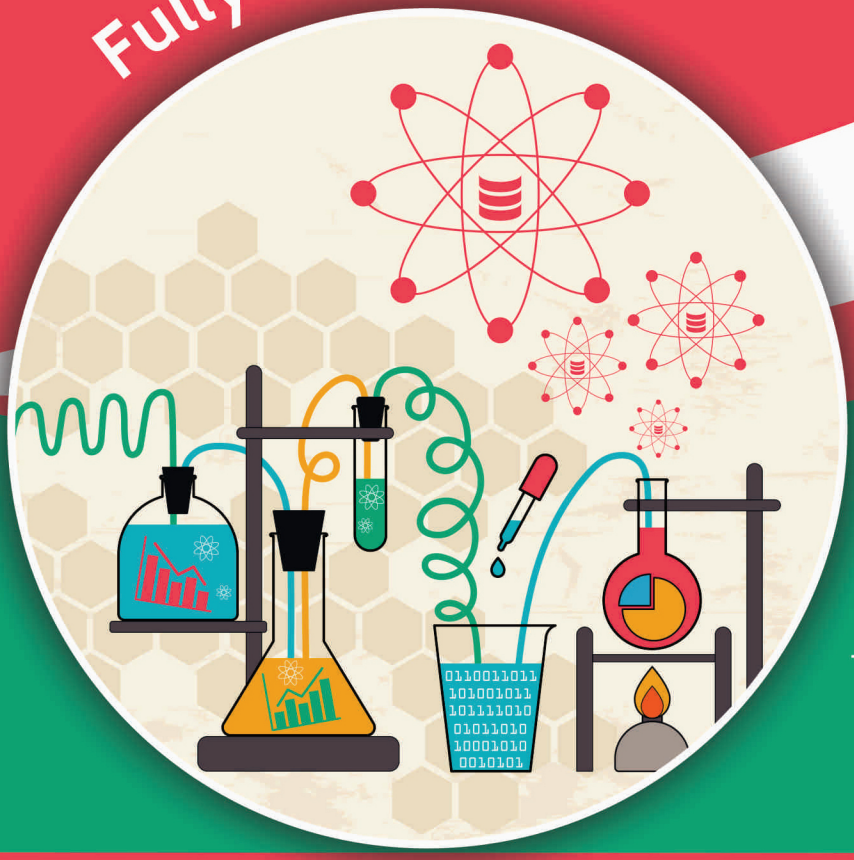
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PREFACE

REVISED EDITION

It gives us immense pleasure and satisfaction to bring out the thoroughly revised and updated edition of the book **"Disha General Organic Chemistry."** The book has been designed to give a better look & feel and to make the text more lucid. The new pattern of JEE Main & Advanced has been kept in mind throughout.

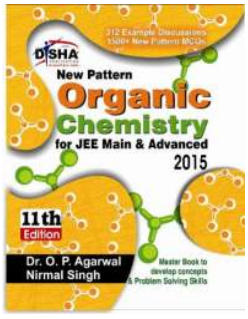
The exercises at the end of each chapter have been designed in the flavour of the new pattern of JEE Main & Advanced. The questions from the previous JEE papers have been incorporated in the different exercises. The book contains three exercises.

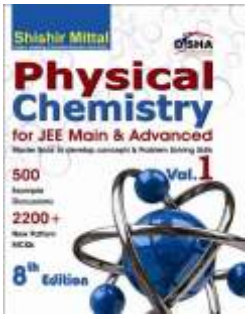
1. **Exercise 1 - MCQ with One correct option :** This exercise contains a collection of questions, which has been very carefully selected and it is ensured that there is no repetition. The exercise has been designed so as to cover all the concepts involved in the chapter.
2. **Exercise 2 :** This exercise contains all the four new variety of questions which have been asked in the last 3-4 JEE examinations. These variety of questions are -
   (i) **MCQ's with one or more than one correct answers :** Around 20-30 well selected problems introduced in each chapter.
   (ii) Comprehension based questions : More than 50 passages which tests the student's comprehension and analytical ability have been added. All these are newly framed problems.
   (iii) Matching type questions : Match the following type of questions with multiple matching have been introduced in each chapter. These are unique and newly framed problems which will definitely pose a big challenge to the student. I feel that this type of problem is the best way to check a student's concept.
   (iv) Assertion & Reason type questions : Assertion and Reason type of questions have been incorporated in each and every chapter.
3. **Exercise 3 - Subjective Problems :** This exercise contains a unique collection of subjective problems which will not only give practice to the students but will also help in revising the complete chapter.

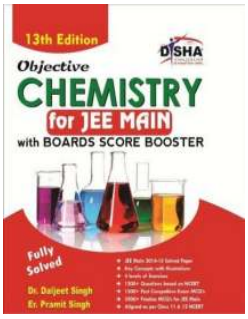
In the end, We would like to request all readers to highlight the printing errors and come forward with suggestions for further improvement of the book.

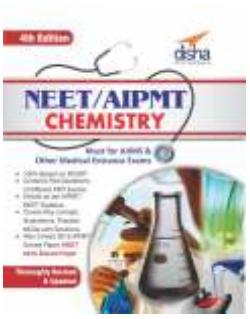
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Other Useful Books









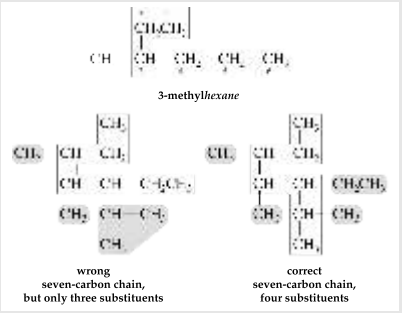
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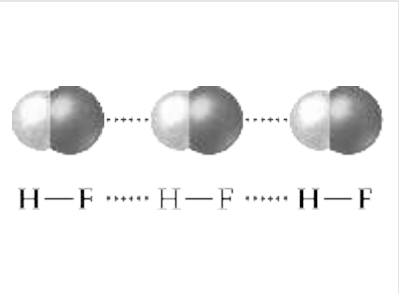
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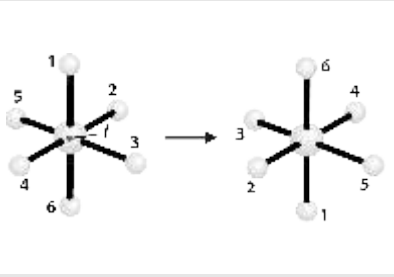
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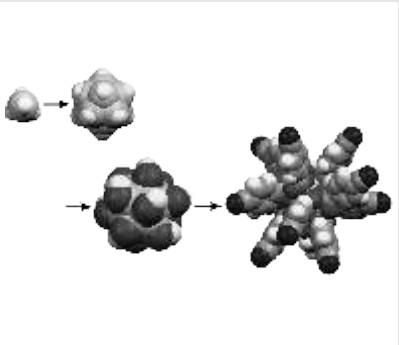
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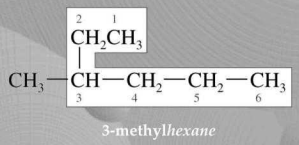


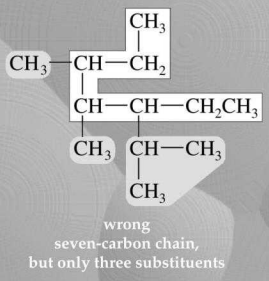
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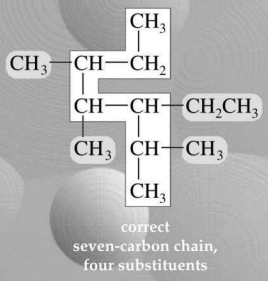
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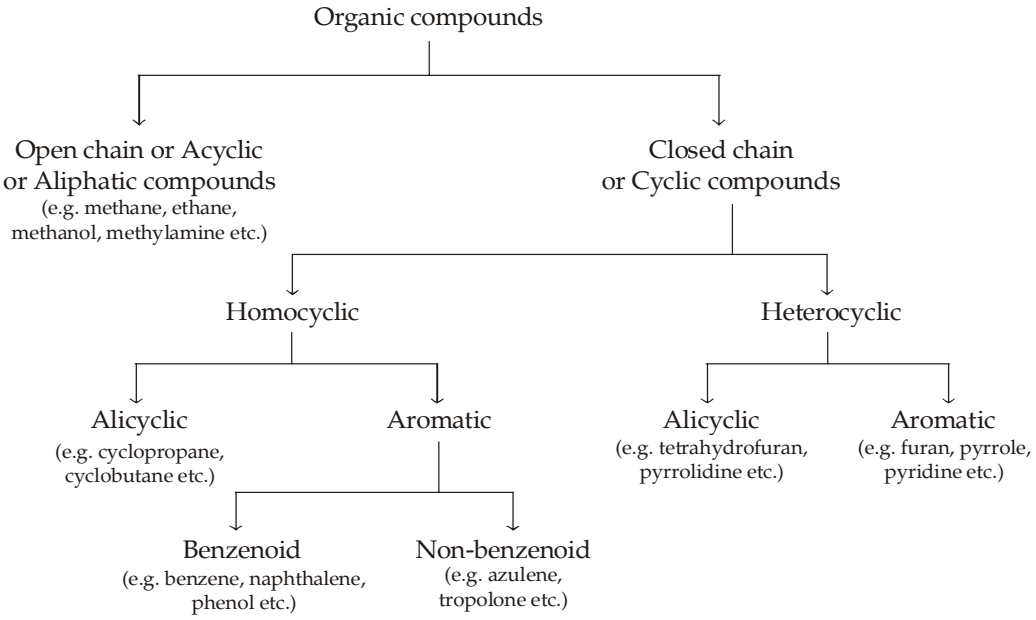
1 Classification and Nomenclature of Organic Compounds

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1.1 Classification of Organic Compounds
1.2 Nomenclature of Organic Compounds
1.3 Alkyl, Alkenyl and Alkynyl Groups
1.4 Bond-Line Formulas
1.5 Nomenclature of Branched Chain Alkanes
1.6 Naming of Compounds having Functional Groups
1.7 IUPAC Names of Some Organic Compounds
1.8 Naming of Polyfunctional Compounds Containing Two or More Similar Carbon-Containing Terminal Groups
1.9 Structural Formula from the IUPAC Name
1.10 Rules for Nomenclature of Alicyclic Compounds
1.11 Nomenclature for Polycyclic Compounds
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EXERCISES
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1.1 Classification of Organic Compounds

All the known organic compounds have been divided into various classes as follows.



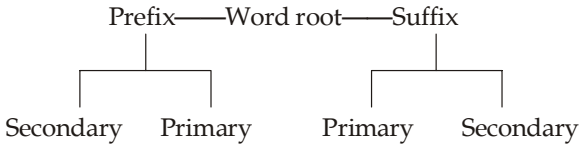
1.2 Nomenclature of Organic Compounds

There are two general ways for naming organic compounds, namely trivial name (common name) and IUPAC name.

Trivial or common names. This is unscientific system in which certain (not all) compounds are named after their source, their property or a historical aspect. These names existed long before organic chemistry became an organized branch of chemical science and structure of organic compounds was not known. Many common names became so popular that they are still widely used by chemists. Methane, ethane, propane, *n*-butane, isobutane, and neopentane are common names.

IUPAC names. A system built on common names is not adequate to communicate structural information of a compound, chemists developed a set of rules for naming organic compounds based on their structures, which we now call the **IUPAC rules**, where IUPAC stands for the "International Union of Pure and Applied Chemistry". Although IUPAC rules were first laid down in 1892, these have been revised at regular intervals to keep them upto-date. The system of nomenclature, based upon IUPAC rules is known as IUPAC system of nomenclature or systematic nomenclature.

The IUPAC name of an organic compound consists of three parts



1.2.1 Word root

A word root indicates the nature of the basic carbon skeleton. Chains containing one to four carbon atoms are known by special word roots, while chains from C_5 onwards are known by Greek numerals.

Chain length	*Word root*	*Chain length*	*Word root*
C_1	Meth–	C_{19}	Nonadec–
C_2	Eth–	C_{20}	Icos–
C_3	Prop–	C_{21}	Henicos–
C_4	But–	C_{22}	Docos–
C_5	Pent–	C_{23}	Tricos–
C_6	Hex–	C_{29}	Nonacos–
C_7	Hept–	C_{30}	Triacont–
C_8	Oct–	C_{31}	Hentriacont–
C_9	Non– or Ennea	C_{32}	Dotriacont–
C_{10}	Dec–	C_{40}	Tetracont–
C_{11}	Undec– or Hendec–	C_{50}	Pentacont–
C_{12}	Dodec–	C_{100}	Hect–
C_{13}	Tridec–		

In general, the word root for any carbon chain is **alk.**

1.2.2 Suffix

There are two types of suffixes *viz.* primary and secondary.

(*i*) **Primary suffixes :** The degree of unsturation or saturation in the carbon chain is indicated by primary suffixes. The primary suffixes for the various saturated and unsaturated carbon chains are mentioned below.

Nature of C chain	C—C	C = C	–C ≡ C–
Primary suffix	*-ane*	*-ene*	*-yne*

It is added after the word root, viz. *ethane*, *ethene*, *ethyne* etc.

In case the parent carbon chain contains two, three, four or more double or triple bonds, numerical prefixes such as *di* (for two), *tri* (for three), *tetra* (for four) etc are added to the primary suffix. For example, *–diene* (for two double bonds), *–triyne* (for three triple bonds).

(*ii*) **Secondary suffixes :** Suffixes, added after the primary suffix to indicate the particular functional group (groups) present in the carbon chain, are known as **secondary suffixes.** Secondary suffixes for some important functional groups are given below.

Class	*Functional group*	*Secondary suffix*	*Class*	*Functional group*	*Secondary suffix*
Alcohols	–OH	–ol	Acid amides	$-CONH_2$	–amide
Aldehydes	–CHO	–al	Esters	–COOR	alkyl... –oate
Ketones	> C = O	–one	Nitriles	–CN	–nitrile
Carboxylic acids	–COOH	–oic acid	Thiols	–SH	–thiol
Acid chlorides	–COCl	–oyl chloride	Amines	$-NH_2$	–amine

The significance of the word root, primary suffix and secondary suffix can be illustrated by the following examples.

Formulae of compound	*Word root*	*Primary suffix*	*Secondary suffix*	*IUPAC name*
CH_3CH_2OH	Eth	ane	ol	Ethanol
CH_3CH_2COOH	Prop	ane	oic acid	Propanoic acid
CH_3NH_2	Meth	ane	amine	Methanamine
$CH_2 = CHCHO$	Prop	ene	al	Propenal
$CH \equiv CCOOH$	Prop	yne	oic acid	Propynoic acid
CH_3CH_2CN	Prop	ane	nitrile	Propaneitrile

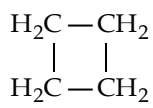
Note that while adding the secondary suffix to the primary suffix, the terminal 'e' of the primary suffix is removed if the secondary suffix begins with a vowel (*a, e, i, o, u* or *y)* but it is retained if the secondary suffix begins with a consonant.

In all above examples except the last the terminal '*e*' of the primary suffix has ben removed because the secondary suffix starts with a vowel, while in the last the secondary suffix (nitrile) starts with a consonant and hence the terminal '*e*' of the primary suffix has been retained.

1.2.3 Prefix

Prefixes are used to indicate (*i*) the cyclic nature of the compound and (*ii*) the nature of the substituent present on the parent chain. Thus like suffixes, prefixes are of two types namely primary and secondary.

(*i*) **Primary prefix.** The primary prefix *cyclo* is added before the word root to indicate the cyclic nature of the carbon skeleton, *e.g.*



Primary prefix	Word root	Prim. suffix	Sec. suffix	IUPAC name
Cyclo	**but**	**ane**	—	**Cyclobutane**

In case the compound is acyclic (open chain), no primary prefix is used.

(*ii*) **Secondary prefix.** The groups which are not considered as functional groups, in IUPAC system of nomenclature, but regarded as substituents are called **secondary prefixes**. These are added before the word root in case of acyclic compounds and before the primary suffix in case of cyclic compounds. Some important secondary prefixes are alkyl (for —R), nitro (for $-NO_2$), halo (for —X), alkoxy (for —OR) etc.

Thus in short, IUPAC name of an organic compound consists of following arrangement.

***pri*-Prefix -*sec*-prefix-word root-*pri*-suffix-*sec*-suffix**

According to the latest rules, the name of an organic compound is derived from the name of the parent hydrocarbon by using suitable suffixes, infixes and prefixes.

1.3 Alkyl, Alkenyl and Alkynyl Groups

These are derived by replacing one hydrogen atom from the corresponding parent compound.

Nature of group	*Primary suffix*	*Generic name*
Alkane minus one H atom	–yl	Alkyl
Alkene minus one H atom	–enyl	Alkenyl
Alkyne minus one H atom	–ynyl	Alkynyl

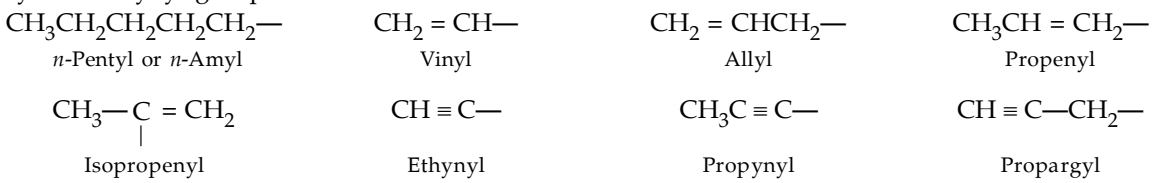
The alkyl groups derived from alkanes having three or more carbon atoms exist in various isomeric structures, *viz.* propyl (or *n*-propyl) and isopropyl; *n*-butyl, isobutyl, *sec*-butyl and *tert*-butyl.



n-Butyl *iso*-Butyl *sec*-Butyl *tert*-Butyl

The prefix *n-*, *iso-*, *sec-*, *tert-*, and *neo-* are although used in common names, these have been integrated into the IUPAC system and are thus acceptable to systematic nomenclature too.

A carbon atom attached to one other carbon atom is known as a **primary (1°) carbon atom**, similarly carbon atoms attached to two, three, and four other carbon atoms are known as **secondary, tertiary and quaternary carbon atom** respectively. Methyl group is although a primary alkyl group, it is always categorised separately. Some typical alkyl, alkenyl and alkynyl groups are



n-Pentyl or *n*-Amyl Vinyl Allyl Propenyl

Isopropenyl Ethynyl Propynyl Propargyl

TEST YOUR UNDERSTANDING - 1.1

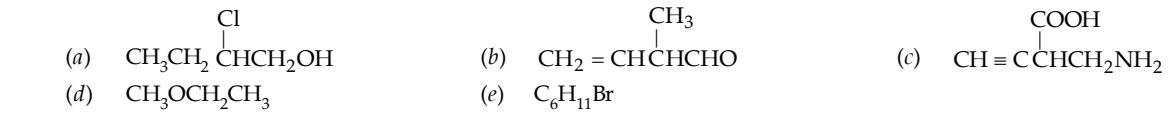
1. Give the total number of carbon atoms present in the following compounds

(*a*) Undecane (a principal component of aggregation pheromone, secreted by cockroaches).

(*b*) Hentriacontane (a principal component of bees wax).

(*c*) Octacosane (a compound present in certain fossil plant).

2. Pick up the word root, suffixes (primary and secondary) and prefixes (primary and secondary) in each of the following structures.



(*a*) (*b*) (*c*)

(*d*) $CH_3OCH_2CH_3$ (*e*) $C_6H_{11}Br$

3. Pick up the word root, suffixes and prefixes in each of the following IUPAC names.

(*a*) 2-Methyl-4-oxobutanoic acid (*b*) 3-(Carbamoylmethyl) pentanediamide

(*c*) 3-(Formylmethyl)hexanedial (*d*) Pentanediel

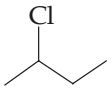
(*e*) 3-Carbamolymethyl) pentanediamide (*f*) 3-(Formylmethyl)hexanedial

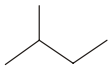
4. (*a*) Give structrues of all the C_5H_{11} alkyl groups and identify them as primary, secondary or tertiary alkyl groups.

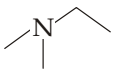
(*b*) Give the structure of the simplest hydrocarbon having all the four types of carbon atoms. Write down its IUPAC name too.

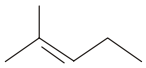
1.4 Bond-Line Formulas

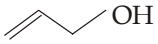
Now-a-days, a very simplified formula called a bond-line formula, is used to represent structural formulas. The bond-line representation is the quickest of all to write because it shows only the carbon skeleton. The necessary number of hydrogen atoms required by each carbon are assumed to be present, and not written ; other atoms (e.g., O, Cl, N) are written inside the skeleton. Each intersection (joint) of two or more lines and the end of a line represent a carbon atom unless some other atom is written in.

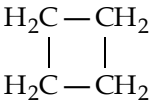
$CH_3CHClCH_2CH_3$ 

$CH_3CH(CH_3)CH_2CH_3$ 

$(CH_3)_2NCH_2CH_3$ 

$(CH_3)_2C = CHCH_2CH_3$ 

$CH_2 = CHCH_2OH$ 





TEST YOUR UNDERSTANDING - 1.2

1. Write the bond-line formula for

(*a*) $(CH_3)_2CHCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2OH$ (*b*) $CH_3COCH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$ (*c*) $(CH_3)_3CH$

(*d*) $CH_3C \equiv CCH_2OH$ (*e*) $CH_3(CH_2)_4\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}HCH_2Cl$ (*f*) $CH_3CH = CH(CH_2)_3\underset{\displaystyle CH_2OH}{\underset{|}{C}}HCHO$

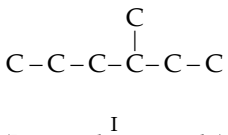
1.5 Nomenclature of Branched Chain Alkanes

There are certain rules for naming a complex organic molecule according to IUPAC system. All organic compounds are regarded as substituted hydrocarbons and, therefore, these names are also known as **substitutive names.** These rules are illustrated below.

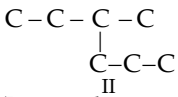
1.5.1 Longest chain rule

The first step for naming an organic compound is to select the longest continuous chain of carbon atoms which may or may not be horizontal (straight). This is called the **parent chain or main chain**, and other carbon chains attached to it are known as **side chain**. On the basis of the number of carbon atoms present in the parent chain, the parent hydrocarbon is determined. For example, if the parent chain contains six carbon atoms, the compound is considered to be a derivative of hexane.

Example - The structure I has the longest chain of six carbon atoms present in a straight line; therefore it is said to be a derivative of hexane. On the other hand, in structure II the straight chain has only four or three carbon atoms while the longest possible chain may have as many as six carbon atoms (zig-zag chain).



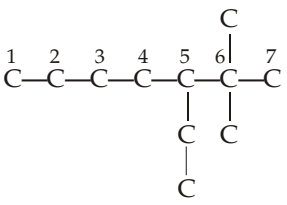
I
(Longest chain, straight)



II
(Longest chain, zig-zag)

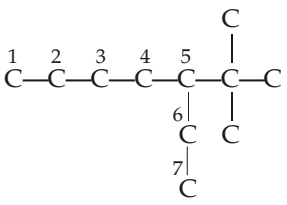
Therefore, both the structures are derivatives of hexane.

In case a molecule contains two equally long carbon chains, the one carrying larger number of side chains is selected. For example, structure III may have two parent carbon chain of equal length (C_7), but the one carrying there substituents is selected.



Straight parent chain of C_7 with three side chains **(Right)**

III



Zig-zag parent chain of C_7 with only one side chain **(Wrong)**

1.5.2 Lowest number *or* lowest sum rule

The longest carbon chain is numbered as 1, 2, 3, 4, ... etc. starting from the end that gives the smallest possible number(s) *to the substituent*(s). For example, in structure IV numbering may be done in two ways ;



IV

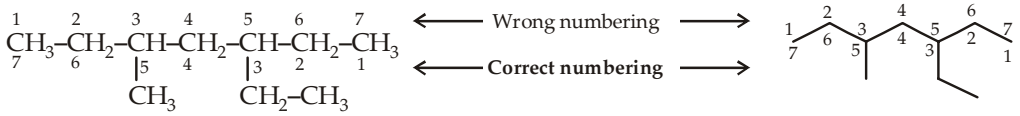
In one case the substituent is assigned position 3, while in other case it is assigned position 4. Hence the former, being smaller, is correct. The number that locates the position of a substituent is known as **locant**. Thus the locant for X in the above correct structure is 3.

In case, the parent chain *has two or more substituents, numbering must be done in such a way that the sum of the locants on the parent chain is the lowest possible.* Thus in structure V numbering may be done in two ways : in one, the sum of locants is 9 while in other it is 12, hence the former is correct while the latter is wrong.



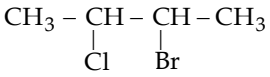
V

Further, if different side chains (alkyl groups) are present on the identical positions in relation to the ends of the chain, numbering must be done in a way that the first cited group (i.e. the group which comes first in alphabetic order) receives the minimum number, *e.g.* the correct name of the following compound is 3-ethyl-5-methylheptane and not 5-ethyl-3-methylheptane.

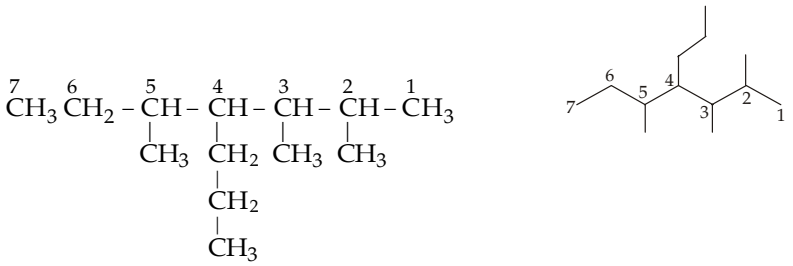


3-Ethyl-5-methylheptane

Similarly, the correct name for the following compound is 2-bromo-3-chlorobutane and not 3-bromo-2-chlorobutane.



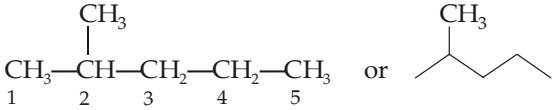
When two chains of equal length compete for selection as the parent chain, choose the chain with the greater number of substituents.



2,3,5-Trimethyl-4-propylhelptane (four substituents)

1.5.3

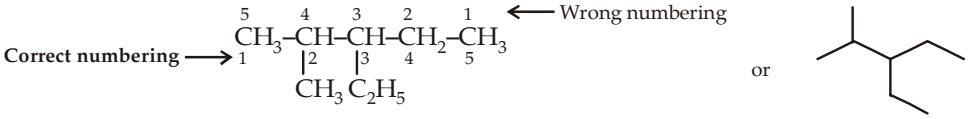
The name of the substituent is prefixed to the name of the parent hydrocarbon and its position on the main chain is indicated by writing the locant before the prefix. A hyphen (–) is inserted between the locant and the substituent name. Thus the compound VI is written as 2-methylpentane.



2-Methylpentane, VI

1.5.4 Alphabetical order of side chains

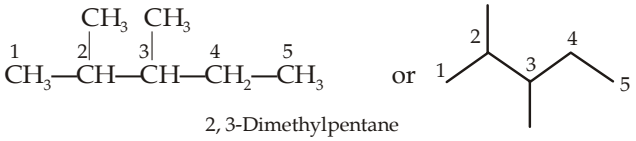
In case two or more alkyl groups (side-chains) are attached to the parent chain, these are prefixed in alphabetic order, *e.g.*



3-Ethyl-2-methylpentane and not as 2-Methyl-3-ethylpentane

1.5.5

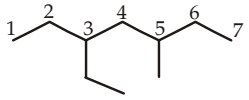
If a substituent is present two or more times, this is indicated by the prefix di–, tri–, tetra–, etc. added to the substituent. The different locants of the substituents are separated by commas. For example,



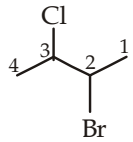
2, 3-Dimethylpentane

1.5.6

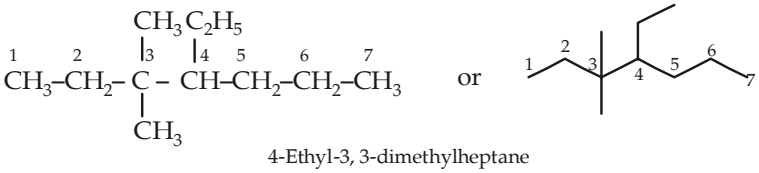
If the same substituent numbers are obtained in both directions, the first cited group receives the lowest number.



3-Ethyl-5-methylheptane *not* 5-Ethyl-3-methylheptane



2-Bromo-3-chlorobutane *not* 3-Bromo-2-chlorobutane

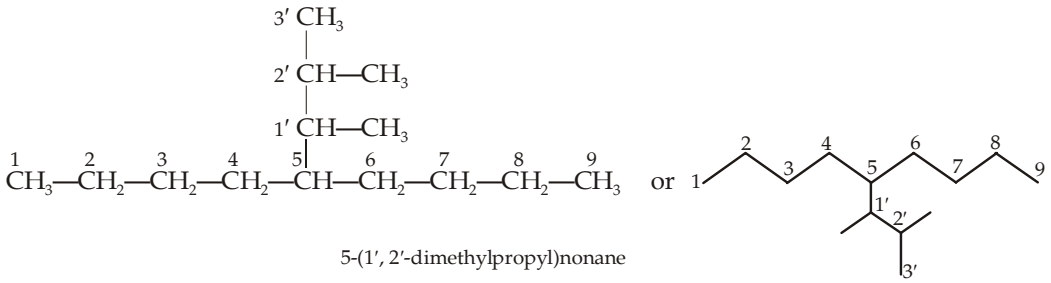


4-Ethyl-3, 3-dimethylheptane

The spelling of the prefixes *di-*, *tri-*, and *tetra-* should not be considered while arranging the substituents alphabetically, as in the above example.

1.5.7

In case the substituent on the parent chain has itself branched chain then it is named as a substituted alkyl group and its carbon chain is numbered from the carbon atom attached to the main chain. The name of this complex substituent is written in bracket to avoid confusion with the numbers of the main chain, *e.g.*



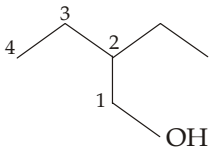
5-(1′, 2′-dimethylpropyl)nonane

The multiplicity of a substituted substituent, *i.e.* when the substituent is itself substituted and there are two or more such substituents, these are indicated by numerical prefixes like '*bis*', '*tris*', '*tetrakis*' etc.

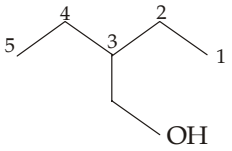
1.6 Naming of Compounds having Functional Groups

After studying the IUPAC nomenclature of saturated hydrocarbons, let us study the rules for naming compounds with functional groups (double and triple bonds are also considered as the functional groups).

(*i*) *The longest carbon chain is selected in such a way as to include the maximum number of functional groups.* Thus in the example given below numbering is done in such a way that the selected carbon chain contains the alcoholic (functional) group, although the longest possible chain (but without functional group) is having five carbon atoms.

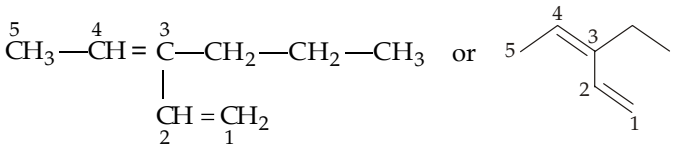


Selected chain has 4 C atoms with functional group (**Right**)



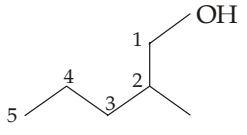
Selected chain has 5 C atoms without functional group **(Wrong)**

Similarly, if the compound contains more than one functional group ; the selected longest chain must have all the functional groups. Thus the following compound is considered as a derivative of pentane and not of hexane.

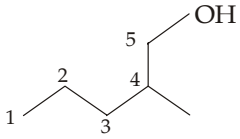


3-Propyl-1, 3-pentadiene

(*ii*) *The numbering of carbon chain is done in such a way that the functional group(s) is (are) given minimum possible number even if it violates the lowest sum rule.* Thus, the following compound is named as

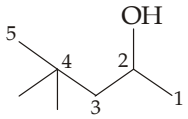


2-Methylpentanol-1 **(Right name)**
(functional group at C_1)

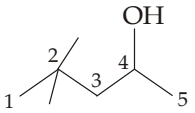


4-Methylpentanol-5 **(Wrong name)**
(functional group at C_5)

Similarly,



4, 4-Dimethylpentanol-2 **(Right name)**
(although sum of locants ; 4 + 4 + 2 = 10)

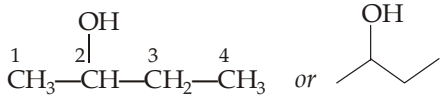


2, 2-Dimethylpentanol-4 **(Wrong name)**
(although sum of locants ; 2 + 2 + 4 = 8)

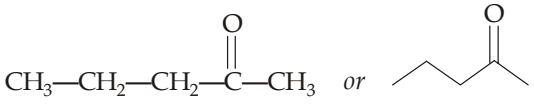
(*iii*) *The name of the substituents are prefixed to the parent hydrocarbon according to IUPAC rules described earlier.*

(*iv*) *The terminal 'e' of the hydrocarbon (alkane) is replaced by the suffix of the corresponding functional group.*

(*v*) *Although the positional number of the functional group may be represented in either of the three ways,* ***in 1993, the IUPAC recommended*** *that the number indicating the position of the functional group should be placed immediately before the suffix, e.g.* ***but-2-ene, butan-2-ol,*** *etc.* ***Although this is the latest convention used by IUPAC system, the older conventions like butene-2 or 2-butene are so widely used, that their replacement will take some time****. So readers should take a note of it throughout the book.*



2-Butanol, Butan-2-ol or Butanol-2



2-Pentanone, Pentan-2-one or Pentanone-2

(*vi*) *Halo, nitro and sometime amino groups are not regarded as functional groups*. They are considered as substituents.

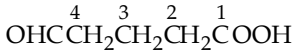
(*vii*) *In case the compound contains two or more different functional groups* (*including C = C and C ≡ C), the principal group forms the suffix of the name while the other functional groups are considered as substituents and indicated as prefixes*. The order of seniority among the principal groups is given in the following table along with their prefix and suffix names.

Seniority table for principal groups

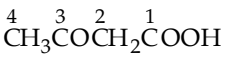
Group	*Prefix name*	*Suffix name*
$-SO_3H$	Sulpho–	sulphonic acid
–COOH	Carboxy–	–oic acid
–COOR	Alkyl-oxycarbonyl	–alkyl---oates
–COX	Haloformyl–	–oyl halide
$-CONH_2$	Carbamoyl–	amide
–CHO	Formyl–	–al
–CN	Cyano–	–nitrile
–CO	Keto- or Oxo	–one
–OH	Hydroxy–	–ol
–SH	Mercapto–	–thiol
$-NH_2$	Amino–	–amine
> C = C < ; —C ≡ C–	–	–ene, –yne
–X (halogen)	Halo–	–
$-NO_2$	Nitro–	–
–NO	Nitroso–	–
–O–	Epoxy–	–
R—	Alkyl–	–

Let us examplify the above rule by some examples.

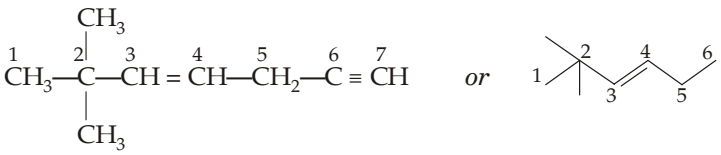
While using prefixes such as formyl (for —CHO), cyano (for —CN), carboxy (—COOH), carbamoyl ($—CONH_2$) etc. the carbon of the substituent group is not counted in the principal chain. However, when prefix —*oxo* (for >C = O) is used, its carbon is counted in the principal chain. This is due to its non-terminal nature.



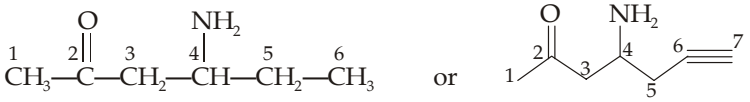
4-Formylbutanoic acid



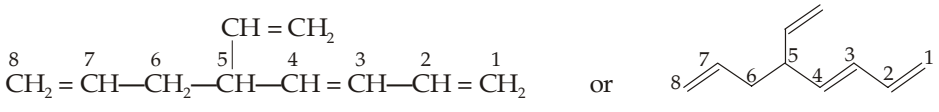
3-Oxobutanoic acid



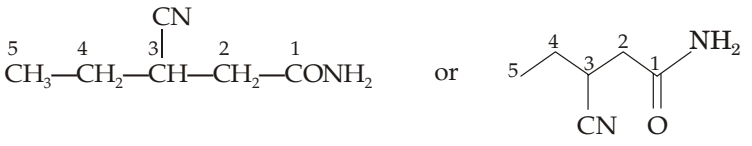
2, 2-Dimethylhept-3-ene-6-yne (Double bond is senior to triple, hence given lower number).



4-Amino-2-hexanone (here ketonic group is senior to amino group)

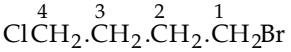


5-Vinyl-1, 3, 7-octatriene



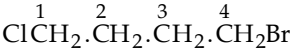
3-Cyanopentamide (here amide group is senior to cyano).

(*viii*) *In case two groups of the same seniority occupy indentical positions in relation to end of the chain, the lowest number should be given to the group in the alphabetical order of their prefixes*. Thus the following compound should be named as 1-bromo-4-chlorobutane.



1-Bromo-4-chlorobutane

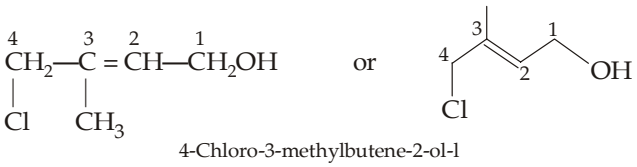
(Right name)



4-Bromo-1-chlorobutane

(Wrong name)

(*ix*) Substituents, side chains and functional groups are named in alphabetical order. In short, first of all mention all substituents in alphabetical manner, then side chains in alphabetical manner, and finally functional group in alphabetical order. For example,

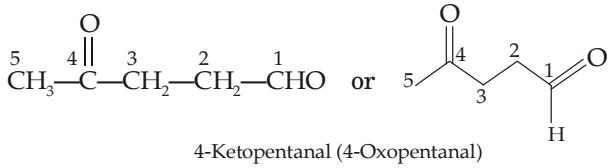


4-Chloro-3-methylbutene-2-ol-l

Thus in the compound given above two functional groups (-ene and -ol) are arranged in the alphabetical order.

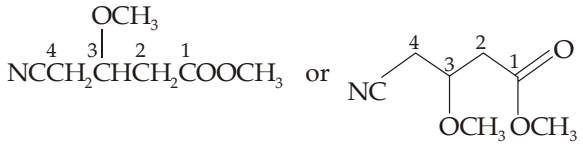
(*x*) *Prefixes like n-, iso-, sec-, tert-, neo-, etc. must be avoided in IUPAC system.*

1.7 IUPAC Names of Some Organic Compounds

1. 

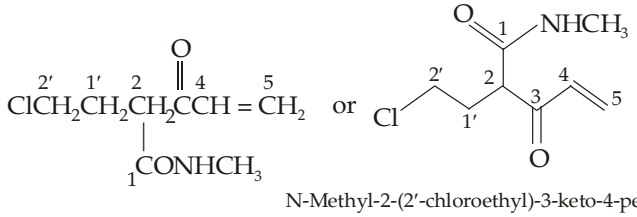
4-Ketopentanal (4-Oxopentanal)

—CHO and >C = O are the principal and secondary functional groups respectively

2. 

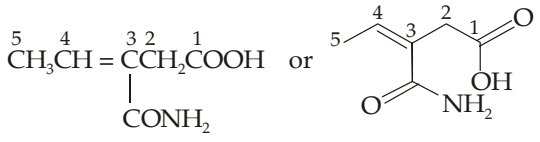
Methyl-4-cyano-3-methoxy butanoate

Note that —$COOCH_3$ is the principal functional group

3. 

N-Methyl-2-(2′-chloroethyl)-3-keto-4-pentenamide

Note that here —$CONHCH_3$ is the principal functional group

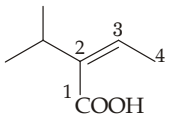
4. 

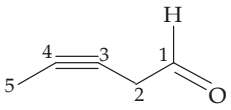
3-Carboxamido-3-pentenoic acid

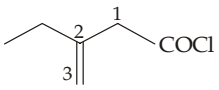
Note that —COOH is the principal functional group while —$CONH_2$ is considered as a substituent

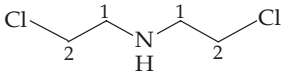
TEST YOUR UNDERSTANDING - 1.3

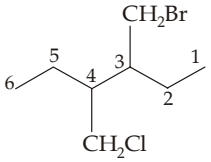
1. Try to justify the selection of the parent carbon chain and elaborate the IUPAC name for each of the following structures :

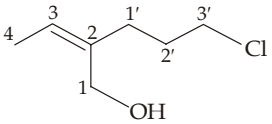
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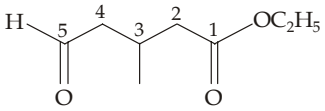
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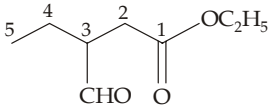
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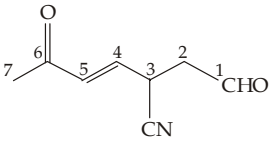
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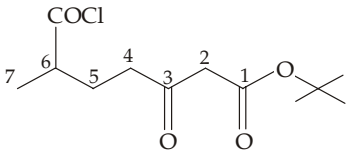
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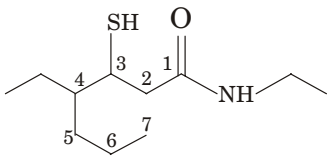
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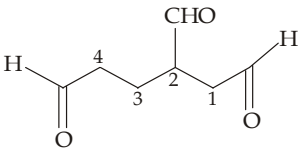
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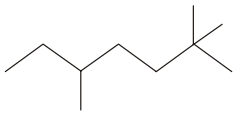
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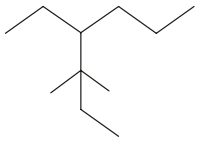
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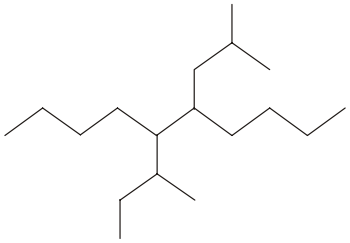
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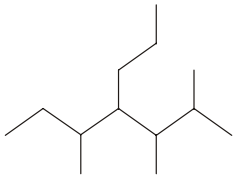
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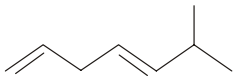
2. Give IUPAC names for the following compounds.

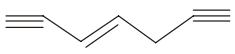
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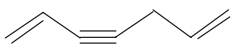
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(*c*) 

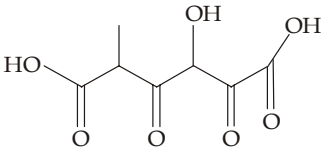
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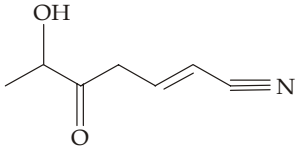
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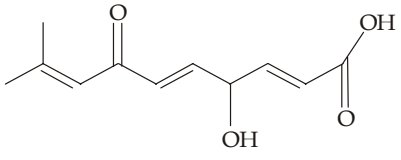
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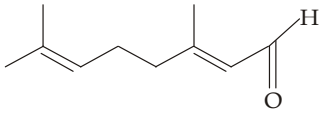
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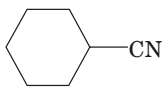
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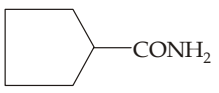
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(*j*) 

(*k*) 

(*l*) 

(*m*) 

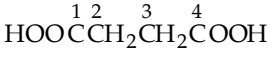
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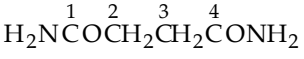
1.8 Naming of Polyfunctional Compounds Containing Two or More Similar Carbon-Containing Terminal Groups

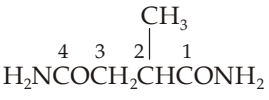
Carbon-containing terminal groups are monovalent groups like —COOH, —COOR, —COCl, —$CONH_2$, —CHO, and —CN. When the compound contains two or more such groups, following special rules must be observed.

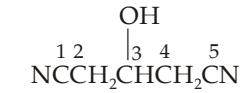
1.8.1

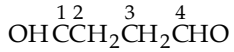
When the compound contains two similar carbon-containing terminal groups, then both of these groups must be counted in the principal chain and it is not necessary to indicate their positions (these are assumed to be present on the terminal carbon atom). For example,

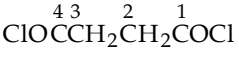

Butanedioic acid

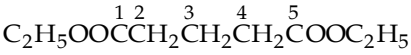

Butanediamide


2-Methylbutanediamide


3-Hydroxypentanedinitrile

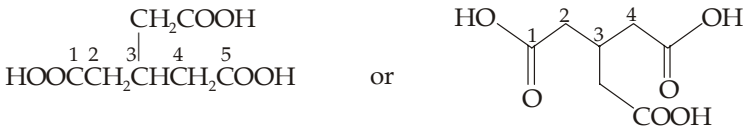

Butanedial

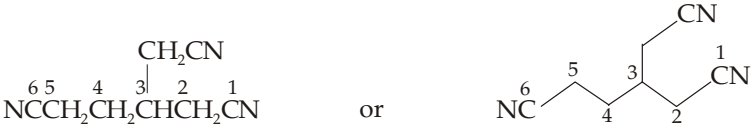

Butanedioyl chloride

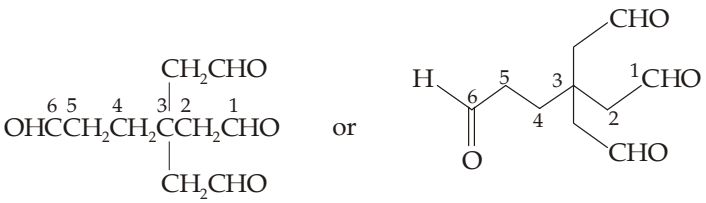

Diethyl pentanedioate

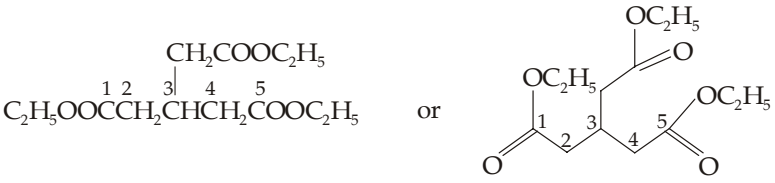
1.8.2

When the compound contains more than two similar terminal groups, all of which are not directly linked to the principal chain, then that longest principal chain should be selected which contains two such similar terminal groups at its two ends. Here the terminal groups are counted in the chain, while the third, present on side chain, is considered as a substituent.


3-(Carboxymethyl)pentanedioic acid


3-(Cyanomethyl)hexanedinitrile

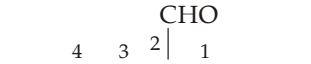

3, 3-Bis(formylmethyl)hexanedial


Diethyl 3-(ethyloxycarbonylmethyl)pentanedioate

1.8.3

When the compound contains more than two similar groups all of which are present on the principal chain, then none of these groups are counted in the principal chain ; and special suffixes are used to indicate the functional group, *viz*.

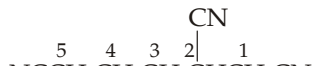
Functional group	*Special suffix*	*Functional group*	*Special suffix*
–COOH	–carboxylic acid	–COX	–carbonyl halide
$-CONH_2$	–carboxamide	–CHO	–carbaldehyde
–COOR	R----carboxylate	–CN	–carbonitrile



Butane-1, 2, 4-tricarbaldehyde

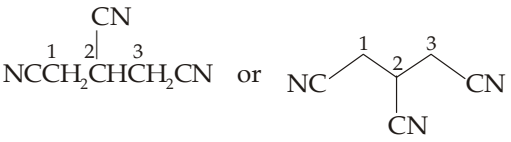


Butane-1, 2, 4-tricarboxylic acid



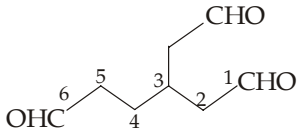
Pentane-1, 2, 5-tricarbonitrile

Few examples are given below for illustration.

1. 

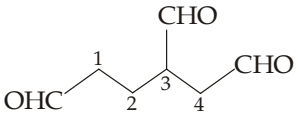
Propane-1, 2, 3-tricarbonitrile

Note that more than two —CN groups are present on the main chain, hence not counted in the main chain

2. 

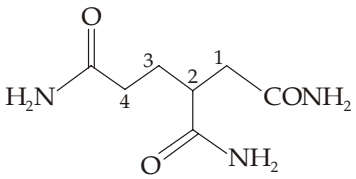
3-(Formylmethyl)hexane-1,6-dial

(Only two —CHO groups are present on the main chain, hence counted in the main chain)

3. 

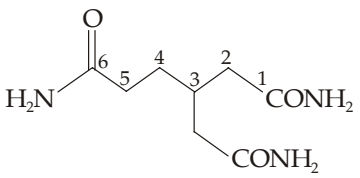
Butane-1, 3, 4-tricarbaldehyde

(More than two —CHO gps. are present on the main chain,hence their C's are not counted in the main chain)

4. 

Butane-1, 2, 4-tricarboxamide

(Three —$CONH_2$ are present on the main chain, hence their C's are not counted)

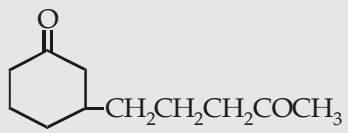
5. 

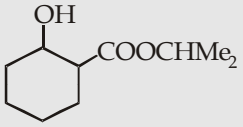
3-(Carbamoylmethyl)hexanediamide

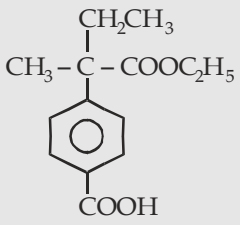
(Only two —$CONH_2$ gps. are on the main chain, the third is on the side chain, hence former two are counted in main chain)

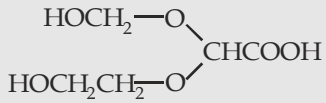
Example 1 :

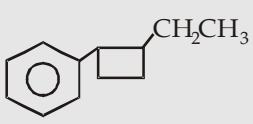
Number the different carbon atoms present in the main and side chain of the following structures and give IUPAC name of the following compounds.

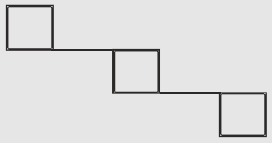
(i) 

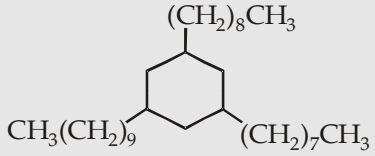
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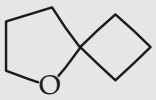
(iii) 

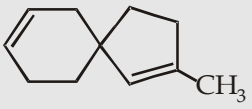
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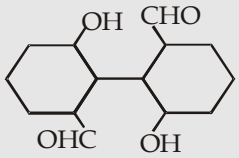
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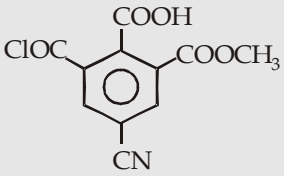
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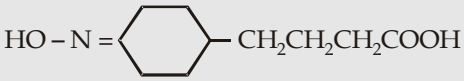
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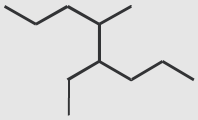
(viii) 

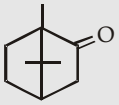
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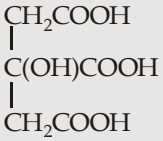
(x) 

(xi) 

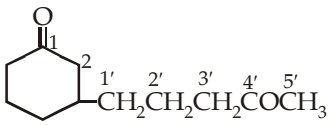
(xii) 

(xiii) 

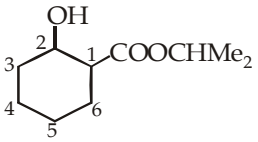
(xiv) 

(xv) 

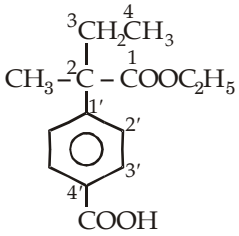
Solution :

(i) 

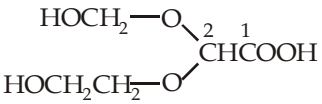
3 – (4′- Oxopentyl)cyclohexanone

(ii) 

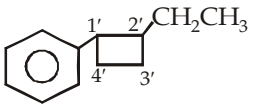
isopropyl-2-Hydroxycyclohexane carboxylate

(iii) 

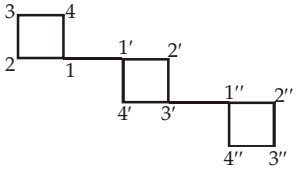
Ethyl, 2-methyl-2-(4′-carboxyphenyl) butanoate

(iv) 

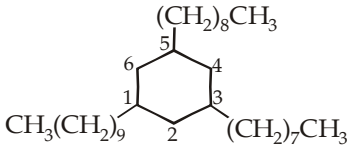
2-Hydroxyethoxy-2-hydroxymethoxyethanoic acid

(v) 

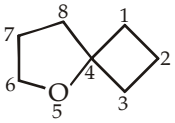
1-(2′-Ethylcyclobutyl)benzene

(vi) 

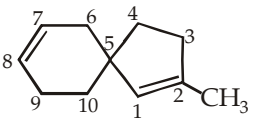
1, 1', 3', 1"-Tercyclobutane

(vii) 

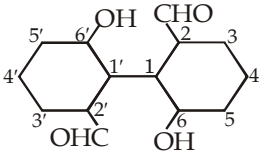
1-Decyl-5-nonyl-3-octylcyclohexane

(viii) 

5-Oxaspiro[3, 4] octane

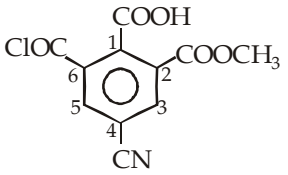
(ix) 

2-Methylspiro [4, 5] deca-1, 7-diene

(x) 

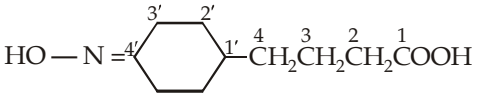
6,6-Dihydroxydiphenyl-2, 2′-dicarbaldehyde

(xi)



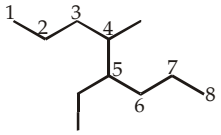
2-Methoxycarbonyl-6-chloroformyl-4-cyanobenzoic acid

(xii)



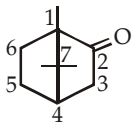
4-(4′- Hydroxyiminocyclohexyl)butanoic acid

(xiii)



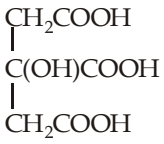
5–Ethyl-4-methyloctane

(xiv)



1, 7, 7 –Trimethylbicyclo [2. 2. 1] heptan -2- one

(xv)



2-Hydroxypropane -1, 2, 3- tricarboxylic acid
(common namecitric acid)

1.9 Structural Formula from the IUPAC Name

Following points should be taken into consideration

1. Identify the word root in the given IUPAC name and draw the corresponding carbon chain and number the chain from either side.

2. Identify the primary suffix (-ane, -ene, or -yne) from the name of the compound and insert the double or triple bond at the carbon atom indicated by the suffix.

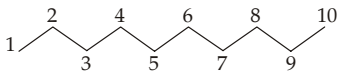
3. Identify the secondary suffix *i.e.* the principal functional group and insert the proper functional group on the carbon atom indicated by the locant in the given IUPAC name. In case the secondary suffix, *i.e.* the principal functional group, does not bear any numerical prefix, it is assumed to be present at C_1.

4. Identify the secondary prefixes, *i.e.* secondary functional group(s) and other substituent(s) indicated by the various prefixes and insert them on the given carbon atom(s) specified by locants.

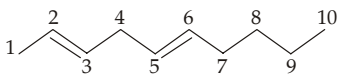
5. Add suitable number of hydrogen atom(s) so that each carbon atom in the chain becomes tetravalent. This step is not necessary in bond line formulae.

Let us illustrate it by taking the example of **3-Hydroxy-7-oxo-8-methyl-2, 5-decadienoic acid.**

(*i*) Here the word root is *deca* which indicates that the compound is a derivative of decane, hence a carbon chain having 10 carbon atoms must be drawn.



(*i*) Chain of 10 C

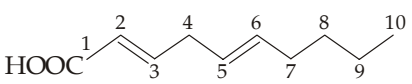


(*ii*) A C_{10} chain having double bonds at C_2 and C_5

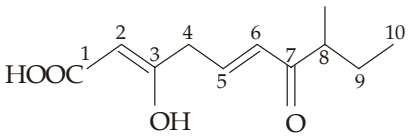
(*ii*) Here primary suffix is *diene* whose positions are indicated by numbers 2 and 5.

(*iii*) Here the secondary suffix, *i.e.* primary functional group is carboxylic acid, indicated by –oic acid which is a secondary suffix for –COOH. Since –oic acid does not bear any number it should be given number 1.

(*iv*) Here the secondary prefixes *i.e.* secondary functional groups and substituents are hydroxy (at C_3), –oxo (at C_7), and methyl (at C_8). Insert these groups at respective carbons. In line-bond formula, each carbon atom is assumed to have required number of H atoms, so there is no necessity for writing hydrogen atoms on C atoms.



(*iii*) A C_{10} chain having double bonds at C_2 and C_5, and a terminal —COOH group



(*iv*) Secondary functional groups at C_3 and C_7; methyl at C_8.
3-Hydroxy-7-oxo-8-methyl-2, 5-decadienoic acid

TEST YOUR UNDERSTANDING - 1.4

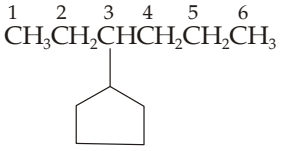
1. Draw structure for the compounds corresponding to following IUPAC names.

(*a*) 3-Ethyl-2-methylheptane
(*b*) 3-Ethyloctene
(*c*) 1, 6-Hexanedioic acid
(*d*) Methyl 2-ethyl-3-hydroxybutanoate
(*e*) *tert*-Butyl-3-hydroxyoct-5-enoate
(*f*) N, N, 2-Trimethyl-3-oxohexanamide
(*g*) 2-Cyclopropyl-1-hexene
(*h*) *tert*-Butylcyclohexane

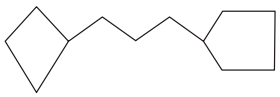
1.10 Rules for Nomenclature of Alicylic Compounds

In addition to rules mentioned earlier, following points should be taken in consideration.

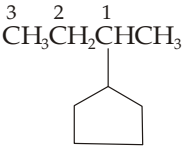
1. If the ring contains fewer carbon atoms than the alkyl group attached to it or when more than one ring system is attached to a single chain, the compound is named as a derivative of alkane and the ring(s) is(are) treated as cycloalkyl substituent(s), otherwise it is named as a derivative of cycloalkane.



3-Cyclopentylhexane
(Ring has 5 C's, while the alkyl group has 6)

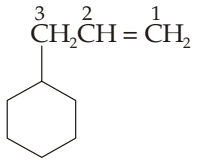


1-Cyclobutyl-
3-cyclopentylpropane

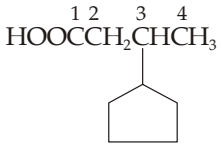


1-Methylpropylcyclopentane
(Ring has 5 C's, while alkyl group has 4)

2. In case, the side chain contains multiple bond or a functional group, the alicyclic ring is treated as substituent irrespective of its size.

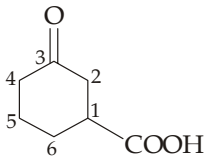


3-Cyclohexylprop-1-ene

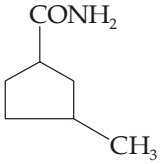


3-Cyclopentylbutanoic acid

3. If the functional group, directly attached to the ring contains carbon atom, it is not counted in the word root ; and special suffixes, mentioned earlier, are used to indicate the presence of such groups.

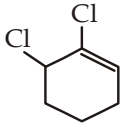


3-Oxocyclohexane-1-carboxylic acid
(Note that here the suffix for —COOH group is –carboxylic acid rather than -oic acid, because its carbon is not counted in word root)

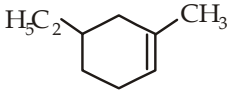


3-Methylcyclopentane-1-carboxamide

In cycloalkenes, the double bond is always given number 1. In case the ring contains other substituent, the numbering should be done in a direction that gives the lower number for the substituent attached on the double bond, no matter it may violate the lowest sum rule. For example,

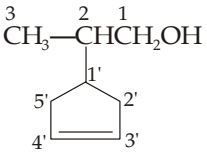


1,6-Dichlorocyclohexene
not
2,3-Dichlorocyclohexene
because 1 < 2

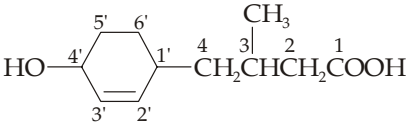


5-Ethyl-1-methylcyclohexene
not
4-Ethyl-2-methylcyclohexene
because 1 < 2

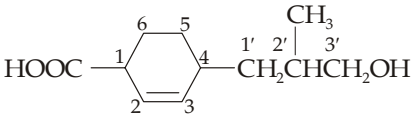
4. Nomenclature of the alicyclic compounds containing double bond or functional in the ring as well as in the side chain. In such cases the compound is considered as a derivative of that part in which principal functional group is present.



2-(Cycloprop-3'-enyl)propanol

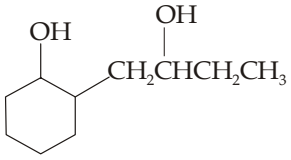


4-(4'–Hydroxycyclohex-2'-enyl)-3-methylbutanoic acid
(Here the principal group, —COOH is present in side chain, so ring is considered as a substituent)

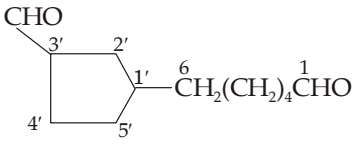


4-(2′-Methyl-3′-hydroxypropyl)cyclohex-2-en-1-carboxylic acid
(Here the principal group —COOH is present in ring, so the side chain is considered as a substituent)

5. When both ring as well as side chain contains the same functional group, then the parent hydrocarbon is decided on the basis of the number of carbon atoms (point 1).



2-(2′ -Hydroxybutyl)cyclohexanol
(Here ring has 6 C's, while side chain has 4)

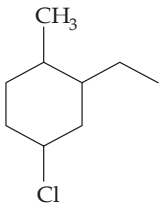


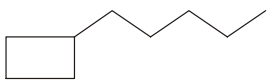
6-(3′ -Formylcyclopentyl)hexanol
(Here ring has 5 C's, while side chain has 6)

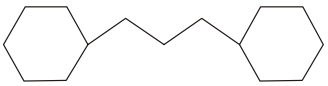
6. If a compound contains an acyclic ring as well as a benzene ring, it is named as a derivative of benzene.

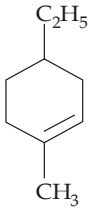
TEST YOUR UNDERSTANDING - 1.5

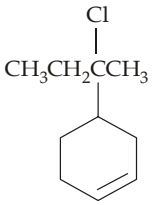
1. Give IUPAC names for the following compounds.

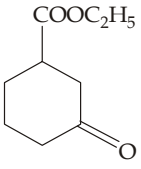
(*a*) 

(*b*) 

(*c*) 

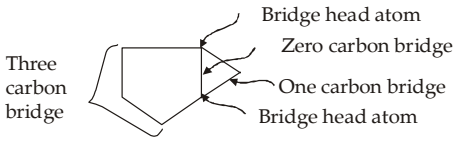
(*d*) 

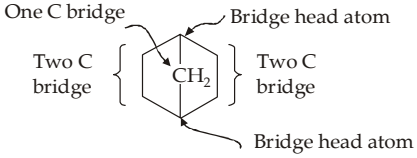
(*e*) 

(*f*) 

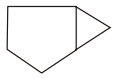
1.11 Nomenclature for Polycyclic Compounds

1. Compounds containing two or more fused alicyclic rings are known as polycyclic compounds. The carbon atoms common to both the rings are called **bridge head atoms**. A bond or a chain of carbon atoms connecting the two bridge heads is called a **bridge**; thus a bridge may contain 0, 1, 2 ... etc. carbon atoms.

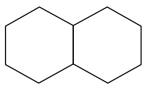




2. A bicyclic compound is named by attaching the prefix *bicyclo* to the name of the hydrocarbon corresponding to the total number of carbon atoms in the two rings. The number of carbon atoms in each of these three bridges connecting the two bridge head carbon atoms is indicated by arabic numerals, *i.e.* 0, 1, 2, 3, ... etc. These arabic numerals are arranged in descending order, separated from one another by full stops (.) and then enclosed in square brackets. These brackets are placed between the prefix bicyclo and the name of the alkane. For example, the above two compounds are named as

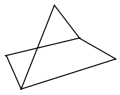

Bicyclo[3.1.0]hexane

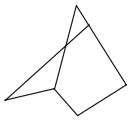

Bicyclo[2.2.1]heptane

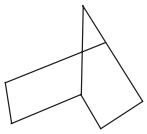

Bicyclo[4.4.0]decane


Bicyclo[3.1.1]heptane

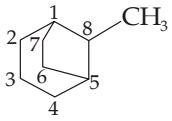

Bicyclo[2.2.2]octane


Bicyclo[1.1.1]pentane

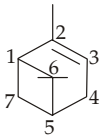

Bicyclo[2.1.1]hexane

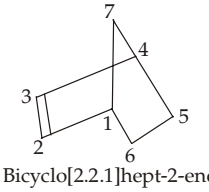

Bicyclo[2.2.1]heptane
(Norborane)

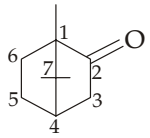
3. If a substituent is present, numbering is done from one of the bridge head atoms, passes first through the longest bridge to the second bridge head atom, then to the next longest bridge and finally to the shortest bridge.



8-Methylbicyclo[3.2.1]octane

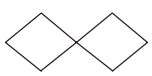

2, 6, 6-Trimethylbicyclo[3.1.1]hept-2-ene

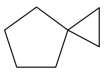

Bicyclo[2.2.1]hept-2-ene

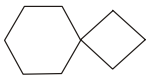


1, 7, 7-Trimethylbicyclo[2.2.1]heptan-2-one

Compounds in which one carbon atom is common to two different rings are called **spiro compounds,** and the common carbon atom is called the **spiro atom**. Their IUPAC name begins with the word spiro followed by brackets containing the number of carbon atoms in *ascending order*, in each ring attached to the common carbon atom and ending with the name of the hydrocarbon corresponding to the total number of carbon atoms in the two rings.


Spiro[3.3]heptane

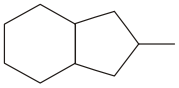

Spiro[2.4]heptane

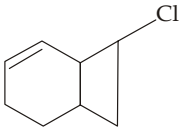

Spiro[3.5]nonane

TEST YOUR UNDERSTANDING - 1.6

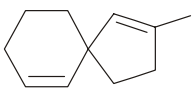
1. Give IUPAC names for the following compounds.

(*a*) 

(*b*) 

(*c*) 

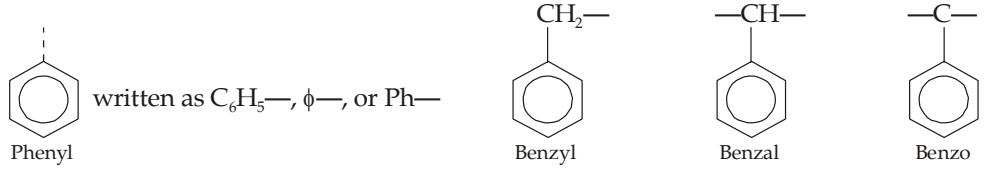
(*d*) 

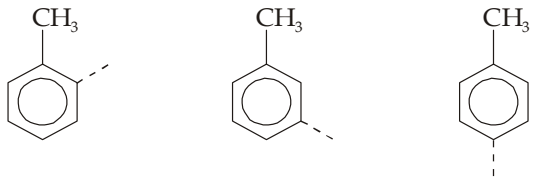
(*e*) 

(*f*) 

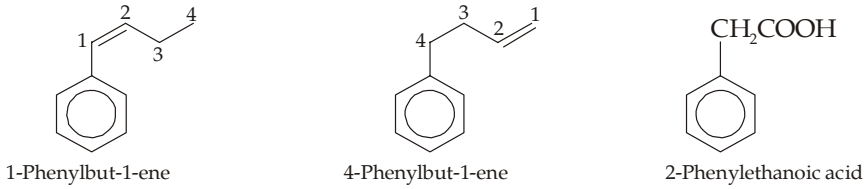
1.12 Nomenclature of Aromatic Compounds

Aromatic compounds are generally named as substituted benzene, however when large and complex groups are attached to the benzene ring, these are named as alkanes, alkenes, etc. and benzene ring is considered as substituent, *i.e.* aryl group. The common aryl groups are



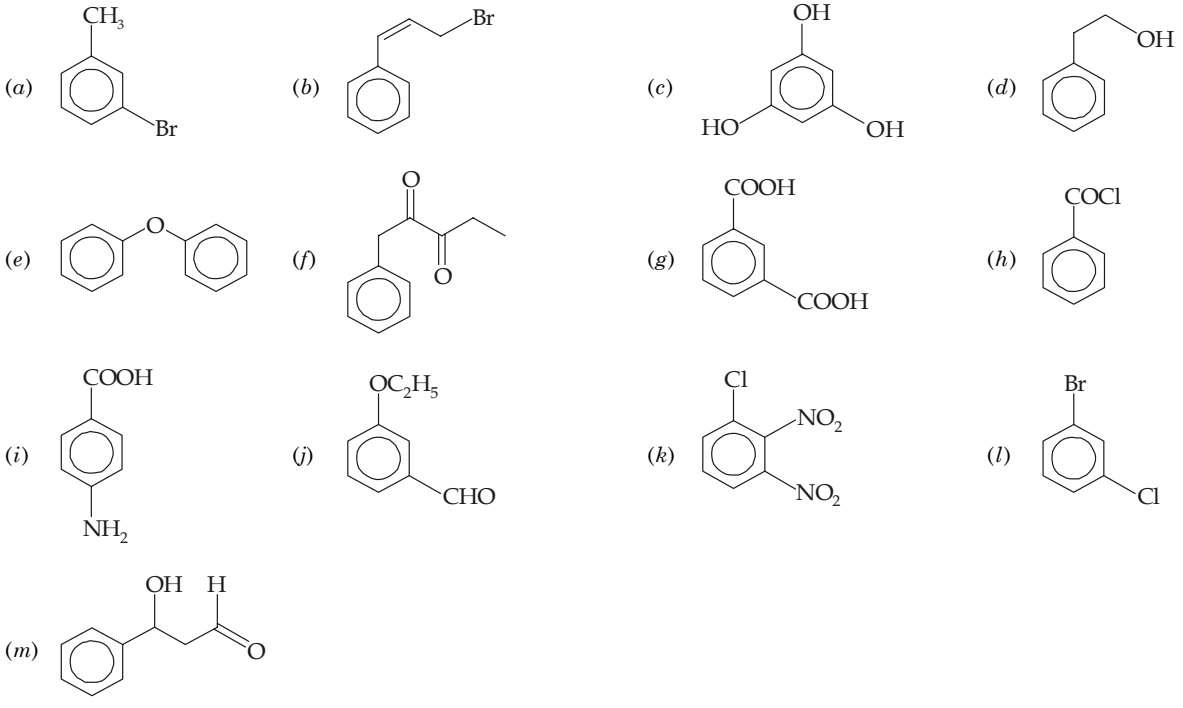


In case benzene ring has a substituted side chain, C_6H_5— is named as a phenyl and the compound is named as an acyclic compound.



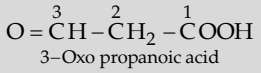
TEST YOUR UNDERSTANDING - 1.7

1. Give IUPAC name for each of the following compounds.

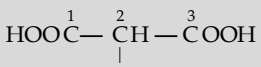


IMPORTANT POINTS

1. In the common system of nomenclature, prefixes iso and neo are used for the groups $Me_2CH–$ (isopropyl) and $Me_3C–$ (*tert*-butyl) groups respectively.
2. Isocyanides or isonitriles or carbylamines have no IUPAC name.
3. The aldehyde group (a terminal group) can be represented by two types of prefixes, i.e., *oxo* (when –CHO is at the end of the carbon chain, here its carbon is counted in the chain) and formyl when –CHO is present as a substituent, its carbon is not counted in the chain). For example,

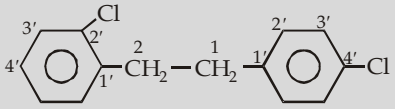


3–Oxo propanoic acid

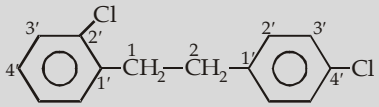


2 – Formylpropane -1, 3 – dioic acid

4. In IUPA**C** system, while using prefixes like carboxy, formyl and oxo, the carbon of the substituent group is not counted in the principal chain.
5. Due to different systems of nomenclature, a given organic compound can have two or more IUPAC names but one IUPAC name can't represent two compounds.

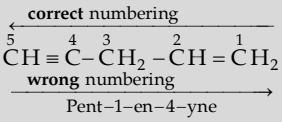


1–(4′–Chlorophenyl)–2–(2′-chlorophenyl)ethane

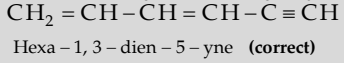


1–(2′–Chlorophenyl)–2–(4′-chlorophenyl)ethane

6. When two or more prefixes consist of identical words, (e.g. chlorophenyl in the given example) the priority for citation is given to that group which contains the lowest locant at the first point of difference.
7. Hydrocarbons containing double as well as triple bond is always named as **alkenyne** and not alkynene. However, in such cases numbering should be done in a way that it follows the lowest locant rule (sum of locants should be minimum). However, if there is a choice, the double bond should be given preference over the triple bond. For example,



Pent–1–en–4–yne



Hexa – 1, 3 – dien – 5 – yne **(correct)**
Hexa – 3, 5 – dien – 1 – yne X**(wrong)**

8. In IUPAC system of nomenclature of **bicyclic compounds**, the numerical prefixes indicating the number of carbon atoms in the two rings and the bridge are written in **descending order**, while in the nomenculature of **spiro** compounds, the numerical prefixes indicating the number of carbon atoms in each ring are written in **ascending order**.

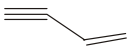
EXERCISE 1.1 (MCQ - ONE option correct)

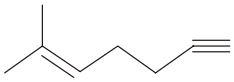
1. The correct IUPAC name for $CH_3CH_2CH_2CH_3$ is
(*a*) *n*-Butane (*b*) Butane
(*c*) Both (*a*) and (*b*) (*d*) None

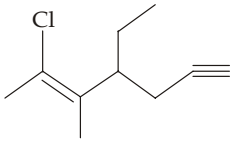
2. Isobutyl group is a ..... alkyl group.
(*a*) primary (*b*) secondary
(*c*) tertiary (*d*) both (*a*) and (*b*)

3. Systematic name for the species, $—CH_2CH_2CH(CH_3)_2$ is
(*a*) Isopentyl (*b*) *sec*-Pentyl
(*c*) 2-Methylbutyl (*d*) 3-Methylbutyl

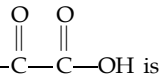
4. Which of the following compound has all the four types (1°, 2°, 3° and 4°) of carbon atoms?
(*a*) 2, 3, 4-Trimethylpentane (*b*) *neo*-Pentane
(*c*) 2, 2, 4-Trimethylpentane (*d*) None of the three

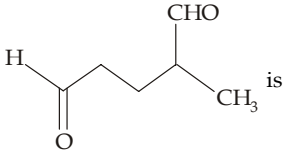
5. IUPAC name of  is
(*a*) 1-Butyne-3-ene (*b*) 1-Butene-3-yne
(*c*) both (*a*) and (*b*) (*d*) Vinylacetylene

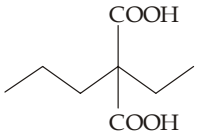
6. Choose the correct IUPAC name for  is
(*a*) 2-Methylhept-6-yn-2-ene (*b*) 2-Methylhept-2-en-6-yne
(*c*) 6-Methyl-5-hepten-1-yne (*d*) 6-Methylhept-1-yn-5-ene

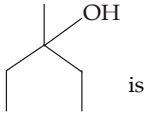
7. The correct IUPAC name for  is
(*a*) 2-Chloro-4-ethyl-3-methyl-6-heptyn-2-ene
(*b*) 6-Chloro-4-ethyl-5-methyl-5-hepten-1-yne
(*c*) 1-Chloro-1, 2-dimethyl-3-ethylhex-1-en-5-yne
(*d*) 1-Chloro-3-ethyl-1, 2-dimethylhex-1-en-5-yne

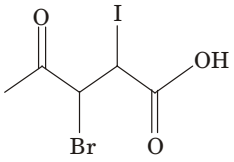
8. The most appropriate IUPAC name for $CH_3CH_2OCH_2CH_2Cl$ is
(*a*) ethyl chloroethyl ether (*b*) 1-Chloro-2-ethoxyethane
(*c*) 2-Ethoxyethyl chloride (*d*) 2-Chloro-1-ethoxyethane

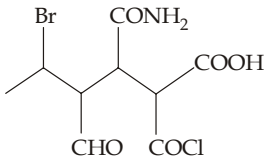
9. IUPAC name for  is
(*a*) Formylmethanoic acid (*b*) 2-Oxoethanoic acid
(*c*) Glyoxalic acid (*d*) 2-Oxomethanoic acid

10. The IUPAC name for  is
(*a*) 2-Formylpentanol (*b*) 2-Methylpentanedial
(*c*) 2-Methyl-4-oxopentanal (*d*) 2, 4-Diformylbutane

11. The IUPAC name for  is
(*a*) 2-Ethyl-2-carboxypentanoic acid
(*b*) 2-Carboxy-2-ethylpentanoic acid
(*c*) 2-Propyl-2-ethylpropanedioic acid
(*d*) 2-Ethyl-2-propylpropanedioic acid

12. IUPAC name for the compound  is
(*a*) 2-Ethyl-1-butanol-2 (*b*) Diethylmethylmethanol
(*c*) 1-Methyl-1-ethylpropanol (*d*) 2-Ethylbutanol

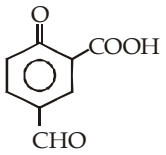
13. IUPAC name for the given structure is 
(*a*) 4-Carboxy-3-bromo-4-iodopentanoic acid
(*b*) 3-Bromo-2-iodo-4-ketopentanoic acid
(*c*) 4-Keto-3-bromo-2-iodopentanoic acid
(*d*) 2-Iodo-3-bromo-4-ketopentanoic acid

14. IUPAC name for the compound 
should be
(*a*) 5-Bromo-3-carbamoyl-2-chloroformyl-4-formylhexanoic acid
(*b*) 2-Bromo-4-carbamoyl-5-chloroformyl-3-formylhexanoic acid
(*c*) 2-Chloroformyl-3-carbamoyl-4-formyl-5-bromohexanoic acid
(*d*) 4-Formyl-2-chloroformyl-3-carbamoyl-5-bromohexanoic acid

15. IUPAC name for $CH_3CON(Br)Cl$ is
(*a*) N-Bromo-N-chloroethanamide
(*b*) N-Chloro-N-bromoethanamide
(*c*) 1-Bromo-1-chloroethanamide
(*d*) N-Bromo-N-chloroacetamide

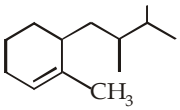
16. Which of the following statement is incorrect ?
(a) –COCl may be represented as carbonyl halide
(b) –COCl may be represented as chloroformyl
(c) –CN may be represented as nitrile, cyano and carbonitrile
(d) None of these

17. Pick up the correct IUPAC name in the following :



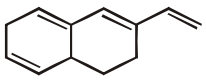
(a) 3-formyl-5-oxocyclohexane carboxylic acid
(b) 5-formyl-2-oxocyclohexane carboxylic acid
(c) 2-carboxy-4-formylcyclohexanone
(d) 3-carboxy-4-oxocyclohexane carbaldehyde

18. Pick up the correct IUPAC name in the following :



(a) 2-methyl-3-(2′, 4′-dimethylbutyl)cyclohexene
(b) 1-methyl-6 (2′, 4′-dimethylbutyl)cyclohexane
(c) 1-methyl-2 (2′, 4′ - dimethylbutyl)cyclohexene
(d) (1'-methylcyclohexenyl)2, 4-dimethylbutane

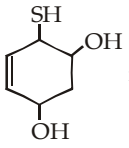
19. Pick up the correct IUPAC name in the following :



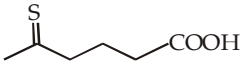
(a) 1-vinyl–5, 8, 9, 10 – tetrahydronaphthalene
(b) 2-ethenylbicyclo [4.4.0] deca–1, 5, 8 – triene
(c) 2-vinyl – 3, 4, 7, 10 – tetrahydronaphthalene
(d) 3-ethenylbicyclo [4.4.0] deca -3, 5, 8-triene

20.  COOH. The correct IUPAC name for the structure is

(a) cyclohexanoic acid
(b) cyclohexane carboxylic acid
(c) both
(d) none

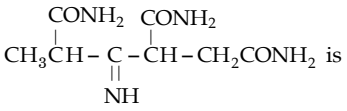
21. The correct IUPAC name for  is

(a) 3, 5-dihydroxy-6-mercaptocyclohexene
(b) 4, 6-dihydroxy-3-mercaptocyclohexene
(c) 3-hydroxy-4-mercaptocyclohex-5-enol
(d) 3-hydroxy-6-mercaptocyclohex-4-enol

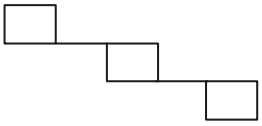
22. The IUPAC name for  is

(a) 5-thiohexanoic acid
(b) 5-thiohexanoic acid
(c) 5-sulphohexanoic acid
(d) None is correct

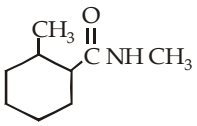
23. The secondary functional group in



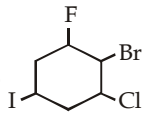
(a) carbanoyl (b) imino
(c) both (d) none

24. The correct IUPAC name for 

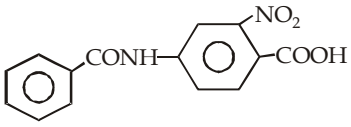
(a) 1, 4-dicyclobutylcyclobutane
(b) 1, 1', 3', 1"-tercyclobutane
(c) *p*-dicyclobutylcyclobutane
(d) 1, 3', 1"-tricyclobutane

25. The IUPAC name of the compound : 

(a) 1-methyl-2-N-methylcyclohexanecarboxamide
(b) 1-(N-methylcarbamoyl)-2-methylcyclohexane
(c) 2-(N-,ethylcarbamoyl)-1-methylcyclohexane
(d) N, 2-dimethylcyclohexanecarboxamide

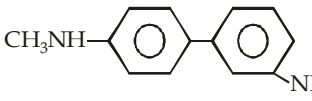
26. The correct IUPAC name for  is :

(a) 2-bromo-1-chloro-3-fluoro-5-iodocyclohexane
(b) 2-bromo-3-chloro-1-fluoro-5-iodocyclohexane
(c) 1-bromo-6-chloro-2-fluoro-4-iodocyclohexane
(d) 1-bromo-2-chloro-6-fluoro-4-iodocyclohexane

27. The correct IUPAC name for 

is

(a) 4-benzamido-2-nitrobenzoic acid
(b) 4-benzoylamino-2-nitrobenzoic acid
(c) 4-benzoylamino-6-nitrobenzoic acid
(d) N-(3-carboxy-4-nitrophenyl) Benzamide

28.  has IUPAC name

(a) 3, 4'-bis (N-methylamino) biphenyl
(b) 3, 4'-bis (methylamino) biphenyl
(c) *p*-methylamino-*m*-methylaminobiphenyl
(d) 3, 4'-bis (aminomethyl) biphenyl

29. The IUPAC name of C_6H_5COCl is

(a) benzene chloro ketone
(b) benzoyl chloride
(c) chloro phenyl ketone
(d) benzene carbonyl chloride

EXERCISE 1.2 (MCQ 1 or >1 option correct, Passage based, Matching, A/R)

DIRECTIONS for Q. 1 to Q. 7 : Multiple choice questions with one or more than one correct option(s).

1. Which of the following statements are true about a homologous series?
(a) Adjacent members of a group differ by a mass of 14
(b) Adjacent members of a group differ by one $-CH_2$ group
(c) members of a homologous series can be prepared by the same general methods
(d) members of a homologous series have the same physical and chemical properties

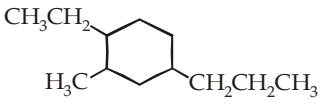
2. Which of the following compounds will have only primary and tertiary carbon?
(a) Pentane (b) 2-Methylbutane
(c) 2, 3-Dimethylbutane (d) 2-Bromo-2-methylpropane

3. Which of the following compounds will have only primary and secondary carbon?
(a) Propane (b) 2,2,3-Trimethylpentane
(c) 2-Methylpropane (d) n-Propylbromide

4. Which of the following statements are true?
(a) Primary carbon atom is bonded to one or no other carbon atom
(b) Secondary carbon atom is bonded to two other carbon atoms
(c) Tertiary carbon atom is bonded to three other carbon atoms
(d) None of above

5. The IUPAC name of the compound $CH_3CHOH.CH_2CH_3$ is
(a) 1-Methylpropanol-1 (b) 2-Butanol
(c) Butan-2-ol (d) Butanol-2

6. The IUPAC name of the compound



(a) 1-Ethyl-2–methyl-4-propylcyclohexane
(b) 2-Ethyl-1-methyl-5-propylcyclohexane
(c) 4-Ethyl-3-methyl-1-propylcyclohexane
(d) All the three

7. The IUPAC name of the compound 
(a) 3-Bromo-3'-chloro-1, 1'-bicyclobutane
(b) 1-Bromo-1'-chloro-4, 4'-bicyclobutane
(c) 1-Bromo-3 (3'-chlorocyclobutyl) cyclobutane
(d) 4-(4'-Chlorocyclobutyl)-1-bromocyclobutane

DIRECTIONS for Q. 8 to Q. 19 : Read the following passages and answer the questions that follows :

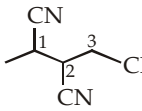
PASSAGE 1

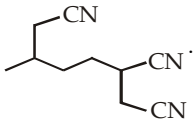
When the compound contains more than two similar groups all of which are present on the principal chain, then none of these groups are counted in the principal chain ; and special suffixes are used to indicate the functional group, *viz.*

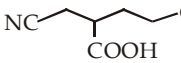
Functional group	*Special suffix*	*Functional group*	*Special suffix*
–COOH	–carboxylic acid	–COX	–carbonyl halide
$-CONH_2$	–carboxamide	–CHO	–carbaldehyde
–COOR	R----carboxylate	–CN	–carbonitrile

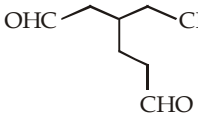
When the compound contains more than two similar terminal groups, all of which are not directly linked to the principal chain, then that longest principal chain should be selected which contains two such similar terminal groups at its two ends. Here the terminal groups are counted in the chain, while the third, present on side chain, is considered as a substituent.

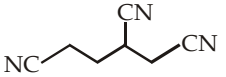
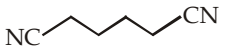
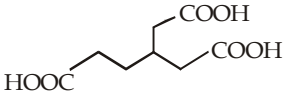
8. This rule can't be applied on the compound containing
(a) aldehydic group
(b) nitrile group
(c) ketonic group
(d) it can be applied to all the three

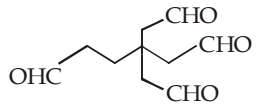
9.  The IUPAC name of this compound is
(a) 2, 3-Dicyanobutanecarbonitrile-4
(b) 1-Methylpropane-1, 2, 3-tricarbonitrile
(c) Butane-1, 2, 3-tricarbonitrile
(d) 2, 3-Dicyanocarbonitrile

10.  The IUPAC name of this compound is
(a) 2-methylhexane-1, 5, 6-tricarbonitrile
(b) 5-methylhexane-1, 2, 6-tricarbonitrile
(c) 3-methyl-6-cyanoctan-1, 8-dinitrile
(d) 6-methyl-3-cyanoctan-1, 8-dinitrile

11.  The IUPAC name of this compound is
(a) 3-Carboxy-4-cyanobutanoic acid
(b) 2-Cyanomethylbutane-1, 4-dioic acid
(c) 3-Cyanomethylbutane-1, 4-dioic acid
(d) 3, 5-Dicarboxypentanenitrile

12.  The IUPAC name of this compound is
(a) pentane-1, 4, 5-tricarbaldehyde
(b) 3-(formylmethyl) hexane-1, 6-dial
(c) 4-(formylmethyl) hexane-1, 6-dial
(d) 4, 4(diformylmethyl) butanal

13. Which of the following is considered as a derivative of hexane?
(i)  (ii) 
(iii) 

(iv) 

(a) (i) and (iii) (b) (ii) and (iii)
(c) (ii), (iii) and (iv) (d) all the four

PASSAGE 2

Although most of the IUPAC rules of open chain compounds are applied to alicyclic compounds, certain points deserve special attention.

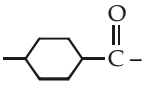
(i) In cycloalkenes, the numbering should be done in a direction that gives the lower number for the substituent attached on the double bond.

(ii) In case the alicyclic compound has functional group in the ring as well as in the side chain, the compound is considered as a derivative of that part in which principal functional group lies.

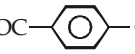
On the basis of the following seniority table for some of the principal groups, answer the questions given below.

Seniority table for principal groups

Group	Prefix name	Suffix name
–COOH	Carboxy–	–oic acid
–COOR	Alkyl-oxycarbonyl	–alkyl---oates
–COX	Haloformyl–	–oyl halide
–$CONH_2$	Carbamoyl–	amide
–CHO	Formyl–	–al
–OH	Hydroxy–	–ol
–X (halogen)	Halo–	–
R—	Alkyl–	–

14.  its correct IUPAC name should be

(a) 4-acetamidocyclohexanol
(b) 4-(N-methylamido)cyclohexanol
(c) 4-hydroxy-N-methylcyclohexanecarboxamide
(d) 4-hydroxycyclohexaneacetamide

15.  . The correct IUPAC name for the structure is :

(a) 4-Carbomylbenzoic acid (b) 4-Amidobenzoic acid
(c) 4-Carboxybenzamide (d) 4-Acetamidobenzoic acid

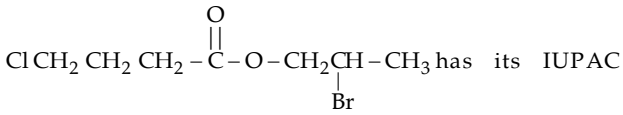
16.  . The correct IUPAC name for the structure is :

(a) 1, 2-Dichlorocyclohexene (b) 1, 6-Dichlorocyclohexene
(c) 2, 3-Dichlorocyclohexene (d) any of the three

17. Accoding to IUPAC system,

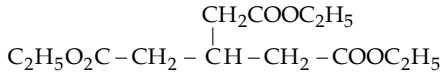
 is named as :

(a) 4-(3-Carboxy-2-methylpropyl)cyclohex-2-enol-1
(b) 4-(4'-Hydroxycyclohex-2-enyl)-3-methylbutanoic acid
(c) 4-Hydroxycyclohexenyl-3-methylbutanoic acid
(d) 4-(4'-Hydroxycyclohex-2'-enyl)-3-methylbutanoic acid

18.  has its IUPAC name as

(a) 4-Chlorobutyl-2-bromopropanoate
(b) 2-Bromopropyl-1-chlorobutanoate
(c) 2-Bromopropyl-3-chlorobutanoate
(d) 2-Bromopropyl-4-chlorobutanoate

19. Name the prefix in the following compound :



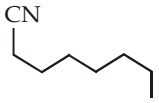
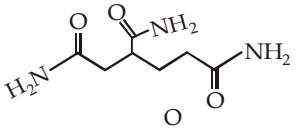
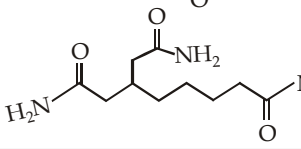
(a) Ethylacetato (b) Ethylacetoxy
(c) Ethyloxycarbonylmethyl (d) Ethoxycarbonylmethyl

DIRECTIONS for Q. 20 to Q. 21 : The following questions are matching type questions. Match Column I with Column II

20.

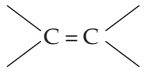
Column I		Column II
(A) Prefix	(a)	carbonyl chloride
(B) Suffix	(b)	carbamoyl
(C) –CN	(c)	carbonitrile
(D) –CHO	(d)	carbaldehyde
(E) –COCl	(e)	chloroformyl

21.

Column I		Column II
(A) 	(a)	carbamoyl-methyl is present
(B) 	(b)	derivative of hexane
(C) 	(c)	name as amide

EXERCISE 1.3 (Subjective Problems)

1. Give the structural formula for a three-carbon compound containing each of the following functional groups.

(*i*)  (*ii*) —C ≡ C—

(*iii*) —C ≡ N (*iv*) —COOH

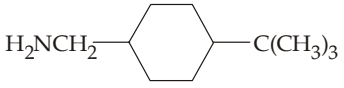
2. Provide a structural formula for the compound with the smallest number of carbons that is

(*a*) a cyclic alcohol (*b*) an amide,
(*c*) a cyclic ether, and (*d*) an alkenylcarboxylic acid

3. Give the bond line structure for the following compounds.

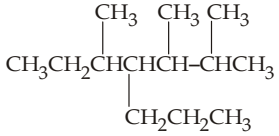
(*a*) $CH_2OH(CH_2)_3COCH_3$

(*b*) $CH_3CH_2NHCOCH_2CH(CH_3)_2$

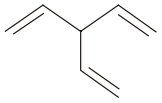
(*c*) 

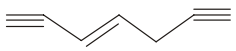
(*d*) $CH_2 = CMe_2$

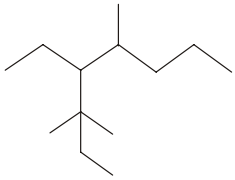
4. Give IUPAC names for the compounds with following structure.

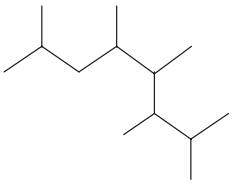
(i) 

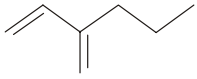
(ii) $CH_3CH_2OCH_2CH_2Cl$ **(iii)** $CH_3CH_2C \equiv CCH_2CHO$

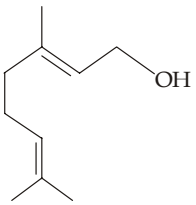
(iv) 

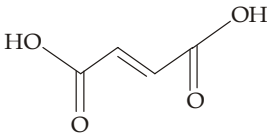
(v) 

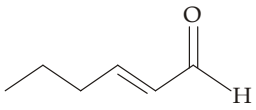
(vi) 

(vii) 

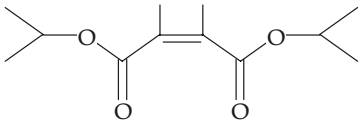
(viii) 

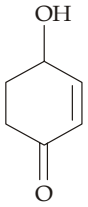
(ix) 

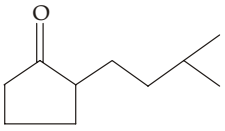
(x) 

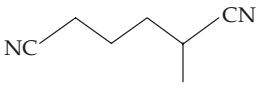
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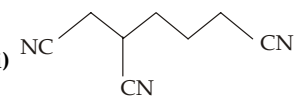
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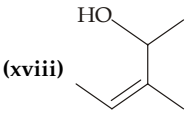
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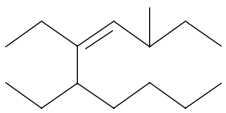
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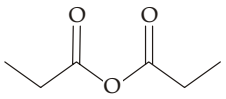
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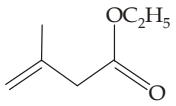
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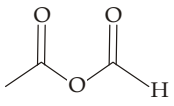
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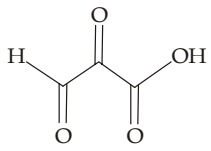
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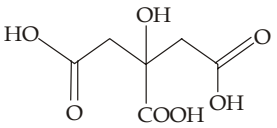
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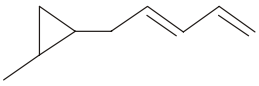
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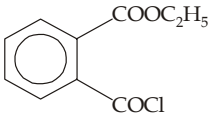
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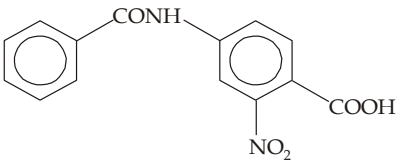
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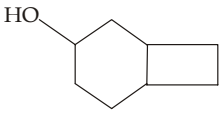
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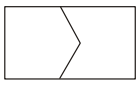
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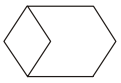
(xxvii) 

(xxviii) 

(xxix) 

(xxx) 

(xxxi) 

(xxxii) 

5. Draw acceptable structure to each of the following compounds.

(*a*) 3-Ethyloctene (*b*) 5-Isobutyl-1-heptene
(*c*) 2-Cyclopropyl-1-heptene (*d*) 3-Ethyl-2-methylhexane
(*e*) 5-*tert*-Butylnonane
(*f*) 2-(1-Cyclobutenyl)-1-hexene
(*g*) Ethyl 2-chloropropanoate
(*h*) Octa-1-ene-4yne (*i*) Bicyclo[4.2.0]octane
(*j*) Spiro[4.5]decane

SOLUTIONS

TEST YOUR UNDERSTANDING - 1.1

1. (*a*) C_{11} (*b*) C_{31} (*c*) C_{28}

2.

	pri-Prefix	*sec.*-Prefix	Word root	*pri*-Suffix	*sec.*Suffix
(*a*)	—	Chloro	but	ane	ol
(*b*)	—	Methyl	but	ene	al
(*c*)	—	Amino	but	yne	oic acid
(*d*)	—	Methoxy	eth	ane	—
(*e*)	Cyclo	bromo	hex	ane	—

3.

	pri-Prefix	*sec.*-Prefix	Word root	*pri*-Suffix	*sec.*Suffix
(*a*)	—	—	but	ene	ol
(*b*)	—	Oxo	but	ane	oic acid
(*c*)	—	Methyl, Oxo	but	ane	oic acid
(*d*)	—	—	pent	ane	al
(*e*)	—	Carbamoyl-methyl —CH_2CONH_2	pent	ane	amide
(*f*)	—	Formylmethyl —CH_2CHO	hex	ane	al

4. (*a*)

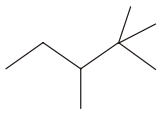
(*i*) $CH_3\overset{1°}{C}H_2CH_2CH_2CH_2-$ (*ii*) $CH_3CH_2\overset{1°}{C}HCH_2-$ (CH_3 branch)

(*iii*) $CH_3CHCH_2\overset{1°}{C}H_2-$ (CH_3 branch) (*iv*) $CH_3\overset{1°}{C}CH_2-$ (CH_3 branch)

(*v*) $CH_3CH_2CH_2\overset{2°}{C}HCH_3$ (*vi*) $(CH_3)_2CH_2\overset{2°}{C}HCH_3$

(*vii*) $CH_3CH_2\overset{2°}{C}HCH_2CH_3$ (*iv*) $CH_3\overset{3°}{C}CH_2CH_3$ (CH_3 branch)

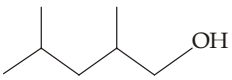
(*b*) $\overset{1°}{C}H_3-\overset{2°}{C}H_2-\overset{3°}{C}H(CH_3)-\overset{4°}{C}(CH_3)_2-CH_3$ or



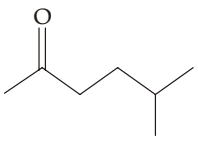
(2, 2, 3-Trimethylpentane)

TEST YOUR UNDERSTANDING - 1.2

1. (*a*)



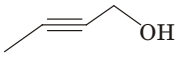
(*b*)



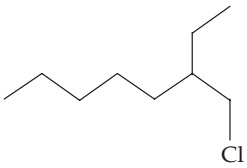
(*c*)



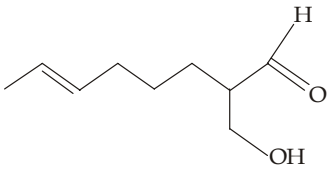
(*d*)



(*e*)



(*f*)



TEST YOUR UNDERSTANDING - 1.3

1. (*a*) 2-Isopropylbut-2-enoic acid

(*b*) Pent-3-ynal

(*c*) 2-Ethylprop-2-enoyl chloride

(*d*) Bis (2-chloroethyl)amine

(*e*) 3-Bromomethyl-4-chloromethylhexane (bromomethyl should get lower locant than chloromethyl because former comes first in alphabet order).

(*f*) 2-(3′-Chloropropyl)but-2-enol (Main chain must contain principal functional group, —OH as well as C = C).

(*g*) Ethyl 3-methyl-5-oxopentanoate (– $COOC_2H_5$ is the principal functional group, —CHO group is present at the end of the chain, so it is counted in the main chain and given the prefix —*oxo*, had it been in the middle of the chain its prefix would have been *formyl*, see example below).

(*h*) Ethyl 3-formylpentanoate.

(*i*) 3-Cyano-6-ketoheptanal (—CHO has priority over >C = O as well as —CN)

(*j*) *tert*-Butyl 3-oxo-6-chloroformylheptanoate (—$COOCMe_3$ is the principal functional group).

(*k*) 4-Ethyl-3-mercapto-N-ethylheptanamide (—CONHR is the principal functional group and the longest chain has 7 carbon atoms).

(*l*) Butane-1, 2, 4-tricarbaldehyde (when more than two —CHO groups are present on the main chain, these are not counted in the principal chain).

2. (*a*) 2,2,5-Trimethylheptane

(*b*) 4-Ethyl-3,3-dimethylheptane.

(*c*) 5-(1′-Methylpropyl)-6-(2′-methylpropyl)decane

(*d*) 2,3,5-Trimethyl-4-propylheptane (in case two or more chains are of equal length, then the chain with greater number of side chains is selected as the principal chain).

(*e*) 6-Methylhepta-1,4-diene

(*f*) Hept-3-ene-1,6-diyne (-*ene* is written first because it comes first in alphabetic order).

(*g*) Hepta-1,6-dien-3-yne

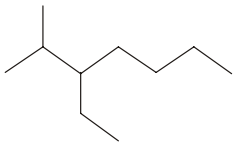
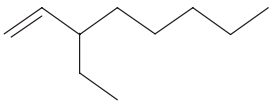
(*h*) Cyclododecane (it is having 12 C's)

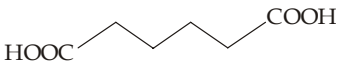
(*i*) 3-Hydroxy-2,4-diketo-5-methylhexanedioic acid

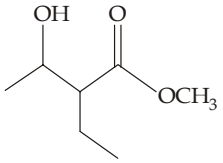
(*j*) 6-Hydroxy-5-oxo-2-heptenenitrile (—CN has priority over >C = O as well as —OH)

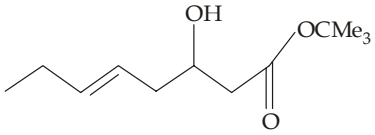
(*k*) 4-Hydroxy-7-oxo-9-methyl-2,5,8-decatrienoic acid
(*l*) 3, 7-Dimethyl-2,6-octadienal
(*m*) Cyclohexylmethanenitrile (Cyclohexanecarbonitrile is its chemical abstract name)
(*n*) Cyclopentanecarboxamide

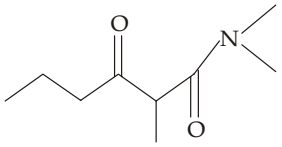
TEST YOUR UNDERSTANDING - 1.4

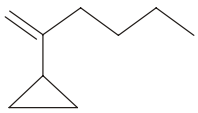
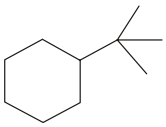
1. (*a*)  (*b*) 

(c) 

(*d*) 

(*e*) 

(*f*) 

(*g*)  (*h*) 

TEST YOUR UNDERSTANDING - 1.5

1. (*a*) 4-Chloro-2-ethyl-1-methylcyclohexane
(*b*) 1-Cyclobutylpentane
(*c*) 1,3-Dicyclohexylpropane
(*d*) 4-Ethyl-1-methylcyclohexene
(*e*) 4-(1-Chloro-1-methylpropyl)cyclohexene
(*f*) Ethyl 3-oxocyclohexane-1-carboxylate

TEST YOUR UNDERSTANDING - 1.6

1. (*a*) Bicyclo[1.1.0]butane
(*b*) 8-Methylbicyclo [4.3.0] nonane
(*c*) 8-Chlorobicyclo [4.2.0]oct-2-ene
(*d*) Spiro [2.2]pentane
(*e*) 2-Methylspiro [4.5]deca-1,6-diene
(*f*) 1,1′-Bicyclopropane.

TEST YOUR UNDERSTANDING - 1.7

1. (*a*) 3-Bromotoluene
(*b*) 1-Phenyl-3-bromopropene
(*c*) Benzene-1,3,5-triol
(*d*) 2-Phenylethanol
(*e*) Phenoxybenzene
(*f*) 1-Phenylpentan-2, 3-dione
(*g*) Benzene-1,3-dicarboxylic acid
(*h*) Benzoyl chloride
(*i*) 4-Aminobenzoic acid
(*j*) 3-Ethoxybenzaldehyde
(*k*) 1-Chloro-2,3-dinitrobenzene (chloro is given lower locant as it comes before nitro in alphabetic order)
(*l*) 1-Bromo-3-chlorobenzene (Br given lower locant)
(*m*) 3-Hydroxy-3-phenylpropanal.

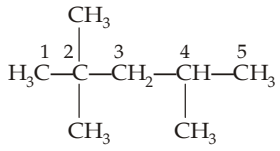
EXERCISE 1.1

1	(b)	**6**	(c)	**11**	(d)	**16**	(d)	**21**	(d)	**26**	(a)
2	(a)	**7**	(b)	**12**	(a)	**17**	(b)	**22**	(b)	**27**	(b)
3	(d)	**8**	(b)	**13**	(b)	**18**	(b)	**23**	(b)	**28**	(a)
4	(c)	**9**	(b)	**14**	(a)	**19**	(b)	**24**	(b)	**29**	(b)
5	(b)	**10**	(b)	**15**	(a)	**20**	(b)	**25**	(d)		

1. The prefix *n*- is not part of the IUPAC system, hence the correct name for $CH_3(CH_2)_2CH_3$ is *butane*, *n*-butane is its common name, although now-a-days, it too is also acceptable to IUPAC system.

2. Isobutyl (Me_2CHCH_2—) is a primary alkyl group because its potential point of attachment is a primary carbon.

3. Numbering should be done with the end having free valency; no matter locant gets higher number.

4. 

C_1 and C_5 are 1°, C_3 is 2°, C_4 is 3°, and C_2 is 4°.

5. A compound containing both a double bond and a triple bond is named as an *enyne*. Numbering is done in a manner which gives the lower locant to the one nearer the end of the chain. In case, both double and triple bonds are located at similar positions with respect to the two ends of the chain, double bond is assigned lower locant because *ene* comes first than *yne*.

7. Numbering should be done from that end of the chain in which double or triple bond gets lower locant, no matter sum of locants may be higher.

8. Among two substituents, lower locant is assigned to that substituent which comes first in alphabetical order.

9. When —CHO is present at the end of a carbon chain, it should be counted in the main chain. Further, here —CHO is not the principal functional group, hence its presence is indicated by the prefix *-oxo*.

10. When two similar carbon-bearing monovalent groups are present in the main chain, both should be counted in the main chain.

11. Since both of the —COOH groups are present on the main carbon chain, these should be counted. Further, *ethyl* should be written first because it comes first in alphabetic order than propyl.

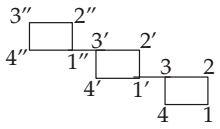
12. Here —OH is the functional group.

13. Here —COOH is the primary functional group, all others are substituents.

14. Here —COOH is the primary functional group, all other groups are substituents, hence indicated by their corresponding prefixes.

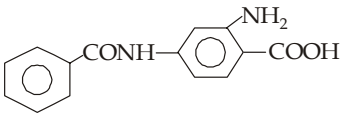
15. When any group is present on an atom other than C, it is indicated by placing such atom like N-methyl, O-methyl, S-methyl, N-bromo etc.

24. Here ter-- is used to indicate Here the numbering is shown

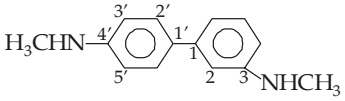


25. The position of two CH_3 (methyl) groups is indicate by N, 2, one - CH_3 is attached to N-atom of $-\overset{\overset{O}{\|}}{C}-\underset{|}{N}H$ group and other at positive number 2 in the ring.

27. The compound formula be



28. The numbering is shown below



Since $-CH_3$ is attached to N– so it is (Methylamine)

29. Carboxylic acids are named as acid chlorides.

EXERCISE 1.2

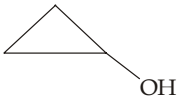
> 1 CORRECT OPTION	1	(a, b, c)	2	(c, d)	3	(a, d)	4	(a, b, c)	5	(b, c, d)	6	(c)
	7	(a,c)										
PASSAGE 1	8	(c)	9	(c)	10	(b)	11	(b)	12	(b)	13	(c)
PASSAGE 2	14	(c)	15	(a)	16	(b)	17	(d)	18	(d)	19	(c)
MATCHING TYPE QUESTIONS	20	(A)-(b); (B)-(c, d); (C)-(c); (D)-(d); (E);(a, e)										
	21	(A)-(b); (B)-(c); (C)-(a,b,c)										

EXERCISE 1.3

1. (*a*) $CH_3CH = CH_2$ (*b*) $CH_3C \equiv CH$

(*c*) $CH_3CH_2C \equiv N$ (*d*) CH_3CH_2COOH

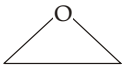
2. (*a*)



(*b*)

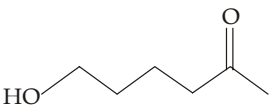


(*c*)

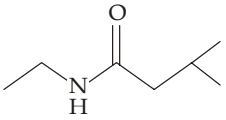


(*d*) $H_2C = CHCOOH$

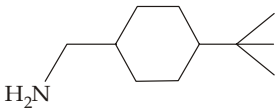
3. (*a*)



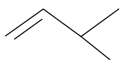
(*b*)



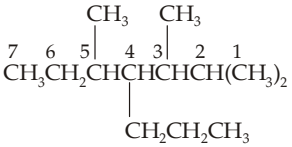
(*c*)



(*d*)

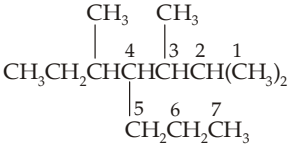


4. (i)



2, 3, 5-Trimethyl-4-propylheptane

Not as



(This numbering is wrong because here number of substituents is less)

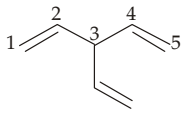
(ii) $CH_3CH_2O\overset{2}{C}H_2\overset{1}{C}H_2Cl$

1-Chloro-2-ethoxyethane

(iii) $\overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}\equiv\overset{3}{C}\overset{2}{C}H_2\overset{1}{C}HO$

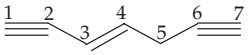
Hex-3-ynal

(iv)



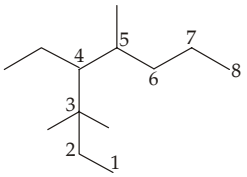
3-Vinylpenta-1, 4-diene

(v)



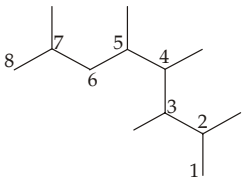
Hept-3-ene-1, 6-diyne

(vi)



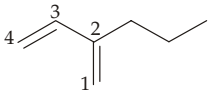
4-Ethyl-3, 3, 5-trimethyloctane

(vii)



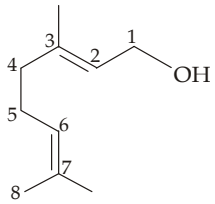
2, 3, 4, 5, 7-Pentamethyloctane

(viii)



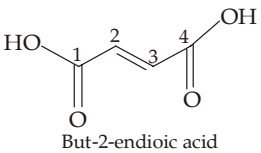
2-Propyl-1, 3-butadiene

(ix)



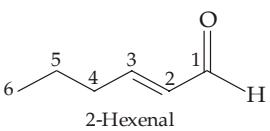
3, 7-Dimethyl-2, 6-octadienol

(x)



But-2-endioic acid

(xi)



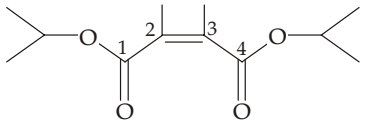
2-Hexenal

(xii)



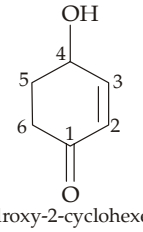
2, 4-Hexdiyne

(xiii)



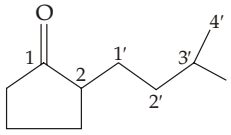
Di-isopropyl-2, 3-dimethyl-2-buten-1, 4-dioate

(xiv)



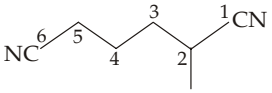
4-Hydroxy-2-cyclohexenone

(xv)



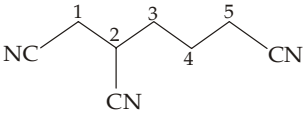
2-(3′-Methylbutyl)cyclopentanone

(xvi)



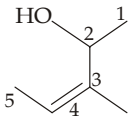
2-Methylhexanedinitrile

(xvii)



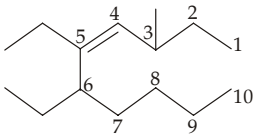
Pentane-1, 2, 5-tricarbonitrile

(xviii)



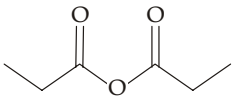
3-Methylpent-3-enol-2

(xix)



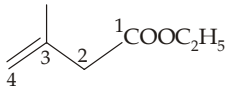
5, 6-Diethyl-3-methyldec-4-ene

(xx)



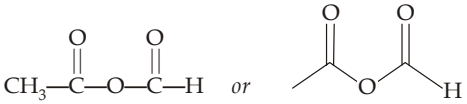
Propanoic anhydride

(xxi)

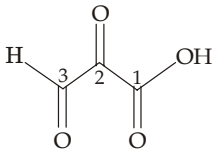


Ethyl-3-methylbut-3-enoate

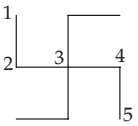
(xxii)



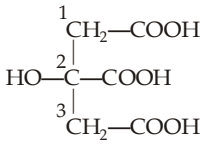
Ethanoicmethanoic anhydride

(xxiii) 

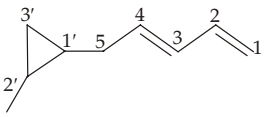
2, 3-Dioxopropanoic acid

(xxiv) 

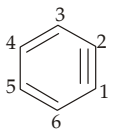
3, 3-Diethylpentane

(xxv) 

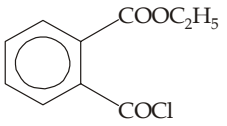
2-Hydroxypropane-1, 2, 3-tricarboxylic acid

(xxvi) 

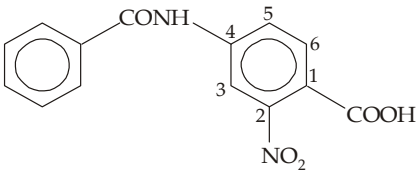
5-(2′-Methylcyclopropyl)penta-1, 3-diene

(xxvii) 

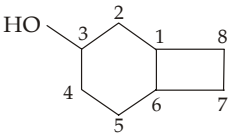
1, 2-Didehydrobenzene

(xxviii) 

Ethyl 2-(chloroformyl)benzoate

(xxix) 

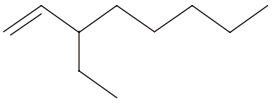
4-(1-Benzoylamino) 2-nitrobenzoic acid

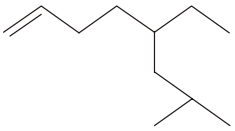
(xxx) 

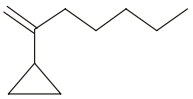
Bicyclo [4.2.0] octan-3-ol

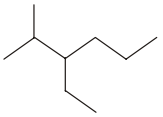
(xxxi) Bicyclo [2.2.1]heptane

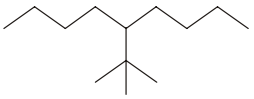
(xxxii) Bicyclo [3.1.1]heptane.

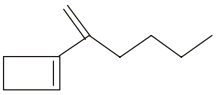
5. (*a*) 

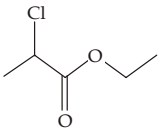
(*b*) 

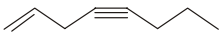
(*c*) 

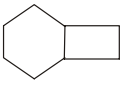
(*d*) 

(*e*) 

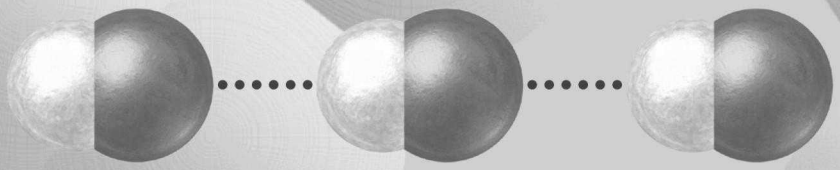
(*f*) 

(*g*) 

(*h*) 

(*i*) 

(*j*) 



H—F ····· H—F ····· H—F

2 Basic concepts in Organic Chemistry

CHAPTER HIGHLIGHTS

2.1 The Covalent Bond
2.2 Effect of Unshared Pair of Electrons
2.3 Electronegativity and Polarity of Bonds
2.4 Polarity of Molecules
2.5 Other Factors for Polarity of Covalent Bonds
2.6 Types of Bonding Among Covalent Molecules (Intermolecular Forces)
2.7 Hydrogen Bonding
2.8 Acids and Bases
2.9 Relative Strength of Acids and Bases
2.10 Structural Isomerism
EXERCISES
SOLUTIONS

2.1 The Covalent Bond

We know that organic compounds are carbon compounds. Electronic configuration of carbon in the ground state (Z = 6 ; $1s^2$, $2s^2p^2$) indicates it to be divalent. However, the tetravalency of carbon atom was explained by the fact that carbon atom forms bonds only in excited state ($1s^2$, $2s^1p^3$). Further this electronic configuration suggests that the tetravalent carbon should have two types of bonds ; one bond is formed by electron present in non-directional orbital (2*s*) and other three identical bonds are formed by electrons present in directional orbital (2*p*). However, all the four bonds formed by carbon in a molecule like methane are equivalent. Finally, it was observed that the carbon atom does not take part in bond formation as such but its outermost orbitals, *i.e.* one 2*s* and three 2*p* orbitals mix or merge together to form new orbitals known as **hybrid orbitals** and the phenomenon in turn is known as **hybridization.** Three types of hybridization are found in organic compounds, namely sp^3, sp^2 and *sp*. It is assumed that students are familiar with the three types of hybridization (sp^3, sp^2 and *sp*) found in alkanes, alkenes, and alkynes respectively, and also with the sigma (σ) and pi (π) bonds.

Type	*Bond angle*	*Geometry*	*Number of unused p orbital(s)*	*% of s orbital*
sp^3	109.28′	Tetrahedral	0	25
sp^2	120°	Trigonal planar	1	33.3
sp	180°	Linear	2	50

POINTS TO REMEMBER

(*i*) Hybrid orbitals (*a*) can overlap better because its head is larger than either lobe of the *p* AO and (*b*) provide greater bond angles, thereby minimize the repulsion between pairs of electrons ; and hence bond formed by a hybrid orbital is more stable than that formed by an atomic orbital.

(*ii*) Since *s* orbitals are closer to nucleus than *p* orbitals, it is reasonable to expect that **greater the *s* character of an orbital the smaller it is.** Thus the decreasing order of the size of the three hybrid orbitals is opposite ($sp^3 > sp^2 > sp$) to that of the decreasing percentage of *s* character in the three hybrid orbitals (given above in the table).

(*iii*) On the basis of the size of the hybrid orbitals, *sp* **orbital should form the shortest and** sp^3 **orbital the longest bond with other atom.** This is evident by the C—H and C—C bond lengths in alkanes (formed by sp^3 hybridized carbon atoms), alkenes (formed by sp^2 hybridized carbon atoms) and alkynes (formed by *sp* hybridized carbon atoms).

Bond type (C—H)	***Bond length***	***Bond type (C—C)***	***Bond length***
sp^3—*s* (alkanes)	1.112 Å	sp^3—sp^3 (alkanes)	1. 54 Å
sp^2—*s* (alkenes)	1.103 Å	sp^2—sp^2 (alkenes)	1.34 Å
sp—*s* (alkynes)	1.08 Å	*sp*—*sp* (alkynes)	1.20 Å

(*iv*) For a given atom, more is the *s* character (or less *p* character) in an orbital, lower is the energy of the electrons in that orbital and the closer are its electrons to the nucleus. In terms of decreasing energy, the order is $p > sp^3 > sp^2 > sp > s$.

(*v*) Further, *the shorter the bond, the greater the compression between atomic nuclei and hence greater is the strength of that bond*. Thus the bond formed by *sp* hybridized carbon is strongest (*i.e.*, it has maximum bond energy), while that formed by sp^3 hybridized carbon is the weakest (*i.e.* it has minimum bond energy). This is evident by the bond energies of the various types of C—H and C—C bonds.

Bond type (C—H)	***Bond energy(kcal/mole)***	***Bond type (C—C)***	***Bond energy(kcal/mole)***
sp^3—*s* (in alkanes)	104	sp^3—sp^3 (in alkanes)	80—90
sp^2—*s* (in alkenes)	106	sp^2—sp^2 (in alkenes)	122—164
sp—*s* (in alkynes)	121	*sp*—*sp* (in alkynes)	123—199

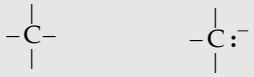
(*vi*) The electronegativity of an orbital increases with increase (or decrease) of *s* (or *p*) contribution in it. Hence electronegativity of the hybrid orbitals follows the order.

$sp > sp^2 > sp^3$ **(Relative electronegativity of hybrid orbitals)**

(*vii*) The type of hybridization of orbitals in organic molecules can be determined on the basis of **hybrid orbital number (HON) rule.** *According to HON rule, every σ bond and an unshared pair of electrons* (but not an unpaired electron) *on an atom uses hybrid orbital.* Thus

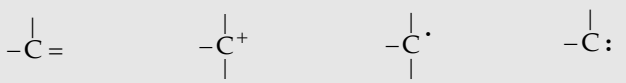
(a) sp^3 hybridization is possible when the atom has

(i) four σ bonds, (ii) three σ bonds and an unshared pair of electrons (carbanions)



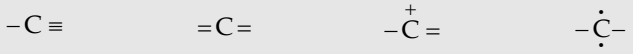
(b) sp^2 hybridization is possible when the atom has

(i) three σ bonds and one π bond, (ii) three σ bonds and a positive charge (carbocations), (iii) three σ bonds and an unpaired electron (free radicals), (iv) two σ bonds and unshared pair of electrons (singlet carbenes)



(c) *sp* hybridization is possible when an atom has

(i) two σ bonds and two π bonds either as a triple bond or as two double bonds on the same carbon, (ii) two σ bonds, one π bond and a positive charge, (iii) two σ bonds and two unpaired electrons (triplet carbenes).

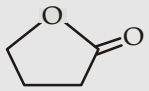


Example 1 :

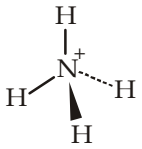
Give the type of hybrid orbitals used by each atom other than hydrogen in each of the following compounds.

(a) NH_4^+, (b) $CH_2 = O$, (c) $CH_2 = NH$, (d) $HC \equiv N$,

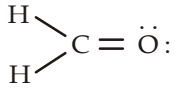
(e) $HO - C \equiv N$, (f) $H_2C = C = CH_2$, (g) $O = C = O$, (h) $H_2C = C = O$,

(i) BF_4^- (j) OH^- (k) 

Solution :

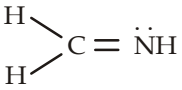
(a) 

N : 4 σ bonds, sp^3

(b) 

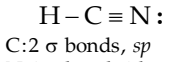
C : 3 σ bonds, sp^2

O : 1 σ bond, 2lp, sp^2

(c) 

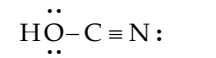
C : 3σ bonds, sp^2

N : 2σ bond, 1 lone pair, sp^2

(d) 

C:2 σ bonds, *sp*

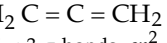
N:1 σ bond, 1 lone pair, *sp*

(e) 

C : 2 σ bonds, *sp*

N : 1 σ bond, 1 lp, *sp*

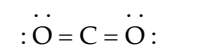
O : 2 σ bonds, 2 lp, sp^3

(f) 

C_1 : 3 σ bonds, sp^2

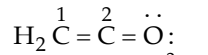
C_2 : 2 σ bonds, *sp*

C_3 : 3 σ bonds, sp^2

(g) 

C : 2 σ bonds, *sp*

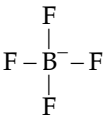
O : 1 σ bond, 2 lp, sp^2

(h) 

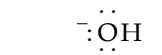
C_1 : 3 σ bonds, sp^2

C_2 : 2 σ bonds, *sp*

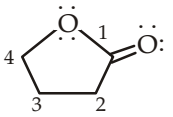
O : 1 σ bond, 2 lp, sp^2

(i) 

B : 4 σ bonds, sp^3

(j) 

O : 1 σ bond, 3 lp, sp^3

(k) 

C_1 : 3 σ bonds, sp^2

$C_2 - C_4$: 4 σ bonds, sp^3

Ketonic O : 1 σ bond, 2 lp, sp^2

Ether O : 2 σ bonds, 2 lp, sp^3

2.2 Effect of Unshared Pair of Electrons

This can be explained by taking the example of ammonia and water.

2.2.1 Ammonia (NH_3)

Electronic configuration of nitrogen ($1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$) indicates that in the formation of NH_3, overlapping of the three pure 2*p* orbitals with 1*s* orbitals of the three hydrogen atoms can take place. If this had been the case, the H—N—H bond angle in ammonia would have been 90°. However, the experimental value for the H—N—H bond angle has been found to be 107°. Since this value (107°) is near to the normal tetrahedral angle of 109.5° in methane, it can be assumed that here also sp^3 hybridisation involving $2s^2$, $2p_x^1$, $2p_y^1$ and $2p_z^1$ atomic orbitals occurs forming four sp^3 hybrid orbitals, one having two (paired) electrons and the other three having one electron each. The latter three orbitals form 3σ bonds with three hydrogen atoms, while the remaining (fourth) sp^3 hybrid orbital retains a pair of electrons commonly known as **lone pair**. Remember that sp^3 hybridisation although normally leads to tetrahedral shape, ammonia is found to have pyramidal shape with nitrogen at the apex and three hydrogens located at the corners of a triangular base.

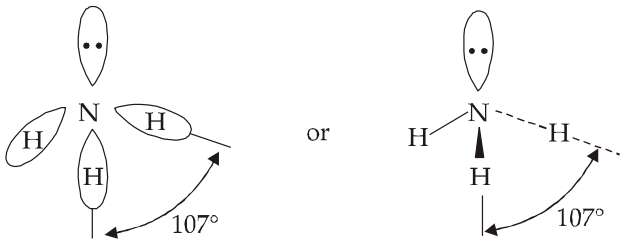


Fig. 1. Pyramidal structure of ammonia molecule.

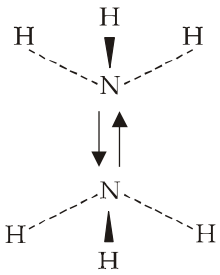


Fig. 2. Inversion of ammonia.

Since the four pairs of electrons in ammonia are not equivalent (three sp^3 bonding and one sp^3 non-bonding), the bond angles are slightly deviated from the ideal value of 109.5°.

Note another important feature of ammonia molecule and that is its **inversion,** *i.e.* it turns inside-out. There is an energy barrier of only 6 kcal/mol between one pyramidal arrangement and the other. This energy is provided by molecular collisions, and even at room temperature the fraction of collisions can do this job. Hence at room temperature rapid transformation between pyramidal arrangements occurs and therefore no amine (even NRR′ R″ of the type) is capable of showing optical isomerism.

2.2.2 Water (H_2O)

Again the electronic configuration of oxygen ($1s^2$, $2s^2$ $2p_x^2$ $2p_y^1$ $2p_z^1$) indicates that in the formation of H_2O molecule, if the two $2p$ atomic orbitals each having one electron overlaps with the $1s$ orbitals of the hydrogen atoms, the H—O—H bond angle would have been 90°.

However, experimental value for this angle is 104.5° pointing to sp^3 hybridisation of $2s^2$ $2p_x^2$ $2p_y^1$ and $2p_z^1$ orbitals. Out of the four sp^3 hybrid orbitals of oxygen, two have one electron each and they form 2σ bonds with the two hydrogen atoms; while the remaining two sp^3 orbitals have a pair of electrons each.

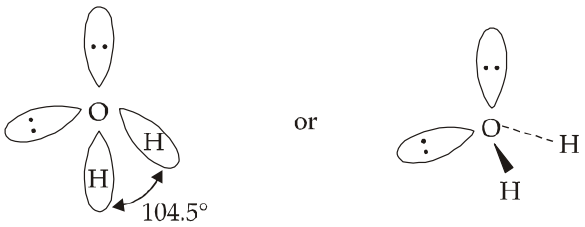


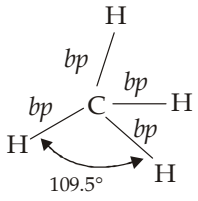
Fig. 3. Structure of water molecule.

Although the four sp^3 orbitals are directed towards the four corners of a tetrahedral, the H—O—H bond angle is found to be 104.5° (less than the regular tetrahedral bond angle of 109.5°). This deviation is due to non-equivalence of the four hybrid orbitals.

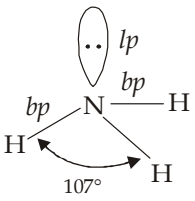
The deviation in bond angle in NH_3 and H_2O from the regular (normal) tetrahedral value (109.5°) as in methane can be explained on the basis of **valence shell electron pair repulsion** (VSEPR) theory. According to this theory, for the maximum stability of a molecule, the valence electrons should be at a maximum distance from each other because of mutual repulsion. Deviation in bond angle occurs due to different type of repulsions in a molecule. However, repulsion between all electron pairs is not equal but it follows the following order.

lp-lp electrons > *lp-bp* electrons > *bp-bp electrons*

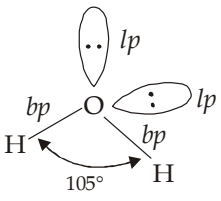
where *lp* stands for lone pair, and *bp* stands for bond pair.



Methane only *bp-bp* repulsion, hence normal tetrahedral angle 109.5°



Ammonia
lp-bp > bp-bp



Water
lp-lp > lp-bp > bp-bp

Thus if the central atom (C, N, O in the above cases) has a lone pair of electrons, the molecule will have a slightly distorted shape (as in case of NH_3 and H_2O). Since nitrogen (in NH_3) has *lp-bp* repulsion which is greater than *bp-bp* repulsion, it will result in the shortening of the H—N—H bond angle (107°). Further, since oxygen (in H_2O) exhibits *lp-lp* repulsion which is greatest, it will result shortening of the H—O—H bond angle from 109.5° to a greater extent which is found to be 104.5°.

TEST YOUR UNDERSTANDING - 2.1

1. Predict the shape of the following molecules

(*a*) BF_3, (*b*) BF_4^-, (*c*) NH_4^+, (*d*) H_3O^+,
(*e*) CH_3NH_2, (*f*) NO_2^+, and (*g*) NO_2^-.

2.3 Electronegativity and Polarity of Bonds

We know that a covalent bond between two atoms is formed by equal sharing of electrons, *i.e.* their nuclei are held together by the same electron cloud. However, once a covalent bond is formed the sharing of electrons between two atoms may be equal (in case the two atoms are same as in case of Cl—Cl, H—H etc.) or different, when the two atoms are different in nature, *viz* H—Cl. Unequal sharing of common electrons by two atoms of different elements is due to their different tendency to attract electrons, a characteristic of elements known as **electronegativity**. The higher the electronegativity, the more effectively does the atom attract and hold electrons. A bond formed by atoms of dissimilar electronegativities is called **polar**, while a bond formed between atoms having similar electronegativity or nearly zero difference in electronegativity is called **non-polar.** Relative electronegativities of a few elements are given below.

F	>	O	>	Cl, N	>	Br	>	S, C, I	>	H
4.0		3.5		3.0		2.8		2.5		2.1

The *more electronegative element of a covalent bond is relatively negatively charged, while the less electronegative element is relatively positively charged.* These charges are indicated by the symbols δ– and δ+ and represent only partial charges (different from complete or ionic charges). Polar bonds are indicated by $\overset{+}{\longleftarrow}$, the head points towards the more electronegative atom.

2.4 Polarity of Molecules

A molecule having polar bonds should be polar, however, this is not true in all cases. For example, O = C = O although has two polar C—O bonds, the CO_2 molecule is **non-polar** ; similarly CCl_4 although has four C—Cl bonds, CCl_4 is a non-polar molecule. A **molecule is said to be polar when the center of negative charge does not coincide with the center of positive charge.** Such a molecule constitutes a *dipole,* two equal and opposite charges are separated in space. The molecule in turn possesses a *dipole moment*, μ, which is equal to the multiple of magnitude of the charge (*e*) and distance (*d*), between the centers of charge.

	μ	=	*e*	×	*d*
in debye units,	(D)		in esu		in cm

Since the charge on an electron is 4.80×10^{-10} electrostatic units (esu) and the distance between charges in a polar bond is of the order of 10^{-8} cm, the product of charge and distance is of the order of 10^{-18} esu. cm. A dipole moment of 1.5×10^{-18} esu. cm is stated on 1.5 D.

Alternatively, 1 debye = 3.34×10^{-30} coulomb meters

Charge on 1 electron = Charge on 1 proton = 1.60×10^{-19} coulomb

If distance between an electron and a proton = 1 Å = 10^{-10} meter

Then $\mu = (1.60 \times 10^{-19}\ \text{coulomb}) \times (10^{-10}\ \text{meter}) = 1.60 \times 10^{-29}$ coulomb meter

Expressing μ in debyes, $$\mu = \frac{1.60 \times 10^{-29}\ \text{C.m.}}{3.34 \times 10^{-30}\ \text{C.m./D}} = 4.8\ \text{D}$$

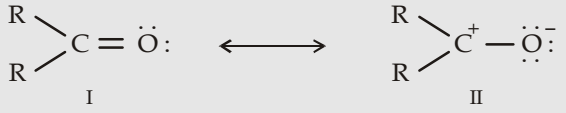
Thus μ (in debyes) = 4.8 × δ (electron charge) × *d* (in Å)

Dipole moments are measured experimentally, and they can be used to calculate bond length and charge separations.

Example 2 :

(a) Determine the charge on the oxygen atom in a C = O bond, whose bond length is 1.22Å and the dipole moment is 2.30 D.

(b) Use this information to evaluate the relative importance of the following two resonance contributions.



I II

Solution :

(a) Dipole moment of the molecule if the bond were 100% ionic, i.e. when oxygen carries a full negative charge

$$\mu_{theoretical} = e \times d = (4.80 \times 10^{-10}\ \text{esu}) \times (1.22 \times 10^{-8}\ \text{cm}) = 5.86 \times 10^{-18}\ \text{esu.cm} = 5.86\ \text{D}$$

$$\text{Actual charge } (\delta) = \frac{\text{Experimental dipole moment}}{\text{Theoretical dipole moment}} = \frac{2.30}{5.86} = 0.39$$

Alternatively,

$$\mu \text{ (in debyes)} = 4.8 \times \delta \text{ (electron charge)} \times d \text{ (in Å)}$$

$$\therefore 2.30\text{D} = 4.8 \times \delta \times 1.22\text{Å} \Rightarrow \delta = \frac{2.30}{4.8 \times 1.22} = 0.39$$

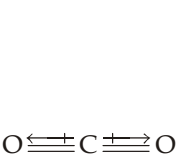
Thus we can say that oxygen atom has an excess of about 0.4 electron and the carbon atom has a deficiency of about 0.4 electron. **Alternatively,** it can be said that the amount δ of charge separation is about 0.40 electronic charge, so the oxygen atom has about 40% of a negative charge and carbon has 40% of a positive charge.

(b) When the value of charge separation is more than 0.5, it indicates that the charged structure is major contributor. Thus here resonance form I must be the major contributor. Although the form II is minor, it is quite significant, explaining in part the high polarity of the C = O.

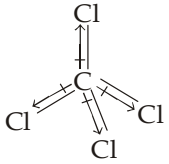
TEST YOUR UNDERSTANDING - 2.2

1. Calculate the charge separation for a typical C–O single bond, with a bond length of 1.43Å and a dipole moment of 0.86 D.

Non-polar molecules always have zero dipole moment because here the value of *e* is zero. This in turn is due to symmetrical structure of the molecule where charge developed by a part of the molecule is cancelled by the equal but opposite charge due to rest part of the molecule.



e = 0, ∴ μ = 0

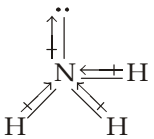


e = 0; ∴ μ = 0

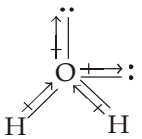
Thus we can say that polarity of the molecule and thus dipole moment also depends upon the shape of the molecule.

Ammonia (NH_3), water (H_2O) and nitrogen trifluoride (NF_3) have different dipole moments because the net dipole moment is a *vector sum* of the individual bond moments and bond moment due to lone pair of electron(s).

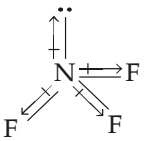
The strongly polar C ≡ N: triple bond has the maximum dipole moment (3.6D).



Ammonia
μ = 1.46 D



Water
μ = 1.84 D



Nitrogen trifluoride
μ = 0.24 D

Dipole moment and geometry of molecule :

1. If a molecular of the type MX_4 has zero dipole moment, it indicates sp^3 hybridisation of M (Z < 21). Examples are CH_4, CCl_4, $SiCl_4$, $SnCl_4$ etc.
2. If a molecule of the type MX_3 has zero dipole moment, it indicates sp^2 hybridisation of M (Z < 21). Examples are BF_3, $AlCl_3$, etc.
3. If a molecule of the type MX_2 has zero dipole moment, it indicates *sp* hybridisation of M (Z < 21). Examples are BeF_2, CO_2, etc.

TEST YOUR UNDERSTANDING - 2.3

1. Although CO_2 and H_2O, both are triatomic, they have considerable difference in their dipole moments. Explain

2. (*i*) Ammonia has dipole moment as 1.46 D, can you predict the dipole moment of nitrogen trifluoride ?

(*ii*) Dipole moment of CH_3F is 1.847 D, can you predict dipole moment of CD_3F ?

2.5 Other Factors for Polarity of Covalent Bonds

We have observed that difference in electronegativity of the two atoms forming a covalent bond produces polarity in a bond and hence in a molecule. In addition to this factor, there are other factors (or effects) which may cause displacement (partial or complete) of the bonding electrons and thus produce polarity in the bond. Some of these effects are **permanent** (*e.g., inductive, mesomeric, and hyperconjugation*) and others are **temporary** (*e.g., electromeric and inductomeric effects*). The former effects are permanently operating in the molecule and are known as **polarisation effects,** while the latter are brought into play by the attacking reagent, and as soon as the attacking reagent is removed, the electronic displacement disappears ; such effects are known as the **polarisability effects.** Here inductive, mesomeric, electromeric effects and hyperconjugation are described.

2.5.1 Inductive effect

It is a well known fact that a covalent bond is formed by the equal sharing of electrons between the two atoms. In case of a covalent bond between two similar atoms, the electron pair of the bond occupies central position between the nuclei of the two concerned atoms. Such a covalent bond is known as non-polar bond, *viz*.

H : H Cl : Cl

On the other hand, in case of a covalent bond between the two dissimilar atoms, the electron pair forming the bond is never shared absolutely equally between the two atoms but is attracted a little more towards the more electronegative atom. For example, in the compound C—X where X is more electronegative than C, the electron pair forming the C—X bond is somewhat more attracted towards the atom X with the result the latter attains partial negative charge (denoted by $\delta -$) while the carbon atom attains a partial positive charge (denied by $\delta +$).

$>C : X$ or $>\overset{\delta+\ \delta-}{C—X}$

On the other hand, in compounds, like C—Z where Z is an electropositive element or group, *i.e.*, C is more electronegative than Z, the electron pair forming the C—Z bond is somewhat displaced towards the carbon atom and thus C and Z attain partial negative and partial positive charges respectively.

$>C : Z$ or $>\overset{\delta-\ \delta+}{C—Z}$

Thus inductive effect causes a certain degree of polarity in the bond which in turn renders the bond much more liable to be attacked by other charged atoms or groups. With reference to inductive effect *it is very important to note that the electron pair, although permanently displaced, remains in the same valency shell.*

Thus, **inductive effect may now be defined as the permanent displacement of electrons forming a covalent bond towards the more electronegative element or group.**

The inductive effect is always transmitted along a chain of carbon atoms. For example, consider a carbon chain in which terminal carbon atom (C_1) is joined to a chlorine atom.

$$\underset{3}{C}—\rightarrow——\underset{2}{C}—\rightarrow——\overset{\delta+}{\underset{1}{C}}—\rightarrow——\overset{\delta-}{Cl}$$

Now since chlorine has greater electronegativity than carbon, the electron pair between C_1 and Cl will be displaced from the middle somewhat to the chlorine atom with the result the latter will acquire a small negative charge, and the C_1 a small positive charge. Now further since C_1 is positively charged, it will attract towards itself the electron pair forming the covalent bond between C_1 and C_2 with the result C_2 will also acquire a small positive charge, but the charge on

C_2 will be smaller than on C_1 since the effect of chlorine atom (source) has been transmitted through C_1 to C_2. Similarly, C_3 will also acquire a small positive charge, but again due to the above reason the charge on C_3 will be smaller than on C_2. This effect can be relayed still further although it would decrease in intensity considerably as the distance from the source increases. In fact, it would be negligible even on C_3 for all practical purposes.

The inductive effect is represented by the symbol $\rightarrow\!\!-$, the arrow pointing towards the more electronegative element or group of elements. Thus in case of *n*-butyl chloride inductive effect may be represented as below.

$$\overset{\delta\delta\delta\delta+}{CH_3}\rightarrow\!\!-\overset{\delta\delta\delta+}{CH_2}\rightarrow\!\!-\overset{\delta\delta+}{CH_2}\rightarrow\!\!-\overset{\delta+}{CH_2}\rightarrow\!\!-\overset{\delta-}{Cl}$$

The decrease in the effect is denoted by using a greater number of the sign δ.

The electron attraction and repulsion are compared with hydrogen as the reference in the molecule R_3C—H as standard. Any atom or group that attracts electrons more strongly than hydrogen is said to have a **– I effect** (electron-attracting or electron-withdrawing), *viz* NO_2, Cl, Br, I, F, COOH, OCH_3, etc. ; while the atom or group that attracts electrons less strongly than hydrogen is said to have **+ I effect** (electron repelling or electron-releasing) *viz.*, CH_3, C_2H_5, Me_2CH and Me_3C groups. The important atoms or groups which cause negative or positive inductive effect are arranged below in the order of decreasing effect.

– I (Electron-attracting) groups.

$$\overset{+}{N}(CH_3)_3 > NO_2 > CN > COOH > F > Cl > Br > I > CF_3 > OR > OH > NH_2 > C_6H_5 > H$$

+ I (Electron-repelling) groups.

$$O^- \text{ (phenoxide)} > COO^- > (CH_3)_3C > (CH_3)_2CH > CH_3CH_2CH_2 > CH_3CH_2 > CH_3 > D > H$$

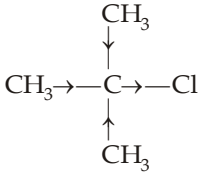
Importance of inductive effect

The phenomenon of inductive effect is very important in organic chemistry as it explains several facts, most important of which are given here.

(*i*) **Reactivity of alkyl halides.** Alkyl halides, in general, are more reactive than the corresponding alkane, the reason being the presence of C—X bond in alkyl halides due to which they undergo inductive effect, *e.g.*, methyl chloride.

$$\overset{\delta+}{CH_3}\rightarrow\!\!-\!\!-\overset{\delta-}{Cl}$$

Thus due to the development of charges, the attack of a reagent on CH_3Cl is facilitated as compared to that on methane. Furthermore, tertiary butyl chloride (a *tert*-halide) is more reactive than the methyl chloride because + I effect of the three methyl groups enhances the – I effect of chlorine atom by supplying electrons towards the tertiary carbon atom.

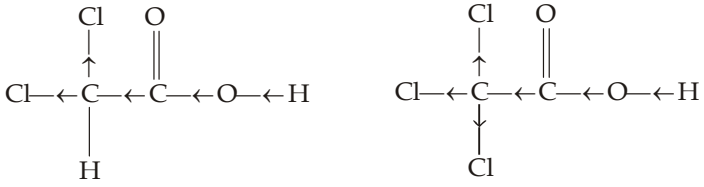

tert-Butyl chloride

Thus *the chlorine atom in tert-butyl chloride can be very easily replaced by other atom as compared to that in methyl chloride* (a primary chloride).

(*ii*) **Strength of carboxylic acids.** An acid is a species that has the tendency to lose proton. Furthermore, the strength of an acid depends upon the ease with which an acid ionises to give proton. Thus any structural unit like strongly electronegative group that helps in removing the proton from the hydroxy group of the acid will have the effect of making the corresponding carboxylic acid a stronger one. For example, halogenated fatty acids are much stronger acids than the parent fatty acid and moreover the acidity among the halogenated fatty acids is increased almost proportionately with the increase in electronegativity of the halogen present. This fact can be visualised by the following table (higher the K_a value, more stronger will be the acid).

Name of the acid	*Formula*	K_a
Iodoacetic acid	$I.CH_2COOH$	75×10^{-5}
Bromoacetic acid	$Br.CH_2COOH$	138×10^{-5}
Chloroacetic acid	$Cl.CH_2COOH$	155×10^{-5}
Fluoroacetic acid	$F.CH_2COOH$	217×10^{-5}

Furthermore, the inductive effect in di- and tri-halogeno substituted acids is still more marked with the result these acids are progressively more stronger than the corresponding monohalogeno substituted acid which is obvious from their dissociation constants, for example, di- and tri-chloroacetic acids are more stronger than the chloroacetic acid.



Actually, the *cumulative inductive* effect of the three chlorine atoms **in trichloroacetic acid makes this substance as strong acid as hydrochloric acid.**

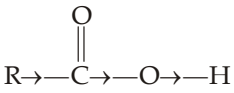
However, since the inductive effect decreases rapidly as the group responsible for the effect (*e.g.* halogen atom in the present case) moves farther from the source (*e.g.* carboxyl group), the strength of the acid is proportionately decreased. Thus the chlorobutyric acids follow the following acidity order which is evident from their dissociation constants.

$$\alpha - \ > \ \beta - \ > \ \gamma - \ > \ n - \text{Butyric acids}$$

Similarly, we can explain the following order of decreasing acidic strength of a few of the fatty acids.

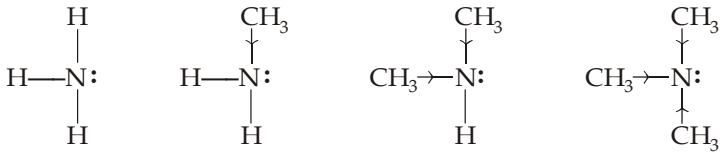
$$HCOOH > CH_3COOH > C_2H_5COOH > n\text{-}C_3H_7COOH$$

The decreasing acidic strength is due to increase in + I effect due to alkyl groups.



Formic acid, having no alkyl group, is the most acidic among these acids.

(*iii*) **Basic character of amines.** *The basic character of amines is due to the presence of unshared electron pair on nitrogen atom which accepts proton ;* the ease with which the lone pair of electrons is available for co-ordination with a proton determines the relative basic strength of amines.



Thus due to + I effect of alkyl group, the nitrogen atom becomes rich in electron with the result the lone pair of electrons on nitrogen atom in amines is more easily available than in ammonia and thus amines are stronger bases than ammonia. However, it is important to note that the relative basic character of amines is not in total accordance with the inductive effect *i.e.* T > S > P, but it is in the following order

$$\text{Secondary} > \text{Primary} > \text{Tertiary} > NH_3 \ \textbf{(Basicity in aqueous solution)}$$

$$\text{Tertiary} > \text{Secondary} > \text{Primary} > NH_3 \ \textbf{(Basicity in gas phase)}$$

For explanation consult, example 3 given below.

(*iv*) **Basic character of alcohols.** On the basis of + I effect of the various alkyl groups, we can explain relative basic character of the following alcohols.

$$CH_3 \rightarrow \ddot{O}H < CH_3CH_2 \rightarrow \ddot{O}H < (CH_3)_2CH \rightarrow \ddot{O}H < (CH_3)_3C \rightarrow \ddot{O}H$$

Thus 3° alcohols are most basic and 1° alcohols least. Therefore, we can now explain the chemistry of Lucas test (Lucas reagent is a mixture of anhydrous $ZnCl_2$ and conc. HCl), where 3° alcohols react fastest and 1° slowest. Since Lucas test involves reaction between an acid (HCl) and a base (ROH), the strongest base (*i.e.* 3° alcohols) will react fastest.

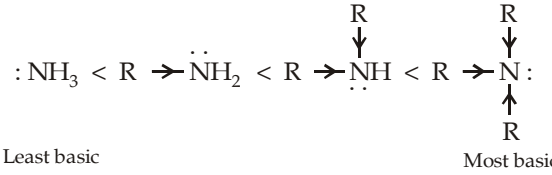
$$\underset{\text{base}}{ROH} + \underset{\text{acid}}{HCl} \xrightarrow{ZnCl_2} \underset{\text{white turbidity}}{RCl\downarrow} + H_2O$$

Example 3 :

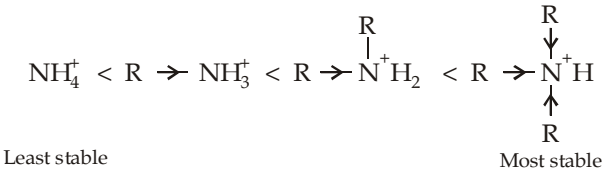
Arrange RNH_2, R_2NH, R_3N and NH_3 in decreasing order of their basic strength in (*a*) aqueous solution and (*b*) gas phase.

Solution :

Two effects, induction and solvation, determine the K_b of an alkyl amine. Inductive effect of alkyl groups increases basic character of alkyl amine with increase in number of alkyl groups. Further, the inductive effect of the alkyl group stabilizes the positive charge on the conjugate base. Thus, it is expected that :



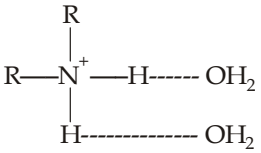
(Relative basic character in gas phase)



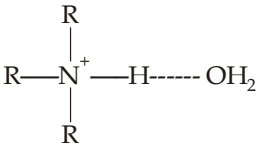
(Stability order)

However, this is true in gaseous phase.

In aqueous solution, both inductive as well as solvation effect, determine the relative basic character of amines. Solvation effect plays important role in stabilising the conjugate acid as they have positive charge and hydrogen.



More stable



Less stable

In terms of solvation alone, more the number of H's in the conjugate acid, the more it is stabilized by H-bonding and thus greater will be basic character of the parent base. Thus, conjugate acid of 2° amines having 2 H's will be more stable than the conjugate acid of 3° amines having only 1 H.

Inductive effect dominates in making all the three amines stronger bases than NH_3, and dimethylamine stronger than methylamine. However, in tertiary amines, the solvation effect has important role.

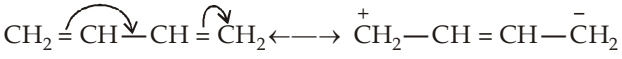
Thus the relative basic character of the three amines in aqueous solution is

$$\underset{\text{Least basic}}{NH_3} < R_3N < RNH_2 < \underset{\text{Most basic}}{R_2NH}$$

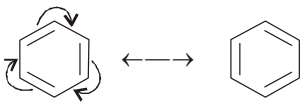
(Basic order in aqeuous solution)

2.5.2 Resonance effect or Mesomeric effect

The phenomenon in which a species (molecule, ion or free radical) can be represented by two or more structures (none of which can alone explain all properties of the species) having same arrangement of atoms but different distribution of electrons is called **resonance.** The various structures are called *resonanting, contributing or canonical structures*. Consider the structure of 1, 3-butadiene and benzene.

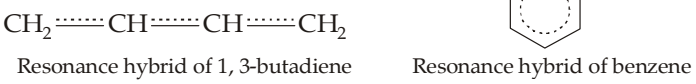


Two canonical structures of 1, 3-butadiene (Note that it is π electrons which are moving)



Two important canonical structures of benzene.

It must be understood that none of the contributing structures of a species has any existence, they exist only on paper. The real structure that can explain all properties of a species is a hybrid of all contributing structures and it is known as **resonance hybrid** of that species.



Resonance hybrid of 1, 3-butadiene Resonance hybrid of benzene

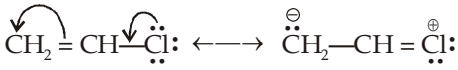
It should be noted that the term resonance does not mean the mixing of formal structures and, therefore, a less confusing term for this phenomenon is **π–π electron delocalisation.**

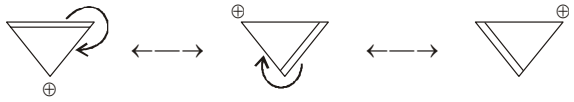
Rules for writing resonance structures :

1. Each resonating structure must conform to real Lewis structures *i.e.* there can be no structure with a penta-covalent carbon and bicovalent hydrogen.

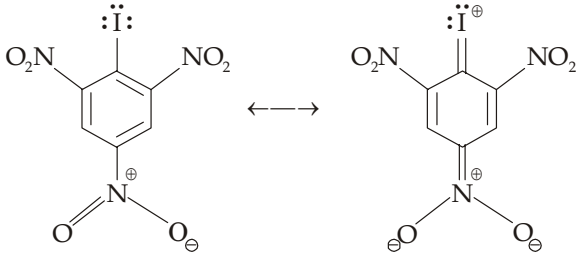
2. Resonance involves movement of only π or *n* electrons and a resonance structure can be derived from another by a series of one or more electron shifts. Thus resonance is possible only when one double is in conjugation with another double bond or an unshared pair of electrons or an electron deficient atom. For example,

(*i*) $CH_2 = CH—CH = CH_2 \longleftrightarrow \overset{+}{C}H_2—CH = CH—\overset{-}{C}H_2 \longleftrightarrow \overset{-}{C}H_2—CH = CH—\overset{+}{C}H_2$

(*ii*) 

(*iii*) 

3. In order to achieve maximum overlap of *p* orbitals, which is necessary for delocalization, it is essential that the *skeleton should be planar* in conjugated system.



Thus any structural feature that destroys this coplanarity of the conjugated system will inhibit resonance. This inhibition is referred to as **steric inhibition of resonance.**

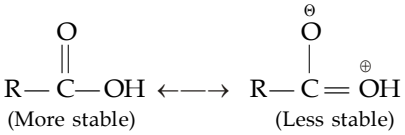
Picryl iodide provides a good example. A comparison of the C—N bond lengths of nitro groups in the *ortho* position (1.45 Å) with that of the nitro group in the *para* position (1.35 Å) reveals that the C—N bond of the nitro group in the *para* position has some double bond character. This is explained on the basis of involvement of the *para* nitro group in resonance because of coplanarity of benzene ring and the nitro group. On the other hand, *ortho* nitro groups do not participate in resonance as they are pushed out of the plane of the ring by bulky iodine atom. Consequently, the C—N bond length of the *ortho* nitro group is very close to that of aliphatic nitro compounds.

4. All resonating structures must have same number of paired electrons.

5. All resonating structures do not contribute equally to the hybrid. Lesser the energy of the structure, more will be its contribution to the hybrid. Relative energies of the contributing structures are assessed by the following rules.

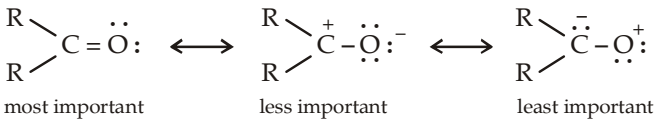
(*a*) Since each covalent bond adds about 50—100 kcal/mole to the stability of the system, it is expected that **structures with more covalent bonds are more stable** than those with fewer. For instance, the non-polar form of butadiene (having 11 covalent bonds) is more stable than the other two polar structures (having 10 double bonds).

(*b*) Non-polar structures have less energy and hence more stable than the polar structures, *e.g.* butadiene, R—COOH etc.



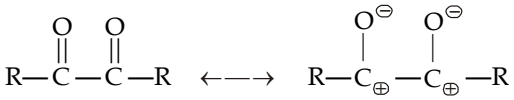
(More stable) (Less stable)

(*c*) If all structures have formal charge, the more stable structure has negative charge on the more electronegative atom and positive charge on the less electronegative (more electropositive) atom. Further structure with the least number (or amount) of formal charge is more stable.



most important less important least important

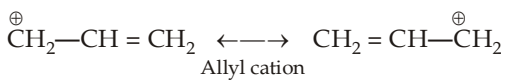
(*d*) Structures with like charges on adjacent atoms have very high energy and hence unimportant. For example,



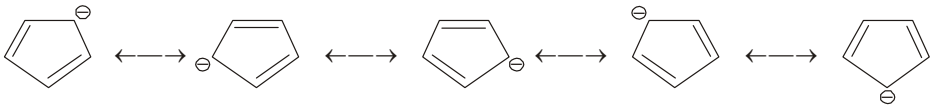
(*e*) Resonating structures with electron deficient, positively charged atom have high energy and hence unimportant.

(*f*) Equivalent contributing structures have nearly equal energies and hence contribute more to the hybrid. Thus phenomenon of resonance is of much significance when two or more **equivalent contributing structures** are possible for a species. For example,





Allyl cation



Cyclopentadienyl anion (all contributing structures are equivalent)

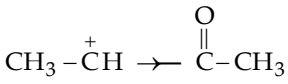
(*g*)



I II

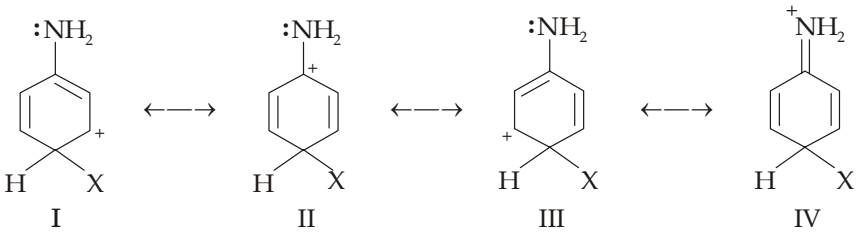
Here, although structure II has positive charge on the electronegative atom, it helps to disperse the charge (positive) on structure I, hence resonance is possible. However, due to positive charge on the electronegative atom (oxygen), contribution of structure II to resonance hybrid is very less.

On the other hand, presence of group which intensifies charge on the atom makes the species less stable.



Here resonance is not possible, and the –I effect of the $-COCH_3$ group intensifies the positive charge on carbon, making it less stable.

(*h*) Structures in which all atoms have a complete octet of electrons are especially stable and make large contribution to the hybrid. For example,



I II III IV

In the above structures, IV is especially stable since here every atom (except hydrogen) has octet.

Example 4 :

Write all possible contributing structures for

(a) hydrazoic acid (HN_3), **(b) nitrate ion (NO_3^-)**

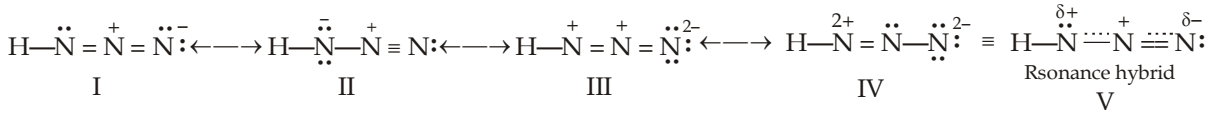
(c) boron trichloride (BCl_3) **(d) formic acid (HCOOH)**

(e) diazomethane.

Comment on the stability of each structure.

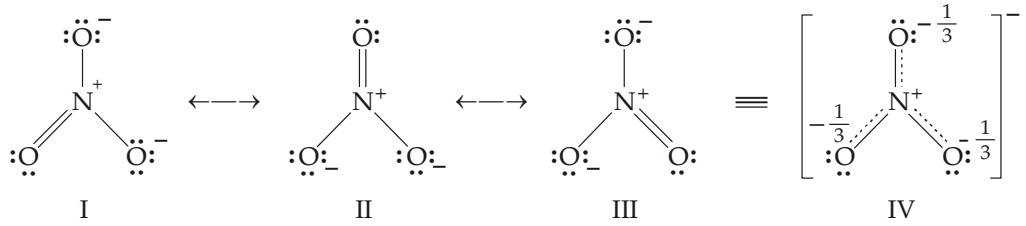
Solution :

(*a*) *Hydrazoic acid, HN_3*



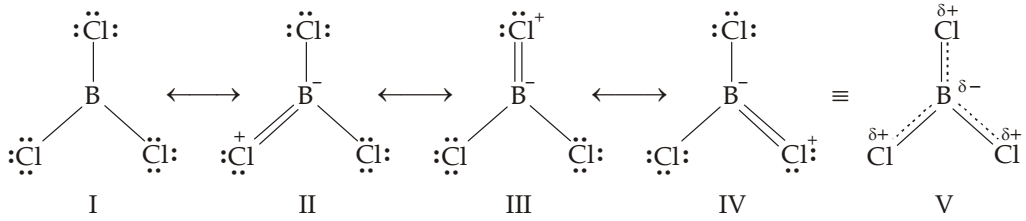
Structrues I and II have least amount of formal charge (total 2), they have nearly similar energy and are the most stable. Structure III has similar charge (+) on adjacent atoms, and moreover it also has a total formal charge of 4, it has a very high energy and hence unstable. Structure IV also has a very high energy because the N bonded to H has only 6 electrons and it has a total formal charge of 4. Thus hydrazoic acid is a hybrid of only two structures, namely I and II and can be represented as V.

(*b*) *Nitrate ion, NO_3^-*



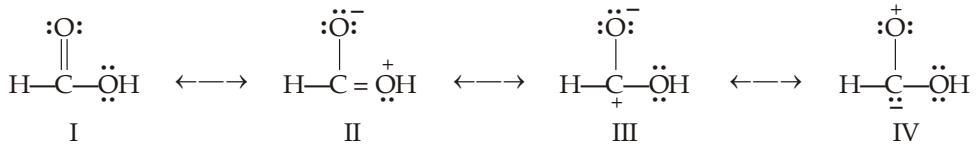
Note that all the three structures of NO_3^- ion are similar to each other and are thus equally stable. Thus resonance hybrid (IV) is composed of all the three structures.

(*c*) *Boron trichloride, BCl_3*



(*d*) *Formic acid, HCOOH*

Structure I is stable because it has no formal charge while the other structures II, III and IV have more number of covalent bonds are equivalent, and so these are equally stable and contribute more to the hybrid, V.



Structures I and II have greater number of covalent bonds, these are more stable than III or IV. Further, structure I has no formal charge it is more stable than II. Among III and IV, III is more stable because here negative charge is on O, a more electronegative element rather than on C (in IV), a lesser electronegative element than O. Structure of carboxylic acids is mainly represented by structure I, *i.e.* resonance is not of much significance in carboxylic acids.

(*e*) *Diazomethane, CH_2N_2*

$$\underset{\text{I}}{H_2C=\overset{+}{N}=\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}:^{-}} \longleftrightarrow \underset{\text{II}}{H_2\overset{-}{\overset{\cdot\cdot}{C}}-\overset{+}{N}\equiv N:} \equiv \underset{\text{III}}{H_2\overset{\delta-}{C}\cdots\overset{\delta+}{N}\equiv\overset{\delta-}{N}}$$

Both have same number of covalent bonds, hence these should be equally stable. However, structure II has negative charge on C, rather than N (a more electronegative element), hence I can said to be more stable than II.

Example 5 :

Pick up the more stable ions among the following pairs with proper explanation.

(i) $\underset{\text{I}}{(CH_3)_2N^+=CH-CH=CH-N(CH_3)_2}$ and $\underset{\text{II}}{(CH_3)_2N^+=CH-CH=CH-OC_2H_5}$

(ii) $\underset{\text{III}}{CH_2=CH-C^-(CH_3)_2}$ and $\underset{\text{IV}}{(CH_3)_2C^- -CHO}$

(iii) $\underset{\text{V}}{CH_3CH_2O^-}$ and $\underset{\text{VI}}{CH_2=CH-O^-}$

Solution :

(i) I is more stable than II because its two resonating structures are equivalent.

$$(CH_3)_2\overset{+}{N}=CH-\overset{\curvearrowleft}{CH}=CH-\overset{\curvearrowleft}{\overset{\cdot\cdot}{N}}(CH_3)_2 \longleftrightarrow (CH_3)_2N-CH=CH-CH-N^+(CH_3)_2$$

Equivalent resonating structures

(ii) IV is more stable than III because its one of the resonating structures has negative charge on oxygen.

$$(CH_3)_2\overset{-}{C}-\overset{\curvearrowleft}{C}-H \longleftrightarrow \underset{\text{More stable}}{(CH_3)_2C=\overset{O^-}{\overset{|}{C}}-H}$$

IV

$$CH_2=CH-\overset{\curvearrowleft}{C^-}(CH_3)_2 \longleftrightarrow \overset{-}{C}H_2-CH=C(CH_3)_2$$

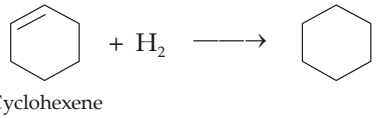
III

(iii) VI is more stable than V because of resonance, while resonance is not possible in V.

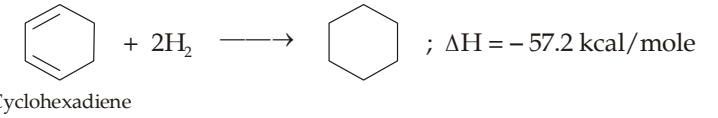
Resonance energy

The most important consequence of resonance is that the resonance hybrid (*i.e.* the actual molecule) has much lower energy than the energy for any of the contributing structures. This lower energy of the resonance hybrid and hence increased stabilisation in such systems is expressed in terms of **resonance energy.** Resonance energy may be defined as the difference between energy of the actual molecule (resonance hybrid) and the energy for the most stable contributing structure. Resonance energy has been computed from the heats of hydrogenation and heats of formation.

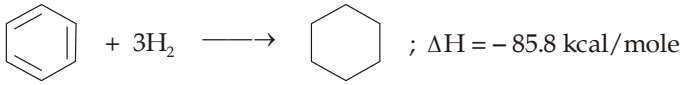
(*i*) **Resonance energy from heats of hydrogenation.** Resonance energy has been calculated by comparing the heat of hydrogenation of the theoretical benzene (cyclohexatriene) with the real molecule of benzene. Heat of hydrogenation of the theoretical benzene (cyclohexatriene) can be calculated as – 85.8 kcal/mole on the basis of the fact that the heat of hydrogenation of C = C is – 28.6 kcal/mole.



Cyclohexene



Cyclohexadiene



Cyclohexatriene
(hypothetical benzene)

However, the heat of hydrogenation of the real benzene molecule as determined experimentally is found to be – 49.8 kcal/mole. Thus we can say that the real structure (resonance hybrid) of benzene has 36.0 kcal/mole (85.8 – 49.8 = 36.00) of energy less than the most stable canonical structure. In other words, benzene molecule is stabilized by 36.0 kcal/mole of energy which is commonly referred to as **resonance energy of benzene.**

In short,

Resonance energy = Theoretical heat of hydrogenation—Experimental heat of hydrogenation.

(*ii*) **Resonance energy from heat of formation.** Resonance energy of a molecule can be computed from heats of formation in the same way as from heat of hydrogenation. For example, for benzene theoretical heat of formation of benzene can be computed from the various bond dissociation energies.

Theoretically,

ΔH_f = 6 (Bond energy of C–H bond) + 3 (Bond energy of C–C bond) + 3 (Bond energy of C = C bond)

= 6 × 98.8 + 3 × 83.1 + 3 × 145 = 1277.1 kcal/mole.

Experimental heat of formation of benzene can be determined from heat of combustion of benzene, heat of formation of CO_2 and heat of formation of O_2 according to the following thermochemical equation.

$$C_6H_6 + 7\frac{1}{2}\ O_2 \longrightarrow 6CO_2 + 3H_2O + 789.1 \text{ kcal}$$

This value is found to be 1313.3 kcal/mole.

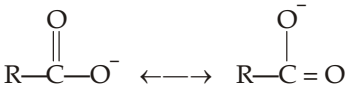
Hence resonance energy of benzene = 1313.3 – 1277.1 = 36.2 kcal/mole.

Effects of resonance :

1. The most important effect of resonance is to induce stability in the molecule, it is due to delocalisation of electrons which decreases reactivity and hence increases stability, of the molecule. Possibility of equivalent (two or more) resonating structrues leads to more stability. Thus we can explain greater stability of the carboxylate ion as compared to carboxylic acids.



Non-equivalent resonating structures of carboxylic acids, resonance less important



Equivalent resonating structures of carboxylate ion, resonance more important leads to greater stability of $RCOO^-$.

Further, more the number of equivalent resonating structures more will be stability of the species (neutral or ionic).

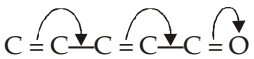
2. The phenomenon of resonance gives identical bonding (concept of partial double bond in resonance hybrid) and hence identical bond lengths. Thus in benzene, carbon-carbon bond length acquires a value which lies between C—C (single bond) length (1.54 Å) and C = C (double bond) length (1.33 Å).

2.5.3 Mesomeric effect

Mesomeric effect is the resonance effect of certain compounds produced under the influence of certain groups attached to the conjugated system. Like inductive effect, mesomeric effect (denoted by M) may be + M and – M. It is + M when the transference of electron pair is away from the hetero atom ; and – M when transference of electron pair is towards the hetero atom. In general,



+ M effect



– M effect

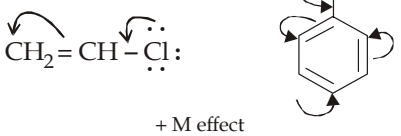
Some common atoms or groups which cause + M and – M effect are given below.

+ M groups. —Cl, —Br, —I, —NH_2, —NR_2, —OH, —OCH_3, –SH

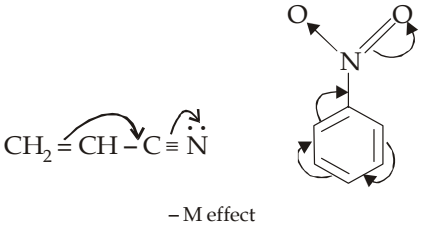
– M groups. —NO_2, —C ≡ N, > C = O, –COOH

The effect is of common occurrence in aromatic compounds and explains orientation in monosubstituted benzenes during electrophilic substitution.

Since **mesomeric effect** is a permanent effect and always operates in a non-reacting molecule, it, **like inductive effect, affects the physical properties of a molecule.** Again, like inductive effect, it may either aid or hinder a particular reaction.

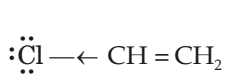


+ M effect

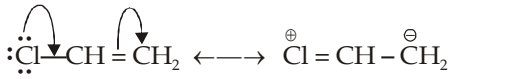


– M effect

The inductive and mesomeric effects, when present together, may act in the same direction or opposite to each other. When the two effects oppose each other, the mesomeric effect is more powerful than the former. For example, in vinyl chloride, chlorine atom attains positive charge, and not negative.



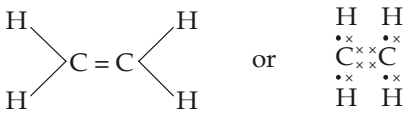
– I effect of chlorine leads to negative charge on chlorine atom



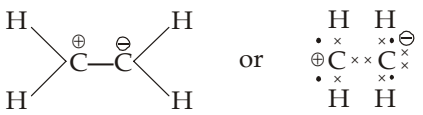
+ M effect due to Cl leads to positive charge on chlorine atom

2.5.4 Electromeric effect

This type of temporary displacement of electrons takes place in compounds containing multiple covalent bonds (*e.g.* C = C, C = O, C ≡ N, etc.) or an atom with a lone pair of electrons adjacent to a covalent bond. The effect involves complete transference of a pair of electrons from a multiple bond to an atom, or from a multiple bond to another bond, or from an atom with a free pair of electrons to a bond. It is the π-electrons of a multiple bond, or the *p*-electrons of an atom, which are transferred. Since the effect involves complete transference of electrons, it leads to the development of full + and – charges within the molecule. It is important to note that the electromeric effect is purely a temporary effect and is brought into play only at the requirement of attacking reagent ; it vanishes out as soon as the attacking reagent is removed from reaction mixture. For example,



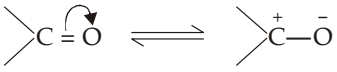
(*a*) Ethylene molecule before adding the reagent



(*b*) Ethylene molecule after adding the reagent.

In the above examples as soon as the attacking reagent is removed, the charged molecule (*b*) reverts to its original condition (*a*).

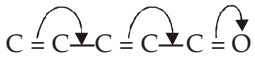
The electromeric effect is generally shown by curved arrow, starting at the original position of the electron pair and ending to the new position (attained by migration) of the electron pair, *e.g.*, in the carbonyl group it operates as



The electromeric effect is represented by the symbol E which may be + E when the displacement of electron pair is away from the hetero atom or – E when the displacement is towards the hetero atom *e.g.*,

+ E effect  (Displacement away from atom X)

Here the attacking species adds on the atom on which electrons are transferred.

– E effect  (Displacement towards atom O)

Here the attacking species does not add on the atom on which electrons are transferred.

Now since the electromeric effect takes place only at the requirement of the attacking reagent it always facilitates the reaction but never inhibits it. It is important to note that **when the inductive and electromeric effects are operating in the same molecule but in the opposite directions, it is the electromeric effect** that usually **overcomes the inductive effect.**

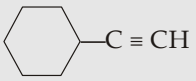
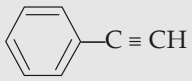
The electromeric effect is of common occurrence during addition of polar reagents on C = C and C = O bonds, and in the orientation of group in monosubstituted benzene during electrophilic substitutions.

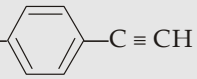
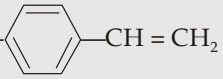
The combined mesomeric and electromeric effects of the atom or group is known as its conjugative effect. Since the conjugative effect was first recognized in connection with the phenomenon of tautomerism, it was previously known as the **tautomeric effect (± T).**

Example 6 :

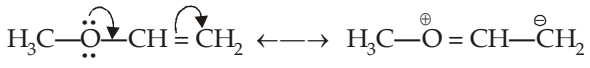
Represent the π-electron transfer due to mesomeric effect in following cases. Assign the + or – sign of effect.

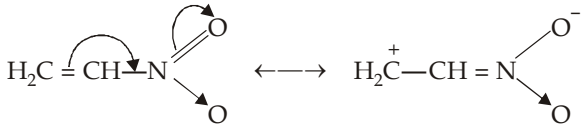
(i) $CH_3O—CH = CH_2$ *(ii)* $CH_2 = CHNO_2$ *(iii)* $CH_2 = CHCH_2NO_2$

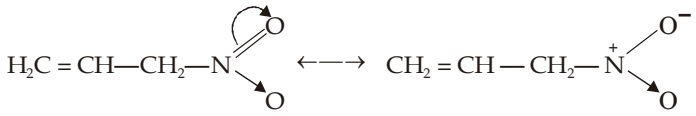
(iv) $CH_2 = CHCl$ *(v)*  *(vi)* 

(vii)  *(viii)*  *(ix)* $CH_3CH = CHCH_2CH_3$.

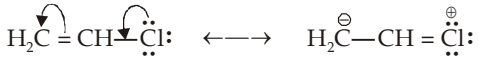
Solution :

(i)  **+ M effect**

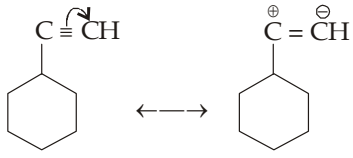
(ii)  **+ M effect**

(iii)  **– M effect**

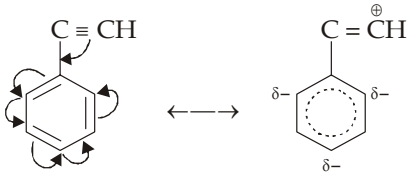
(Note that C = C is not conjugated, hence π–electron transfer will not proceed to $– NO_2$; $– NO_2$ will independently undergo – M effect)

(iv)  **+ M effect**

Note that here + M effect and – I effect opposes each other. But + M > – I

(v) 

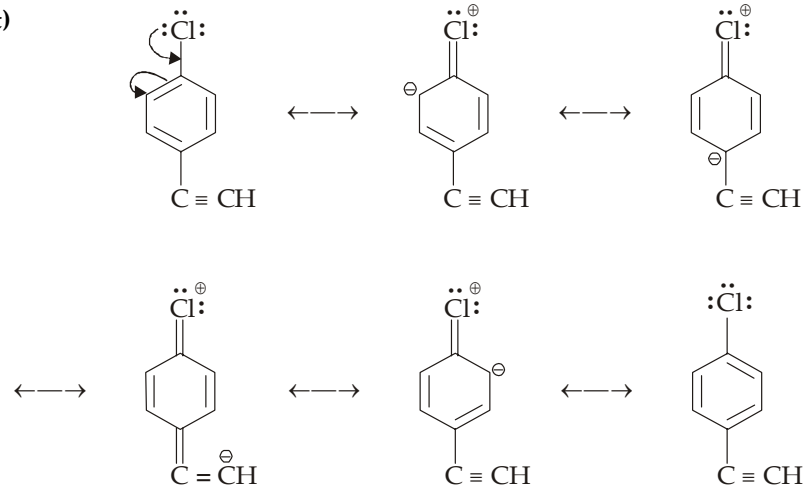
No mesomeric effect displacement of electrons is due to + I effect

(vi) 

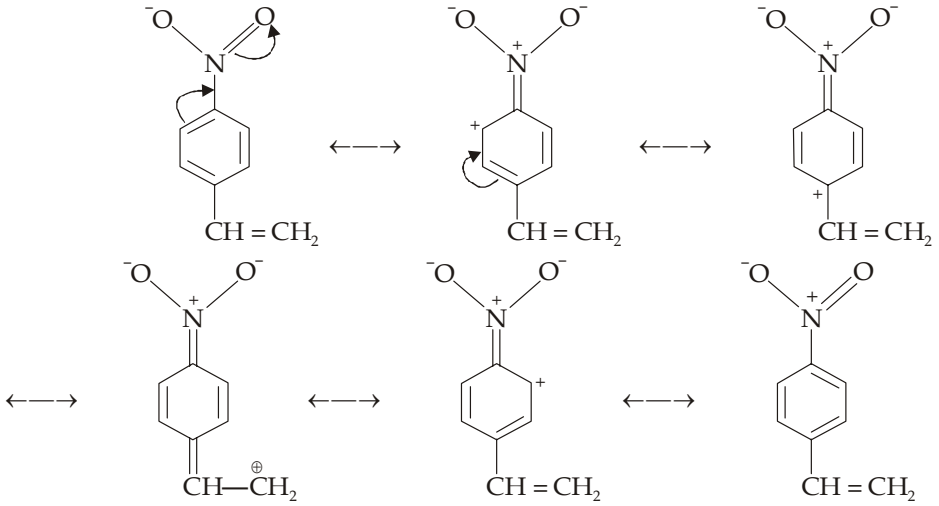
Mesomeric effect due to - I effect

It is not given + or – sign because hetero atom (other than C) is not involved.

(*vii*) **(+ M effect)**



(*viii*) **(– M effect)**

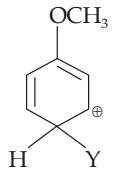


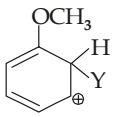
(*ix*) $CH_3—\overset{\curvearrowleft}{CH}=CH—CH_2CH_3 \longleftrightarrow CH_3—\overset{\ominus}{C}H—\overset{\oplus}{C}H—CH_2CH_3$

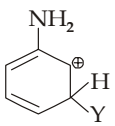
No mesomeric effect, displacement of electrons is governed by —CH_2CH_3 group which has more + I effect than the —CH_3.

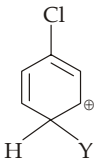
TEST YOUR UNDERSTANDING - 2.4

1. Write down the various mesomeric structures of the following species, and also mention which one is especially stable or unstable, if any

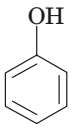
(*i*) 

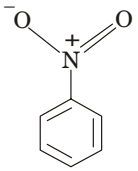
(*ii*) 

(*iii*) 

(*iv*) 

2. Write down the resonance hybrid of the following structures.

(*i*) Allyl carbonium ion (*ii*) Acetamide (*iii*) 

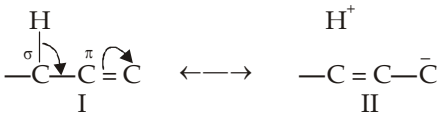
(*iv*) 

3. Draw the resonating structure of the carbonium ion ($CH_3OCH_2^+$) and discuss the relative stability of different canonical structures.

4. Explain why $CHCl_3$ is more acidic than CHF_3.

2.5.5 Hyperconjugation

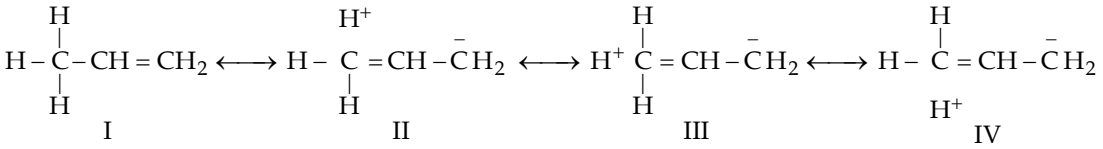
Baker and Nathan suggested that alkyl groups with at least one hydrogen atom on the α-carbon atom, attached to an sp^2 hybridised carbon atom (alkenes, carbocations or alkyl free radicals), are able to release electrons in the following way.



I ⟷ II

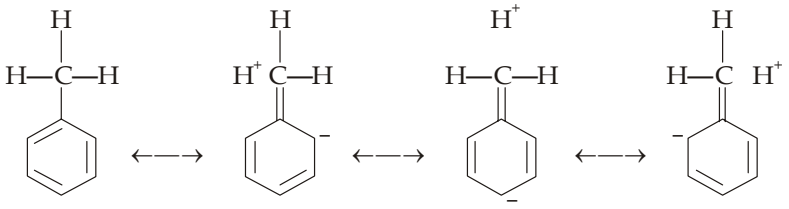
Note that the delocalisation involves σ and π bond orbitals (or *p* orbitals in case of carbocation and free radicals); thus it is also known as **σ – π conjugation.** This type of *electron release due to the presence of the system* H—C—C = C is known as **hyperconjugation** or **Baker-Nathan effect.** Note that in structure II there is no definite bond between one of the carbon atoms and one of the hydrogen atoms, hence hyperconjugation is also known as **no-bond resonance.** It is a permanent effect. It is also known as **anchimeric effect.**

Hyperconjugation in propene



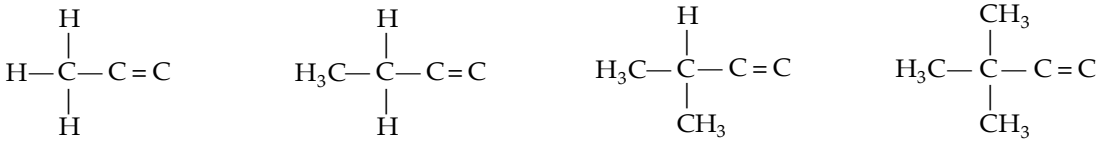
I ⟷ II ⟷ III ⟷ IV

Hyperconjugation in toluene



I ⟷ II ⟷ III ⟷ IV

More the number of H—C bonds attached to the unsaturated system more will be the probability of electron release by this mechanism. Thus the electron release by this mechanism will be greater in methyl (possessing three hyperconjugated H—C bonds), less in ethyl (having two such bonds) and *iso*-propyl (one) and essentially zero in *tert*-butyl (no hyperconjugated H—C bond) group.



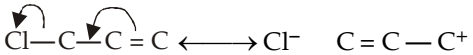
Methyl compound	Ethyl compound	*iso*-Propyl compound	*tert*-Butyl compound
(containing 3 H – C hyperconjugated bonds)	(containing 2 H – C hyperconjugated bonds)	(containing 1 H – C hyperconjugated bond)	(containing no H – C hyperconjugated bond)

It is important to note that although hyperconjugation like inductive effect causes the release of electrons and thus the two effects reinforce each other in this respect, the magnitude of the two effects changes in opposite directions in passing along a series of alkyl groups.

CH_3—, CH_3CH_2—, $(CH_3)_2CH$—, $(CH_3)_3C$—

Increasing inductive effect, Decreasing hyperconjugation ⟶

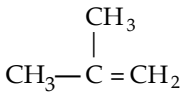
The phenomenon of hyperconjugation can also be applied to group, Cl—C—C = C (*cf.* H—C—C = C) where the effect operates in the reverse direction.



Effects of hyperconjugation*.

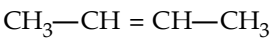
(*i*) **Stability of alkenes.** Hyperconjugation explains the stability of certain olefins over other alkenes. For example, propene is more stable than ethene because in propene there are three H—C hyperconjugated bonds and thus the σ-electron of C—H bond can delocalise over three different structures (structures drawn above).

Further greater the number of alkyl groups attached to the doubly-bonded carbons, the more stable the alkene is. Thus 2-methylpropene and butene-2 are more stable than propene.



2-Methylpropene

(6 H—C hyperconjugated bonds)



Butene-2

(6 H—C hyperconjugated bonds)

In general, alkenes follow the following order of stability.

$$R_2C = CR_2 > R_2C = CHR > RCH = CHR > R\,CH = CH_2 > CH_2 = CH_2$$

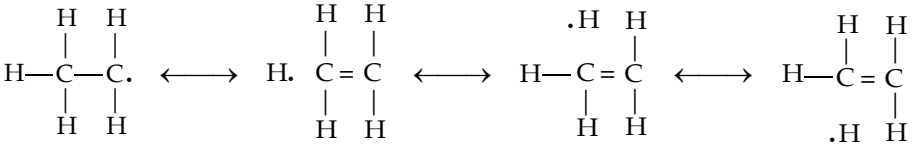
(*ii*) **Stability of carbocations and alkyl free-radicals.** The concept of hyperconjugation can also be extended to explain the following relative stabilities of alkyl radicals and carbocations.

tert-Alkyl > *sec*-Alkyl > *pri*-Alkyl > Methyl radical

e.g., $(CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3$

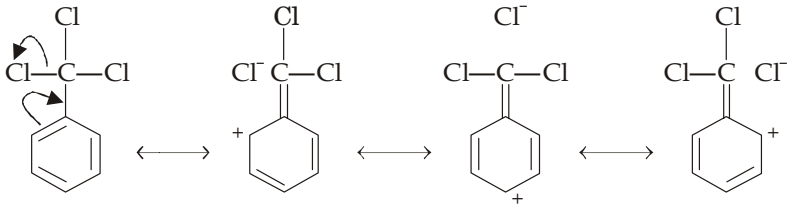
Similarly, $(CH_3)_3\,C^+ > (CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2 > \overset{+}{C}H_3$

In general, more the number of hyperconjugative structures of a species higher is its stability. Thus ethyl radical may be regarded as a hybrid of the following hyperconjugative structures.

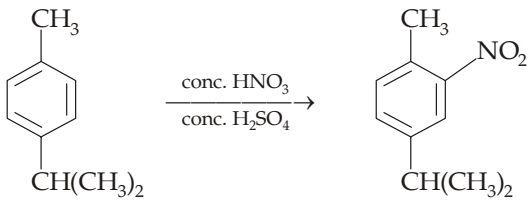


(*iii*) **Orienting influence of alkyl group in *o, p*-positions and of —CCl_3 group in *m*-position.** Observe the hyperconjugative structures of toluene, given earlier you will find high electron density on *o*- and *p*-positions.

Hyperconjugation in $C_6H_5CCl_3$ causes electron deficiency in *o*-, *p*-positions and thus *m*-positions become relatively electron rich.



The role of hyperconjugation in directive influence can be realised by knowing the fact during nitration of *p*-isopropyltoluene and *p*-*tert*-butyltoluene, —NO_2 group is introduced mainly in the *o*-position with respect to the —CH_3 group and not to isopropyl or *tert*-butyl group.



* Hyperconjugative effect is a much weaker effect as compared to resonance effect.

TEST YOUR UNDERSTANDING - 2.5

1. Represent the movement of electrons in allyl bromide on additions of HBr.

2.6 Types of Bonding Among Covalent Molecules (Intermolecular Forces)

In an ionic compound, the structural units are ions. For example, solid sodium chloride is made up Na^+ and Cl^- ions. Each Na^+ ion is attached to six Cl^- ions around it and each Cl^- ion is attached to six Na^+ ions around it. The *interionic forces are very powerful electrostatic forces and hold each ion in position.* However, in non-ionic (covalent) compounds, the structural units are molecules which *are hold together through very weak forces* of the following three types.

2.6.1 Dipole-dipole interaction

In polar molecules, positive end of one polar molecule is attracted by the negative end of another polar molecule and vice versa. As a result of this, dipole-dipole interaction, polar molecules are generally held to each other more strongly than the nonpolar molecules of comparable molecular mass.

2.6.2 Hydrogen bond

Hydrogen bond is formed between hydrogen atom linked to highly elecronegative element, X (F, O or N), and another highly electronegative element, Y (F, O or N), X—H ------ Y. Hydrogen bond may be intermolecular or intramolecular. Intermolecular hydrogen bonding causes association of the molecules and thus increases its m.p. or b.p.

2.6.3 London (van der Waals) forces

In non-polar compounds there is a weak intermolecular attraction due to electrostatic attraction between the nuclei of one molecule and electrons of the other. The electrostatic attraction is largely compensated by electrostatic repulsion between electrons of the two neighbouring molecules, as well as by repulsion between nuclei of the two neighbouring molecules. Thus the van der Waals forces are very weak and are significant only when the molecules are very close together. They act only between portions of different molecules which are in close contact, *i.e.,* between the surface molecules. Thus van der Waal forces are proportional to

(*a*) *surface area of a molecule.* Greater is the surface area of a molecule, greater is the number of interactions and hence stronger will be van der Waal forces. This explains why boiling point decreases on the increase in branching of a compound.

(*b*) *molecular weight of compound.* The greater the molecular weight of the molecule, the greater is the number of electrons and the greater these forces.

The relative order of attraction of the three intermolecular forces is :

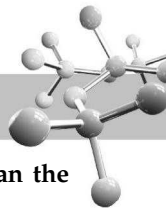
hydrogen bond > dipole-dipole > van der Waals

The physical properties especially m.p., b.p. and solubility depend largely upon the nature of the bond present in the molecule, nature of the intermolecular forces and molecular weight of the compound.

(*a*) **Melting and boiling points.** A solid melts when the thermal energy of its particles is large enough to overcome the interparticle forces which hold them in position. Similarly, a liquid boils when the thermal energy of its particles is enough to overcome the cohesive forces which hold them in position. Since ionic compounds have very strong interionic forces which are overcome only at very high temperatures, they melt (or boil) at high temperatures. On the other hand, non-ionic (covalent) compounds have weak intermolecular forces (H-bond, dipole-dipole interaction or van der Waals forces) which are overcome at relatively low temperatures, these compounds melt (or boil) at low temperatures.

$$\overset{\delta+}{H}-\overset{\delta-}{F}$$

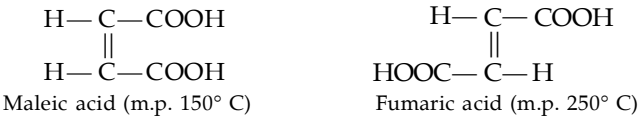
Melting points depend not only on molecular weight but also on molecular shape. Following important general relationship exists between melting point and structure of aromatic compounds.



(*i*) **Among isomeric disubstituted benzenes the para isomer generally melts considerably higher than the corresponding ortho and para.**

The higher melting point (and lower solubility) of a *para* isomer is due to molecular symmetry. The more symmetrical a compound, the better it fits into a crystal lattice and hence higher will be the melting point (and lower is the solubility). Among disubstituted benzenes, *para* isomers are the most symmetrical and hence possess highest melting point among the three isomers.

(*ii*) *trans*-Isomers have higher m.p. than the corresponding *cis*-isomer, *e.g.*

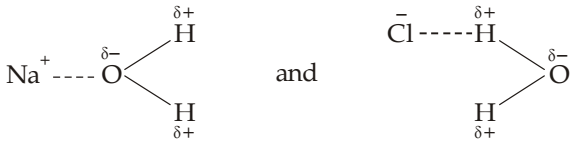


(*iii*) In carboxylic acids, even numbered member has higher melting point than the higher molecule having odd number of carbon atoms.

(*b*) **Solubility.**

(*i*) Ionic compounds are generally soluble in water due to following reason.

In the strongly polar solvent H_2O, each positive ion is surrounded by water molecules due to ion-dipole attraction, and each negative ion is H-bonded to water.



These interactions, called **solvation** (more specifically, **hydration**, since the solvent is water), causes the ions to separate and disperse in the solvent. Once the ions are hydrated, water lowers the attraction between oppositely charged ions due to its high dielectric constant.

(*ii*) Non-ionic compounds are governed by solubility rule *''like dissolves like''*. Thus non-polar, weakly polar and highly polar substances are generally soluble in non-polar, weakly polar and highly polar solvents respectively. Solubility of organic compounds in water can be predicted on the basis of H-bonding.

(*a*) Compounds containing —OH, —COOH, —NH_2 and ethers are soluble in water because these functional groups are capable of forming hydrogen bonding with water.

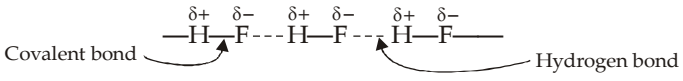
(*b*) Hydrocarbons are almost insoluble in water ; in general larger the hydrocarbon part of an organic molecule, lower is its solubility in water. However, lower alkanes (*e.g.* CH_4) are sparingly soluble in water due to their similar (smaller) size with that of water molecules.

2.7 Hydrogen Bonding

A hydrogen atom, with only 1*s* orbital at first sight is expected to form only one valency bond but it has been found to possess the special property of forming weak bonds with certain electronegative atoms to which it is not directly attached by formal chemical bonds. There is a lot of evidence to show that in some cases hydrogen atom can, in fact, bind two atoms together, apparently forming two bonds.

Consider the hydrogen–fluorine bond in hydrogen fluoride, HF. This is a polar covalent bond in which hydrogen is attached to a strongly electronegative element. As a result, the fluorine acquires partial negative charge hydrogen acquires a partial positive charge.

The positive charge on hydrogen in a molecule of hydrogen fluoride will be attracted electrostatically by the negative charge on the fluorine atom in another molecule of hydrogen fluoride. This electrostatic attraction (dipole-dipole attraction) between different molecules of hydrogen fluoride continues resulting in the formation of a large aggregate.



Thus we see that hydrogen in hydrogen fluoride is bonded to two highly electronegative flourine atoms; the linkage between hydrogen and one of the fluorine atoms is a usual covalent bond while the linkage between hydrogen and the other fluorine is simply due to electrostatic forces of attraction which results a weak bond, commonly known as **hydrogen bond** (protonic bridge). The new type of linkage is represented by dotted line (-------).

Thus **hydrogen bond** *is an electrostatic attractive force between covalently bonded hydrogen atom of one molecule and an electronegative atom (such as* F, O, N*) of another molecule.* Hydrogen bond is merely a strong electrostatic attractive force and not a normal chemical bond. It is very weak (strength about 2—10 kcal mol^{-1} or 8.4—42 kJ mol^{-1}) as compared to a covalent bond (strength 50—100 kcal mol^{-1} or 209—418.4 kJ mol^{-1}).

Conditions for hydrogen bonding

(*i*) *The molecule must possess a higher electronegative atoms such as* F, O *or* N, *directly linked to hydrogen atom.*

(*ii*) *The size of the electronegative atom should be small.*

These conditions are met only by F, O and N* atoms and only these atoms form effective hydrogen bonding. Thus hydrogen bonds are usually encountered in hydrogen fluoride (HF), water (H_2O), ammonia (NH_3), alcohols (ROH), carboxylic acids (RCOOH), and amines (RNH_2). Further, greater the electronegativity and smaller the size of the atom (F, O, N), the stronger is the hydrogen bond which is evident from the relative order of energies of hydrogen bonds in the three elements.

$$\underset{10\ \text{kcal/mole}}{H—F\cdots H} > \underset{7\ \text{kcal/mole}}{H—O\cdots H} > \underset{2\ \text{kcal/mole}}{H—N\cdots H}$$

Comparison of hydrogen bonding formed by halogens. Among halogens, only fluorine forms hydrogen bonding because other halogens are not too electronegative to form hydrogen bonding. The non-existence of hydrogen bonding in HCl, HBr and HI explains the non-existence of molecules like KCl– – –HCl ($KHCl_2$), KBr – – –HBr ($KHBr_2$) and KI– – –HI (KHI_2), although KF– – –HF (KHF_2) has been isolated. Actually, the HF_2^- anion has the strongest known hydrogen bond (bond energy = 27 kcal/mole).

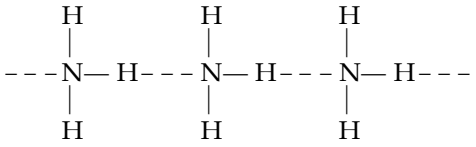
$$[F\text{------}H—F]^-$$

Experimentally, it has been found that hydrogen atom is in midway between the two fluorine atoms. The HF_2^- ion consists of two F^- ions shielded from each other by a proton (H^+).

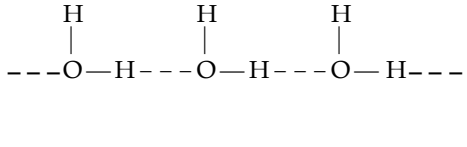
Types of hydrogen bonding. Generally, the hydrogen bonds are classified into two groups, *viz*. intermolecular and intramolecular.

2.7.1 Intermolecular hydrogen bonding

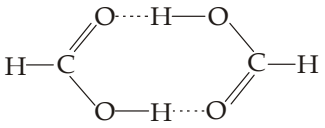
In such type of linkage the two or more than two molecules of the same compound combine together to give a polymeric aggregate. For example,



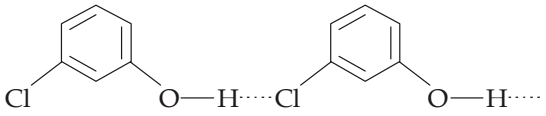
Hydrogen bonding in ammonia



Hydrogen bonding in water



Hydrogen bonding in formic acid (dimerisation)



Hydrogen bonding in *m*-chlorophenol

Intermolecular hydrogen bonding between molecules of the same type (*association*) *increases the boiling point of the compound.* The increase in boiling point is because of association of several molecules of the compound with the result the effective molecular weight of the compound increases and hence more energy (large amount of heat) is required to dissociate the molecules for vaporization.

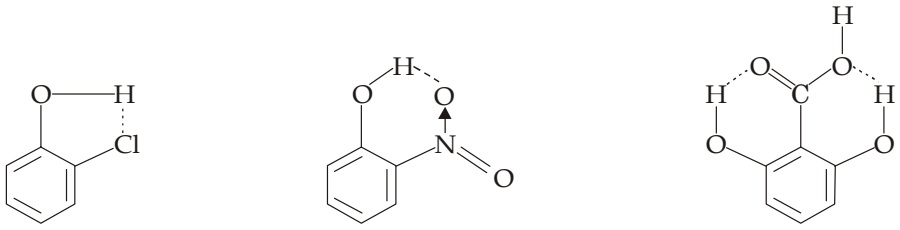
Intermolecular hydrogen bonding between molecule of a compound and water molecule, increases solubility of that compound in water (remember *a compound is said to be soluble in water if it is capable forming hydrogen bonding with water*).

2.7.2 Intramolecular hydrogen bonding

In this type, hydrogen bonding occurs within two atoms of the same molecule. This type of hydrogen bonding is commonly known as **chelation** and frequently occurs in organic compounds. Intramolecular hydrogen bonding is possible when a six or five-membered ring can be formed. Some examples are given below.

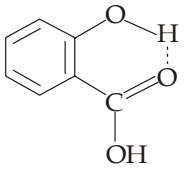
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* Although Cl has same electronegativity as nitrogen, it does not form effective hydrogen bonds. This is because of its larger size than that of N with the result its electrostatic attractions are weak. Similarly, sulphur forms a very weak hydrogen bond due to its low electronegativity, although oxygen present in the same group forms a strong hydrogen bond.

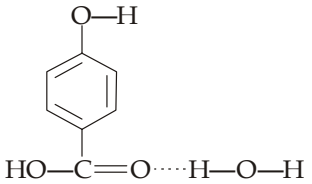


Intramolecular hydrogen bonding in *o*-chlorophenol, *o*-nitrophenol and 2, 6-dihydroxybenzoic acid.

Intramolecular hydrogen bonding (chelation) *decreases the boiling point of the compound and also its solubility in water.* This is because of fact that the chelation between the *ortho* substituted groups restricts the possibility of intermolecular hydrogen bonding and thus prevents association of the molecules which would have raised the melting and boiling points. Chelation is not possible in the corresponding *m*- and *p*-isomers because the two groups (atoms) are far away from each other. Hence in such cases, intermolecular hydrogen bonding takes place which in turn increases the boiling point. Thus we can explain *the low m.p. and b.p. of the ortho isomers of hydroxy and nitro-carbonyl compounds than the corresponding m-and p-isomers.* Decrease of solubility in water is again due to chelation which prevents hydrogen bonding between compound and water.



Intramolecular hydrogen bonding in *o*-hydroxybenzoic acid (Note that —CO group not available to form hydrogen bond with water)



Intermolecular H-bonding between *p*-hydroxybenzoic acid and water (—CO group is available to form hydrogen bond with water)

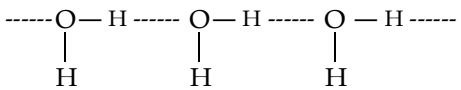
EFFECTS OF HYDROGEN BONDING

1. **Boiling point.** The boiling point of a liquid is the temperature at which kinetic energy of the molecule is sufficient to overcome the intermolecular attractive forces. Thus it seems to be reasonable that heavier the molecule and stronger the intermolecular forces higher will be the boiling point of the compound. Thus, if the intermolecular forces are equal, the melting and boiling points of similar compounds should increase with the increase in molecular weight of the compound. This explains why the melting and boiling points generally increase with increase in number of carbon atoms in most of the homologous series.

On the other hand, if the two similar compounds under study are having different intermolecular forces, their melting and boiling points differ very much. It is due to the fact that molecules of the compound having greater attractive intermolecular force have a greater tendency of association with the result the effective molecular weight and subsequently melting and boiling* points of the compound increase. Best familiar examples of this type of compounds are water, alcohols, hydrogen fluoride, amines and amides.

(*a*) ***Water.*** Although water has minimum molecular weight amongst hydrides of the 16th group of the periodic table, it has the highest melting and boiling points and is liquid (while others are gases) under ordinary conditions.

This is explained on the basis that water molecules associate through hydrogen bonding and thus require more energy to get separated for vaporization.



As far as sulphur is concerned, its lesser electronegative nature than oxygen gives S—H bond a smaller ionic character than the O—H bond and thus H_2S forms very weak hydrogen bond.

---

* Alternatively, since extra energy is required to break the hydrogen bond, intermolecular hydrogen bonding increases the melting and boiling points of substances.

The two unusual properties of water, namely (*a*) low density in the solid state than that in the liquid state, and (*b*) contraction when heated between 0°C and 4°C, can be explained on the basis of hydrogen bonding in water.

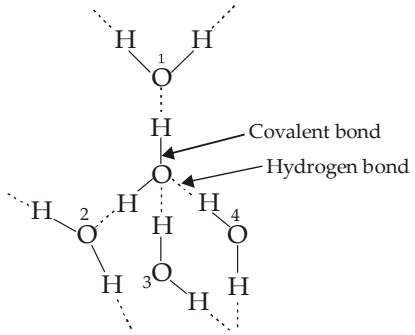
Note the following features of the above structure.

(*i*) The H_2O molecules are tetrahedrally oriented with respect to one another.

(*ii*) Each oxygen atom is surrounded tetrahedrally by four H atoms.

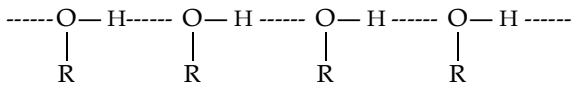
(*iii*) One water molecule is capable of forming four hydrogen bonds.

(*iv*) Hydrogen bonds are weaker and, therefore, longer than the covalent bonds.



The tetrahedral open cage-like structure of ice.

(*b*) ***Alcohols.*** The boiling points of alcohols are higher than those of the corresponding thiols (mercaptans) and ethers. Higher boiling point of an alcohol than that of the corresponding thiol is due to the association of alcohol molecules in the same way as in water.



Similarly, we can explain the higher boiling points of polyhydric alcohols than their ethers. The successive replacement of hydrogen atom of the OH group of alcohol by alkyl group to form ether blocks the probability of hydrogen bonding, and thus the boiling points of the products (*i.e.* ethers) progressively decrease in spite of increase in molecular weights.

	CH_2OH | CH_2OH	CH_2OCH_3 | CH_2OH	CH_2OCH_3 | CH_2OH_3
b.p.	197°C	125°C	84°C

Now let us compare the hydrogen bonding in water and alcohols (*e.g.*, ethyl alcohol). Although both the compounds are having the hydroxyl group responsible for forming hydrogen bonds, water having low molecular weight boils at a high temperature than ethyl alcohol having higher molecular weight.

	H_2O	C_2H_5OH
Mol. wt.	18	46
b.p.	100°C	78°C

The higher boiling point of water than ethyl alcohol is because of greater degree of hydrogen bonding in water than in alcohol with the result greater number of water molecules are associated than the ethyl alcohol.

The high degree of hydrogen bonding in water is due to more contribution of —OH group in water (H — OH) molecule than that in alcohol (R—OH) molecule where a larger alkyl group is present in place of smaller hydrogen atom. The alcohols, due to alkyl group, behave somewhat like hydrocarbons as far as hydrogen bonding is concerned. This is further evidenced by the fact that larger the alkyl group or more the number of alkyl groups in an alcohol, lesser will be its tendency of forming hydrogen bonding. Thus primary alcohols have the highest boiling point while the tertiary alcohols have the lowest boiling point in the isomeric alcohols.

$CH_3CH_2CH_2CH_2OH$	$CH_3CH(OH)CH_2CH_3$	$CH_3-C(OH)(CH_3)-CH_3$
1-Butanol (1° alcohol) b.p. 118°C	2-Butanol (2° alcohol) b.p. 99°C	Methyl-2-propanol (3° alcohol) b.p. 83°C

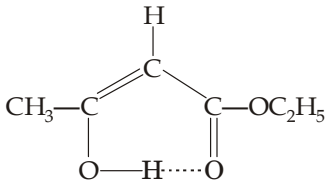
Glycerol, $CH_2OHCHOHCH_2OH$, having three — OH groups per molecule can form more hydrogen bonds per molecule than that of water. This increases attraction between all the molecules and hence increases the resistance of flow, *i.e.* viscosity.

(*c*) ***Hydrogen fluoride.*** Like the hydride of oxygen (water) among the hydrides of group 16 elements, hydrogen fluoride among the hydrides of group 17 elements, although has the lowest molecular weight, yet it is liquid and has the highest boiling point while others are gaseous in nature with low b.p.The abnormally high boiling point of HF is explained on the basis of the fact that due to greater electronegativity and smaller size, fluorine forms much stronger intermolecular hydrogen bonds than other halogens.

(*d*) ***Amines.*** Like water and alcohols, primary and secondary amines, but not tertiary, are capable of forming intermolecular hydrogen bonding (— N—H ------N) and thus primary and secondary amines boil at higher temperatures than the isomeric tertiary amine.

By now we have discussed the examples where the boiling points is increased due to hydrogen bonding (*intermolecular*) **but there are certain cases where the boiling point is decreased due to hydogen bonding** (*intramolecular*). For example, *the ortho-hydroxy- nitro,-carbonyl,-carboxylic or -chloro compounds have lower melting and boiling points than the respective meta or para isomer.* The reason being that intramolecular hydrogen bonding takes place between the two ortho substituted groups and thus prevents association of the molecules which would have raised the melting and boiling points.

On the other hand, intramolecular hydrogen bonding is not possible in case of *m*- and *p*-isomers because of the size of the ring which would have been formed. Thus here the intermolecular hydrogen bonding takes place which causes some degree of association with the result the *m*- and *p*-isomers melt and boil at higher temperatures.

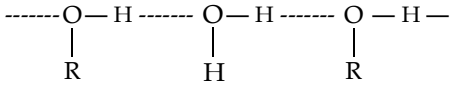


Hydrogen bonding in enolic form of acetoacetic ester.

Chelation also explains low boiling point of the enolic form of acetoacetic ester than that of the ketonic form (although usually alcohols possess higher boiling points than that of the corresponding ketones, *e.g.* isopropyl alcohol boils at 82°C while acetone at about 56°C).

2. Water solubility. *A substance is said to be soluble in water if it is capable of forming hydrogen bonding with water molecules.* On the other hand, compounds in which hydrogen bonding with water is not possible (or restricted due to intramolecular hydrogen bonding) would be insoluble or less soluble in water.

Thus organic compounds like alkenes, alkanes and ethers which lack the formation of hydrogen bonds with water are insoluble in water while alcohols and acids which are capable of forming hydrogen bonds with water are readily soluble in water.



Hydrogen bonding between alcohol and water

However, it is important to note that when the alkyl group (R —) in alcohols has four or more carbon atoms, the alkyl group predominates and hydrogen bond formation is restricted with the result the solubility of such alcohols in water decreases. Alcohols containing more than seven carbon atoms are insoluble in water, while methyl, ethyl and propyl alcohols are fairly soluble in water.

When a compound has a large ratio of — OH groups to hydrocarbon group, it will be very much soluble in water. Thus sugars, certain starches and polyvinyl alcohol are quite soluble in water.

Thus we can explain the solubility of alcohols, phenols, primary and secondary amines in water since these compounds easily form hydrogen bonds with water molecules. The success of non-ionic detergents[1] is due to the powerful solubilizing effect of hydroxyl groups. Since the water soluble portion of these detergents has neutral hydorxy, ether or amino groups, they are easily dissolved in water as a result of hydrogen bonding.

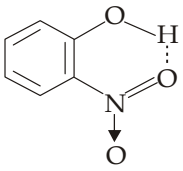
The insolubility of tertiary amines[2] in water is probably due to a steric effect rather than lack of N - - - - -H—O bonding because tertiary amines with the alkyl groups tied back by ring formation, such as pyridine, are soluble in water.

It is important is note that while *the intermolecular hydrogen bonding increases solubility of the compound in water, the intramolecular hydrogen bonding decreases.* This is due to the fact that the formation of internal hydrogen bond prevents hydrogen bonding between the compound and water which thus reduces solubility of the compound in water.

One practical application of the contrasting effects of chelation and association upon boiling point and water solubility is made in the separation of a mixture of *ortho*- and *para*-hydroxy-carbonyl or-nitro compounds by steam distillation. In case of *ortho* isomers, association of the hydroxyl group with water molecules is prevented due to chelation and thus these isomers are only sparingly soluble in water and possess lower boiling point and

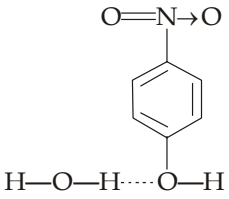
1. Non-ionic detergents are the derivatives of di- and tri-ethanolamines or the condensation products of ethylene oxide with alcohols or phenols.
2. However, the first member of the series, trimethylamine is about 41% soluble in water.

are thus much volatile that the *para* isomers with the result the *ortho* isomers can be steam distilled so much rapidly than the *para* isomers that a practical separation of the two isomers can be achieved.



o-Nitrophenol

Due to chelation, —OH group is not available to form hydrogen bond with water hence it is sparingly soluble in water. Further, association of the molecules due to intermolecular hydrogen bonding is also not possible hence it has lower boiling point.



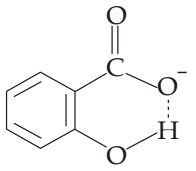
p-Nitrophenol

—OH group available to form hydrogen bond with water, hence it is completely soluble in water. Chelation is not possible, hence association of the molecules is possible due to intermolecular hydrogen bonding. Hence it has high boiling point.

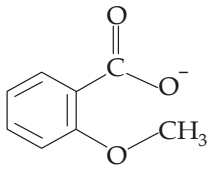
3. **Strength of acids.** The dissociation of an acid and hence its acidity is sufficiently increased, if its anion is stabilized by chelation. This can be proved by the ionization constants of the three isomeric hydroxy-and methoxy-benzoic acids in water.

	ortho	*meta*	*para*
$OH . C_6H_4 . COOH$	105×10^{-5}	8.3×10^{-5}	2.9×10^{-5}
$OCH_3 . C_6H_4 . COOH$	8.1×10^{-5}	8.2×10^{-5}	3.4×10^{-5}

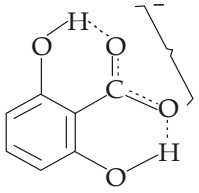
The abnormally high dissociation constant of the *o*-hydroxybenzoic acid in the above table is due to the fact its anion is stabilized by chelation. Its dissociation is 17 *times more than that of benzoic acid. The fact that hydrogen bonding increases the acidity of the o-isomer is proved by the very low dissociation constant of the o-methoxybenzoic acid where hydrogen is not available for hydrogen bonding. Furthermore, the dissociation of 2, 6-dihydroxybenzoic acid is 800 times as large as that of benzoic acid which is again due to greater stabilization of its anion by hydrogen bonding.*



Salicylate ion



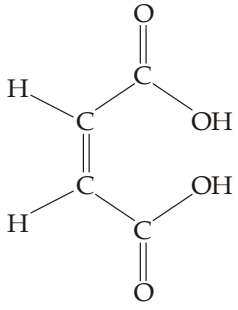
o-Methoxybenzoate anion
(Hydrogen bonding is not possible)



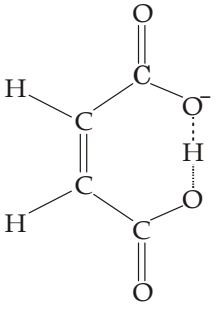
2, 6-Dihydroxybenzoate anion

Similarly, we can explain very strong acidic character of maleic acid than fumaric acid. If one proton is removed from each of the acids, the corresponding ions are formed. But the maleate ion can be stabilized by chelation because hydrogen and oxygen responsible for forming hydrogen bond are very near to each other. On the other hand, fumarate ion can not stabilise by chelation because hydrogen and oxygen are on the opposite sides to each other, hence the formation of fumarate ion does not take place. This explains why maleic acid is a stronger acid than its isomer, fumaric acid.

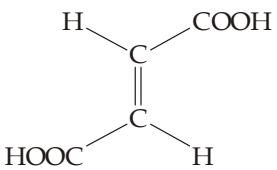
In case, the dissociating hydrogen atom is involved in hydrogen bond, enough energy will be required for its removal and thus the dissociation constant will be abnormally low. This explains why the *o*-halogenophenols are weaker acids than the *m*- or *p*-isomers. It also explains why the second dissociation constant of maleic acid is very low as compared to that of K_{a_1}.



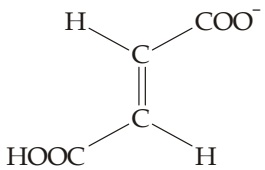
Maleic acid



Maleate ion
(chelation possible)



Fumaric acid

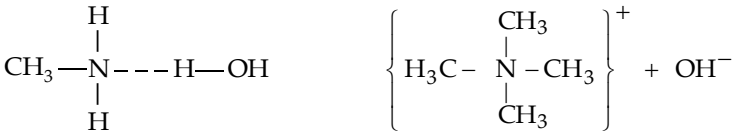


Fumarate ion
(chelation not possible)

Similarly, we can explain why HF is a less stronger acid than any other halogen acid. Since HF is capable of forming strong hydrogen bonds, its proton is dissociated with a great difficulty as compared to other halogen acids. Thus acidity among halogeno acids follows the following order :

$$HF < HCl < HBr < HI$$

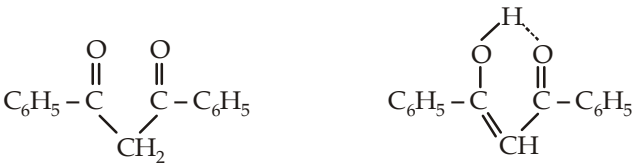
4. **Basic strength of amines.** Compounds like NH_3, $MeNH_2$, Me_2NH and Me_3N are weak bases, while the quaternary compound $Me_4N^+OH^-$ is a very strong base can be explained in the following way. When dissolved in water, the first four bases combine with water to yield species I which owing to the formation of hydrogen bond can not be regarded as fully ionic.



I II

On the other hand, the tetramethylammonium hydroxide, lacking a hydrogen atom on the nitrogen, cannot exist in a form analogous to I. It exists only in the completely ionized form II with the result the compound is a strong base, quite comparable in strength to potassium hydroxide.

5. **Chemical properties :** Hydrogen bonding also affects chemical properties of certain compounds. For example, dibenzoylmethane $C_6H_5COCH_2COC_6H_5$ neither gives certain typical reactions of the ketonic group, viz. it does not add HCN and $NaHSO_3$, nor some typical reactions of the enolic group, viz. acetylation and reaction with Grignard reagent. It is due to enolisation and hydrogen bonding.



(keto form) (enol form)

Dibenzoylmethane

6. **Hydrogen bonding in biological systems.** Hydrogen bonding also plays a very important role in biological systems. Most of water (which generally constitutes over 50% of the weight of the plant or animal) present in plants and animal is attached to proteins by hydrogen bond. The significance of hydrogen bonding in biological system can best be illustrated by its role in the structure of proteins and nucleic acids. Hydrogen bonding stabilises the usual structure of proteins and nucleic acids.

TEST YOUR UNDERSTANDING - 2.6

1. Account for the following :
   (*i*) Although CH_3Cl molecule is more polar than CH_3Br and CH_3I, it has lowest boiling point among the three.
   (*ii*) Although *n*-pentane and neopentane have same molecular weight and similar polarity, they differ in their boiling points.
   (*iii*) Ethyl alcohol boils at 78.3°C, while its isomer dimethyl ether boils at a very low temperature (– 24°C).
   (*iv*) Mineral oil, a mixture of high-molar mass hydrocarbons, dissolves in *n*-hexane but not in ethanol.

2.8 Acids and Bases

The terms acids and bases have been defined in a number of ways, however, here we shall take up only two ways.

2.8.1 Lowry-Bronsted definition

An acid is a substance that donates a proton, and a base is a substance that accepts a proton. The strength of acids or bases is measured by the extent to which they lose or gain protons, respectively. In acid-base reactions, acids and bases are converted to their conjugate bases and conjugate acids respectively. Remember that a strong acid (base) has always a weak conjugate base (acid), and a weak acid (base) always has a strong conjugate base (acid).

	Stronger acid		Stronger base(conjugate base)		Weaker acid (conjugate acid)		Weaker base
(*i*)	H_2SO_4	+	H_2O	$\rightleftharpoons$	H_3O^+	+	HSO_4^-
(*ii*)	HCl	+	NH_3	$\rightleftharpoons$	NH_4^+	+	Cl^-
(*iii*)	H_3O^+	+	OH^-	$\rightleftharpoons$	H_2O	+	H_2O
(*iv*)	NH_4^+	+	OH^-	$\rightleftharpoons$	H_2O	+	NH_3

Following important conclusions are drawn from the above examples.

(*a*) *A substance acts as an acid only when another substance capable of accepting a proton (i.e.,* a base) *is present.* For example, hydrogen chloride or acetic acid solution in benzene is not acidic (but neutral) because benzene is not in a position to take up protons. On the other hand, HCl or CH_3COOH solution in water is definitely acidic because HCl or CH_3COOH can ionise in water.

(*b*) *In aqueous solution,* H^+ *ion exists as hydrated ion* H^+H_2O *or* H_3O^+ **(hydronium ion)** and not as free H^+ ion.

(*c*) *Not only molecules but even ions may act as acids or bases.*

Table 3.1. Bronsted-Lowry Acids and Bases

Type	Acid	Base
Molecular	HCl, HBr, $HClO_4$, H_2SO_4, H_3PO_4, H_2O	NH_3, NH_2NH_2, amines, H_2O
Cationic	NH_4^+, $[Fe(H_2O)_6]^{3+}$, $[Al(H_2O)_6]^{3+}$	$[Fe(H_2O)_5(OH)]^{2+}$, $[Al(H_2O)_5(OH)]^{2+}$
Anionic	HS^-, HCO_3^- , HSO_4^-, $H_2PO_4^-$	Cl^-, Br^-, OH^-, HSO_4^-, CO_3^{2-}, SO_4^{2-}

(*d*) *Water,* the most common solvent, *can act both as an acid as well as a base* because it can give off a proton [example (*iv*)] as well as can receive it [example (*i*)]. Its dual behaviour may be represented by the following equation.

$$\underset{\text{Acid}_1}{H_2O} + \underset{\text{Base}_2}{H_2O} \rightleftharpoons \underset{\text{Acid}_2}{H_3O^+} + \underset{\text{Base}_1}{OH^-}$$

(*e*) The strength of an acid (or a base) depends upon the tendency of the base (or the acid) which accept (or donate) proton, *i.e.*, on medium which acts as base (or acid), *e.g.*

(*i*) $HCl + H_2O \longrightarrow H_3O^+ + Cl^-$ (*ii*) $HCl + NH_3 \longrightarrow NH_4^+ + Cl^-$

(*iii*) $HCl + C_6H_6 \longrightarrow$ No Reaction (*iv*) $HCl + CH_3COOH \longrightarrow CH_3COOH_2^+ + Cl^-$

(*v*) $HCl + HF \longrightarrow H_2Cl^+ + F^-$

Thus it is obvious that HCl acts as

an acid in water as in the above equation No. (*i*)

a stronger acid in NH_3 as in the above equation No. (*ii*)

a neutral in C_6H_6 as in the above equation No. (*iii*)

a weak acid in CH_3COOH as in the above equation No. (*iv*)

a weak base in HF as in the above equation No. (*v*)

(*f*) In acid-base reactions, equilibrium favours the formation of the weaker acid and weaker base.

Classification of solvents on the basis of proton

(*i*) *Protophilic.* Solvents which have a greater tendency to accept proton *e.g.*, H_2O, alcohol, liquor ammonia etc.

(*ii*) *Protogenic.* Solvents which have a greater tendency to donate proton, *e.g.*, H_2O, HCl(*l*), glacial acetic acid etc.

(*iii*) *Amphiprotic.* Solvents which can both accept and donate a proton, *e.g.*, H_2O, liquor ammonia, alcohol etc.

(*iv*) *Aprotic.* Solvents which can neither accept nor can donate a proton, *e.g.*, benzene, CS_2, CCl_4, etc.

TEST YOUR UNDERSTANDING - 2.7

1. Write down the conjugate acids and bases in the reaction of H_2O with gaseous (*a*) HCl and (*b*) NH_3.

Also mention the direction in which the reaction will mainly occur in each case.

2. Rewrite the following equations to show the Lowry-Bronsted acids and bases actually involved. Represent in which direction the reaction will mainly proceed.

(*a*) $NH_3(aq) + HNO_3(aq) \longrightarrow NH_4NO_3(aq)$ (*b*) $NaCN(aq) \longrightarrow HCN(aq) + NaOH(aq)$

(*c*) $NaH + H_2O \longrightarrow H_2 + NaOH$ (*d*) $CaC_2 + H_2O \longrightarrow Ca(OH)_2 + C_2H_2$.

Strength of acids and bases. The ease with which an acid loses a proton is known as its strength and similarly the ease with which a base takes up a proton is known as the strength of a base. The strength of an acid or a base is usually measured in terms of their ionisation constants (K_a and K_b). Furthermore, since the K_a values are very small and are expressed in negative powers of 10, they are converted into pK_a ($pK_a = -\log_{10} K_a$), *e.g.* K_a and pK_a values of CH_3COOH in water are 1.79×10^{-5} and 4.76 respectively. In general, the stronger an acid (base), the larger is its $K_a(K_b)$ and smaller is its $pK_a(pK_b)$ *value.* The ionisation constant of acid and base are related as below.

$$pK_a + pK_b = pK_w = 14.00 \text{ (at } 25°C).$$

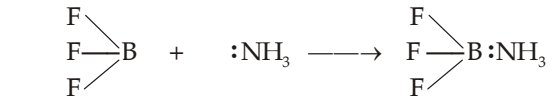
If pK_a or pK_b value is negative, it indicates that the acid (or base) is completely ionised (strong acid or base).

2.8.2 Lewis definition

According to Lewis, an acid is a substance that can take up an electron pair, while a base is a substance that can furnish an electron pair to form *a covalent bond. Thus a Lewis acid is an electron-pair acceptor (electrophile or electron deficient) and a Lewis base is an electron-pair donor (nucelophile or electron rich).* This is the most fundamental and most general concept for acids and bases.

Remember that **all the Bronsted-Lowry bases are also Lewis bases but all Bronsted-Lowry acids are not Lewis acids.** Thus according to Lewis, an acid may also be a species without any proton **(aprotic).** Actually, **Lewis acids** may be of several types.

(*i*) *Compounds whose central atom has an incomplete octet*. In other words, acids of this type are electron deficient molecules such as BF_3, $AlCl_3$, $GaCl_3$, etc.



Acid (electron acceptor) Base (electron donor)

Strength of such Lewis acids increases with

(*a*) an increase in nuclear charge (*i.e.* positive charge) on the central atom, *e.g.* $H_3O^+ > H_2O > OH^- > O^{2-}$

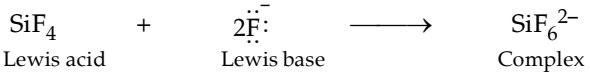
(*b*) an increase in the number and relative electronegativity of atom attached on the central atom, *e.g.* $SO_2 < SO_3$.

However, note the anomaly in case of relative acidic character of BX_3.

$$BF_3 < BCl_3 < BBr_3 < BI_3$$

(*c*) a decrease in atomic radius of the central atom.

(*ii*) *Compounds in which the central atom has available d-orbitals and may acquire more than an octet of valence electrons ;* SiF_4, $SnCl_2$ and $SnCl_4$ are typical examples.



Lewis acid Lewis base Complex

Some other examples of this type are PF_3, PF_5, SF_4, SeF_4, $TeCl_4$, TiX_4 and GeX_4.

(*iii*) *All simple cations, e.g.* Na^+, Ag^+, Cu^{2+}, Al^{3+}, Fe^{3+} etc. They can combine with electron pair, *e.g.*

$$Ag^+ + 2:NH_3 \longrightarrow (H_3N:Ag:NH_3)^+$$

Acid strength of simple cations increases with

(*a*) an increase in positive charge on the ion, *e.g.* $Fe^{2+} < Fe^{3+}$

(*b*) a decrease in ionic radius, *e.g.* $K^+ < Na^+ < Li^+$

(*c*) an increase in nuclear charge on atoms, *e.g.* $Li^+ < Be^{2+} < B^{3+}$

(*iv*) *Molecules with a multiple bond between atoms of dissimilar electronegativities.* Examples are O = C = O, O = S = O, etc.

Here positive end of the π bond dipole acts as an acid, *e.g.* $\overset{\delta-}{O} = \overset{\delta+}{C} = \overset{\delta-}{O}$.

(*v*) *Elements with an electron sextet.* Oxygen and sulphur atoms contain six electrons in their valency shells and, therefore, act as Lewis acids.

Lewis bases may be of following types.

(*i*) *All the simple negative ions, such as* $:\ddot{C}l:^-$, $:\ddot{F}:^-$

(*ii*) Molecules with one or two unshared pair of electrons, *e.g.* H_2O, NH_3, PH_3, ROH, R_2O, R_2S, pyridine, NX_3 etc.



The Lewis base nature of nitrogen trihalides follows the order : $NF_3 < NCl_3 < NBr_3 < NI_3$

This can be explained in terms of electronegativity of halogens. More is the electronegativity difference in the N—X bond, more is partial positive charge on N atom and thus lesser is the tendency of the electron pair to be donated by N.

(*iii*) Molecules with a multiple bond between atoms of dissimilar electronegativity, *e.g.*O = C = O, O = S = O, etc.

Here negative end of a π bond dipole acts as a base, *e.g.* $\overset{\delta-}{O} = \overset{\delta+}{C} = \overset{\delta-}{O}$.

(*iv*) Unsaturated hydrocarbons like $CH_2 = CH_2$, HC ≡ CH etc. Here π electrons are available to Lewis acids.

2.9 Relative Strength of Acids and Bases

To be acidic in the *Lowry-Bronsted sense*, a molecule must of course contain hydrogen. Thus degree of acidity of these acids is determined largely by the ability of the atom holding hydrogen to accommodate the electron pair left behind after removing proton. The better this atom accommodates these electrons, the greater the extent to which the conjugate base is formed, and hence stronger will be the original acid. Two factors that mainly determine the ability of an atom to accommodate electrons are

(*a*) *Electronegativity.* By definition, a more electronegative atom has a greater avidity for electrons. Since among atoms of the row of the periodic table, electronegativity increases from left to right, we can explain following acidic order.

(*i*) $H—CH_3 < H—NH_2 < H—OH < H—F$ (*ii*) $H—SiH_3 < H—PH_2 < H—SH < H—Cl$

(*b*) *Size of the atom.* Since a bigger atom permits greater dispersal of the charge of the electrons, it tends to stabilize a charged species. Further since among atoms of the same family, size increases on moving down the group, acidity also increases on moving down the group.

(*i*) $H—F < H—Cl < H—Br < H—I$ (*ii*) $H—OH < H—SH < H—SeH < H—TeH$

Among **organic acids**, appreciable Lowry-Bronsted acidity can be expected from compounds containing O—H, N—H and S—H groups. Factors responsible for relative acidic character of organic acids are hybridisation, inductive effect, resonance, hydrogen bonding etc.

To be acidic in the **Lewis sense,** a molecule must be electron deficient, *i.e.* it should have an atom having only a sextet of electrons.

(*i*) *Electronegativity.* More is the electronegativity of the atom holding the electron pair less will be its basicity.

(*ii*) *Size of the atom.* The bigger the atom, weaker will be base.

(*iii*) *Charge on atom.* For a given atom, availability of electrons is greatest in an electron-rich, negatively charged molecule, and least in an electron-poor, positively charged molecule as in the following example.

$OH^- > H_2O > H_3O^+$; $S^{2-} > HS^- > H_2S$; $NH_2^- > NH_3$

TEST YOUR UNDERSTANDING - 2.8

1. Predict the relative acidity of

(*a*) CH_3OH and CH_3SH (*b*) NH_4^+ and H_3O^+ (*c*) NH_4^+ and NH_3 (*d*) H_2O and OH^-.

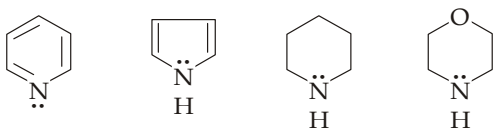
2. Arrange the following in the order of increasing acidity.

(*a*) H_2O, NH_3, HF and CH_4 (*b*) HCl, HBr, HF and HI

3. Arrange the following in order of decreasing basic character.

(*i*) CH_3OH, CH_3NH_2 and CH_3F (*ii*) OH^-, NH_2^-, CH_3^- and F^- (*iii*) OH^-, SH^- and SeH^-

(*iv*) F^-, Cl^-, Br^- and I^-. (*v*)



4. Explain the fact that neither pure H_2SO_4 nor pure $HClO_4$ conducts electric current, but a mixture of the two does.

5. Account for the fact that nearly every oxygen containing organic compound dissolves in cold conc. H_2SO_4 to give a solution from which the compound can be recovered by dilution with water.

To be basic in either the **Lowry-Bronsted** *or* **the Lewis sense,** a molecule must have an electron pair available for sharing. The better an atom accommodates the electron pair, less will be the availability of this pair for sharing and hence weaker will be the base. The availability of these unshared electrons is determined largely by the following characteristics of the atom holding this pair.

ISOMERISM

The existence of two or more compounds with the same molecular formula but different properties (physical, chemical or both) is known as isomerism ; and the compounds themselves are called *isomers*. The term was given by Berzelius. The difference in properties of the two isomers is due to the difference in the arrangement of atoms within their molecules. Isomerism may be of two types : structural isomerism and stereoisomerism. Here only structural isomerism is discussed, stereoisomerism is discussed in a separate chapter.

2.10 Structural Isomerism

When the isomers differ only in the arrangement of atoms or groups within the molecule, without any reference to space, these are known as **structural isomers** and the phenomenon as **structural isomerism.** Thus the structural isomers have the same molecular formula, but possess different structural formulae. Structural isomerism may again be of several types.

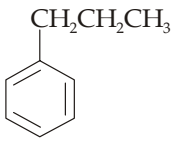
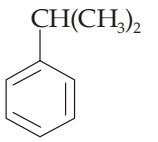
2.10.1 Chain, nuclear or skeleton isomerism

This type of isomerism is *due to the difference in the nature of the carbon chain (i.e. straight or branched)* which forms the nucleus of the molecule, *e.g.*,

(*a*) $CH_3CH_2CH_2CH_3$ and $CH_3CH(CH_3)CH_3$

(*b*) $CH_3CH_2CH=CH_2$ (1-Butene) and $CH_3C(CH_3)=CH_2$ (Isobutene)

(c) $CH_3CH_2CH_2CH_2OH$ (*n*-Butanol) and $CH_3CH(CH_3)CH_2OH$ (Isobutanol)

(*d*)  (*n*-Propylbenzene) and  (Isopropylbenzene)

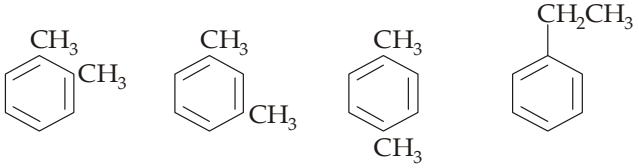
2.10.2 Position isomerism

It is due to the difference in the position of the substituent atom, group or an unsaturated linkage in the same carbon chain. Such isomers are also called **regiomers**. Examples are

C_3H_7OH : $CH_3—CH_2—CH_2—OH$ (*n*-Propanol (Propanol-1)) and $CH_3—CH(OH)—CH_3$ (*iso*-Propanol (Propanol-2))

C_4H_8 : $CH_2=CH—CH_2—CH_3$ (Butene –1) and $CH_3—CH=CH—CH_3$ (Butene -2)

C_6H_{14} : $CH_3CH_2CH_2CH(CH_3)CH_3$ (2-Methylpentane) and $CH_3CH_2CH(CH_3)CH_2CH_3$ (3-Methylpentane)

C_8H_{10} 

o-Xylene, *m*-Xylene, *p*-Xylene, Ethylbenzene

Example 7 :

Write the total number of isomeric alkenes corresponding to molecular formula C_5H_{10}.

Solution :

For knowing the possible number of isomers of a compound, follow the following points.

(*i*) First write down the possible number of isomeric parent alkanes.

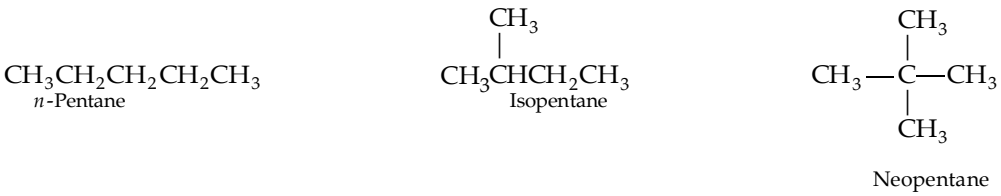
(*ii*) Take one isomeric alkane, introduce the given functional group (*e.g.* double bond) at different positions so as to get different isomeric compounds.

(*iii*) Repeat the procedure for other isomeric alkanes.

(*iv*) Observe the possibility of geometrical and optical isomerism in all the isomeric compounds, so obtained.

Take the example of C_5H_{10}.

(*i*) The parent hydrocarbon, pentane, has three isomers.

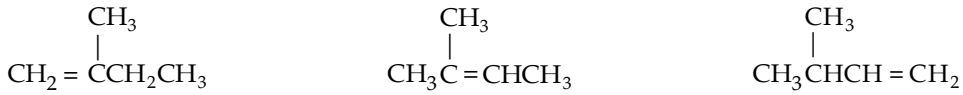


(*ii*) Now introduce one double bond, first in *n*-pentane for which there are two possibilities.



From the formula of pentene-2, it is obvious that it can exist in *cis* and *trans* forms.

(*iii*) Now introduce one double bond in various possible positions in isopentane.

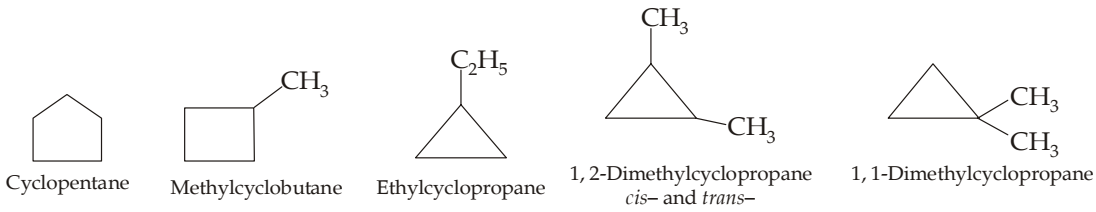


Observe that none of them can exhibit geometrical and optical isomerism.

(*iv*) From the formula of neopentane it is evident that a double bond can't be introduced at any position.

So total number of isomeric alkenes corresponding to C_5H_{10} is **six**.

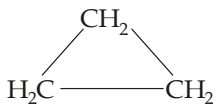
Remember that C_5H_{10} can also exist as cycloalkanes of following structures :



2.10.3 Ring-chain isomerism

This type of isomerism is *due to difference in mode of linkage of carbon atoms and the isomers may have either open chain or closed structure, e.g.,*

C_3H_6 : $CH_3—CH = CH_2$ (Propene)



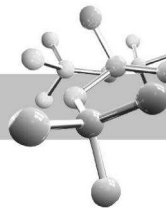
Cyclopropane

C_4H_6 : $CH_3CH_2C \equiv CH$ (1-Butyne)

$CH_2=CH—CH=CH_2$ (1, 3-Butadiene)



Cyclobutene



2.10.4 Functional isomerism

This type of isomerism is *due to difference in the nature of functional group present in the isomers.* The following pairs of compounds always form functional isomers with each other.

(*i*) Dienes, allenes and alkynes
(*ii*) Alchols and ethers
(*iii*) Aldehydes, ketones and unsaturated alchols
(*iv*) Carboxylic acids and esters
(*v*) 1°, 2° and 3° amines
(*vi*) Nitroalkanes and alkyl nitrites
(*vii*) Cyanides and isocyanides
(*viii*) Aromatic alcohols, phenols and ethers

Few examples of each pair are given below.

(*a*) **C_4H_6 :** $CH_2=CH—CH=CH_2$, $CH_2=C=CHCH_3$, $CH_3—C\equiv C—CH_3$

Buta -1, 3-diene (note the presence of two C = C linkage) — 1,2–Butadiene (allene) — Butyne-2 (note the C ≡ C linkage)

(*b*) **C_2H_6O :** $CH_3—CH_2OH$ Ethyl alcohol (note the alcoholic group); $CH_3—O—CH_3$ Dimethyl ether (note the ether group)

(*c*) **C_3H_6O :** CH_3CH_2CHO Propanal; CH_3COCH_3 Acetone; $CH_2=CH—CH_2OH$ Allyl alcohol

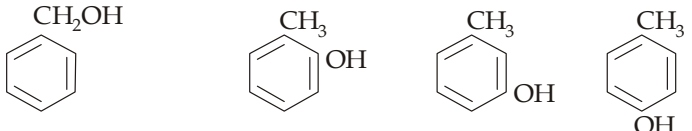
(note the different functional groups in 3 isomers)

(*d*) **$C_3H_6O_2$:** CH_3CH_2COOH Propanoic acid (note the acidic group); CH_3COOCH_3 Methyl acetate (note the ester group)

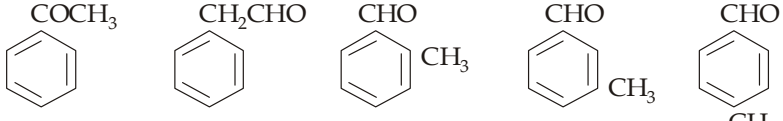
(*e*) **C_3H_9N :** $CH_3CH_2CH_2NH_2$ *n*-Propylamine (a primary amine); $CH_3NHC_2H_5$ Methylethylamine (a sec. amine); $(CH_3)_3N$ Trimethylamine (a *tert*-amine)

(*f*) **RNO_2 :** RNO_2 Nitroalkanes (Note the nitro group); $RONO$ Alkyl nitrites (Note the nitrite group)

(*g*) **RCN :** $RC\equiv N$ Alkyl cyanides (Note the cyanide group); $RN\overset{+}{=}C$ Alkyl isocyanides (Note the isocyanide group)

(*h*) **C_7H_8O :** 

Benzyl alcohol (Note the **alcoholic group**) — *o*-, *m*-, *p*- Cresols (Note the **phenolic group**)

(*i*) **C_8H_8O :** 

Acetophenone — Phenylacetaldehyde — *o*-, *m*-, *p*-Methylbenzaldehydes

2.10.5 Metamerism

It is due to difference in nature of alkyl groups attached to the same functional group. This type of isomerism is shown by compounds of the same homologous series. For example,

$CH_3—O—C_3H_7$-*n* Methylpropyl ether; $CH_3—O—CH(CH_3)_2$ Methylisopropyl ether; $C_2H_5—O—C_2H_5$ Diethyl ether

2.10.6 Tautomerism

Tautomerism[1] *may be defined as a phenomenon in which a single compound exists in two readily interconvertible structures that differ markedly in the relative position of at least one atomic nucleus, generally hydrogen.* The two different structures are known as tautomers of each other. Sometimes the term tautomerism is also called as **desmotropism** (Greek *desmos-bond ;* tropos-*turn*), since the interconversion of the two forms involves a change of bonds, or **dynamic isomerism** as the two forms are in dynamic equilibrium with each other. Other uncommon names for the tautomerism are *kryptomerism, allelotropism* or *merotropy ;* however, tautomerism is the most widely accepted term.

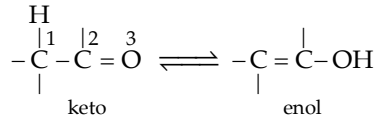
Alternatively, tautomerism may be of two types.

(a) **Dyad system.** When the hydrogen atom migrates from atom number one to atom number two, e.g.

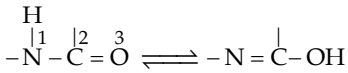


(b) **Triad system.** When the hydrogen atom migrates from atom one to atom three in a chain. It may again be of several types, viz.

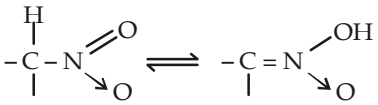
(i) Keto-enol system :



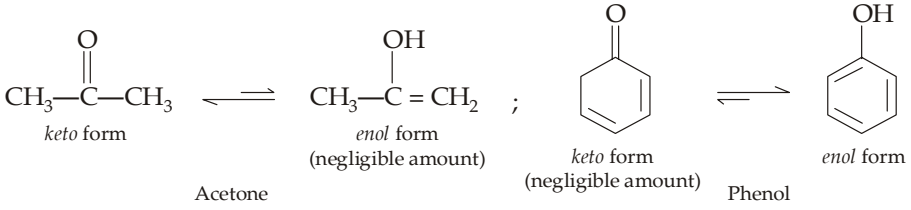
(ii) Lactam-lactim or amido-imido system :



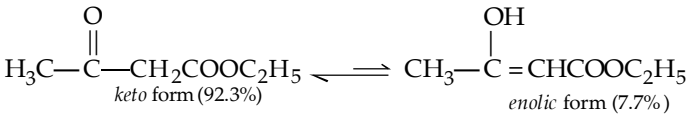
(iii) Nitro-acinitro system :



Among the several types of tautomerism *keto-enol tautomerism* is the most important. In this type, one form (tautomer) exists as a *ketone* while the other exists as an enol[2]. The two simplest examples are of acetone and phenol.



However, the most widely studied example of keto-enol tautomerism is that of acetoacetic ester (ethyl acetoacetate).



Acetoacetic ester

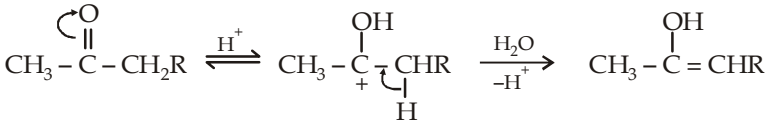
The two forms are readily interconvertible by acid or base catalyst, and under ordinary conditions surface of the glass is sufficient to catalyse the interconversion. The exact composition of the equilibrium depends upon the nature of the compound, solvent, temperature, etc. *The conversion of a keto form into enol form is known as* **enolisation.** The two forms of the acetoacetic ester have been isolated under suitable conditions.

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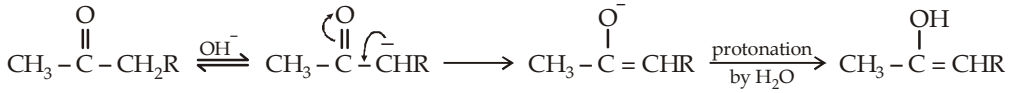
1. The term was introduced by Laar.
2. When the hydroxyl group is attached to a carbon atom which in turn is attached to another carbon atom by means of a double bond, its nature becomes acidic (difference from alcoholic hydroxyl group which is neutral). This type of hydroxyl group is known as enolic. In short,



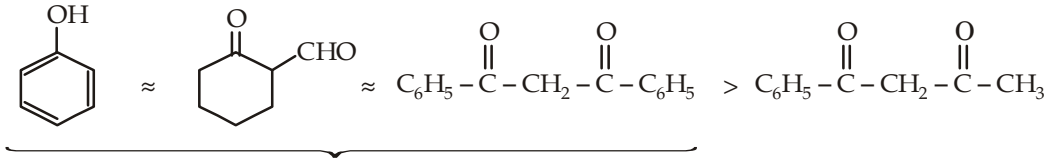
Mechanism of acid catalysed enolisation :



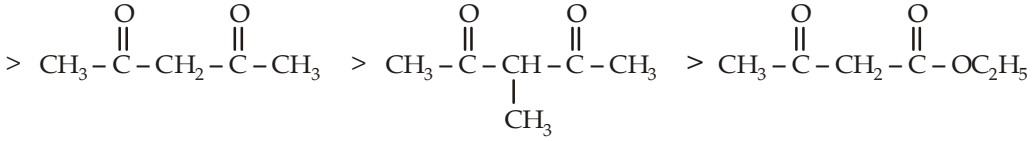
Mechanism of base catalysed enolisation :



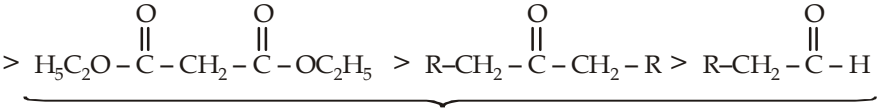
The decreasing ease of enolisation of the various ketones is



Nearly 100% enolic form

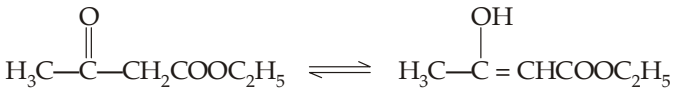


Steric hindrance decreases stability



Negligible enolic form

Keto-enol tautomerism in acetoacetic ester is proved by the fact that under ordinary conditions, the compound gives the properties of the ketonic group (reaction with hydroxylamine to form oxime, reaction with phenylhydrazine to form phenylhydrazone, reduction to form secondary alcohol etc.) as well as that of the enolic group (reaction with PCl_5, NH_3, bromine water, $FeCl_3$, acidic character etc.)

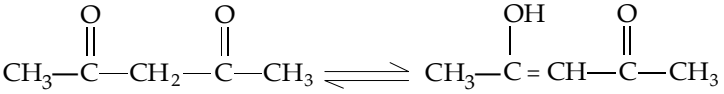


ketonic form (note the presence of a ketonic group)

enolic form (note the presence of a double bond and acidic —OH group)

Note that in *all the examples of keto-enol tautomerism the two isomeric forms are interconvertible by the migration of a proton from one atom (carbon) to other with the simultaneous shifting of bonds.* Remember that *keto-enol tautomerism is possible only in those* **aldehydes and ketones which have at least one α-hydrogen atom** which can convert the ketonic group to the enolic group. Examine the following compounds.

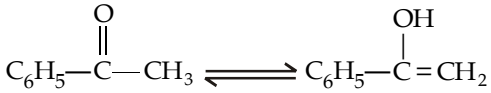
(*i*)



ketonic form — enolic form

Acetylacetone

(*ii*)



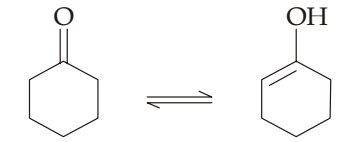
ketonic form — enolic form

Acetophenone

(*iii*) $CH_3—CH_2—\overset{\overset{O}{\|}}{C}—H \rightleftharpoons CH_3—CH=\overset{\overset{OH}{|}}{C}—H$

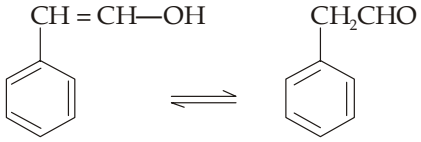
ketonic form ⇌ enolic form

Propionaldehyde

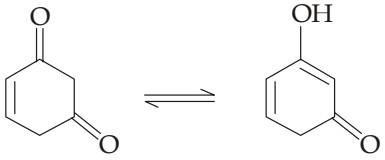
(*iv*) 

ketonic form ⇌ enolic form

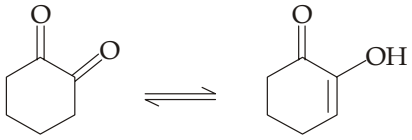
Cyclohexanone

(*v*) 

(Tautomerism possible)

(*vi*) 

(Tautomerism possible)

(*vii*) 

(Tautomerism possible)

(*viii*) $C_6H_5-\overset{\overset{O}{\|}}{C}-H$

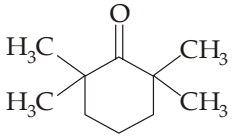
Benzaldehyde

(tautomerism not possible)

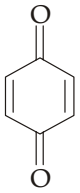
(*ix*) $C_6H_5-\overset{\overset{O}{\|}}{C}-C_6H_5$

Benzophenone

(tautomerism not possible)

(*x*) 

(Tautomerism not possible)

(*xi*) 

(Tautomerism not possible)

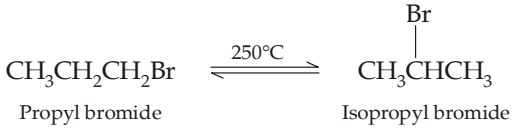
Distinction from resonance*. The tautomeric forms are quite chemically distinct entites and can be separated (in suitable cases *e.g.* acetoacetic ester) and characterised. On the other hand, resonating forms differ only in the distribution of electrons and can never be separated from one another since neither of them has any real existence. Moreover, the position of an ion (cation, generally H^+ or anion) in tautomers differs by several Angstrom units whereas the position of the nuclei in resonating structures never differ by more than 0.3 Angstrom units *e.g.* in the two resonating structures of benzene the two extremes for the carbon-carbon bond differ only by 0.20 Å (C—C, 1.54 Å ; C = C, 1.34 Å). The important differences between resonance and tautomerism can be summarised below.

1. Tautomerism involves a change in the position of atom (generally hydrogen), while resonance involves a change in the position of the unshared or π electron only.
2. Tautomers are definite compounds and may be separated and isolated. Resonating structures are only imaginary and can't be isolated.
3. The two tautomeric forms have different structures (*i.e.* functional groups). The various resonating structures have the same functional group.
4. Tautomers are in dynamic equilibrium with each other, resonating structures are not in dynamic equilibrium.
5. Tautomerism has no effect on bond lengths, while resonance affect the bond lengths (single bond is shortened while the double bond becomes lengthier).
6. Tautomerism does not lower the energy of the molecule and hence does not play any role in stabilising the molecule, while resonance decreases the energy and hence increases the stability of the molecule.
7. Tautomerism is indicated by '$\rightleftharpoons$' while resonance by '$\longleftrightarrow$'.
8. Tautomerism may occur in planar or non-planar molecules, while resonance occurs only in planar molecules.

---

* When two or more structures have practically the same position of all the atomic nuclei but differ only in the average distribution of electrons, the structures are known as resonating structures and the phenomenon as resonance.

Distinction from isomerism. In fact there is no sharp line of distinction between isomers and tautomers since some substances which are isomers under normal conditions can be converted into tautomeric forms under more drastic conditions. For example, propyl and iso-propyl bromides are isomeric compounds under normal conditions but form an equilibrium mixture on heating at 250°C in a sealed tube.



Propyl bromide Isopropyl bromide

And hence the *dynamic isomerism* represents the better term for this phenomenon than *tautomerism*.

Distinction from molecular rearrangement. Although there is no sharp difference between tautomerism and molecular rearrangement, yet the two can be distinguished by the fact that the former is a rapid and reversible phenomenon whereas the latter needs neither be reversible nor rapid.

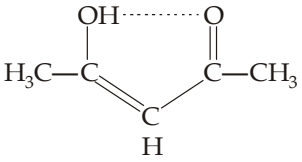
Percentage composition of tautomeric mixture. The percentage composition of keto-enol tautomeric mixture depends upon the relative stabilities of the two forms.

(*i*) Ketonic form predominates in simple monocarbonyl compounds like acetaldehyde, acetone and cyclohexanone. This is due to greater strength (about 364 kJ mol^{-1}) of the carbon oxygen double bond present in the ketonic form than the carbon-carbon double bond (250 kJ mol^{-1}) present in enolic form.

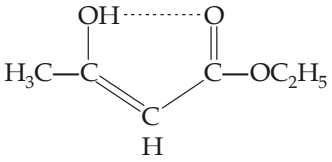
(*ii*) Enolic form predominates in compounds containing two carbonyl groups separated by a —CH_2— group ; *i.e.* 1, 3-dicarbonyl compounds, *viz.* acetoacetic ester, acetylacetone, benzoylacetophenone. This is due to greater stabilization of the enolic form due to following two factors.

(*a*) Presence of conjugation which increases stability of molecule due to resonance.

(*b*) Formation of intramolecular hydrogen bonds between enolic hydroxyl group and second carbonyl group which leads to stabilisation of the molecule.



Intramolecular hydrogen bonding in the enolic form of acetylacetone



Intramolecular hydrogen bonding in acetoacetic ester

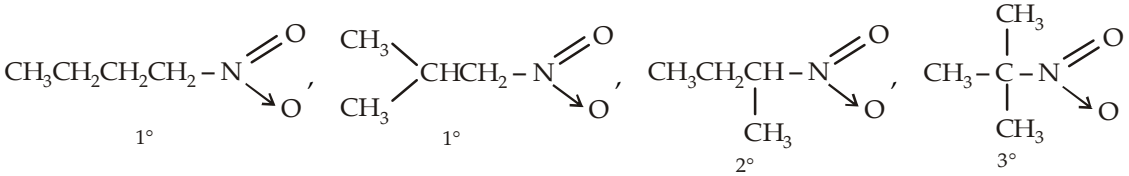
Thus polar protic solvent (like water, methanol, acetic acid etc.) which tends to stabilise the keto form relative to the enol form will reduce the enol content. On the other hand, non-polar solvents (like benzene, hexane etc.) which do not form hydrogen bonds, tend to increase the enol content. Thus the enol content of acetylacetone in ethanol is only 76%, while in hexane it is as much as 92%.

Example 8 :

Write down structures of the isomeric nitroalkanes of the formula $C_4H_9NO_2$. Which of them will show phenomenon of tautomerism?

Solution :

$C_4H_9NO_2$ (Nitrobutane) can have following isomeric structures



1° 1° 2° 3°

The last one, 3° nitroalkane, can't exhibit tautomerism.

Example 9 :

Give mechanism of the following reactions : $C_6H_5-\overset{\overset{O}{\|}}{C}-CD_2CH_3 \xrightarrow{H^+}$

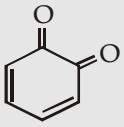
Solution :

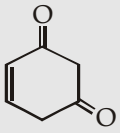
$$C_6H_5-\overset{\overset{O}{\|}}{C}-CD_2CH_3 \overset{H^+}{\rightleftharpoons} C_6H_5-\overset{OH}{\overset{|}{C^+}}-CDCH_3 \longrightarrow C_6H_5-\overset{OH}{\overset{|}{C}}-\overset{+}{C}DCH_3 \longrightarrow C_6H_5-\overset{OH}{\overset{|}{C}}=CDCH_3 + D^+$$

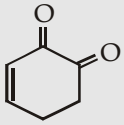
(D is the migrating group)

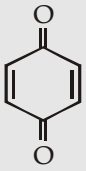
Example 10 :

Which of the following compound can exhibit tautomerism?

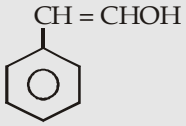
(a) 

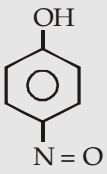
(b) 

(c) 

(d) 

(e) $H_2N-\overset{\overset{O}{\|}}{C}-NH_2$

(f) 

(g) 

(h) $H_2N-\overset{\overset{S}{\|}}{C}-NH_2$

Solution :

All except (a) and (d) show tautomerism, (a) and (d) do not have any α-H.

EXERCISE 2.1 (MCQ - ONE option correct)

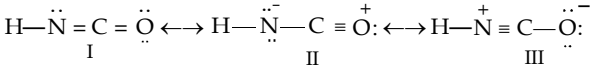
1. In ammonia, nitrogen is sp^3 hybridised. Which statement is true about the hybrid orbitals of nitrogen in ammonia?
(*a*) All the four sp^3 hybrid orbitals are equivalent
(*b*) One sp^3 hybrid orbital is different from the remaining three
(*c*) Two sp^3 hybrid orbitals are different from the remaining two
(*d*) All the four sp^3 orbitals are non-equivalent.

2. In which of the following you would expect, the normal tetrahedral bond angle (109.5°) ?
(*a*) NH_3 (*b*) H_2O
(*c*) BF_4^- (*d*) None of the three.

3. Which of the following statements is true ?
(*a*) Toluene has zero dipole moment
(*b*) Toluene has a definite dipole moment due to + I character of the $-CH_3$ group
(*c*) Toluene has a definite dipole moment due to difference in electronegativity of the carbon atom of the nucleus and that of the side chain.
(*d*) Toluene has a definite dipole moment due to resonance.

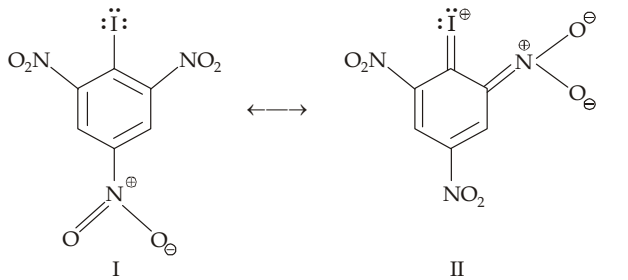
4. Which of the following is true regarding the direction of the dipole ?
(*a*) $C \rightleftharpoons H$ and $C \rightleftharpoons D$
(*b*) $C \leftrightharpoons H$ and $C \leftrightharpoons D$
(*c*) $C \rightleftharpoons H$ and $C \leftrightharpoons D$
(*d*) $C \leftrightharpoons H$ and $C \rightleftharpoons D$.

5. Isocyanic acid, HNCO can be represented by the following three contributing structures

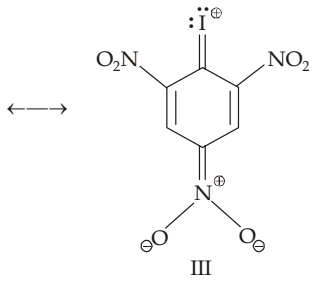


Order of stability of the three contributing structures is
(*a*) I > II > III (*b*) I > III > II
(*c*) I > II = III (*d*) I = II = III.

6. Which of the following resonating structure is not possible for 2, 4, 6-trinitroiodobenzene



I II



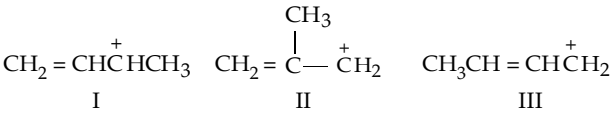
III

(*a*) I (*b*) II
(*c*) III (*d*) None of them.

7. Which of the following statement is true regarding the stability of NH_4^+ and CH_3^+ ?
(*a*) Both are equally stable
(*b*) NH_4^+ ion is less stable than CH_3^+ ion because is the former +ve charge is present on the more elecronegative element
(*c*) NH_4^+ ion is more stable than CH_3^+ because the former is an inorganic ion, while the latter is an organic ion
(*d*) NH_4^+ ion is more stable because here N has complete octet of electrons, while H has duet.

8. The carbon-oxygen bond length in sod. formate and $CaCO_3$ is respectively
(*a*) 1.27 Å and 1.31 Å (*b*) 1.31 Å and 1.27 Å
(*c*) 1.27 Å and 1.27 Å (*d*) 1.31 Å and 1.31 Å.

9. Which is the correct order of stability of the following three carbonium ions ?



I II III

(*a*) I > II > III (*b*) II > I > III
(*c*) I ≈ III > II (*d*) All are equally stable.

10. Hyperconjugation is not possible in
(*a*) $CH_3C \equiv CH$ (*b*) CH_3CH_2CHO
(*c*) CH_3CN (*d*) $(CH_3)_3CCH = CH_2$.

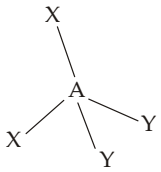
11. Which of the forces is responsible for the solubility of NaCl in water?
(*a*) Ion-dipole attraction (*b*) Hydrogen bond
(*c*) Both (*a*) and (*b*) (*d*) None of the two.

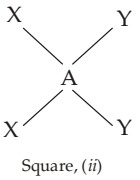
12. Stain produced by butter on a cloth is removed by
(*a*) rubbing with water because of formation of hydrogen bond
(*b*) benzene because of dipole-dipole interaction
(*c*) carbon tetrachloride because of presence of very weak forces between butter and carbon tetrachloride
(*d*) none of the above.

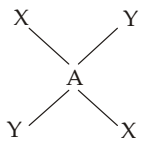
13. Which of the following statement is true?
(*a*) Lithium acetylacetonate and beryllium acetylacetonate are soluble in chloroform and have very high melting points
(*b*) Both are insoluble in chloroform and have low melting points
(*c*) The two differs in their melting points and resemble in solubility
(*d*) None of the above is true.

14. Which of the following statement is true for *n*-butanol and diethyl ether ?
(*a*) Both have same solubility in water & also boil at high temperature than expected from their molecular weight
(*b*) *n*-Butanol is more soluble in water and boils at a higher temperature than diethyl ether
(*c*) Both have same solubility in water, but *n*-butanol boils at a higher temperature than diethyl ether
(*d*) None of the above is true.

15. Which of the following structures are expected to have a net dipole moment ? Assuming that electronegativities of atoms A, X and Y are 5, 3 and 1 respectively.


Tetrahedral, (*i*)

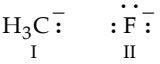

Square, (*ii*)


Square, (*iii*)

(*a*) (*i*) and (*ii*) (*b*) (*ii*) and (*iii*)
(*c*) (*i*) and (*iii*) (*d*) All the three.

16. Among closely related molecules where the same atom loses proton, which of the following statement is true ?
(*a*) Increase in positive charge decreases acidity
(*b*) Increase in negative charge decreases acidity
(*c*) Increase in negative charge increases acidity
(*d*) Nothing can be said.

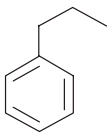
17. Which of the following is true regarding basic character of the two species ?


I II

(*a*) I and II have nearly equal basic character
(*b*) I is much more stronger base than II
(*c*) II is much more stronger base than I
(*d*) II is slightly more basic than I.

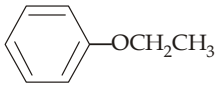
18. Which of the following is true ?
(*a*) Acetic acid is a stronger acid in water than in methanol
(*b*) Acetic acid is a stronger acid in methanol than in water
(*c*) Acetic acid is as acidic in water as in methanol
(*d*) None of the above in true.

19. The total number of chain isomers for the compound shown in side is



(*a*) 2 (*b*) 4
(*c*) 5 (*d*) 8.

20. The possible number of metamers of the compound shown in side is



(*a*) 2 (*b*) 3
(*c*) 4 (*d*) 5.

21. Predict the product P



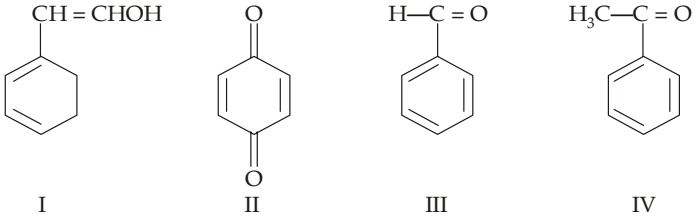
(*a*) $CH_3C(OH) = CHCOOC_2H_5$
(*b*) $CH_3C(OD) = CHCOOC_2H_5$
(*c*) $CH_3C(OH) = CDCOOC_2H_5$
(*d*) $CH_3C(OD) = CDCOOC_2H_5$.

22. In which of the following property *cis*-3-hexene differs from *trans*-3-hexene ?
(*a*) melting point (*b*) dipole moment
(*c*) solubility in ethanol (*d*) All of the three.

23. The number of isomers possible for C_4H_8 is
(*a*) 2 (*b*) 3
(*c*) 4 (*d*) 5

24. The possible number of isomers for $C_4H_4O_4$ is
(*a*) 2 (*b*) 3
(*c*) 4 (*d*) 5

25. Keto enol tautomerism is observed in


I II III IV

(*a*) IV (*b*) I, III, IV
(*c*) I, IV (*d*) II, III, IV.

26. Which one of the following has most acidic α-hydrogen atom?
(*a*) CH_3CHO (*b*) CH_3COCH_3
(*c*) $CH_3COCH_2COOC_2H_5$ (*d*) CH_3COCH_2CHO.

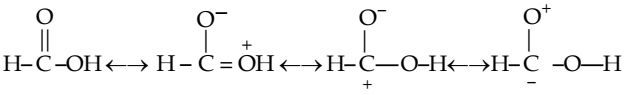
27. Urea can show which type of isomerism ?
(*a*) Position (*b*) Functional
(*c*) Keto-enol tautomerism (*d*) both (*b*) and (*c*).

28. Which of the following has a bond formed by overlap of sp^3 –*sp* hybrid orbitals ?
(*a*) $CH_3—C \equiv C—H$ (*b*) $CH_3—CH = CH—CH_3$
(*c*) $CH_2=CH—CH=CH_2$ (*d*) $HC \equiv CH$.

29. The hybridisation of carbon atoms in C—C single bond of $HC \equiv C—CH = CH_2$ is
(*a*) sp^3–sp^3 (*b*) $sp^2 - sp^3$
(*c*) $sp - sp^2$ (*d*) $sp^3 - sp$.

30. In the compound $CH_2 = CH—CH_2—CH_2—C \equiv CH$, the $C_2—C_3$ bond is of the type
(*a*) $sp - sp^2$ (*b*) $sp^3 - sp^3$
(*c*) $sp - sp^3$ (*d*) $sp^2 - sp^3$.

31. Formic acid is considered as a resonance hybrid of the four structures.


I II III IV

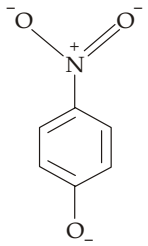
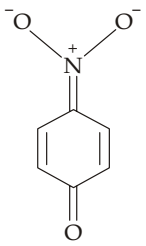
Which of the followings order is correct for the stability of the four contributing structures ?
(*a*) I > II > III > V (*b*) I > II > IV > III
(*c*) I > III > II > IV (*d*) I > IV > III > II.

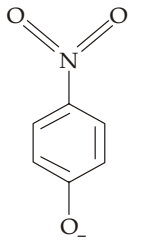
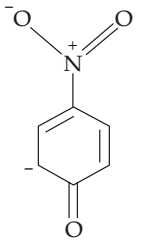
32. Examine the following two structures for the anilinium ion and choose the correct statement from the ones, given below.


I II

(*a*) II is not an acceptable canonical structure because carbonium ions are less stable than ammonium ion
(*b*) II is not an acceptable canonical structure because it is non-aromatic
(*c*) II is not an acceptable canonical structure because the nitrogen has 10 valence electrons
(*d*) II is an acceptable canonical structure.

33. The most unlikely representation of resonance structures of *p*-nitrophenoxide ion is

(*a*)  (*b*) 

(*c*)  (*d*) 

34. The total number of isomers for the compound of the formula C_7H_8O is

(*a*) 3 (*b*) 4

(*c*) 5 (*d*) 6.

35. The enolic form of acetone contains

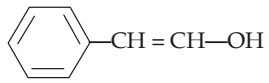
(*a*) 9 σ bonds, 1 π bond and 2 lone pairs

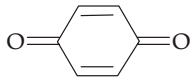
(*b*) 8 σ bonds, 2 π bonds and 2 lone pairs

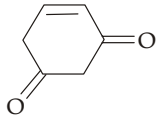
(*c*) 10 σ bonds, 1 π bond and 1 lone pair

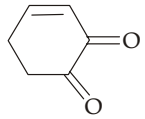
(*d*) 9 σ bonds, 2 π bonds and 1 lone pair.

36. Tautomerism is not shown by

(*a*) 

(*b*) 

(*c*) 

(*d*) 

37. Which of the following statement is true regarding acidity of $CH_3COCH_2CH_3$(I) and $CH_2(CN)_2$(II).

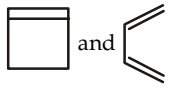
(a) I > II (b) I < II

(c) I = II (d) Not definite

38. Which of the following pairs represent the phenomenon of resonance?

(a) $CH_3CH_2-\overset{\overset{O}{\|}}{C}-H$ aend $CH_3CH=\overset{\overset{OH}{|}}{C}-H$

(b) $CH_3\overset{+}{C}HOH$ and $CH_3CH=\overset{+}{O}H$

(c) 

(d) None

39. Cyanate ion, CNO^- has three important resonating structures

$$\underset{I}{O=C=N^-} \longleftrightarrow \underset{II}{^-O-C\equiv N} \longleftrightarrow \underset{III}{^+O\equiv C-N^{2-}}$$

Which of the above structures contributes more to the resonance hybrid?

(a) I (b) II

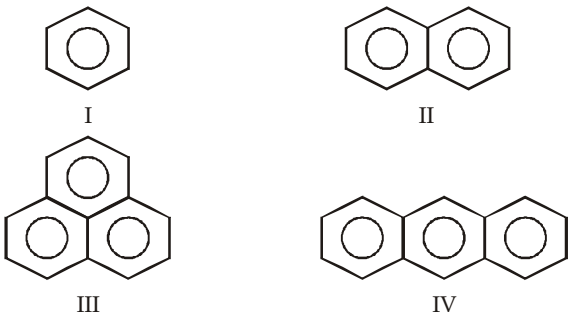
(c) I and II equal (d) All equal

40. The oxidation states of O, C and N in the above II structure respectively are

(a) –2, +4, 3 (b) –2, +4 and –3

(c) –1, +4 and zero (d) –2, +4 and +5

41. Arrange the following structures in decreasing order of σ to π bond ratio



I II III IV

(a) IV > III > I > II (b) III > I > II > IV

(c) III = IV > II > I (d) III = IV > I > II

42. The carbon-chlorine bond length is shortest in

(a) CH_3Cl (b) CH_2Cl_2

(c) $CHCl_3$ (d) CCl_4

43. The number of *p*-orbitals in $\overset{+}{C}H_3$ is

(a) 2 (b) 3

(c) 4 (d) zero

44. In which of the following C – C bond distance is maximum?

(a) $H_2C=CH_2$ (b) BrHC = CHBr

(c)  (d) $H_2C=CBr_2$

45. The bond between Li and F is ionic, while that between Li and Cl it is covalent, what should be the nature of bond between Li and Br?

(a) ionic (b) covalent

(c) coordinate (d) nothing certain

46. Which of the following involves cleavage of covalent bond?

(a) melting of KCN (b) melting of silica

(c) boiling of H_2O (d) boiling of CF_4

47. A diatomic molecule has a dipole moment of 1.2 D, if the bond distance between the atoms is 1Å, the percentage of electronic charge on each atom would be

(a) 29% (b) 25%

(c) 20% (d) 15%

48. Let the heat of hydrogenation of benzene is 61 kcal/mol. and its resonance energy is 36 kcal/mol., then the heat of hydrogenation of cyclohexene and cyclohexadiene per mole respectively are

(a) 20.3, 40.6 (b) 40.6, 20.3

(c) 32.3, 64.6 (d) 25, 50

49. The average bond energy of the C–H bond in methane is the mean of the four bond dissociation energies, viz. CH_3–H to CH_3; CH_2–H to CH_2; CH–H to CH and CH to C; which bond cleavage has minimum bond dissociation energy?

(a) $H_3C \dagger H$ (b) $H_2C \dagger H$

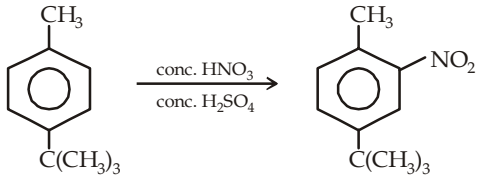
(c) $HC \dagger H$ (d) $C \dagger H$

50. Which of the following has minimum dipole moment?

(a) CH_3CH_2Cl (b) $CH_2=CHCl$

(c) $CH_2=CHCH_2Cl$ (d) CH_3Cl

51.



Introduction of $-NO_2$ group at the given position in the above reaction can be explained on the basis of

(a) inductive effect (b) hyperconjugation

(c) both (d) resonance

52. The $C_2 - C_3$ bond length in 1,3-butadiene is

(a) 1.54Å (b) 1.35Å

(c) 1.46Å (d) 1.20Å

53. Arrange the following carbocations in decreasing order of stability

$CH_3\overset{+}{C}HOCH_3$ (I) $\quad CH_3\overset{+}{C}HCOCH_3$ (II)

$CH_3\overset{+}{C}HCH_3$ (III)

(a) III > I > II (b) I > III > II

(c) I > II > III (d) III > I = II

54. Resonance has impact on the stability or unstability of which carbocation?

(a) $CH_3\overset{+}{C}HCH_3$ (b) $CH_3\overset{+}{C}HOCH_3$

(c) $CH_3\overset{+}{C}HCOCH_3$ (d) All the three

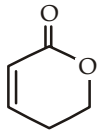
55. How many cyclic isomers are possible for C_5H_{10}?

(a) 3 (b) 4

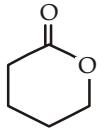
(c) 5 (d) 6

56. Which of the following compounds cannot show tautomerism?

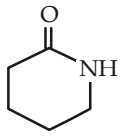
(a) $CH_2 = CHOH$ (b)



(c)



(d)



57. $C_6H_5-\overset{O}{\overset{\|}{C}}-CH_2CD_3 + D_3O^+ \longrightarrow$ Product is

(a) $C_6H_5-\overset{OD}{\overset{|}{C}}=CDCD_3$ (b) $C_6H_5-\overset{OD}{\overset{|}{C}}=CHCD_3$

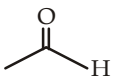
(c) $C_6H_5-\overset{OH}{\overset{|}{C}}=CDCD_3$ (d) $C_6H_5-\overset{OD}{\overset{|}{C}}=CDCH_2D$

58. Maximum enol content is in

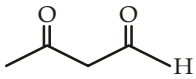
(a)



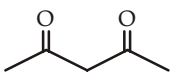
(b)



(c)



(d)



59. Which of the following has a bond formed by overlap of sp^3–sp hybrid orbitals?

(a) $CH_3 - C \equiv C - H$

(b) $CH_3 - CH = CH - CH_3$

(c) $CH_2 = CH - CH = CH_2$

(d) $HC \equiv CH$

60. Carbon tetrachloride has no net dipole moment because of

(a) its planar structure

(b) its regular tetrahedral structure

(c) similar size of carbon and chlorine atoms

(d) similar electron affinities of carbon and chlorine

61. What is the decreasing order of strength of the bases $OH^-, NH_2^-, H-C\equiv C^-$ and $CH_3-CH_2^-$?

(a) $CH_3 - CH_2^- > NH_2^- > H - C \equiv C^- > OH^-$

(b) $H - C \equiv C^- > CH_3 - CH_2^- > NH_2^- > OH^-$

(c) $OH^- > NH_2^- > H - C \equiv C^- > CH_3 - CH_2^-$

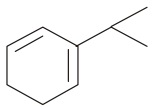
(d) $NH_2^- > H - C \equiv C^- > OH^- > CH_3 - CH_2^-$

62. Among the following compounds, the strongest acid is

(a) $HC \equiv CH$ (b) C_6H_6

(c) C_2H_6 (d) CH_3OH

63. How many types of H's are present in the structure of the compound drawn below?



(a) 3 (b) 4

(c) 5 (d) 6

64. The increasing order of boiling points of the below mentioned alcohols is

(I) 1,2-dihydroxy benzene

(II) 1,3-dihydroxy benzene

(III) 1,4-dihydroxy benzene

(IV) Hydroxy benzene

(a) I < II < IV < III (b) I < II < III < IV

(c) IV < II < I < III (d) IV < I < II < III

65. The number of structural isomers for C_6H_{14} is

(a) 3 (b) 4

(c) 5 (d) 6

66. Hyperconjugation involves overlap of the following orbitals

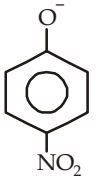
(A) σ-σ (B) σ - p

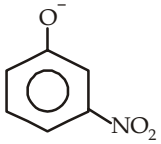
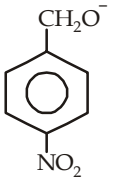
(C) p- p (D) π-π

EXERCISE 2.2 (MCQ 1 or >1 option correct, Passage based, Matching, A/R)

DIRECTIONS for Q. 1 to Q. 18 : Multiple choice questions with one or more than one correct option(s).

1. Resonance can explain the stability of

(a) $(CH_3)_2\overset{+}{C}OH$ (b) 

(c)  (d) 

2. Pick up the correct statement

(a) The k_1 of maleic acid is high than that of fumaric acid, while the k_2 of maleic acid is very low than that of fumaric acid

(b) Fluorine forms stronger H-bond than oxygen, hence HF should boil at a higher temperature than H_2O

(c) Delocalisation of π electrons does not always lead to stabilisation

(d) Delocalisation of π electrons always leads to stabilisation

3. In which of the following pairs of carbocations, the second carbocation is less stable than the first?

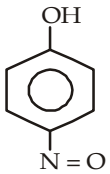
(a) $CH_2=CH\overset{+}{C}H_2$ and $CH_2=CHCH_2\overset{+}{C}H_2$

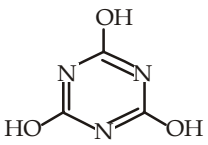
(b) $CH_3NH\overset{+}{C}H_2$ and $\overset{+}{C}H_2OH$

(c) $CH_3\overset{+}{C}HCH_2CH_2CH_3$ and $CH_3CH_2\overset{+}{C}HCH_2CH_3$

(d) $CH_3OCH_2\overset{+}{C}H_2$ and $CH_3O\overset{+}{C}H_2$

4. Which of the following compounds show tautomerism?

(a)  (b) $H_2N-\overset{O}{\overset{\|}{C}}-NH_2$

(c) $H_2N-\overset{S}{\overset{\|}{C}}-NH_2$ (d) 

5. Enolic form of methyl 3-oxobutanoate is more stable than its keto form, this is due to

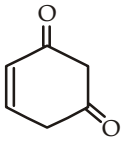
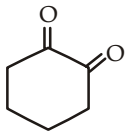
(a) resonance stabilization of the enol form

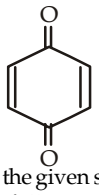
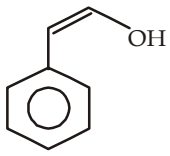
(b) intermolecular hydrogen bonding

(c) intramolecular hydrogen bonding

(d) carbonyl group on each side of $-CH_2-$ group

6. Tautomerism is exhibited by

(a)  (b) 

(c)  (d) 

7. All of the given structures show ring-chain tautomerism, in which of the following cyclic form is more stable than the open chain form?

(a) $CHOCH_2CH_2OH$

(b) $CH_3COCH_2CH_2OH$

(c) $CHOCHOHCHOHCH_2OH$

(d) $CH_2OHCOCHOHCHOHCH_2OH$

8. Which of the following compounds have only one type of hybrid carbon?

(a) $CH_2=CH-CH=CH_2$ (b) $HC\equiv C-C\equiv CH$

(c) $CH_3-CH_2-CH_2-CH_3$ (d) $CH_3-C\equiv C-CH_3$

9. In which of the following compounds are all the carbon atoms in the sp^3 state of hybridization

(a) CH_4 (b) C_2H_6

(c) C_3H_8 (d) C_4H_{10}

10. Resonance structure of a molecule should have

(a) identical arrangement of atoms

(b) nearly the same energy content

(c) the same number of paired electrons

(d) identical bonding

11. Hydrogen bonding is possible in

(a) Ethers (b) Hydrocarbons

(c) Water (d) Alcohols

12. Dipole moment is shown by :

(a) 1, 4-dichlorobenzene

(b) *cis* 1, 2-dichloroethane

(c) *trans* 1, 2-dichloroethene

(d) *trans* 1, 2-dichloro-2-pentene

13. Which of the following will show hyperconjugation :

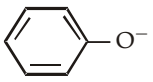
(a) $CH_3-CH=\underset{|}{C}-$

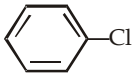
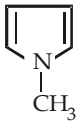
(b) $CH_3-CH_2-CH=\underset{|}{C}-$

(c) $CH_3-\underset{|}{\underset{CH_3}{CH}}-CH=C-$

(d) $CH_3-\underset{|}{\overset{CH_3}{C}}-CH=\underset{|}{C}-$
$\quad\quad\quad

15. Resonance stabilised compounds are :

(a)  (b) $CH_2 = CH - Cl$

(c)  (d) 

16. The compounds which is(are) isomeric with diethyl ether is (are)

(a) n-propyl methyl ether (b) butan-1-ol

(c) 2-methylpropan-2-ol (d) butanone

17. Out of the following compounds, which will not have a zero dipole moment?

(a) 1, 1-dichloroethylene

(b) *cis*-1, 2-dichloroethylene

(c) *trans*-1, 2-dichloroethylene

(d) All have zero dipole moments

18. The type of hydrogen present in the above structure is

(a) 2° allylic (b) vinylic

(c) 3° allylic (d) benzylic

INSTRUCTION for Q. 19 to 56 : Read the passages given below and answer the questions that follow.

PASSAGE 1

The statement that molecule having polar bonds should be polar, is not always true; e.g. O = C = O has two polar C – O bonds, yet CO_2 is non-polar. A molecule is said to be polar when the centre of negative charge does not coincide with the centre of positive charge. The polarity of every bond results in dipole moment which can be calculated as below.

μ (in debye) = *charge* (in esu unit) × *d* (in Å)

Alternatively, μ (in debyes) = 4.8 × electron charge × *d* (in Å)

Dipole moment is a vector quantity, and thus the net dipole moment of a polyatomic molecule is the vector sum of the dipole moments of various bonds. The magnitude of the resultant dipole moment is dependent upon the spatial orientation of various bonds present in the molecule. If the molecule is symmetrical, the resultant dipole moment of the molecule is zero.

19. Dipole moment can be used for calculating

(a) bond length between two atoms

(b) charge on the more electronegative atom

(c) charge on both of the atoms

(d) polar nature of the molecule

20. The central atom in each of the three molecules CCl_4, H_2O, and NH_3 is sp^3 hybridised; carbon tetrachloride has zero dipole moment, what do you expect about the dipole moment of H_2O and NH_3?

(a) Water has zero dipole moment, while NH_3 has a definite dipole moment

(b) NH_3 has zero dipole moment, while H_2O has definite dipole moment

(c) H_2O and NH_3, both have zero dipole moments

(d) H_2O and NH_3, both have definite dipole moments

21. The dipole moment of NH_3 is 1.46D, what should be the dipole moment of NF_3?

(a) 1.70D (b) 0.24D

(c) zero (d) 1.46D

22. Different values of dipole moment of NH_3 (1.46 D) and H_2O (1.84D) is due to

(a) difference in electronegativities of N and O

(b) difference in lone pair on electrons on N and O

(c) different direction of dipole in the N – H and O – H bonds

(d) difference in hybridisation of the central atom

23. Which has least dipole moment?

(a) H – Cl (b) H – F

(c) H – Br (d) H – I

(size of the four halogen is I > Br > Cl > F)

24. A diatomic molecule has a dipole moment of 1.98D and bond length of 0.92Å; the bond between two atoms should have ..... ionic character.

(a) 52.5% (b) 50%

(c) 44.8% (d) 26.6%

PASSAGE 2

Hydrogen bond is an electrostatic attractive force between covalently bonded hydrogen atom of one molecule and electronegative atom of small size of another molecule. The three atoms satisfying these conditions are F, O and N. Hydrogen bonding may be intermolecular as well as intramolecular. Intramolecular hydrogen bonding, also known as chelation, is possible when a 6- or 5-membered ring can be formed. Intermolecular hydrogen bonding increases the boiling point of the compound and also solubility of the compound in water. Intramolecular hydrogen bonding decreases boiling point and also its solubility in water.

25. Strongest hydrogen bond is possible in case of

(a) higher electronegativity and greater size of the atom

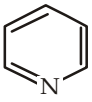
(b) lesser electronegativity and lesser size of the atom

(c) higher electronegativity and smaller size of the atom

(d) higher electronegativity irrespective of size of the atom

26. Which of the following compound is soluble in water?

(a)  (b) 

(c)  (d) none

27. Among the following pairs, pick up the incorrect order with reference to boiling points.

(a) $CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3 > CH_3\overset{\displaystyle O}{\overset{\|}{C}}CH_3$

(b) $H_2O > H_2S$

(c) $CH_3\underset{\displaystyle OH}{\underset{|}{C}} = CHCOOC_2H_5 > CH_3\overset{\displaystyle O}{\overset{\|}{C}}CH_2COOC_2H_5$

(d) None of the three

28. The relative acidic character of halogen acids (HX) can be explained on the basis of

(a) inductive effect (b) hydrogen bonding

(c) hybridization (d) all the three

29. HCl does not form H-bonding, while HF does so because

(a) HCl is less polar than HF

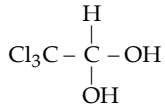
(b) of weak electrostatic attraction between Cl and H

(c) larger size of Cl

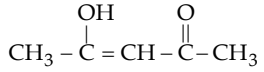
(d) any other reason

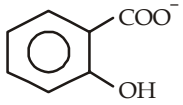
30. Tetramethylammonium hydroxide is as basic as potassium hydroxide because
(a) it exists only in ionized form
(b) it can't form hydrogen bonding
(c) both of the factors
(d) none of the two

31. Intramolecular hydrogen bonding is possible in

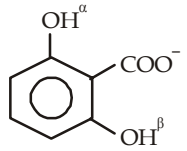
(a) 

(b) CH_3COOH

(c) 

(d) 

32. Which hydrogen atom of 2,6-dihydroxybenzoate can form intramolecular hydrogen bond?

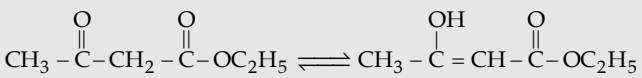


(a) α (b) β
(c) both (d) none

33. Which of the following molecules dimerises in non-polar solvents?
(a) HCOOH (b) ArCOOH
(c) CH_3COOH (d) ArOH

PASSAGE 3

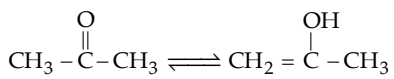
Tautomerism may be defined as a phenomenon in which a single compound exists in two readily interconvertible structures that differ in the relative position of hydrogen. It is broadly of two types :- dyad system in which hydrogen migrates from atom one to atom two, and similarly defined *triad system*. Keto-enol tautomerism is the most important and its most usual example is ethyl acetoacetate.

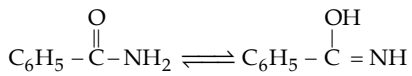


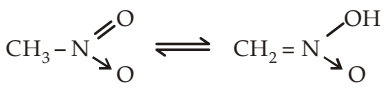
The two forms are readily interconvertible under ordinary conditions by acid or base catalyst.

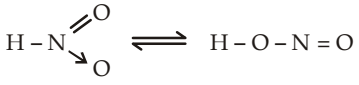
Stability of the enolic form depends upon several factors, viz. its stabilization (through resonance) and nature of solvent. Non-polar solvents generally stabilise the enolic form, while polar protonic solvent stabilises the ketonic form.

34. Which of the following is not an example of triad system of tautomerism?

(a) 

(b) 

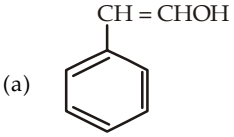
(c) 

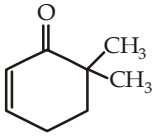
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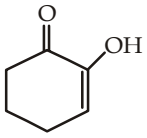
35. In which of the following enol content is maximum?
(a) $CH_3COCH_2COOC_2H_5$ (b) $CH_3COCH_2COCH_3$
(c) $C_6H_5COCH_2COCH_3$ (d) $C_6H_5COCH_2COC_6H_5$

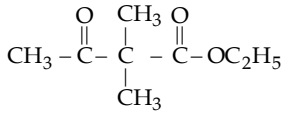
36. Which of the following statement is/are incorrect about ethyl acetoacetate?
(a) It reacts with $NaHCO_3$ to form addition product
(b) It does not discharge bromine solution
(c) It has an ester linkage
(d) It has two ketonic groups

37. Tautomerism is not possible in

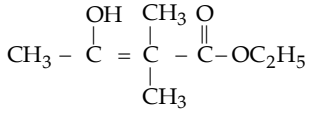
(a) 

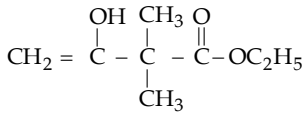
(b) 

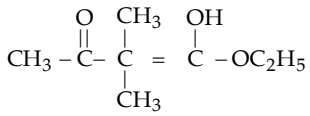
(c) 

(d) 

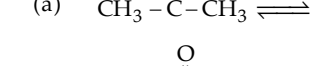
38. Which of the following constitutes enolic form of dimethyl acetoacetic ester?

(a) 

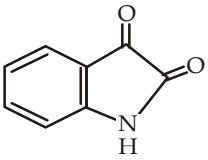
(b) 

(c) 

(d) None of the three

39. You are given two samples of acetylacetone,  in different solvents, namely ethyl alcohol and *n*-hexane. Which of the following statement is true?
(a) Both samples have equal percentage of the keto form
(b) Sample in ethanol has higher percentage of the keto form than that in the *n*-hexane sample
(c) Sample in *n*-hexane has higher percentage of the keto form than that in ethanol sample
(d) Sample in ethanol does not have keto form at all

40. Phenols and amines undergo methylation when treated with CH_3I. How many methylated products can be formed when isatin is methylated?



(a) One (b) Two
(c) Three (d) Four

41. The species formed during enolisation of ethyl acetoacetate in presence of acids is

(a) $CH_3-\overset{+OH}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5$

(b) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{+OH}{\overset{\|}{C}}-OC_2H_5$

(c) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-\overset{+}{O}C_2H_5$

(d) All the three

PASSAGE - 4

Conditions for hydrogen bonding

(*i*) *The molecule must possess a higher electronegative atoms such as* F, O *or* N, *directly linked to hydrogen atom.*

(*ii*) *The size of the electronegative atom should be small.*

Types of hydrogen bonding. Generally, the hydrogen bonds are classified into two groups, *viz*. intermolecular and intramolecular.

1. **Intermolecular hydrogen bonding.** In such type of linkage the two or more than two molecules of the same compound combine together to give a polymeric aggregate.
2. **Intramolecular hydrogen bonding.** In this type, hydrogen bonding occurs within two atoms of the same molecule. Intramolecular hydrogen bonding is possible when a six or five-membered ring can be formed.

42. Hydrogen bonding is possible in
(a) *o*-chlorobenzoic acid (b) HCl
(c) HF (d) KF

43. Which of the following explains the high boiling point of *m*-chlorophenol than the *o*-chlorophenol?
(a) Intermolecular H-bond
(b) Intramolecular H-bonding
(c) Both
(d) None

44. Which of the following factor explains insolubility of salicyclic acid in water?
(a) Its bulky aryl group
(b) Chemical reaction between –OH and –COOH groups
(c) Chelation
(d) Association

PASSAGE 5

A molecule having polar bonds should be polar, however this is not true in all cases. A molecule is said to be polar when the center of negative charge does not coincide with the center of positive charge. A polar molecule has a dipole moment, μ, which is equal to the multiple of magnitude of the charge (*e*) and distance (*d*) between the centers of charge.

$$\mu = e \times d$$

45. The correct order of the dipole moments of the four alkyl halides should be

$\underset{I}{CH_3F}$ $\underset{II}{CH_3Cl}$ $\underset{III}{CH_3Br}$ $\underset{IV}{CH_3I}$

(a) I > II > III > IV (b) IV > III > II > I
(c) II > I > III > IV (d) II > III > I > IV

46. Which of the following statement is false about BCl_3?
(a) It has three polar bonds
(b) It is a polar molecule
(c) It is a non-polar molecule
(d) Its central atom has no lone pair of electrons

47. Dipole moment can be used for
(a) calculating bond length between two concerned polar atoms
(b) calculating the percentage ionic character of the concerned bond
(c) differentiating between ionic and covalent bond
(d) all the above three purposes

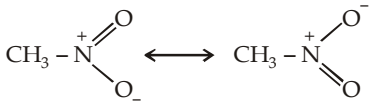
PASSAGE – 6

Following criteria should be taken in consideration for resonance.

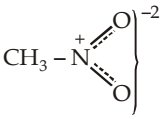
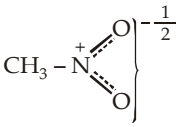
The major contributor is the one with the lowest energy. Good contributors generally have all octets satisfied, as many bonds as possible and as little charge separation as possible. Negative charges are more stable on the more electronegative atoms.

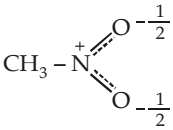
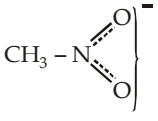
Resonance stabilization is most important when it serves to delocalize a charge over two or more atoms.

48. The two important resonating structures of nitromethane are:



the resonance hybrid of nitromethane can be written as

(a)  (b) 

(c)  (d) 

49. Observe the following structures :

$$\underset{I}{H_2C=\overset{+}{N}H_2} \longleftrightarrow \underset{II}{\overset{+}{C}H_2-NH_2}$$

(a) Structure I is major contributor in the two resonating structures
(b) Structure II is major contributor in the two resonating structures
(c) Both are equal stable
(d) Resonance is not possible

50. How many resonating structures can be drawn for 2, 4-pentadienyl radical?
(a) 1 (b) 2
(c) 3 (d) 4

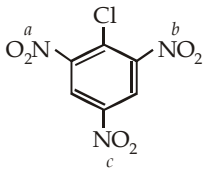
PASSAGE 7

Resonance involves movement of only π or *n* electrons and a resonance structure can be derived from another by a series of one or more electron shifts. Thus resonance is possible only when one double bond is in conjugation with another double bond or an unshared pair of electrons or an electron deficient atom.

Further for resonance, it is essential that the *skeleton should be planar* in conjugated system. Thus any structural feature that destroys this coplanarity of the conjugated system will inhibit resonance. This inhibition is referred to as **steric inhibition of resonance.**

Structures in which all atoms have a complete octet of electrons are especially stable and make large contribution to the hybrid.

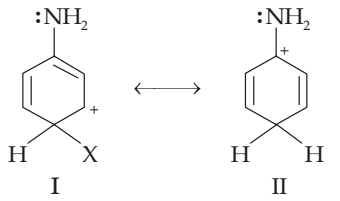
51. In picryl chloride which of the $-NO_2$ group (as indicated by a, b, c) is involved in resonance.

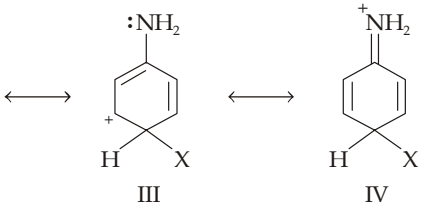


(a) a (b) b
(c) c (d) all

52. The C–Cl bond length in CH_2 = CHCl and CH_2=$CHCH_2Cl$ respectively is most likely to be
(a) shorter, longer (b) longer, shorter
(c) equal (d) shorter, shorter

53. Which of the following is more stable than others





(a) I (b) II
(c) IV (d) all equal

PASSAGE 8

Alkyl groups with at least one hydrogen atom on the α-carbon atom, attached to an unsaturated carbon atom, are able to release electrons in the following way.



Note that the delocalisation involves σ and π bond orbitals (or *p* orbitals in case of free radicals) ; thus it is also known as σ – π **conjugation.** This type of *electron release due to the presence of the system* H—C—C = C is known as **hyperconjugation.**

The phenomenon of hyperconjugation can also be applied to group, Cl—C—C = C, where the effect operates in the reverse direction.

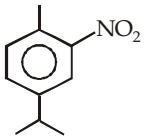
More the number of H—C bonds attached to the unsaturated system more will be the probability of electron release by this mechanism. Thus the electron release by this mechanism will be greater in methyl (possessing three hyperconjugated H—C bonds), less in ethyl (having two such bonds) and *iso*-propyl (one) and essentially zero in *tert*-butyl (no hyperconjugated H—C bond) group.

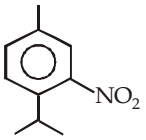
It is important to note that although hyperconjugation like inductive effect causes the release of electrons and thus the two effects reinforce each other in this respect, the magnitude of the two effects changes in opposite directions in passing along a series of alkyl groups.

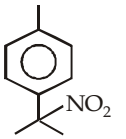
More is the number of hyperconjugative structures, more will be the stability of the species.

54. On the basis of hyperconjugation which of the following alkene is more stable ?
(a) 2-Methylpropene (b) Butene - 2
(c) Both equal
(d) Hyperconjugation has nothing to do with the relative stability of the two alkenes.

55.  $\xrightarrow{\text{Nitration}}$ P. P is most likely to be

(a) 

(b) 

(c) Both in equal amounts (d) 

56. Which of the following statements is regarding the electron substitution in toluene and benzotrichloride, $C_6H_5CCl_3$. Substitution takes place in o-position in toluene and m-position in $C_6H_5CCl_3$.
(a) This can be explained by both inductive as well as hyperconjugation.
(b) This can be explained only by inductive effect.
(c) This can be explained only by hyperconjugation.
(d) This can be explained by inductive effect and mesomeric effect.

Instructions for Q. 57 to 63 : Following questions are Multiple Matching type Questions :

57.

	Column I		*Column II*
(A)	Enol form of $CH_3COCH_2COOC_2H_5$	(a)	resonance stabilization
(B)	Higher acidity of maleic acid than fumaric acid	(b)	Hydration
(C)	Higher acidity of potassium fumarate than sodium maleate	(c)	Intramolecular hydrogen bonding
(D)	Solubility of NaCl in water	(d)	Intermolecular hydrogen-bonding

58.

	Column I		*Column II*
(A)	O = C = O	(a)	C is sp hybridised
(B)	OH^-	(b)	O has two lone pair of electrons
(C)	HCHO	(c)	C is sp^2 hybridised
(D)	$CH_2 = C = CH_2$	(d)	O is sp^3 bybridised

59.

	Column I		*Column II*
(A)	Inductive effect	(a)	Temporary effect
(B)	Hyperconjugation	(b)	Lucas's test for the three types of alcohols
(C)	Mesomeric effect	(c)	Involves σ electrons
(D)	Electronic effect	(d)	Involves π electrons

60.

	Column I		*Column II*
(A)	H_2O	(a)	Protophilic solvent
(B)	Liquid ammonia	(b)	Amphiprotic solvent
(C)	Benzene	(c)	Aprotic solvent
(D)	C_2H_5OH	(d)	Protogenic solvent

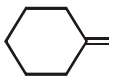
61.

	Column I		*Column II*
(A)	*sp* hybridization	(a)	square planar
(B)	sp^2 hybridization	(b)	tetrahedral
(C)	sp^3 hybridization	(c)	octahedron
(D)	dsp^2 hybridization	(d)	trigonal bipyramidal
(E)	d^2sp^3 hybridization	(e)	linear
(F)	dsp^3 hybridization	(f)	triangluar planar

62.

	Column I		*Column II*
(A)	o - Hydroxybenzoic acid	(a)	Tautomerism
(B)	p- hydroxybenzoic acid	(b)	Intramolecular H- bonding
(C)	Acetylacetone	(c)	Intermolecular H- bonding
(D)	Acetoacetic ester	(d)	Soluble in water

63.

	Column I		*Column II*
(A)	CH ≡ CH	(a)	Markownikoff addition
(B)		(b)	Acidic hydrogen
(C)	$CH_3COCH_2COOC_2H_5$	(c)	Wohl-Ziegler reaction
(D)	CH_3NO_2	(d)	Tautomerism

Instructions for Q. 64 to 70 : Following questions are Assertion and Reasoning Type Questions :

Note : Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 5 choices (a), (b), (c), (d) and (e) out of which ONLY ONE is correct.

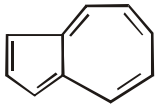
(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.

(c) Statement -1 is True, Statement-2 is False.

(d) Statement -1 is False, Statement-2 is True.

(e) Statement -1 is False, Statement-2 is False.

Q.64 Statement - 1 : Dipole moment of Azulene  is more than naphthalene.

Statement- 2 : Azulene exists as dipolarion due to the aromatic nature obtained in both rings.

65. **Statement I :** 3-Phenylbutan-2-one racemises in presence of dilute acid or dilute base.

Statement II : Its keto form is thermodynamically more stable form then the enol form.

66. **Statement - 1 :** CH_3OH boiling point is more than CH_3SH while $CH_3–O–CH_3$ boiling point is less than $CH_3–S–CH_3$.

Statement - 2 : Hydrogen bonding is stronger in CH_3OH than CH_3SH while no hydrogen bonding exist in $CH_3–O–CH_3$ and $CH_3–S–CH_3$.

67. **Statement I :** 2,4,6 trinitro N, N-diemethylaniline is 40,000 times more basic than 2,4,6-trinitroaniline.

Statement II : In the former steric inhibition or resonance causes the availability of ℓp on N whereas in the later due to H-bonding of NH_2 with NO_2 groups make NH_2 planar with benzene ring, so easy delocalisation of electron pair of N in benzene ring.

68. **Statement 1** : p-Hydroxybenzoic acid has a lower boiling point than o-hydroxybenzoic acid.

because

Statement 2 : o-Hydroxybenzoic acid has intramolecular hydrogen bonding.

69. **Statement 1 :** Trichloroacetic acid is stronger than acetic acid.

Statement 2 : Electron withdrawing substituents decrease the activity.

70. **Statement 1:** Neopentane forms one mono substituted compound.

Statement 2 : Neopentane is isomer of pentane.

Instructions for Q. 71 to 82 : The following questions are True/False Type Questions :

71. Vinyl chloride has higher dipole moment than allyl chloride.

72. The relative values of dipole moment of vinyl chloride and allyl chloride is due to resonance which here decreases dipole moment.

73. The *meta*-directing influence of $–CCl_3$ group in benzotrichloride is due to inductive as well as hyperconjugation.

74. Both $CH_3\overset{+}{C}HCH_2CH_3$ and $CH_3\overset{+}{C}HCH_3$ are 2° carbocations, hence equally stable.

75. Maleic and fumaric acids have similar acidic character, while fumarate ion is a stronger acid than maleate ion.

76. $CH_3O\overset{+}{C}H_2$ is more stable than $CH_3OCH_2\overset{+}{C}H_2$.

77. Resonance effect involves delocalisation of π or *p* electrons, while inductive effect involves delocalisation of σ electrons.

78. In $CH_2 = CH\overset{+}{N}H_3$, the π electrons are delocalised in the following way.

$$\underset{\text{I}}{CH_2 = CH - \overset{+}{N}H_3} \longleftrightarrow \underset{\text{II}}{\overset{+}{C}H_2 - CH = NH_3}$$

79. 1,3-Butadiene is stabilised by resonance, while cyclobutadiene is destabilised by resonance.

80. Boiling points of hydrogen halides follow the order HF > HCl > HBr > HI.

81. Chelation may explain increasing acidic character as well as decreasing acidic character of certain compounds.

82. Stability of enolic form of acetylacetone is due to resonance as well as hydrogen bonding.

EXERCISE 2.3 (Subjective Problems)

1. Predict the shape of the following species.

(*i*) $(CH_3)_3B$ (*ii*) CH_3^- (*iii*) CH_3^+
(*iv*) NH_2^- (*v*) BF_4^- (*vi*) $(CH_3)_2O$.

2. Write the conjugate acid and conjugate base of the following :

(*a*) HNO_3 (*b*) $H:^-$ (*c*) $:CH_3^-$
(*d*) Cl^- (*e*) $H_2C = CH_2$ (*f*) CH_3O^-.

Which of the following species is amphoteric in nature ?

3. Which is the stronger base in each of the following pairs ?

(*a*) NH_3 and PH_3

(*b*) NH_2^- and OH^-

(*c*) HS^- and F^-.

4. Ethanol and water both form hydrogen bond and ethanol has high molecular weight than water, even then water boils at a much higher temperature than ethanol. Explain

5. Arrange the following alkenes in increasing order of stability. Explain you answer with proper reason.

$CH_3CH = CH_2$, $CH_2{=}CH_2$, $(CH_3)_2C = CH_2$, $(CH_3)_2C = CHCH_3$, $(CH_3)_2C = C(CH_3)_2$

6. Explain the following :

(*i*) Guanidine behaves as a strong base.

(*ii*) Vinyl alcohol is acidic in nature

(*iii*) Acidic nature of α-hydrogen of aldehydes and ketones

(*iv*) The F^- of dissolved NaF is more reactive in dimethyl sulphoxide, $(CH_3)_2SO$ or acetonitrile than in methanol.

(*v*) Melting point of NaCl is much higher than that of $AlCl_3$.

(*vi*) In acylium ion, the structure $R{-}C \equiv O^+$: is more stable than $R{-}C^+ = O$.

7. Give the enolic forms of acetylacetone, ethyl acetoacetate and diethyl malonate and explain their stability involving intramolecular H—bonding.

8. Indicate the type of hybridisation of each carbon atom in the following compounds.

(*i*) CH_3CN (*ii*) $CH_3CH = CH_2$
(*iii*) $CH_3{-}C \equiv C - CH_3$ (*iv*) $HC \equiv C{-}CH = CH_2$.

9. (*a*) Write the structural formulae of all the possible isomers of $C_2H_2Cl_2$ and indicate which of them is non-polar.

(*b*) What effect should the following resonance of vinyl chloride have on its dipole moment ?

$$CH_2 = CH{-}Cl \longleftrightarrow \overset{\ominus}{C}H_2{-}CH = \overset{\oplus}{C}l$$

(*c*) Write the tautomeric forms for phenol.

10. (*a*) Write the two resonance structures of ozone which satisfy the octet rule.

(*b*) Write all possible resonance structures of the following that satisfy the octet rule.

NO_3^- and N_3^-.

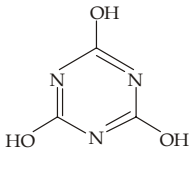
11. Arrange 2, 2-dimethylbutane, 3-methylpentane and *n*-hexane in order of decreasing boiling point. Explain your answer with proper reasoning.

12. Arrange the following in order of increasing boiling point

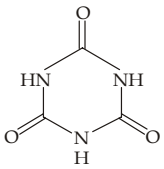
(*i*) *n*-butane, *n*-butanol, *n*-butyl chloride and isobutane
(*ii*) *n*-butane, ethanol, water and propane.

13. Arrange the following in increasing order of expected enol content in CH_3CH_2CHO, CH_3COCH_3,CH_3CHO, $CH_3COCH_2COCH_3$.

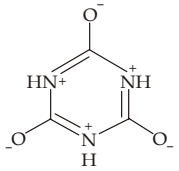
14. Is there any relationship between following three structures?



I



II



III

SOLUTIONS

TEST YOUR UNDERSTANDING - 2.1

1. For predicting the shape of each molecule, one must know the number of orbitals required by the central atom for holding the atoms attached to it and also unshared pairs of electrons, if any. For example, if the molecule requires 4 orbitals, sp^3 hybridisation is indicated.

(*a*) **BF_3.**

$_5B = 1s^2\ 2s^2\ p_x^1\ p_y^0\ p_z^0$ (ground state)

$_5B = 1s^2\ 2s^1\ p_x^1\ p_y^1\ p_z^0$ (excited state)

Thus BF_3 molecule will be trigonal planar, each F—B—F bond angle is 120° and the empty p_z orbital is at right angles to the plane of the molecule.

(*b*) **BF_4^-.**

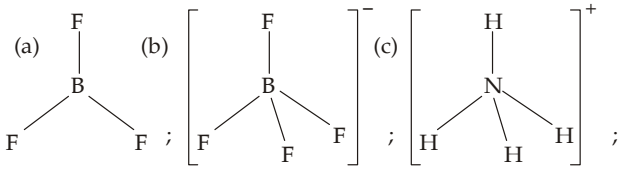
$$_5B = 1s^2 \quad \underbrace{2s^1\ 2p_x^1\ 2p_y^1\ 2p_z}_{sp^3\ \text{Hybridisation}}$$

The empty sp^3 hybrid orbital overlaps with a filled orbital of F^- holding two electrons. The shape is regular tetrahedral with a bond angle of 109.5°.

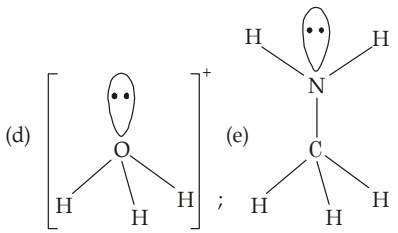
(*c*) **NH_4^+.** Four hydrogen atoms of N indicate sp^3 hybridisation, NH_4^+ species has no lone pair of electrons, giving regular tetrahedral shape with the normal tetrahedral bond angle of 109.5°.

(*d*) **H_3O^+.** In H_3O^+, oxygen is sp^3 hybridised and the shape of the molecule is a distorted tetrahedral (pyramidal) due to the presence of lone pair of electrons.

(*e*) **CH_3NH_2.** The central atom (N) is sp^3 hybridised ; three sp^3 orbitals form the usual N—H, N—H and N—C sigma bonds, the fourth sp^3 orbital has a lone pair of electrons. Thus here again shape of CH_3NH_2 will be distorted tetrahedral.



BF_3 BF_4^- NH_4^+



H_3O^+ CH_3NH_2

(*f*) **NO_2^+ ($:\ddot{O} = \overset{+}{N} = \ddot{O}:$).** Here the central atom (N) has two σ bonds and no lone pair of electrons ; thus it needs two hybrid orbitals which indicates *sp* hybridised state of N. Thus NO_2^+ will be linear in shape.

(*g*) **NO_2^- ($:\ddot{O} = \ddot{N}—\ddot{O}:^-$).** Here N has two σ bonds and one unshared pair of electrons and, thus it requires three hybrid orbitals indicating sp^2 hybridisation of N. Thus NO_2^- will have a trigonal planar shape.

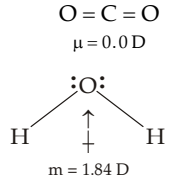
TEST YOUR UNDERSTANDING - 2.2

1. 0.86 D = 4.8 × δ × 1.43 Å; δ = 0.125 e

Thus the amount of charge separation is about 0.125 electronic charge, so the carbon atom has about an eighth of a positive charge, and the oxygen atom has about an eighth of a negative charge.

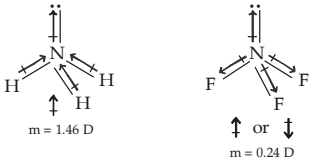
TEST YOUR UNDERSTANDING - 2.3

1. Carbon dioxide (CO_2) has zero dipole moment while water (H_2O) has a considerably large value of dipole moment (1.84 D). This is due to difference in their shape, CO_2 is a linear molecule (dipole moment of one C—O bond cancels that of the other C—O bond), while water has



a bent shape distorted tetrahedral, hence the dipole moment of the one O—H bond does not completely cancel that of other.

2. (*i*) In ammonia, dipole moment due to N—H bonds and due to lone pair of electrons reinforce each other

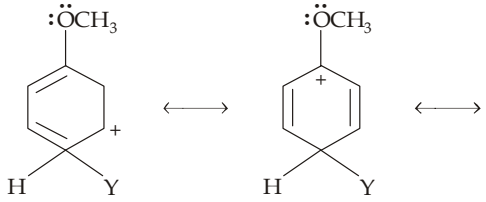


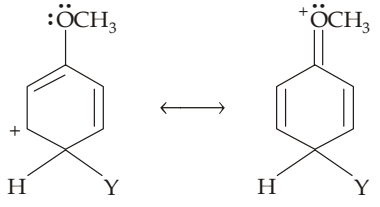
On the other hand, in NF_3, dipole moment due to N—F bonds is opposed by the dipole moment due to unshared pair of electrons. These opposing moments are *nearly* of the same size which produces a small moment, in any direction. However, remember in NH_3 the observed moment is mainly due the unshared pair, augumented by the sum of the bond moments.

(*ii*) Dipole moment of CD_3F will be higher (1.858 D) than that of CH_3F (1.847 D). The higher μ for CD_3F is due to higher value of charge (*e*) because *d* is same for the two molecules. Higher value of *e* in turn is due to the fact that F pulls electrons from D more easily than from H, *i.e.* D is more electron-releasing than H.

TEST YOUR UNDERSTANDING - 2.4

1. (*i*)

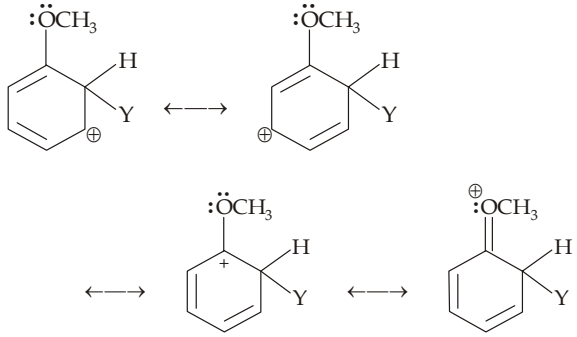




Especially stable every atom has octet

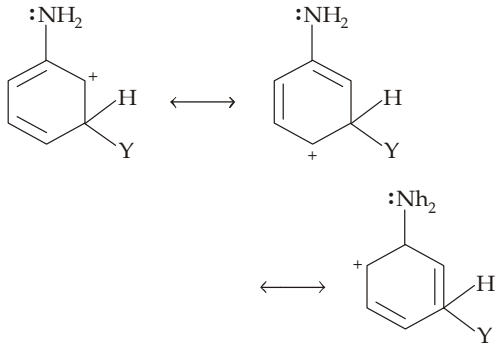
For writing resonating structures of an ion or a free radical, put the charge or odd electron in the various alternate positions. Remember that whenever in a structure every atom has a complete octet of electrons, it is considered to be more stable ignoring the fact that the charge is present on the more or less electronegative atom.

(*ii*)

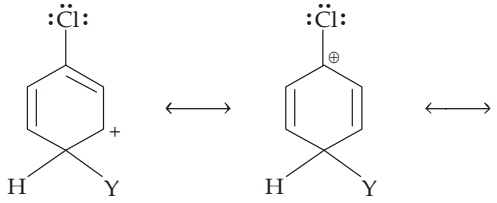


Especially stable every atom has octet

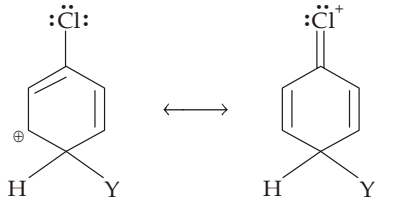
(*iii*)



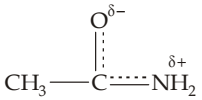
(*iv*)

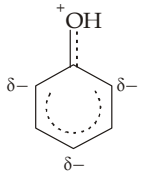
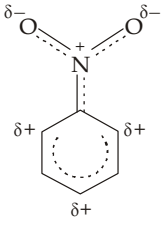


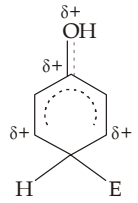
Especially unstable + charge on C bearing – I group



Comparatively stable every atom has octet

2. (*i*) $\overset{\delta+}{CH_2}\cdots\cdots CH\cdots\cdots\overset{\delta+}{CH_2}$ (*ii*) 

(*iii*)  (*iv*) 

(*v*) 

3. $CH_3—\ddot{O}—\overset{+}{C}H_2 \longleftrightarrow CH_3—\overset{+}{O}=CH_2$

Carbonium ion — Oxonium ion. Especially stable every atom has complete octet

This situation is comparable with the CH_3^+ and H_3O^+ where again latter is more stable due to complete octet of electrons of oxygen.

4. $Cl_3C:^-$ is less basic than $F_3C:^-$. This can be explained in terms of delocalization ; F can disperse charge only by an inductive effect, while Cl can disperse charge by an inductive as well as by *p-d* π bonding (F has no *d* orbital hence delocalization by *p-d* π bonding is not possible).

TEST YOUR UNDERSTANDING - 2.5

1. $CH_2=CH—CH_2 \rightarrow —Br \xrightarrow{HBr} \overset{+}{C}H_2—\overset{-}{C}H—CH_2—Br$

Electromeric effect due to – I effect



Electromeric effect due to hyperconjugation

Here hyperconjugative effect is strong than the inductive effect of Br, so mainly electromeric effect takes place in the second way.

TEST YOUR UNDERSTANDING - 2.6

1. For determining the relative boiling points, try to know the type of intermolecular force present among molecules of the same type. Higher is the attraction, greater is the force and more will be the boiling point. Relative order of attraction for the three important intermolecular forces is H-bond >> dipole-dipole > London forces. In case, two or more compounds have similar type of intermolecular force, then consider the molecular weight of such compounds, higher is the molecular weight more will be the boiling point.

(*i*) Order of polarity of the three alkyl halides is

$$CH_3Cl > CH_3Br > CH_3I$$

while the order of molar mass is

$$CH_3I > CH_3Br > CH_3Cl$$

However, here order of molar mass predominates, thus the boiling points of the three halides will be governed by their molar masses rather than the weak dipole-dipole attraction.

(*ii*) *n*-Pentane and neopentane are structural isomers, hence they have similar molar mass and polarity (both are non-polar). Thus here, shape of the molecule should be considered. The shape of *n*-pentane is rod-like, while that of neopentane is sphere-like. Now we know that rods can touch along their entire length, and thus provide larger surface area while spheres touch only at a point and thus have lower surface area. More is the surface area, greater will be the London forces and hence higher will be the boiling point.

(*iii*) Both, ethyl alcohol (C_2H_5OH) and dimethyl ether (CH_3OCH_3) are polar molecules and hence exhibit dipole-dipole attraction. However, hydrogen bonding (a strong intermolecular force) is possible only in ethyl alcohol, hence it boils at a higher temperature. In CH_3OCH_3, no hydrogen is present on O, hence hydrogen bonding is not possible.

(*iv*) Attractive forces between nonpolar molecules such as mineral oil and *n*-hexane are very weak ; hence *such molecules can mutually mix and hence formation of solution is easy.* Actually, the nonpolar molecules cannot overcome the strong H-bonds present between polar solvent (*e.g.* ethanol) molecules and therefore nonpolar molecules do not dissolve in polar protic solvents like C_2H_5OH and water.

TEST YOUR UNDERSTANDING - 2.7

1. (*a*) $\underset{\text{Acid}_1\text{ (Stronger)}}{HCl} + \underset{\text{Base}_2\text{ (Stronger)}}{H_2O} \rightleftharpoons \underset{\text{Acid}_2\text{ (Weaker)}}{H_3O^+} + \underset{\text{Base}_1\text{ (Weaker)}}{Cl^-}$

Conjugate

Conjugate

The reaction goes in the right direction because HCl is a good proton donor and hence a strong acid. Remember that an acid-base reaction goes in the direction of weak acid-weak base.

(*b*) $\underset{\text{Acid}_1\text{ (Weaker)}}{H_2O} + \underset{\text{Base}_2\text{ (Weaker)}}{NH_3} \rightleftharpoons \underset{\text{Acid}_2\text{ (Stronger)}}{NH_4^+} + \underset{\text{Base}_1\text{ (Stronger)}}{OH^-}$

Conjugate

Conjugate

The reaction goes in the left direction because NH_3 is a poor proton acceptor (a weak base). Note the amphoteric (acidic as well as basic) character of H_2O.

2. (*a*) $\underset{\text{Stronger base}}{NH_3} + \underset{\text{Stronger acid}}{H_3O^+} \rightleftharpoons \underset{\text{Weaker acid}}{NH_4^+} + \underset{\text{Weaker base}}{H_2O}$

(*b*) $\underset{\text{Weaker base}}{CN^-} + \underset{\text{Weaker acid}}{H_2O} \rightleftharpoons \underset{\text{Stronger acid}}{HCN} + \underset{\text{Stronger base}}{OH^-}$

(*c*) $\underset{\text{Stronger base}}{H^-} + \underset{\text{Stronger acid}}{H_2O} \longrightarrow \underset{\text{Weaker acid}}{H_2} + \underset{\text{Weaker base}}{OH^-}$

(*d*) $\underset{\text{Stronger base}}{C_2^{2-}} + \underset{\text{Stronger acid}}{H_2O} \longrightarrow \underset{\text{Weaker base}}{2OH^-} + \underset{\text{Weaker acid}}{C_2H_2}$

TEST YOUR UNDERSTANDING - 2.8

1. Consider the conjugate base of the various species

(*a*) CH_3O^- and CH_3S^- are conjugate bases of CH_3OH and CH_3SH respectively. Here oxygen and sulphur are in the same family of the periodic table, and sulphur is bigger than oxygen causing greater dispersal of the charge. Thus formation of CH_3S^- will be easier *i.e.* it is more stable. Hence *Acidity* $CH_3OH < CH_3SH$.

(*b*) Conjugate bases of NH_4^+ and H_3O^+ are NH_3 and H_2O respectively. Here N and O are in the same row (period) of the period table, and oxygen is more electronegative than nitrogen, thus H_2O will be more stable than NH_2. Hence *Acidity* $NH_4^+ < H_3O^+$.

(*c*) Conjugate bases of NH_4^+ and NH_3 are NH_3 and NH_2^- respectively. Here lone pair of electrons formed by loss of proton is better accommodated in : NH_3 (a neutral species) than in : NH_2^- (a negatively charged species). Hence

Stability $NH_2^- < NH_3$; Acidity $NH_3 < NH_4^+$

(*d*) Conjugate bases of H_2O and OH^- are OH^- and O^{2-} respectively. Here lone pair of electrons due to loss of proton is better accommodated in OH^- (single negative charge) than in O^{2-} (a doubly negatively charged). Hence

Stability $O^{2-} < OH^-$; Acidity $OH^- < H_2O$

2. First write down the conjugate base.

(*a*) The four species are H_2O, NH_3, HF and CH_4. Their conjugate bases are OH^-, NH_2^-, F^- and CH_3^-. The central atoms of these species (O, N, F and C) are present in the same row *i.e.* in the same periodic table. Hence their electronegativity will determine their stability.

Electronegativity order $C < N < O < F$

Hence stability order $CH_3^- < NH_2^- < OH^- < F^-$

Hence acidity order $CH_4 < NH_3 < H_2O < HF$

(*b*) The four species are HCl, HBr, HF and HI. Their conjugate bases are Cl^-, Br^-, F^- and I^-.

Atoms of these ions belong to the same group of the periodic table, hence their size increases on going down the group. Thus

Size order $F < Cl < Br < I$

Stability order $F^- < Cl^- < Br^- < I^-$

Remember that bigger the size of the ion, more will be its stability.

Hence *acidity* $HF < HCl < HBr < HI$.

3. For determining the relative basic character, follow the following points.

(*a*) In case the atoms bearing electron pair are in the same row of the periodic table, observe their *electronegativity* (more is the electronegativity of the atom less will be the basic character of the species bearing it).

(*b*) In case the atoms bearing electron pair are in the same family (group) of the periodic table, observe their *size* (the bigger the atom, more its ability to accommodate the electron pair and hence lesser will be the basic character of the species bearing it).

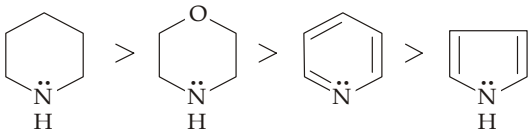
(*i*) *Basic character* $CH_3NH_2 > CH_3OH > CH_3F$

(*ii*) *Basicity* $CH_3^- > NH_2^- > OH^- > F^-$

(*iii*) *Basicity* $OH^- > SH^- > SeH^-$

(*iv*) *Basicity* $F^- > Cl^- > Br^- > I^-$

(*v*) Decreasing basic character.



I II III IV

We know that more the availability of lone pair of electrons, more is the basic character. Structures I and II do not exhibit resonance, and thus lone pair of electrons is localised and easily available for protonation, compound II is less basic than I because of presence of electronegative oxygen atom.

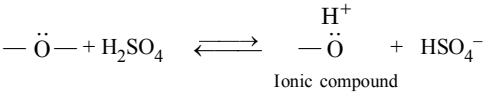
In compound III also, although lone pair of electrons on N is not involved in resonance but it is present on N attached to C by a double bond, hence it is less available than the N of I and II. In IV, lone pair of electrons on N is involved in resonance and hence least available for protonation.

4. Neither pure acid is ionized. However, in the mixture of $HClO_4$ and H_2SO_4, the stronger one ($HClO_4$) acts as an acid and thus donates a proton to H_2SO_4 (here a weaker acid) to form a mixture of ions.

$\underset{\text{Acid}_1}{HClO_4} + \underset{\text{Base}_2}{H_2SO_4} \rightleftharpoons \underset{\text{Acid}_2}{H_3SO_4^+} + \underset{\text{Base}_1}{ClO_4^-}$

$HClO_4$ is a stronger acid than H_2SO_4 because of the two conjugate bases (ClO_4^- and HSO_4^-), ClO_4^- is a weaker base than HSO_4^- because of more electronegativity of Cl than that of S. Hence here H_2SO_4 is acting as a base.

5. Reversible protonation of an unshared electron pair on an oxygen atom converts the organic compound into an ionic compound, a salt, which is soluble in the highly polar solvent, conc. H_2SO_4.



Ionic compound

EXERCISE 2.1

1	(b)	**6**	(b)	**11**	(c)	**16**	(b)	**21**	(b)	**26**	(d)	**31**	(b)	**36**	(b)	**41**	(b)	**46**	(b)	**51**	(b)	**56**	(b)	**61**	(a)
2	(c)	**7**	(d)	**12**	(c)	**17**	(b)	**22**	(d)	**27**	(b)	**32**	(c)	**37**	(b)	**42**	(d)	**47**	(b)	**52**	(c)	**57**	(b)	**62**	(d)
3	(c)	**8**	(a)	**13**	(d)	**18**	(a)	**23**	(d)	**28**	(a)	**33**	(c)	**38**	(b)	**43**	(d)	**48**	(c)	**53**	(b)	**58**	(c)	**63**	(b)
4	(c)	**9**	(c)	**14**	(c)	**19**	(d)	**24**	(c)	**29**	(c)	**34**	(d)	**39**	(b)	**44**	(c)	**49**	(d)	**54**	(b)	**59**	(a)	**64**	(d)
5	(b)	**10**	(d)	**15**	(a)	**20**	(d)	**25**	(c)	**30**	(d)	**35**	(a)	**40**	(b)	**45**	(b)	**50**	(b)	**55**	(d)	**60**	(b)	**65**	(c)
																								66	(b)

1. In ammonia, $2s^2\ 2p_x^1$, $2p_y^1$ and $2p_z^1$ orbitals of nitrogen undergo hybridisation to form four sp^3 orbitals, one having 2 electrons and the remaining three have 1 electron each.

2. In BF_4^-, the central atom (B) has only bonding electrons, *i.e.* no lone pair of electrons is present on the sp^3 hybridised B.

3. Dipole moment is due to difference in electronegativity of the two atoms. In toluene carbon atom of nucleus is sp^2 hybridised and hence more electronegative than that of side chain which is sp^3 hybridised.

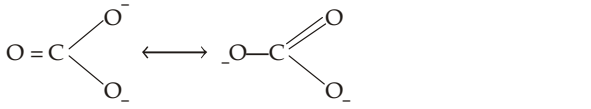
4. D is more electron-releasing than H ; hence relative to the C— H bond, the C—D bond has a dipole from D to C.

5. Structure I is most stable as it has no formal charge, while structure II is least stable because the negative charge is present on N rather than the more electronegative O as in III.

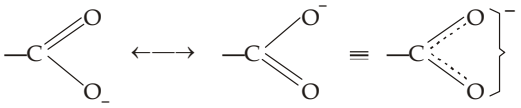
6. Structure II is not possible because the bulky iodine atom will push the *ortho* —NO_2 groups out of the plane of the ring, hence the two —NO_2 groups can't participate in resonance (*steric inhibition of resonance*).

7. An ion in which all atoms have complete octet of electrons and hydrogen has duet is more stable than the other.

8. The carbonate ion is a hybrid of three equivalent structures ; each carbon-oxygen bond is double (C = O) in one structure and single (C—O) in the other two. Thus each carbon-oxygen bond has less double bond character and hence is longer, than the bonds in formate ion which is hybrid of two equivalent structures.

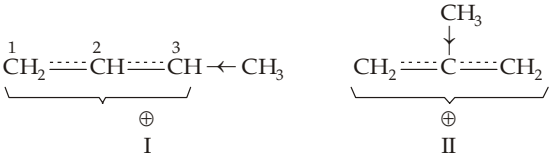


Resonating structures of CO_3^{2-}

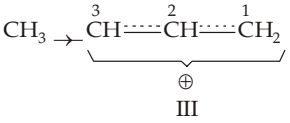


Resonating structures of $—COO^-$ ion

9. Let us first write the resonance hybrid of the three allyl carboniun ions.

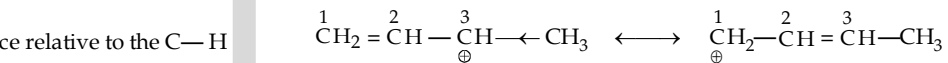


I II



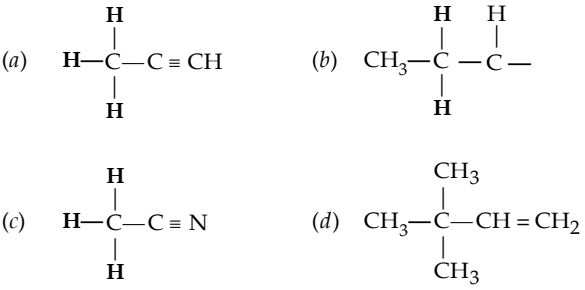
III

We know that better the dispersal of + charge, more will be the stability of the carbonium ion. Further, we know that C_1 and C_3 carry most of the positive charge which is

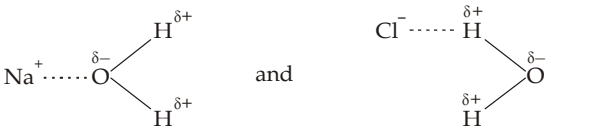


dispersed by the methyl group (+ I group) present on I and III, thus these two are more and equally stable than the II in which methyl group is present on C_2 which carry little of the positive charge.

10. In all structures except (*d*), π bond is in conjugation with the hyperconjugated H—C bonds represented by bold H.



11. Solution of a salt, such as NaCl, necessitates separation of the attracting ions (*i.e.* Na^+ and Cl^- ions). In presence of strong polar solvents like H_2O, both ions (Na^+ as well as Cl^-) are surrounded by water molecules in the following ways :



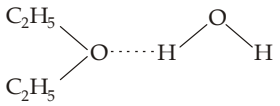
Ion-dipole attraction and Hydrogen bond between Cl^- and H_2O

12. Butter and CCl_4, both have very weak forces between them, hence they mix with each other.

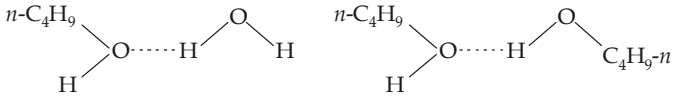
13. Lithium compounds are ionic, hence are insoluble in organic solvents and have high melting points ; while beryllium salts are covalent, hence soluble in organic solvents and will melt at low temperatures.

14. *n*-Butanol molecules can form hydrogen bonding between themselves (association) raising its boiling point, it can also form hydrogen bonding between water molecules (intermolecular hydrogen bonding) leading to its solubility in water. Diethyl ether, on the other hand, can't associate because of absence of H atom on O, hence its b.p. will be low than the isomeric *n*-butanol ;

however it can form H-bonding with water through its O with the H of water.

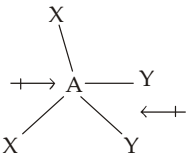


(*a*) Diethyl ether

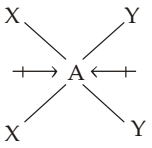


(*b*) *n*-Butanol

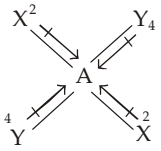
15.



Tetrahedral, (*i*)
Net moment



Square, (*ii*)
Net moment



Square, (*iii*)
Net moment = 0

In (*i*) and (*ii*) bond moments in opposite directions are not cancelled, while in (*iii*) individual bond moments are cancelled.

16. Increase in positive charge in closely related species increases acidity while increase in negative charge decreases acidity because the conjugate base (formed by loss of proton) will become less stable with the increase in negative charge.

$$O^{2-} < OH^- < H_2O$$

Stability of the three conjugated bases.

This is because the electron pair left behind upon the loss of proton is easily accommodated in a neutral conjugate base, followed by univalent ion, then bivalent ion, and so on.

Hence $OH^- < H_2O < H_3O^+$

Stability of the three conjugate acids

17. $H_3C:^-$ is much stronger base than $:\ddot{F}:^-$ due to following two factors.

(*a*) F is much more electronegative than C.

(*b*) Electron density of F^- is dispersed over its entire surface (100%), while that of H_3C^- is dispersed over only one-fourth of its surface (25%), the remaining three-fourth surface is occupied by three hydrogens. Thus electrons of F^- are more dispersed (and hence less available for protonation) than that of CH_3^-.

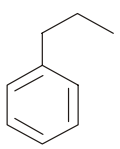
18. The difference of CH_3COOH as an acid in water and methanol is due to difference in solvation of the ions. Water solvates ions better than does methanol, hence

(*i*) $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

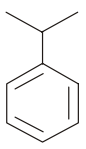
(*ii*) $CH_3COOH + CH_3OH \rightleftharpoons CH_3COO^- + CH_3OH_2^+$

reaction (*i*) is shifted more toward the right than the reaction (*ii*)

19.



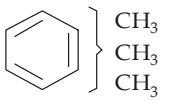
n-Propylbenzene



*iso*propylbenzene

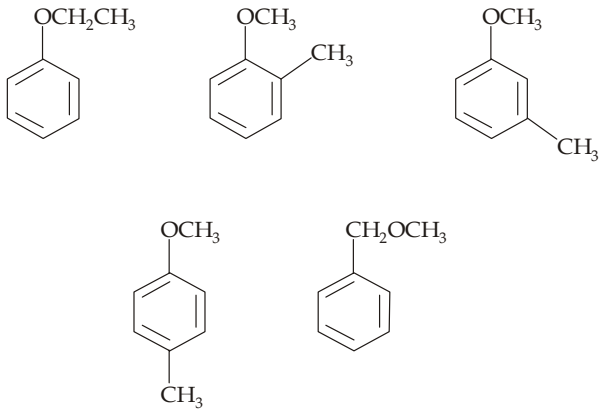


o-, *m*- and *p*-Ethyltoluenes

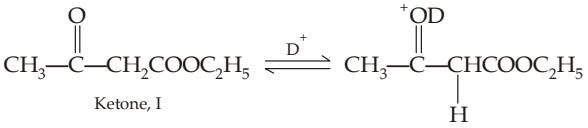


1, 2, 3-, 1, 2, 4- and 1, 3, 5-Trimethylbenzenes

20.

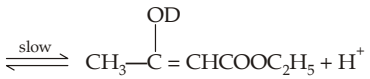


21. For this we must know the mechanism of enolisation. Note that α–H atom in II is more labile than in the ketone I



Ketone, I

Conjugate acid, II

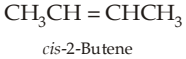


22. Geometrical isomers differ in all physical properties.

23.



1-Butene



cis-2-Butene
trans-2-Butene

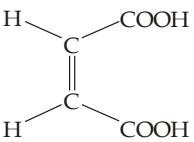


Cyclobutane

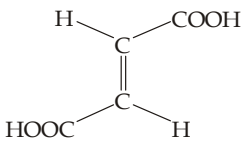


Methylcyclopropane

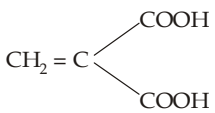
24.



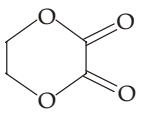
Maleic acid



Fumaric acid



Unsaturated dicarboxylic acid

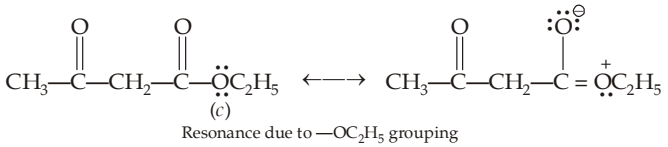


Cyclic ester

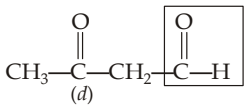
25. Only I and IV have α-hydrogen atoms.

26. Carbanion of all the four compounds are stabilised by resonance, hence α-hydrogen atom of all will be acidic. However, resonance stabilisation of the carbanion formed by (*c*) and (*d*) is more than that from (*a*) and (*b*). Further among (*c*) and (*d*), parent compound

(c) also shows resonance due to $—\ddot{O}C_2H_5$ group, hence its carbanion will be relatively less stable than that of the (d).



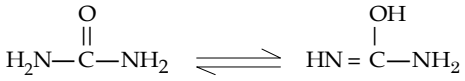
Resonance due to $—OC_2H_5$ grouping



no resonance is possible in this group.

Hence compound (d) will have more tendency to be converted to carbanion.

27. Urea, H_2NCONH_2 can show lactam-lactim tautomerism, or functional isomerism with NH_4CNO (ammonium cyanate).



30. Since olefinic bond has upper position in the seniority table, it should be given lower number in numbering than the acetylenic linkage. C^2 is having double bond one side *i.e.* it is sp^2 hybridised while C^3 has single bonds on both sides, it is sp^3 hybridised.

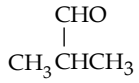
31. I and II have greater number of covalent bonds and thus more stable than either III or IV. Further I has no formal charge, thus it is more stable than II having formal charges. Further IV is less stable because here negative charge is present on carbon (a lesser electronegative atom than oxygen) and positive charge on oxygen (a more electronegative element) ; while it is reverse in III which is in accordance with the nature of the two atoms (oxygen and carbon).

32. A resonating structure in which every atom has 8 valence electrons (octet) is said to be the most stable, on the contrary a structure having more than 8 valence electrons in any of its atoms is said to be most unstable.

33. Structure (c) has 10 valence electrons in N.

34. C_4H_8O corresponds to general formula, $C_nH_{2n}O$ for aldehydes and ketones. Thus different isomeric aldehydes, ketones and unsaturated alcohols are

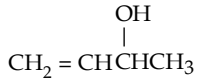
(i) $CH_3CH_2CH_2CHO$ — 1° aldehyde

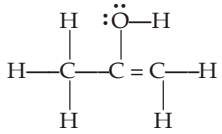
(ii)  — 2° aldehyde

(iii) $CH_3COCH_2CH_3$ — ketone

(vi) CH_2= $CHCH_2CH_2OH$ — 1° alcohol

(v) $CH_3CH = CHCH_2OH$ — 1° alcohol

(vi)  — 2°alcohol

35. 

Acetone (enolic form)

No. of σ bonds = 9

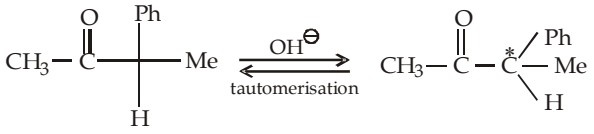
No. of π bond = 1

No. of lone pairs = 2

36. Enolisation is possible only in those structures which have at least one α-hydrogen atom to the ketonic group ; in structure (b) α-hydrogen atom to ketonic group is not present.

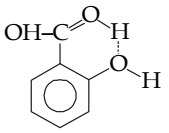
EXERCISE 2.2

>1 CORRECT OPTION	1	(a,b,c)	2	(a,c)	3	(a,b,c)	4	(a,b,c,d)	5	(a,c)	6	(a,b,d)
	7	(c,d)	8	(a, b, c)	9	(a,b,c,d)	10	(a, b, c)	11	(c, d)	12	(b, d)
	13	(a, b, c)	14	(a, b)	15	(a,b,c,d)	16	(a,b,c)	17	(a,b)	18	(a,b,c)
PASSAGE 1	19	(a,b,c,d)	20	(d)	21	(b)	22	(a,b)	23	(d)	24	(c)
PASSAGE 2	25	(c)	26	(b)	27	(d)	28	(b)	29	(b, c)	30	(a,b,c)
	31	(a,b,c)	32	(a,b,c)	33	(a,b,c)						
PASSAGE 3	34	(d)	35	(d)	36	(b,d)	37	(b)	38	(b)	39	(b)
	40	(b)	41	(a)								
PASSAGE 4	42	(a, c)	43	(a)	44	(c)						
PASSAGE 5	45	(c)	46	(b)	47	(d)						
PASSAGE 6	48	(c)	49	(a)	50	(c)						
PASSAGE 7	51	(c)	52	(a)	53	(c)						
PASSAGE 8	54	(b)	55	(a)	56	(a)						
MATCHING TYPE QUESTIONS	57	(A) - a, c; (B) - c; (C) - c; (D) - b, d					58	(A) - a, b ; (B) -d ; (C) - b, c ; (D) - a				
	59	(A) - b, c ; (B) - c, d ; (C) -d (D) - a,d					60	(A) – a,b,d; (B) – a,b; (C) – c; (D) – a,b				
	61	(A)-e; (B)-f; (C)-b; (D)-a; (E)-c; (F)-d					62	(A) - b ; (B) - c, d ; (C) -a, b (D) -a, b				
	63	(A)-a, b ; (B)-a, c ; (C)-b, d ; (D)-b, d										
A/R	64	(a)	65	(b)	66	(a)	67	(a)	68	(d)	69	(c)
	70	(b)										
TRUE/FALSE	71	FALSE	72	**TRUE**	73	TRUE	74	**FALSE**	75	FALSE	76	**TRUE**
	77	FALSE	78	**FALSE**	79	TRUE	80	**FALSE**	81	TRUE	82	**TRUE**

65. 

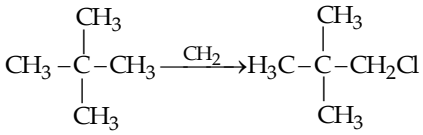
Statement-1 is True, Statement-2 is True but reason is not the correct explanation of assertion.

68. p-Hydroxybenzoic acid has higher boiling point than o-hydroxybenzoic acid due to intermolecular hydrogen bonding. Thus, statement-1 is false. o-Hydroxybezoic acid shows intramolecular H-bonding thus, statement-2 is true.



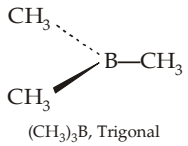
69. Trichloro acedic acid is stronger acid as three chloro substituents are electron withdrawing.

70. Neopentane forms one mono substituted compound as shown below :

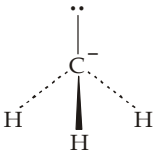


It is 1-chloro 2, 2-dimethyl propane.
It forms only one mono substituted compound not because it is isomer of pentane but because its structure is symmetrical (all the form carbons are symmetrically situated around central carbon).

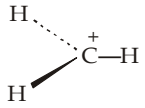
EXERCISE 2.3

1. (*i*) 

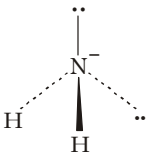
$(CH_3)_3B$, Trigonal

(*ii*) 

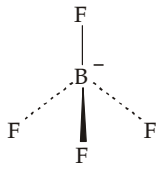
CH_3^-, Tetrahedral

(*iii*) 

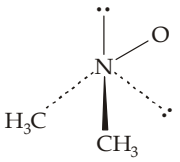
CH_3^+, Trigonal

(*iv*) 

NH_2^-, Tetrahedral

(*v*) 

BF_4^-, Tetrahedral

(*vi*) 

$(CH_3)_2O$, Tetrahedral

2.

	Species	*Conjugate acid*	*Conugate base*
(*a*)	HNO_3	$H_2NO_3^+$	NO_3^-
(*b*)	$H:^-$	H_2	None
(*c*)	$:CH_3^-$	CH_4	$:\ddot{C}H_2^{2-}$
(*d*)	Cl^-	HCl	None
(*e*)	$CH_2 = CH_2$	$CH_3—CH_2^+$	$CH_2 = \ddot{C}H^-$
(*f*)	CH_3O^-	CH_3OH	$:CH_2O^{2-}$

However, practically conjugate bases in (*c*) and (*f*) are difficult to form, hence it can be said that CH_3O^- and $:CH_3^-$ have no conjugate bases.

Thus HNO_3 and $CH_2 = CH_2$ are amphoteric.

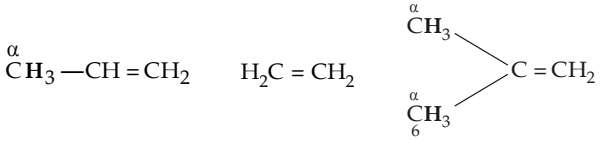
3. (*a*) NH_3 is stronger base than PH_3 because of smaller size of N.

(*b*) NH_2^- is stronger base than OH^- because of less electronegativity of N than that of O. Moreover in $:NH_2^-$, electron density is dispersed over one-third (33%) of the surface while in OH^- electron density is dispersed over half (50%) of the surface.

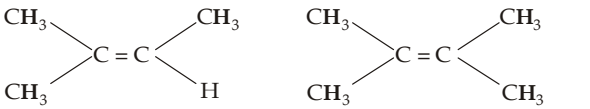
(*c*) Basic character of HS^- and F^- cannot be compared because F and S are in different groups and different periods of the periodic table.

4. Degree of association is very high in water as compared to that in ethanol because presence of bulky alkyl groups hinders the formation of intermolecular hydrogen bonding.

5. Relative stability of alkenes can be explained on the basis of hyperconjugation, more the number of hyperconjugative structures (*i.e.* α—H atoms, written, below the each member), more will be the stability of the alkene.



3-Hyperconjugative structures | No | 6-Hyperconjugative structures

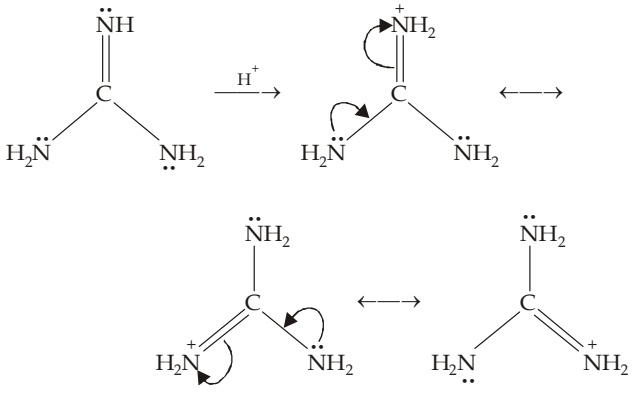


9 Hyperconjugate structures | 12 Hyperconjugative structures

Hence order of stability is

$(CH_3)_2C = C(CH_3)_2 > (CH_3)_2C = CHCH_3 > (CH_3)_2C = CH_2 > CH_3CH = CH_2 > CH_2 = CH_2$.

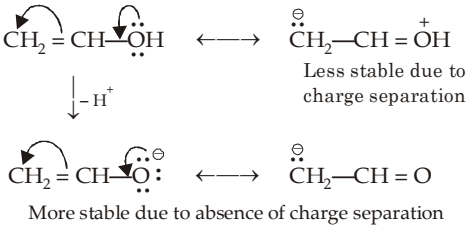
6. (*i*) Guanidine is a strong base because it can accept proton very easily and the protonated guanidine is quite stable as it is a resonance hybrid of three equivalent structures.



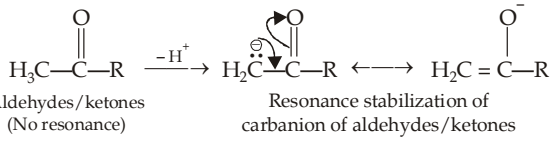
Three equivalent resonating structures

Note that protonation occurs only at sp^2 hybridised nitrogen atom because this leads to a species very much stabilised by three *equivalent* resonating structures. Protonation on sp^3 hybridised N atom gives species which is not stabilised by resonance to any significant extent.

(*ii*) Vinyl alcohol behaves as a weak acid because the ion formed by deprotonation is more stable than the parent compound.



(*iii*) α-Hydrogen atom of aldehydes and ketones is acidic in nature because the carbanion formed by its loss is stablised by resonance.

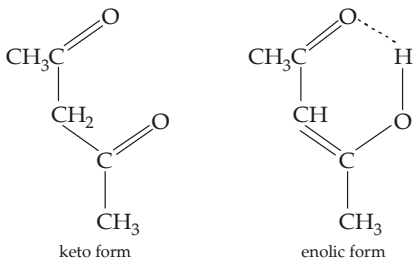


(*iv*) In methanol, fluoride ion is linked to CH_3OH via H—bond (CH_3OH - - - F^-) with the result reactivity of F^- is decreased. The other two solvents are incapable of forming H—bond.

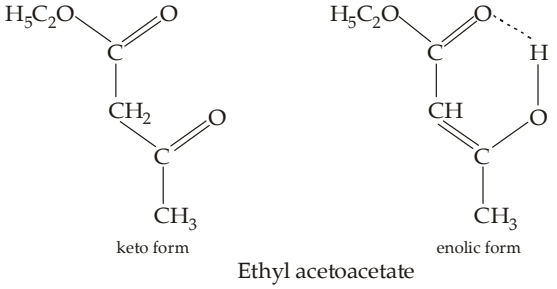
(*v*) NaCl is electrovalent, while $AlCl_3$ is covalent.

(*vi*) In acylium ion, $R—C \equiv O^+$: is more stable than $R—\overset{+}{C} = O$, the ordinary carbonium ion, because in the former the octet of every atom is complete while in the later, the carbon atom has only 6 electrons.

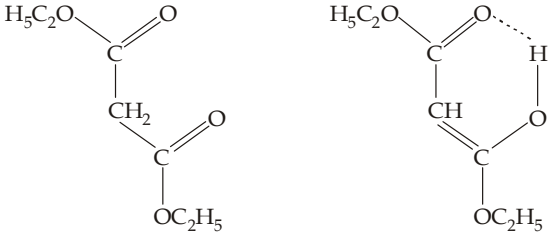
7. If a structure is capable of forming 5- or 6-memberd ring structure it is said to be stable. In the enolic form of the given compounds 6-membered ring is formed due to hydrogen bonding, thus the enolic forms of these compounds are said to be stable.



Acetylacetone



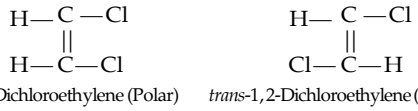
Ethyl acetoacetate



Diethyl malonate

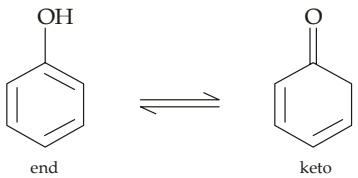
8. (*i*) sp^3, sp (*ii*) sp^3, sp^2, sp^2
(*iii*) sp^3, sp, sp, sp^3 (*iv*) sp, sp, sp^2, sp^2.

9. (*a*)

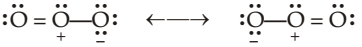


(*b*) Resonance decreases the dipole moment of vinyl chloride. The positive charge on Cl and a negative charge on C (developed by resonance) oppose each other and hence diminish the electronegativity of Cl and thus polarity (and dipole moment) of the bond. The dipole moments of vinyl chloride and chlorobenzene are 1.4 D and 1.7D respectively, while the dipole moment of alkyl halides is 2– 2.2 D.

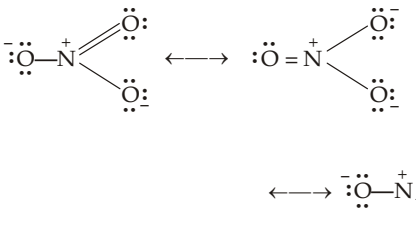
(*c*)



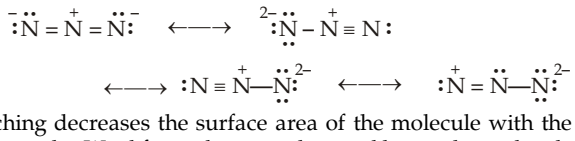
10. (*a*)



(*b*)



and



11. Branching decreases the surface area of the molecule with the result vander Waal forces becomes less and hence the molecule boils at lower b.p. Thus the boiling point order is

n-Hexane > 3-Methylpentane > 2, 2-Dimethylbutane

12. (*i*)

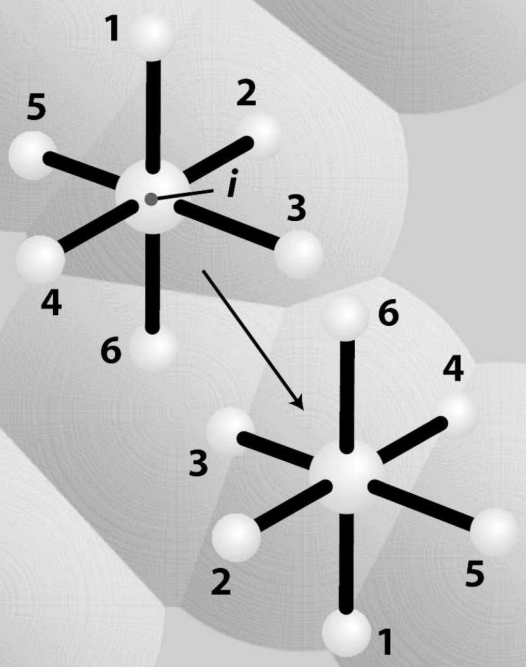
	iso-Butane	<	*n*-Butane	<	*n*-Butyl chloride	<	*n*-Butanol
Intermolecular forces	Weaker vander Waal		Stronger vander Waal		Dipole-dipole		H-bond

(*ii*)

	Propane	<	*n*-Butane	<	Ethanol	<	Water
Intermolecular forces	Weaker vander Waal		Stronger vander Waal		Weaker H-bond		Stronger H-bond

13. $CH_3CHO < CH_3COCH_3 < CH_3COCH_2CHO < CH_3COCH_2COCH_3$

14. I and II are tautomers (lactam-lactim type) ; II and III are resonating structures.



3

Stereochemistry

CHAPTER HIGHLIGHTS

3.1 Conformational Isomers

3.2 Configurational Isomers

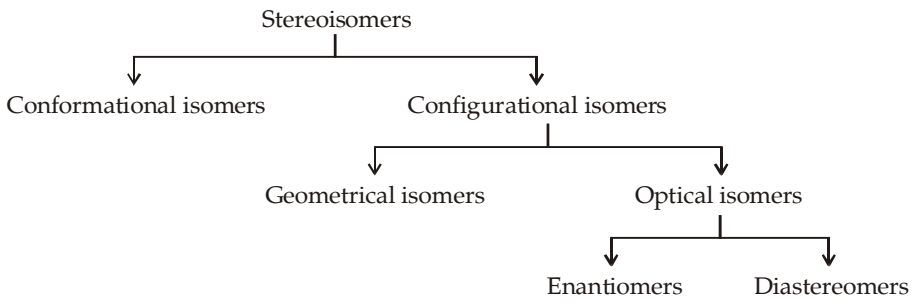
3.3 Enantiomers and Chiral Molecules

3.4 Diastereomers

EXERCISES

SOLUTIONS

Stereochemistry is the study of the three-dimensional structure of molecules. The foundation of organic stereochemistry was laid by Van't Hoff and Le Bel in 1874. They, independently, proposed that the four bonds to carbon were directed towards the corners of a tetrahedron. Stereochemistry explains the existence of *stereochemical isomers* or *stereoisomers*, namely *conformational* (those that can be interconverted by rotation about a sigma bond) and *configurational* (those that can be interconverted only by breaking and reforming of bonds). Two important sub-classes of configurational isomers are *geometrical isomers* (those in which restricted rotation in a ring or at a multiple bond determines the relative spatial arrangement of atoms) and *optical isomers* (those that differ in the three-dimensional relationship of substituents about one or more atoms).



Diastereomers (steroisomers that are not enantiomers) may not necessarily be optical isomers, geometrical isomers are also examples of diastereomers.

3.1 Conformational Isomers

The isomers which differ in the conformation are known as conformational isomers. Conformational isomers are rapidly interconverted at room temperature, so **they cannot be sparated**. Conformational isomers are also called **conformers**. There are two kinds of conformational isomers.

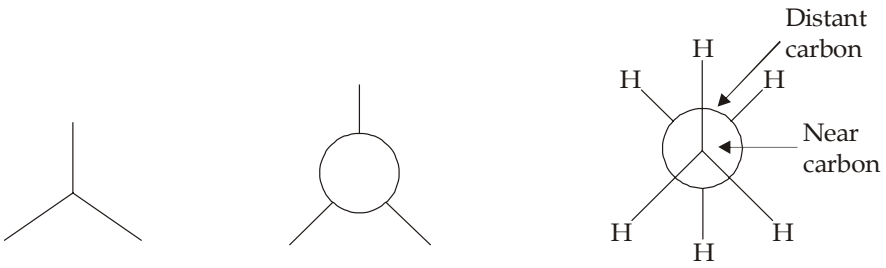
(a) Conformational isomers due to free rotation about carbon-carbon single bonds. This is found in alkanes, cycloalkanes and their substituted derivatives.

(b) Conformers due to amine inversion, discussed in enantiomers.

Conformations of alkanes. There is restricted (but not free) rotation about a single bond. *The restricted rotation leads to the existence of a single compound of one configuration into more than one spatial arrangements* **(conformations).** So now **conformation** *may be defined as the term used to denote any one of the infinite number of spatial arrangements of the atoms of a molecule that can arise from rotation about a single bond.*

Difference between conformation and configuration. The term conformation should not be confused with the **configuration** *which relates to those spatial arrangements of the atoms of a molecule that can be changed only by the breaking and making of bonds* whereas the *spatial arrangements in* **conformation** *are changed simply by rotation about a single bond.* In other words we can say that the various stereoisomers that differ in configuration can be interconverted only by the breaking and making of bonds whereas the conformational arrangement may be interconverted by rotation of one part of the molecule with respect to the rest of the molecule about a single bond joining these two parts. The various conformations of some of the important compounds are dealt in the book to clarify the point.

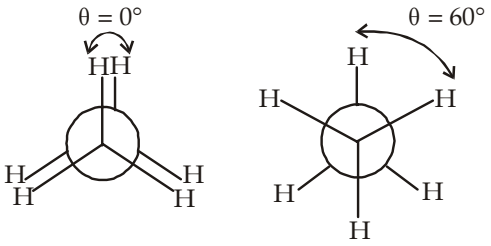
Representation of conformation. Conformation of alkanes can best be represented with the help of Newmann projection formulae since eclipsing (overlapping or crowding) of hydrogen atoms can best be represented by this formula. In the Newmann projection formula, the carbon atoms nearer to the eye (*i.e.*, the front carbon) and the groups attached to it are represented by equally spaced radii and the distant carbon atom (*i.e.* the carbon atom farther from the eye or the rear carbon) and the groups attached to it are represented by a circle with three equally spaced radial extensions.



Front carbon Rear carbon Newmann projection formula for $H_3C—CH_3$

(a) Conformations of ethane. The conformation of ethane, $H_3C—CH_3$ affords the simplest possible introduction of the subject. Imagine that one of the methyl groups is rotated along the C—C axis keeping the rest of molecule undisturbed. An infinite number of possible arrangements of the rotated methyl group with respect to the undisturbed methyl group are possible, each of these possible arrangement represents a **conformation.**

Any conformation can be specified by its **torsion angle or dihedral angle** (θ), the angle between the C–H bonds on the front carbon atom and the C–H bonds on the back carbon in the Newmann projection.



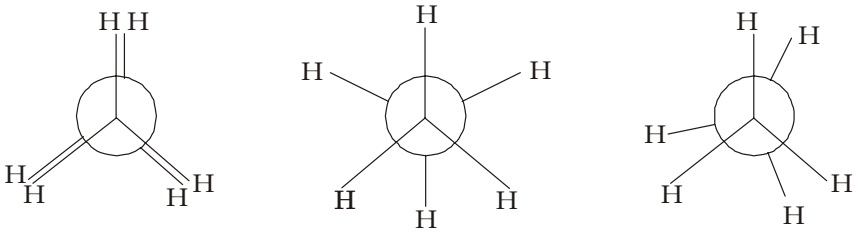
* It is important to note that the bonds of the rear carbon in the eclipsed form in the Newmann projection formula are shown slightly displaced simply to make them visible otherwise in practice they eclipse (overlap) completely. However, this can beautifully be realised in the ball-and-stick model of the eclipsed form of ethane.

In ethane, the conformation with θ = 0° is called the **eclipsed conformation**, while the conformation with θ = 60° is called the **staggered conformation**.

However, for the sake of convenience each rotation is done in the instalment of 60°. Thus in such case we will obtain six different conformations of ethane. Of these six conformations, the two extreme ones are worth studying because these are very much different from each other, while the intermediate four conformations are almost similar to each other but of course different from the two extreme forms. Thus in short there will be three conformations of ethane, the two extremes and the third which will be the intermediate of the two extremes.

1. One extreme conformation will be such in which the rear methyl group is completely eclipsed by the front methyl group and thus only the front methyl group, *i.e.*, three hydrogen atoms of the methyl group nearer to the eye are visible. Such conformation is known as **eclipsed conformation.** In the Newmann projection formula of the eclipsed form, the hydrogen atoms are crowded, *i.e.* the two hydrogen atoms come close to each other.

2. Another extreme conformation will be such in which the rear methyl group has been rotated upside down and thus both the methyl groups, *i.e.*, all the six hydrogen atoms are visible and are as far apart from each other as possible. Such conformation is known as **staggered.**



3. The infinite number of possible intermediate conformations between the two extreme conformations are referred to as **skew conformations.** In these conformations, hydrogen atoms are closer than in staggered but away than in eclipsed conformation.

It is important to note that all the above conformations of ethane are not equally stable. Among the infinite number of conformations the *staggered conformation* in which hydrogen atoms are as far apart as possible *is the most stable* while the *eclipsed conformation* in which hydrogen atoms are perfectly eclipsed *is the least stable ;* stabilities of the skew conformations lie in between these two extreme limits. Hence the relative stabilities of the various conformations of ethane are in the following order.

Staggered > Skew > Eclipsed

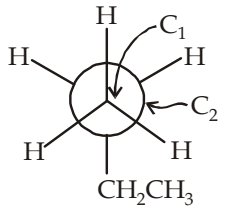
This stability order can be explained in terms of repulsive interactions (non-bonded) between bonding pairs of electrons, *i.e.* electrons pair which form six C—H bonds in ethane. In the staggered conformation, the electron clouds of six carbon-hydrogen bonds are as far apart as possible with the result there is minimum repulsive interactions between these electron clouds. Hence this conformation is quite stable. On the other hand, in the skew and eclipsed conformations, the electron clouds start coming closer. This causes repulsive interactions which is maximum in the eclipsed conformation where there is minimum separation of the electrons of the six C—H bonds. Hence the potential energies of the skew and eclipsed conformations increase and thus their stabilities decrease which is minimum in case of eclipsed conformation.

The repulsive interaction between the electron clouds which affects the stability of a conformation is known as **torsional strain.** Of all the conformations of ethane, staggered conformation has the least torsional strain and hence most stable while eclipsed conformation has the maximum torsional strain and hence least stable. Due to torsional strain, certain energy called **torsional energy**, is required to allow rotation around the C—C single bond. In other words, an ethane molecule having staggered conformation will have to cross an energy barrier equivalent to the torsional energy for being converted into eclipsed conformation.

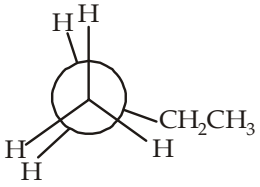
The energy difference between the staggered and eclipsed conformations of ethane is found to be 2.8 kcal/mole which constitutes the energy barrier to rotation about the C—C bond, *i.e.*, for the conversion of staggered to eclipsed conformation. However, this energy barrier of 2.8 kcal/mole is too small for either form to remain stable, *i.e.*, the two forms are interconvertible because even at ordinary temperature, ethane molecules have an average energy of 15—20 kcal/mole which can easily overcome the small barrier of 2.8 kcal/mole. This implies that *rotation about the carbon-carbon single bond in ethane is almost free for all practical purposes,* and it is not possible to separate the different conformations of ethane. Remember that ordinarily, ethane is mostly in staggered form.

(b) **Conformations of butane :** Butane has three carbon-carbon single bonds, and the molecule can rotate about each of them. One of the staggered and one of the eclipsed conformations of butane due to rotation about the C_1–C_2 bond are drawn below.

$$\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{3}{CH_2}-\overset{4}{CH_3}$$

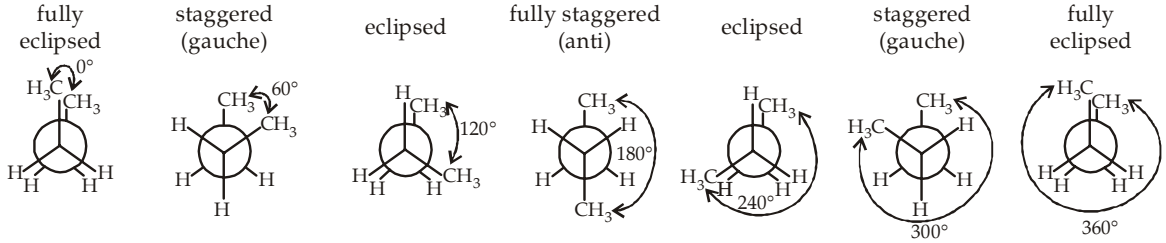


A staggered conformation due to rotation about the C_1-C_2 bond in butane



An eclipsed conformation due to rotation about the C_1-C_2 bond in butane

It is important to note that all the staggered conformers due to rotation about the C_1–C_2 bond in butane have same energy (difference from the staggerred conformers due to rotation about the C_2–C_3 bond). The six important conformations of butane obtained due to rotation about the C_2–C_3 bond are drawn below.



Note that six different configurations are broadly of two types.

(i) **Staggered :** Structures B, D and F in which the substitutents on the C_2 and C_3 are as far apart as possible. Hence they have less **steric strain** (**steric hindrance**) and thus more stable than the other three (A, C and E).

Further among the three staggered conformers, the conformer D is different from the other two staggered conformers B and F because in D the two methyl (bulky) groups are maximum possible away from each other, hence this conformation exerts less steric strain than the D and F, and thus it has less energy and more stable. The two types of staggered conformers are known as **anti** (D) and **gauche** (B and F) **conformers.**

(ii) **Eclipsed :** Like the three staggered conformers (B, D and F), there are three eclipsed conformers (A, C and E) in which the substituents on C_2 and C_3 are closest to each other. Thus they have more steric strain, more energy and less stability. Further among the three eclipsed conformers, the eclipsed conformer A has two large (CH_3) groups closest to each other, while the other two (C and E) has two CH_3 groups away from each other. Hence A (called totally eclipsed) is less stable than the C and E (called eclipsed), although all the three A, C and E are less stable than B, D and F.

The order of stability of these conformations is

$$\underset{D}{\text{Anti}} > \underset{B=F}{\text{Gauche}} > \underset{C=E}{\text{Eclipsed}} > \underset{A}{\text{Fully eclipsed}}$$

In an alkane, most molecules are in staggered conformations, and further more molecules are in an anti conformation than in a gauche conformation (the two types of staggered conformers). The preference for a staggered conformation causes carbon chains to orient themselves in a zigzag fashion.

TEST YOUR UNDERSTANDING - 3.1

1. (a) What structural features are necessary for a compound to exhibit conformational isomerism? Which of the following compounds have conformations?

(i) CH_3Cl (ii) H_2O_2 (iii) H_2NOH (iv) $CH_2 = CH_2$

(b) Draw the two important conformational isomers of methanol.

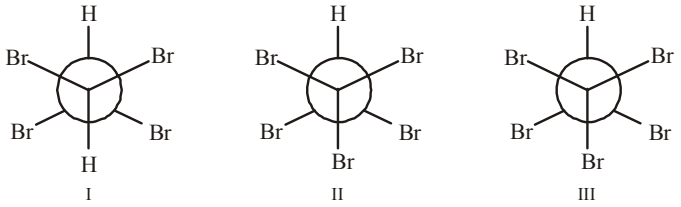
2. Draw the six conformations of propane.

3. Using Newmann projections, draw the most stable conformer for the following.

(a) 3-Methylbutane, considering rotation about the $C_2 - C_3$ bond.

(b) 3,3-Dimethylhexane, considering rotation about the $C_3 - C_4$ bond.

4. Three conformations of 1, 1, 2, 2-tetrabromoethane are given below.



Answer the following regarding these.

(*i*) Can any of the above conformation exhibit optical isomerism ?

(*ii*) Is there any known relation between the three, if so mention it ?

5. Complete the following reactions

(*i*) $CH_2OH.CHOH.CH = CH_2 \xrightarrow[\text{alk. } KMnO_4]{\text{Cold}} \underset{\text{Optically active}}{A} + \underset{\text{Optically inactive}}{B}$

(*ii*) $CH_2OH.CHOH.CHOH.CH_2OH \xrightarrow{1 \text{ mole HBr}} \underset{\text{(Optically active)}}{C}$

(*iii*) 2-Ethyl-3-methyl-1-pentene $\xrightarrow{H_2}$ $\underset{\text{(Optically active)}}{D} + \underset{\text{(Optically inactive)}}{E}$

6. 1, 2-Dibromoethane has a zero dipole moment, while ethylene glycol has a measurable dipole moment. Explain.

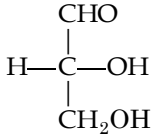
3.2 Configurational Isomers

These isomers differ in the configuration (arrangement of substituents around a central atom). Since these isomers are not readily interconverted at room temperature, they can be separated. There are two kinds of configurational isomers : (a) *cis-trans isomers*, and (b) *isomers due to chirality centre (optical isomers).* Before going into details of the two types of configurational isomers, we must be familiar with the concept of configuration.

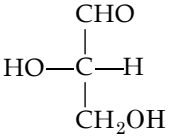
Configuration : In the study of the optical isomerism among organic compounds three different conventions are frequently used : D and L- ; *d*- and *l*- and (+) and (–)- ; the latter two have the same significance and are used to indicate the sign of rotation of the two enantiomers. The first convention, *i.e.*, D- and L-, is used to show the *configuration* of the compound. *By the term configuration we mean the arrangement of atoms or groups around the chiral centre* which is most commonly a carbon or nitrogen atom. It must be very clear to the reader that there is no significant relation between the sign of rotation and the configuration of an enantiomer because a compound and its derivatives having the same configuration may have different sign of rotation, *e.g.*, lactic acid and its esters, although having same configuration, possess opposite sign of rotation, *viz.* + 3.82° and – 8.25°, respectively. Two systems have been developed for studying the configuration of organic compounds.

3.2.1 Relative configuration (D, L-Nomenclature)

Before 1951, there was no method for determining the **absolute configuration** (actual arrangement of atoms in space) of a compound and hence the configuration of all the compounds were studied with respect to glyceraldehyde[1] **(relative configuration),** the configuration of which was taken as an arbitrary standard. (+) – Glyceraldehyde, having the —OH group on the right and the hydrogen atom on the left, the —CHO and —CH_2OH groups being at the top and bottom, respectively, was arbitrarily given the configurational symbol D. The mirror image compound (–)- gylceraldehyde, in which the –OH group is on the left and hydrogen on right was given the configuration, L.



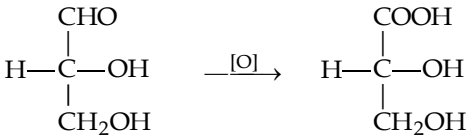
D-(+)-Glyceraldehyde[2]
(having —OH to the right)



L-(–)-Glyceraldehyde[2]
(having —OH to the left)

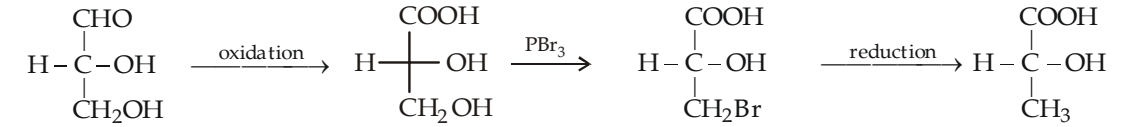
1. Rosanoff chose glyceraldehyde as arbitrary standard for studying relative configuration because of its relationship to carbohydrates.
2. (+)- and (–)-signs indicate that the two forms are dextro- and laevorotatory, respectively, but it must also be taken in mind that it is not necessary that all the compounds belonging to D- and L-series will be dextro- and laevorotatory, respectively.

Any compound that can be prepared from, or converted into D- (+)-glyceraldehyde will belong to the D-series, and similarly any compound that can be prepared from, or converted into, L–(–)-glyceraldehyde will belong to the L-series **(relative configuration).** For example, D-glyceraldehyde can be converted to glyceric acid by simple oxidation and thus the configuration of glyceric acid obtained must be D.



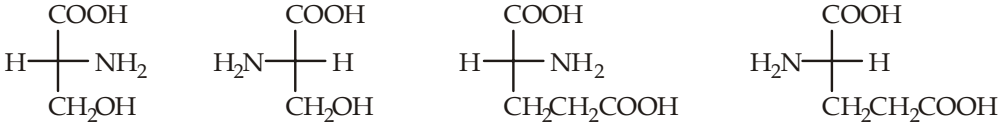
D–(+)-Glyceraldehyde D–(–)-Glyceric acid

Similarly, lactic acid obtained from D- (+)-glyceraldehyde in the following way is also assigned D-configuration.



D–(+)–Glyceraldehyde D-(–)-Glyceric acid D–(–)–3–Bromo–2–hydroxypropanoic acid D–(–)–Lactic acid

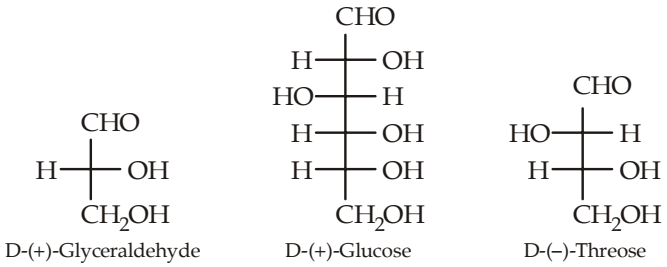
Although D,L-nomenclature also known as Fischer-Rosanoff convention is ambiguous, it is still widely used in the chemistry of amino acids and sugars. The D,L-configuration of all α-amino acids can be represented below.



D-(+)-Serine L-(–)-Serine D-(–)-Glutamic acid L-(+)-Glutamic acid

Most naturally occuring amino acids have the L configuration but it never means that all L-amino acids will be (–)-enantiomer. Actually there is no relation between configuration (D, L) and sign of rotation [(+) and (–)]; as is evident from the example of glutamic acid.

In case of sugars, when the bottom asymmetric carbon atom has H on left and OH on right, it is said to belong to D series, if the configuration at the bottom asymmetric carbon atom is opposite (H on right and OH on left), it is said to belong to L series. Most naturally occurring sugars belong to D series.



D-(+)-Glyceraldehyde D-(+)-Glucose D-(–)-Threose

3.2.2 Absolute configuration (R and S System of Nomenclature)

The D, L system of relating the configuration has a basic defect that sometimes the configuration of the same molecule may not be related to both D and L series. Moreover, it is cumbersome to apply it to molecules having complicated structure and to compounds having more than one chiral carbon atoms. These difficulties are, however, removed by an unambiguous system devised by Cahn, Ingold and Prelog ; which is based *on the actual three-dimensional formula.* The system of assigning configuration involves the following steps.

Step I

The four atoms or groups attached to the chiral carbon atom are assigned a sequence of priorities in accordance with a set of rules, known as **sequence rules** (described below).

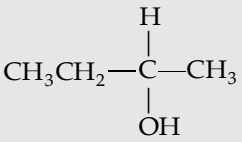
Sequence rule 1.

In case all the four atoms directly attached to the chiral carbon atom are different from one another, sequence of priorities is determined by their atomic numbers. The atom of highest atomic number gets the highest priority while the atom having the lowest atomic number is given the least order of priority. Thus the sequence of priority of the four atoms in bromochloroiodomethane (BrCHCll) is I (Z = 53), Br (Z = 35), Cl (Z = 17) and H (Z = 1).

In case the chiral centre has two isotopic atoms, such as deuterium (D) and hydrogen (H), the isotopes of higher mass number gets higher priority.

Sequence rule 2.

If two or more atoms directly attached to the chiral carbon atom have the same atomic number, the priority may be determined by comparing the next atom in the group. If even this does not solve the problem, the comparison is extended to the next atom and so on.

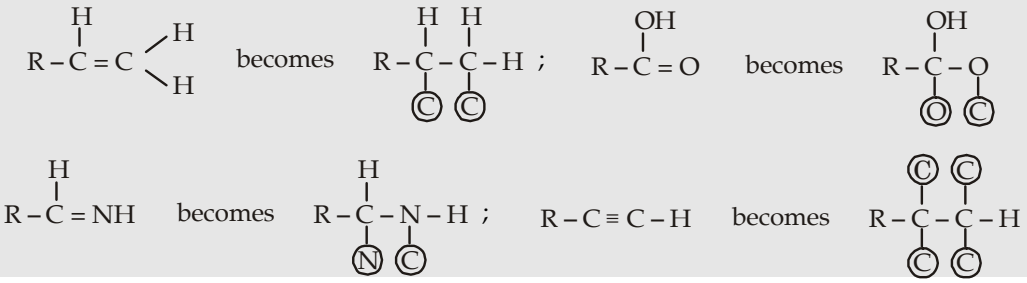


Let us consider the case of *sec*-butyl alcohol in which the four atoms or groups attached to the chiral centre are CH_3CH_2—, H, —CH_3 and — OH.

The relative priorities of the —CH_3 and —C_2H_5 groups can't be decided by the first atom linked to the chiral carbon which is carbon in both cases. The next atoms in —CH_3 group are H, H and H while in CH_3—CH_2— group the next atoms are C, H and H. Now since C has a higher atomic number than H, CH_3CH_2 — (having C, H and H atoms) gets higher priority to CH_3 (having H, H and H atoms).

Sequence rule 3.

Treat double and triple bonds as if each were a singly bonded to two (or three) of those atoms. For this method, imagine that each π bond is broken and the atoms at both ends duplicates. Note that when you break a bond, you always add two imaginary atoms.



By the application of these rules, some common substituents are arranged in the following priority sequence.

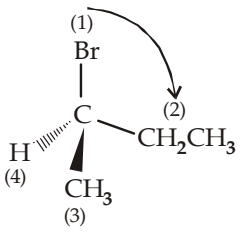
I, Br, Cl, SO_3H, F, OCOR, OR, OH, NO_2, NR_2, NHCOR, NHR, NH_2, CCl_3, COCl, COOR, COOH, $CONH_2$, COR, CHO, CH_2OH, CN, C_6H_5, CR_3, CHR_2, CH_2R, CH_3, D and H.

Step II.

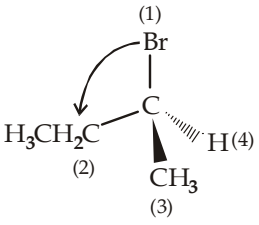
After assigning priorites to the four groups or atoms attached to the chiral carbon, proceed as below.

For structures drawn as a perspective formule :

If the group (or atom) with the lowest priority (4) is bonded to a hatched wedge, draw a curved arrow from the group (or atom) with the highest priority (1) to the group/atom with the second highest priority (2). If the arrow points in a clockwise direction, the compound has the *R* (*R* is for *rectus*, which is Latin for "right") of configuration, in case it points to anticlockwise direction, the compound has the *S* (*S* is for *sinister*, which is Latin for "left") configuration.

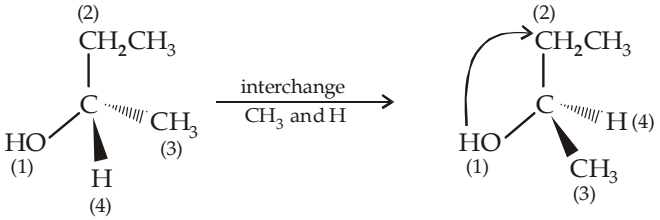


(*R*)–2-Bromobutane



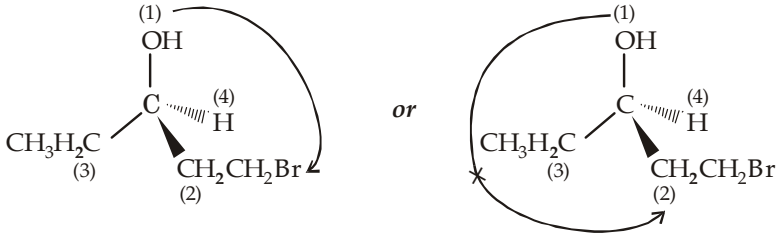
(*S*)–2-Bromobutane

However, if the group/atom with the lowest priority (4) is not bonded by a hatched wedge, interchange a pair of groups so that group (4) is bonded by a hatched wedge and then proceed as mentioned above. The configuration now you get will be the *configuration of the enantiomer of the original molecule*, hence the configuration of the original molecule will be other than that of enantiomer.



(*R*)–2-Propanol which means the configuration before interchanging had the (*S*)-configuration

Sometimes there are two options for drawing the arrow from group (1) to group (2).

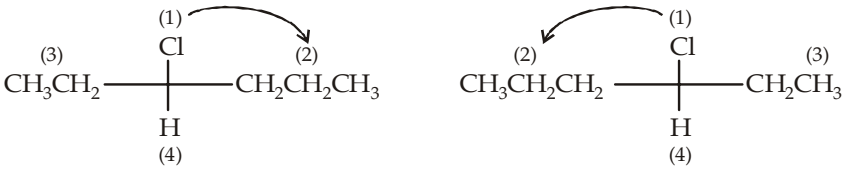


(*R*)–1-Ethyl-3-bromopropanol **(correct)** (*S*)– **(wrong)**

In such case, remember that while drawing an arrow you can pass over (*ignore*) the lowest priority group (4) but never the next lowest priority group (3). Thus in the above example, the correct configuration is *R* but not *S*.

For structures drawn as a Fischer projection :

If we assume that a clockwise arrow specifies an *R* configuration and a counterclockwise arrow specifies an *S* configuration, the configuration of Fischer projection formulas can be remembered by a mnemonic "**V**ery true when the lowest priority group (4) is present on a **V**ertical bond and **H**orribly wrong if the lowest priority group is present on a **H**orizontal bond. Thus remember that when the lowest priority group is present on a horizontal bond clockwise direction of the arrow signifies *S* configuration, not the *R* configuration.



(*R*)-3-Chlorohexane (*S*)-3-Chlorohexane

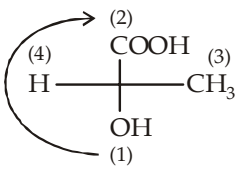
Note that here lowest priority group is on a vertical bond.



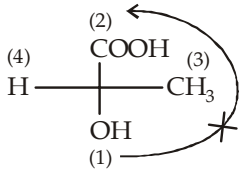
(*S*)-2-Butanol (*R*)-2-Butanol

Note that here lowest priority group is on a horizontal bond.

As in perespective projection, while drawing an arrow you can pass over the group with the lowest priority (4), but never the group (3).



Correct drawing of arrow
(*S*)-Lactic acid



Wrong drawing of arrow

Here since the lowest priority group is on a horizontal bond, so clockwise direction of arrow signifies *S*-configuration, the enantiomer of this will be having *R*-configuration.

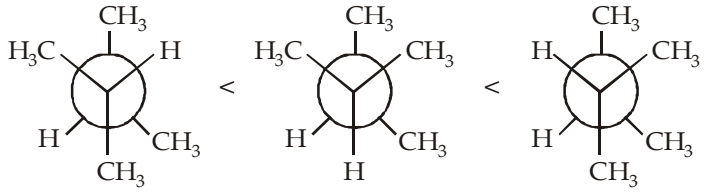
Thus the easiest way to determine whether two molecules (drawn on a two-dimensional piece of paper) with one chirality center and with the same set of substituents are enantiomers or identical molecules is to know their configuration. If one has the *R* configuration and the other has the *S* configuration, we can say that they are enantiomers but which one is dextro-and which one is laevo can be ascertained only by polarimeter. If the two molecules have the same (*R* or *S*) configuration, they are identical.

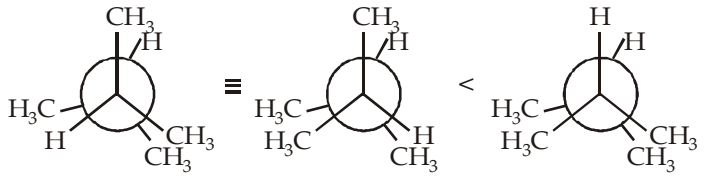
Example 1 :

(a) Draw the staggered conformations of 2,3-dimethylbutane in order of increasing energy.

(b) Draw the eclipsed conformations of 2,3-dimethylbutane in order of increasing energy.

Solution :

(a) 

(b) 

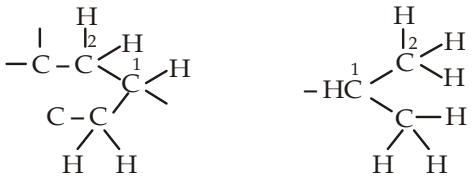
Example 2 :

Arrange the following groups (ligands) in decreasing order of priority.

(a) $(CH_3)_2CH–$ and cyclohexyl (b) Cyclohexyl and phenyl (c) Phenyl and tert-butyl

Solution :

(a) Cyclohexyl > $–HC(CH_3)_2$



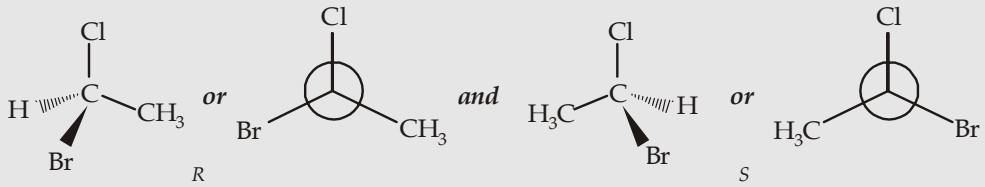
First point of difference lies at C_2; in cyclohexyl C_2 has only two H and one C, while C_2 of $(CH_3)_2CH–$ has three H.

(b) Phenyl – > Cyclohexyl–. Here first point of difference lies at C_1 because the C_1 of phenyl is doubly bonded and hence counted as attached to three C's.

(c) Phenyl – > $(CH_3)_3C–$. Here first point of difference lies at C_2.

Example 3 :

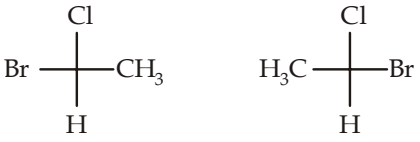
Convert the following structures to the Fischer projection formulas.



R *S*

Solution :

In the Fischer formula, the chiral carbon is assumed to be present at the crossing of a horizontal and a vertical line. The horizontal bonds project out of the plane of the paper, toward the viewer, while the vertical bonds project behind the plane of the paper, away from the viewer. Now put the Cl back so the H and Cl are behind the plane with the Cl on the top and the H below. The Me and Br project in front of the paper on the horizontal bond, the Me to the right and Br to the left of the viewer.



R *S*

Example 4 :

Draw the Fischer projection formula for (S)-2-butanol. What happens when

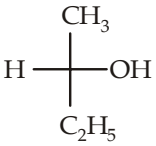
(a) ligands across the horizontal bond are exchanged

(b) ligands across the vertical bond are switched

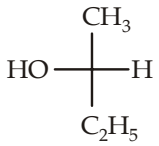
(c) both of the above switches are performed

(d) a ligand attached to a horizontal bond is switched with the ligand attached to a vertical bond.

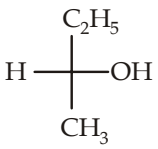
Solution :



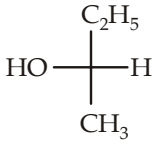
(*S*)-2-Butanol

(a) 

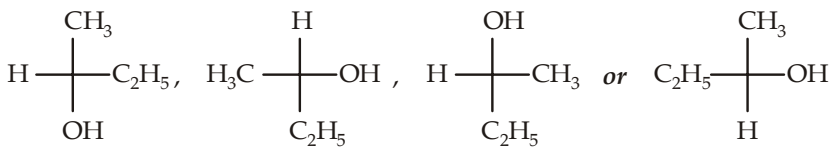
(*R*)-2-Butanol

(b) 

(*R*)-2-Butanol

(c) 

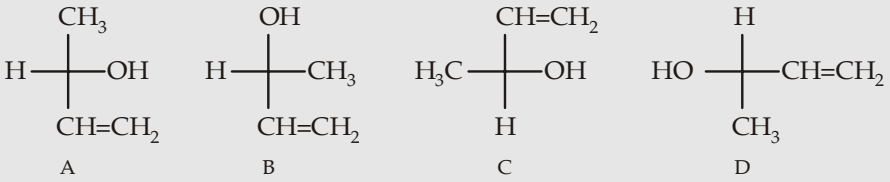
(*S*)-2-Butanol

(d) 

All are (*R*)-2-Butanol

Example 5 :

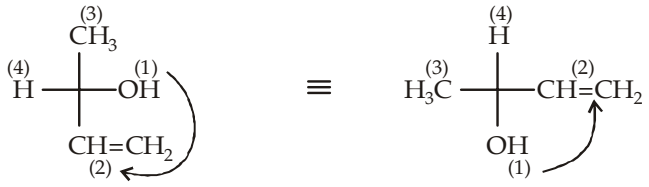
(a) Designate the compound A as R or S and then give its relation with the three other structures B, C and D for the same compound.



(b) How many interchange(s) are required for the conversion of A to other structures, namely B, C and D?

Solution :

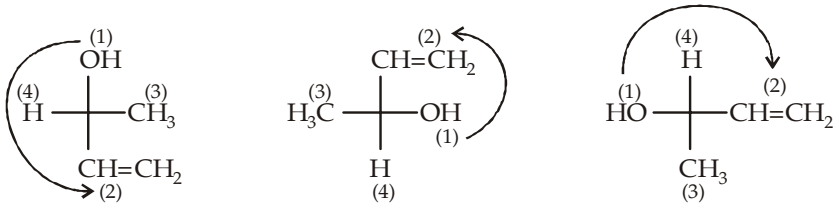
(a) The priority order for the four groups is OH > CH = CH_2 > CH_3 > H. In the given structure, the direction of arrangement of groups i.e. from highest priority (1) to the second highest priority (2) is clockwise.



A — Clockwise direction imparts *R* but H is on horizontal bond, so it should be *S*

A — Counterclockwise direction gives *S*

However, here the lowest priority substituent (H) is on the horizontal side, so correct configuration of A should be *S*. **Alternatively** bring lowest priority substituent (H) on the vertical bond by making **two** switches; now the arrangement of groups (1) to (2) is counterclockwise giving it *S* configuration.

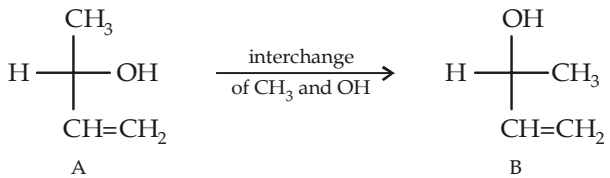


B — *S*, but H on horizontal position, therefore correct configuration is *R*

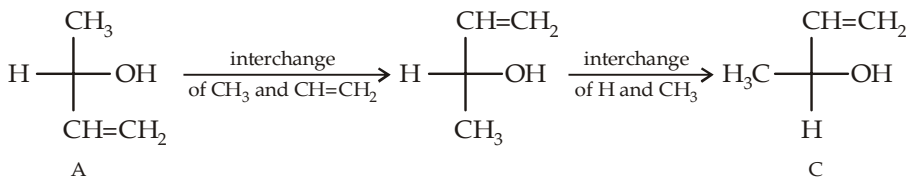
C — *S* configuration, H is in vertical position

D — *R* configuration, H is in vertical position

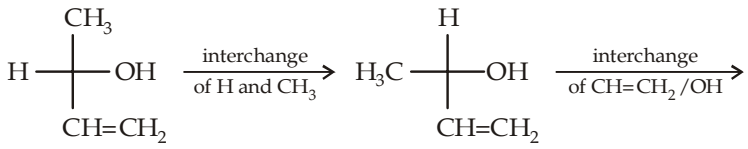
(b)



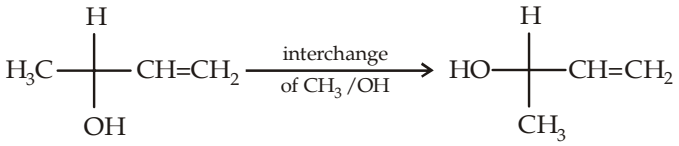
Therefore number of interchange is **one**.



Therefore number of interchanges is **two**.



A

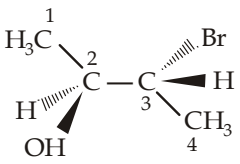


D

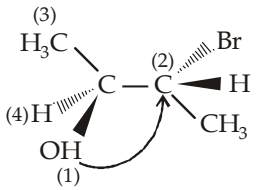
Therefore number of interchanges is **three**.

The R, S system of nomenclature for isomers with more than one chirality center :

If a compound has more than one chirality center, we analyze each center separately and decide whether it is (*R*) or (*S*). As an example, let us name the following stereoisomer of 3-bromo-2-butanol.



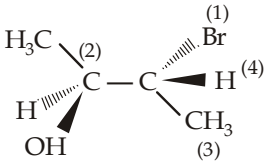
3-Bromo-2-butanol



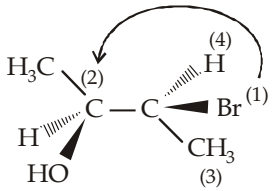
Priority orders of the four substituents at C-2

Configuration at the chiral carbon-2 : The priority order of the four groups at C-2 is shown above. Here the lowest priority substituent (4) is bonded by a hatched wedge, so draw an arrow from the group (1) to group (2) and note that the direction of arrow is counterclockwise indicating the configuration at C-2 as *S*.

Configuration at the chiral carbon-3 : Analyse the priority order of the four substituents at C-3, and observe that the lowest priority substituent (4) is not bonded by a hatched wedge so bring it temporarily on a hatched bond by interchanging H and Br.



Priority orders of the four substituents at C-3



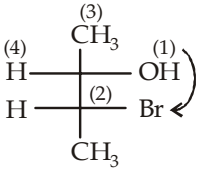
S-configuration on the imaginary structure, so the configuration at C-3 on the original (left) structure should be *R*

Counterclockwise indicating *S*-configuration

Thus the stereoisomer in question is (2*S*, 3*R*)-3-bromo-2-butanol.

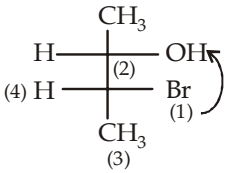
Let us study the configurations at the two chiral carbons of 3-bromo-2-butanol, when drawn according to Fischer projection.

Configuration at C-2



Clockwise direction indicates (*R*) configuration. However, note that group(4) is present on horizontal bond, so the correct configuration at C-2 will be (*S*).

Configuration at C-3



Counterclockwise direction indicates (*S*) configuration which is obtained when substituent (4) is present on horiztonal bond (Horribly wrong) so correct configuration at C-3 is opposite to (*S*), i.e. (*R*)

Example 6 :

Draw perspective formulas for the following compounds -

(a) (S)-2-Butanol and (R)-2-Butanol **(b) (2R, 3S)-3-Chloro-2-pentanol.**

Solution :

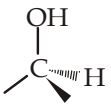
(a) (i) Write down the structural formula for the given compound to know what groups are bonded to the chirality center $CH_3\overset{*}{C}H(OH)CH_2CH_3$

(ii) Assign the priority order to the four substituents; –OH (1),–CH_2CH_3 (2), –CH_3 (3), and –H (4).

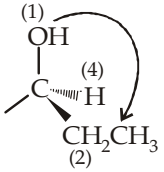
(iii) Draw the tetrahedral carbon atom;



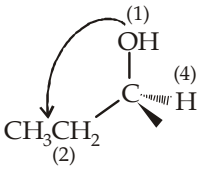
(iv) Put the lowest priority substituent on the hatched wedge; and the highest priority group (1) on any of the remaining three bonds.



(v) Now take into consideration the configuration, you want, if you want *R* enantiomer, draw an arrow clockwise from the highest priority group (1) to the next available bond and put the group with the next priority (2) on that bond. In case you want *S* configuration, draw an arrow anticlockwise from the highest priority group (1) to the next available bond and put the group (2) on that bond.

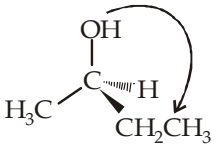


Clockwise arrow for *R*

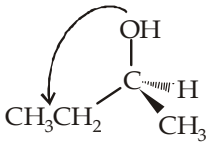


Counterclockwise arrow for *S*

(vi) Put the remaining substituent on the bond available.

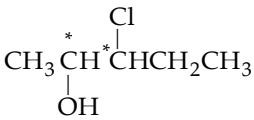


(*S*)-2-Butanol



(*R*)-2-Butanol

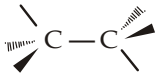
(b) (i)



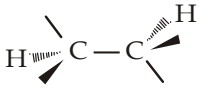
3-Chloro-2-pentanol

(ii) The priority order of the four groups on the two carbon atoms are –OH(1), –$CHClCH_2CH_3$ (2), –CH_3 (3) and –H (4) on one carbon; and –Cl (1), –$CHOHCH_3$ (2), –CH_2CH_3 (3) and –H (4).

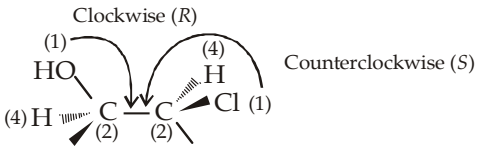
(iii) The perspective respresentation of the two chiral carbon atoms.



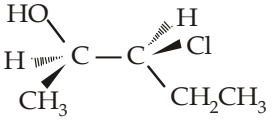
(iv) Putting the lowest priority group (4) on the hatched wedge of each chirality center.



(v) For each chirality center, put the highest priority group (1) on that bond from which when arrow is drawn to the nexty priority group (2) gives clockwise direction (for *R* configuration) or counterclockwise direction (for *S* configuration).

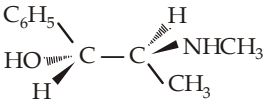


(vi) Place the remaining group on each chiral carbon.

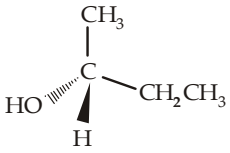


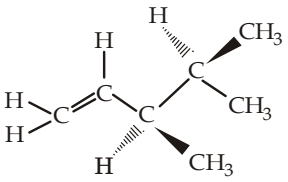
TEST YOUR UNDERSTANDING - 3.2

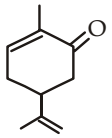
1. Ephedrine is the principal constituent of the herb Ephedra and used for treating asthma. It has two chiral carbon atoms and thus has four stereoisomers. However, the isomer having following configuration is pharmacologically active. Assign the configuration at each of the carbon atoms.

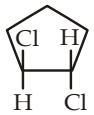


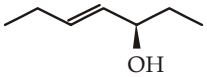
2. Star (*) the asymmetric carbon atom(s) in each of the following structures, and determine whether it has the (*R*) or the (*S*) configuration.

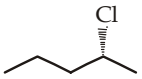
(a) 

(b) 

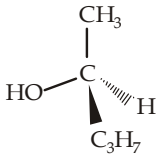
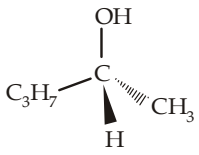
(c) 

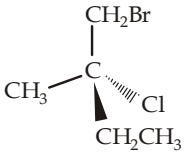
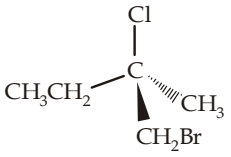
(d) 

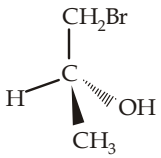
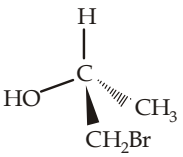
(e) 

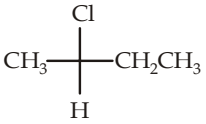
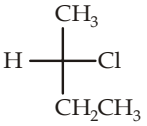
(f) 

3. Do the following structures represent identical molecules or a pair of enantiomers?

(a)  and 

(b)  and 

(c)  and 

(d)  and 

4. Account for the fact that chlorination of *n*-butane to 2-chlorobutane (*sec*-butyl chloride) gives racemic mixture, while chlorination of any one enantiomer 2-chlorobutane (*sec*-butyl chloride) gives optically active product.

5. Detrmine the percentage composition of a mixture of enantiomers of 2-bromo-octane having specific rotation of + 18° ; given the specific rotation of the (R)-(–)-2-bromo-octane is – 36°.

6. (*a*) Give priority order of the 1°, 2°, 3° alkyl and CH_3 groups according to sequence rule.

(*b*) Draw cross formula (Fischer projection formula) for the following compounds and assign configuration R/S to the fromula drawn.

(*i*) α-Deuterioethyl brimide (*ii*) 3-Chloro-1-pentene (*iii*) Malic acid

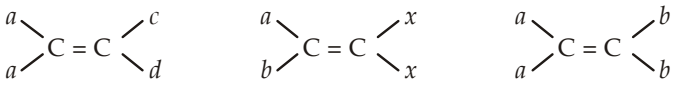
(*iv*) Alanine (*v*) Methylethyl-*n*-propylisopropylmethane (*vi*) 1- Amino-1-phenylethane.

7. Give the number of isomers formed during free radical mono-chlorination of isopentane. Predict which isomer(s) will be obtained in racemic form ? Draw their R/S formulae.

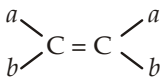
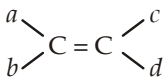
Geometrical isomerism is due to hindered rotation either due to two doubly bonded atoms (e.g. C = C, C = N and N = N) or due to cyclic structure.

3.2.3 Geometrical isomerism in alkenes

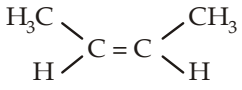
Due to absence of rotation about a carbon-carbon double bond, an alkene in which each of the two doubly bonded carbon atoms is differently substituted can exist in two different configurations. Thus following types of compounds cannot exist as geometrical isomers.

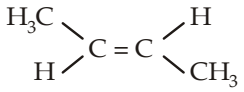


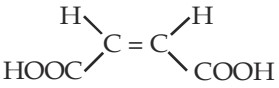
On the other hand, following types of compounds can exist as geometrical isomers.

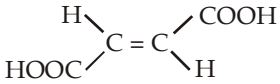



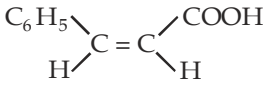
When the similar substituents are on the same side, the isomer is called *cis*-, while when the similar substituents are on the opposite sides, the isomer is called *trans*. Hence geometrical isomerism is also known as *cis-trans* isomerism. Few examples are given below.

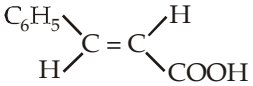

cis-2-Butene

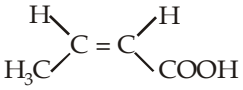

trans-2-Butene

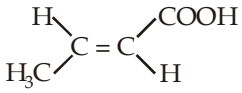

Maleic acid (*cis*)


Fumaric acid (*trans*)

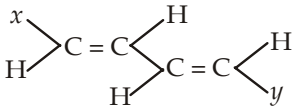

Cinnamic acid (*cis*)

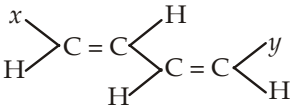

(*trans*)

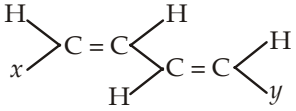

Isocrotonic acid (*cis*)

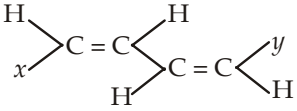

crotonic acid

When a compound contains *n* number of dissimilarly substituted double bonds, the number of geometrical isomers is 2^n, *e.g.*

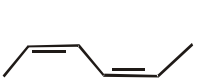

tanns-trans

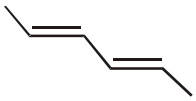

tanns-cis

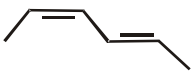

cis-trans

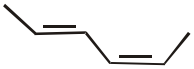

cis-cis

However, the number of geometrical isomers is less than 2^n when the two double bonds are substituted by similar groups, viz. 2,4-hexadiene, $CH_3CH = CHCH = CHCH_3$, having two double bounds have only three geometrical isomers instead of four.


cis-cis, I


trans-trans, II


cis-trans, III


trans-cis, IV

Structures III and IV are identical.

TEST YOUR UNDERSTANDING - 3.3

1. Draw the *cis*- and *trans*- isomers for the following compounds :

(a) 3,4-Dimethyl-3-heptene (b) 2-Methylbut-2-en-1,4-dioic acid

2. Some of the following examples can show geometric isomerism, and some cannot. Draw the line bond structures for all and name as *cis* and *trans* isomers for those that show geometric isomerism.

(a) 3-Hexene (b) 2,4-Dimethyl-2-pentene (c) 1,3-Butadiene

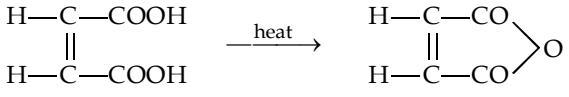
(d) 1-Chloro-2-butene (e) 4,5-Dibromo-1-pentene (f) 1,4-Dichloro-2-pentene

3. Draw the structures for the *cis-trans* isomers of the following compounds

(a) 1-Ethyl-3-methylcyclobutane (b) 1-Bromo-3-chlorocyclohexane

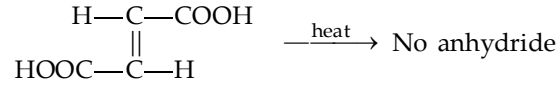
Distinction between *cis*- and *trans*-isomers.

(i) **By cyclization method.** Generally, the *cis*-isomers are comparatively less stable because of mutual repulsion between the groups. Hence, the *cis*-isomer (*e.g.* maleic acid) cyclises on heating to form the corresponding anhydride while the *trans*-isomer does not form its anhydride at all.



Maleic acid (*cis*) Maleic anhydride

Note that the two reacting groups (—COOH) are near to each other.



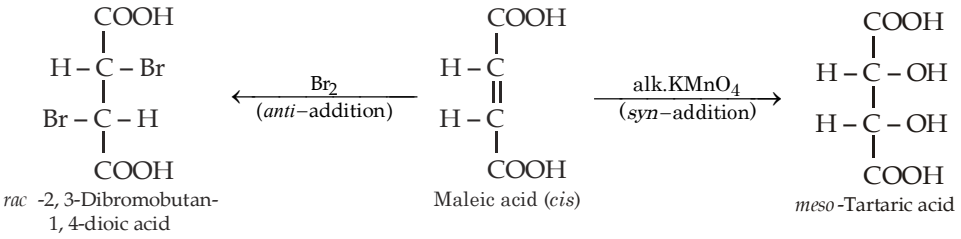
Fumaric acid (*trans*)

Note that the two reacting groups (—COOH) are quite apart form each other, hence cyclisation is not possible.

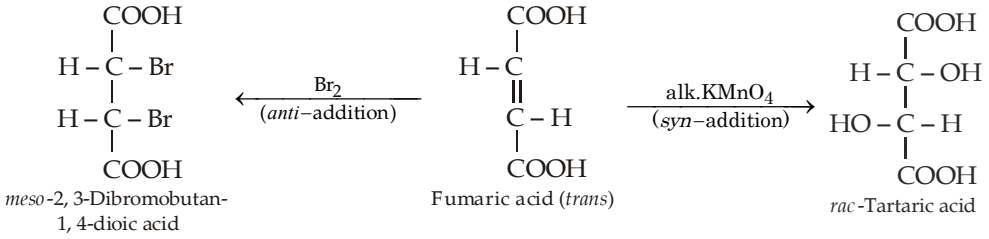
(*ii*) **By hydroxylation** (*Oxidation by mean of* $KMnO_4$, OsO_4 *or* H_2O_2 *in presence of* OsO_4). Oxidation (hydroxylation) of alkenes by means of these reagents proceeds in the *syn*-manner. Thus the two geometrical isomers of an alkene lead to different products by these reagents.

However, addition of Br_2 and halogen acid (HX) on alkenes gives *anti*-addition product. Thus here also, the two geometrical isomers of an alkene lead to different products.

The term *syn* addition means the two atoms or groups are added on available sites, i.e. on the same side on *cis* and on different sides on *trans* isomer. On the other hand, the term *anti* addition means the two atoms or groups are added on different sides on *cis* isomer, and on same side on *trans* isomer.



rac -2, 3-Dibromobutan-1, 4-dioic acid Maleic acid (*cis*) *meso* -Tartaric acid



meso -2, 3-Dibromobutan-1, 4-dioic acid Fumaric acid (*trans*) *rac* -Tartaric acid

(*iii*) **By studying their dipole moments.** The *cis*-isomer of a symmetrical alkene (alkenes in which both the carbon atoms have similar groups) has a definite dipole moment, while the *trans*-isomer has zero dipole moment. For example, 1, 2-dichloroethylene and butene-2.



cis-1, 2-Dichloroethylene (μ = 1.9 D) *trans*-1, 2-Dichloroethylene (μ = 0.0 D) *cis*-Butene-2 *trans*-Butene-2

In *trans*-isomer of the symmetrical alkenes, the effect produced in one half of the molecule is cancelled by that in the other half of the molecule.

In case of unsymmetrical alkenes, the *trans*-isomer has lower dipole moment than the corresponding *cis*-isomer. For example,



cis-2, 3-Dichloropentene-2 (high dipole moment) *trans*-2, 3-dichloropentene-2 (less dipole moment)

Similar is the case with pentene-2.



cis-pentene-2 (more polar) *trans*-pentene-2 (more ploar)

Note that the $—CH_2CH_3$ has more + I effect than the $—CH_3$ group, hence dipole moment of the two polar bonds do not cancel each other in the *trans* isomer. Thus *trans*-isomer is also polar, but less than he corresponding *cis*-isomer.

(*iv*) **By studying other physical properties.**

(*a*) The *cis*-isomer of a compound has higher boiling point and higher solubility in water due to higher polarity, higher density, higher heat of hydrogenation, higher heat of combustion and higher refractive index than the corresponding *trans*-isomer **(Auswers-skita rule).**



	cis-2-Butene	*trans*-2-Butene	*cis*-1, 2-Dichloroethene	*trans*-1, 2-Dichloroethene
b.p.	4°C	1°C	60°C	48°C
m.p.	– 139°C	– 106°C	– 80°C	– 50°C

(*b*) The *trans*-isomer has higher melting point than the *cis*-isomer due to symmetrical nature and more close packing of the *trans*-isomer.

3.2.4 Geometrical Isomerism in Oximes (compounds containing C = N group)

Oximes are the condensation products of aldehydes/ketones with hydroxylamine.

Aromatic aldoximes and aromatic ketoximes also show geometrical isomerism. In aldoximes, when H and OH groups are on the same side, the isomer is known as *syn* (analogous to *cis*) and when these groups are on the opposite sides, the isomer is known as *anti* (analogous to *trans*).



syn-Benzaldoxime *anti*-Benzaldoxime

In ketoximes the prefixes *syn* and *anti* indicate which group of ketoxime is *syn* (on the same side) or *anti* (on the opposite side) to the OH group.

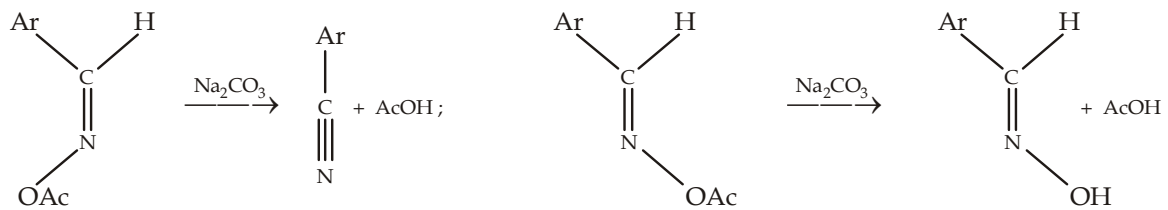


syn-Phenyl-*p* tolylketoxime (*anti*-*p*-Tolylphenylketoxime) *syn*-*p*-Tolylphenylketoxime (*anti*-phenyl-*p*-tolylketoxime)

However, remember that all aromatic ketoximes do not show geometrical isomerism *e.g.*, $(C_6H_5)_2C = NOH$, benzophenone oxime having two similar aryl groups does not show geometrical isomerism.

Determination of configuration of aldoximes

The two forms (*syn* and *anti*) of aromatic aldoximes resemble each other in many ways, but differ in the behaviour of their acetyl derivatives towards sodium carbonate solution. The acetyl derivative of the *anti*-isomer gives cyanide, whereas that of *syn*-isomer is reconverted into aldoxime back on treatment with aqueous sodium carbonate.



Acetate of *anti*-aldoxime Cyanide Acetate of *syn*-aldoxime Aldoxime

Behaviour of aldoxime acetate towards aqeous Na_2CO_3

Determination of configuration of ketoximes.

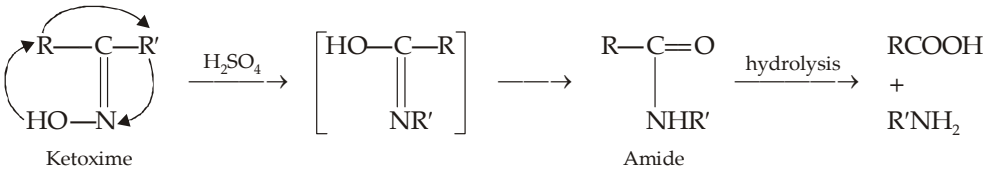
Like aliphatic and aromatic aldoximes, aliphatic and aromatic ketoximes also occur in one and two forms, respectively. But it must be noted that unlike aromatic aldoximes, the aromatic ketoximes can exist in two isomeric forms only when one aryl and another alkyl or two different aryl groups are present. The aromatic ketoxime having two same aryl groups do not show the phenomenon of geometrical isomerism, *e.g.* benzophenone oxime, $Ph_2C = NOH$, does not show the phenomenon of geometrical isomerism. The configuration of geometrical isomerism is determined with the help of Beckmann rearrangement.

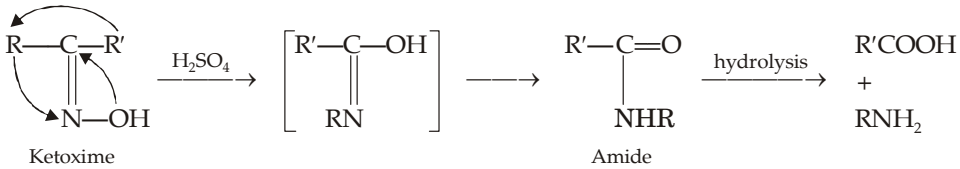
Beckmann rearrangement.

The Beckmann rearrangement consists in the conversion of ketoximes to N-substituted amides by heating with some acidic reagent, *viz.* conc. H_2SO_4, BF_3, polyphosphoric acid (PPA), P_2O_5, PCl_5, SO_3, $SOCl_2$, $C_6H_6SO_2Cl$, etc.



The two different amides, thus formed, can be identified by their hydrolysis to different acids and amines. In this rearrangement the shift or migration of groups is always *trans*-(*anti*) to the leaving group [*e.g.* —OH].





Geometrical isomerism due to N = N bond.

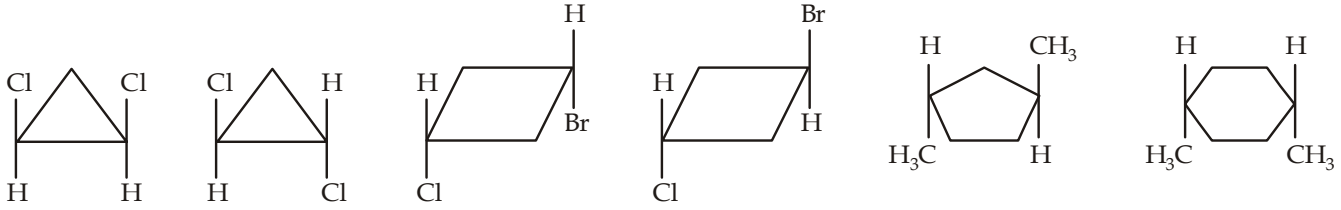


syn-Azobenzene *anti*-Azobenzene

3.2.5 Geometrical isomerism in cyclic compounds

Like double bonds, cyclic system prevents free rotation about the single bond. In the cyclic system, the group attached to the top of the vertical line is said to be above the plane of the ring and the group attached to the bottom of the vertical line is said to be below the plane of the ring. Thus properly substituted cycloalkanes show geometrical isomerism; the *cis* isomer has substituents on the same side **of the ring**, whereas the *trans* isomer has substituents on opposite sides of the ring.

Disubstituted cyclobutanes and cyclopentanes show two position isomers (1, 2- and 1, 3-) each of which can exhibit geometrical isomerism. Disubstituted cyclohexanes show three position isomers (1, 2-, 1, 3- and 1, 4-) each of which can exihibit geometrical isomerism.



cis- *trans*- 1,2-Dichlorocyclopropane

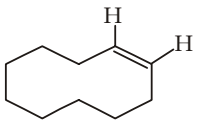
cis-1-Bromo-3-chlorocyclobutane

trans-1-Bromo-3-chlorocyclobutane

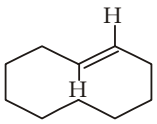
trans-1,3-Dimethyl-cyclopentane

cis-1,4-Dimethyl-cyclohexane

In cycloalkenes, *cis-trans* isomerism is possible only in large rings (at least 8 carbon atoms) because *trans* cycloalkenes with less than 8 carbon atoms are unstable at room temperature. *trans*-Cyclo-octene is stable at room temperature, although the *cis* isomer is still more stable. For cyclodecene and larger cycloalkenes, the *trans* isomer is nearly as stable as the *cis* isomer.



cis-Cyclodecene



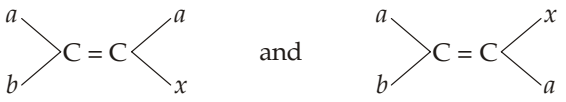
trans -Cyclodecene

3.2.6 The *E* and *Z* Nomenclature of Geometrical Isomers

As discussed earlier, the geometrical isomerism is possible in structures of the following three types.

Type 1. 

cis *trans*

Type 2. 

cis *trans*

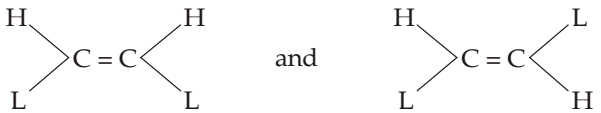
Type 3. 

cis *trans*

In the first two types, the geometrical isomers are labelled as *cis* and *trans* on the basis of the fact that the common groups are on the same or opposite sides of the double bond. But in type 3 where all the four substituents are different, *cis-trans* type of isomerism cannot be applied. Moreover, the *cis-trans* system (also *syn-anti* system in oximes) is often ambiguous because the configurational descriptions have not been defined according to any general and clear set of rules. So an unambiguous system of configurational assignments for all types of structures showing geometrical isomerism was developed in 1968. This system is known as E-Z system of nomenclature and is based upon the sequence rules of Cahn, Ingold and Prelog originally developed for naming optical isomers on the R-S system. The following procedure is followed in specifying the configuration of such compounds.

(*i*) Assign the priority order to the two groups attached to each of the doubly bonded carbon in accordance with the sequence rules, discussed earlier.

(*ii*) Select the atom/group with higher priority on each doubly bonded carbon. If the atoms/groups of higher priority (denoted by H) on each carbon are on the same side of the double bond, the isomer is assigned the configuration Z (from the German word, *zusammen* meaning together). On the other hand, if the atoms/groups of higher priority on each carbon are on the opposite sides of the double bond, the isomer is assigned the configuration E (from the German word *entgegen* meaning against).



Z-isomer *E*-isomer

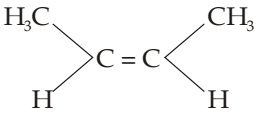
Where H and L represent the atoms (groups) of higher and lower priority respectively.

Now let us consider example of an alkene in which one of the doubly bonded carbon atom has Br and I and the other has F and Cl. Now since I has a higher atomic number than Br, it is assigned higher priority ; similarly Cl is of higher priority than F on the second olefinic carbon atom. Thus the E and Z configurations of the two isomers of 1-bromo-2-chloro-2-fluoro-1-iodoethene are assigned.

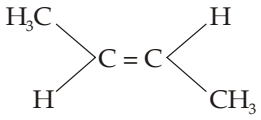


Z *E*

Thus the *cis*- and *trans*-isomers of 2-butene become Z- and E-2-butenes respectively.

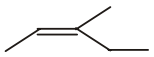


Z-2-Butene

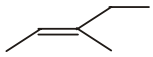


E-2-Butene

Remember that there is no relation between *cis-trans* isomers and *E, Z* isomers.



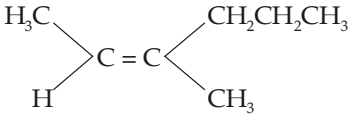
(*Z*)-3-Methylpent-2-ene



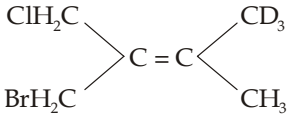
(*E*)-3-Methylpent-2-ene

Note that here, the similar groups (CH_3) is on the same side in the (*E*)-isomer, so it should be *cis*- on the basis of *cis-trans* isomerism. However, in 2-butene the *cis*-2-butene is *Z*-2-butene.

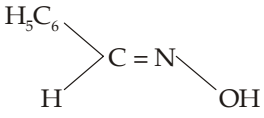
Similarly, following structures are assigned to the configuration mentioned below them.



Z-isomer



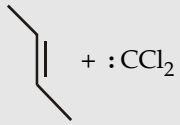
E-isomer

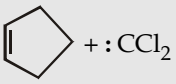


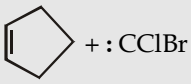
E-isomer

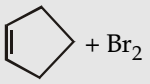
Example 7 :

Write down the structure of the product, mentioning stereochemistry in each case.

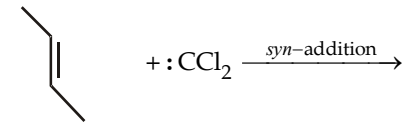
(i) 

(ii) 

(iii) 

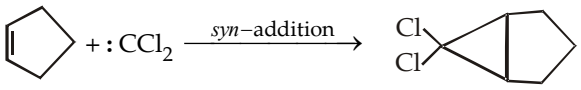
(iv) 

Solution :

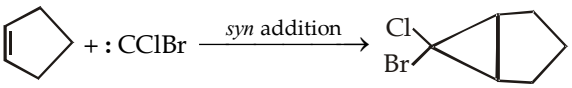
(i) 

trans-Butadiene

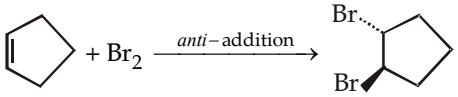
trans-1, 1-dichloro-2, 3-dimethylcyclopropane

(ii) 

meso

(iii) 

race-

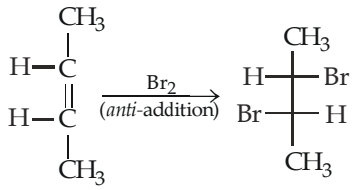
(iv) 

rac

Example 8 :

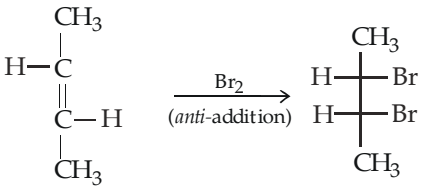
Three isomeric hydrocarbons of the formula C_4H_8 decolorise bromine water. Write down the structure in each case, mentioning stereochemistry. Also give structure of the other isomer (if possible) for the compound.

Solution :



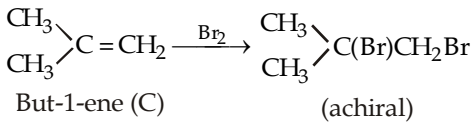
cis-But-2-ene
(A)

rac-



trans-But-2-ene
(B)

meso-



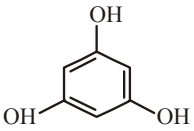
But-1-ene (C) (achiral)

Two other isomers of C_4H_8 are  and 

cyclobutane methylcyclo-propane

TEST YOUR UNDERSTANDING - 3.4

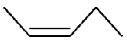
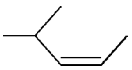
1. (*a*) How many isomeric nitroalkanes are possible for the molecular formula $C_4H_9NO_2$? Also draw the structure of tautomer of each isomer.

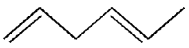
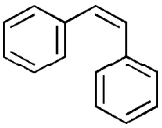
(*b*) Draw structure of the tautomer of 

.

2. Draw structures of the possible geometrical isomers of 2, 4-hexadiene.

3. Assign E or Z configuration to the following structures.

(*i*)  (*ii*)  (*iii*) 

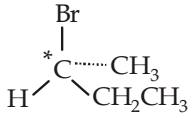
(*iv*)  (*v*)  (*vi*) 

3.3 Enantiomers and Chiral Molecules

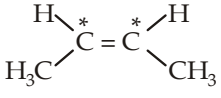
The word chiral comes from the Greek word Cheir, meaning "hand"; thus chiral objects and chiral molecules are said to possess "handedness".

Handedness means analogy of the two isomers of a molecule, of course chiral, with the left and right hand. Just as the left hand is a non-superimposable mirror image of the right hand, the structure of an isomer of a chiral molecule is the non-superimposable mirror image of the other isomer. Thus **a chiral molecule** *is defined as one that is not identical with a mirror image; a non-identical (non-superimposable) mirror image is called an* ***enantiomer*** of the original molecule; and a pair of non-identical mirror images is called **a pair of enantiomers**. Objects (and molecules) that are superimposable on their images are **achiral**. Note that gents socks are achiral while ladies socks with fingers and thumb and gloves are chiral.

How to know the possibility of enantiomers with one chirality centre? A pair of enantiomers is always possible for molecules that contain one tetrahedral atom, with four different groups attached to it. A tetrahedral atom with four different groups is known as a **chirality centre** (the latest IUPAC name approved for the earlier names like *stereogenic centre, stereocentre, a chiral centre, and an asymmetric atom).* Actually, the term chirality centre belongs to a broader term called stereocentre. **A stereocentre (or stereogenic atom) is any atom at which the interchange of any two groups gives a stereoisomer.** Asymmetric carbon and the doubly-bonded carbon atoms in *cis-trans* isomers are the most common types of stereocentre.



* Carbon is a stereocentre as well as chirality centre



* Carbons are stereocentres but not chirality centre

* It must be noted that aliphatic oximes exist only in one form and that is the *anti* form.

In a cyclic compound, a carbon atom can be stereogenic if it has two different substituents, and the path traced around the ring from that carbon in clockwise direction is different from that traced in anticlockwise direction.

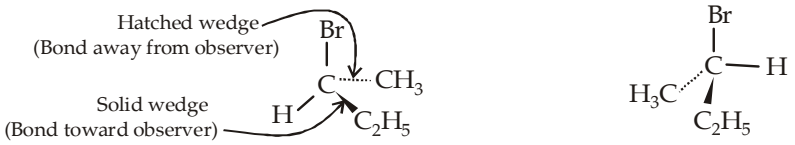
However, remember that this is the one way but not the only way for assessing the possibility of enantiomerism because as we will see that some of the molecules containing more than one tetrahedral chiral carbon show enantiomerism while some do not exhibit enantiomerism, even though they contain chiral center.

Interchanging of any two groups present on a chirality centre converts one enantiomer into other. However, an interchange of groups requires the breaking and reforming of σ bonds at the centre of chirality, which in turn require a large input of energy, hence enantiomers do not interconvert spontaneously (difference from **conformational isomers** which are interconverted spontaneously by rotations about σ bonds).

3.3.1 Drawing of enantiomers

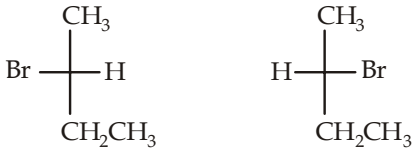
(*i*) Perspective formulas

Show two of the bonds to the chirality center in the plane of the paper, one bond as a solid wedge coming out of the paper, and the fourth bond as a hatched wedge projecting back from the paper. The four groups may be attached to the chirality center in any order. If any two of the groups (or atoms) bonded to the chirality center are interchanged, the molecule obtained will be the enantiomer of the parent molecule



Perspective (three-dimensional) formulas of the enantiomers of 2-bromobutane
(Here H and CH_3 are interchanged)

(*ii*) Fischer projection formulas : Use the point of intersection of two perpendicular lines to represent the chirality centre; horizontal lines represent the bonds that project out of the plane of the paper toward the viewer, and vertical lines represent the bonds that project back from the plane of the paper away from the viewer. The carbon chain is drawn vertically with C – 1 at the top of the chain :



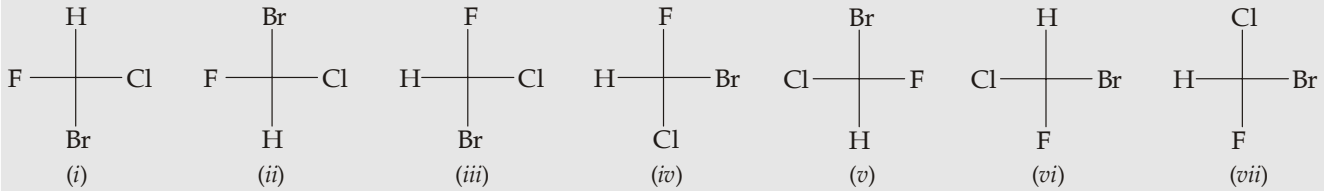
Fischer projections for the enantiomers of 2-bromobutane

Here also interchange of the two groups (or atoms) of an enantiomer gives the second enantiomer, however many organic chemists prefer to interchange the two horizontal groups because the enantiomers then look like mirror images on paper. Note that **interchanging one pair of groups gives enantiomer,** while interchanging two pairs of groups (or atoms) gives an identical (original) molecule.

In short, **if two structural formulas of a compound differ by an odd number of interchanges, they are enantiomers; if by an even number, they are identical.**

Example 9 :

Seven Fischer projection formulas are drawn below for CHBrFCl. Give the relation of structures (ii) to (vii) with respect to (i).



Solution :

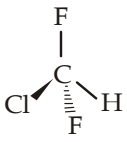
It two structural formulas differ by odd number of interchanges, they are enantiomers; if by an even number, they are identical.

Structure	*Sequence of group interchange*	*Number of interchanges*	*Relationship to (i)*
(*ii*)	H, Br	1 (odd)	enantiomer
(*iii*)	H, F	1 (odd)	enantiomer
(*iv*)	H, F ; Br, Cl	2 (even)	identical
(*v*)	H, Br ; Cl, F	2 (even)	identical
(*vi*)	F, Br ; Br, Cl	2 (even)	identical
(*vii*)	F, Br; Br, Cl ; H, Cl	3 (odd)	enantiomer

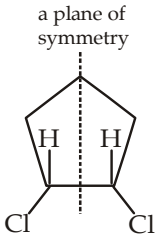
3.3.2 Tests for chirality

The ultimate test for molecular chirality of a molecule is non-superimposability over its mirror image. If two structures are mirror image of each other, and these are not superimposable over each other, these are said to be chiral. However, certain structural features related to molecular symmetry can **sometimes** help us in knowing whether a molecule is chiral or achiral. For example, a molecule having either a plane of symmetry or a center of symmetry is superimposable on its mirror image, and thus it will be **achiral**.

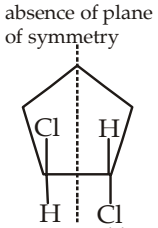
A plane of symmetry, also called internal mirror plane of symmetry is defined as an imaginary plane that bisects a molecule in such a way that the two halves of the molecule are mirror images of each other. The plane may pass through atoms, between atoms, or both. For example, difluorochloromethane has a plane of symmetry (defined by the atoms H–C–Cl) and thus the molecule is **achiral**.



Difluorochloromethane
(it has a plane of symmetry along the atoms Cl–C–H)



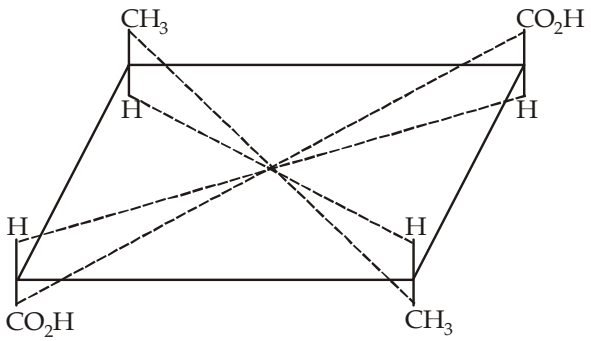
cis-1,2-Dichloro-cyclopentane



trans-1,2-Dichloro-cyclopentane

Similarly, *cis*-1,2-dichloropentane has a plane of symmetry while the corresponding *trans*-isomer does not have any plane of symmetry so the former is achiral whereas the latter is chiral.

A center of symmetry is an imaginary point in the center of a molecule from which if lines are drawn, on any group, on both the sides to an equal distance, it divides the molecule into two equal halves which are the mirror images of each other. For example, 2,4-dimethylcyclobutane-1,3-dicarboxylic acid has a center of symmetry which is the center of the ring.



Thus from the above discussion, we can generalize the principle that *any molecule with a plane of symmetry or a center of symmetry is achiral, even though it may contain asymmetric carbon atoms.* However, the converse is not always true i.e. the absence of these symmetry elements does not necessarily mean that the molecule is chiral. Thus remember that a molecule lacking a plane of symmetry or a center of symmetry is likely (**not necessarily**) to be chiral.

TEST YOUR UNDERSTANDING - 3.5

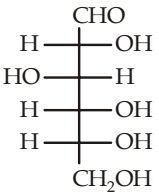
1. Locate any plane of symmetry or center of symmetry in each of the following compounds. Which of the following compounds are chiral/achiral?

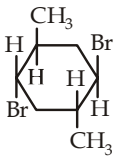
(a) (*E*)-1,2-Dichloroethene (b) (*Z*)-1,2-Dichloroethene

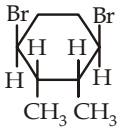
(c) *cis*-1,2-Dichlorocyclopropane (d) *trans*-1,2-Dichlorocyclopropane

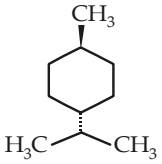
2. Which of the following compounds are chiral? Star all asymmetric carbon atoms in the molecule. Point out plane of symmetry or center of symmetry in the structure of the molecule, also predict whether the molecule is optically active or inactive.

(a) *meso*-2,3-Dibromo-2,3-dichlorobutane (b) (2*R*, 3*S*) $\overset{4}{C}H_2OH\overset{3}{C}HBr\overset{2}{C}HOH\overset{1}{C}H_2OH$

(c) 

(d) 

(e) 

(f) 

3.3.3 Optical activity

Since the molecules of enantiomers are not superimposable one over the other, these are considered to be different compounds. However, the two enantiomers have most of their physical properties (e.g. melting points, boiling points, solubilities, etc.) similar because these properties depend on the magnitude of the intermolecular forces operating between the molecules which is identical in the enantiomers. Enantiomers show different rates of reaction when they interact with other chiral substances. They also differ in solubilities in solvents that consist of a single enantiomer or an excess of a single enantiomer. The easily observable way in which enantiomers differ is their behaviour toward plane-polarized light.

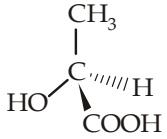
What is plane-polarized light? Ordinary light consists of electromagnetic waves vibrating randomly in all directions. Plane-polarized light is composed of waves that vibrate in only one plane. Plane-polarized light is produced by passing normal light through a polarizer such as a polarized lens or a Nicol prism. When plane-polarized light passes through a solution of an achiral compound, the light emerges from the solution with its plane of polarization unchanged because there is no asymmetry in the molecules. Thus in short *an achiral compound does not rotate the plane of polarization and hence called* ***optically inactive***.

However, when plane-polarized light passes through a solution of a chiral compound, the light emerges with its plane of polarization changed (rotated) because of *asymmetric* nature of the molecules. Thus, a chiral compound rotates the plane of polarization either in clockwise or in counterclockwise direction. If one enantiomer rotates the plane of polarization in clockwise direction, its mirror image will rotate the plane of polarization exactly to the same extent but in counterclockwise direction. *A compound that rotates the plane of polarized light is said to be* ***optically active***. Before the relationship between chirality and optical activity was known, enantiomers were called **optical isomers** *because they rotate the plane of polarized light through some angle.* However, now this ambiguous term (*optical isomers*) has been replaced by the well defined term ***enantiomers***.

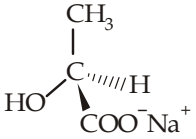
3.3.4 Stereochemistry of molecules with one chiral centre

If an optically active compound rotates the plane of polarization in a clockwise direction, it is called ***dextrorotatory***, indicated by (+). If an optically active compound rotates the plane of polarization in a counterclockwise direction, it is called **levorotatory**, indicated by (–). *Dextro* and *levo* are latin prefixes for "to the right" and "to the left", respectively; these are sometimes abbreviated by a lowercase *d* or *l* respectively.

Do not confuse (+) and (–) with *R* and *S*. The (+) and (–) symbols indicate the direction in which an optically active compound rotates the plane-polarized light, whereas *R* and *S* indicate the arrangement of the groups about a chirality center. There is no relation between these two conventions. Some compounds with the *S* configuration are (+) and some are(–). For example, (*S*)-lactic acid is dextrorotatory whereas (*S*)-sodium lactate is levorotatory.



(*S*)-(+)-Lactic acid



(*S*)-(–)-Sodium lactate

By looking at the structure of a compound we can tell whether it has the *R* configuration or the *S* configuration, but whether a compound is detxtrorotatory, (+) or levorotatory, (–) can be known only with the help of a polarimeter.

The angular rotation of polarized light by a chiral compound is a characteristic property of that compound. The rotation (α) observed in a polarimeter depends on the concentration of the sample solution, the length of the cell, optical activity of the compound, temperature and the wavelength of the light source. To use the rotation of polarized light as a characteristic property of a compound, the rotation is measured under the specific condition and called **specific rotation**, [α].

$$[\alpha]_D^{25} = \frac{\alpha \text{ (observed)}}{c.\ell}$$

where, α (observed) = Rotation observed c = Concentration in g/mL

ℓ = Length of sample cell (path length) in decimeters D = Represents the D line of the sodium spectrum

25 = Represents that the measurement is made at 25°C.

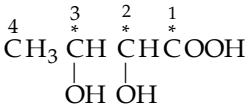
TEST YOUR UNDERSTANDING - 3.6

1. If (*S*)-lactic acid is dextrorotatory and the corresponding sodium salt is levorotatory, then can you predit the nature of (*R*)-lactic acid and its sodium salt?

2.. A chiral sample gives a rotation that is close to 180°. How will you tell whether this rotation is +180° or –180°?

3.3.5 Stereochemistry of molecules with more than one chirality centre

When a molecule contains two stereocentres, as in 2,3-dihydroxybutanoic acid, it can exist in four stereoisomeric forms. These four isomers are simply all the permutations of (*R*) and (*S*) configurations at the two chiral carbon atoms, C2 and C3.



2,3-Dihydroxybutanoic acid

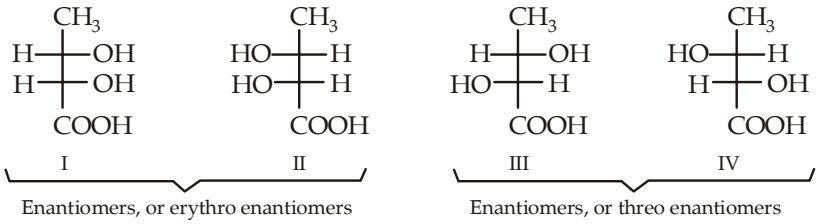
(2R, 3R) (2S, 3S) (2R, 3S) (2S, 3R)

I II III IV

Enantiomers Enantiomers

In order to convert a molecule with two stereogenic centres to its enantiomer, the configurations at both centres must be changed. Reversing the configuration at only one stereogenic centre converts it to a disastereomeric structure (diastereomers are stereoisomers that are not enantiomers). Thus here I and III, I and IV, II and III, and II and IV are diastereomers.

A compound with n dissimilar chiral carbon atoms can have a maximum of 2^n stereoisomers. Thus 2,3-dihyroxybutanoic acid having 2 chiral carbon atoms can have as many as four ($2^2 = 4$) stereoisomers.



I II

Enantiomers, or erythro enantiomers

III IV

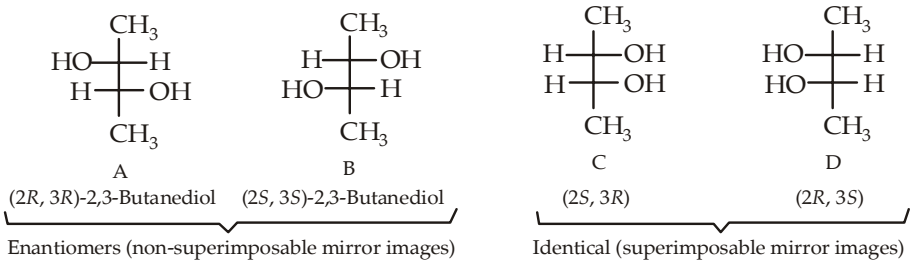
Enantiomers, or threo enantiomers

Here I and III, I and IV, II and III, and II and IV all are diastereomers. Remember that *cis-trans* isomers of a compound are also considered as diastereomers because they are stereomers but not enantiomers.

However, remember that when two of the chiral carbon atoms have identical substituents and opposite configuration, the number of stereoisomers will be less than 2^n.

3.3.6 Meso compounds (Achiral molecules with two stereogenic centres)

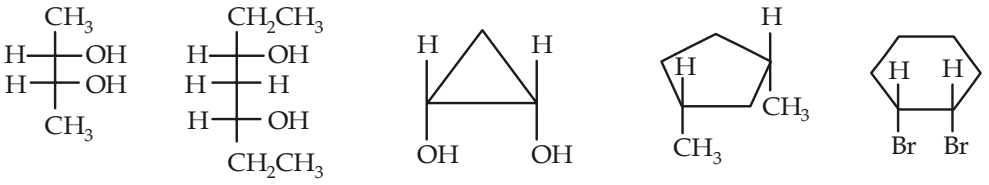
A structure with two stereocenters does not *always* have four possible stereoisomers. The formula 2^n gives correct number of stereoisomers only when all the chiral carbon atoms are differently substituted. In case when a molecule has two chiral centers that are equivalently substituted as in 2,3-butanediol, the number of stereoisomers will be *three instead of four*. Of the four theoretically possible structures, two (A and B) are enantiomers of each other, while the *remaining two* (C and D) *are not enantiomers* because the mirror image of one superimposes over its original form, i.e. the two structures are superimposable. Thus in short, structures C and D are same and represent only one molecule, hence the compound has only three stereoisomers.



To know whether the two structures are identical or not, rotate one of the structures by 180° in the plane of the paper, if now it superimposes over the other then two structures are identical. It is found to be so in case of structures C and D.

The molecules represented by structure C or D is not chiral even though it contains two chiral carbons. Such molecules are called ***meso compounds*** *(achiral compounds that have chirality centers)*. The ultimate test for molecular chirality is to construct a model (or write the structure) of the molecule and then test whether the model (or structure) is superimposable on its mirror image. If it is superimposable, the molecule is achiral, if not superimposable, the molecule is chiral.

The achiral nature of the *meso* isomer is due to the presence of a ***plane of symmetry***. Because of the plane of symmetry, a meso compound does not rotate the plane of polarized light, and hence it is optically inactive. Few examples of *meso* compounds are given below.



3.3.7 Erythro and threo nomenclature

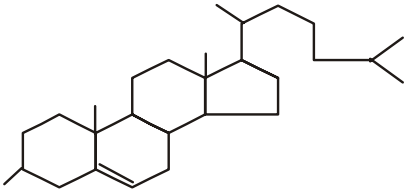
When Fischer projections are drawn for stereomers with two adjacent chirality centres, the pair of enantiomers with similar groups on the same side of the carbon chain is called the **erythro enantiomers**. The pair of enantiomers with similar groups on opposite sides is called **threo enantiomers**. Thus, the above drawn I and II stereoisomers in (e) are the *erythro* enantiomers, while the III and IV are the *threo* enantiomers.

TEST YOUR UNDERSTANDING - 3.7

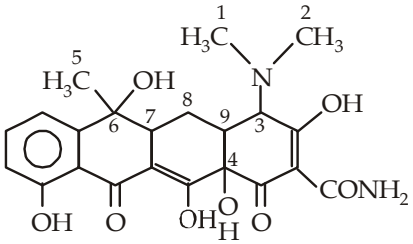
1. Cholesterol, an important compound, has I as its structure

(a) How many chirality centers does it have?

(b) Also predict the maximum number of stereoisomers of cholesterol?



I, Cholesterol



II, Tetracycline

2. Tetracycline is a broad-spectrum antibiotic. It is assigned structure II. How many chirality centers does tetracycline have?

3. Cholic acid, an important constituent of bile acids, has eleven chiral carbon atoms. Can you predict the possible number of diastereomers of cholic acid?

3.3.8 Properties of enantiomers and diastereomers

Enantiomers have identical physical properties (except for the direction in which they rotate plane-polarized light) and identical chemical properties - they react at the same rate with a given *achiral* reagent.

Since diastereomers are not mirror images of each other, they have different physical properties (like m.p., b.p., solubilities, specific rotations, and so on) and different chemical properties - they react with the same reagent at different rates. In this respect, these diastereomers resemble diasteromeric alkenes like *cis*- and *trans*-2-butene. Because diastereomers have different physical properties, they can be separated by ordinary methods like distillation and recrystallization (note that enantiomers can't be separated by either of the two methods).

TEST YOUR UNDERSTANDING - 3.8

1. Predict the nature of the two stereoisomers in each of the following case of a compound having two chirality centers.
   (a) The configuration of both chirality centers in the two isomers is same.
   (b) When the configuration of both chirality centers in one isomer is opposite to that of the configuration of the chirality centers in the other isomer.
   (c) When the configuration of one of the chirality centers has the same configuration in the both isomers but the other chirality center has opposite configuration in the two isomers.
2. (a) Draw Fischer projections of the four stereoisomeric 3-amino-2-butanols and label each as erythro or threo.
   (b) The (2*R*, 3*R*)-3-amino-2-butanol is liquid while the (2*R*, 3*S*)-isomer is a crystalline solid. Name the remaining two stereomers with their physical state.
3. Using *R* and *S* descriptors, write all the possible combinations for a molecule with three stereogenic centers.

3.3.9 Prediction of number of optical isomers in compounds having chiral centre

1. When the molecule is chiral.

Number of *d* and *l* isomers (a) = 2^n , Number of meso forms (m) = 0

$\therefore$ Total number of optical isomers = ($a + m$) = 2^n

Where n is the number of differently substituted chiral carbon atom(s).

Common example is CH_3.CHBr.CHBr.COOH

2. When the molecule is symmetrical and has even number of chiral carbon atoms.

Number of *d* and *l* isomers (a) = $2^{(n-1)}$, Number of meso forms (m) = $2^{(n/2)-1}$

$\therefore$ Total number of optical isomers = ($a + m$)

Common example is tartaric acid, HOOC.CHOH.CHOH.COOH

3. When the molecule is symmetrical and has an odd number of chiral carbon atoms.

Number of *d* and *l* forms $(a) = 2^{(n-1)} - 2^{(n/2)-0.5}$ Number of meso forms $(m) = 2^{(n/2)-0.5}$

$\therefore$ Total number of opital isomers $= (a + m) = 2^{(n-1)}$

Common example is

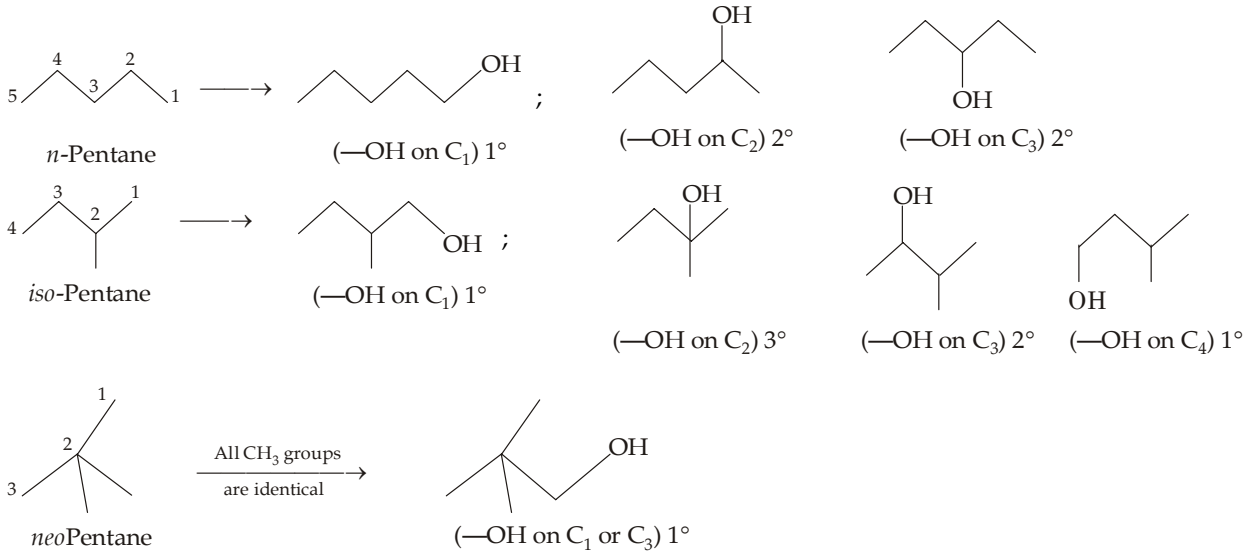
$$HOOC - \overset{*}{C}HOH - \overset{*}{C}HOH - \overset{*}{C}HOH - COOH$$

A carbon atom which is attached to two different atoms or groups as well as two identical carbon atoms is called **pseudo chiral carbon atom**. For example, in trihydroxyglutaric acid, the central carbon atom is *pseudo chiral* while the terminal carbon atoms are chiral.

Example 10 :

How many monohydric primary alcohols can be derived from the hydrocarbon C_5H_{12}. Draw their structures.

Solution :



Hence total number of monohydric 1° alcohols = 1 + 2 + 1 = 4.

Example 11 :

Draw structures of the following compounds in line bond notations.

(*i*) Z-1, 3-Pentadiene **(*ii*) E-1, 3-Pentadiene**

(*iii*) 2E, 4E-3-Ethyl-2,4-hexadiene **(*iv*) 2Z, 4E-3-Ethyl-2,4-hexadiene**

(*v*) 2Z, 4Z-3-Ethyl-2,4-hexadiene.

Solution :

For drawing line bond formulae for geometrical isomers, proceed according to following points.

(*a*) Write down the structure of the compound. Pick up the doubly bonded carbon atoms responsible for geometrical isomerism. In case the compound has two or more such centres, take one by one.

(*b*) Observe the atom or group attached on each carbon atom and determine their priority according to sequence rule.

(*c*) Draw the line representing other group in the same direction for *Z* or *cis* isomer, or in opposite direction for the *E* or *trans* isomer.

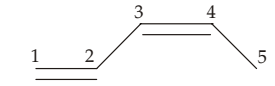
(*d*) In case compound has more than one double bond causing geometrical isomers, repeat steps (*b*) and (*c*) for each such double bond.

Let us illustrate the above points on *Z*-1-, 3-pentadiene and *E*-1, 3-pentadiene.

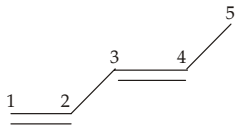
(*a*) $\overset{1}{C}H_2 = \overset{2}{C}H - \overset{3}{C}H = \overset{4}{C}H - \overset{5}{C}H_3$. Here only double bond between C_3 and C_4 can produce geometrical isomers.

(*b*) C_3 has H and —CH = CH_2 group where —CH = CH_2 has priority over H ; while C_4 has H and CH_3 group where —CH_3 has priority over H.

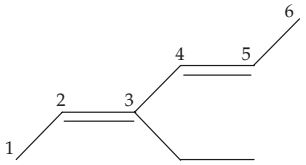
(*c*) For *Z* isomer draw lines in such manner that lines representing —CH = CH_2 and —CH_3 lie on the same side ; similarly for *E*, draw lines on opposite directions.

(*i*) 

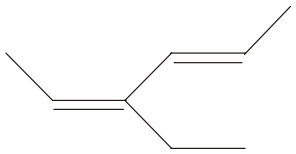
Z-1, 3-pentadiene (*cis*-1, 3-pentadiene)
CH_2 = CH— and —CH_3
are on same side

(*ii*) 

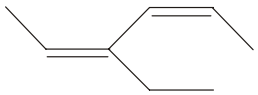
E-1, 3-Pentadiene (*trans*-1, 3-pentadiene)
CH_2 = CH— and —CH_3
are on opposite sides

(*iii*) 

2E, 4E-3-ethyl-2, 4-hexadiene

(*iv*) 

2Z, 4E-3-ethyl-2, 4-hexadiene

(*v*) 

2Z, 4Z-3-ethyl-2, 4-hexadiene

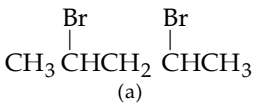
Example 12 :

Which of the following compounds has a meso stereoisomer?

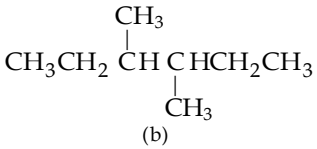
(a) 2,4-Dibromopentane **(b) 3,4-Dimethylhexane** **(c) 2-Bromo-3-methylpentane**
(d) 1,3-Dichlorocyclohexane **(e) 1,4-Dichlorocyclohexane** **(f) 1,2-Dichlorocyclohexane**
(g) 3,4-Dimethylhexane **(h) 1-Chloro-2-methylcyclohexane**

Solution :

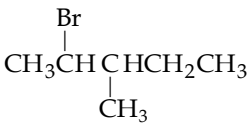
First of all draw structure for each of the compound



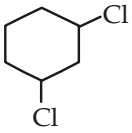
(a)



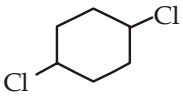
(b)



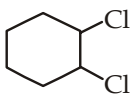
(c)



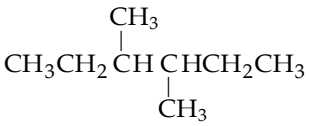
(d)



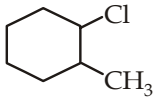
(e)



(f)



(g)



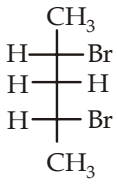
(h)

The essential condition for a compound to exist in meso stereomeric form is the presence of two equivalently substituted chiral centers. Thus here

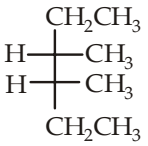
(i) Compounds (e) and (g) do not have any chiral carbon so they do not show even stereoisomerism, what to speak of meso compound.

(ii) Compounds (c) and (h) have two chiral centers, but the two chiral carbons of each compound are different, so they do not have any meso isomer.

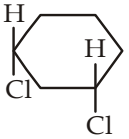
(iii) Each of the compounds (a), (b), (d) and (f) have two equivalently substituted two chiral centers. Further, the meso isomer has a plane of symmetry which can be easily observed in acyclic compound when drawn as a Fischer projection, and in cyclic compounds when drawn with a flat ring.



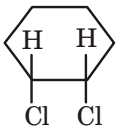
(a)



(b)



(d)



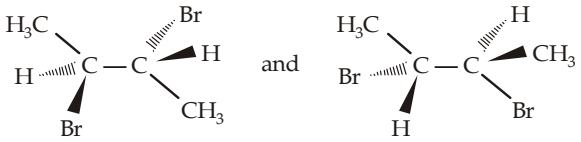
(f)

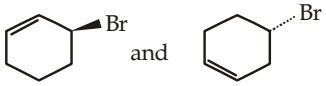
TEST YOUR UNDERSTANDING - 3.9

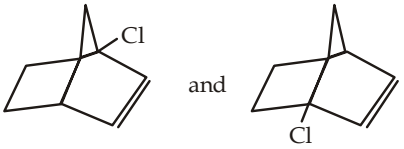
1. Classify each of the following pair as enantiomers, diastereomers or identical.

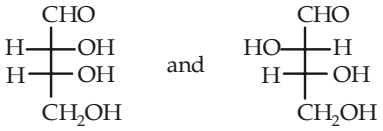
(a) (2*R*, 3*S*)-2,3-dibromohexane and (2*S*, 3*R*)-2,3-dibromohexane

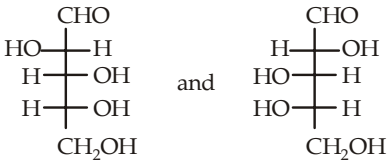
(b) (2*S*, 3*R*)-2,3-dichlorohexane and (2*R*, 3*R*)-2,3-dichlorohexane

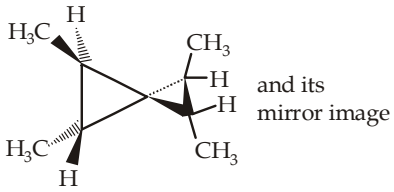
(c) 

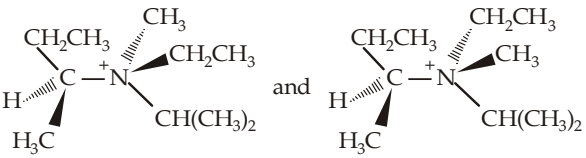
(d) 

(e) 

(f) 

(g) 

(h) 

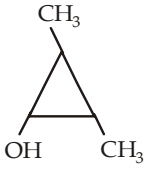
(i) 

2. Draw all the distinct stereoisomers for each structure and show their relationship as enantiomers, diastereomers, etc. Label any meso isomer, if any and draw in any mirror plane of symmetry.

(a) $CH_3CHClCHOHCOOH$

(b) COOH.CHOH.CHOH.COOH

(c) HOOC.CHBr.CHOH.CHOH.COOH

(d) 

3. Which of the following compounds has meso as one of the stereoisomers in each case?

(a) 2,3-Dimethylbutane (b) 3,4-Dimethylhexane (c) 2-Bromo-3-methylpentane

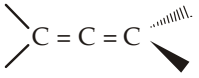
(d) 1,3-Dimethylcyclohexane (e) 1,4-Dimethylcyclohexane (f) 1,2-Dimethylcyclohexane

(g) 3,4-Dimethylhexane (h) 1-Bromo-2-methylcyclohexane

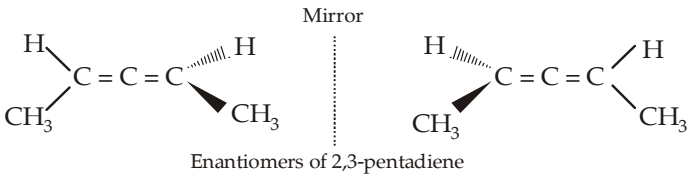
3.3.10 Enantiomerism in Compounds having no chiral centre

We have learnt that the essential condition for a molecule to be chiral is that it is not superimposable on its mirror image. The most important and common examples of chiral compounds contain a tetrahedral atom with four different substituents. However, several chiral molecules are known which although do not contain any chiral (asymmetric) atom, yet they are chiral. In these types of compounds, chirality to the molecule is associated with the molecular shape. Here the chirality is better known as **disymmetry**.

Allenes : Dienes containing double bonds between successive carbon atoms are called allenes or cumulenes.



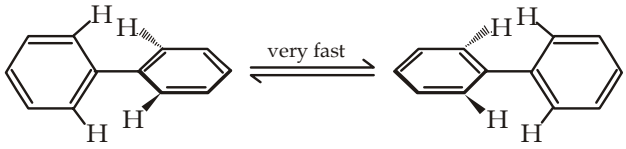
The central carbon atom is in *sp* hybrid state and thus the two π bonds lie in mutually perpendicular planes. This geometry of the π bonds causes the groups attached to the end carbon atoms to lie in perpendicular planes. Thus allenes with different substituents on the end carbon atoms are chiral and hence show enantiomerism (allenes do not show *cis-trans*-isomerism).



Enantiomers of 2,3-pentadiene

Conformational enantiomerism in biphenyls :

Although the two benzene nuclei of the biphenyl are different, they can't be distinguished because of very fast rotation around the C–C single bond.



However, this rotation can be avoided by placing bulky groups on the *ortho* positions of the two benzene rings, and thus such biphenyls can exist in two structures.



However, these two structures are superimposable mirror images over each other, hence they do not show enantiomerism. In case, the *ortho*-positions of each of the benzene rings are differently substituted by bulky groups, the biphenyls show enantiomerism.

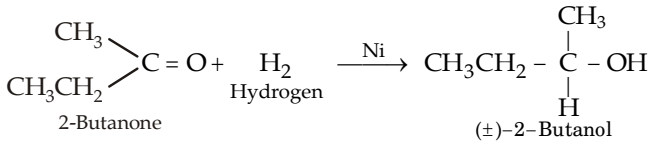


Thus it is concluded that *the essential condition for enantiomerism is the molecular disymmetry or molecular chirality and not the mere presence of chiral centre.*

3.3.11 Racemic Mixture

A mixture of equal amounts of the two enantiomers is called a **racemic mixture, a racemic modification, or a racemate**. A racemic mixture does not rotate plane-polarized light. They are optically inactive because for every molecule in a racemic mixture that rotates the plane of polarized light in one direction, there is a mirror-image molecule that rotates the plane in the opposite direction; hence these are often designated as being (**±**) or ***d, l***. For example, a racemic form of (*R*)-(–)-2-butanol and (*S*)-(+)-2-butanol is designated as (±)-2-butanol or (*d,l*)-2-butanol.

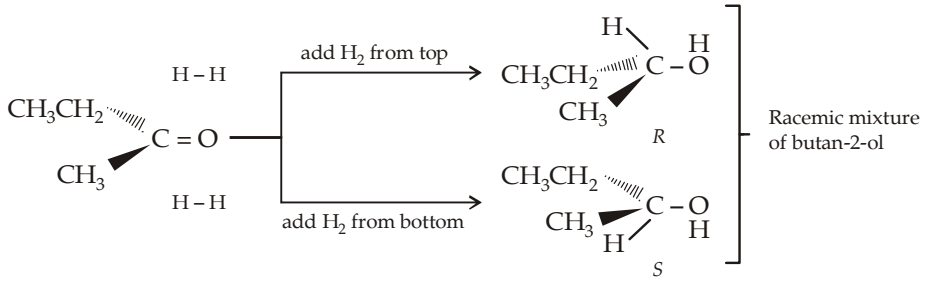
Many reactions lead to racemic products, especially when an achiral molecule is converted to a chiral molecule in absence of any chiral reagent or solvent. For example, addition of hydrogen across the C=O double bond of a ketone produces a racemic mixture of the alcohol.



2-Butanone
(achiral molecule)

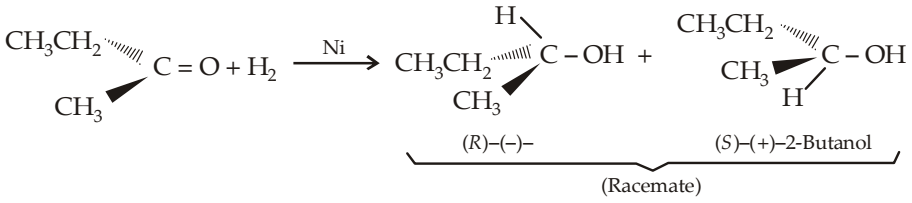
(±)–2–Butanol
[chiral molecules but 50:50 mixture of (*R*) and (*S*)]

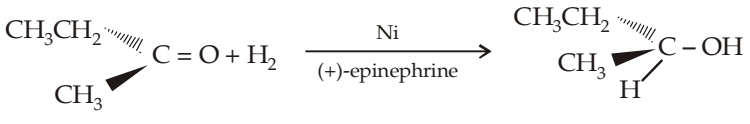
The formation of racemic mixture can be explained by the fact that if the addition of hydrogen to one face of the double bond of a carbonyl group (a flat molecule) produces the *R*-enantiomer, addition of hydrogen to the other face forms the *S*-enantiomer.

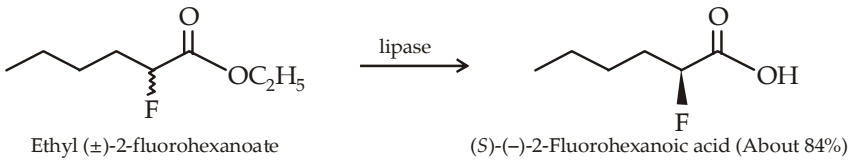


3.3.12 Enantioselective synthesis

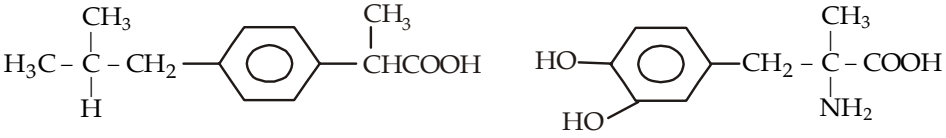
If a reaction that leads to the formation of enantiomers produces a preponderance of one enantiomer over its mirror image, it is called **enantioselective**. For a reaction to be enantioselective, a chiral reagent, solvent, or catalyst must assert an influence on the course of the reaction. The enantioselective syntheses taking place in nature is due to the chiral influence of proteins, present in enzymes. The active site of proteins (enzymes) is chiral, and hence ***only one enantiomer of a chiral reactant fits it properly*** causing the reaction to occur. For example,

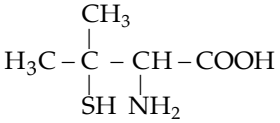






On similar ground, the therapeutic use of only the (*S*)-enantiomer of the following drugs can be explained.





TEST YOUR UNDERSTANDING - 3.10

1. Draw three dimensional representations of the following compounds. Which one has asymmetric carbon atom and which has no asymmetric carbon atom but still chiral?
   (a) 1-Chloro-3-methyl-1,2-butadiene (b) 1-Chloro-1,3-butadiene
   (c) 2,2'-Dibromo-6-iodo-6'-methylbiphenyl (d) 2,2'-Dideuteriobiphenyl
2. Write three-dimensional formula for the (*S*)-enantiomers of
   (a) ibuprofen, (b) methyldopa, and (c) penicillamine

3.3.13 Enantiomeric excess and optical purity

Sometimes we deal with mixtures that are neither optically pure (all molecules are of one enantiomer) nor racemic (equal amounts of two enantiomers). In these cases, we specify optical purity (**o.p.**) of the mixture. The optical purity of a mixture is defined as the ratio of its rotation to the rotation of a pure enantiomer.

$$\text{Optical purity} = \frac{\text{Observed specific rotation}}{\text{Specific rotation of pure enantiomer}}$$

For example, if a sample of 2-bromobutane whose (*S*)-enantiomer has specific rotation of +23.1° has an observed specific rotation of +9.2°, its optical purity will be 0.40, i.e. it will be 40% optically pure.

$$\text{Optical purity} = \frac{+9.2°}{+23.1°} = 0.40 \text{ or } 0.40 \times 100 = 40\%$$

The positive specific rotation (+9.2°) of the sample indicates that the sample has excess amount of (*S*)-(+)-2-bromobutane. Thus the optical purity (40%) of the mixture indicates the following composition of the mixture.

40% (+) enantiomer + 60% (±)-mixture

or 40% (+) + 30% (+) + 30% (–) enantiomer

or 70% (+) enantiomer + 30% (–) enantiomer

In other words, the mixture has 40% excess of one enantiomer, hence this amount (40%) which is equal to optical purity is also known as **enantiomeric excess (e.e.)**.

Algebraically, we use the following formula

$$\text{O.p} = \text{e.e.} = \frac{[d-l]}{(d+l)} \times 100\% = \frac{\text{Excess of one over the other}}{\text{Entire mixture}} \times 100\%$$

Since in the above calculation, units cancel out, the formula can be used whether the amounts of the enantiomers are expressed in concentrations, grams or percentages.

TEST YOUR UNDERSTANDING - 3.11

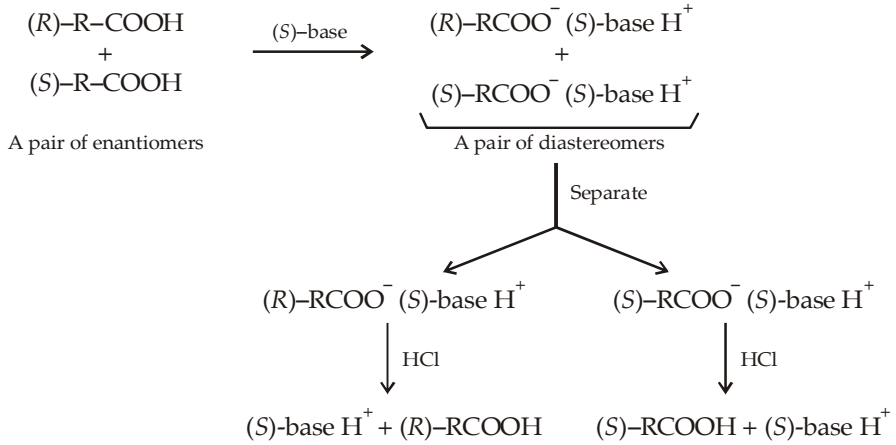
1. (+)-Mandelic acid has a specific rotation of +158°. What would be the observed specific rotation of a mixture having 25% (+)-mandelic acid and 75% (–)-mandelic acid?
2. If the observed specific rotation of a mixture of (*R*)-glyceraldehyde and (*S*)-glyceraldehyde is +1.4°, determine the percentage composition of (*R,S*)-glyceraldehyde; the $[\alpha]_D^{25}$ for (*S*)-(–)-glyceraldehyde is –8.7°C.
3. Calculate the enantiomeric excess and the specific rotation of a mixture containing 6 g of (+)-2-butanol and 4g of (–)-2-butanol. The specific rotation of the pure (–)-2-butanol is –13.5°.
4. A solution having 10 mL of 0.10 M solution of the *R* enantiomer and 30 mL of a 0.10 M solution of the *S* enantiomer has a specific rotation of +4.8°. Determine the specific rotation of each of the enantiomer.
5. Catalytic reduction of 2-butanone in presence of (–)-epinephrine gives a product with a specific rotation of –0.45°. Calculate the percentage composition of the product, (+)-2-butanol and (–)-2-butanol, obtained. The specific rotation of (+)-2-butanol is +13.5°.

3.3.14 Separation of Enantiomers

The separation of a mixture of enantiomers into pure enantiomers is called **resolution**. Since enantiomers have identical boiling points and solubilities, they can't be separated by the conventional separation techniques, such as crystallization and distillation.

Pasteur separated racemic mixture of the crystalline sodium ammonium tartrate by using a microscope and a pair of tweezers. The separation was based on the fact that the crystals of the two enantiomers were not identical, crystals of one enantiomer were "right-handed" while that of other enantiomer were "left-handed".

However, separation of enantiomers by hand is not universally useful method of resolving a racemic mixture because only a few compounds form asymmetric crystals. A more commonly used method is to convert the enantiomers into diastereomers. Diastereomers can be separated by the usual conventional methods like distillation and fractional crystallization because they have different physical properties. After separation, the individual diastereomers are converted back into the original enantiomers. For example, a racemic mixture of a carboxylic acid can be separated (resolved) into two enantiomers by using a naturally occurring 100% optically pure base (a resolving agent); morphine, strychnine, and brucine are naturally occurring chiral bases commonly used for this purpose.



Enantiomers can also be separated by **chromatography**. The racemic mixture to be separated is dissolved in a solvent and the solution is then passed through a column packed with a ***chiral*** adsorbent. The two enantiomers move through the column at different rates because of their different affinities (adsorption) for the chiral adsorbent (a right hand prefers a right-hand glove), so one enantiomer will emerge from the column before the other.

TEST YOUR UNDERSTANDING - 3.12

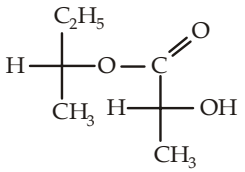
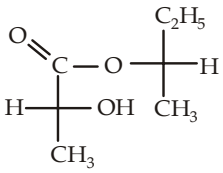
1. (*R, S*)-2-Butanol is treated with (*R, R*)-tartaric acid to form salts.

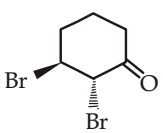
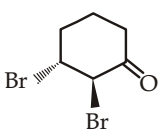
(a) How many different salts can be formed? (b) Predit the total number of chirality centers in each salt.

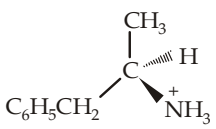
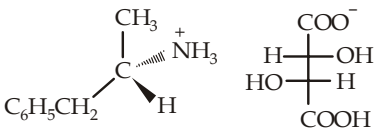
(c) How many chirality centers are identical to that in the other salt and how many are different?

2. Which of the following pairs of compounds can be separated by recrystallisation or distillation?

(a) (±)-Tartaric acid and *meso*-tartaric acid.

(b)  and 

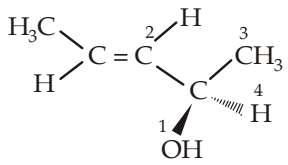
(c)  and 

(d)  and 

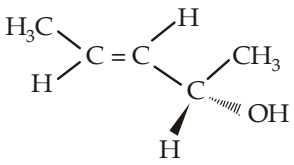
3. Draw the structures of (*R*)-2-butyl-(*R,R*)-tartrate, (*S*)-2-butyl-(*R,R*)-tartrate, and their mirror images. Give the relationship of the four compounds as enantiomers, diastereomers, or identical.

3.3.15 Compounds capable of Showing Enantiomerism as well as Geometric Isomerism

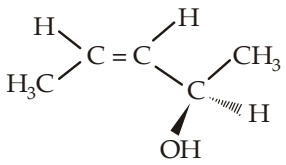
A molecule having both stereogenic centers and double bonds will show enantiomerism as well as geometric isomerism, provided each of the doubly bonded atom is differently substituted. For example, 3-penten-2-ol may be either *R* or *S*, and *R* may be *R*, *E* or *R*, *Z*; similarly *S* may be *S*, *E* or *S*, *R*. Thus there are four stereoisomers of 3-penten-2-ol, although it has only one stereogenic center.



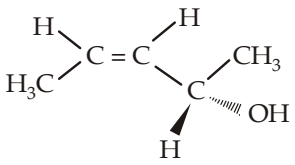
(2*R*, 3*E*)-3-penten-2-ol



(2*S*, 3*E*)-3-penten-2-ol



(2*R*, 3*Z*)-3-penten-2-ol

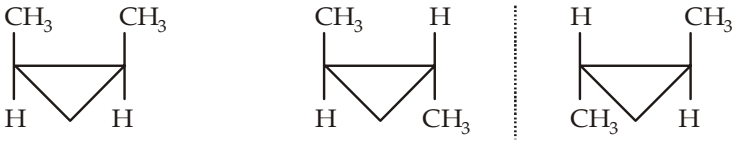


(2*S*, 3*Z*)-3-penten-2-ol

3.3.16 Stereoisomerism in Carbocyclic Compounds

(i) Monosubstituted carbocyclic compounds do not have stereoisomers.

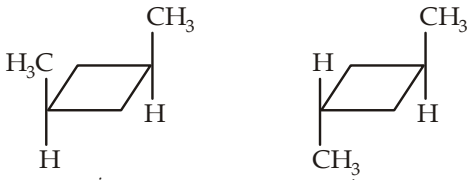
(ii) 1,2-Dimethylcyclopropane have three stereoisomers



cis (meso) *trans* (enantiomers)

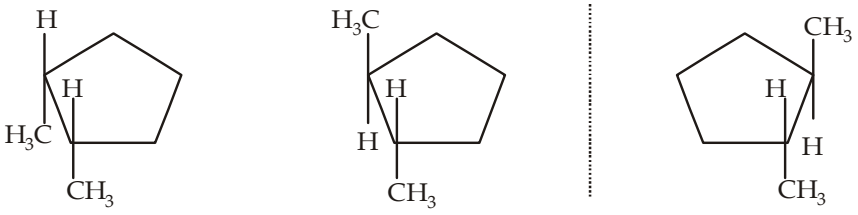
(iii) 1,2-Dimethylcyclobutane has also three stereoisomers : *cis* (meso) and *trans* (enantiomers).

(iv) 1,3-Dimethylcyclobutane has two stereoisomers.



cis *trans*

(v) All *cis*-isomers of 1,2- and 1,3-dimethylcyclopentanes are *meso*, while all *trans*-isomers exist as a pair of enantiomers.



cis (meso) *trans* (enantiomers)

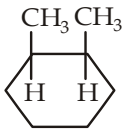
However, when the two carbons are differently substituted, both *cis*- and *trans*- isomers exist as pair of enantiomers.



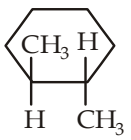
cis-1-Chloro-2-methylcyclopentane *trans*-1-Chloro-2-methylcyclopentane

(vi) Stereoisomers in the various substituted disubstituted cyclohexanes.

1,2-Dimethylcyclohexane

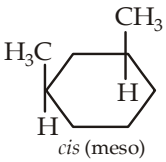


cis (meso)

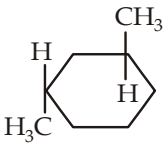


trans (racemate)

1,3-Dimethylcyclohexane

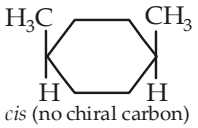


cis (meso)

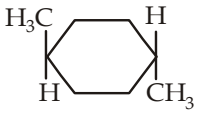


trans (racemate)

1,4-Dimethylcyclohexane



cis (no chiral carbon)



trans (no chiral carbon)

TEST YOUR UNDERSTANDING - 3.13

1. How many stereoisomers are possible for the following compound. Draw their structures.

$$CH_3CH_2CH(Br)CH_2CH = CHCH_3$$

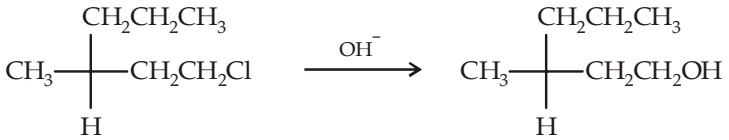
2. Draw the enantiomers of

(a) 3-bromocyclohexene, and (b) 4-bromocyclohexene

3.3.17 Reactions of compounds bearing chirality center (Relative and absolute configuration)

When a compound that contains a chirality center undergoes a reaction, two situations may arise.

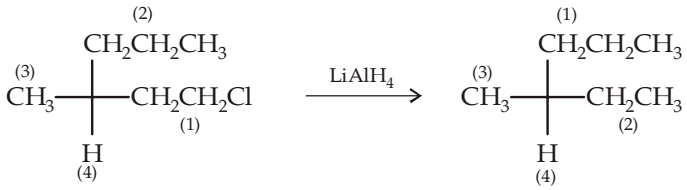
(a) The reaction takes place without cleavage of any of the four bonds to the chirality center. In such cases, the relative positions of the groups bonded to the chirality center will not change. For example,



(*S*)-1-Chloro-3-methylhexane (*S*)-3-Methyl-1-hexanol

Relative configuration of reactant and product is same.
Absolute configuration of reactant and product is same.

However, it is very important to note that although the relative positions of the four groups same in the reactant as well as product, it does not **always** mean that an *S*-reactant will always yield an *S* product. For example,

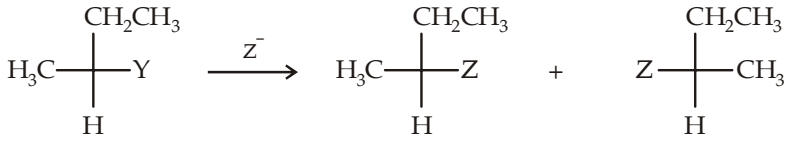


(*S*)-1-Chloro-3-methylhexane (*R*)-3-Methylhexane

Relative configuration of reactant and product is same.
Absolute configuration of reactant and product is different.

In this example, although the four groups bonded to chirality center maintained their relative positions (**relative configuration**) during the reaction, the absolute configurations of the two are opposite; one is *S* and the other is *R*. This is due to change in the relative priorities of the four groups as indicated by the encircled numbers.

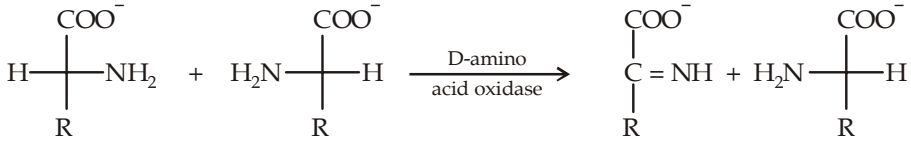
(b) If a bond to the chirality center is broken, the product may have the same or opposite relative configuration to the reactant. The nature of the product actually depends upon the mechanism of the reaction.



Relative configuration of reactant and product may be same or different.

Rate of reaction of a chiral compound :

Enantiomers have the same chemical properties, so they react with **achiral** reagents (e.g. OH^-) at the same rate. However, if the reagent is *chiral*, the enantiomers react at different rates. The common example of chiral reagent is an enzyme. The enzyme, being chiral, reacts only with one enantiomer, leaving another unchanged. If we imagine an enzyme to be a right-handed glove, then it will fit ***only*** into the right-handed hand (enantiomer), not at all into the left-handed hand (enantiomer).

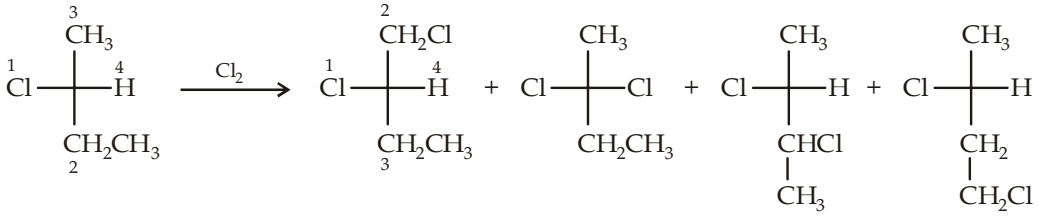


R-enantiomer | *S*-enantiomer | oxidized *R*-enantiomer | *S*-enantiomer

Example 13 :

How many stereoisomers are formed when (R)-2-chlorobutane is monochlorinated? Give the stereochemistry of each stereoisomer.

Solution :



A (*R*)-2-Chlorobutane | B (*S*) | C | D (2R, 3R and 2R, 3S) | E (*R*)

(i) Compound B is chiral having the same relative configuration at C_2 as A, but it is S since priority order is changed ($CH_2Cl > CH_2CH_3$), in A the priority order was $CH_2CH_3 > CH_3$.

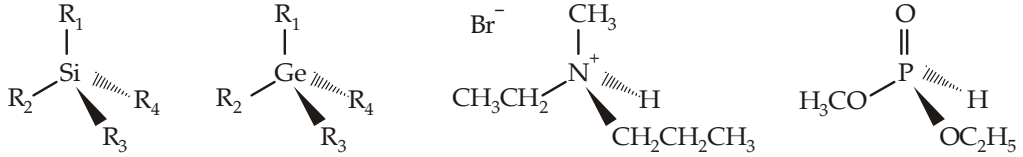
(ii) Compound C is achiral.

(iii) In D, a new chiral carbon is introduced hence it can exist in two diastereomeric forms: 2*R*, 3*R* (optically active), and 2*R*, 3*S* (meso).

(iv) E has same relative configuration at C_2 as in A, further like A it is also *R* because the priority order is not changed. It was $CH_2CH_3 > CH_3$ in A; it is $CH_2CH_2Cl > CH_3$ in E.

3.3.18 Compounds with stereocentres other than Carbon

A tetrahedral atom with four different groups attached to it is a stereocenter (**chirality center**). Thus when an atom like silicon, germanium, nitrogen or phosphorus has four different substituents bonded it, it becomes chiral and the molecule bearing such atom will show enantiomerism and the enantiomers can be separated.



Enantiomerism in tetrahedral molecules other than carbon.

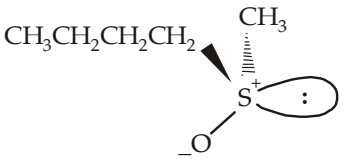
Trigonal pyramidal molecules (molecules in which one of the four positions is occupied by a pair of non-bonding electrons) are also chiral provided the central atom bears three different groups. Hence, such molecules should also show enantiomerism, however the two enantiomers can't be separated at the same ease in all cases because of different rate of pyramidal inversion that interconverts enantiomers.

(a) In case of amines, pyramidal inversion at nitrogen is very rapid (E_{act} = 24 – 40 kJ mol^{-1} or 6 to 10 kcal mol^{-1}) and thus an enantiomer of amines (having no stereogenic center other than nitrogen) is rapidly converted to other enantiomer causing immediate racemization.



(b) Tricoordinate phosphorus compounds (phosphines), however, undergo pyramidal inversion much more slowly than amines (E_{act} = 120 – 140 kj mol^{-1} or 30-35 kcal mol^{-1}), and thus a number of optically active phsophines have been prepared.

(c) Tricoordinate sulphur compounds bearing three different substituents around sulphur have also been resolved because the rate of pyramidal inversion at sulphur is rather slow. Optically active sulphoxides are examples of this type.



(*S*)-(+)-Butyl methyl sulphoxide

3.4 Diastereomers

All stereomers that are not mirror images are called diastereomers. Diastereomers include (a) all geometric isomers, and (b) compounds containing two or more chiral centers (usually asymmetric carbons). These have been discussed earlier in detail.

Stereochemistry of Reactions

When we study the stereochemistry of a reaction, we are concerned with the following questions.

(a) If a chiral center or a double bond is generated during a reaction, there are possibilities that a single stereoisomer or all possible stereoisomers are formed. In case the reaction leads to the preferential formation of one stereoisomer over another, it is called a **stereoselective reaction**. Depending on the degree of preference for a particular stereoisomer, a reaction can be described as *moderately stereoselective, highly stereoselective, or completely stereoselective.*

A stereoselective reaction : $A \longrightarrow B + C$, where B and C are stereoisomers.

(b) If the reactant can exist as stereoisomers, it is just possible that one stereoisomer reacts while the other does not react, or the two isomers form different products, the reaction is said to be **stereospecific**.

A stereospecific reaction : $A \longrightarrow B$, $C \longrightarrow D$ where A and C are stereoisomers and B and D are stereoisomers.

In the above reaction, we observe that stereoisomer A forms only the stereoisomer B but not the D, so, in addition to stereospecific, the reaction is also stereoselective. Many reactions (like addition of bromine on the carbon-carbon double bond) *are both stereoselective and stereospecific*. But this is not always true; some reactions are stereoselective but not stereospecific, one particular stereoisomer is the predominant product regardless of the stereochemistry of the reactant, or regardless of whether the reactant even exists as stereoisomers.

Some reactions are stereospecific but not stereoselective because (i) although the stereoisomers may react at different rates, but form the same stereoisomers as the product, or (ii) form products that differ in ways other than in their stereochemistry. Sometimes one stereoisomer reacts readily, while the other does not react at all, as in the biological reactions.

Further stereospecificity toward enentiomers is called **enantiospecificity**, and stereospecificity toward diastereomers is called **diastereospecificity**.

Whenever a reaction can lead to the formation of two structural (constitutional) isomers, one of which predominates the other, the reaction is called **regioselective reaction**.

TEST YOUR UNDERSTANDING - 3.14

1. Draw the structure of the reactant and products formed in the following reaction. Give the R/S designations to each

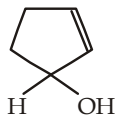
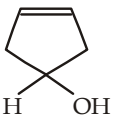
$$(R)-C_2H_5CH(CH_3)CH=CH_2 + D_2 \xrightarrow{Pd}$$

EXERCISE 3.1 (MCQ - ONE option correct)

1. Which of the following statements is true?
(a) All stereocenters are chiral
(b) All chiral centers are stereocenters
(c) Both of the above
(d) None of the two

2. Which of the following is false?
(a) A compound with a stereocenter is always optically active
(b) A compound with a stereocenter may or may not be optically active
(c) A compound with a stereocenter is never optically active
(d) Both (a) and (c)

3. Which of the following has stereogenic center?

(a)  (b) 

(c) Both (d) None

4. Theoretically, which type of intermediate can serve as a chiral center?
(a) $R^1R^2R^3C^+$ (b) $R^1R^2R^3C:^-$
(c) $R^1R^2R^3C^\bullet$ (d) None of these

5. Which of the following type of compound can be resolved?

(a) $\overset{1}{R}\overset{2}{R}\overset{3}{R}\overset{+}{\underset{\cdot\cdot}{S}}X^-$ (b) $\overset{1}{R}\overset{2}{R}\overset{3}{R}\overset{\cdot\cdot}{P}$

(c) $\overset{1}{R}\overset{2}{R}\underset{\cdot\cdot}{S}=O$ (d) All of these

6. Which of the following can show optical activity?
(a) 3-Methylpentene-1 (b) 3-Methylpent-1-yne
(c) 2,3-Dimethylpentane (d) All the three

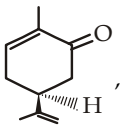
7. The observed rotation of a solution of coniine (0.75 g/10 mL) in a 1 decimeter tube at 25°C (D line) is found to be +1.2°. The specific rotation of the coniine present will be
(a) +1.2° (b) –1.2°
(c) +16° (d) –16°

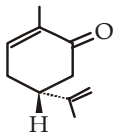
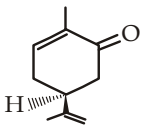
8. Find the observed rotation of a solution of coniine containing 0.35 mg/mL as measured in a 5.0 cm tube (D line), assuming the specific rotation of the sample coniine as –16°
(a) +16° (b) –1.2°
(c) +2.8° (d) –2.8°

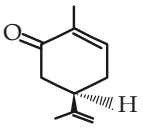
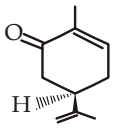
9. Which of the following statement is true?
(a) Doubling the concentration of the solution doubles the observed and specific rotation
(b) Doubling the concentration of the solution halves the observed and specific rotation
(c) Doubling the concentration of the solution doubles the observed rotation without affecting the specific rotation
(d) Doubling the concentration of the solution and doubling the length of the tube increases the observed rotation by four times

10. Preparation of a compound X leads to a mixture with 20% racemization and 80% retention. What should be the observed rotation of the mixture, if $[\alpha]_D = -12°$?
(a) +9.6° (b) –9.6°
(c) +2.4° (d) –2.4°

11. The fact that two enantiomers of carvone have different smells suggests that
(a) the two enantiomers are associated with different impurity.
(b) the two have different volatility
(c) the receptor sites in the nose are achiral
(d) the receptor sites in the nose are chiral

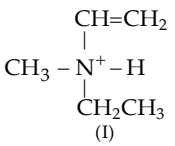
12. If the structure of (+)-carvone is  , the structure for (–)-carvone will be

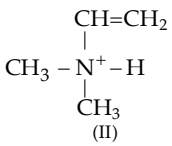
(a)  (b) 

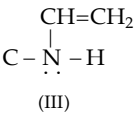
(c)  (d) 

13. Which of the following is most reliable test for assessing the enantiomerism in a compound?
(a) Absence of plane of symmetry or center of symmetry
(b) Nonsuperimposability of the mirror image
(c) Both of these
(d) None of these

14. Which of the following has two stereoisomers?

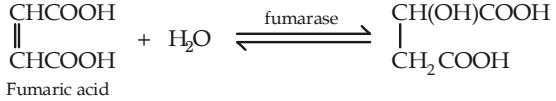
 (I)

 (II)

 (III)

(a) None of these (b) Only I
(c) Only III (d) I and III

15. Which of the following reaction produces optically inactive product?

(a) 
Fumaric acid

(b) $(\pm)\text{–}CH_3CHOHC_2H_5 + (R)\text{–tartaric acid} \longrightarrow$ Tartrate

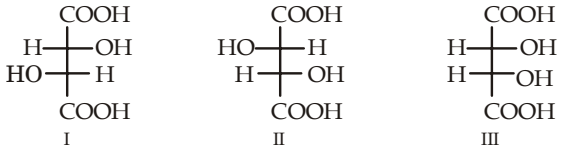
(c) $CH_3CH=CH_2 \xrightarrow{CH_3CO_3H} CH_3\underset{\diagdown O \diagup}{CH}-CH_2$

(d) All the above three

16. Meso stereoisomer is possible in which of the following compounds?
(I) 2,4-Dibromopentane (II) 2,3-Dibromopentane
(III) 3-Bromo-2-pentanol (IV) *cis*-1,3-Dimethylcyclohexane
(V) *trans*-1,3-Dimethyl cyclohexane
(a) I (b) I and III
(c) I and IV (d) None of these

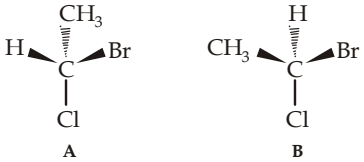
17. In the resolution of 1-phenylethylamine using (–)-malic acid, if the compound obtained by recrystallization of the mixture of diastereomeric salts is (*R*)-1-phenylethylammonium (*S*)-malate, the configuration of the more soluble salt will be
(a) (*R*)-1-phenylethylammonium (*R*)-malate
(b) (*S*)-1-phenylethylammonium (*R*)-malate
(c) (*S*)-1-phenylethylammonium (*S*)-malate
(d) (*S*)-1-phenylethylammonium (*R*)-malate

18. From the structures of the three stereoisomers of tartaric acid, which statement should be true?



(a) I is (+)–, II is (–)–, and III is optically inactive
(b) I is (–)–, II is (+)–, and III is optically inactive
(c) I is (+)–, II is (–)–, and III is meso
(d) III is optically inactive, but nothing can be said about I and II

19. Compounds A and B are related as

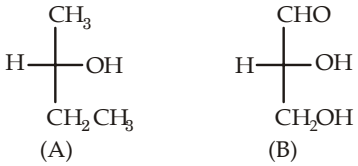


(a) diastereomers (b) conformational isomers
(c) enantiomers (d) same compound

20. The priority sequence of the alkyl groups is
(a) 1° > 2° > 3° > CH_3 (b) CH_3 > 1° > 2° > 3°
(c) 3° > 2° > 1° > CH_3 (d) 3° > 2° > CH_3 > 1°

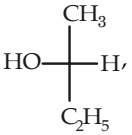
21. The first point of difference in determining the priority order among C_6H_5– and $(CH_3)_3C$– is at
(a) C_1 (b) C_2
(c) C_3 (d) C_4

22. The configurations of the compounds A and B respectively are

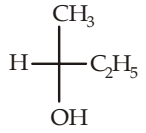


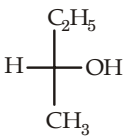
(a) *R* and *R* (b) *S* and *S*
(c) *R* and *S* (d) *S* and *R*

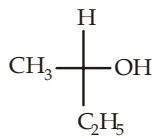
23. (*R*)-2-Butanol has the structure as



then the structure for (*S*)-2-butanol should be

(a) 

(b) 

(c) 

(d) None of these

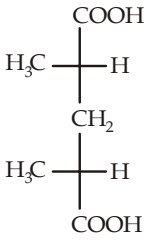
24. Reaction of (–)-lactic acid with methyl alcohol gives (+)-methyl lactate

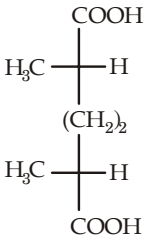
$$\underset{\text{(–)–Lactic acid}}{CH_3CH(OH)COOH} + CH_3OH \xrightarrow{HCl} \underset{\text{(+)–Methyl lactate}}{CH_3CH(OH)COOCH_3}$$

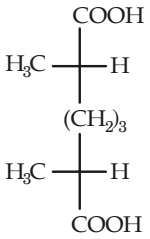
This reaction involves
(a) change in observed rotation
(b) change in configuration
(c) both (a) and (b)
(d) racemization

25. Which of the *R* / *S* designation for *meso*-2,3-butanediol is incorrect?
(a) 2*R*, 3*S* (b) 2*S*, 3*R*
(c) *R*, *S* (d) None of these

26. Which of the following stereoisomers is *meso*?

(a) 

(b) 

(c) 

(d) All of these

27. The number of stereoisomers formed during monochlorination of butane is
(a) 1 (b) 2
(c) 3 (d) 4

28. $(S)-C_3H_7CH(OH)CH=CH_2 + H_2 \xrightarrow{\text{Pt catalyst}} C_3H_7CH(OH)CH_2CH_3$

From the above reaction, we can definitely say that
(a) the product and reactant are *S*
(b) the product and reactant have same specific rotation
(c) the product and reactant have same sign of specific rotation
(d) (a) and (c) are correct

29. What would happen when (+)-2-iodobutane is kept in a solution of NaI?
(a) (–)-2-iodobutane will be formed
(b) (±)-2-iodobutane will be formed
(c) (+)-2-iodobutane will be major product
(d) Nothing will happen

30. The two enantiomers of 3,4-hexanediol can form as much as
(a) two diastereomers (b) three diastereomers
(c) four diastereomers (d) only one diastereomer

31. Select the compound which shows *cis-trans* isomerism but can't be named as *cis* and *trans*?
(a) 3-Octene (b) 3-Chloropent-2-ene
(c) 1,3-Butadiene (d) 4,5-Dibromo-1-pentene

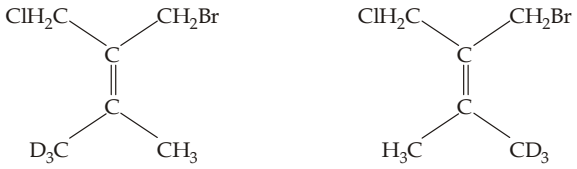
32. Which of the following compound does not show *cis-trans*-isomerism?
(a) 1,4-Dimethylcyclohexane
(b) 1,3-Dimethylcyclohexane
(c) 1-Vinyl-3-methylcyclopentane
(d) Vinylcyclopentane

33. Which of the following does not show geometric isomerism?
(a) 1,2-Dimethylcyclohexane
(b) 1,4-Dimethylcyclohexane
(c) 1-Bromo-3-chlorocyclohexane
(d) None of the three

34. Which of the following statement is true regarding *cis*- and *trans*-2-butenes?
(a) Both have similar vander Waals attractions
(b) Both have similar dipole-dipole attractions
(c) Both are true
(d) Both isomers have similar van der Waals attractions, but only the *cis* isomer has dipole-dipole attractions

35. A hydrocarbon with the minimum number of carbon atoms, capable of showing geometric isomerism as well as optical isomerism is
(a) 3-Methylpentene (b) 3-methylpentene-2
(c) 4-Methylhexene-2 (d) 4-Methylheptene-3

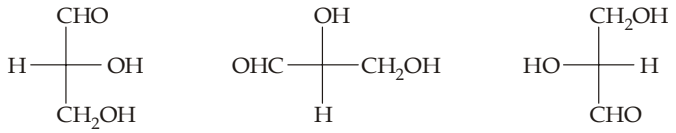
36. Following isomeric pair constitutes an example of



(*a*) Structural isomers (*b*) Enantiomers
(*c*) Functional isomers (*d*) Diastereomers.

37. How many stereoisomers are possible for monochloroisopentane?
(*a*) 2 (*b*) 4
(*c*) 6 (*d*) zero.

38. Which of the following statement is true regarding following structures ?



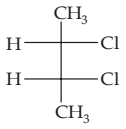
I II III

(*a*) I, II and III are identical
(*b*) I and II are identical, while I and III are enantiomers
(*c*) I and III are identical, while I and II are enantiomers
(*d*) II and III are identical, while I and II are enantiomers.

39. Which of the following statement is true ?
(*a*) The two enantiomers of 2-methyl-1-butanol react with acetic acid at the same rate
(*b*) The two enantiomers of 2-methyl-1-butanol react with (+)-lactic acid at the same rate
(*c*) A molecule containing chiral carbon atom is always chiral
(*d*) A chiral molecule always has at least one chiral atom.

40. In which of the following compounds meso form is possible ?
(*i*) 3, 4-Dibromo-3, 4-dimethylhexane
(*ii*) 2, 3-Dihydroxybutan-1, 4-dioic acid
(*iii*) 2, 4-Dibromopentane
(*iv*) 1, 2, 3, Tribromobutane
(*a*) (*i*) and (*ii*) (*b*) only (*ii*)
(*c*) (*i*), (*ii*) and (*iii*) (*d*) All the four.

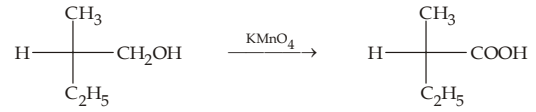
41. Structure written below, has which of the following R, S configuration ?



(*a*) 2(R)– 3(R)– (*b*) 2(S) – 3(S)–
(*c*) 2(R) –3(S)– (*d*) 2(S) – 3(R)–.

42. When (+)-2-butanol is allowed to stand in an aqueous acidic solution for some time, the product will be
(*a*) dextro-rotatory (*b*) laevo-rotatory
(*c*) optically inactive (*d*) either of the these.

43.



(S)-(–)-2-Methyl-1-butanol (+)-2-Methylbutanoic acid

The above reaction indicates that the configuration of the product is
(*a*) R (*b*) S
(*c*) RS (*d*) can't be predicted.

44. Which of the following reaction can be used to establish relative configuration ?
(*a*) (R)–$CH_3CH_2C(CH_3)(OH)CH_2Cl$
$\xrightarrow{PCl_5}$ $CH_3CH_2C(CH_3)(Cl)CH_2Cl$
(*b*) (S)–$CH_3CHClCH_2CH_3$
$\xrightarrow{CH_3ONa}$ $CH_3CH(OCH_3)CH_2CH_3$
(*c*) (R)–$CH_3CH_2CHOHCH_3$
$\xrightarrow{Na}$ $CH_3CH_2CH(O^-Na^+)CH_3$
(*d*) (S)–$(CH_3)_2C(OH)CHBrCH_3$
$\xrightarrow{CN^-}$ $(CH_3)_2C(OH)CHCNCH_3$.

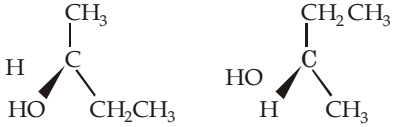
45. Which of the following compounds will exhibit geometrical isomerism ?
(*a*) 1-Phenyl-2-butene (*b*) 3-Phenyl-1-butene
(*c*) 2-Phenyl-1-butene (*d*) 1, 1-Diphenyl-1-propene.

46. Number of stereoisomeric forms of the compound $CH_3.CH = CH. CHBr.CH_3$ is
(*a*) 3 (*b*) 6
(*c*) 2 (*d*) 4.

47. The optically active tartaric acid is named as D –(+) – trataric acid because it has a positive
(*a*) optical rotation and is derived from D-glucose
(*b*) pH in organic solvent
(*c*) optical rotation and is derived from D – (+) – glyceraldehyde
(*d*) optical rotation only when substituted by deuterium.

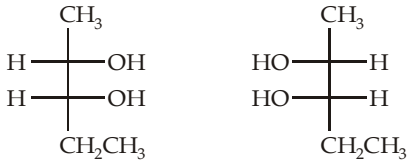
48. A solution of (+) – 2-chloro-2-phenylethane in toluene racemises slowly in the presence of small amount of $SbCl_5$ due to formation of
(*a*) carbanion (*b*) carbene
(*c*) free radical (*d*) carbocation.

49. The following pair of structures are examples of :



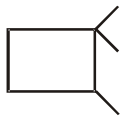
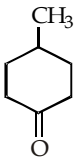
(a) same molecule (b) enantiomers
(c) diastereomers (d) regiomers

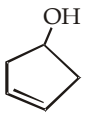
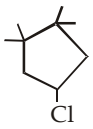
50. The following compounds are :



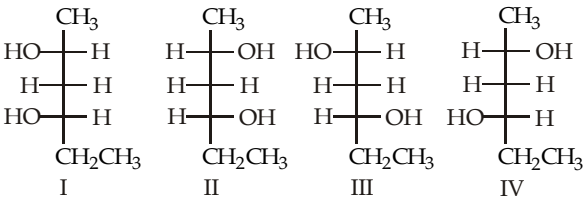
(a) enantiomers (b) diastereomers
(c) identical (d) epimers

51. Which of the following has a stereogenic centre?

(a)  (b) 

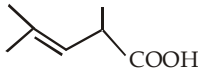
(c)  (d) 

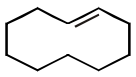
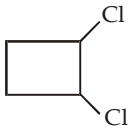
52. Which of the following represents enantiomeric pair?



(a) I and II (b) I and III
(c) I and IV (d) II and III

53. Which of the following structures can show geometrical as well as optical isomerism?

(a)  (b) HO – N =N – OH

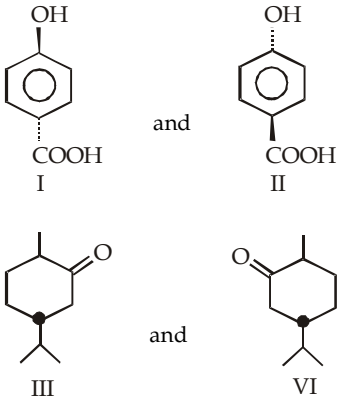
(c)  (d) 

54. An enantiomerically pure acid is treated with racemic mixture of an alcohol having one chiral carbon. The ester formed will be
(a) optically active mixture
(b) pure enantiomer
(c) meso compound
(d) racemic mixture

55. 2-Methylpenta-2, 3-diene is achiral because it has
(a) a plane of symmetry
(b) a centre of symmetry
(c) a C_2 axis of symmetry
(d) both a plane and a centre of symmetry

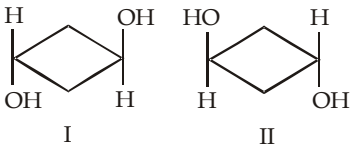
56. *n*-Heptane can be made chiral by introducing a substituent on
(a) C_1 (b) C_3
(c) C_4 (d) any of the carbon

57. Pick up the correct statement regarding following two pairs.



(a) I and II as well as III and IV are enantiomers,
(b) I and II are enantiomers, while III and IV are identical.
(c) I and II as well as III and IV are identical.
(d) I an II are identical, while III and IV are diastereomers.

58. The compounds I and II are



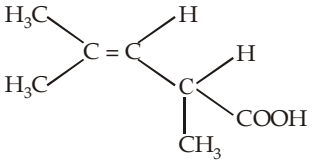
(a) same
(b) enantiomers
(c) achiral identical mirror images
(d) geometrical isomers

59. The number of chiral carbon atoms in 1, 2-dimethyl-cyclohexane (A), 3-methylcyclohexene (B) and 4-methylcyclopentene (C) respectively are
(a) 1, 1, 1 (b) 2, 1, 0
(c) 2, 0, 1 (d) 2, 1, 1

60. Optical isomerism is shown by
(a) butanol-1 (b) butanol-2
(c) 3-pentanol (d) 4-heptanol

61. meso-Tartaric acid is optically inactive due to the presence of
(a) two chrial carbon atoms
(b) molecular unsymmetry
(c) molecular symmetry
(d) external compensation

62. Which of the following compounds will exhibit cis-trans (geometrical) isomerism?
(a) 2-butene (b) 2-butyne
(c) 2-butanol (d) butanal

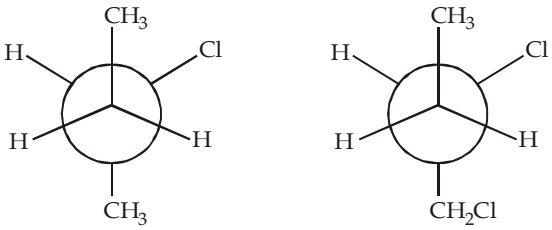
63. The structure  shows
(a) geometrical isomersism
(b) optical isomerism
(c) geometrical & optical isomerism
(d) tautomerism.

64. Which of the following compounds exhibits stereoisomerism?
(a) 2-methylbutene-1 (b) 3-methylbutyne-1
(c) 3-methylbutanoic acid (d) 2-methylbutanoic acid

EXERCISE 3.2 (MCQ 1 or >1 option correct, Passage based, Matching, A/R)

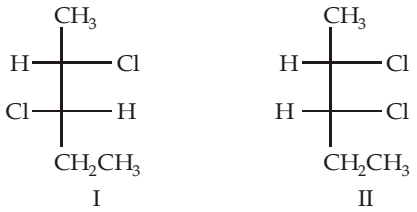
DIRECTIONS for Q. 1 to Q. 22 : Multiple choice questions with one or more than one correct option(s).

1. Observe the following structures and pick up the correct option(s) mentioned below :



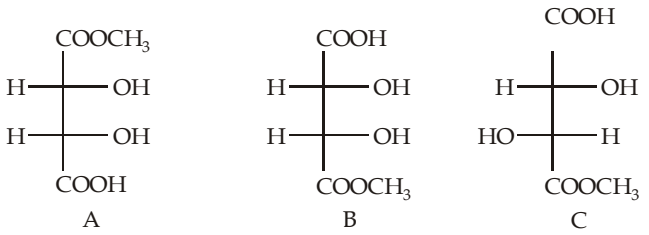
(a) The two are position isomers
(b) None of the two shows optical isomerism
(c) Only A shows optical isomerism
(d) The two are not related to each other regarding isomerism

2.



(a) I and II are enantiomers
(b) I is 2S, 3S; while II is 2S, 3R
(c) I is 2R, 3R; while II is 2R, 3S
(d) I and II are diastereomers

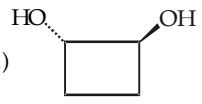
3. Which of the following statements are true regarding following structures?

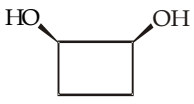


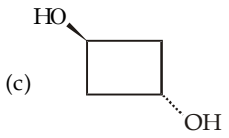
(a) A and B are diastereomers
(b) A and C are diastereomers
(c) B and C are diastereomers
(d) A and B are enantiomers

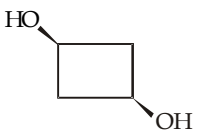
4. The R and S enantiomers of an optically active compound differ in
(a) their reactivity with chiral reagents
(b) their melting points
(c) their optical rotation of plane polarized light
(d) their solubility in achiral reagents

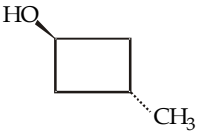
5. Which of the following is (are) chiral?

(a) 

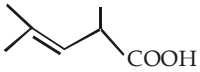
(b) 

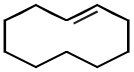
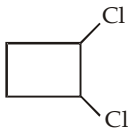
(c) 

(d) 

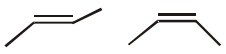
(e) 

6. Which of the following can show diastereoisomerism?

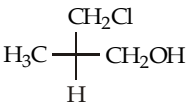
(a) 

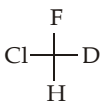
(b) HO – N =N – OH
(c) 
(d) 

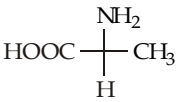
7. Pick up the correct statements.
(a) Sodium potassium tartarate will show enantio-merism.
(b) $CH_3-\underset{\underset{H}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_2CH_3$ and $Cl-\underset{\underset{CH_2CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-H$ are enantiomers.
(c) CH_3COCH_3 on reaction with HCN followed by acidic hydrolysis gives racemic mixture.
(d) $CH_3CH_2NO_2$ will show functional isomerism and tautomerism.

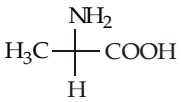
8. 
X Y
Which of the following statments(s) is (are) incorrect?
(a) X is *cis*- and Y is *trans*
(b) X is Z and Y is *E*
(c) X is *trans* and Y is *cis*
(d) X and Y are diastereomers

9. Which of the following has S configuration?

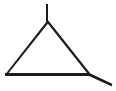
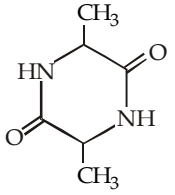
(a) 

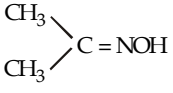
(b) 

(c) 

(d) 

10. Which of the following shows *cis*-*trans* isomerism?

(a) 
(b) 

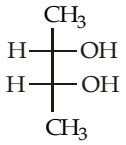
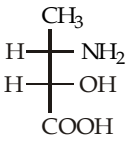
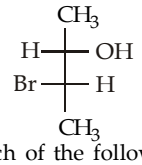
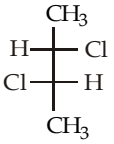
(c) 

(d) 1, 2-Dimethylcyclobutane

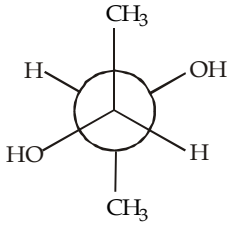
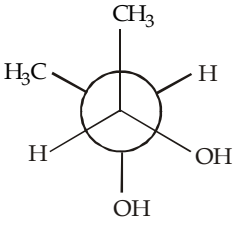
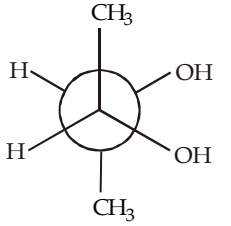
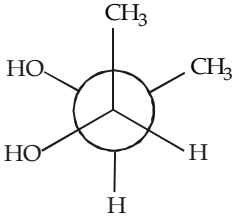
11. Which of the following statement(s) is (are) incorrect?
(a) Malic acid is less soluble in water than fumaric acid.
(b) The presence of chiral carbon is an essential condition for enantiomerism.
(c) Reduction of butanone with a chiral reagent gives (R)- and (S)-2-butanols in equal amounts.
(d) Diastereoisomers are always optically active.

12. Which of the following have different rates of reaction?
(a) Reaction of (+) and (–)- enantiomers with a chiral reagent.
(b) Reaction of diastereomers with a chiral reagent.
(c) Reaction of distereomers with an achiral reagent
(d) Reaction of (+) and (–) enantiomers with an achiral reagent.

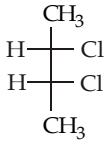
13. Which of the following is (are) threo isomers (s)?

(a) 
(b) 
(c) 
(d) 

14. Which of the following Newmann projections represent *meso* isomer?

(a) 
(b) 
(c) 
(d) 

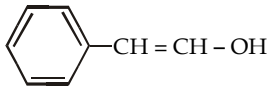
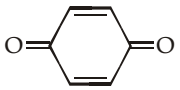
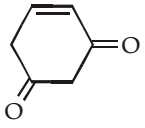
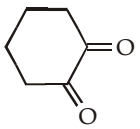
15. Select the correct statement(s) about the following compound

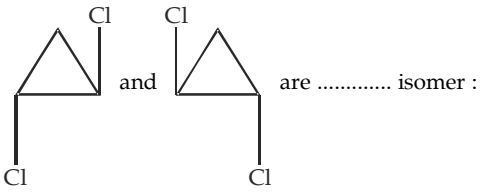


(a) It is an achiral molecule
(b) It is erythro isomer
(c) It has three stereoisomers
(d) It has no plane of symmetry

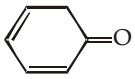
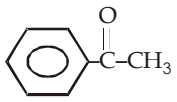
16. Which of the following compounds will show geometrical isomerism?
(a) 2–butene (b) propene
(c) 1–phenylpropene (d) 2–methyl–2–butene

17. Tautomerism is exhibited by

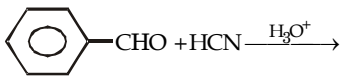
(a) 
(b) 
(c) 
(d) 

18.  are ..... isomer :
(a) position (b) optical
(c) geometrical (d) diastereomer

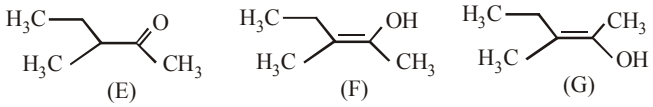
19. Which can show tautomerism?

(a) $CH_3CH_2NO_2$ (b) 
(c)  (d) HCN

20. In which case chiral carbon is generated?

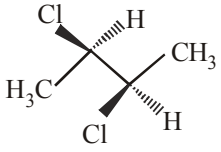
(a) $CH_3COCH_3 + HCN \xrightarrow{H_3O^+}$
(b) $CH_3CHO + HCN \xrightarrow{H_3O^+}$
(c) $CH_3COCOOH + HCN \xrightarrow{H_3O^+}$
(d) 

21. The correct statements(s) concerning the structures E,F and G is (are) –


(E) (F) (G)

(a) E,F, and G are resonance structures
(b) E,F and E, G are tautomers
(c) F and G are geometrical isomers
(d) F and G are diastereomers

22. The correct statement(s) about the compound given below is (are)

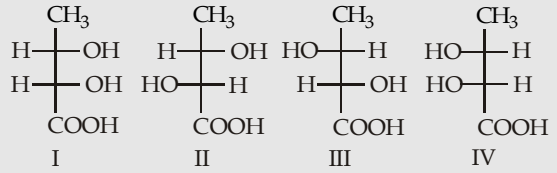


(a) The compound is optically active
(b) The compound possesses centre of symmetry
(c) The compound possesses plane of symmetry
(d) The compound possesses axis of symmetry

INSTRUCTION for Q. 23 to 32 : Read the passages given below and answer the questions that follow.

PASSAGE 1

A compound with n dissimilar chiral carbon atoms can have maximum of 2^n stereomers.



Since all of the above structures are devoid of plane of symmetry, they are chiral and hence optically active. Reversing of configuration at one of the stereogenic centres results in a diastereoisomer, while reversing of configuration at both stereogenic centres results in enantiomer. Diastereomers are stereoisomers that are not enantiomers. Since enantiomers are mirror image of each other they have identical physical and chemical properties; thus they have same b.p., solubilities and identical reactivity with achiral reagents.

23. Which of the following pairs are not diastereomers?
(a) I and II (b) II and IV
(c) I and IV (d) II and III

24. If COOH group is replaced by CH_3, which pair structure will be achiral?
(a) I (b) IV
(c) II (d) None

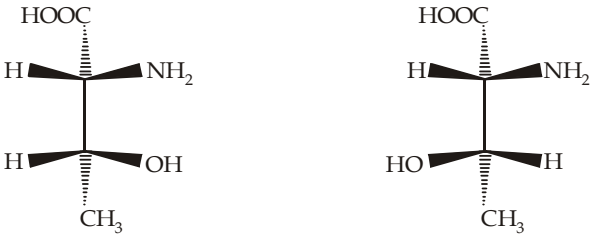
25. All of the above compounds are treated (separately) with an optically active base, which of them will react at different rates?
(a) I and II (b) II and IV
(c) I and IV (d) All the three

26. All of the above compounds are treated (separately) with an achiral acid, which of them will react at different rate?
(a) I and II (b) II and IV
(c) I and IV (d) All the three

PASSAGE 2

Isomers are compounds that have the same chemical formula but different structures. There are two fundamental types of isomerism: constitutional isomerism and stereoisomerism. Constitutional isomers are compounds whose atoms are connected differently. Stereoisomers are compounds whose atoms are connected in the same order but with a different geometry. Sub-types of stereoisomers include enantiomers (mirror-image stereoisomers) and diastereomers (non-mirror-image stereoisomers). Further, diastereomers can be classified as either cis-trans diastereomers or configurational diastereomers

27. What kind of isomers are the two compounds below?



(a) Configurational diastereomers
(b) Enantiomers
(c) Constitutional isomers
(d) cis-trans diastereomers

28. What kind of isomers are the two compounds below?



(a) Configurational diastereomers
(b) Enantiomers
(c) Constitutional isomers
(d) They are exactly the same compound

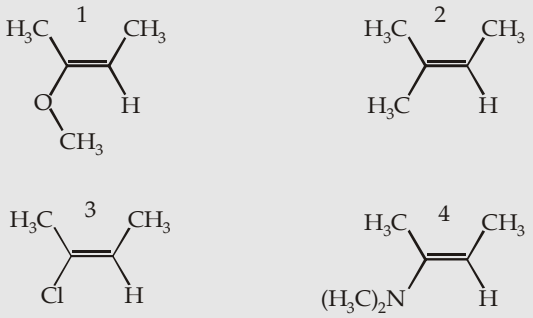
29. What kind of isomers are the two compounds below?



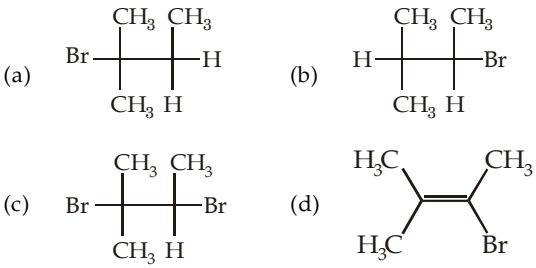
(a) Configurational diastereomers
(b) Enantiomers
(c) cis-trans diastereomers
(d) They are exactly the same compound

PASSAGE 3

Alkenes are characterized by C=C bonds. As such, they are subject to electrophilic addition reactions. Most electrophilic additions obey Markovnikov's rule; however, there are some exceptions. Examples of alkenes are shown below

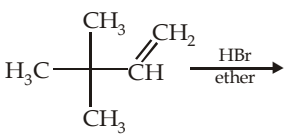


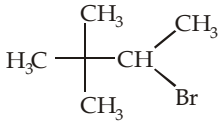
30. When HBr adds to compound 2 above, the main product is

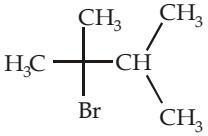


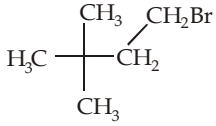
31. What is the order of reactivity of the compounds above to electrophilic addition of HBr?
(a) 1 > 2 > 3 > 4 (b) 3 > 1 > 4 > 2
(c) 4 > 1 > 2 > 3 (d) 2 > 4 > 1 > 3

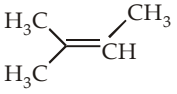
32. What is the major product of the following reaction?



(a) 

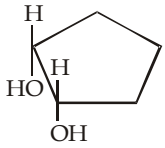
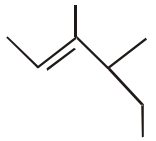
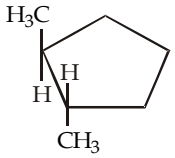
(b) 

(c) 

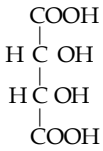
(d) 

Instructions for Q. 33 to 35 : Following questions are Multiple Matching type Questions :

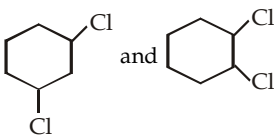
33.

	Column I		*Column II*
(A)	Dimethylcyclo -hexane	(a)	Position isomerism
(B)		(b)	Plane of symmetry
(C)		(c)	Enantiomerism
(D)		(d)	Geometrical isomerism

34.

	Column I		*Column II*
(A)	$CH_3NHC_2H_5$	(a)	Enantiomerism
(B)	$CH_3CH(Cl)C_2H_5$	(b)	Resolvable
(C)	$CH_3CH = C = CHCH_3$	(c)	Non-resolvable
(D)		(d)	Enantiomerism not possible

35.

	Column I		*Column II*
(A)	Geometrical isomers	(a)	Diastereomers
(B)	Enantiomers	(b)	Same properties
(C)	Meso compounds	(c)	Different properties
(D)	Tautomers	(d)	

Instructions for Q. 36 to 40 : Following questions are Assertion and Reasoning Type Questions :

Note : Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 5 choices (A), (B), (C), (D) and (E) out of which ONLY ONE is correct.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.

(c) Statement -1 is True, Statement-2 is False.

(d) Statement -1 is False, Statement-2 is True.

(e) Statement -1 is False, Statement-2 is False.

36. **Statement I :** 3-Phenyl-butan-2-one racemises in presence of dilute acid or dilute base.
Statement II : Its keto form is thermodynamically more stable form then the enol form.

37. **Statement I :** Restricted rotation about a bond is the necessary condition for geometrical isomerism.
Statement II : Two different orientations are possible due to restricted rotation about a bond if the end groups are different.

38. **Statement I :** Compounds having only one chiral centre can have both enantiomer and diastereomer.
Statement II : Diastereomer may or may not have chirality.

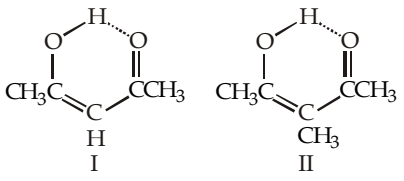
39. **Statement I :** Cis-1, 3-dihydroxy cyclohexane exists in boat conformaton.
Statement II : In the chair form, there will not be hydrogen bonding between the two hydroxyl groups.

40. **Statement I :** Diastereoisomers have different physical properties.
Statement II : They are non-superimposable mirror images.

Instructions for Q. 41 to 46 : The following questions are True/False Type Questions :

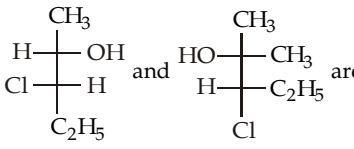
41. Dichlorocyclopentane does not exhibit structural isomerism but only stereoisomerism.

42. Maleic acid and fumaric acid are diastereomers.

43. 

The above two structures are equally stable.

44. Dimethylcyclohexanes do not have any plane of symmetry, hence show enantiomerism.

45.  are identical.

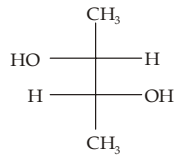
46. $CH_3\ddot{\underset{\cdot\cdot}{C}}HCH_2CH_3$ and $CH_3\ddot{\underset{\cdot\cdot}{C}}HCOCH_3$ are optically inactive.

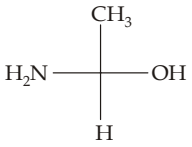
EXERCISE 3.3 (Subjective Problems)

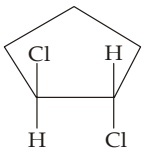
1. Draw structures of the various possible geometrical isomers of 2, 4-heptadiene.

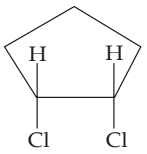
2. An optically active dichloro derivative of propane (A), on further chlorination gives trichloro derivative. Suggest the structure of A, write down structures of the various possible trichloro derivatives and predict which isomer, if any, is optically active.

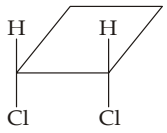
3. Assign R/S configuration to the chiral carbon atoms in the following compounds.

(*i*) 

(*ii*) 

(*iii*) 

(*iv*) 

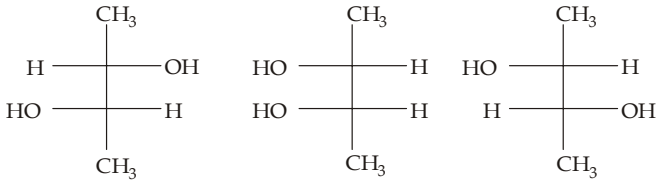
(*v*) 

4. (*a*) Write down structures of stereoisomers of the following compounds.

(*i*) 2, 3-Dihydroxybutane

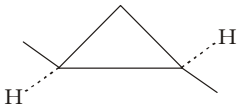
(*ii*) 3-Phenyl-2-propenoic acid.

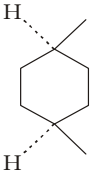
(*b*) Identify the pairs of enantiomers and diasteromers from the following compounds, I, II and III.



5. Acetophenone on reaction with hydroxylamine hydrochloride can produce two isomeric oximes. Write structures of the oximes.

6. Write down the name of the following compounds.

(*a*) 

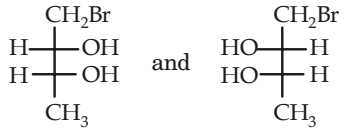
(*b*) 

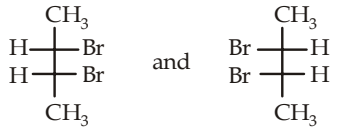
7. How many enantiomeric pairs are possible in the simplest possible alkene?

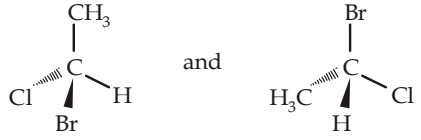
8. Give the stereochemical relationships between each pair of isomers.

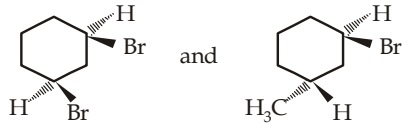
(*i*) CH_3CN (*ii*) $CH_3CH = CH_2$

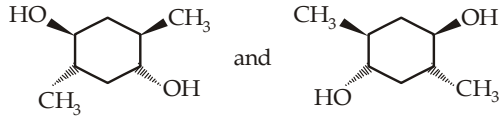
(*iii*) $CH_3—C \equiv C — CH_3$ (*iv*) $HC \equiv C—CH = CH_2$.

(*a*) 

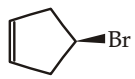
(*b*) 

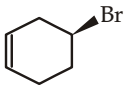
(*c*) 

(*d*) 

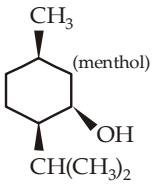
(*e*) 

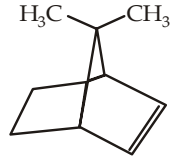
9. In each of the following structure, star (*) any asymmetric carbon atom. Draw any internal mirror planes of symmetry, if any.

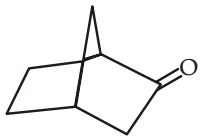
(a) 

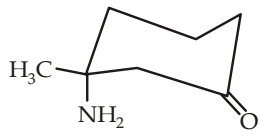
(b) 

(c) 

(d) 

(e) 

(f) 

(g) 

10. Draw the structure of each of the following compounds and its enantiomer. Also draw the structure of the diastereomer(s), where possible

(a) (2*R*, 3*S*)-2,3-Dibromohexane

(b) *meso*-3,4-Dibromohexane

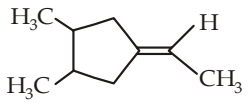
(c) (*R*)-1,1,2-Trimethylcyclohexene

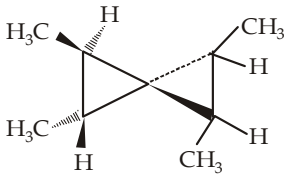
(d) (1*R*, 2*R*)-1,2-Dibromocyclohexane

11. (a) Draw all stereoisomers of 2,3,4-tribromopentane and give the relationship between them. Star (*) the asymmetric carbon atom(s) in each.

(b) Give the stereogenic and chirality character of C_3 in the various isomers.

12. Draw all stereoisomers for the following structures.

(a) 

(b) 

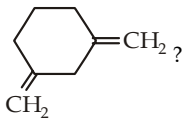
13. Each of the two optically active alkenyl chlorides, A and B, of the same molecular formula, C_5H_9Cl takes up one mole of hydrogen to form compound C (optically inactive) and D (optically active) respectively. Assign structures to the two alkenes.

14. How many stereoisomers are possible for 2,3,4,5-tetrahydroxyhexane-1,6-dioic acid? Give their *R* / *S* designations. How many of these are optically active and how many are optically inactive?

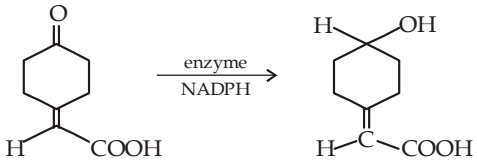
15. Does tri-*sec*-butylmethane show stereoisomerism?

16. How many *meso* diastereomers are possible for the compound with the formula $C_6H_{12}Cl_2$?

17. How many stereoisomers can be obtained by catalytic hydrogenation of both double bonds in the following compound



18. The following cyclohexanone was enzymatically reduced to form a cyclohexanol derivative.

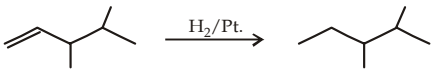


(a) How many stereocenter(s) is(are) present in the product?

(b) Does the product possess any asymmetric carbon atom?

(c) What is the fate of the product regarding its optical activity?

19. Observe the following reaction and answer the questions given below :



(a) Mark the star (*) on the chiral carbon(s).

(b) Predict the *R,S* designation of the two compounds.

(c) On the basis of structure of the molecules, can we ascertain whether the molecules are *d- or* l- *rotatory?*

20. (a) An aqueous solution of pure stereoisomer A of concentration 0.10 g/mL had observed rotation –30° in a 10 dm tube at 589.6 mm (the sodium D line) and 25°C. How do you calculate its specific rotation at 25°C?

(b) Under identical conditions but with concentration 0.050 g/mL, a solution of A had observed rotation +165°. Rationalize how this could be and recalculate the specific rotation for the stereoisomer *A*.

(c) If the optical rotation of a substance studied at only concentration is 0°, can it definitely be concluded to be achiral or racemic?

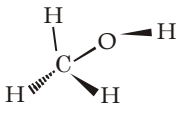
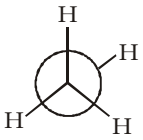
21. An organic compound X ($C_3H_6O_2$) is found containing one –OH group, but no carbonyl group, can exist in two stereoisomeric forms. Assign structure to the two stereoisomers.

SOLUTIONS

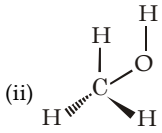
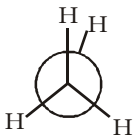
TEST YOUR UNDERSTANDING - 3.1

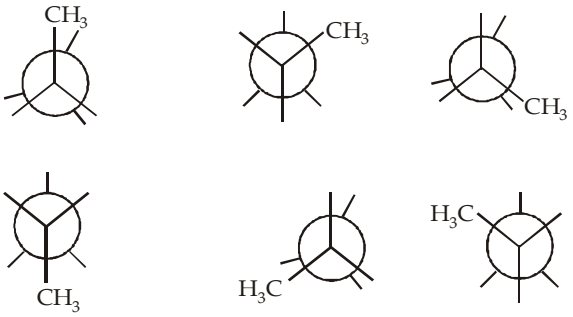
1. (a) There must be four atoms bonded sequentially only by *sigma bonds*, i.e. A-B-C-D.

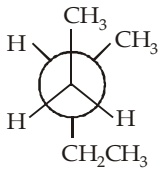
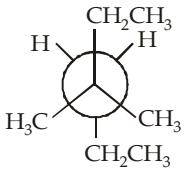
CH_3Cl has only three atoms bonded sequentially, and $CH_2 = CH_2$ has a π bond in addition to a sigma bond between the two carbons. Thus only H_2O_2 and H_2NOH have conformations.

(b) (i)  *or* 

O is behind C, hence not visible

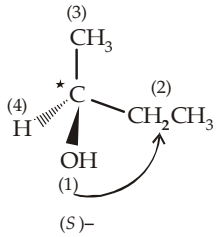
(ii)  *or* 

2. 

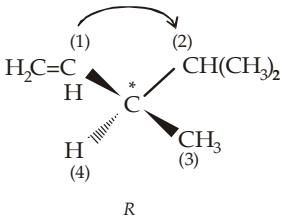
3. (a)  (b) 

TEST YOUR UNDERSTANDING - 3.2

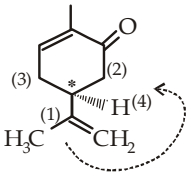
1. C_1 has *R*, while C_2 has *S* configuration.

2. (a) 

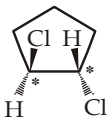
(*S*)–

(b) 

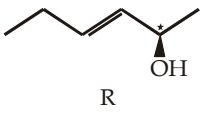
R

(c) 

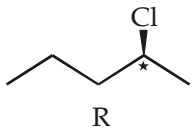
(*S*)-

(d) 

Both * atoms are *S* configuration

(e) 

R

(f) 

R

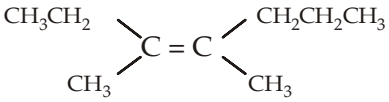
3. (a) The first structure has the *S* and the second has the *R* configuration, hence the two structures represent a pair of enantiomers.

(b) Enantiomers

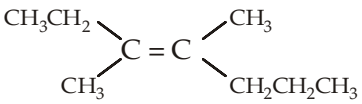
(c) Enantiomers

(d) Enantiomers

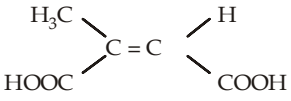
TEST YOUR UNDERSTANDING - 3.3

1. (a) 

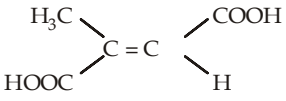
cis



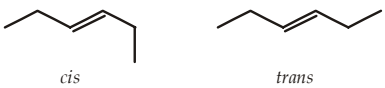
trans

(b) 

cis

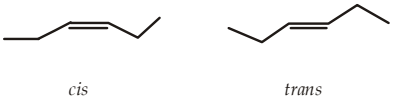


trans

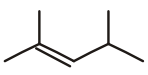
2. (a) 

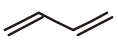
cis *trans*

or



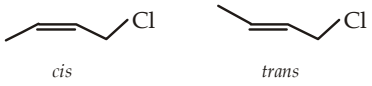
cis *trans*

(b) 

(c) 

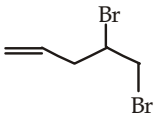
Geometric isomerism not possible in (b) and (c).

(d)



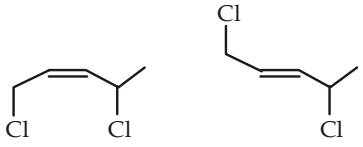
cis *trans*

(e)



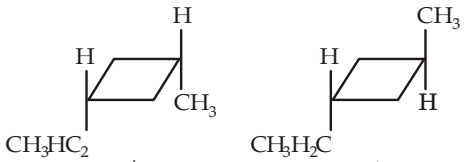
Geometric isomerism not possible

(f)



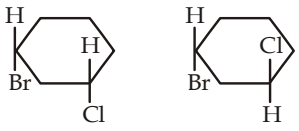
cis *trans*

3. (a)



cis *trans*

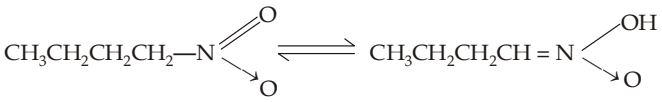
(b)



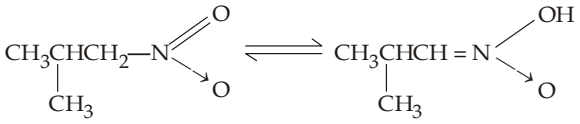
cis *trans*

TEST YOUR UNDERSTANDING - 3.4

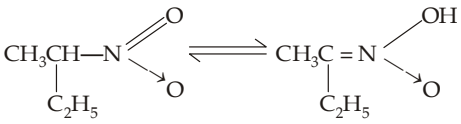
1. (a)



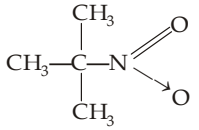
1° Nitroalkane



1° Nitroalkane



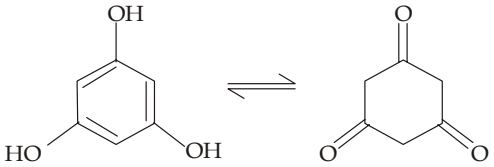
2° Nitroalkane



Tautomerism not possible because of absence of α–H atom

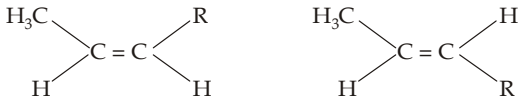
3° Nitroalkane

(*b*)



2. 2, 4-Hexadiene ($CH_3CH = CHCH = CHCH_3$) can exist in three geometrical isomeric forms.

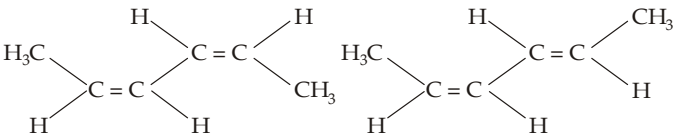
(*i*) Take one of the double bonds at a time and draw structures of the possible geometrical isomers, by taking rest of structure as a substituent.



cis *trans*

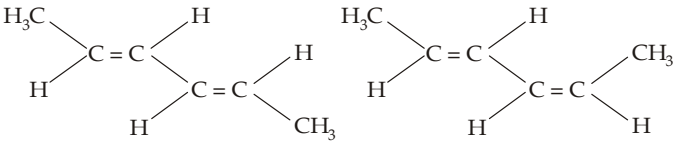
(*ii*) Now draw structure(s) of the possible isomers by considering next double bond, in each of the above two isomers.

For *cis*



cis-cis, I *cis-trans*, II

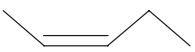
For *trans*



trans-trans, III *trans-cis*, IV

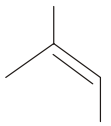
(*iii*) In case, identical structures are obtained, take only one isomer. Thus here structure II and IV are same because both alkyl groups are similar, hence only one of them should be considered. Thus three geometrical isomers (I, II and III) are possible for 2, 4-hexadiene

3. (*i*)



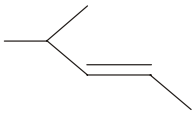
Z-2-Pentene
(*cis*-2-Pentene)

(*ii*)



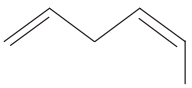
2-Methylbutene-2
(geometrical isomerism not possible)

(*iii*)



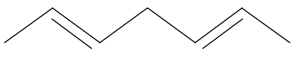
E-4-Methyl-2-butene
(*trans*-4-Methyl-2-pentene)

(*iv*)



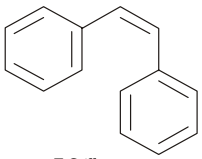
Hexa-1, 4 (E)-diene

(*v*)



Hepta-1 (E), 5(E)-diene

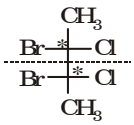
(*vi*)



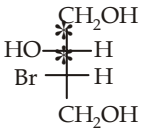
Z-Stilbene

TEST YOUR UNDERSTANDING - 3.5

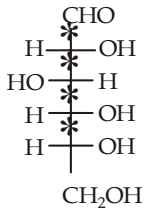
1. (a) (*E*) - 1,2-Dichloroethene is a planar molecule. The molecular plane is a plane of symmetry. Further, the molecule also has a center of symmetry located at the center of the carbon-carbon double bond. It is an *achiral* molecule.
   (b) (*Z*)-1,2-Dichloroethene is *achiral*. The plane of the molecule is a plane of symmetry. A second plane of symmetry is perpendicular to the plane of the molecule and bisects the carbon-carbon double bond.
   (c) *cis*-1,2-Dichlorocyclopropane has a plane of symmetry that bisects the C_1-C_2 bond and passes through C_3. It is *achiral*.
   (d) *trans*-1,2-Dichlorocyclopropane has neither a plane of symmetry nor a center of symmetry. It is a *chiral* molecule.

2. (a) 

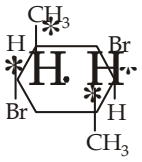
meso structure
(not optically active)

(b) 

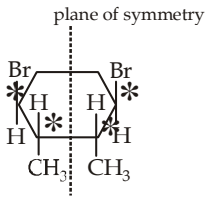
optically active

(c) 

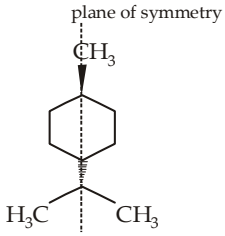
(optically active)

(d) 

center of symmetry present
(not optically active)

(e) 

meso
(not optically active)

(f) 

meso
(not optically active)

TEST YOUR UNDERSTANDING - 3.6

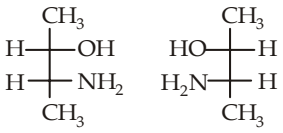
1. Yes, when (*S*)-lactic acid is dextrorotatory, the (*R*)-isomer should be levorotatory. Similarly, when the (*S*)-sodium lactate is levorotatory the (*R*)-sodium lactate should be dextro.
2. Dilute the solution to about one-fourth of its concentration and then measure the rotation which will give the value of either +45° or –45°.

TEST YOUR UNDERSTANDING - 3.7

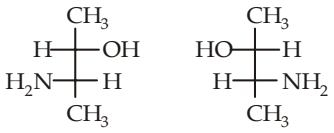
1. (a) Eight (b) $2^8 = 256$
2. It has 5 chiral centers.
3. Cholic acid has $2^{11} = 2048$ stereoisomers of which one is an enantiomer of cholic acid. Now since an object can have only one mirror image, so the number 2048 has (+)-cholic acid, (–)-cholic acid and 2046 other stereoisomers which are not enantiomers. Thus the number of diastereomers of cholic acid = 2046.

TEST YOUR UNDERSTANDING - 3.8

1. (a) Identical (b) Enantiomers
   (c) Diastereomers

2. (a) 

Erythro Erythro

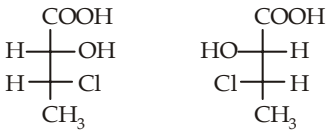


Threo Threo

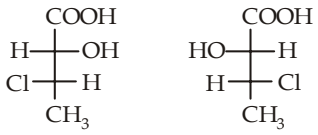
   (b) (2*S*, 3*S*) is liquid, (2*S*, 3*R*) is solid.
3. No. of isomers with three stereogenic centers = $2^3 = 8$.
   RRR, RRS, RSR, SRR, SSS, SSR, SRS, RSS

TEST YOUR UNDERSTANDING - 3.9

1. (a) Configurations at both chiral carbons inverted – **enantiomers.**
   (b) Configuration at only one chiral carbon inverted – **diastereomers.**
   (c) Configuration at only one chiral carbon (the left one) inverted – **diastereomers**.
   (d) The position of C=C bond shifted – **constitutional isomers.**
   (e) Chiral, the two are mirror images – **enantiomers**.
   (f) Configuration at only one chiral carbon (the top one) inverted – **diastereomers**.
   (g) Configurations at all chiral carbon inverted – **enantiomers**.
   (h) Superimposable mirror images – **same compound**.
   (i) Configuration at only one chirality center (nitrogen) inverted - **diastereomers**.
2. (a) Total number of stereoisomers = $2^2 = 4$



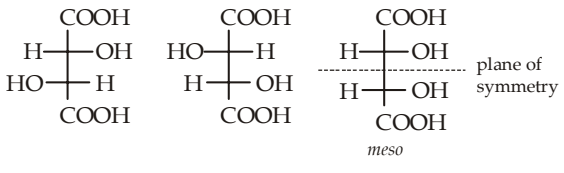
I II



III IV

I and II; III and IV are **enantiomers.** I and III, I and IV, II and III, and II and IV are **diastereomers**.

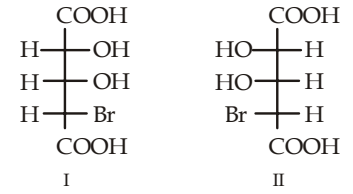
   (b) Compound has two identical chiral carbon, therefore number of stereoisomers will be **less than (2^2) 4**.

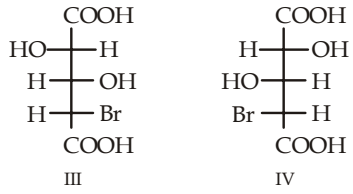


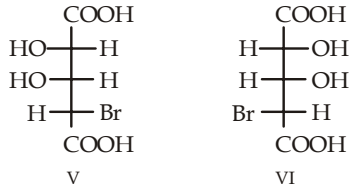
meso
I II III

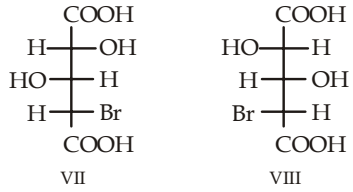
I and II are **enantiomers**, I and III; II and III are **diastereomers**.

(c) Here no chiral carbons are identical, therefore, number of stereoisomers = $2^3 = 8$.







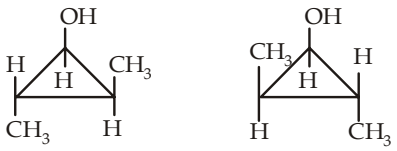


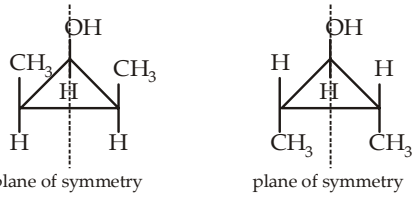
Enantiomers : I and II; III and IV; V and VI; VII and VIII.

Diastereomers : Any pair which is not enantiomeric, e.g. I and III, I and IV, I and V, I and VI,

I and VII, I and VIII, II and III, and so on.....

(d)





meso (III) *meso* (IV)

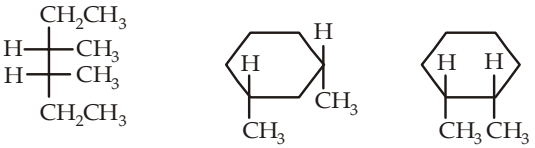
Enantiomers : I and II

Diastereomers : I and III, I and IV, II and III, II and IV, III and IV.

3. (i) Compounds *a*, *e* and *g* do not have any chiral center, so they will not show enantiomerism, hence no question of *meso* form.

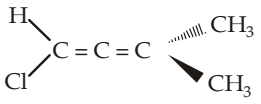
(ii) Compounds *c* and *h*, each have two different chiral centers, so they will not have *meso* stereoisomer.

(iii) Compounds *b*, *d* and *f*, each will have *meso* stereoisomer because each contains two identical chiral carbons; and hence possess a plane of symmetry.



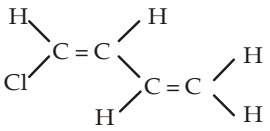
TEST YOUR UNDERSTANDING - 3.10

1. (a)



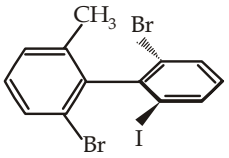
no asymmetric carbon, but the allene has a plane of symmetry between the two methyls. Hence the molecule is not chiral

(b)



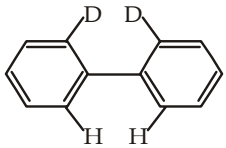
planar molecule, no asymmetric carbon, not a chiral molecule

(c)



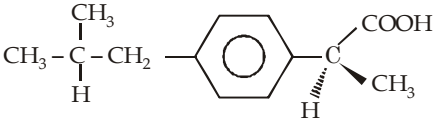
no asymmetric carbon, but the molecule is chiral due to restricted rotation

(d)

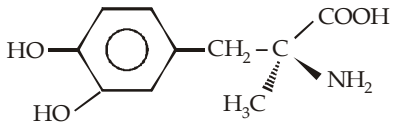


No asymmetric carbon, and the substituents at *ortho* positions are not large enough to restrict rotation, hence the molecule is not chiral

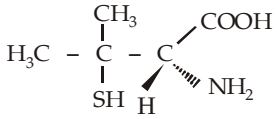
2. (a)



(*S*)–Ibuprofen

(b) 

(*S*)–Methyldopa

(c) 

(*S*)–Penicillamine

TEST YOUR UNDERSTANDING - 3.11

1. o.p. = $\frac{75-25}{100} = 0.5$

   ∴ Observed rotation of the mixture = Rotation of pure enantiomer × o. p. = –158 × 0.5 = –79°.

2. o.p. = $\frac{+1.4}{+8.7} = 0.16$ or 16%

   Optical purity of 16% means that the mixture has 16% (*R*) and 84% (*RS*)–; i.e. 16 + 42 = 58% of *R* and 42% of *S* enantiomer.

3. o.p. = e.e. = $\frac{(6-4)}{(6+4)} = 0.2$ or 20%

   Enantiomeric excess of 20% indicates that the (+)–enantiomer is 20% excess; in other words the composition of the mixture is 20% (+)–enantiomer + 80% (±)-mixture ***or*** 20% (+)-enantiomer + 40% (+)–enantiomer + 40% (–)–enantiomer

   Observed rotation = rotation of pure * enantiomer × o.p. = +13.5° × 0.2 = +2.7°.

   *Since the mixture has excess amount of (+)–enantiomer, rotation of (+)–pure enantiomer should be taken which is +13.5°.

4. The given solution has

   (i) 10 mL × 0.10 M = 1 mmol. of the *R* enantiomer, and

   (ii) 30 mL × 0.10 M = 3 mmol. of the *S* enantiomer.

   Thus the solution has total of 4 mmoles of which 1 + 1 = 2 mmol. are present as racemic mixture and 2 mmol. as pure *S* enantiomer.

   ∴ o.p. = $\frac{\text{excess of one enantiomer over the other}}{\text{entire mixture}} = \frac{2}{4} = 0.5$

   We know that

   o.p. = $\frac{\text{observed specific rotation}}{\text{specific rotation of the pure enantiomer}}$

   $0.50 = \frac{+4.8°}{x}$; $x = +9.6°$

   It is important to note that here the *S* enantiomer is in excess, hence +9.6° is the specific rotation of the *S* enantiomer and –9.6° will be the specific rotation of the *R* enantiomer.

5. The specific rotation of (–)–2-butanol = –13.5°

   o.p. = $\frac{-0.45°}{-13.5°} = 0.33$ or 3.3%

   Thus the product has 3.3% excess of one of the enantiomers of 2-butanol which is (–)–enantiomer because the product has (–)–specific rotation. Thus the product has 3.3% (–)–enantiomer + 96.7% (±)–mixture or 3.3% + 48.4% (–)–enantiomer + 48.3% (+)–enantiomer or 51.7%(–)–enantiomer + 48.3% (+) enantiomer.

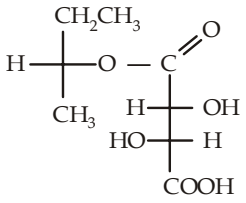
TEST YOUR UNDERSTANDING - 3.12

1. (a) Two (a diastereomeric pair)

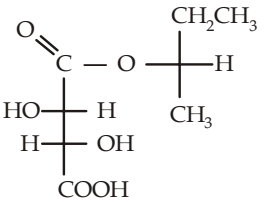
   (b) Three

   (c) Two chirality centers are identical due to same *R*,*R*-tartaric acid component, and one chirality center due to 2-butanol component is different.

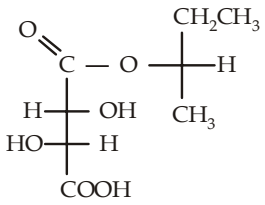
2. Any diastereomeric pair could be separated by a physical process like distillation or crystallization. Diastereomers are found in parts *(a)*, *(b)* and *(d)*. Since the two structures in *(c)* are enantiomers, they could not be separated by normal physical means.

3. 

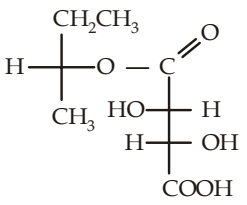
   (*R*)-2-Butyl (*R*, *R*)-tartrate

   (*S*)-2-Butyl (*S*, *S*)-tartrate

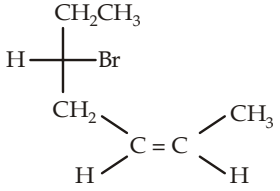
   (*S*)-2-Butyl (*R*, *R*)-tartrate

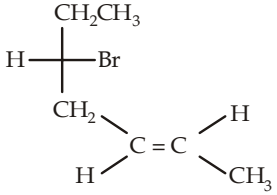
   (*R*)-2-Butyl (*S*, *S*)-tartrate

TEST YOUR UNDERSTANDING - 3.13

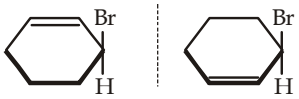
1. The compound has a carbon-carbon double bond whose each sp^2 hybridised carbon is differently substituted, so it will show geometrical isomerism. Further, it also has one chiral carbon, each of the geometric isomer (*cis* and *trans*) can exist in (*R*) and (*S*) form. So on the whole, there will be 4 stereomeric isomers.

   cis - *R*
   cis - *S*

   trans - *R*
   trans - *S*

2. (a) 

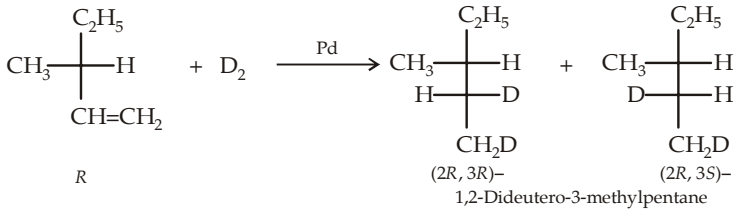
   3-Bromocyclohexene

   (b) 

   4-Bromocyclohexene

TEST YOUR UNDERSTANDING - 3.14

1.



1,2-Dideutero-3-methylpentane

EXERCISE 3.1

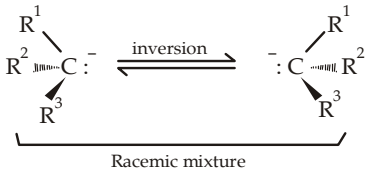
1	(b)	**6**	(d)	**11**	(d)	**16**	(c)	**21**	(b)	**26**	(d)	**31**	(b)	**36**	(d)	**41**	(d)	**46**	(d)	**51**	(a)	**56**	(b)	**61**	(c)
2	(b)	**7**	(c)	**12**	(d)	**17**	(c)	**22**	(d)	**27**	(c)	**32**	(d)	**37**	(b)	**42**	(c)	**47**	(c)	**52**	(a)	**57**	(d)	**62**	(a)
3	(a)	**8**	(d)	**13**	(b)	**18**	(d)	**23**	(d)	**28**	(a)	**33**	(d)	**38**	(c)	**43**	(b)	**48**	(d)	**53**	(d)	**58**	(c)	**63**	(b)
4	(b)	**9**	(c)	**14**	(b)	**19**	(c)	**24**	(a)	**29**	(a)	**34**	(d)	**39**	(a)	**44**	(c)	**49**	(a)	**54**	(a)	**59**	(b)	**64**	(d)
5	(d)	**10**	(b)	**15**	(c)	**20**	(c)	**25**	(d)	**30**	(d)	**35**	(c)	**40**	(c)	**45**	(a)	**50**	(a)	**55**	(c)	**60**	(b)		

1. When switching (interchanging) of two ligands attached to an atom result in a new stereoisomer, the atom is called *stereocenter*. If the new stereocenter is an enantiomer, the stereocenter is a chiral center, otherwise not. Thus all stereocenters are not chiral but the reverse is true, i.e. all chiral centers are stereocenters.

2. Note the definitions from the above question. Maleic acid has a stereocenter, but not optically active, $CH_3CH(OH)COOH$ has a stereocenter and is optically active.

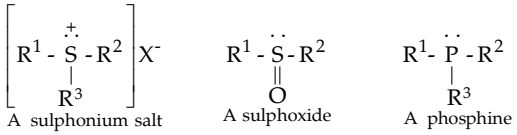
3. A tetrahedral atom bearing four different substituents is known as stereogenic center. In (b) the tetrahedral carbon bears two identical substituents.

4. The carbon of a carbocation and a free radical (C^+, $C^{\bullet}$) is sp^2 hybridized leading to a flat geometry. Thus such carbon has a plane of symmetry and is achiral, no matter it may have three different groups. On the other hand, carbon of carbanion is sp^3 hybridised and thus theoretically it can exist as a pair of enantiomers provided the three ligands attached to carbon are different. However, in practice a rapid "umbrella" type inversion converts either enantiomer to a racemic mixture.



The energy required for this inversion is very low in carbon, thus leading to rapid inversion.

5. The energy required for inversion about S and P (third period elements) is sufficiently high so the properly substituted sulphur and phosphorus compounds can be resolved.



A sulphonium salt | A sulphoxide | A phosphine

6. (a) $CH_3CH_2\overset{*}{C}HCH=CH_2$ (b) $CH_3CH_2\overset{*}{C}HC\equiv CH$

(c) $CH_3CH_2\overset{*}{C}H\ CHCH_3$ (with CH_3 and CH_3)

7. $[\alpha]_D = \dfrac{[\alpha]_{obs.}}{\ell c}$, where c is concentration in g/mL and ℓ is length of the tube in dm (decimeters).

$\therefore [\alpha]_D = +1.2°/(1)(0.075) = +16°$

8. $[\alpha]_{obs.} = [\alpha]_D \times \ell c = -16° \times 0.50 \times 0.35 = -2.8°$

9. Observed rotation depends on the concentration of the solution and the length of the tube containing the solution. Specific rotation is a constant and is independent of concentration and path length.

10. $\alpha_{obs.} = 0.80(-12°) = -9.6°$

11. The fact that the carvone enantiomers smell differently is due to the fact that the receptor sites in the nose are chiral, and only the correct enantiomer will fit its particular site (just as a hand requires a glove of the correct chirality for a proper fit).

12. Structure (d) is the non superimposable mirror image of the given structure of (+)-carvone.

13. Nonsuperimposability of mirror image is the sole criteria for enantiomerism.

14. A rapid umbrella type inversion rapidly converts the structure III to its enantiomer; hence the two enantiomers are not separable.

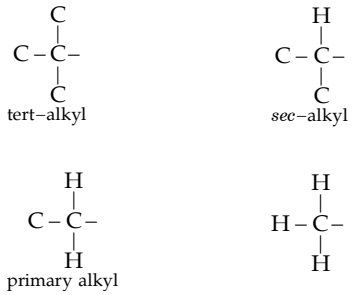
15. Reaction (a) is enzyme catalysed so it will form only one enantiomer of malic acid, reaction (b), again involves a chiral reagent, so the product will give two diasteromers, reaction (c) is an example where achiral reactant is converted into chiral product without the use of any chiral reagent, so the resultant product will be a racemic mixture.

16. I and IV, both are symmetric molecules.

17. Racemic mixture to be resolved is (*R*,*S*)-1-phenylethylamine, while the resolving agent that remains common in the two diastereomers formed is (–)-malic acid.
The resolving agent (–)– malic acid is found to be (*S*)- as shown by the name of one of the diastereomer, so the other diastereomer will be (*S*)-1-phenylethylammonium (*S*)-malate.

18. III is *meso* so it is certain that it is optically inactive. Although I and II are enantiomers, it is not certain which one is (+)-stereoisomer and which one is (–)–. It can be determined only by polarimeter.

19. Structure A is converted into B by switching two groups.

20. 

21. Each carbon of phenyl group is doubly bonded, hence it is counted to have three C's. In $(CH_3)_3C$– group the C_1 has three C's while all other carbons are having only one C and three H.

22. The priority order of the four groups is different in two cases
(A) OH, CH_2CH_3, CH_3, H
(B) OH, CHO, CH_2OH, H

23. Each of the three structures can be obtained from the parent compound (*S*)-2-butanol by two switches, hence all the three are (*S*)-2-butanol.

24. Sign of rotation is a molecular property unrelated to configuration.

25. For *meso* structure the 2*R*, 3*S* is identical with the 2*S*, 3*R*, it is not necessary to indicate the number and thus *R*, *S* or *S*, *R* designation is also correct.

26. The stereoisomers (a) and (c), i.e. those where $n = 1$ or an odd number, have a plane of symmetry cutting through the central carbon. The stereoisomer where $n = 2$ or an even number has the symmetry plane cutting through the central C–C bond.

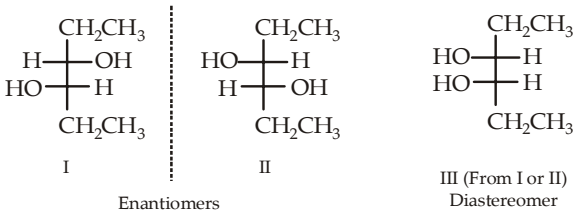
27. $CH_3CH_2CH_2CH_2Cl$, $CH_3CH_2CHClCH_3$ (enantiomers)

28. Sign of rotation and R/S designation of different compounds have no relation. Here the reactant and product belong to the same designation because there is no change in the priority order of the four substituents.

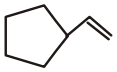
29. Optically active 2-iodobutane reacts with I^- with inversion at chiral carbon, leading to racemization.

$$(+)-CH_3CHICH_2CH_3 + I^- \rightleftharpoons (-)-CH_3CHICH_2CH_3$$

30. An enantiomer can be converted into diastereomer by inverting two groups on the asymmetric carbon atom.



31. $CH_3CH = C(Cl)CH_2CH_3$. Here all the four groups around doubly bonded carbon are different, so *cis-trans* nomenclature is not possible.

32.  Vinylcyclopentane

33. All show geometric isomerism

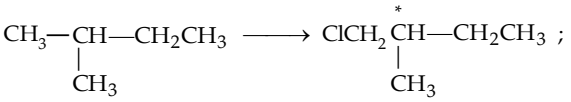
34. Since *trans*-2-butene is non-polar, it does not have dipole-dipole attraction.

35. Hydrocarbon with minimum carbon, and capable of showing *cis*, *trans* as well as optical isomerism should have following structure.

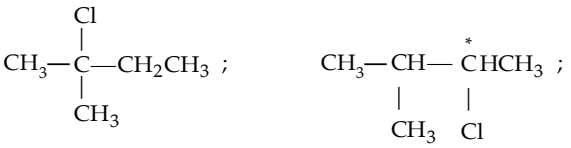
$$CH_3CH = CH\underset{\displaystyle CH_3}{\underset{|}{C}}HC_2H_5$$

36. Stereoisomers which are not enantiomers are known as diastereomers. The former is E–(*trans*)– isomer while the latter is *Z*-(*cis*-) isomer.

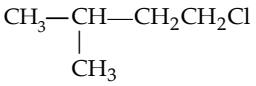
37. First of all write down all possible isomers of monochloroisopentane ; observe the chiral carbon atom(s) in all isomers



Isopentane
I



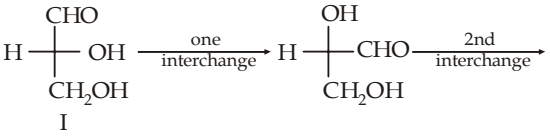
II III



IV

Thus only structures I and III can exhibit optical isomerism. Further each is having 1 chiral carbon atom, so 2 stereoisomers (*d* and *l*) are possible for each compound.

38. Structure I is changed to II by three (even number) interchange of groups, thus they should be enantiomers.

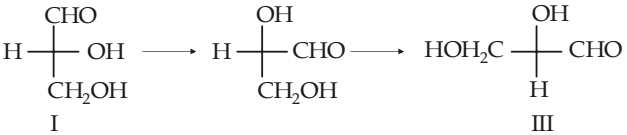


I



II

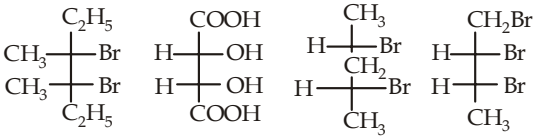
On the other hand, structure III is derived from I by two interchanges, thus they should be identical.



I III

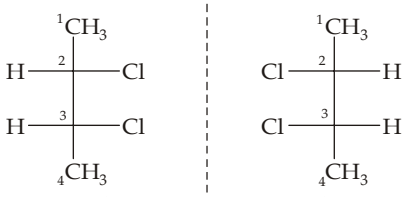
39. Rate of reaction between a chiral molecule and an achiral reagent is same with both of the enantiomers, while it is different with a chiral reagent in the two enantiomers. Every molecule containing chiral carbon atom is not chiral, *e.g.* mesotartaric acid has two chiral carbon atoms yet the molecule is achiral. A chiral molecule does not necessarily have chiral atom, *e.g.* properly disubstituted allenes have no chiral atom, yet they show enantiomerism.

40. A compound having two similar chiral atoms can form *meso* form. The first three compounds have two similar chiral atoms, while in (*iv*) the chiral atoms are different.



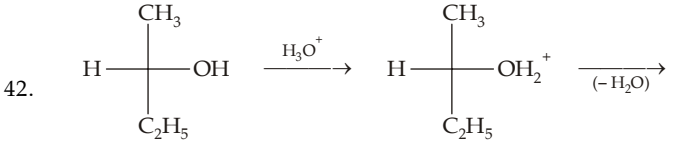
(i) (ii) (iii) (iv)

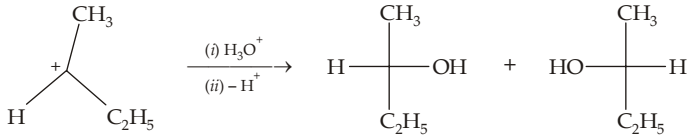
41.



2(S) – 3(R) – 2(R) – 3(S) –

42.



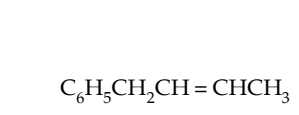


Racemic modification (optically inactive)

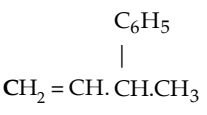
43. Configuration of the product changes (from that of reactant) only when the bond attached to the chiral atom is broken during the reaction. Since, here configuration of the reactant is S, the product should also have S configuration, no matter the sign of rotation is different.

44. Only reaction *c* does not involve breaking of bonds to the chiral C, other reactions involve breaking of bonds to the chiral C.

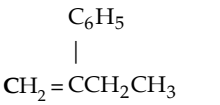
45. Draw structure and observe each of the doubly bonded carbon atom. Geometrical isomerism is not possible in compounds *b*, *c* and *d* due to carbon atom represented by bold letter.



1-Phenyl-2-butene (*a*)



3-Phenyl-1-butene (*b*)

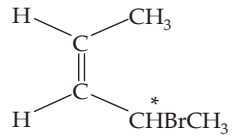


2-Phenyl-1-butene (*c*)

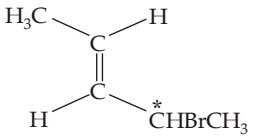


1, 1-Dipenyl-1-propenen (*d*)

46.



cis- ; (+)- and (–)-

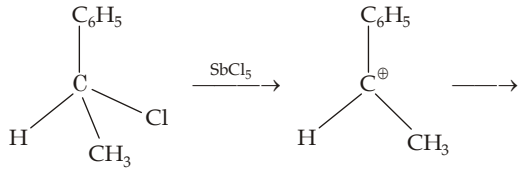


trans- ; (+)- and (–)-

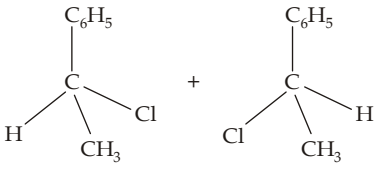
(+) – and (–) – isomers in each is possible because of presence of chiral carbon atom, marked by asterisk.

47. D – (+) – Glyceraldehyde is taken as arbitrary standard for D, L-nomenclature of configuration.

48. $SbCl_5$, being a Lewis acid, will take up chlorine as chloride ion forming a carbocation as an intermediate, which, being planar, can be attacked on either side of the plane forming equal amount of the two enantiomers.

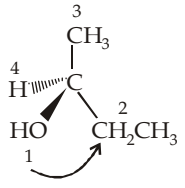


(+)-2-Phenyl-2-chloroethane Carbocation (planar)

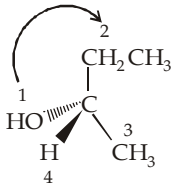


Racemic mixture

49.



Here the lowest priority group (H) is away from the observer, hence usual R/S nomenclature is applicable. Thus it is *S*.



Here the lowest priority group is towards the observer, hence the usually assigned (R) configuration is reversed to *S*.

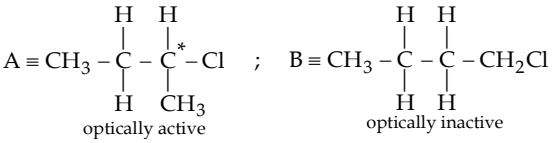
Thus the two structures are *S*, *S*, hence identical.

Regiomers are those structural isomers which differ in the position of the functional group.

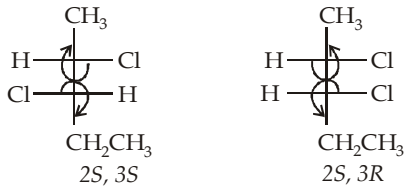
EXERCISE 3.2

>1 ONE CORRECT OPTION	1	(a,c)	2	(b,d)	3	(b,c,d)	4	(a,c)	5	(b,c,d,e)
	6	(a,b,c,d)	7	(a,d)	8	(a,b)	9	(a,b,d)	10	(a,b,d)
	11	(b,c,d)	12	(a,b,c)	13	(a,b)	14	(a,d)	15	(a,b)
	16	(a, c)	17	(a, c, d)	18	(b, c)	19	(a, b, c, d)	20	(b, c, d)
	21	(b, c, d)	22	(a, d)						
PASSAGE 1	23	(c,d)	24	(c)	25	(d)	26	(a,b)		
PASSAGE 2	27	(b)	28	(a)	29	(c)				
PASSAGE 3	30	(a)	31	(c)	32	(b)				
MATCHING TYPE QUESTION	33	(A) - a, b, c, d; (B) - b, d; (C) - c, d; (D) - c, d								
	34	(A) - a, c ; (B) - a, b ; (C) - a, b (D) - d, c								
	35	(A) - a, c ; (B) - b ; (C) - d, c (D) - c								
A/R	36	(b)	37	(a)	38	(d)	39	(d)	40	(c)
True / False	41	FALSE	42	TRUE	43	FALSE	44	FALSE	45	TRUE
	46	FALSE								

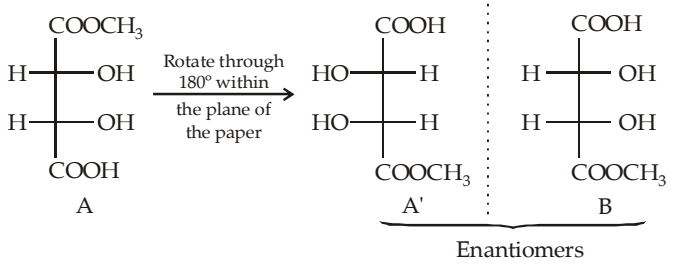
1. Convert these Newmann projections into open chain structures.



2.



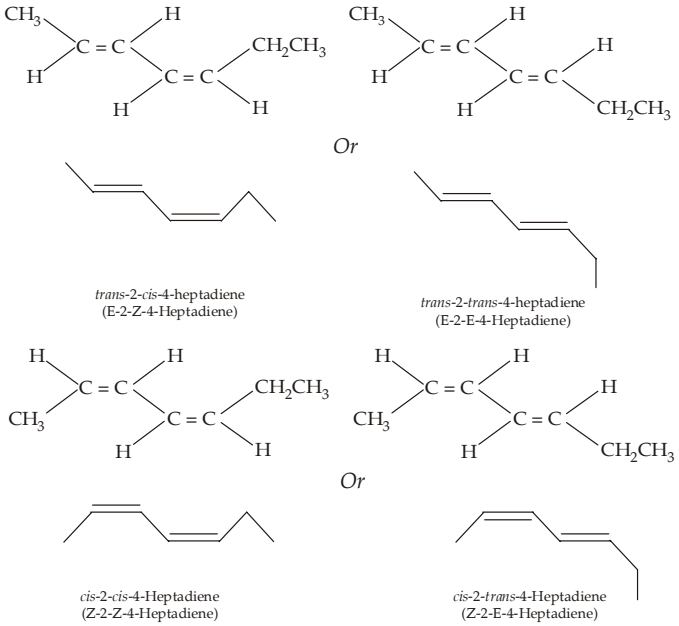
3. Rotation of A through 180° within the plane of the paper gives A´. Now since A = A´, hence A is an enantiomer of B.



Further C is diastereomer of A and B.

EXERCISE 3.3

1. Four geometrical isomers are possible.



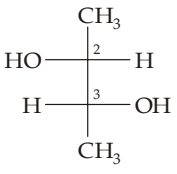
2. $CH_3CH_2CH_3 \xrightarrow{Cl_2} CH_2Cl\overset{*}{C}HClCH_3 \xrightarrow{Cl_2}$

Optically active (A)

$CH_2ClCHClCH_2Cl$ + $CHCl_2\overset{*}{C}HClCH_3$ + $CH_2ClCCl_2CH_3$

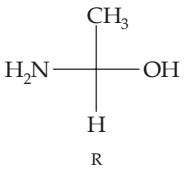
Optically inactive Optically active Optically inactive

3. (*i*)



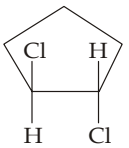
2R, 3R

(*ii*)



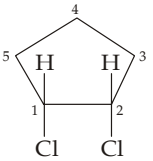
R

(*iii*)



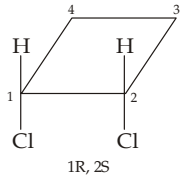
1(R), 2(R)

(*iv*)



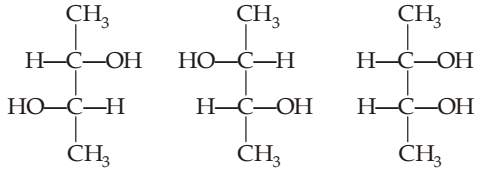
1(R), 2(S)

(*v*)



1R, 2S

4. (*a*) (*i*) $CH_3.\overset{OH}{CH}.\overset{OH}{CH}.CH_3$. Like tartaric acid, it can exist in three stereoisomeric forms (*d*-, *l*-and *m*-).



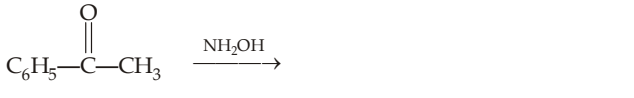
(*ii*) $C_6H_5.CH = CH.COOH$. It can exist in two stereoisomeric forms (*cis*- and *trans*)



cis *trans*

(*b*) I and III are enantiomers ; while I and II ; and II and III are diastereomeric pairs.

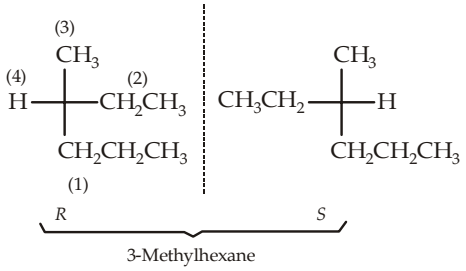
5.



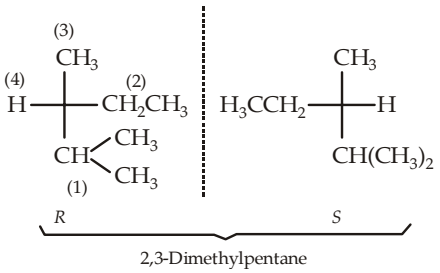
syn- and *anti*-Ketoximes

6. (*a*) *trans*-1, 2-Dimethylcyclopropane.
(*b*) *cis*-1, 2-Dimethylcyclohexane.

7. The simplest possible optically active alkane has H, CH_3, C_2H_5 and C_3H_7 as ligands.



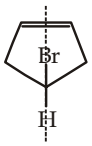
3-Methylhexane



2,3-Dimethylpentane

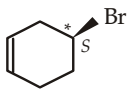
8. (a) Enantiomers (b) Same
(c) Enantiomers (three exchanges)
(d) Diastereomers
(e) Same (one can be converted to other when rotated through 180°).

9. (a)



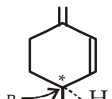
Achiral
(plane of symmetry)

(b)



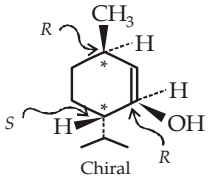
Chiral

(c)



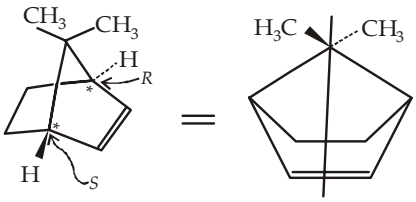
Chiral

(d)



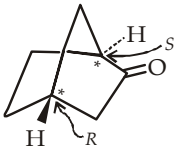
Chiral

(e)



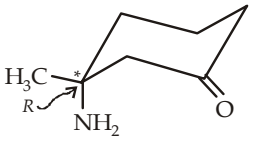
Plane of symmetry
meso, achiral

(f)



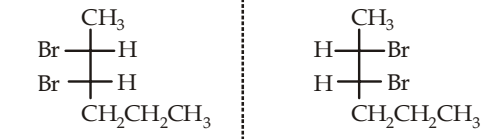
Chiral

(g)

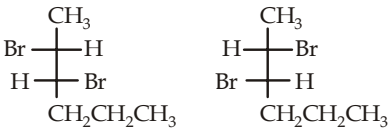


Chiral

10. (a)

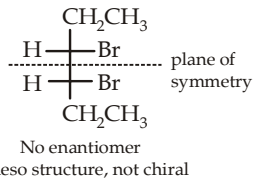


no plane of symmetry — Enantiomers — chiral structure

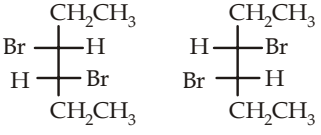


chiral structure
(diastereomers)

(b)

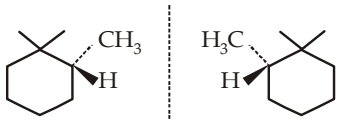


No enantiomer
a meso structure, not chiral



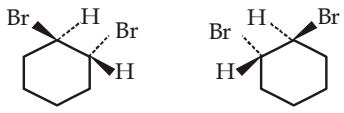
chiral structure
Diastereomers

(c)

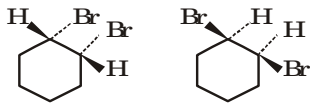


Enantiomers
Chiral structure, no plane of symmetry
no diastereomer

(d)

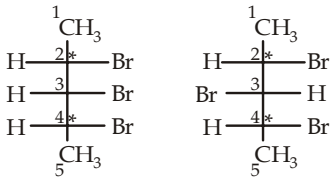


No plane of symmetry
Chiral structure



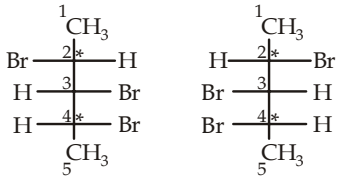
Chiral structure
Diastereomers

11. (a)



A (2*S*, 4*R*) B (2*S*, 4*R*)

meso, diastereomers

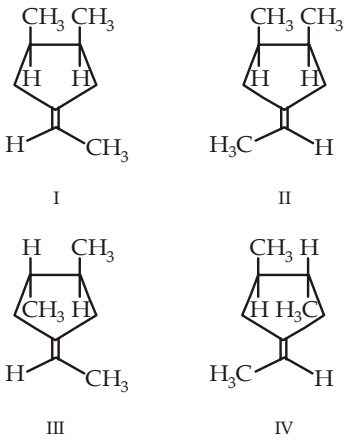


C (2*R*, 4*R*) D (2*S*, 4*S*)

enantiomers

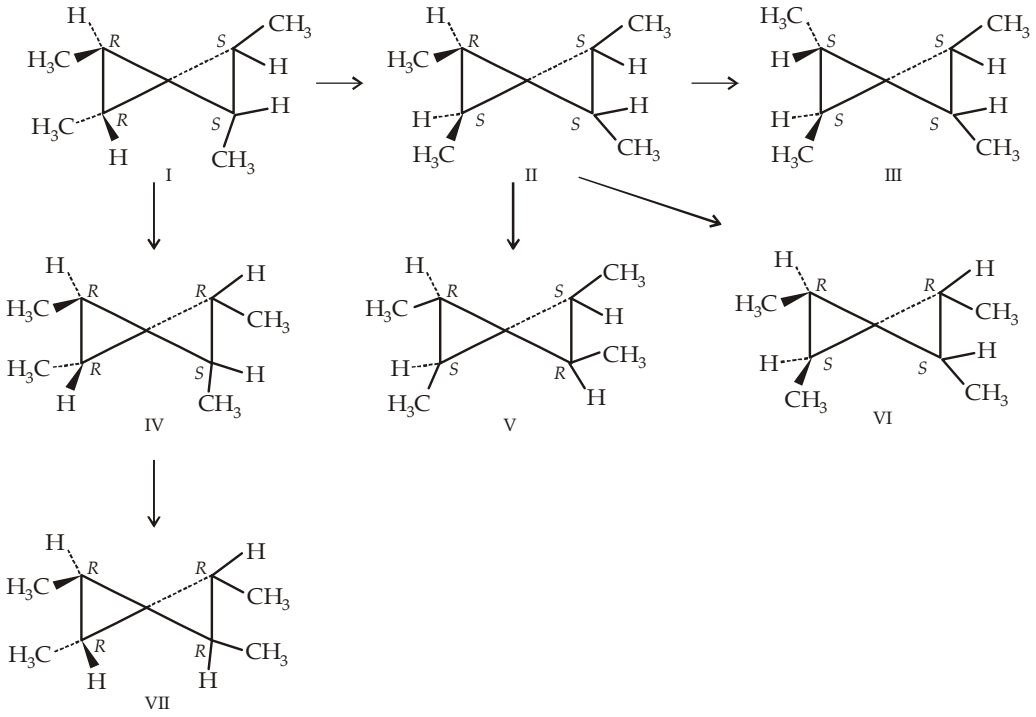
(b) In structures A and B, **C–3** is not chiral because it has two identical groups. However, it **is stereogenic** because interchanging the H and Br at C–3 in A gives the different meso (diastereomer) structure B.
In structures C and D, C–3 is not stereogenic because when H and Br at C–3 are interchanged and the structure is rotated through 180°, C is converted into D. Hence, **C–3 is not stereogenic**.

12. (a)



I and II; III and IV are enantiomers. All other pairs are diastereomers.

12. (b)

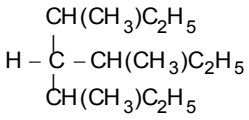


II and IV; III and VII; V and VI are enantiomers; I is *meso*.

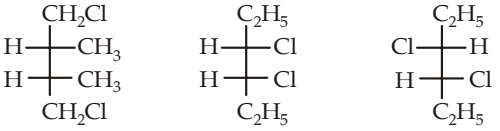
13. $CH_3CH_2\underset{A}{\overset{Cl}{\underset{|}{C}}}HCH = CH_2$ $\qquad$ $ClCH_2\underset{B}{\overset{CH_3}{\underset{|}{C}}}HCH = CH_2$

14. ^1COOH / ^2CHOH / ^3CHOH / ^4CHOH / ^5CHOH / ^6COOH It has four chiral carbons, of which C_2 and C_5 are identical, and C_3 and C_4 are identical. The total number of stereoisomers is 10, of which 8 (four enantiomeric) are optically active and two are optically inactive (*meso*). Four enantiomeric pairs are *RRRR* and *SSSS; RRRS* and *SSSR; RRSR* and *SSRS; RSSR* and *SRRS*; the two *meso* isomers are *RRSS* and *RSRS*.

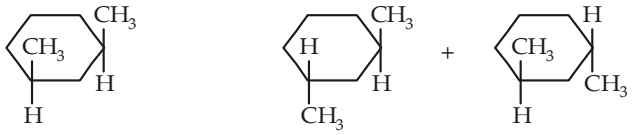
15. Yes;



Note the presence of three chiral carbons, one on each *tert*-butyl group. Since all three alkyl groups are equivalent, *RSR* = *SRR* = *RRS*, so only two enantiomeric pairs are possible; *RRR* and *SSS*; *RRS* and *SSR*.

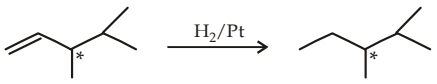
16. 

17. Three. If H_2 adds to both double bonds from the same face, the product will be *meso*. If H_2 adds to the double bond from opposite faces, the product will be racemic.



meso racemate

18. (a) The product has three stereocenters; the carbon bearing H and OH, and the two carbons bearing double bond.
    (b) No, the product has no asymmetric carbon atom.
    (c) Although the product has no asymmetric carbon atom, yet the molecule is chiral and hence it is optically active. Interchange of two bonds of any of the stereocenter makes the enantiomer.

19. (a) 

    (b) The four ligands on the chiral carbon are $CH_2 = CH$, H, CH_3, $CH(CH_3)_2$ whose priority order in decreasing sequence is $CH = CH_2$, $CH(CH_3)_2$, CH_3 and H. However, in the product the decreasing priority order of the groups is changed : $CH(CH_3)_2$, CH_2CH_3, CH_3 and H, so the product will be *R*.
    (c) Specific rotation is a molecular property which can be determined only by polarimeter.

20. (a) $$[\alpha]_D = \frac{-30^\circ}{(0.10\ g/\ mL)\,(1.0\ dm)} = -300^\circ$$

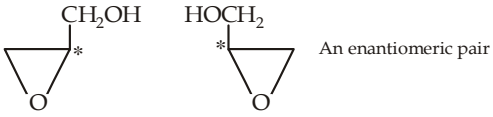
    (b) $$[\alpha]_D = \frac{+165^\circ}{(0.05\ g/\ mL)\,(1.0\ dm)} = +3300^\circ$$

    The two rotation values can be explained by recognizing that the substance is a powerful optically active substance. The first reading (–30°) was really +330° (+360° – 30°).

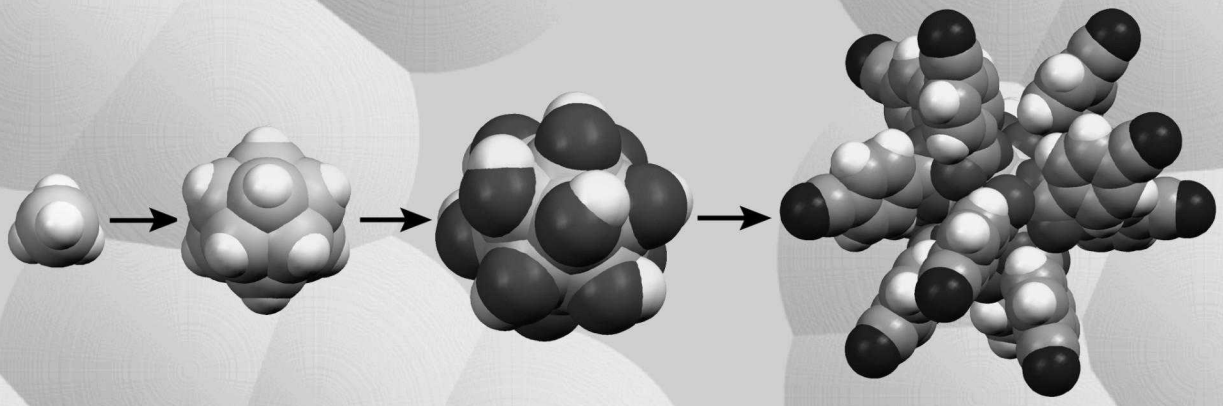
    $$[\alpha]_D = \frac{+330^\circ}{(0.10\ g/\ mL)\,(1.0\ dm)} = +3300^\circ$$

    Thus the specific rotation in both cases is +3300°.
    (c) No, the apparent 0° rotation could be +360° or –360°, or an integral multiple of these values.

21. The molecular formula $C_3H_6O_2$ of X indicates that it has an index of hydrogen deficiency of 1. Thus compound X could possess a carbon-carbon double bond, or a ring. Stereoisomeric forms are not possible in a C_3 compound having carbon-carbon double bond. Hence, the compound X should be a cyclic compound containing oxygen in the ring (oxirane).



An enantiomeric pair



4 Organic Reactions and their Mechanism

CHAPTER HIGHLIGHTS

4.1 Types of Reaction Intermediates
4.2 Types of Reagents
4.3 Types of Organic Reactions
4.4 Energetics of Organic Reactions
4.5 Competitive Reactions (Thermodynamic and Kinetic Control)
4.6 Mechanism of Substitution Reactions
4.7 Mechanism of Addition Reactions
4.8 Mechanism of Elimination Reactions
EXERCISES
SOLUTIONS

4.1 Types of Reaction Intermediates

Reactions involving organic compounds are known as organic reactions. Generally, organic reactions involve two steps : (*i*) breaking of the old bond and (*ii*) formation of new bond. Breaking of old bond may take place either homolytically (one electron remains with each of the two atoms) leading to the formation of **free radicals** as intermediate or heterolytically (both the bonding electrons go to the electronegative atom) leading to the formation of *ions* (**carbocations** or **carbanions**).

$H_3C\cdot$ (Free radical) $H_3C^{\oplus}$ (Carbocation) — electron deficient

$H_3C:^{-}$ Carbanion — electron rich (nucleophiles)

Thus on the whole, there are three reaction intermediates, all of which are trivalent and have a tendency to become tetravalent accounting for high reactivity of these species.

When above types of reaction intermediates are formed, formation of the new bond may take place in a separate and next step by combining other reagent. However, in some cases, both steps (breaking of old bond as well as formation of new bond) occur simultaneously. Thus in such cases, well known intermediates are not formed but an imaginary **transition state** having zero life time is formed.

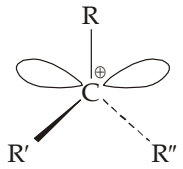
$$HO^{-} + CH_3{-}Cl \longrightarrow \underset{\text{Transition state}}{HO^{\delta-} \cdots CH_3 \cdots Cl^{\delta-}} \longrightarrow HOCH_3 + Cl^{-}$$

Reactions involving formation of free radicals are known as **free radical reactions,** while those involving ions are known as **ionic reactions.**

Free radical reactions occur in gas phase or in non-polar solvents. These are initiated and catalysed by light, high temperature, oxygen or peroxides and their rate is not influenced by change in temperature. Ionic reactions occur in presence of polar solvents. These are not effected by light, oxygen or peroxides but catalysed by acids and bases. Generally, rate of ionic reactions increase with increase in temperature.

4.1.1 Carbocations, Carbonium ions or Carbenium ions

Carbocations are defined as species with a positively charged carbon having only three covalent bonds. The carbon atom of carbocation is sp^2 hybridized. The three sp^2 orbitals are utilised in forming bonds with three substituents, the remaining p orbital of carbon remains empty. Thus during reaction of a carbonium ion with a nucleophile, the latter may attach to it on either side of the plane leading to the formation of racemic mixture (of course, if the parent compound is chiral).



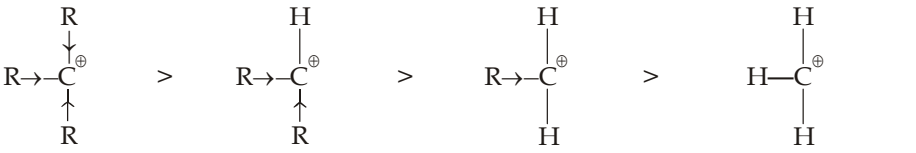
Formation : Carbocations are generally formed in acid catalysed reactions and in solvolysis of the C—X bond.

(a) (*i*) $CH_2 = CH_2 \overset{H^+}{\rightleftharpoons} CH_3 - \overset{+}{C}H_2$ (*ii*) $R - OH \overset{H^+}{\rightleftharpoons} R - \overset{+}{O}H_2 \rightleftharpoons \overset{+}{R} + H_2O$

(b) (*i*) $(CH_3)_3C - \overset{\curvearrowright}{Cl} \longrightarrow (CH_3)C^+ + Cl^-$

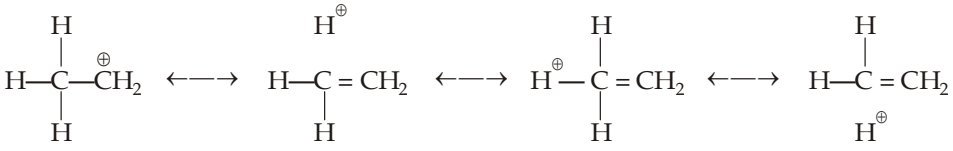
(*ii*) $C_6H_5 - N^+ \equiv NCl^- \longrightarrow C_6H_5 - \overset{\curvearrowright}{N^+} \equiv N \longrightarrow C_6H_5^+ + N_2$

On the basis of relative stability*, carbocations are classified into two types, *viz.* less stable or transient (*e.g.* simple alkyl) and stable (*e.g.* aryl substituted methyl and allyl) carbocations. **Relative stability of simple alkyl carbocations is explained on the basis of inductive effect** and **hyperconjugation**.



tert-Alkyl (+ charge dispersed by 3 alkyl groups) > *sec*-Alkyl (+ charge dispersed by 2 alkyl groups) > *pri*-Alkyl (dispersed only by 1 alkyl group) > Methyl carbocation (+ charge not dispersed)

Similarly, due to **hyperconjugation,** positive charge on different types of carbocations is dispersed on different number of hydrogen atoms, *e.g.* on ethyl carbocation the positive charge can disperse over 4 positions.

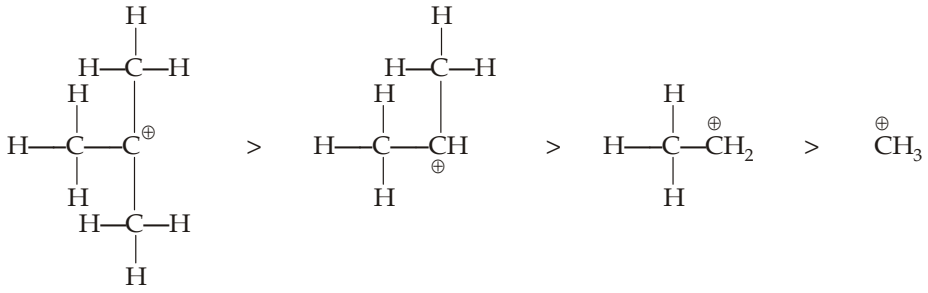


Dispersal of positive charge over 4 positions in ethyl carbocation

In case of *sec*-carbocation, more equivalent structures can be written than for ethyl carbocation (a primary carbocation); further still greater number of such structures can be written for a tertiary carbocation. Hence the relative stability of the simple alkyl carbocations will follow the following order.

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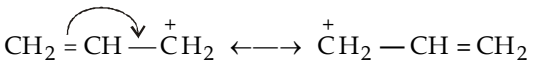
* Remember that greater the probability of the positive charge (in case of carbocations), negative charge (in case of carbanions) or an odd electron (in case of free radicals) to be neutralised or dispersed in a species, more will be its stability. Conversely, greater is the probability of the charge to be concentrated over a particular atom, lesser will be the stability of that species. In other words, dispersal of the charge or the odd electron present on a species produces stability, while concentration of the charge produces unstability.



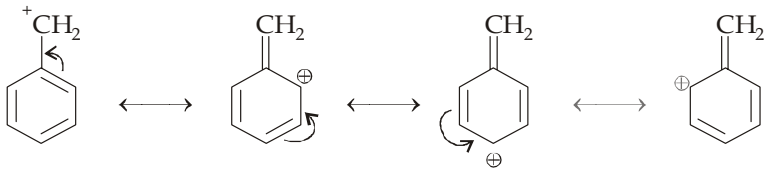
tert-Butyl carbocation (+ charge can disperse over 9 other positions) > *sec*-Isopropyl carbocation (+ charge can disperse over 6 other positions) > Ethyl carbocation (+ charge can disperse over 3 other positions) > Methyl carbocation (No dispersal of + charge)

A carbocation is more electron deficient (they have 6 electrons) than a free radical (with 7 electrons); hence stability of alkyl carbocations due to hyperconjugation is greater than that of radicals.

Higher stability of allyl and aryl substituted methyl (*e.g.* $Ph_3\overset{+}{C} > Ph_2\overset{+}{C}H > Ph\overset{+}{C}H_2$) carbocations is due to dispersal of positive charge due to resonance.

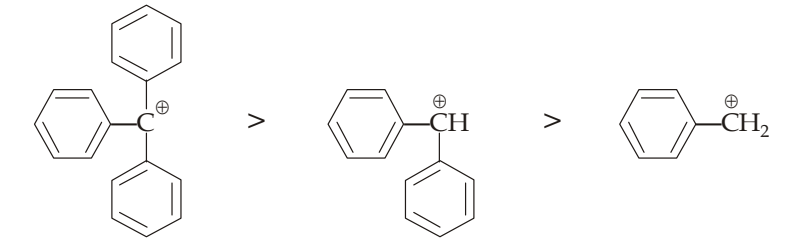


Resonating structures of allyl carbocation



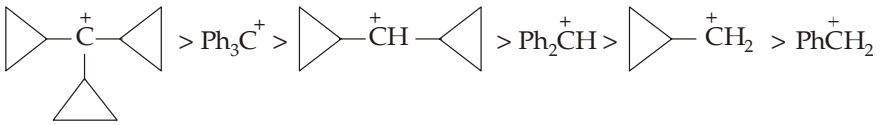
Resonating structures of benzyl carbocation

Since positive charge on $Ph_2\overset{+}{C}H$ can disperse over 7 positions, while that on $Ph_3\overset{+}{C}$ over 10 positions, relative stability of these carbocations follows the order.



Triphenylmethyl carbocation (dispersal of + charge on 9 other positions) > Diphenylmethyl carbocation (7 other positions) > Benzyl carbocation (3 other positions)

The overall stability order of carbocations is



$$3^\circ > CH_2 = CH\overset{+}{C}H_2 > 2^\circ > 1^\circ > \overset{+}{C}H_3$$

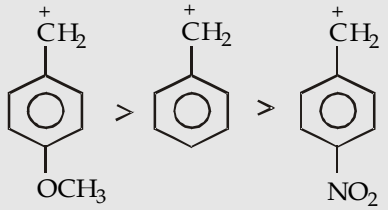
Stability of *tert*-carbocations as well as *tert*-radicals is largely due to *steric relief* achieved in their formation. In the parent compound (*e.g. tri*-isopropylmethyl chloride), carbon atom is tetrahedral and thus has a bond angle of 109.5° with the result the three bulky (isopropyl) groups are pushed by each other producing *steric strain.* When this compound is converted into carbocation or a free radical, the bond angle extends from 109.5° (sp^3) to 120° (sp^2) resulting in the relief of this strain due to increase in space between the bulky groups. Actually such a carbocation would resist addition of a nucleophile because it would again result in the crowding of bulky groups together.

Important Points regarding Stability

(i) Stability of the carbocation decreases with the increase in *s*-character of the carbon bearing positive charge. Thus

% *s*-character $\underset{25}{CH_3\overset{+}{C}H_2} > \underset{33.3}{CH_2=\overset{+}{C}H} > \underset{50}{CH\equiv\overset{+}{C}}$

(ii) Presence of electron-donating substituents tends to stabilize the carbocation as it helps in dispersing the positive charge. Presence of electron-withdrawing groups destabilize the carbocation since it intensifies the positive charge. Thus



(iii) If a hetero atom (O, N etc.) having a lone pair of electrons is present next to positively charged carbon, stability of the carbocation increases due to resonance.

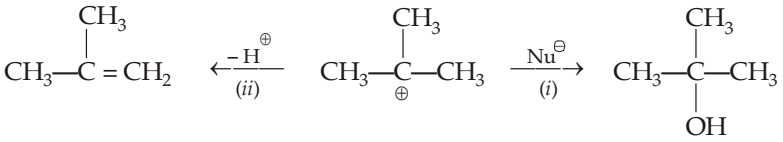
$$CH_3-\overset{+}{C}H-\ddot{O}CH_3 \longleftrightarrow CH_3-CH=\overset{+}{\ddot{O}}CH_3$$

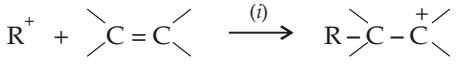
(iv) Because of resonance, acylium ion is almost as stable as *tert*-butyl carbocation

$$CH_3-\overset{+}{C}=O: \longleftrightarrow CH_3-C\equiv\overset{+}{O}:$$

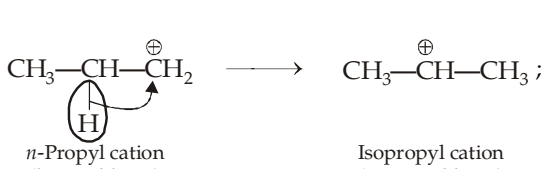
Reactions :

Carbocations undergo mainly three reactions, *viz.* (*i*) combination with a nucleophile,(*ii*) elimination of a proton, if any, from the α-carbon atom, and



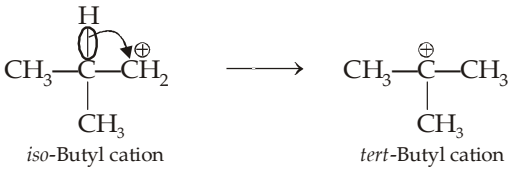


(*iii*) wherever possible, a less stable carbocation (1° or 2°) rearranges to the more stable (2° or 3°) carbocation. This is possible by 1, 2-hydride shift or by 1, 2- $:CH_3^-$ shift



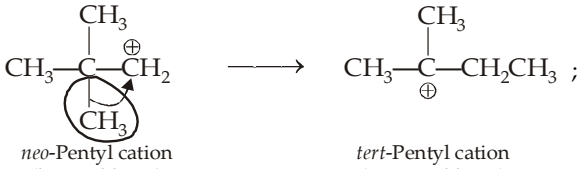
n-Propyl cation (less stable, 1°)

Isopropyl cation (more stable, 2°)



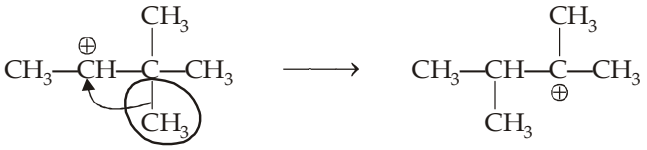
iso-Butyl cation (less stable, 1°)

tert-Butyl cation (more stable, 3°)



neo-Pentyl cation (less stable, 1°)

tert-Pentyl cation (more stable, 3°)

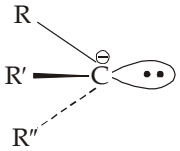


(less stable, 2°)

(more stable, 3°)

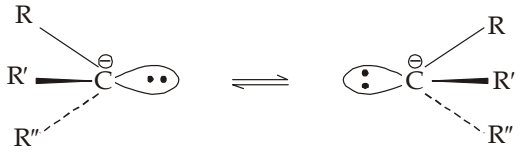
4.1.2 Carbanions

Carbanions are anions of carbon generated by the removal of one of the group attached to a carbon without removing the bonding electrons. The, a carbanion possesses one unshared pair of electrons and three pairs of bonding electrons around the central carbon atom which is sp^3 hybridised.



However, the bond angle between two bonding orbitals is slightly less than 109.5° due to two types of repulsions (*bp-bp* and *lp-bp;* and *lp-bp* > *bp-bp*). The methyl anion is similar to ammonia in shape (pyramidal) ; the two are also *isoelectronic*. Due to tetrahedral geometry, carbanion having three different substituents (chiral carbanion) should show enantiomerism but it is not so because the unshared pair of electrons and central carbon rapidly oscillate from one side of the plane to the other.

This rapid equilibrium between enantiomeric pyramidal structures thus explains the loss of optical activity associated with the asymmetric carbanions.



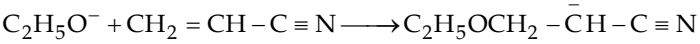
Rapid equilibrium between two enantiomers of a carbanion

Although unconjugated carbanions are sp^3 hybridised, conjugated carbanions are sp^2 hybridised because electron delocalisation results in formation of a double bond in which all involved atoms should be coplanar.

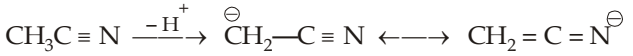


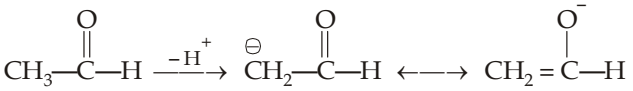
Thus such carbanions will be optically inactive even when it has three different groups (chiral carbanion), because asymmetry of the negative carbon is destroyed with the formation of a carbon-carbon double bond.

When formed – Carbanions are formed by compound having group like –CN, $-NO_2$, etc. On a doubly bonded carbon atom.

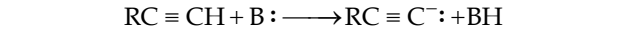


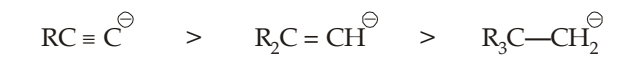
(*a*) having electrons attracting substituents such as —NO_2, —CN or carbonyl which render α-hydrogen atoms relatively acidic. Further once the carbanion is formed by these compounds, it is stabilised by delocalisation of the negative charge.





(*b*) having acetylenic hydrogen atom so that the negative charge is present on acetylenic carbon atom which can accommodate it easily because of its greater *s* character. Thus the relative stability of the following carbanions can be explained.





Acetylenic C (50% *s* character) > Alkenyl C (33.3% *s* character) > Alkyl C (25% *s* character)

(*c*) whose one hydrogen atom is removed forming anion which along with π electrons of the molecule can form *delocalised aromatic system*, characteristic stability of aromatic compounds, *e.g.* cyclopentadiene.



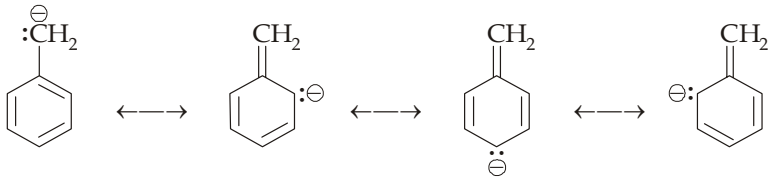
Cyclopentadiene Cyclopentadienyl anion

Triphenylcarbanion (Triphenylmethylanion)

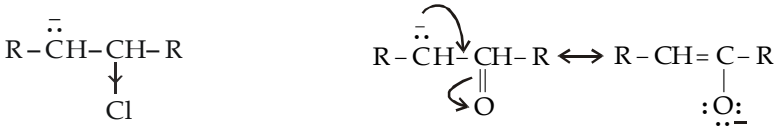
Stability :

Usually, a carbanion is stabilised by resonance if a double bond is located α- to the anionic carbon. This explains the stability of allylic and benzylic carbanions.





If the α-position of a carbanion has an electronegative element (like halogen) or a functional group with a multiple bond, viz. C = C, C = O, $C \equiv N$, NO_2 etc. such carbanions are stabilized by resonance.

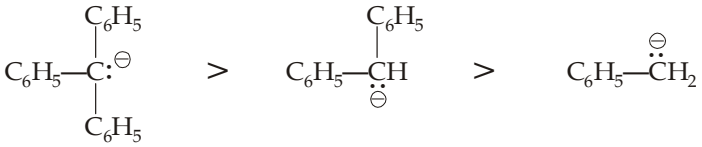


–ve charge is dispersed due to –I effect –ve charge is dispersed due to resonance

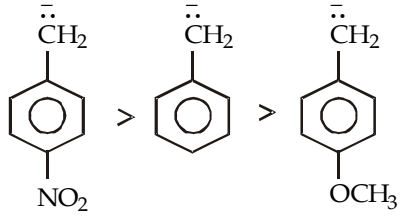
The stability effect of the various α-substituents follows the order :

$$-NO_2 > -COR > -COOR > -CN > -X \text{ (halogen)}$$

Thus the relative stability of carbanion having different number of phenyl groups on anionic carbon can also be explained on the basis of resonance.



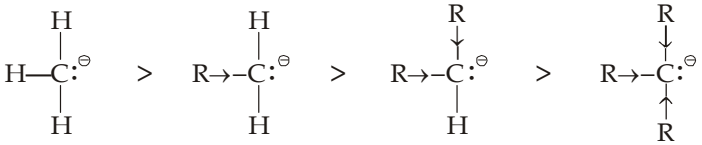
Presence of electron-donating substituents in bezene ring decreases the stability of the carbanion, while presence of electron-withdrawing substituents increases the stability (reverse to the order of corresponding carbocations). For example,



Stability of the carbanions increases with the increase in *s*-character of the carbon bearing negative charge.

$$CH_3\ddot{C}H_2 < CH_2 = \ddot{C}H < CH \equiv \ddot{C}$$

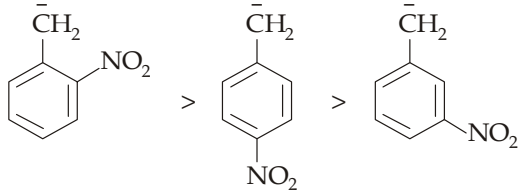
Since presence of electron withdrawing groups increases stability of carbanion as they help in dispersing negative charge on C, presence of electron-pushing groups (alkyl groups) will decrease the stability of carbanions as they concentrate (increase) negative charge on C. Thus the stability order of the simple carbanions is



Methyl 1°-Alkyl 2°-Alkyl 3°-Alkyl

Remember that here the stability order is exactly reverse to that of carbocations and free radicals.

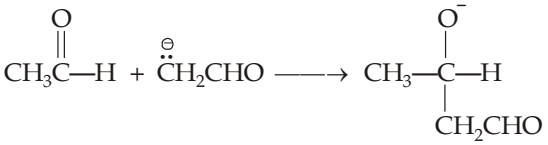
(*i*) $HC \equiv \bar{C} > Ph_3\bar{C} > Ph_2\bar{C}H > Ph\bar{C}H_2 > CH_2 = CH\bar{C}H_2 > C_6H_5^- > CH_2 = \bar{C}H > CH_3^-$

(*ii*) 

Reactions :

Among common reactions of carbanions are their nucleophilic character, viz. (*i*) nucleophilic substitution, and (*ii*) nucleophilic addition (addition to carbonyl carbon, *aldol condensation*).

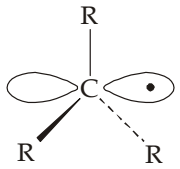
(*i*) $CH_3CH_2Br + CH \equiv C^{\ominus} \longrightarrow CH_3CH_2C \equiv CH$

(*ii*) 

Usually, carbanions do not undergo rearrangement reactions.

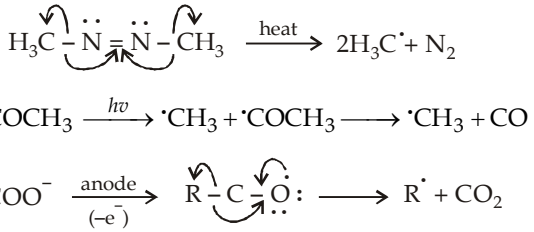
4.1.3 Free Radicals

Free radicals are neutral species having an odd or unpaired electron which imparts it paramagnetism. A free radical is found to have a **planar** configuration in which the carbon atom bearing the odd electron is sp^2 hybridised (as in carbocations) and the odd electron remains in the *p* orbitals.



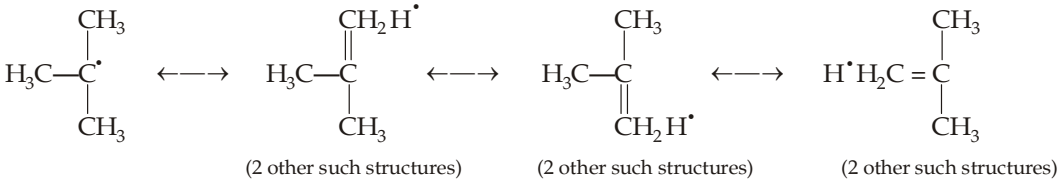
Formation :

Free radicals are often produced when a molecule is supplied sufficient energy (thermal or photochemical). In addition, oxidation-reduction reactions involving the gain or loss of a single electron can also generate free radicals.



Stability :

Stability of free radicals is explained on the basis of resonance (in case of allyl and aryl substituted methyl free radicals) and hyperconjugation (in case of alkyl radicals : 3° > 2° > 1°).



(2 other such structures) (2 other such structures) (2 other such structures)

Hyperconjugation in *tert*-butyl radical

Since allyl and benzyl radicals are stabilized by resonance, these are more stable than alkyl free radicals.



Reactions :

Among the important chemical reactions of free radicals are : (*i*) formation of new free radicals, (*ii*) combination with other free radical, and (*iii*) disproportionation (possible only in selected higher radicals).

(*i*) $CH_4 + Cl\cdot \longrightarrow HCl + \cdot CH_3$ (*ii*) $\cdot CH_3 + \cdot CH_3 \longrightarrow CH_3CH_3$

$\cdot CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl\cdot$ (*iii*) $\cdot CH_3CH_2 \longrightarrow CH_3CH_3 + CH_2 = CH_2$ (Disporportionation)

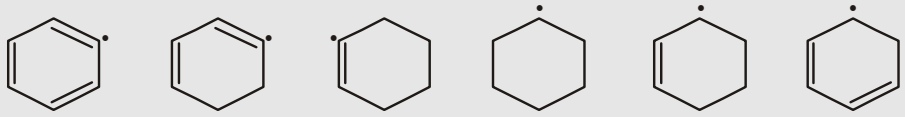
Free radicals have lesser tendency for rearrangement because of the fact that the difference in stability between a primary and a tertiary radical is not as much as that between a primary and a tertiary carbocation.

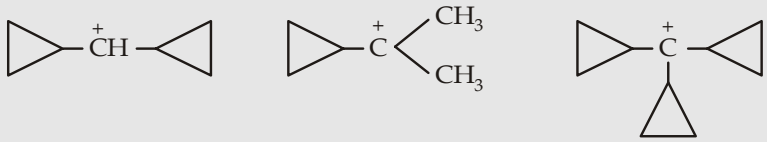
Radical ions :

A free radical obtained by the addition of an electron to a π system is called *radical anion*, while the free radical obtained by the removal of an electron from a π bond is called *radical cation*.

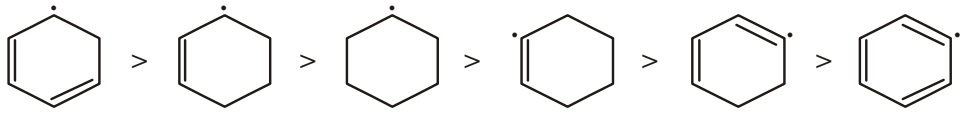
Example 1 :

Arrange the following free radicals / carbocations in decreasing order of stability.

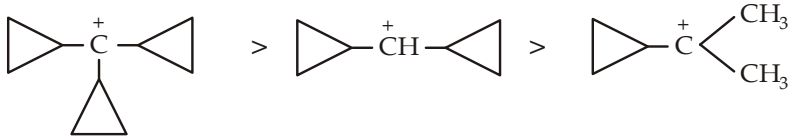
(a) 

(b) 

Solution :

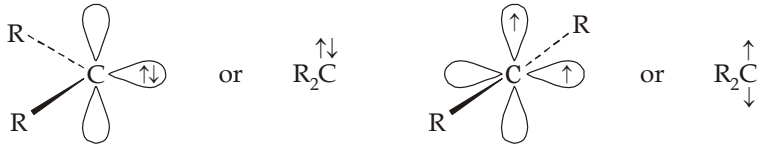
(a) 

2° allylic radical with two conjugated double bond | 2° allylic radical with one conjugated double bond | vinylic | vinylic | vinylic

(b) 

4.1.4 Carbenes

Carbenes are neutral, divalent carbon intermediates in which a carbon is covalently bonded to two atoms and has two non-bonding orbitals containing two electrons between them. Carbenes are of two types, singlet and triplet. Singlet carbene has sp^2 hybridised carbon atom, two of which are used in forming covalent bonds with the two substituents, the third one has the unshared pair of electrons ; while the *p*-orbital remains vacant. Thus a *singlet carbene* is *diamagnetic* and *resembles carbocation.*



Singlet carbene Triplet carbene

Triplet carbon has *sp* hybridised carbon atom, the two hybrid orbitals form covalent bonds with two groups and two electrons are placed, one each, in the equivalent, mutually perpendicular p_y and p_z orbitals, i.e. here the two unshared electrons are not paired, thus a triplet carbene is paramagnetic and resembles a free radical (diradical).

In a singlet carbene, two electrons are present in the same orbital i.e. electrons are paired, interelectronic repulsion takes place and hence a singlet carbene is generally less stable than the triplet carbene.

Formation :

Carbenes are formed during alkaline hydrolysis of chloroform and decomposition of diazo compounds and ketenes.

(*i*) $CHCl_3 \overset{OH^-}{\rightleftharpoons} \overset{\ominus}{C}Cl_3 \rightleftharpoons :CCl_2 + Cl^-$ (Dichlorocarbene)

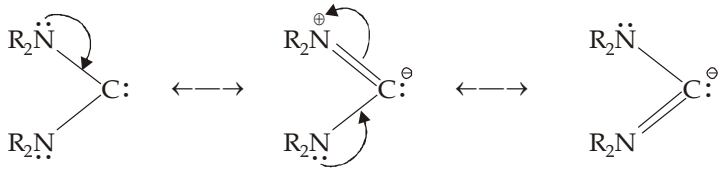
(*ii*) $CH_2=\overset{\oplus}{N}=\overset{\ominus}{\underset{\cdot\cdot}{N}}: \xrightarrow{heat} :CH_2 + N_2$ (Carbene)

(*iii*) $CH_2=C=O \xrightarrow{heat} :CH_2 + CO$

Carbenes have never been purified or even made in a high concentration, because when two carbenes collide, they immediately dimerize to given an alkene.

$$R_2C: + :CR_2 \xrightarrow{very\ fast} R_2C=CR_2$$

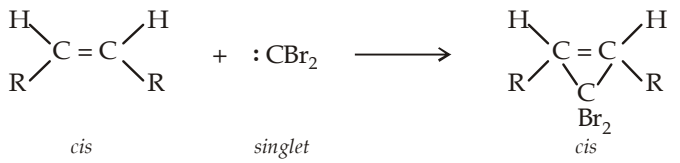
Carbenes in which the carbene carbon is attached to two atoms, each having a lone pair of electrons are relatively more stable than the carbene itself due to resonance.



Reactions :

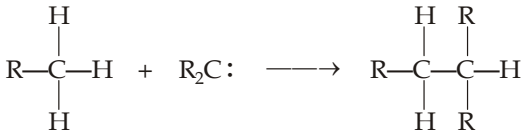
Carbenes undergo mainly two types of reactions ; *cycloaddition* with an alkene and *insertion* between the C—H bond.

$$H_2C=CH_2 + :CH_2 \longrightarrow \underset{\text{(due to cycloaddition)}}{H_2C\!\!\!\diagup\!\!\!\diagdown CH_2} + \underset{\text{(due to insertion)}}{CH_3CH=CH_2}$$

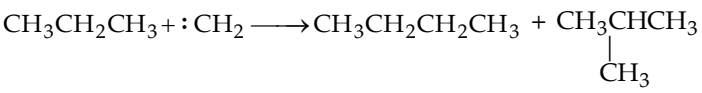


cis *singlet* *cis*

Insertion reaction :



Further it can be inserted in all the possible positions (1°, 2°, 3°).

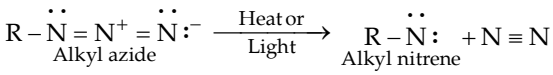


Carbenes are involved as intermediates in some well reactions like Riemer-Tiemann reaction, carbylamine reaction, Wittig reaction and Wolff rearrangement.

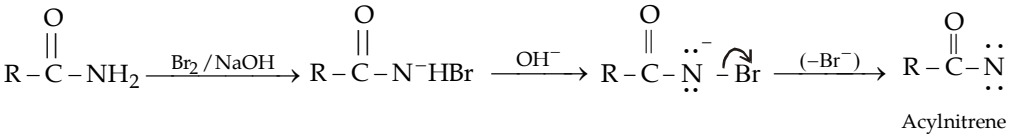
4.1.5 Nitrenes (*Imidogens*)

Nitrenes are neutral monovalent nitrogen species i.e. these are analogs of carbenes. These are electron deficient species and thus act as strong electrophiles. Like carbenes, nitrenes also exist in singlet and triplet states. Triplet state is the ground state and most nitrenes exist in this state. These can be generated in situ by the following methods.

(i) By the decomposition of azides in presence of heat or light.



(ii) By the action of bromine in presence of base on a 1° amide (Hofmann bromamide reaction).

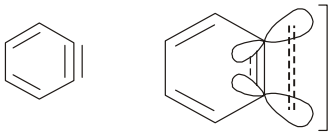


Nitrenes, particularly acyl nitrenes are formed as intermediates in Hofmann, Curtius and Lossen rearrangements.

4.1.6 Arynes

Arynes may be defined as aromatic compounds containing a formal carbon-carbon triple bond. The best known example is benzyne which is benzene minus two ortho hydrogens and thus sometimes it is also called *dehydrobenzene.*

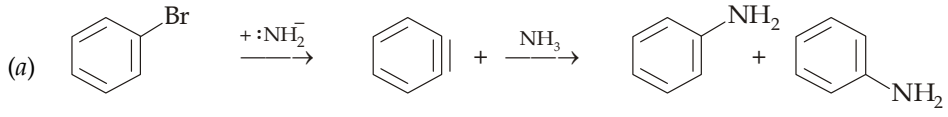
Remember that the benzyne bond is not like the triple bond of acetylene. In benzyne, one of the π components of the bond is part of delocalized π system of the aromatic ring. The second π component is obtained by overlapping of two sp^2 hybridized orbitals (not *p-p* overlap). These two sp^2 orbitals lie in the plane of the ring and does not interact with the aromatic π system. Further the two contributing sp^2 orbitals are not oriented properly for effective overlap, the π bond formed is relatively weak and hence benzynes are not stable but extremely reactive.

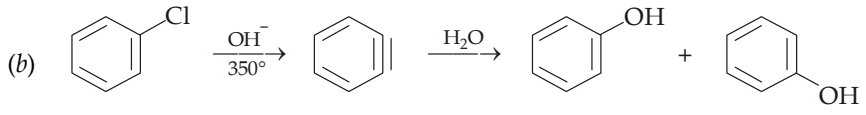


The degree of overlap of these sp^2 orbitals is smaller than in the triple bond of an alkyne

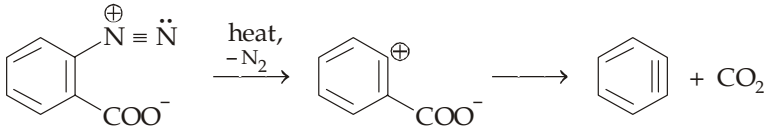
Benzyne formation has been observed in following reactions.

(*i*) Reaction of aryl halides with a strong base as during formation of (*a*) aniline from bromobenzene and (*b*) phenol from chlorobenzene.



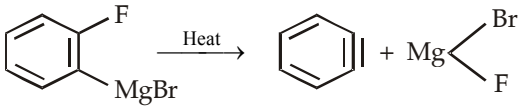


(*ii*) By heating benzenediazonium-2-carboxylate.

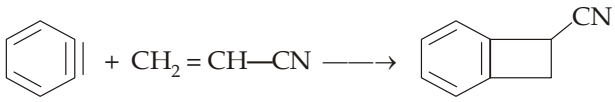


Benzene diazonium-2-carboxylate

(*iii*) By heating *o*-fluorophenyl magnesium bromide



Benzynes undergo nucleophilic addition with a wide variety of nucleophiles like H_2O, NH_3, RNH_2, C_6H_5Li etc. They also undergo dimerization reactions and react with olefins to form addition bicyclic compounds.



4.2 Types of Reagents

Heterolysis of a covalent bond is carried out by two types of reagents : electrophiles and nucleophiles.

4.2.1 Electrophiles

An electrophile (electron loving) *is a reagent that is deficient in electrons* and thus they attack at the electron rich site of the molecule. They are also called cationoid reagents and either carry a positive charge or have incomplete valence shell or have an atom which can acquire more electrons, *e.g.* SiF_4. Some commonly used electrophilic reagents are $H^{\oplus}$, $H_3O^{\oplus}$, $NO_2^{\oplus}$, R_3C^+, $X^{\oplus}$, RC^+O, BF_3, $AlCl_3$, $ZnCl_2$, $FeCl_3$, SiF_4, ICl, $R^{\bullet}$ (free radicals), :CR (carbenes), $:\ddot{N}R$ (nitrenes), etc. Since electrophiles are capable of accepting electron pair, they are **Lewis acids.**

Positively charged electrophiles are more reactive than the neutral ones. Since presence of electron withdrawing substituents tends to concentrate positive charge on the reacting site of the electrophile, such electrophiles will be more reactive. Smaller cations are stronger electrophiles than the larger cations belonging to the same group because the positive charge is dispersed over a smaller surface.

In addition to the above list, **cation carriers** like Br – Br, H – Br, Cl – OH, etc. and oxidising agents like Fe^{3+}, O_3, R – O – O – R, etc. also act as electrophilic reagents.

4.2.2 Nucleophiles

A *nucleophile* (nucleus loving) *is a reagent that has at least one unshared pair of electrons on one of its atoms.* They are also called anionoid reagents. These are negatively charged species, neutral compounds of oxygen, nitrogen or sulphur which always carry at least one unshared pair of electrons on them or compounds having π electrons. Common examples are

OH^-, OR^-, Br^-, CN^-, NH_2^-, $RCOO^-$, $RC \equiv C^-$, $CH_3COCH_2^-$, $(COOC_2H_5)_2CH^-$, $H_2\ddot{O}:$, ROH, ROR, RSH, NH_3, $H_2C = CH_2$,etc.

As expected, nucleophiles react at a positive or a partially positive site of a reactant. Fully charged ions like OR^- and OH^- are stronger nucleophiles than neutral substances like alcohols and water. Nucleophilic character is also enlarged by the presence of electron-donating groups (*e.g.* alkyl) which tend to concentrate negative charge on the reacting site of the nucleophile, *e.g.*, OCH_3^- is a better nucleophile than OH^-.

Reactions instigated by nucleophiles and electrophiles are respectively known as *nucleophilic and electrophilic reactions*.

In addition, **anion carriers**, e.g. R – MgX, H – H_3AlLi, H – C_6H_5, > C = C < etc. and reducing agents like Fe^{2+}, $[Fe(CN)_6]^{4-}$ etc. also act as nucleophilic reagents.

4.2.3 Ambiphiles or Ambidents

Reagents having both electron attracting (electrophilic) as well as electron-repelling (nucleophilic) site have dual (amphoteric) nature and known as **ambiphiles**. For example, HOH, ROH, RPH_2, organic compounds having C = O or $C \equiv N$ linkage etc.

Electrophile

$CH_3 - \overset{\delta+}{C} \equiv \overset{\delta-}{N}:$

Nucleophile

Other important examples of ambident nucleophiles are $^{-}O-\ddot{N}=O$, $-\overset{\|}{C}-\overset{\ominus}{C}H-\overset{\|}{C}-$ etc.

4.2.4 Comparison of Nucleophilicity and Basicity

Both of these two characteristics depend upon the availability of a lone pair of electrons. If this lone pair of electrons is donated to a hydrogen atom, it is called **basicity** and if it is donated to a carbon atom, it is called **nucleophilicity**. For example,

$$Nu:^{-} + \overset{|}{\underset{|}{C}}\!\!-\!\!X \longrightarrow Nu\!-\!\overset{|}{\underset{|}{C}} + X:^{-} \quad \text{[Nucleophilicity]}$$

$$Nu:^{-} + H\!-\!A \rightleftharpoons Nu\!-\!H + A:^{-} \quad \text{[Basicity]}$$

Thus, nucleophilicity depends upon the rate constant of the reaction, while basicity depends upon the equilibrium constant (K_b). In other words, nucleophilicity governs the kinetics of a reaction while basicity determines its thermodynamics. Nucleophilicity and basicity may be similar or different as indicated by the following points.

(*i*) If the nucleophilic centre of two or more species is same, nucleophilicity parallels basicity, *i.e.* more basic the species, stronger is its nucleophilicity

$$CH_3O^- > HO^- > CH_3COO^- > H_2O$$

— Basicity and nucleophilicity decrease ⟶

In all of the above species, nucleophilic atom is same, hence nucleophilicity parallels basic strength which in turn depends upon the relative strength of the conjugate acid (stronger the conjugate acid, weaker will be the base).

(ii) For the same nucleophilic centre, the basicity increases but due to steric hindrance the nucleophilicity decreases as the size of the nucleophile increases. For example,

⟵ increasing basicity ⟶

$$CH_3O^-, (CH_3)_2CHO^-, (CH_3)_3CO^-$$

⟵ increasing nucleophilicity ⟵

(*iii*) In going from left to right across a period, the basicity and nucleophilicity are directly related. Both of the characteristics decrease as the electronegativity of the atom bearing lone pair of electrons increases. For example,

$$H_3C:^- > H_2N:^- > H\ddot{O}:^- > \ddot{F}:^-$$

⟵ Basicity and nucleophilicty decrease ⟶

(*iv*) In moving down a group, the basicity and nucleophilicity are inversely related, *i.e.* nucleophilicity increases while basicity decreases. For example,

$$F^-, Cl^-, Br^-, I^- ; \quad NH_3, PH_3 ; \quad H_2O, H_2S$$

⟵ Basicity decreases, while nucleophilicity increases ⟶

This opposite behaviour is because of the fact that basicity and nucleophilicity depend upon different factors. Basicity is directly related to the strength of the H–Element bond, while nucleophilicity is indirectly related to the electronegativity of the atom to which proton is attached.

Bond dissociation energy of the H–Element : H—F > H—Cl > H—Br > H—I

Thus basicity follows the order : $F^- > Cl^- > Br^- > I^-$

Electronegativity of the atom : F > Cl > Br > I

Thus nucleophilicity follows the order : $I^- > Br^- > Cl^- > F^-$.

(*v*) When the atom bonded to the nucleophilic centre also has a lone pair of electrons, the nucleophilicity increases while the basicity decreases. For example, $H-\ddot{O}-\ddot{O}:^-$ (peroxide ion) is more nucleophilic than OH^- ion but it is less basic than the OH^- ion. Similarly, hydrazine $(H_2\ddot{N}-\ddot{N}H_2)$ is more nucleophilic but less basic than NH_3.

Effect of solvent on nucleophilicity : Anionic nucleophiles are less reactive in protic solvents (viz. ROH, HOH) than in aprotic solvents (viz. acetonitrile CH_3CN, DMF, $HCONH_2$, acetone). For example, fluoride ion is a poor nucleophile in protic solvents, however it is a good nucleophile in an aprotic solvent. The reason is very simple, anionic nucleophiles, especially smaller one like F^-, are solvated through H-bonds in protic solvents and hence their attack on the substrate will require breaking of some of the hydrogen bonds which reduce their nucleophilicity.

Example 2 :

Are base strength and nucleophilicity, both inolving reaction of an electron pair with a positive site, identical? Explain.

Solution :

No, although they are parallel quantities, they differ from each other because

(i) **Strength of a base** is based on the *K* for the reaction of the base with a proton-donating Bronsted acid;

$$B:^- + HA \rightleftharpoons B:H + A:^-$$

(ii) **nucleophilicity** is measured by the rate of reaction with an electrophile, usually a carbon atom.

$$B:^- + -\overset{|}{\underset{|}{C}}-Br \longrightarrow B-\overset{|}{\underset{|}{C}}- + Br^-$$

Example 3 :

Compare the basicities of the following pairs of bases :

(a) F^- **and** I^- **(b)** OH^- **and** SH^- **(c)** OH^- **and** NH_2^-

(d) $CH \equiv C^-$ **and** $CH_2 = CH^-$ **(e)** NH_2OH **and** NH_3 **(f)** Cl_3C^- **and** F_3C^-

Solution :

(a) For elements in the same group of the periodic table, the larger the basic site atom higher will be the possibility of delocalization of the charge, hence lesser will be its availability for proton. Thus

$$I^- < F^-$$

(b) Here also S and O lies in the same group, but S lies in higher period than O.

$$SH^- \quad < \quad OH^-$$

(S lies in 3rd period) (O lies in 2nd period)

(c) When the basic site elements are in the same period of the periodic table and carry negative charge, more the number of electron pairs on the site atom, more will be delocalization of the negative charge and thus weaker is the base. Thus

$$:\ddot{N}H_2^- < :\ddot{O}H^-$$

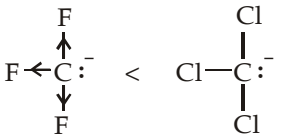
(d) More is the *s*-character of the orbital having unshared (lone) pair of electrons, more it will be closer to carbon and thus lesser will be the basicity.

$$CH \equiv \underset{sp}{\ddot{C}:^-} < CH_2 = \underset{sp^2}{\ddot{C}H^-}$$

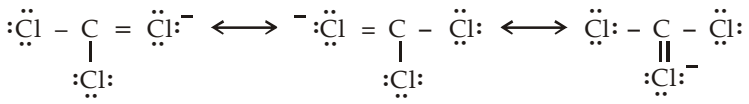
(e) When the basic site has no negative charge, but has a group like –X, –OH, –OR which causes electron-attraction due to inductive effect decreases electron density on the basic site leading to decrease in basicity. Thus

$$H_2\ddot{N} \longrightarrow OH \quad < \quad \ddot{N}H_3$$

(f) At first sight, one would conclude that $^{-}CF_3$ is less basic than $^{-}CCl_3$ due to more electron-withdrawing nature of F than Cl.



However, this is not true because in $Cl_3C:^{-}$, the unshared electron pair on C in the *p*-orbital undergoes extended *p*-dπ bonding into an empty *d*-atomic orbital of each of the three chlorines (*p*-*d*π bonding is not possible in $F_3C:^{-}$ because F has no *d*-orbital). Thus $Cl_3C:^{-}$ is in a weaker base than $F_3C:^{-}$.



Remember that resonance stabilization is more important than the inductive effect.

Example 4 :

Explain the following :

(a) NH_3 is more basic than PH_3. Explain it on the basis of their bond angle; bond angle in NH_3 and PH_3 are 107° (app.) and 90° (app.) respectively.

(b) Methaneselanate, $CH_3SeO_3^{-}$ is a stronger base than methanesulphonate, $CH_3SO_3^{-}$.

Solution :

(a) Both N and P are in group 5 of the periodic table, but P lies in third period while N in second period. Thus P, being larger in size than N, its hydride (PH_3) will be less basic than NH_3.

Explanation on the basis of bond angle : The 90° H–P–H bond angle indicates that P uses *p* AO's for bonding and hence the unshared electron pair lies in *s*-orbital which being closer to nucleus, is less available for protonation. The 107° H–N–H bond angle indicates that N uses sp^3 HO's, hence electron pair lies in sp^3 orbital having 25% *s*-character. Thus unshared electron pair on N (in NH_3) is more available than the unshared electron pair on P (in PH_3).

(b) Both S and Se atom are capable of forming *p*-*d*π bonds, causing dispersal (delocalization) of negative charge. However, *p*-*d*π bonding is more important in $CH_3SO_3^{-}$ which involves overlapping of 2*p* AO's of oxygen with 3*d*-orbital of S, overlapping in $CH_3SeO_3^{-}$ involves 2*p*-orbital of oxygen and 4*d*-orbital of Se, hence it is less effective. Thus there is less effective overlap and delocalization of the negative charge in $CH_3SeO_3^{-}$, hence it is stronger base than $CH_3SO_3^{-}$.

Example 5 :

(a) Write chemical equations for the reaction of CH_3NH_2 with (i) H_2O; (ii) gaseous HCl and (iii) $(CH_3)_3B$.

(b) Whether the amine is behaving as a base or as a nucleophile in the three cases.

Solution :

(a) (i) $\underset{\text{base}}{CH_3NH_2} + \underset{\text{acid}}{H_2O} \rightleftharpoons \underset{\text{salt}}{CH_3NH_3^{+}OH^{-}}$ (ii) $\underset{\text{base}}{CH_3NH_2} + \underset{\text{acid}}{HCl(g)} \longrightarrow \underset{\text{salt}}{CH_3NH_3^{+}Cl^{-}}$ (solid)

(iii) $\underset{\text{nucleophile}}{CH_3NH_2} + \underset{\substack{\text{electrophile}\\ \text{(B is electron deficient)}}}{B(CH_3)_3} \longrightarrow \underset{\text{complex compound}}{CH_3NH_2^{+} - B^{-}(CH_3)_3}$

(b) In (i) and (ii) CH_3NH_2 acts as a Bronsted base; while in (iii), it is acting as a nucleophile.

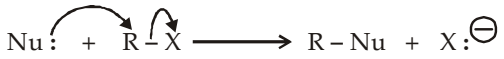
4.3 Types of Organic Reactions

The most common organic reactions can be classified into four groups namely substitution, addition, elimination and rearrangements.

4.3.1 Substitution Reactions

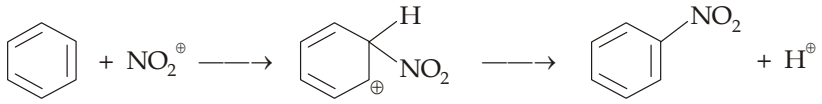
The replacement of an atom or group from a molecule by a different atom or group is known as **substitution** or **displacement reaction.** The species to be substituted may be either a nucleophile, an electrophile or a free radical.

In **nucleophilic substitution,** a nucleophile provides an electron pair to the substrate and the leaving group departs with an electron pair.



These are usually written as S_N (S stands for substitution and N for nucleophilic) and are common in aliphatic compounds especially in alkyl halides and acyl halides.

In **electrohphilic substitution,** the attacking species is an electrophile and the departing group leaves the molecule without pair of bonding electrons. These are usually written as S_E (S stands for substitution and E for electrophilic) and are more common in aromatic compounds which provides electron rich site.



In **free radical substitution,** a free radical attacks the substrate to form new free radical which is converted into substituted product, the leaving atom departs the substrate with an electron. These reactions are initiated by sunlight, oxygen and other free radical producing agents. Most common examples are halogenation of alkanes.

$$CH_4 + Cl_2 \xrightarrow{\text{light}} CH_3Cl + HCl$$

4.3.2 Addition Reactions

In addition reactions, the reagent adds to a molecule which generally has a multiple bond. Like substitution, here also the attacking species may be a nucleophile, electrophile or a free radical.

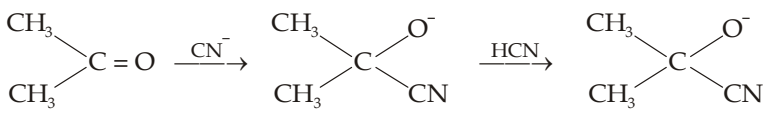
$$CH_2 = CH_2 + HBr \longrightarrow CH_3 - CH_2Br$$

In **electrophilic addition,** an electrophile approaches a multiple bond (source of electrons) to form a carbocation which in the next step combines with a nucleophile to give addition product.

$$CH_2 = CH_2 \xrightarrow{H^{\oplus}} CH_3—CH_2^{\oplus} \xrightarrow{Br^{\ominus}} CH_3—CH_2Br$$

However, when the addition of HBr to alkenes is carried out in presence of peroxides, addition occurs through *radical mechanism.*

In **nucleophilic additions,** a nucleophile provides a pair of electrons to a carbon atom joined to oxygen by a multiple bond.



Free radical addition reactions are initiated by free radicals. For example,

$$CH_3CH = CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3CH_2CH_2Br$$

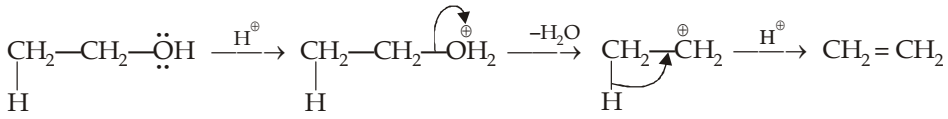
4.3.3 Elimination Reactions

An elimination reaction involves removal of two atoms from the same molecule, thus it is said to be reverse of an addition reaction. For example,

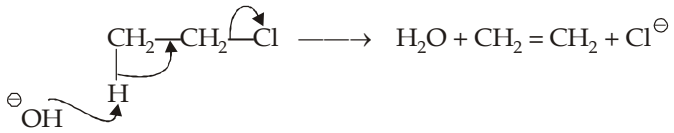
$$CH_3CH_2Cl \xrightarrow{\text{alc. KOH}} CH_2 = CH_2 + HCl$$

Generally, two atoms or groups are lost from adjacent carbon atoms to form an unsaturated compound, such reactions are known as β-**elimination.** Acid-catalyzed dehydration of alcohols and base-catalysed dehydrohalogenation of alkyl halides are common examples.

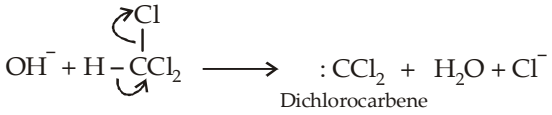
(*i*)



(*ii*)



In few elimination reactions, two atoms or groups are lost from the same carbon atom to form highly reactive species, known as *carbenes* (α-**elimination**). For example,

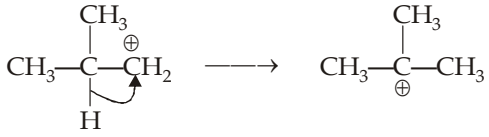


4.3.4 Molecular Rearrangements

A rearrangement reaction involves the migration of an atom or a group (including a double bond) within the molecule.

(*i*) $CH_3CH(X)CH = CH_2 \longrightarrow CH_3CH = CHCH_2X$

(*ii*)



(*iii*) $NH_4CNO \longrightarrow NH_2CONH_2$

TEST YOUR UNDERSTANDING - 4.1

1. Pick up the species which can act as (*a*) an electrophile, (*b*) a nucleophile, (*c*) both *i.e.* electrophile as well as nucleophile and (*d*) neither electrophile nor nucleophile.

H^+, H_2, H_2O, Cl^+, Cl^-, Cr^{3+}, CH_4, NO_2^+, $BeCl_2$, CH_2O, $CH_3CH = CH_2$, $SnCl_4$, CH_3CN, SiF_4

2. Some of the commonly used reagents are given below. Identify which part of the reagent can act as an electrophile ?

Cl_2, H_2O, HBr, HOCl, CH_3COOH, CH_3COCl, $C_6H_5SO_2OH$

3. In CH_3COCl and ICl, every atom has complete octet of electrons, even then they behave as electrophiles. Explain.

4. Classify the following reactions as addition, substitution, elimination, rearrangement or redox, note that a single reaction may belong to more than one type

(*i*) $H_2C = CH_2 + HCl \longrightarrow CH_3CH_2Cl$

(*ii*) $H_2C = CH_2 + H_2 \xrightarrow{Pt} CH_3CH_3$

(*iii*)  $\longrightarrow CH_3CH = CH_2$

(*iv*) $CH_3CHClCHClCH_3 + Zn \longrightarrow CH_3CH = CHCH_3 + ZnCl_2$

(*v*)  $+ Br_2 \longrightarrow BrCH_2CH_2CH_2Br$

(*vi*) $NH_4CNO \longrightarrow H_2NCONH_2$

(*vii*) $CHCl_3 + OH^- \longrightarrow :CCl_2 + H_2O + Cl^-$

(*viii*) $CH_3CH_2Br + H^- \longrightarrow CH_3CH_3 + Br^-$

(*ix*) 

5. Think of the intermediate formed during following reactions :

(*i*) $(CH_3)_3COH + H^+ \longrightarrow$ [Intermediate] $+ H_2O$

(*ii*) $CH_2I_2 + Zn \longrightarrow [\ ] + ZnI_2$

(*iii*) $(CH_3)_3CCl + AlCl_3 \longrightarrow [\ ] + AlCl_4^-$

(*iv*) $CH_3—N = N—CH_3 \longrightarrow [\ ] + N_2$

(*v*) $CH_2N_2 \longrightarrow [\ ] + N_2$

(*vi*) $CH_2 = CH_2 + DBr \longrightarrow [\ ] + Br^-$

(*vii*) $(CH_3)_2Hg \longrightarrow [\ ] + .Hg.$

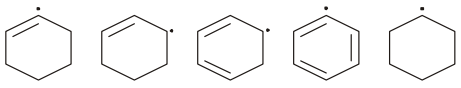
(*viii*) $C_2H_2 + Na \longrightarrow [\ ] + Na^+ + \frac{1}{2}H_2$

6. The rate expression for the following reaction is given by the expression $r = k[Me_3CBr][Ag^+]$.

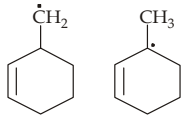
$Me_3CBr + CH_3COO^- + Ag^+ \longrightarrow$ Products

Write down the product of the reaction and explain it by a plausible mechanism showing the reacting electrophiles and nucleophiles.

7. Arrange the following free radicals in decreasing order of stability.

(*i*) 

I II III IV V

(*ii*) $CH_2 = \dot{C}H$ $CH_2 = \dot{C}H—CH_2$ 

I II III IV

4.4 Energetics of Organic Reactions

Every chemical reaction can proceed in either direction, even if it goes in one direction to a microscopic extent. Thus for every reaction, a **state of equilibrium** is reached when the concentrations of A, B, C and D no longer change even though the reverse and forward reactions are taking place. The equilibrium constant of a reaction depends upon following thermodynamic quantities.

$$e\,A + f\,B \rightleftharpoons g\,C + h\,D$$

(*i*) **Enthalpy change (ΔH).** It is the quantity of heat released or absorbed when a mole of reactant is converted into a mole of product. Alternatively, ΔH of a chemical reaction is the difference in the enthalpies of the products, H_P and the reactants, H_R, *i.e.* $\Delta H = H_P - H_R$.

If the bonds in the products are more stable than the bonds in the reactants, *i.e.* when the sum of bond energies of the products are more than that of the reactants, ΔH is negative and the reaction is **exothermic.**

$$H_3C—H + Cl—Cl \longrightarrow H_3C—Cl + H—Cl$$

Bond energy 435 243 339 431 ; $\Delta H = -92$ kJ mol^{-1}

678 kJ mol^{-1} 770 kJ mol^{-1}

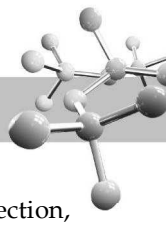
(*ii*) **Entropy change (ΔS).** Since entropy is a measure of randomness, change in entropy is the measure of the energy consumed (or released) in the reaction to create more order (or randomness) in products relative to reactants. For a reaction,

$$\Delta S = S_P - S_R$$

(*iii*) **Free energy change (ΔG).** When entropy change is taken with the absolute temperature (T), it gives the free energy change (ΔG) according to the following relation.

$$\Delta G = \Delta H - T\Delta S$$

A reaction proceeds in the forward direction only when ΔG is negative that is there is overall release of energy. A positive ΔG, on the other hand, indicates that the reaction has a tendency to go backward.



Rates of reactions

Although a negative value of ΔG tell us that the reaction is thermodynamically feasible in the forward direction, it does not necessarily tell us that the reaction will proceed at a measurable rate. The **rate of reaction** and its dependence on the concentration of the various reacting species is predicted by kinetic studies. Consider the following reaction.

$$e\,A + f\,B \longrightarrow g\,C + h\,D$$

The rate of the above reaction is given by

$$\text{rate} = k\,[A]^x\,[B]^y$$

where k is the rate constant at temperature T. The numerical values of the exponents x and y are determined experimentally, they need not be the same as e and f, the coefficients of the chemical reaction. The sum of the values of the exponents is defined as the order of the reaction.

Under a given set of conditions (concentration, temperature, nature of solvent, presence of catalyst etc.), following factors determine the rate of a given reaction.

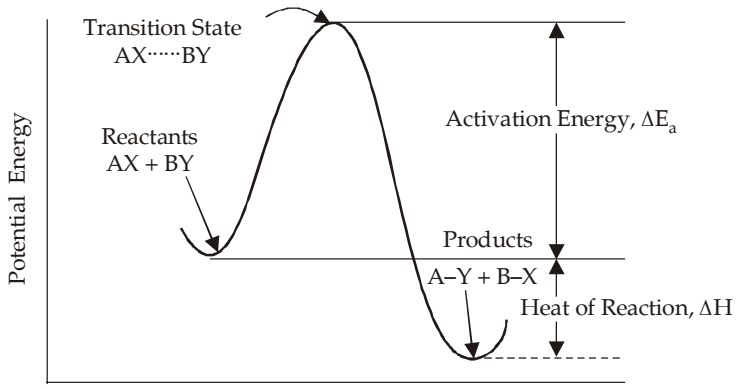
(*i*) **Number of collisions per unit time.** The greater the chances for molecular collision, the faster the reaction. Probability of collision is proportional to the molar concentrations.

(*ii*) **Enthalpy of activation** (activation energy, E_{act}, $\Delta H^{\neq}$). Reaction may take place only when colliding molecules have some enthalpy content in excess of average (E_{act}). The smaller the value of E_{act}, the more successful will be the collisions and the faster the reaction.

(*iii*) **Entropy of activation** ($\Delta S^{\neq}$). All collisions between molecules possessing requisite E_{act} does not result the reaction. Collisions between molecules must also occur in certain orientation, reflected by the value of entropy of activation. The more organized or less random is the required orientation of the colliding molecules, lower is the entropy of activation and thus slower is the reaction.

Transition state and enthalpy diagrams

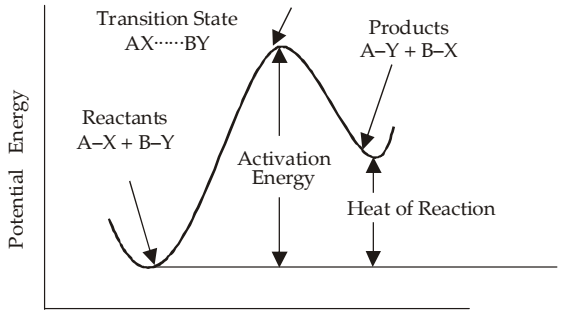
When reactants having sufficient enthalpy of activation and proper orientation collide, they pass through a hypothetical transition state in which some bonds are breaking while others are being formed. The relationship of the transition state to the reactants and products is shown by energy (enthalpy) diagrams.



Enthalpy diagram for exothermic reactions.

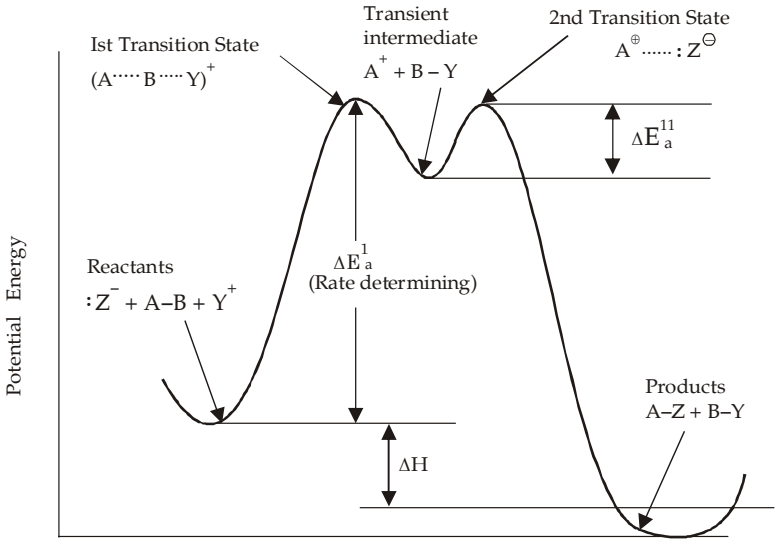
From the above plot it is obvious that for the reaction to proceed, energy must be supplied to the reactants in order to carry them over the hump. This energy is required, essentially, to stretch and ultimately to break any bond as may be necessary in the reactants. This amount of work necessary to get the reactants upto the top of the hump is called the **free energy of activation, activation energy or energy of activation.** Therefore, reactions with high activation energies occur more slowly than those with low activation energies, since at ordinary temperature the kinetic energy of only a small fraction of the reactant molecules will be great enough to provide sufficient energy on collision to reach the transition state. Thus we see that it is the activation energy and not the heat of reaction which determines the reaction. The top of the energy hump corresponds to the least stable configuration through which the reactants pass on their way to products and this is generally known as the **transition state or activated complex.** The activated complex is not a true molecule. It contains partial bonds, and the energy content of the system is maximum. Its life is extremely short, and hence it cannot be isolated; it always decomposes into reactants or products.

An endothermic reaction similarly has a specific activation energy required to reach its transition state. But here the activation energy must be greater or least equal to the heat of reaction.



Enthalpy diagram for endothermic reaction

However, many common reactions are not so simple and do not proceed through a single transition state as the above two examples, but involve the formation of one or more actual intermediates. The overall such reactions consist of two or more separate reactions, *viz.* (*i*) reactants → intermediate, and (*ii*) intermediate → products, and thus two or more activation energies will be involved–one leading to a transition state for formation of the intermediate, and a second leading to a transition state between the intermediate and the final products. The step with the highest activation energy will usually be the slower and therefore the **rate determining step** of the over-all reaction.



Enthalpy diagram for an exothermic reaction with a transient intermediate

If a reaction proceeds through a true intermediate, there will be a minima in the energy diagram. The greater the dip, the more stable will be the intermediate, and *vice versa i.e.*, the shallower the dip, the less stable will be the intermediate. In the extreme case, the dip may be so shallow that the intermediate is indistinguishable from the transition state. It should be noted here that each intermediate has its own transition state.

TEST YOUR UNDERSTANDING - 4.2

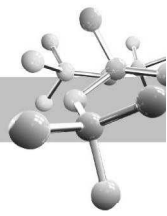
1. Predict the sign of ΔS (positive or negative) in the following reactions :

(*i*) $CH_2 = CH_2 + H_2 \longrightarrow CH_3CH_3$ (*ii*) $H_2C\overset{CH_2}{\diagup\diagdown}CH_2 \xrightarrow{\text{heat}} CH_3CH = CH_2$

(*iii*) $CH_3COO^{-}(aq) + H_3O^{+}(aq) \longrightarrow CH_3COOH + H_2O$

2. Predict the effect on the rate of a reaction if a change in the solvent causes (*i*) a decrease in $\Delta H^{\neq}$ and an increase in $\Delta S^{\neq}$, (*ii*) an increase in $\Delta H^{\neq}$ and a decrease in $\Delta S^{\neq}$, (*iii*) an increase in $\Delta H^{\neq}$ and $\Delta S^{\neq}$, and (*iv*) a decrease in $\Delta H^{\neq}$ and $\Delta S^{\neq}$.

3. Catalyst generally speeds up reactions by lowering $\Delta H^{\neq}$. Explain how this occurs in terms of reactant and transition state enthalpies.



4. The rate of the reaction (A + B → C + D) can be expressed in three ways.
(*i*) rate = k[A][B], (*ii*) rate = k[A], or (*iii*) rate = k[B]. Give plausible mechanisms consistent with the above expressions.

5. Give mechanism for the reaction, 2A + 2B ⟶ C + D, whose rate = $k[A]^2[B]$, assuming that no step is termolecular.

6. The rate of the reaction A + 2B ⟶ C + D is expressed as rate = $k[A][B]^2$. If the rate determining step of the reaction is unimolecular, give the possible mechanism of the reaction.

4.5 Competitive Reactions (Thermodynamic and Kinetic Control)

Many reactions produce a mixture of products formed from a common intermediate. For example, hydrogen halides add to 1, 3-butadiene to give a mixture of two regioisomeric allylic halides.

$$\underset{\text{1, 3-Butadiene}}{CH_2=CHCH=CH_2} \xrightarrow[(-\,80°C)]{HBr} \underset{\substack{\text{3-Bromo-1-butene (81\%)}\\\text{(1, 2-Addition)}}}{CH_3\overset{Br}{\overset{|}{C}}HCH=CH_2} + \underset{\substack{\text{1-Bromo-2-butene (19\%)}\\\text{(1, 4-Addition)}}}{CH_3CH=CHCH_2Br}$$

Both of the above products are derived from the same allylic carbocation.

$$\underset{\text{2° (More stable)}}{[CH_3\overset{+}{C}HCH=CH_2} \longleftrightarrow \underset{\text{(1° Less stable)}}{CH_3CH=CH\overset{+}{C}H_2]} \xrightarrow{Br^-} \underset{\substack{\text{3-Bromo-1-butene (81\%)}\\\textbf{(Major)}}}{CH_3\overset{Br}{\overset{|}{C}}HCH=CH_2} + \underset{\substack{\text{1-Bromo-2-butene (19\%)}\\\textbf{(Minor)}}}{CH_3CH=CHCH_2Br}$$

The secondary carbocation is more stable than the primary *i.e.* it bears more of the positive charge than does the primary carbon, hence attack by the nucleophile (Br^-) is faster at 2° carbocation forming 1, 2-addition product as the major product.

When the major product of a reaction is that which is formed at the fastest rate, it is known as **kinetically controlled** or **rate-controlled product,** *and the reaction is known as kinetically controlled reaction.* Such reactions take place at low temperature. Most organic reactions fall into this category, and the addition of HBr to 1, 3-butadiene at low temperature is a kinetically controlled reaction.

However, addition of HBr to 1, 3-butadiene at room temperature gives 1-bromo-2-butene (1, 4-addition product) as the major product.

$$\underset{}{CH_2=CHCH=CH_2} \xrightarrow[\text{room temp.}]{HBr} \underset{\substack{\text{3-Bromo-1-butene (44\%)}\\\text{(1, 2-addition)}}}{CH_3\overset{Br}{\overset{|}{C}}HCH=CH_2} + \underset{\substack{\text{1-Bromo-2-butene (56\%)}\\\text{(1, 4-addition)}}}{CH_3CH=CHCH_2Br}$$

When the major product of the reaction is that which is relatively more stable, it is known as **thermodynamically-controlled** or **equilibrium controlled product,** and the reaction is known as *thermodynamically-controlled reaction.* Such products are formed at room temperature (high temperature).

Thus, it can be concluded that the temperature of the reaction exerts a major influence on the product composition. This can be explained on the basis of the fact that at elevated temperature, the 1, 2 and 1, 4-addition products *interconvert rapidly* by allylic rearrangement. Heating the product mixture to 45°C in the presence of hydrogen bromide leads to a mixture in which the ratio of 3-bromo-1-butene to 1-bromo-2-butene is 15 : 85.

$$\underset{\substack{\text{3-Bromo-1-butene}\\\text{(Less stable)}}}{CH_3\overset{Br}{\overset{|}{C}}HCH=CH_2} \rightleftharpoons \underset{\substack{\\\\Br^-}}{CH_3CH\overset{H}{\overset{|}{=}}\overset{+}{C}CH_2} \rightleftharpoons \underset{\substack{\text{1-Bromo-2-butene}\\\text{(More stable)}}}{CH_3CH=CHCH_2Br}$$

The predominance of the 1, 4-addition product (1-bromo-2-butene) is due to its high stability owing to the presence of *internal double bond* than the 1, 2-addition product (3-bromo-1-butene) which has a terminal double bond.

When addition occurs under such conditions where the products can equilibrate, the composition of the product is not in accordance to the relative rates of formation of the products (or the relative stability of the intermediate carbocation) but tends to reflect their relative stabilities.

However, it must be remembered that if the conditions of the reaction do not permit interconversion (like low temperature), *i.e.* when the reaction is irreversible the kinetically controlled product will invariably predominate. The irreversible nature of the reaction at low temperature is because of slow isomerization which in turn in due to insufficient thermal energy to permit the products to surmount the energy barrier for ionization. At higher temperatures, isomerization is possible and the more stable product predominates.

4.6 Mechanism of Substitution Reactions

As described earlier substitution reactions may follow of free-radical or ionic path. Further, ionic mechanism may be nucleophilic (when the reagent is nucleophile) or electrophilic. Thus, on the whole there are three types of substitution reactions namely free radical, nucleophilic and electrophilic depending upon the nature of the reactant, reagent and reaction conditions.

4.6.1 Free-Radical Mechanism

This mechanism occurs when the reaction conditions or reagent are free-radical producing, *viz.* UV light, high temperature or presence of certain free radical initiators (*e.g.* peroxides, tetraethyl lead, etc.). This mechanism is observed in halogenation of alkanes. For details of halogenation, readers are referred to Ch. on 'Alkanes'. However, here three necessary steps encountered in halogenation of alkanes are summarised below.

(*i*) *Initiation step (Formation of free-radical).* A reactive particle, typically an atom or free-radical, is needed to start the reaction. It is the generation of this reactive particle that requires the vigorous conditions, *viz.* presence of UV light, high temperature etc.

$$X - X \xrightarrow[\text{or } 250\text{-}400^\circ C]{\text{UV light}} 2X\cdot$$

(*ii*) *Propagation steps.* $X\cdot + H{-}CH_3 \longrightarrow HX + \cdot CH_3$

$$\cdot CH_3 + X_2 \longrightarrow CH_3X + X\cdot$$

These two steps are repeated until finally a chain is terminated.

(*iii*) *Termination step.* The above propagation steps, *i.e.* chain reaction stops by coupling of any two radicals.

$$X\cdot + X\cdot \longrightarrow X - X$$

$$\cdot CH_3 + X\cdot \longrightarrow CH_3{-}X$$

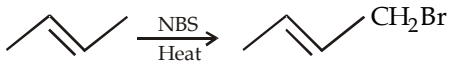
$$\cdot CH_3 + \cdot CH_3 \longrightarrow CH_3{-}CH_3$$

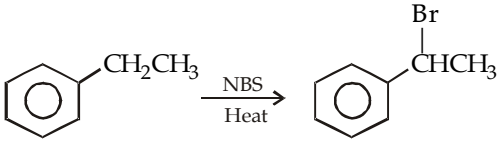
When the ratio of CH_4 to X_2 is high, CH_3X is formed predominantly and when X_2 is in excess, CCl_4 is the final product.

Relative reactivity of hydrogens toward free radical halogenation : It is in accordance with the relative stability of the free radicals.

Benzyl > allyl > 3° > 2° > 1° > vinyl > methyl

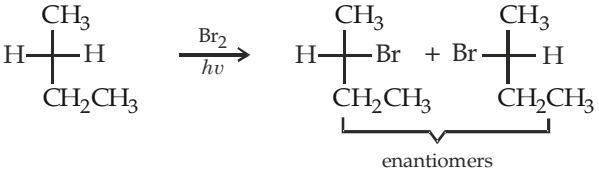
Halogenation at allylic or benzylic carbon takes place by means of Cl_2 or Br_2 at high temperatures (500-800°C). However, allylic bromination is carried out more easily with NBS (N-bromosuccinimide). The weak N-Br bond in NBS can be cleaved homolytically into radical upon warming or exposure to visible light. For more details of allylic bromination consult (6.4.15).



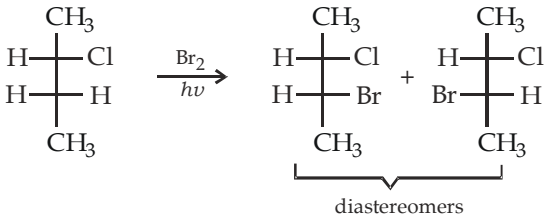


Stereochemistry :

(i) If the reaction creates a chirality centre in the product both the R and S enantiomers are formed.



(ii) In case, the parent compound already has a chiral centre, and another chirality centre is developed, a pair of diastereomers is formed.



4.6.2 Nucleophilic Substitution (S_N) Reactions

These reactions occur when the attacking agent is a nucleophile. Such reactions are mainly encountered in alkyl halides and acyl halides.

Nucleophilic substitution in alkyl halides : The carbon-halogen bond in an alkyl halide is polar ($\overset{\delta+}{R}—\overset{\delta-}{X}$) and cleaved heterolytically on attack by a nucleophile.

$$R—\ddot{X}: + Y:^- \xrightarrow{\text{Solvent}} R—Y + \ddot{X}:^-$$

Nucleophiles may be anions or neutral molecules having lone pair of electrons. Relative reactivity of different nucleophiles will be discussed at a later stage. The **leaving group** in alkyl halides is halide ion (X^-). Relative leaving ability of the halide ion, *i.e.* reactivity of alkyl halides follows the order : RI > RBr > RCl >> RF which can be explained in two ways.

(*a*) Leaving-group ability of an anion is related to basicity. A strongly basic anion is usually a poorer leaving group than a weakly basic one. Fluoride is the most basic and the poorest leaving group, while iodide is the least basic and the best leaving group.

(*b*) Iodine has the weakest bond to carbon and thus iodide is the best leaving group ; on the contrary fluorine has the strongest bond to carbon and thus fluoride is the poorest leaving group. Alkyl fluorides are rarely used as substrates in nucleophilic substitution because they are several thousand times less reactive than alkyl chlorides.

In order to ensure that reaction occurs in homogeneous solution, such **solvents** are chosen which dissolve both the alkyl halide (organic compounds) and nucleophiles (generally ionic salts). Two such solvents are ethanol-water mixtures and dimethyl sulphoxide, $(CH_3)_2S = O$ (DMSO).

Kinetic studies (study of rate of reaction with change in concentration) of nucleophilic substitution show that methyl and other primary halides react by second-order kinetics (*i.e.* rate is dependent upon the concentration of two substances, *viz.* alkyl halide and nucleophile) ; while *tert*-alkyl halides react by first-order kinetics (*i.e.* rate depends upon the concentration of only one substance, the alkyl halide). In short,

rate = $k[RX][OH^-]$ (For CH_3X and 1° alkyl halides)

rate = $k[RX]$ (For 3° alkyl halides)

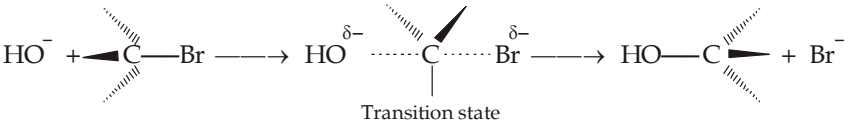
Secondary alkyl halides show border line behaviour : sometimes sceond-order, sometimes first-order, often a mixture of the two.

The above facts led to the conclusion that nucleophilic aliphatic substitution can proceed by two different mechanisms, named as biomolecular and unimolecular.

4.6.3 Bimolecular Mechanism of Nucleophilic Substitution (S_N2)

As mentioned earlier, the rate of such reaction is found to be directly proportional to the concentration of both reactants (alkyl halide and nucleophile). Thus we can say that the reaction is first-order with respect to each reactant or second-order overall. The overall second-order kinetic behaviour points out that the rate-determining step of the reaction is *bimolecular.*

The S_N2 reactions are believed to be completed in one step. The nucleophile (*e.g.* OH^-) starts to share its electrons with the substrate carbon from the side opposite* to the bromine atom (*back side attack*), and simultaneously the bromine atom starts removing its shared pair of electrons from the carbon atom **(concerted process).** This leads to the formation of a transition state.



The S_N2 reaction (Note that the nucleophile, OH^- attacks the back side of the bromine atom)

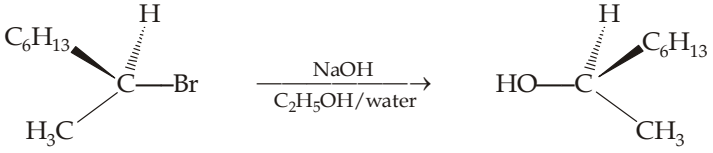
In the transition state, carbon atom is partially bonded to the nucleophile (OH^-) as well as to the leaving group (—Br) ; —OH has a diminished negative charge since it has begun to share its electrons with carbon, while —Br has developed a partial negative charge as it has partly removed a pair of electrons from carbon. The —OH and —Br are located as far apart as possible ; the three substituents and the carbon lie in a single plane, all bond angles being 120°. Thus note the carbon atom in the transition state is pentavalent. The C-substituent bonds are thus arranged like the spokes in a wheel, with the C—OH and the C—Br bonds lying along the axle.

Finally, the C—Br bond is fully cleaved by the energy liberated by the C—OH bond formation, the —OH group takes the position just opposite to that occupied by the —Br. The negative charge on bromine (the leaving group) is stabilised by hydrogen bonding with the solvent.

The S_N2 mechanism is believed to describe most substitution of simple primary alkyl halides and to some extent secondary alkyl halides.

Stereochemistry of S_N2 reactions :

Stereochemistry of S_N2 reactions can best be demonstrated by taking alkyl halide having chiral carbon, *e.g.* 2-bromooctane. When (+)-2-bromooctane is allowed to react with NaOH under S_N2 conditions, (–)-2-octanol is obtained.

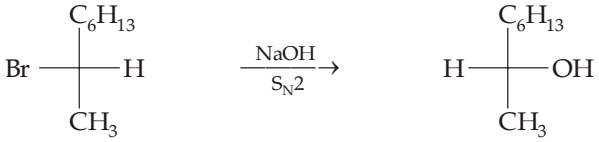


(+)-2-Bromooctane (–)-2-Octanol

The change in the sign of specific rotation from (+)- to (–)- indicates that the configuration changes during the reaction. Thus it can be concluded that *an* S_N2 *reaction proceeds with inversion of configuration usually referred to as* **Walden inversion.**

Remember that there is no distinct relation between the sign of rotation and R/S specification of different compounds. They may be having different sign of rotation but same specification (R or S), although in the above particular example inversion in configuration (*i.e.* change in specific rotation, happens to be accompanied by a change in specification from S-(+)-2-bromooctane to R-(–)-2-octanol.

It is important to note that during S_N2 reaction, configuration of every molecule is inverted *i.e. an* S_N2 *reaction proceeds with complete inversion of configuration.* This can be proved by the fact that a sample of 83% optically pure (+)-2-bromooctane gives 83% optically pure (–)-2-octanol on S_N2 reaction.



S-(+)-2-Bromooctane
$[\alpha] = +32.9°$
(Optical purity 83%)

R-(–)-2-Octanol
$[\alpha] = -8.55°$
(Optical purity 83%)

* Attack by OH^- on the oppsoite side to that of bromine is because of the fact that both of them are electron rich. It is, therefore, natural that they will remain away as far apart as possible.

TEST YOUR UNDERSTANDING - 4.3

1. Determine the specific rotation of (–)-2-octanol obtained by the reaction of (+)-2-bromooctane (of specific rotation = + 24.9°) with aqueous sodium hydroxide. Given [α] for optically pure (+)-2-bromooctane and (–)-2-octanol have specific rotations of + 39.6° and – 10.3° respectively.

Steric effects in S_N2 reactions : There is a very large difference in reactivity between different types of alkyl halides towards S_N2 reactions under the given state of conditions. For example, reactivity of some alkyl bromides with lithium iodide in acetone differs widely.

	CH_3Br	CH_3CH_2Br	$(CH_3)_2CHBr$	$(CH_3)_3CBr$
Relative rate	**221000**	**1350**	**1**	**too small to measure**

The above large difference in rate is because of degree of **steric hindrance** offered by increasing number of alkyl groups on the carbon bearing the leaving group, to the nucleophile. This is further evidenced by studying the rate of reaction of different 1° halides with lithium iodide in acetone.

1° Alkyl halides :	$CH_3—CH_2Br$	$C_2H_5—CH_2Br$	$(CH_3)_2CH—CH_2Br$	$(CH_3)_3C—CH_2Br$
Relative rate :	**1.0**	**0.8**	**0.036**	**0.00002**

In the above example, we see that although neopentyl bromide, $(CH_3)_3CCH_2Br$, is a primary alkyl halide, it is practically inert to substitution by S_N2 mechanism because of steric hindrance. Thus remember that *difference in rate between two* S_N2 *reactions are mainly due to steric factors, and not to polar factors.*

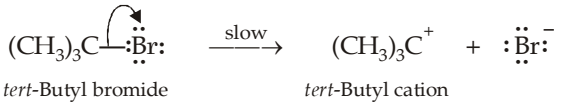
4.6.4 Unimolecular Mechanism of Nucleophilic Substitution (S_N1)

In the above discussion, it is observed that *tert*-alkyl halides are practically inert to substitution by S_N2 mechanism because of steric hindrance. It does not mean that such halides do not undergo nucleophilic substitutions. Actually, it was observed that the hydrolysis of *tert*-alkyl halides occurs by a different mechanism. It follows *first-order* kinetics, that is, the rate depends upon the concentration of only one reactant, the *tert*-alkyl halide which is proved by the fact that the rate does not change either on adding the stronger nucleophile like OH^- ion or increasing the concentration of OH^-.

$$(CH_3)_3CBr + H_2O \longrightarrow (CH_3)_3COH + HBr \text{ ; rate } = k[(CH_3)_3CBr]$$

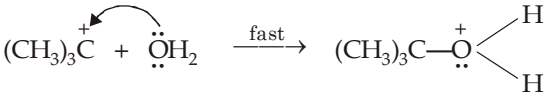
The observations led to the fact that the reaction takes place according to following steps.

Step 1. The carbon-halogen bond breaks heterolytically without any assistance from the nucleophile forming a carbocation.

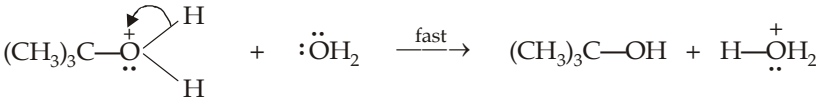


tert-Butyl bromide — *tert*-Butyl cation

Step 2.



Step 3.



tert-Butyl oxonium ion (acts as an acid) — Water (acts as a base) — *tert*-Butyl alcohol

Step 3 does not occur when the nucleophile is an anion. In this mechanism, since the rate-determining step (slow step which is first) involves only one molecule, it is known as **unimolecular nucleophilic substitution (S_N1).**

Relative reactivity of different alkyl halides towards S_N1 mechanism : Since S_N1 reactions involve the formation of carbocation as intermediate in the rate determining step, **more is the stability of carbocation higher will be reactivity of alkyl halides towards S_N1 route.** Now we know that stability of carbocations follows the order : 3° > 2° > 1°, so S_N1 reactivity should also follow the same order.

$$3° > 2° > 1° > \text{Methyl} \quad \textbf{(}S_N\textbf{1 reactivity)}$$

This is also proved experimentally by carrying out substitution of different alkyl halides by chosing conditions under which S_N1 route is very slow as solvolysis in aqueous formic acid (both H_2O and HCOOH are weak nucleophiles)

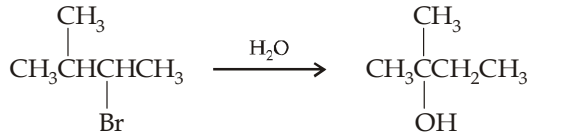
$$RX + H_2O \xrightarrow{HCOOH} ROH + HX$$

The relative rate of hydrolysis (which is mainly S_N1) of different alkyl halides under these conditions are found as below.

Alkyl bromide	Class	Relative rate
CH_3Br	Unsubstituted	1
CH_3CH_2Br	Primary	2
$(CH_3)_2CHBr$	Secondary	43
$(CH_3)_3CBr$	Tertiary	100,000,000

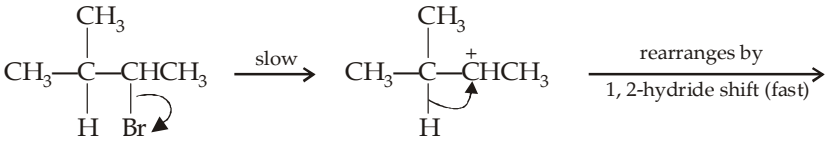
This suggests that **steric crowding** that **influences reaction rate in S_N2 processes** plays no role in S_N1 reactions. On the other hand, **in S_N1 reactions, electronic effect,** specifically the stabilization of carbocation intermediate by alkyl substituents **is the decisive factor.**

Additional evidence for the formation of carbocations as intermediates comes from the observations that in certain cases rearranged products are the main products (recall that carbocations undergo rearrangement to the more stable). For example, hydrolysis of 2-bromo-3-methylbutane (a secondary alkyl halide) yields 2-methyl-2-butanol (a tertiary alcohol) as the exclusive product of hydrolysis.

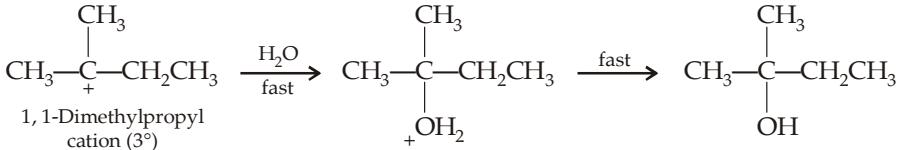


2-Bromo-3-methylbutane — 2-Methyl-2-butanol (93%)

Mechanism :

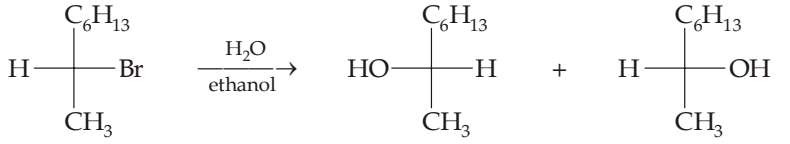


2-Bromo-3-methylbutane — 1, 2-Dimethylpropylcation (2°)



1, 1-Dimethylpropyl cation (3°) — 2-Methyl-2-butanol (3° alcohol)

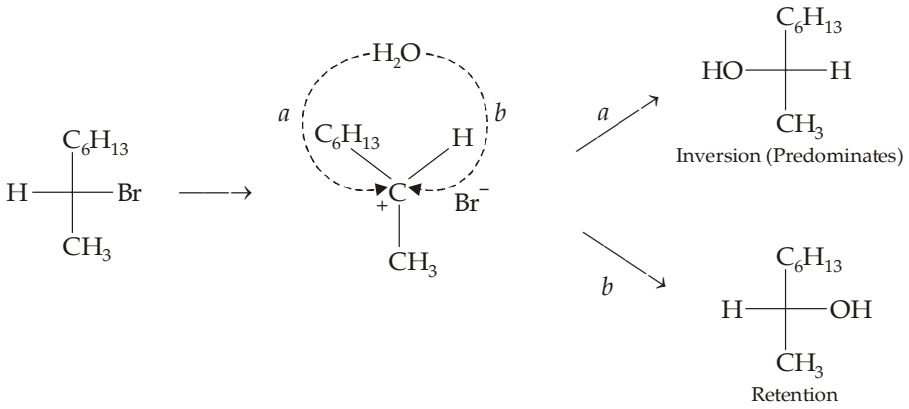
Stereochemistry of S_N1 reactions : We have observed that S_N1 reactions involve the formation of carbocations as intermediates. Further, since carbocations are planar, they can be attacked by the nucleophile in the second (fast) step on either side of the face. Thus if the starting alkyl halide is optically active, the product should be racemic mixture with no optical activity. However, this is rarely observed in practice. Normally, the two enantiomers of the product are not formed in equal amount ; the enantiomer having inverted configuration with respect to the alkyl halide predominates and the second enantiomer of the product is present in lesser amount. Thus the product contains a racemic modification and some amount of the enantiomer having inverted configuration. Hence it can be said that **S_N1 reactions proceed with inversion plus partial racemization.** In short, we can say that S_N1 reactions proceed both with inversion as well as retention of configuration, number of inverted molecules are always more than the molecules having original configuration. For example, hydrolysis of optically pure (–)-2-bromooctane gives 83% (+)- and 17% (–)-2-octanols, *i.e.* reaction proceeds with 66% net inversion.



(–)-2-Bromooctane — (+)-2-Octanol (83%) + (–)-2-Octanol (17%)

Net inversion = 66%

Partial but not complete loss of optical activity in S_N1 reactions suggests that the carbocation is not completely free of its halide ion counterpart when it is attacked by the nucleophile. Actually ionization of the alkyl halide gives a carbocation halide ion pair. The anion of the leaving group shields one side of the carbocation, and thus the nucleophile attacks the carbocation faster from the side opposite to the leaving group.



Thus more amount of the inverted configuration is formed than that of retained configuration. (The more stable carbocation gives more racemization). Thus note that the products of S_N1 reactions are not stereospecific (difference from S_N2 products which are stereospecific).

TEST YOUR UNDERSTANDING - 4.4

1. (*a*) Which of the alkyl halide in each of the following pairs will react faster in S_N1 reaction ?

(*i*) Cyclopentyl iodide or 1-methylcyclopentyl iodide

(*ii*) Cyclopentyl bromide or 1-bromo-2, 2-dimethylpropane

(*iii*) *tert*-Butyl iodide or *tert*-butyl chloride.

(*b*) Which of the alkyl halide in each of the following pairs will react faster with sodium iodide in acetone ?

(*i*) 1-Bromopentane or 3-bromopentane (*ii*) 1-Chlorohexane or cyclohexyl chloride

(*iii*) 2-Chloropentane or 2-fluoropentane (*iv*) 1-Bromodecane or 2-bromopropane

(*v*) 2-Bromo-2-methylhexane or 2-bromo-5-methylhexane.

2. In the hydrolysis of 2-bromo-3-methylbutane, the intermediate carbocation rearranges by a hydride shift, but not by a methyl shift, explain.

3. R-α-Phenylethyl chloride, $C_6H_5CHClCH_3$, of specification rotation – 34° is treated with dilute aqueous NaOH to give alcohol of [α] + 1.7°. If the specific rotations of the optically pure (R)-α-phenylethyl chloride and (R)-α-phenylethyl alcohol are – 109° and – 42.3° respectively, calculate (*a*) the optical purity of the reactant and product and (*b*) the percentage of inversion and of retention.

4. Suggest the mechanism whether S_{N^1} or S_{N^2} in the following reactions :

(*i*) $CH_3CH_2CH_2X \xrightarrow{:Z} CH_3CH(Z)CH_3$ (*ii*) $(CH_3)_2CHCH(X)CH_3 \xrightarrow{:Z} (CH_3)_2C(Z)CH_2CH_3$

(*iii*) $(CH_3)_3CCH_2Br \xrightarrow{C_2H_5O^-} (CH_3)_3CCH_2OC_2H_5$ (*iv*) $(CH_3)_3CCH_2Br \xrightarrow{C_2H_5OH} (CH_3)_2\underset{\displaystyle OC_2H_5}{\overset{\displaystyle |}{C}}—CH_2CH_3$

5. Neopentyl halides undergo nucleophilic substitutions very slowly, whatever might be the experimental conditions. Explain.

S_N2 versus S_N1 reactions

	S_N2		S_N1
1.	These follow second-order kinetics.	**1.**	These follow first order kinetics
2.	Here the nucleophile attacks on the alkyl halide from back side.	**2.**	Here the nucleophile attacks on the carbocation which are first formed by heterolysis of the C–X bond.
3.	These involve complete stereochemical inversion.	**3.**	These involve partial racemization.
4.	These form unrearranged products.	**4.**	Rearrange products are formed, where possible.
5.	The order of reactivity is $CH_3W > 1° > 2° > 3°$.	**5.**	Order of reactivity is $3° > 2° > 1° > CH_3W$.
6.	These require strong nucleophiles	**6.**	Weak nucleophiles are OK.
7.	Wide variety of solvents are used.	**7.**	These require good ionising solvent
8.	The reaction is stereoselective as well as stereospecific.	8.	The reaction is neither stereoselective nor stereospecific.

4.6.5 Factors Affecting S_N Reactions

However, before going to details of the factors favouring S_N1 or S_N2 reaction, we must know that the main difference in the two mechanisms lies in the way the nucleophile attacks on substrate. In S_N2 mechanism, nucleophile attacks the alkyl halide from back-side of the substrate ; while in S_N1, nucleophile attacks on the carbocation, hence here the alkyl halide first undergoes heterolytic cleavage. Thus whichever of these two processes (back-side attack by the nucleophile or heterolysis to form a carbocation) goes faster for a particular alkyl halide determines which mechanism predominates.

$$R-X+:Z \xrightarrow{\text{Solvent}} R-Z+X^-$$

The relative ease of these two processes in turn depends upon nature of substrate (alkyl group as well as leaving group), nature of nucleophile and of course also nature of solvent.

1. Nature of alkyl group (R). The nature of the alkyl group of the substrate exerts a profound effect on the type of mechanism. In alkyl groups, two structural factors are at work.

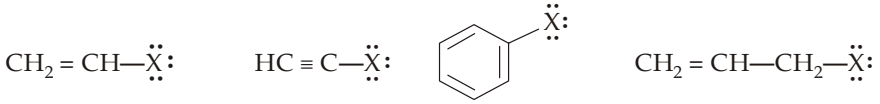
(*i*) *Steric factor.* It largely determines the ease with which a nucleophile can attack the alkyl group from back-side. Larger an alkyl group, more will be difficult for the nucleophile to attack it from back-side.

(*ii*) *Accommodation of positive charge.* This factor determines the ease of formation of a carbocation (*i.e.* ease of heterolysis). More is the ability of accommodating positive charge (by delocalization) by a carbocation, more will be the ease of heterolysis.

Thus as we proceed along the simple alkyl series (CH_3, 1°, 2° and 3°), the group becomes progressively bulky, steric hindrance increases and hence back side attack becomes more difficult and hence slower, this explains why S_N2 mechanism follows the order : $CH_3X < 1° < 2° < 3°$. At the same time, progressive branching in the alkyl group increases ability to accommodate positive charge ; hence heterolysis becomes easier and hence faster. This explains why S_N1 mechanism follows the order : $3° > 2° > 1° > CH_3X$.

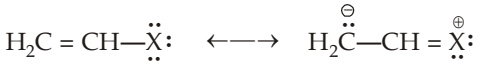
As mentioned earlier secondary alkyl halides may follow both (S_N1 and S_N2) or either of the two mechanisms.

Here, we must also consider the reactivity of unsaturated alkyl halides, which are of two types : (*a*) those having unsaturation at α-carbon atom, *viz.* vinyl, alkynyl and aryl halides, and (*b*) those having unsaturation at carbon other than α-, *e.g.* allyl halides.



Former are inert towards nucleophilic substitutions because of two factors.

(*i*) Resonance stabilization of the substrate which results in strengthening of the bond between carbon and halogen.



(*ii*) The halogen is attached to more electronegative carbon (sp^2 or sp) which thus makes departure of X difficult than in alkyl halides where it is attached on sp^3 carbon.

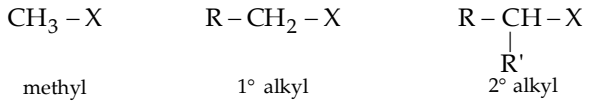
On the other hand, allyl halides undergo nucleophilic substitution easily mainly by S_N1 mechanism.

$$CH_3CH=CH—CH_2X \longrightarrow [CH_3CH=CH—\overset{+}{C}H_2 \longleftrightarrow CH_3\overset{+}{C}H—CH=CH_2]$$

$$\xrightarrow{OH^-} \underset{\text{Normal product } (S_N1)}{CH_3CH=CHCH_2OH} + \underset{\text{Rearranged product } (S_N1')}{CH_3CH(OH)—CH=CH_2}$$

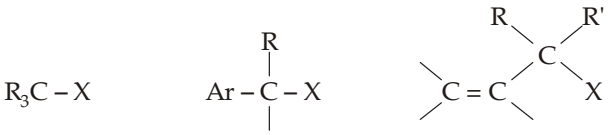
Summary of alkyl, allylic and benzylic halides and S_N reactions :

(a) Halides showing mainly S_N2 reactions :



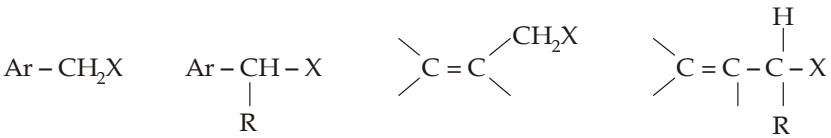
methyl 1° alkyl 2° alkyl

(b) Halides showing mainly S_N1 reactions :



3° alkyl 3° benzylic 3° allylic

(c) Halides showing either S_N1 or S_N2 reactions :



1° benzylic 2° benzylic 1° allylic 2° allylic

2. Nature of the leaving group. The nature of the leaving group has little effect on the type of mechanism. However, it effects the rate of reaction in both S_N1 as well as S_N2 reactions to same extent. In both cases, leaving group is removed, hence better the leaving group, faster will be the reaction.

Since the leaving group breaks away as a base, it is easier to displace weaker bases as compared to stronger bases. Thus we can say that the less basic the substituent, the more easily it is displaced (by the solvent in S_N1 reactions or by an attacking nucleophile in S_N2 reactions). This explains why alcohols are resistant to nucleophilic displacement *in non-acidic media* because strongly basic nature of the OH^- group makes it a poor leaving group. However, in presence of acids, the oxygen of the —OH group gets protonated and thus here the leaving group (H_2O), being a very weak base displaced easily. Thus alcohols undergo nucleophilic substitutions only in acidic medium. Thus, in general **the weaker the base, the better is the leaving group.** Relative leaving group abilities of the important groups are tabulated below.

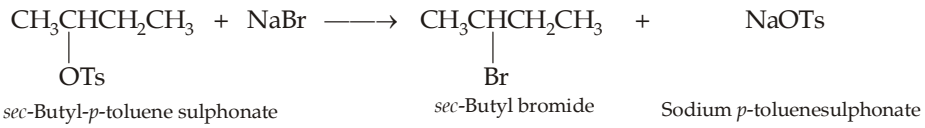
Relative Leaving-Group Abilities

Leaving group	*Relative rate*	*Conjugate acid* of leaving group*	*K_a of conjugate acid*
F^-	10^{-5}	HF	3.5×10^{-4}
Cl^-	10^{10}	HCl	10^7
Br^-	10^1	HBr	10^9
I^-	10^2	HI	10^{10}
H_2O	10^1	H_3O^+	55
TsO^-	10^5	TsOH	6×10^2
$CF_3SO_2O^-$	10^8	CF_3SO_2OH	10^6

TsO^- is *p*-toluenesulphonate ; their esters are called tosylates ; $CF_3SO_2O^-$ is trifluoromethanesulphonate (esters of the latter are called *triflates*).

* Any species whose conjugate acid has K_a less than 1 cannot be a leaving group in a nucleophilic substitution; *viz.* OH^-, H^-, OR^-, NH_2^-, NR_2^-.

Since *p*-toluenesulphonates (easily prepared by the reaction of alcohol and *p*-toluenesulphonyl chloride, commonly known as tosyl chloride) are better leaving groups than halides, alkyl halides (chloride, bromide or iodide) can be prepared from alkyl *p*-toluenesulphonates using corresponding NaX as nucleophile.



Tosylates undergo nucleophilic substitution (S_N1 as well as S_N2) in the same way as alkyl halides.

Other good leaving groups are phenoxide ion or 2, 4-dinitrophenoxide ion ; these are weak bases due to dispersal of negative charge on the benzene ring.

Example 6 :

Arrange the following in decreasing order of their leavability.

CH_3COO^-, $C_6H_5O^-$, Cl_3CCOO^- and $C_6H_5SO_3^-$

Solution :

Weaker the base (or stronger the conjugate acid of the base), more will be its leaving capacity. The conjugate acids of the given anions are

CH_3COOH C_6H_5OH Cl_3CCOOH $C_6H_5SO_3H$

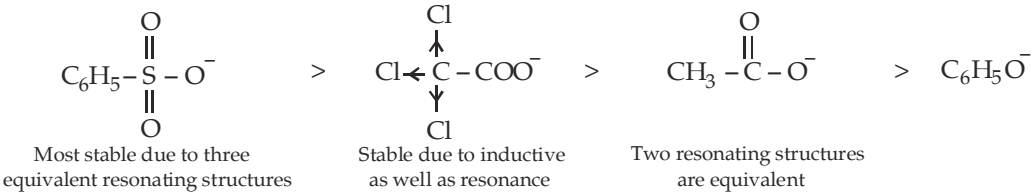
The relative acidic character of the four conjugate acids is

$$C_6H_5SO_3H > Cl_3CCOOH > CH_3COOH > C_6H_5OH$$

Thus the leavability (fugacity) of the four groups is

$$C_6H_5SO_3^- > Cl_3CCOO^- > CH_3COO^- > C_6H_5O^-$$

Alternatively, more the stability of the anion (base), higher is its leavability. Thus



TEST YOUR UNDERSTANDING - 4.5

1. Give chemical equation showing preparation of octadecyl *p*-toluenesulphonate ; and its reaction with (*a*) potassium acetate and sodium butanethiolate ($CH_3CH_2CH_2CH_2SNa$).

3. **Nature and concentration of the nucleophile.** Remember that S_N2 and S_N1 reactions differ in the respect that in the former, nucleophile participates in the rate-determining step, while in S_N1 reactions it participates after the rate-determining step. So, nature and concentration of nucleophiles mainly affects S_N2 reactions, and it does not play directly any role in S_N1 reactions.

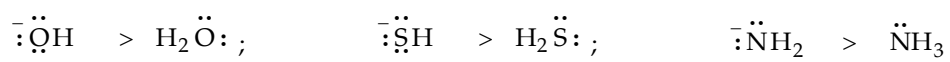
In S_N2 reactions, a nucleophile transfers its electron pair to carbon of the substrate leading to the formation of transition state. Hence, a stronger nucleophile will react with the substrate faster. Nucleophilic strength or nucleophilicity is a measure of how fast a Lewis base displaces a leaving group from a suitable substrate. By measuring the rate at which various Lewis bases react with methyl iodide in methanol, a list of their nucleophilicity relative to methanol as the standard nucleophile has been compiled.

Nucleophilicity of some common nucleophiles in water and alcohol

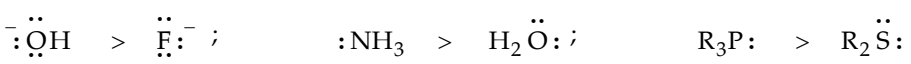
Class of nucleophile	*Nucleophile*	*Relative reactivity*
Very good	R_3P:, I^-, HS^-, RS^-	$> 10^5$
Good	R_2NH, HO^-, RO^-, CN^-, N_3^-	10^4
Fair	Br^-, NH_3, Cl^-, $RCOO^-$	10^3
Weak	F^-, H_2O, ROH	1
Very weak	RCOOH	10^{-2}

Trends in nucleophilicity :

(*i*) A species with a negative charge is a stronger nucleophile than a similar neutral species. In particular, a base is a stronger nucleophile than its conjugate acid.



(*ii*) With increase in electronegativity, nucleophilicity decreases from left to right in the periodic table.



(*iii*) Nucleophilicity increases down the periodic table, following the increase in size and polarizability.

$$I^- > Br^- > Cl^- > F^- \; ; \qquad {}^-SeH > {}^-SH > {}^-OH \; ; \qquad R_3P: > R_3N:$$

The rate of S_N1 is independent of the nature of the nucleophile (stronger or weaker) because here the nucleophile attacks on the carbocation (a fast step). The net result is that, other things being equal, *a strong nucleophile favours the S_N2 reaction, and a weak nucleophile favours the S_N1 reaction.*

Thus we can explain that why neopentyl bromide, Me_3CCH_2Br gives unrearranged product (S_N2 reaction) with ethoxide ion (a strong nucleophile), but a rearranged product (S_N1 mechanism) with C_2H_5OH (a weak nucleophile).

In S_N2 reactions, since a nucleophile is involved in the rate determining step, its concentration will directly effect the rate of reaction.

$$\text{rate} = k[RX][:Z]$$

Hence an increase in the concentration will speed up the reaction and also fraction of the reaction undergoing S_N2 reaction. On the other hand, a decrease in [: Z] slows down the S_N2 reaction and also the fraction of the reaction undergoing S_N2 reaction. The net result is that, other things being equal, *a high concentration of nucleophile favours S_N2 reaction, and a low concentration favours the S_N1 reaction.*

4. Effect of solvent. Solvents play a dominant and sometimes decisive role in deciding the rate and mechanism of nucleophilic substitution. Change in solvent in a particular reaction may increase or decrease the rate of reaction, even in some cases it may change the mechanism as is evident from following examples.

(*i*) $\underset{(>91\%\text{ yield})}{C_6H_{13}CN} \xleftarrow[<20\text{ mts.}]{DMSO} CH_3(CH_2)_4CH_2Br + NaCN \xrightarrow[>20\text{ hrs.}]{\text{aq. } CH_3OH} \underset{(71\%\text{ yield})}{C_6H_{13}CN}$

It is an example of S_N2 reaction.

(*ii*) $CH_3OH \xleftarrow[S_N1]{HCOOH/H_2O} CH_3Br \xrightarrow[S_N2]{H_2O,\,OH^-} CH_3OH$

Although no generalisation can be made, following point should be noted, of course with reservations.

(*a*) In presence of good ionizing solvents which increases the rate of ionization of the alkyl halide, rate of S_N2 reaction decreases while that of S_N1 reaction increases.

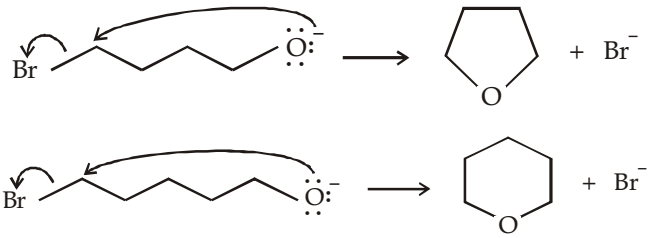
Dielectric constants and ionization rates of *t*-butyl chloride in common solvents.

Solvent	*Dielectric constant*	*Relative rate of ionization*
Water	78	8000
Methanol	33	1000
Ethanol	24	200
Acetone	21	1
Diethyl ether	4.3	0.001
Hexane	2.0	<0.0001

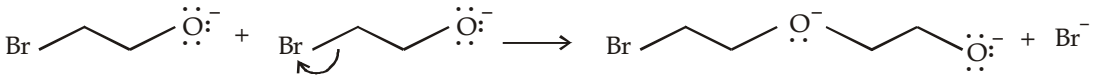
(*b*) Rate of S_N2 reactions is fastest in presence of polar aprotic solvents. Aprotic solvents are those polar solvents which do not have —OH group, *viz.* dimethylsulphoxide (DMSO, $Me_2S = O$), N, N-dimethylformamide (DMF, Me_2NCHO), acetonitrile (CH_3CN) etc.

Intermolecular versus intramolecular nucleophilic substitution

A molecule having two functional groups one of which acts as nucleophile and other leaving group can undergo intermolecular or intramolecular nucleophilic substitution. If the two such groups are separated from each other by four or five carbon atoms, intramolecular reaction occurs leading to the formation of five or six membered (*stable*) rings (*intramolecular* S_N).



Since three- and four-membered rings are strained (unstable) when the two groups are separated by one, two or three carbon atoms, intermolecular nucleophilic substitution takes place.



4.6.6 Nucleophilic Substitution in Acyl Compounds

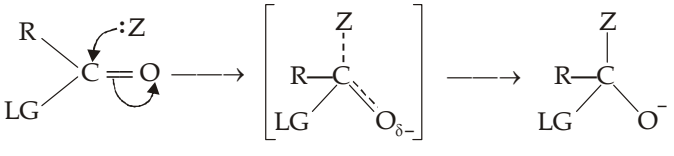
Acyl compounds (compounds containing acyl group, $R-\overset{\overset{O}{\|}}{C}-$ *viz.* carboxylic acids and their derivatives namely acid chlorides, anhydrides, amides and esters) undergo nucleophilic substitution in which —OH, —Cl, —OCOR, —NH_2 or —OR′ is replaced by some other basic group. Substitution at acyl carbon (unsaturated) takes place much more readily than at alkyl carbon (saturated) atom. High reactivity of acyl carbon towards nucleophilic substitution is due to electronic and steric factors.

(*a*) Tendency of oxygen to acquire electrons even at the expense of gaining negative charge.

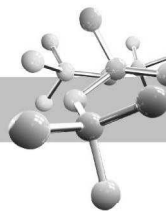
(*b*) Relatively unhindered transition state is formed ; in acyl substitution a tetrahedral intermediate (a stable situation) is formed from trigonal reactant, while in alkyl substitution a transition state having pentavalent carbon (an unstable situation) is formed from tetrahedral reactant.

The nucleophilic acyl substitution involves two steps.

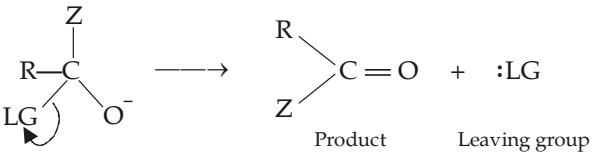
First step :



Transition state (Becoming tetrahedral) Intermediate (Tetrahedral)



Second step :



(*i*) Generally, the overall rate is affected by the rate of both steps, but the first step is more important.

(*ii*) The first step is favoured by the presence of electron withdrawl group on R which stabilizes the developing negative charge, and it is hindered by the presence of bulky groups which become crowded together in the transition state.

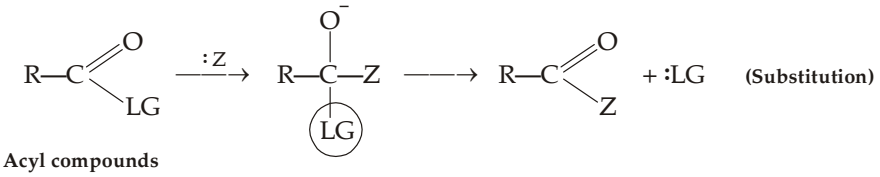
(*iii*) The second step depends on the basicity of the leaving group (:LG) ; the weaker the base the better the leaving group. For acid chlorides, acid anhydrides, esters and amides, **:**LG is respectively

	Cl^-	^-OCOR	^-OR	$^-NH_2$
Basic character	Very weak	Moderately weak	Strong bases	

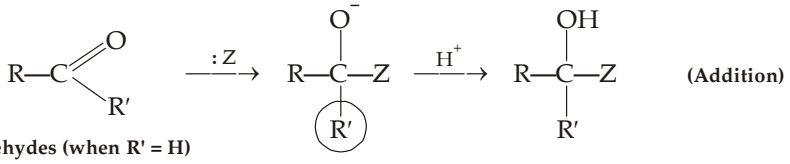
Increasing basic character ⟶
Decreasing leaving property

Thus acids chlorides undergo nucleophilic substitution most easily, while amides with most difficulty.

Relation between basicity and leaving capacity of the group also explains why aldehydes and ketones undergo nucleophilic addition rather than nucleophilic substitution, although first step is similar to that in acyl nucleophilic substitution.



Acyl compounds

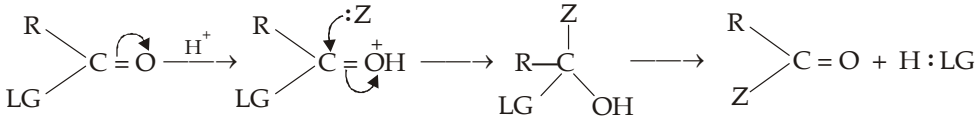


Aldehydes (when R' = H) or ketones

Note that if aldehydes and ketones, undergo substitution, the leaving group would have been hydride ion (**:**H^-) or alkyde ion (**:** R'^-) which, as we know, are the strongest bases of all, hence these are most difficult to be removed and instead aldehydes and ketones undergo addition reactions easily.

(*iv*) Nucleophilic acyl substitution neither involves the formation of carbocations, as in S_N1 reactions of alkyl halides nor pentavalent transition state as in S_N2 reactions of alkyl halides.

Acyl nucleophilic substitution takes place more easily in presence of acid, because here H^+ becomes attached to carbonyl oxygen making the carbonyl grup more electrophilic and thus more susceptible to the nucleophilic attack.



Undergoes nucleophilic attack more readily, even by weak nucleophiles

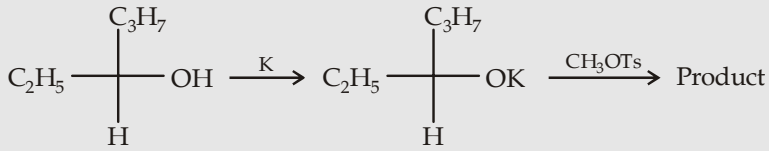
Thus we can explain why acid derivatives are hydrolysed more readily in presence of acids than in neutral medium; easy hydrolysis of acid derivatives in presence of alkali than in neutral medium is due to strong nucleophile ($^-$OH), and discussed in **chapter on acid derivatives.**

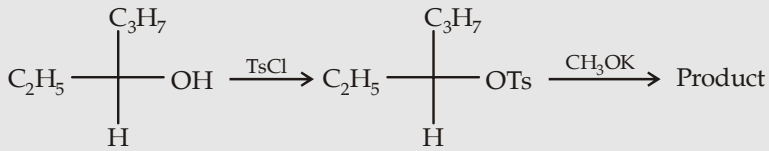
4.6.7 Electrophilic Substitution Reactions (S_E)

These reactions are mainly found in aromatic compounds. For details, consult Ch. 7.

Example 7 :

Observe the following two reactions and answer the questions mentioned below :

(i) 

(ii) 

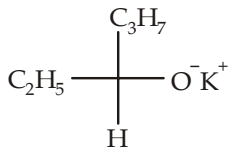
(a) Pick up the nucleophile in both reactions.

(b) Write the structure of the product in the two reactions and assign their R, S configurations.

(c) Is there any relation between the two products, if yes then mention it.

Solution :

(a) The nucleophile in the two reactions are



in (i); and $CH_3O^-K^+$ in (ii).

(b) In *(i)*, the chiral carbon is in the nucleophile and none of its bonds are cleaved, leading to the same configuration as reactant. However, in *(ii)* the CH_3O^- attacks the chiral carbon of the substrate from back side leading to inversion in configuration.

(c) 

Product from (*i*) *S* Product from (*ii*) *R*

The two products are enantiomers.

TEST YOUR UNDERSTANDING - 4.6

1. Among the following pairs, pick up the species that undergo nucleophilic substitution more easily

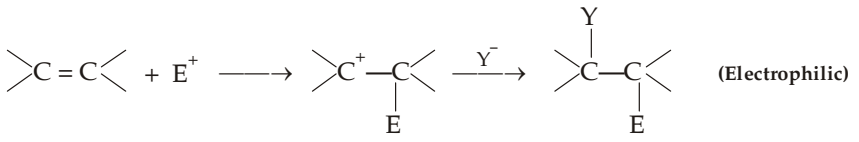
(*i*) CH_3COCl and CH_3Cl (*ii*) CH_3CONH_2 and CH_3NH_2 (*iii*) $CH_3COOC_2H_5$ and $CH_3OC_2H_5$

2. For each of the following pairs, pick up the compound (I or II) which undergoes S_N2 reaction more easily than the other.

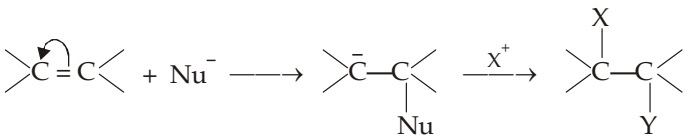
	I	II
(a)	$CH_3Cl + OH^-$	$CH_3Br + OH^-$
(b)	$CH_3CH_2Cl + H_2O$	$CH_3CH_2Cl + OH^-$
(c)	$CH_3CH_2Br + CH_3S^-$	$CH_3CH_2Br + CH_3O^-$
(d)	$CH_3CH=\underset{\displaystyle CH_3}{\underset{\vert}{C}}H-CH-Br$	$CH_3CH=\underset{\displaystyle CH_3}{\underset{\vert}{C}}Br$

4.7 Mechanism of Addition Reactions

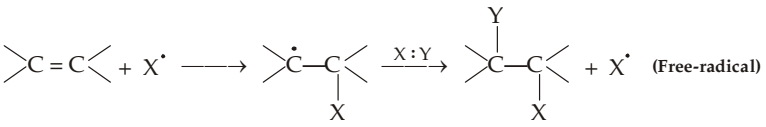
Like substitution reactions, addition reactions may be initiated by electrophiles, nucleophiles or free radicals. Hence addition reactions may also be of three types, *viz.* electrophilic addition reactions, nucleophilic addition reactions and free radical addition reactions.



(Electrophilic)



(Nucleophilic)

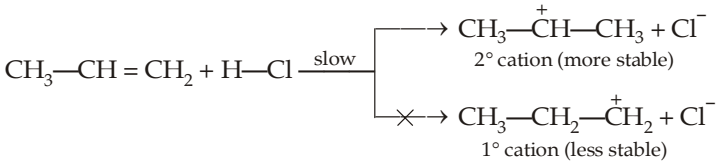


(Free-radical)

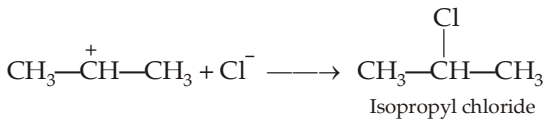
4.7.1 Mechanism of Electrophilic Addition

Since a multiple bonded carbon atom can readily supply the comparatively loosely held π electrons to the electrophile, *electrophilic additions are characteristic reactions of alkenes and alkynes.* Moreover, π electron cloud tends to shield the molecule from attack by nucleophiles. The general mechanism given above for electrophilic addition is applicable for addition of protic acids, *viz.* HCl, HBr, HI, H_2SO_4 and H_3O^+ (hydration in presence of acid). Let us examplify it by addition of HCl on propene.

First step :

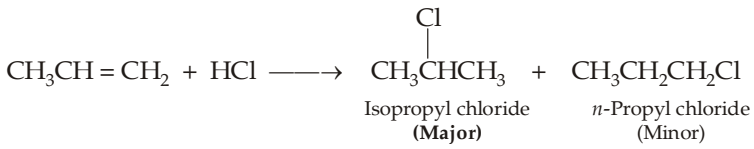


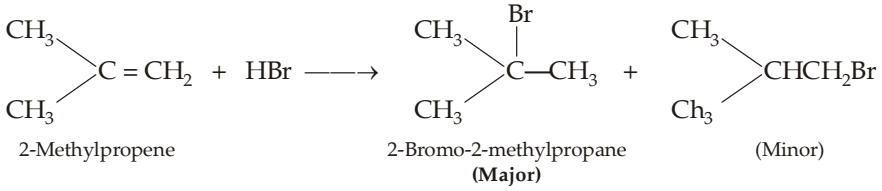
Second step :



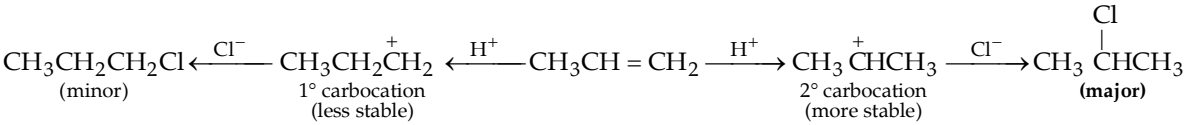
Order of reactivity among HX is : HI > HBr > HCl > HF

Such reactions (as that of addition of HX on propene) which can produce two or more isomers, but gives one of them in greater amount than the other, are called **regioselective**, a reaction which is 100 percent regioselective is termed **regiospecific.** For example,





In such cases, *i.e.* when an unsymmetrical reagent adds on an unsymmetrical alkene, major product is given by **Markownikov's rule** *according to which the negative part of the reagent adds on that carbon atom which has minimum number of hydrogen atom(s).* Alternatively, the compound corresponding to the more stable carbocation is the major product, viz.

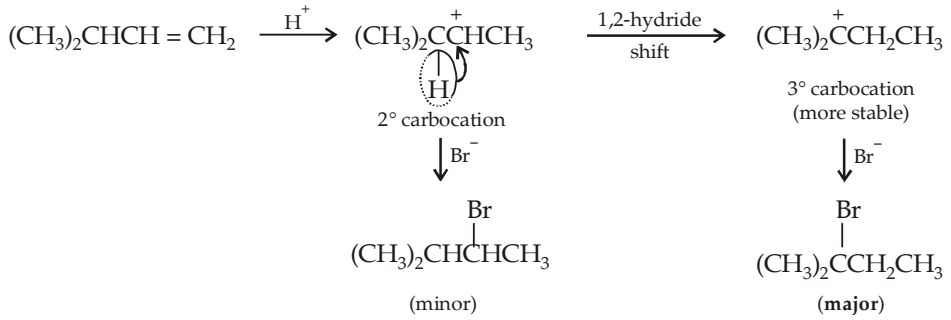


Since carbocations are formed as intermediate in the above electrophilic addition reactions, such reactions are liable to form rearranged product, where possible, by the 1,2-hydride, 1,2-methyl or 1,2-phenyl shift. Such shifts are possible only when a less stable carbocation is changed to more stable (3° > 2° > 1°). The preference of shifts follow the order

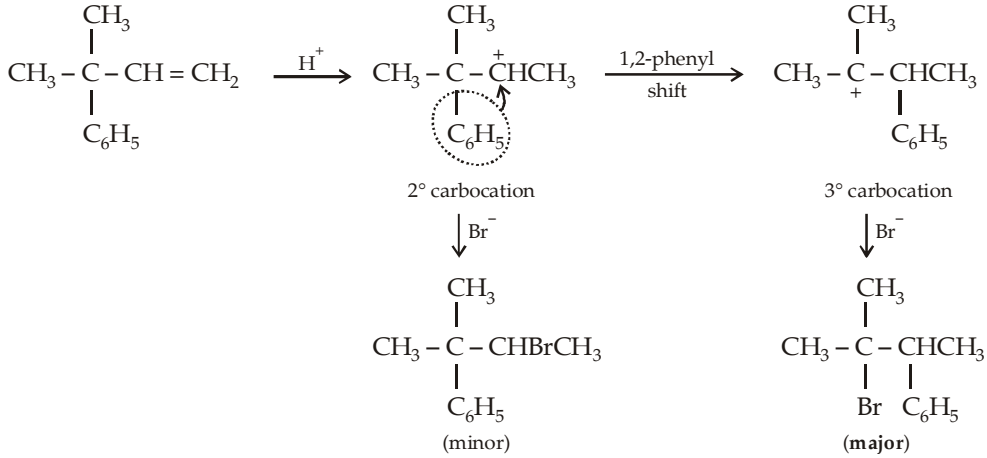
1,2-phenyl > 1,2-hydride > 1,2-methyl

For example,

(i)



(ii)

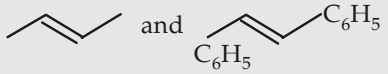


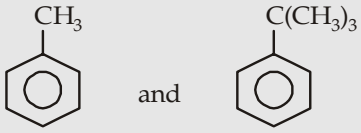
Example 8 :

Which compound of each pair is more reactive toward reaction given against each.

(a)  **(addition of HBr)**

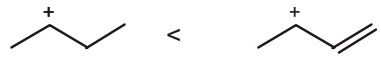
(b)  **(addition of HCl)**

(c)  **(addition of HCl)**

(d)  **(nitration)**

Solution :

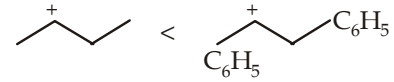
The first three reactions are examples of electrophilic addition, so higher the stability of the carbocation greater will be its reactivity towards given reagents.

(a) 

2° carbocation < 2° allylic carbocation (more stable)

(b) 

2° carbocation < 3° carbocation more stable

(c) 

2° carbocation < 2° benzyl carbocation (more stable)

(d) Here the two effects (inductive and hyperconjugation) operate in opposite directions. Since hyperconjugation dominate over inductive effect, so nitration (electrophilic substitution) will be governed by hyperconjugation, hence toluene will undergo nitration faster than *ter*-butylbenzene.



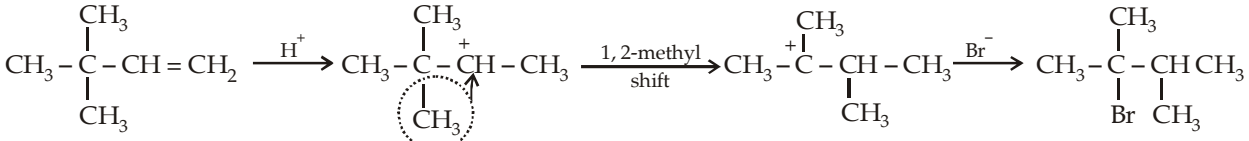
Three hyperconjugative H's — Zero hyperconjugative H

Example 9 :

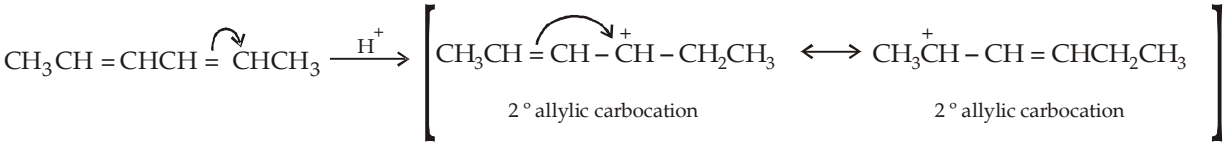
Give mechanism for the following reactions :

(i) $(CH_3)_3CCH = CH_2 + HBr$ **(ii) $CH_3CH = CHCH = CHCH_3 + HBr$**

Solution :

(i) 

2° carbocation — 3° carbocation — 2-Bromo-2, 3-dimethylbutane

(ii) 

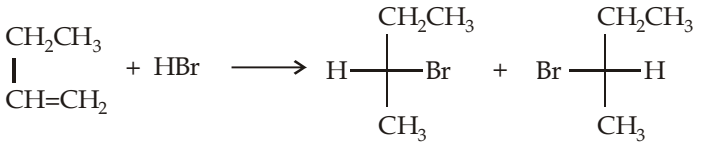
2 ° allylic carbocation ⟷ 2 ° allylic carbocation



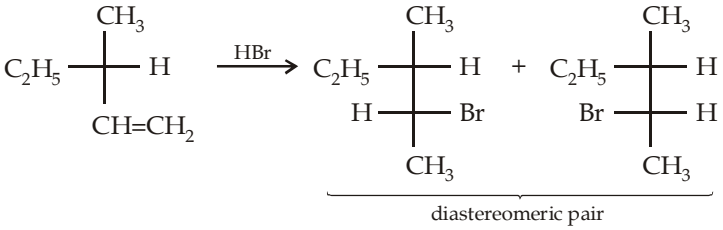
4-bromo-2-hexene + 2-bromo-3-hexene

Stereochemistry of Addition of HX on Alkenes

(i) When a chiral centre is created due to addition of HX on alkenes, having no chiral carbon, a racemic mixture of the product is formed, because the intermediate is sp^2 hybridised carbocation (or sp^2 hybridised free radical) either of which is liable to be attacked by the X^- ion (or $X^\bullet$) either from above the plane or below the plane.



(ii) In case the alkene has a chirality centre and the addition reaction results in another chiral centre, a pair of diastereomers will be formed.

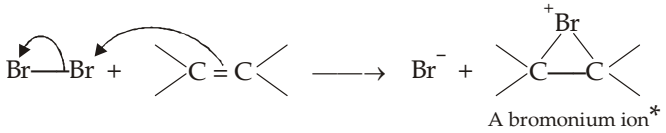


However, the two diastereomers will be formed in unequal amounts because one face of the intermediate carbocation will be more sterically hindered and hence less available for the Br^- ion than the other which is less sterically hindered.

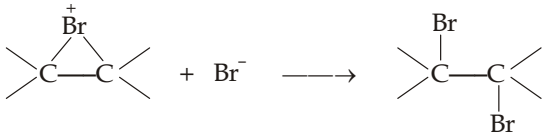
(iii) For the stereochemistry of the addition reactions on the alkene having no chiral centre but gives two chiral centres, consult **Chemical Properties of Alkenes**.

Addition of halogens (*e.g.* Br_2) on alkenes is somewhat different from the above general mechanism of electrophilic addition. Here, again the first step involves the formation of a cation, a cyclic bromonium ion*, but not a carbocation. Note that here also bromine is transferred as positive bromine (electrophile), *i.e.* without a pair of electrons which are left behind on the second bromine atom released as bromide ion. In the second step, the cyclic bromonium ion is attacked by the available nucleophile which may be Br^- or any other species added from outside to form the final product(s).

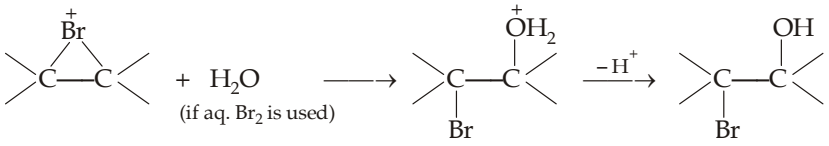
First step :



Second step :

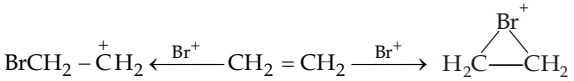


Or



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* In cyclic bromonium ion, all of its atoms have octet of electrons, while carbon has only six electrons in the carbocation, $BrCH_2—\overset{+}{C}H_2$.

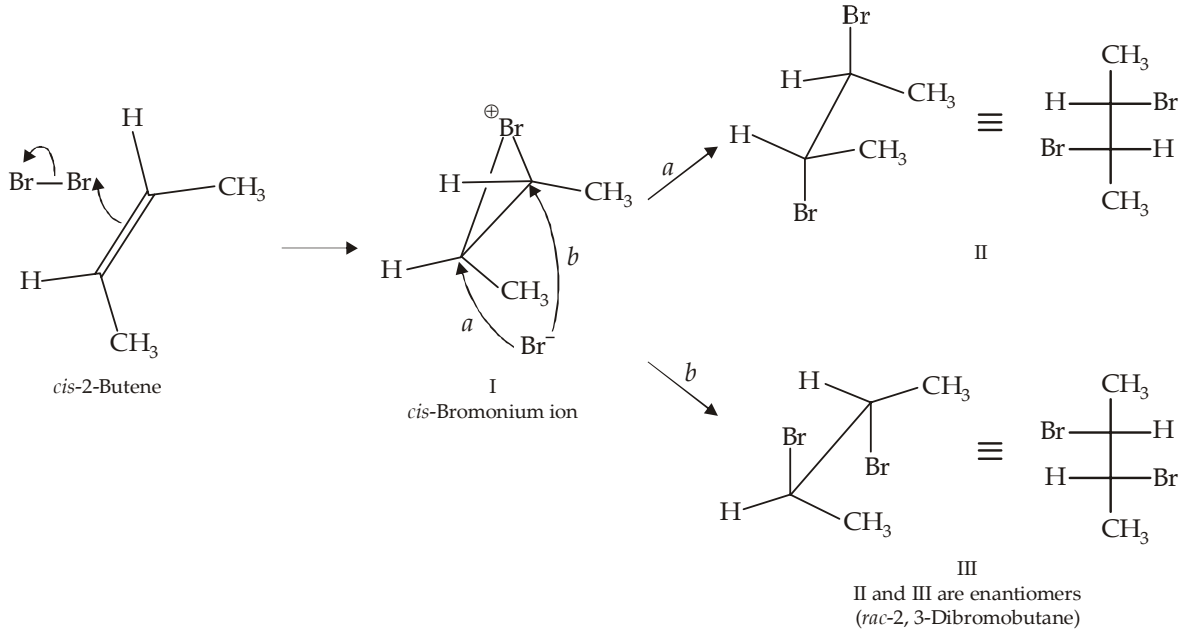


This is the same reaction which involves the formation of halohydrins (addition of OH^- and Br^+ parts of $\overset{-\delta}{H}O\overset{+\delta}{Br}$ used as ($H_2O + Br_2$).

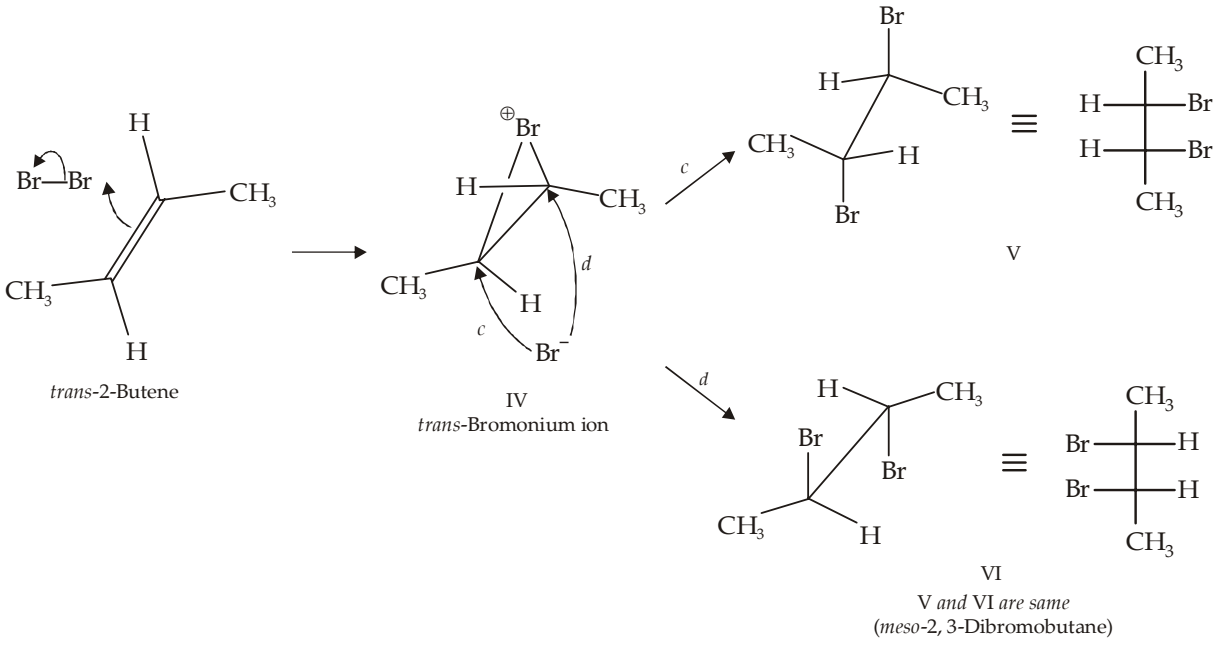
Addition of halogens on alkenes follows the order : $F_2 > Cl_2 > Br_2 > I_2$. However, fluorine is so reactive that it not only adds to the double bond but also replaces all the hydrogens with fluorine. On the other hand, iodine adds slowly to alkenes at low temperature and further the di-iodides, being unstable due to large size of iodine present on adjacent carbon atoms, decompose back to give alkene and iodine at room temperature. Inert solvents like CCl_4 and CH_2Cl_2 are used for halogen addition because these solvents dissolve both halogens as well as alkenes.

Special features of halogen addition

Addition of two bromine (in case of Br_2) or Br and OH (in case of $Br_2 + H_2O$) takes place in *anti*-manner proving the formation of cyclic bromonium ion. Thus addition of bromine on *cis*-2-butene gives only *racemic*-2, 3-dibromobutane, while *trans*-2-butene gives only *meso*-2, 3-dibromobutane. Thus addition of bromine to alkenes is both *stereospecific* as well as *stereoselective.*



Addition of bromine to *cis*-2-butene *via* a cyclic bromonium ion. Opposite-side attacks [(a) and (b)] are equally likely, and give enantiomers in equal amounts.

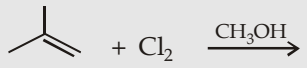


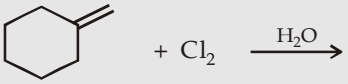
Addition of bromine to *trans*-2- butene via a cyclic bromonium ion. Opposite-side attacks [(c) and (d)] give the same product.

A reaction in which stereoisomeric starting molecules gives stereoisomeric products is called **stereospecific reaction.** Terms like *syn* addition, *anti* elimination and inversion of configuration describe stereospecific reactions. On the other hand, a reaction in which a single starting material can form two or more stereoisomeric products but one of them predominates is called a **stereoselective reaction.** Terms such as addition to the less hindered side describe stereoselectivity.

Example 10 :

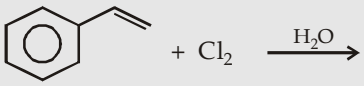
Write the major product in each of the following reactions :

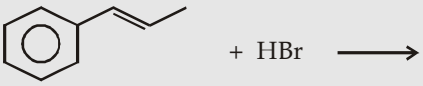
(a) 

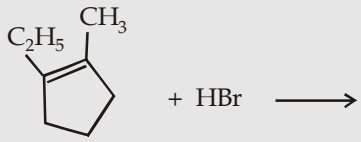
(b) 

(c) 

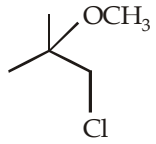
(d) 

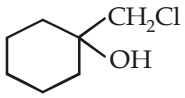
(e) 

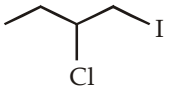
(f) 

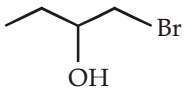
(g) 

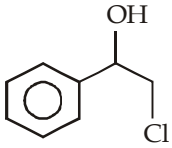
Solution :

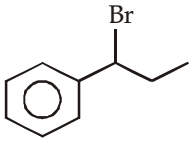
(a) 

(b) 

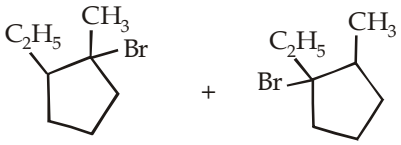
(c) 

(d) 

(e) 

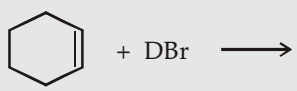
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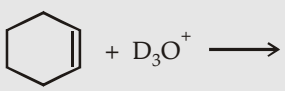
(Benzylic carbocation as intermediate)

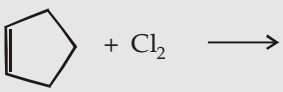
(g) 

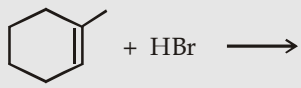
Example 11 :

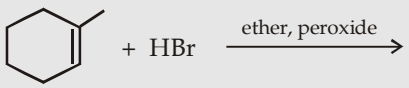
Give the stereochemistry of the product(s) formed in each of the following reaction :

(a) 

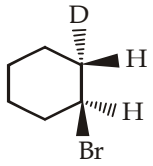
(b) 

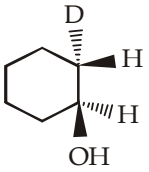
(c) 

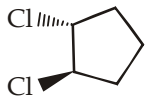
(d) 

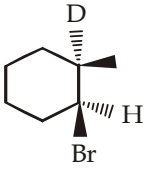
(e) 

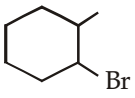
Solution :

(a)  + enantiomer

(b)  + enantiomer

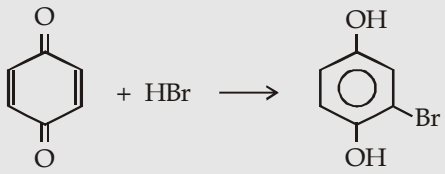
(c)  + enantiomer

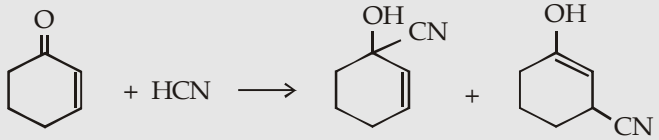
(d)  + enantiomer

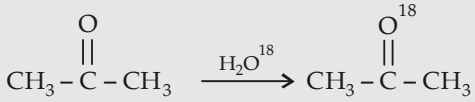
(e) 

Example 12 :

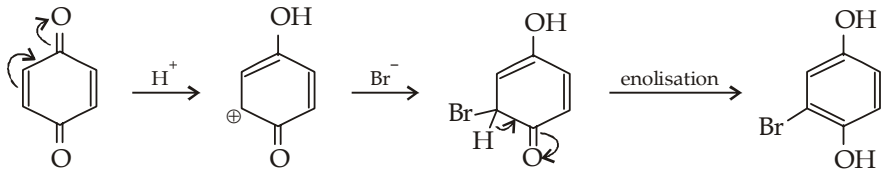
Propose mechanism for the following reactions :

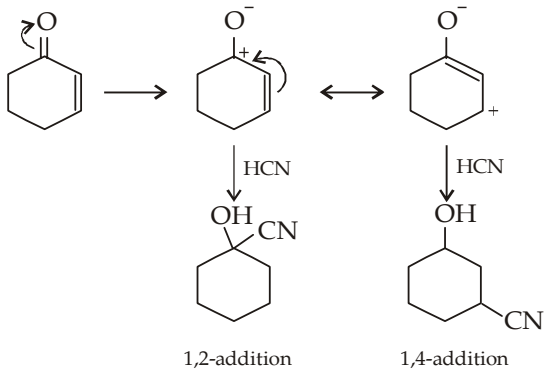
(a) 

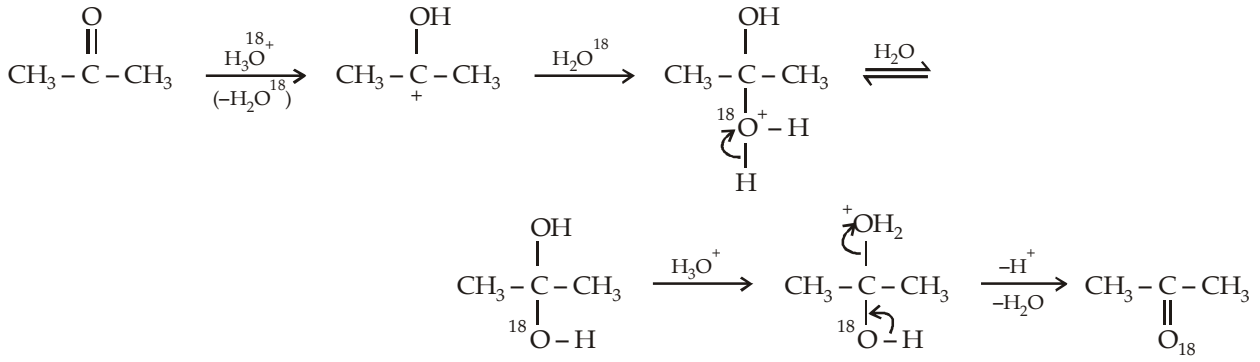
(b) 

(c) 

Solution :

(a) 

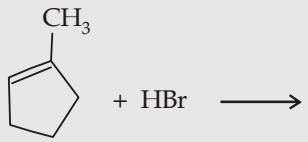
(b) 

(c) 

Example 13 :

Give the addition product for each of the following reactions with the stereochemistry of the product.

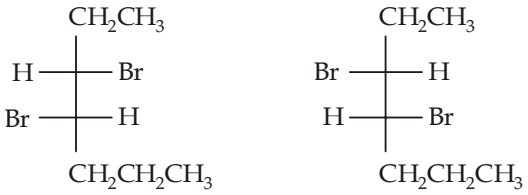
(a) ***cis*-3-Heptene + Br_2 ⟶** **(b) 3-Methyl-3-hexene + HBr ⟶**

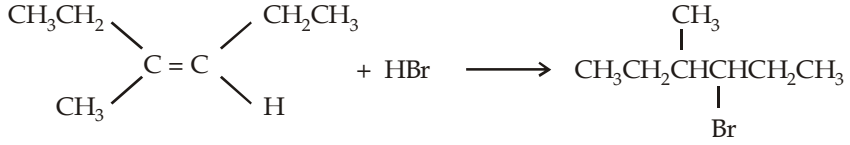
(c) 

Solution :

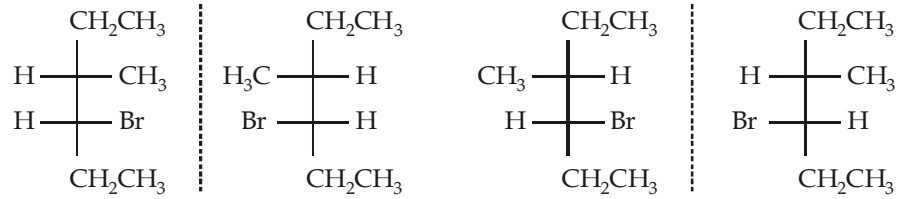
(a) $CH_3CH_2CH=CHCH_2CH_2CH_3 + Br_2 \longrightarrow CH_3CH_2\overset{Br}{\underset{|}{C}}H\overset{*}{C}H\overset{Br}{\underset{|}{C}}HCH_2CH_2CH_3$

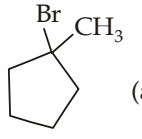
Here although two chiral centres are created, only two isomers (one enantiomeric pair) will be formed because the cyclic bromonium ion is liable to be attacked by the Br^- only from the opposite side, i.e. only *anti* addition (not *syn* addition) is possible.



(b) 

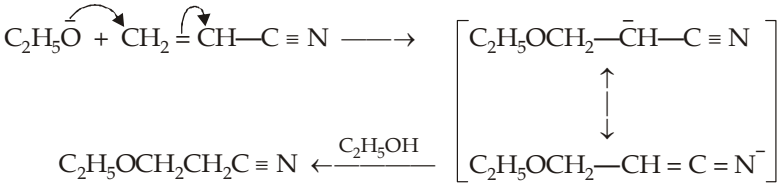
Two chirality centres have been created in the product, the number of stereoisomers formed will be four, which are two enantiomeric pairs.



(c)  (achiral molecule)

4.7.2 Mechanism of Nucleophilic Addition

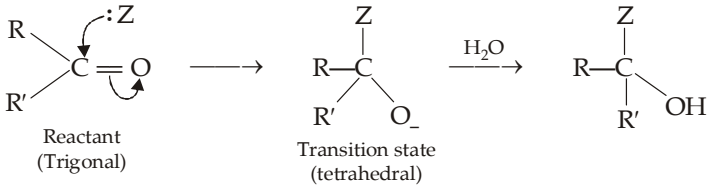
Presence of electron-withdrawing group in an alkene deactivates a carbon-carbon double bond towards electrophilic addition reactions, but at the same time it makes alkene more susceptible to attack by a nucleophile. If the electron-withdrawing group is in conjugation with the carbon-carbon double bond, the intermediate carbanion, formed by the attack of nucleophile stabilizes due to resonance. Hence such alkenes undergo nucleophilic addition reactions. Examples are addition reactions of α, β-unsaturated nitriles, aldehydes, ketones and esters. Addition of ethanol to acrylonitrile in presence of strong base is a typical example. The base converts the weaker nucleophile (C_2H_5OH) to a stronger nucleophile ($OC_2H_5^-$).



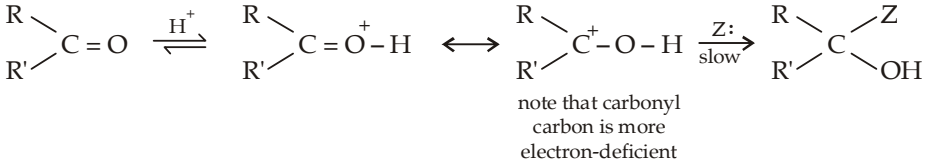
Similarly, $(CH_3)_2\ddot{N}H + CH_2 = CHCN \longrightarrow (CH_3)_2NCH_2CH_2CN$

Important example is Michael reaction.

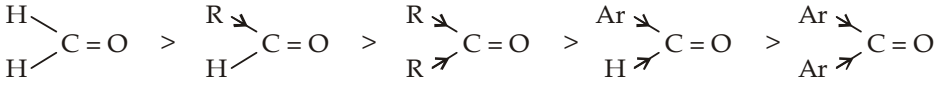
However, nucleophilic additions are typical reactions of aldehydes and ketones. The real cause of reactivity of the carbonyl group towards nucleophiles is the tendency of oxygen to acquire electrons and its ability to carry a negative charge. This makes carbonyl carbon electron-deficient and liable to be attacked by a nucleophile. Further, carbonyl group, being flat, is open to relatively unhindered attack from above or below. The reaction takes place in the following two steps.



Nucleophilic addition to carbonyl group takes place easily in presence of acids because the latter protonates the carbonyl oxygen which thus causes carbonyl carbon more electron deficient.



Since alkyl groups are electron-releasing, their presence makes the carbonyl carbon less electron-deficient, and less reactive towards nucleophilic substitution hence nucleophilic substitution on carbonyl group follows the order :



Since the nucleophile attacks only on the carbonyl carbon rather than on oxygen, the addition to carbonyl group is **regioselective**. In case, the carbonyl compound has two different alkyl groups i.e. $R \neq R'$, the product will be a mixture of the two enantiomers.

4.7.3 Mechanism of Free Radical Addition

Free radical addition reactions are encountered during addition of HBr (not HCl or HI) on alkenes in presence of peroxides* (recall that in absence of peroxides, additon is electrophilic), hence the reaction is commonly known as **peroxide effect.** The salient features of the mechanism are

(*i*) peroxides initiate the free-radical reactions.

(*ii*) hydrogen and bromine add to the double bond homolytically rather than hetero-lytically.

(*iii*) the intermediate is a free radical rather than a carbocation.

(*iv*) addition occurs against Markownikov rule.

---

* Free-radical additon also takes place in presence of light of a wavelength liable to dissociate H—Br into $H^{\bullet}$ and $Br^{\bullet}$.

The essential steps of the reaction are as follows.

$$\underset{\text{Peroxide}}{RO—OR} \longrightarrow 2\dot{O}R$$

} **Chain - initiating steps**

$$R\dot{O} + HBr \longrightarrow ROH + Br.$$

$$CH_3CH = CH_2 + Br. \longrightarrow \underset{\text{2° free radical (more stable)}}{CH_3—\dot{C}H—CH_2Br}$$

$$CH_3—\dot{C}H—CH_2Br + H—Br \longrightarrow CH_3—CH_2—CH_2Br + Br.$$

} **Chain - propagating steps**

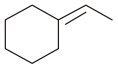
Peroxide effect is neither shown by H—Cl (because bond energy of the H—Cl bond is too high to break on approach of free radicals) nor by H—I because I**.** radicals are very unstable and hence combine to form I_2 moleccule.

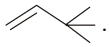
Polymerisation of ethylene to polyethylene and vinyl monomers to polyvinyl monomers are also free radical addition reactions.

$$nCH_2 = CH_2 \xrightarrow{\text{Catalyst}} -[-CH_2—CH_2-]_n-$$

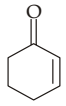
TEST YOUR UNDERSTANDING - 4.7

1. Give structural formula for the carbocation intermediate that leads to the major product in the following reactions :

(*i*) 2-Methyl-1-butene + HCl (*ii*) *cis*-2-Butene + HBr (*iii*)  + HBr

2. Give mechanism for the additon of HCl on  .

3. Identify compounds A to E in the following reactions :

(*i*)  + HCN ⟶ A + B

(*ii*) $CH_3CH = CH_2 + CCl_4 \xrightarrow{\text{peroxide}} C$

(*iii*) $CH_3CH = CH_2 + CBrCl_3 \xrightarrow{\text{peroxide}} D$

(*iv*) $CH_3CH = CH_2 + CHCl_3 \xrightarrow{\text{peroxide}} E$

4.8 Mechanism of Elimination Reactions

Elimination reactions involve the loss of atoms(s) or group(s) from a molecule to form an unsaturated species (generally double or triple bonds), thus these reactions may said to be reverse of addition reactions. These reactions may proceed in the following two ways.

1. **α-Elimination or 1, 1-elimination.** Here the two atoms or groups are eliminated from the same carbon atom leading to the formation of carbenes, *e.g.*

$$CHCl_3 \longrightarrow :CCl_2 + HCl$$

This type of reactions is very rare.

2. **β-Elimination or 1, 2-elimination.** Here two atoms or groups are removed from two adjacent carbon atoms leading to the formation of a double bond. These are the common elimination reactions and can take place by either of the two mechanisms, namely E2 and E1.

(a) $H_3C—CH_2Cl + :B \longrightarrow H_2C = CH_2 + H:B + Cl^-$

(b) $RCH_2CH_2OH \xrightarrow{H^+} RCH = CH_2 + H_2O$

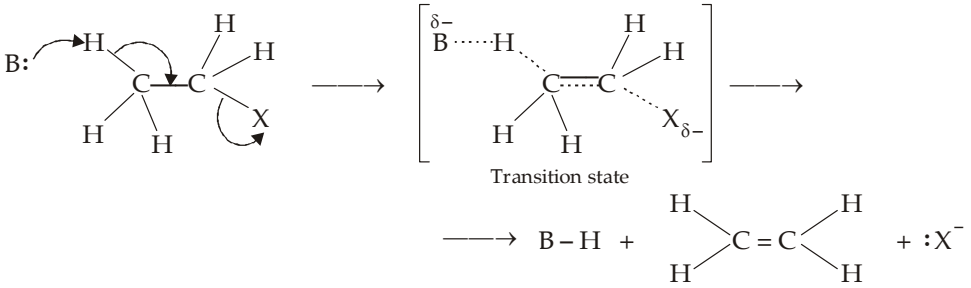
(c) $RCH_2CH_2\overset{+}{N}R_3OH^- \xrightarrow{\text{heat}} RCH = CH_2 + R_3N + H_2O$ (**Hofmann degradation**)

4.8.1 E2 Mechanism

The reaction following this mechanism exhibits second-order kinetics.

$$\text{Rate} = k[\text{Alkyl halide}]\,[\text{Base}]$$

Thus doubling the concentration of either the alkyl alhalide or the base doubles the reaction rate, while doubling the concentration of both reactants increases the rate by a factor of 4. Such reactions involve a single step ; base pulls a proton away from carbon and simultaneously a halide leaving group departs from the molecule forming the double bond.



Among different halide leaving groups, reactivity of alkyl halides increases with decreasing strength of the carbon-halogen bond, *i.e.*

R—I > R—Br > R—Cl > R—F

Weakest C—halogen bond, I^- the best leaving group

Strongest C—halogen bond, F^- the poorest leaving group

Hence iodides are most reactive towards elimination reaction, while fluorides the least which explains why fluorides are not used as starting materials in the preparation of alkenes.

In case, dehydrohalogenation of alkyl halide yields more than one alkene, *the alkene having greater number of alkyl groups to the doubly bonded carbons will be preferred product* **(Saytzeff rule,** which can also be defined as '*in dehydrohalogenation the more stable the alkene, the faster it is formed*'). The more stable alkene is thus known as **Saytzeff product,** while the less stable alkene is known as **Hoffmann product.**

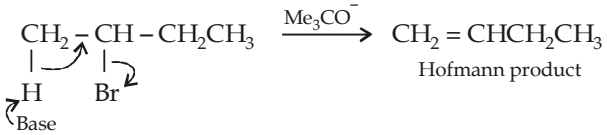
$$CH_3CH_2\underset{\underset{Br}{|}}{C}HCH_3 \xrightarrow{(CH_3)_3COK} \underset{\text{(Saytzeff product)}}{CH_3CH=CHCH_3} + \underset{\text{(Hoffmann product)}}{CH_3CH_2CH=CH_2}$$

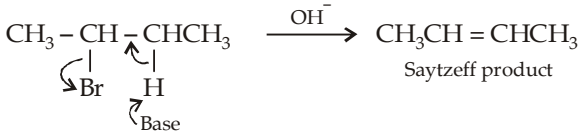
Thus the ease of formation and stability of various alkenes is

$$R_2C=CR_2 > R_2C=CHR > R_2C=CH_2, RCH=CHR > RCH=CH_2$$

Most E2 reactions give Saytzeff product, however, Hofmann product is preferred under one of the following conditions :

(*i*) The base used is large, e.g. Me_3CO^-.





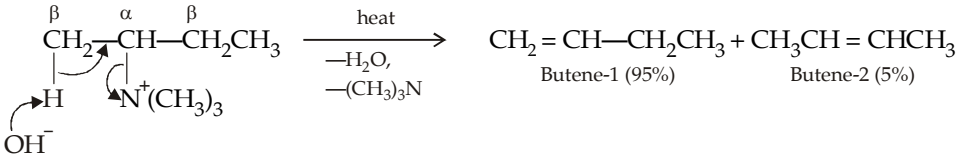
(*ii*) The alkyl halide is an alkyl fluoride.

(*iii*) The alkyl halide contains one or more double bonds. Remember that a conjugated alkene is always preferred to non-conjugated alkene.

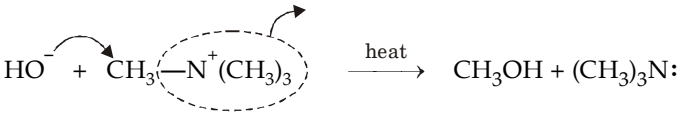
(*iv*) Eliminations involving charged substances, e.g. when a quaternary hydroxide is heated strongly (to 125°C or higher), it decomposes to form an alkene and a tertiary amine.

$$\underset{\underset{N^+(CH_3)_3OH^-}{|}}{CH_3CHCH_2CH_3} \xrightarrow{\text{heat}} \underset{\text{1-Butene(95\%)}}{CH_2=CHCH_2CH_3} + (CH_3)_3N + H_2O$$

This reaction, known as **Hofmann elimination**, is an E2 reaction in which hydroxide ion functions as a base. A novel aspect of the Hofmann elimination is its *regioselectivity*. Elimination in alkyltrimethylammonium hydroxides proceeds in the direction that gives the less substituted alkene (opposite to Saytzeff rule) ; this is known as **Hofmann rule** *or* **Hofmann orientation**.



The base (OH^-) attacks the most acidic hydrogen ; a primary hydrogen atom is more acidic because its carbon atom bears only one electron-releasing group. Alternatively, it is the less sterically hindered β hydrogen that is attacked by the base (OH^- or any other base). Methyl groups are deprotonated in preference to methylene groups which in turn are deprotonated in preference to methines. In case the 4° ammonium hydroxide does not have any β-hydrogen, alkene formation is impossible, rather alcohol is formed by S_N2 reaction.



As we have observed, E2 mechanism resembles S_N2 mechanism, however the two differ in their relative order. Reactivity of RX toward E2 is 3° > 2° > 1° (opposite to that of S_N2 reactions) which is evident from the following relative rates.

Alkyl halide		*Product*	*Relative rate*	*Relative rate per H*
(1°) CH_3CH_2Br	⟶	$CH_2 = CH_2$	1.0	1.0
(1°) $CH_3CH_2CH_2Br$	⟶	$CH_3CH = CH_2$	3.3	5.0
(2°) $CH_3CHBrCH_3$	⟶	$CH_3CH = CH_2$	9.4	4.7
(3°) $(CH_3)_3CBr$	⟶	$(CH_3)_2C = CH_2$	120	40

This relative order, 3° > 2° > 1°, is due to following two factors.

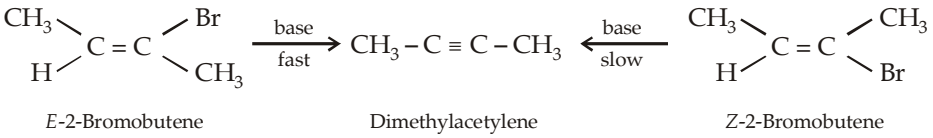
(*a*) Increased branching (from 1° alkyl halide to 3° halide) successively provides greater number of β-hydrogens for attack by base (probability factor).

(*b*) Increased branching leads to a more highly branched, *i.e.* more stable alkene.

4.8.2 Stereochemistry of E2 Reactions

The two groups or atoms are eliminated from *anti* (opposite) positions (*anti elimination*) because *anti* elimination requires the molecule to be in a staggered conformation (a more stable conformer), while *syn* elimination requires eclipsed conformation.

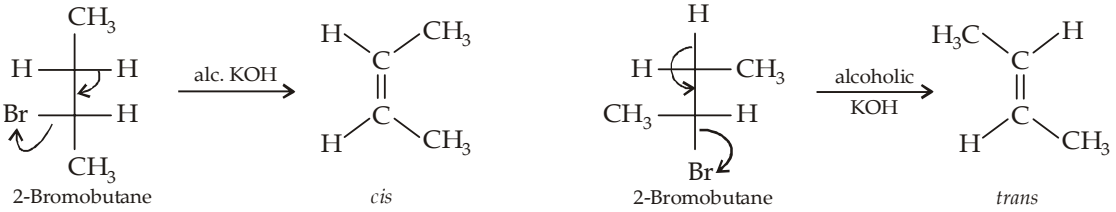
In other words, for *anti* elimination, the two leaving groups must be as far apart as possible. Thus *E*-2-bromobutene forms dimethylacetylene more rapidly than the *Z*-isomer.



E-2-Bromobutene Dimethylacetylene *Z*-2-Bromobutene

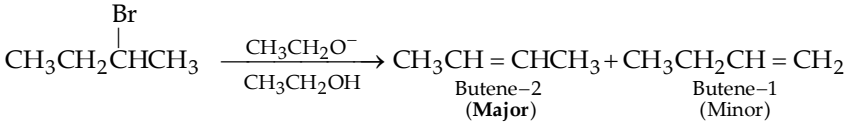
This example indicates that E2 reaction is *stereospecific*, i.e. different stereoisomer of the starting material gives different stereoisomer of the product. This is also reflected from compounds having chiral carbon atoms ; *meso*-isomer gives *cis*-isomer while *d*- or *l*-gives *trans*-isomer on E2 elimination.

Following examples also indicate stereospecificity of E2 reactions.



2-Bromobutane *cis* 2-Bromobutane *trans*

Other interesting example of E2 reaction is dehydrohalogenation of alkyl halides leading to two products.



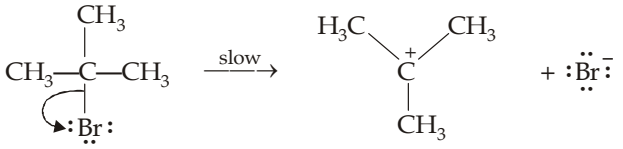
Butene–2 (**Major**) Butene–1 (Minor)

Further, of the two isomeric butene-2 (*E* and *Z*), *E*-butene-2 (having bulkier groups on opposite sides) is major because it has less steric strain and thus more stable, while *Z*-butene-2 is minor. Thus it can be said that E2 reactions are regioselective (dominance of butene-2 over butene-1) as well as stereoselective (dominance of *E*-butene-2 over *Z*-butene-2).

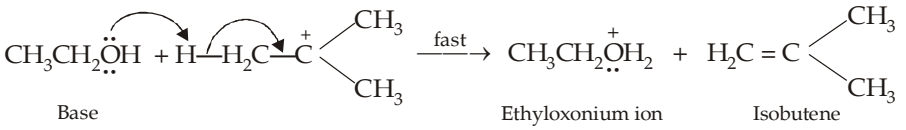
4.8.3 E1 Mechanism

E1 reaction proceeds by first-order kinetics. The mechanism is similar to that of S_N1 reactions except that here the carbocation loses a proton to form alkene (*cf.* in S_N1 reactions, carbocation takes up nucleophile). Since here carbocations are formed as intermediates, the relative order of reactivity of alkyl halides towards E1 should be 3° > 2° > 1°.

First step :



Second step :



Base Ethyloxonium ion Isobutene

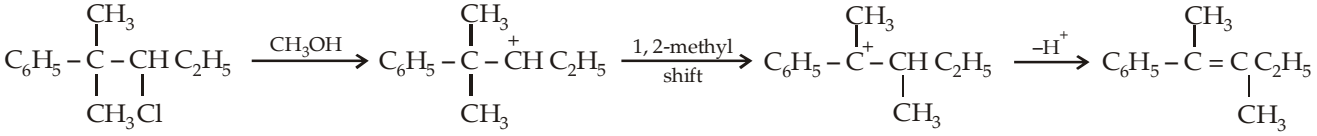
4.8.4 Characteristics of E1 Reactions

(i) Since in the rate-determining step of E1 reaction, the leaving group is removed, and a carbocation is formed as an intermediate, the rate of E1 reaction depends on both of these factors and follows the order.

3° benzylic ≈ 3° allylic > 2° benzylic ≈ 2° allylic ≈ 3° > 1° benzylic ≈ 1° allylic ≈ 2° > 1° > vinyl

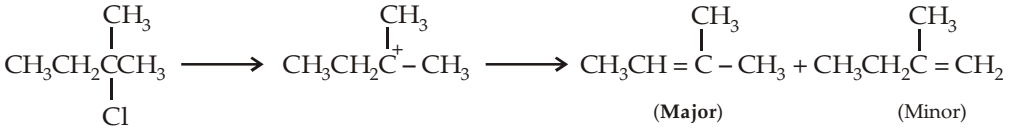
(ii) E1 reactions occur in presence of either a weak base or a base in low concentration.

(iii) Further, formation of carbocation may result rearranged product, in case when less stable carbocation may change to the more stable by 1, 2-shift. For example,



2° carbocation

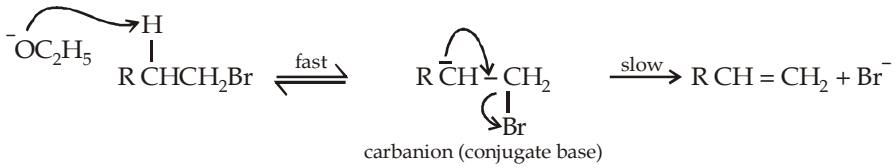
(iv) In case the removal of proton (second step), can form two products, the major product is formed according to Saytzeff rule. For example,



(v) **Stereochemistry of E1 reactions :** Since the carbocation is planar, the electrons from the departing hydrogen can move towards the positively charged carbon from either side and thus both *syn*- as well as *anti*-elimination can occur. However, here also *E*-isomer having bulkier groups on the opposite sides will be major product because of its higher stability than the *Z*-isomer.

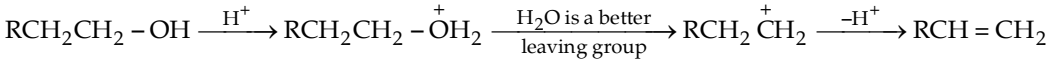
4.8.5 E1cB Mechanism

This is a two step reaction. The first step involves the rapid formation of carbanion by an alkyl halide under the influence of a base. The second step is slow and involves the lose of leaving group (halide ion).



Since the rate determining step (slow step) is dependent on the concentration of the conjugate base of the substrate (carbanions) and thus unimolecular, the reaction is known as E1cB **(elimination, unimolecular from conjugate base)**. Reactions proceeding by E1cB pathway are exceedingly rare.

Acid-catalysed dehydration of alcohols :

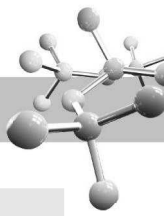


However, since 1° carbocations are not quite stable, the above mechanism (E1) is applicable to 2° and 3° alcohols and 1° alcohols follow E2 mechanism, where loss of water and proton take place simultaneously.

4.8.6 E2 vs E1

We have already observed that both mechanisms follow the same order (1° < 2° < 3°), although reactivity by both mechanisms increases for different reasons. Reactivity by E2 increases mainly because of greater stability of the more highly branched alkenes being formed ; reactivity by E1 increases because of greater stability of the carbocation being formed in the rate-determining step. Thus it becomes somewhat difficult to know whether an alkyl halide undergoes elimination by E2 or E1. However, this problem can be somewhat solved on the basis of the role by the other reagent, *i.e.*, the base.

We know that E2 is a second-order reaction, *i.e.* here base takes part in the rate determining step; while in E1 base does not take part in rate determining step. Thus the rate of E2 depends upon the nature as well as concentration of the base. On the other hand, the rate of E1 is independent of the nature and concentration of the base. Thus **for a given substrate, the more concentrated the base or the stronger the base the more E2 mechanism is favoured over E1.** Thus *E1 mechanism is encountered only with tertiary or secondary substrates and that too in presence of either a weak base or a base in low concentration.*



Example 14 :

Mention the type of elimination mechanism in each of the following :

(a) $CH_3CH_2(CH_3)CHBr + CH_3OH \longrightarrow$

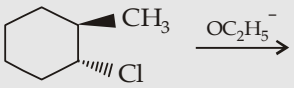
(b) $CH_3CH_2(CH_3)CHBr + CH_3ONa \xrightarrow{DMSO}$

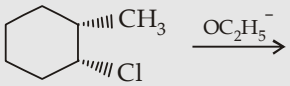
(c) $Me_3C\,Br + OH^- \xrightarrow{DMF}$

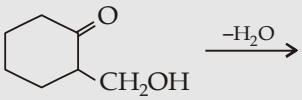
(d) $Me_3C\,Br + H_2O \longrightarrow$

(e) $Me_2C(Br)CH_2CH_3 \xrightarrow{Me_3CO^-}$

(f) $CH_3CH(F)CH_2CH_3 \xrightarrow{OH^-}$

(g) 

(h) 

(i) 

Solution :

(a) E1 (CH_3OH is a weak base)

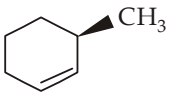
(b) E2 (CH_3O^- is a strong base)

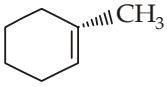
(c) E2 (OH^- is a strong base)

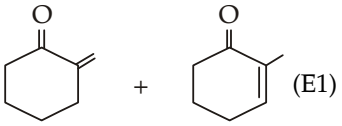
(d) E1 (H_2O is a weak base)

(e) $CH_2 = C(CH_3) - CH_2CH_3$ (E2, base is strong)

(f) $CH_2 = CHCH_2CH_3$ (E2, halide is fluoride)

(g)  (E2, *anti* elimination gives only Hofmann product)

(h)  (E2, *anti* elimination gives more preferred Saytzeff product)

(i)  (E1)

Example 15 :

Which of the alkyl halide (I or II) will be more reactive toward E2 reaction?

	I	**II**
(a)	$CH_3CH_2CH(Br)CH_2CH_3$	$CH_3CH(Br)CH_2CH_3$
(b)	$C_6H_5CH_2CH(Br)CH_2CH_3$	$C_6H_5CH_2CH(Br)CH_3$

Solution :

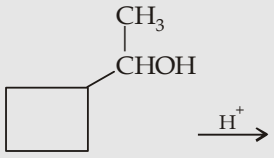
(a) II (C bearing Br is less sterically hindered).

(b) I (newly developed double bond is conjugated to benzene ring).

Example 16 :

Predict the product formed in each of the following reaction and give mechanism :

(a) $(CH_3)_3C-\underset{\displaystyle OH}{\underset{|}{C}}H\,CH_3 \xrightarrow{H^+}$

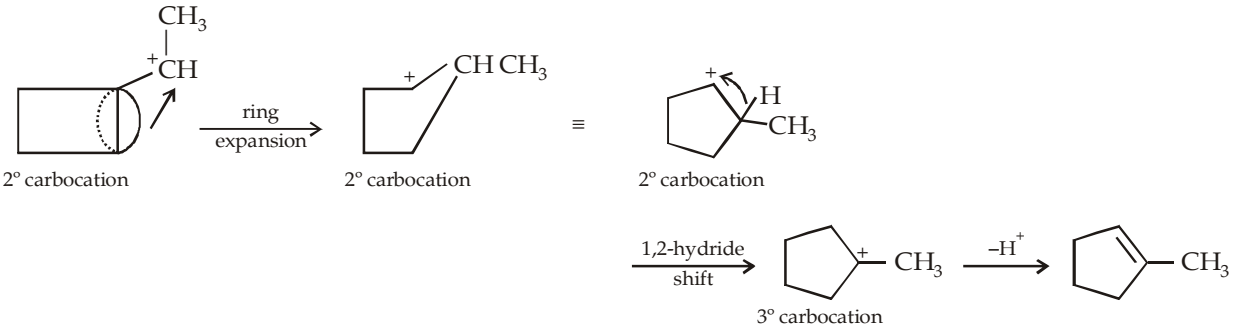
(b) 

(c) $C_6H_5-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CHCH_3 \xrightarrow{Me_3CO^-}$

Solution :

(a) $(CH_3)_3C-\overset{+}{C}HCH_3 \xrightarrow[\text{shift}]{\text{1, 2-methyl}} (CH_3)_2\overset{+}{C}-\underset{\displaystyle CH_3}{\underset{|}{CH}}CH_3 \xrightarrow{H^+} (CH_3)_2C=C(CH_3)_2$

2° carbocation 3° carbocation

(b) 

(c) $C_6H_5-\underset{\displaystyle H}{\underset{|}{CH}}-\overset{+}{C}H-\underset{\displaystyle CH_3}{\underset{|}{CH}}CHCH_3 \longrightarrow C_6H_5\overset{+}{C}HCH_2\,CH(CH_3)_2 \xrightarrow{-H^+} C_6H_5CH=CH\,CH\,(CH_3)_2$

2° carbocation Benzal carbocation Hofmann product

4.8.7 Elimination vs substitution

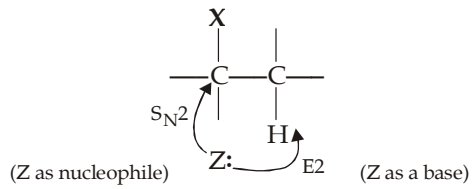
We have observed that the most common substrate for 1, 2-elimination as well as for substitution are **alkyl halides and alkyl sulphonates.** Furthermore, the reagent required for the two reactions (bases and nucleophiles) are similar. Both reagents (bases and nucleophiles) are electron-rich, bases are nucleophilic and nucleophiles are basic. Thus, it is expected that there will nearly always be a competition between substitution and elimination.

Let us consider first the S_N2 and E2 reactions both of which involve attack of the reagent **:Z** on the substrate. While acting as a nucleophile, the reagent **:Z** attacks the substrate on carbon and causes substitution, while acting as a base it attacks the substrate on hydrogen and brings about elimination.

Now we know that the relative order of reactivity for the two kinds of reactions is

3° > 2° > 1° **For E2 reactions**

1° > 2° > 3° **For S_N2 reactions**



E2 *versus* S_N2

So it can be concluded that primary substrates undergo elimination slowest and substitution fastest, while tertiary substrates undergo elimination fastest and substitution slowest. From the above relative order, it can further be concluded that in bimolecular reactions, the proportion of elimination increases as the structure of the substrate changes from primary to secondary to tertiary.

$$CH_3CH_2Br \xrightarrow{^-OC_2H_5} \underset{91\%}{CH_3CH_2OC_2H_5} + \underset{9\%}{CH_2=CH_2}$$

$$(CH_3)_2CHBr \xrightarrow{^-OC_2H_5} \underset{87\%}{CH_3CH=CH_2} + \underset{13\%}{(CH_3)_2CHOC_2H_5}$$

Like the nature of substrate, the nature of the reagent :Z also influences the ratio of the two products.

(*a*) A bulky nucleophile or bulky alkyl halide (even primary) will favour E2 reactions, because of steric factor (*cf.* mechanism of S_N2 reactions) *e.g.*

$$\underset{1^\circ \text{ Alkylhalide}}{CH_3(CH_2)_{15}CH_2CH_2Br} \xrightarrow[C_2H_5OH]{^-OCMe_3} \underset{(87\%)}{CH_3(CH_2)_{15}CH=CH_2} + \underset{(13\%)}{CH_3(CH_2)_{15}CH_2CH_2OC_2H_5}$$

$$(CH_3)_2CHCH_2Br + CH_3O^- \xrightarrow{CH_3OH} \underset{(60\%)}{(CH_3)_2C=CH_2} + \underset{(40\%)}{(CH_3)_2CHCH_2OCH_3}$$

(*b*) Nucleophiles which are also strong bases like ^-OH favour elimination while good nucleophiles, which are weak bases (*e.g.* CN^-, azide N_3^-, ^-SH etc.) favour substitution.

2-Chloropropane when treated separately with acetate ion or ethoxide ion undergoes different reactions.

$$\underset{\substack{\text{Isopropyl acetate}\\(100\%)}}{CH_3\overset{\overset{OCOCH_3}{|}}{C}HCH_3} \xleftarrow[CH_3COOH]{CH_3COO^-} \underset{\substack{\text{2-Chloropropane}}}{CH_3\overset{\overset{Cl}{|}}{C}HCH_3} \xrightarrow[C_2H_5OH]{C_2H_5O^-} \underset{\substack{\text{Propene}\\(75\%)}}{CH_3CH=CH_2}$$

(S_N2) (E2)

This is because CH_3COO^- is a weaker base than $C_2H_5O^-$ (recall that CH_3COOH is a stronger acid than C_2H_5OH).

Further, a less polar solvent and high temperature tend to favour elimination, while more polar solvent and a low temperature favour substitution. This explains why hot alc. KOH is used for dehydrohalogenation, while aqueous KOH is used for substitution. So favourable conditions for E2 are bulkiness at either of the two reagents (alkyl halide and nucleophile), strongly basic nucleophiles like OH^- and $OC_2H_5^-$, less polar solvent and relatively high temperature.

(c) A tertiary alkyl halide is the least reactive toward S_N2 reaction but most reactive toward E2 reaction, thus when a *tert*-alkyl halide is treated with a nucleophile under $S_N2/E2$ conditions, only the elimination product is formed.

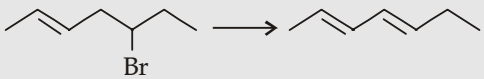
$$(CH_3)_3CBr + CH_3CH_2O^- \xrightarrow{CH_3CH_2OH} \underset{\text{Methylpropene}}{(CH_3)_2C=CH_2} + CH_3CH_2OH + Br^-$$

Now let us take S_N1 and E1 reactions, both of which involve the formation of carbocation in the rate-determining step. Hence the least stable carbocation (1°) will react immediately with the anion to form substitution product. On the other hand, the 3° cation, having sufficient stability will lose proton to form the more stable (more branched) alkene.

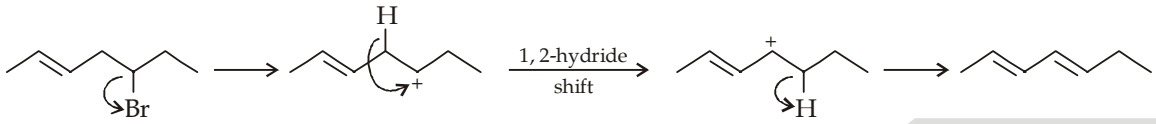
In short, for a particular alkyl halide substitution reactions are favoured by nucleophiles which are weak bases, *viz.* H_2O, C_2H_5OH, CN^-, N_3^-, RS^-, HS^- etc., and using low temperature (room temperature) ; while elimination reactions are favoured by strong bases like OH^-, $^-OC_2H_5$ etc. and using high temperature.

Example 17 :

Propose a mechanism for the following reaction :



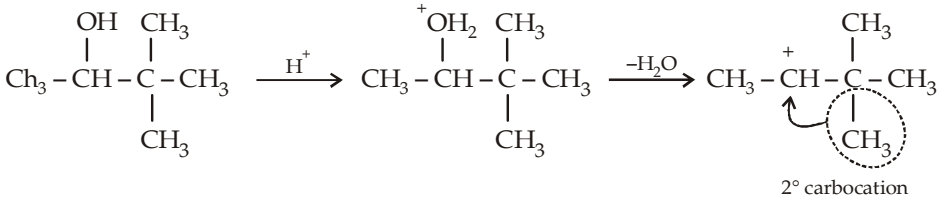
Solution :

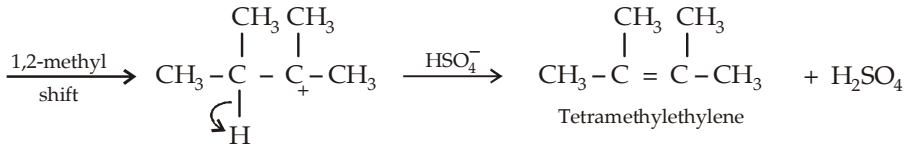


Example 18 :

3,3-Dimethylbutanol-2 loses a molecule of water, when treated with concentrated sulphuric acid to give tetramethylethylene. Suggest a mechanism. (IIT 1996)

Solution :





Summary of S_N1, S_N2, E1, E2 and E1cB Reactions

Type of alkyl halide	Poor nucleophile (e.g. H_2O, ROH)	Weak basic nucleophile (e.g. I^-, RS^-)	Strongly basic unhindered nucleophile (e.g. RO^-)	Strongly basic hindered nucleophile (e.g. Me_3CO^-)
Methyl halide	No reaction	S_N2	S_N2	S_N2
1° unhindered RX	No reaction	S_N2	S_N2	E2
1° hindered RX	No reaction	S_N2	E2	E2
2° alkyl halide	S_{N^1}, E1(slow)	S_N2	E2	E2
3° alkyl halide	E1 or S_N1	S_N1, E1	E2	E2
O X ‖ | CH_3 C CH_2 CH CH_3	E1cB	E1cB	E1cB	E1cB

TEST YOUR UNDERSTANDING - 4.8

1. Predict the major product of each of the following reactions :

(*i*) Cyclohexyl bromide and potassium ethoxide

(*ii*) *sec*-Butyl bromide solvolysis in methanol

(*iii*) *sec*-Butyl bromide solvolysis in methanol containing 2M sodium ethoxide.

2. Give various steps involved in the acid-catalysed dehydration of 2, 2-dimethylcyclohexanol to form the major product.

3. Give various steps involved in the acid-catalysed dehydration of the following alcohols to different alkenes

(*a*) 1-Methylcyclohexanol (*b*) 9-Decanol.

EXERCISE 4.1 (MCQ - ONE option correct)

1. Which of the following is not an electrophile ?
(*a*) Ag^+ (*b*) H_2C:
(*c*) SiF_4 (*d*) None

2. Consider the following sequence of steps
(*i*) A ⟶ B (*ii*) B + C ⟶ D + E
(*iii*) E + A ⟶ 2F
Product of the reaction is/are
(*a*) B, D, E and F (*b*) D, E and F
(*c*) D and F (*d*) F.

3. Addition of bromine on ethylene is generally represented as
$CH_2 = CH_2 + Br_2 \longrightarrow CH_2BrCH_2Br$
The nucleophilic species present or formed as intermediate in the above reaction are
(*a*) $CH_2Br\,\bar{C}H_2$ and Br^- (*b*) $CH_2 = CH_2$ and Br^-
(*c*) only $CH_2 = CH_2$ (*d*) only Br^-.

4. Cyclohexene has three types of hydrogen atoms, marked as 1, 2 and 3. Which hydrogen atom can be removed most easily and which with most difficulty as H**.** ?
(*a*) 1 and 2 respectively (*b*) 2 and 3 respectively
(*c*) 2 and 1 respectively (*d*) All with same ease.

5. Insertion of methylene in isobutane, $(CH_3)_2CHCH_3$ can form how many compounds ?
(*a*) 1 (*b*) 2
(*c*) 3 (*d*) 4

6. Extra stability of *tert*-carbocation can be explained due to
(*a*) inductive effect (*b*) hyperconjugation(*c*)
steric relief (*d*) all the three

7. In methyl anion ($:CH_3^-$), carbon is sp^3 hybridised. The angle between bonding pairs should be
(*a*) 109.5° (*b*) < 109.5°
(*c*) > 109.5° (*d*) any of the three.

8. Which of the following three intermediates have nearly similar geometry ?

$\overset{\oplus}{C}H_2CH_3$ (I) $\quad :\overset{\ominus}{C}H_2CH_3$ (II) $\quad :\overset{\ominus}{C}H_2COCH_3$ (III) $\quad CH_2 = CH\overset{\ominus}{\ddot{C}}H_2$ (IV)

(*a*) I and III (*b*) II and IV
(*c*) II, III and IV (*d*) I, III and IV.

9. Which of the following compound can form carbanion easily ?

CH_3CH_3 (I) $\quad CH_3CHO$ (II) $\quad CH_3CH_2Cl$ (III) $\quad$  (IV)

(*a*) II only (*b*) II and III
(*c*) I, II and III (*d*) II and IV

10. $(+)\text{-}C_2H_5CH(CH_3)COC_6H_5 \xrightarrow[(ii)\ Br_2]{(i)\ Base} C_2H_5CBr(CH_3)COC_6H_5$
Here the product is
(*a*) (+) – (*b*) (–)
(*c*) (±) – (*d*) Not definite.

11. Consider the following species

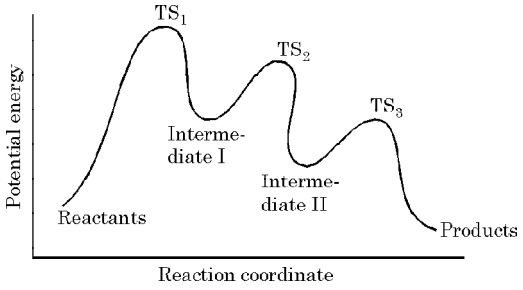
H^+	OH^-	H_3O^+	$AlCl_3$
I	II	III	IV

Which of the following is/are cationoid ?
(*a*) I and III (*b*) I and IV
(*c*) II (*d*) I, III and IV.

12. Chlorobenzene having chlorine on heavy carbon is treated with sodamide, the product is
(*a*) aniline having —NH_2 group on heavy C atom
(*b*) aniline having —NH_2 group on C-12
(*c*) both (*a*) and (*b*)
(*d*) reduction takes place to from benzene.

13. The transition state of the rate determining step of a multi-step reaction has
(*a*) lowest enthalpy (*b*) highest enthalpy
(*c*) medium enthalpy (*d*) unpredictable.

14. Enthalpy diagram of a multi-step reaction is drawn below. Can you predict the rate determining step in the reaction ?



(*a*) No (*b*) Yes, first step
(*c*) Yes, second step (*d*) Yes, third step.

15. The decreasing order of nucleophilicity of HS^-, $RCOO^-$, RCOOH and ROH is
(*a*) $RCOO^- > HS^- >$ RCOOH > ROH
(*b*) $HS^- > RCOO^-$ > RCOOH > ROH
(*c*) $HS^- > RCOO^-$ > ROH > RCOOH
(*d*) $RCOO^- > HS^-$ > ROH > RCOOH.

16. During dehydration of *tert*-butanol with an acid, which of the following carbocation is more likely to be formed as an intermediate ?
(*a*) $CH_3CH_2CH_2\overset{+}{C}H_2$ (*b*) $CH_3CH_2\overset{+}{C}HCH_3$
(*c*) Both (*d*) None.

17. Polarisation of electrons in acrolein may be written as
(*a*) $\overset{\delta-}{C}H_2 = CH - \overset{\delta+}{C}H = O$ (*b*) $\overset{\delta-}{C}H_2 = CH - CH = \overset{\delta+}{O}$
(*c*) $\overset{\delta-}{C}H_2 = \overset{\delta+}{C}H - CH = O$ (*d*) $\overset{\delta+}{C}H_2 = CH - CH = \overset{\delta-}{O}$.

18. In CH_3CH_2OH, the bond that undergoes heterolytic cleavage most readily is
(*a*) C—C (*b*) C—O
(*c*) C—H (*d*) O—H.

19. The bond dissociation energy needed to form the benzyl radical from toluene is ..... the formation of methyl radical from methane.
(*a*) equal to (*b*) less than
(*c*) greater than (*d*) not certain.

20. Which of the following reaction leads to complete racemization?
(*a*) Free radical substitution
(*b*) S_N1
(*c*) S_N2
(*d*) All the three.

21. Which of the following process involves inversion of configuration ?
(*a*) S_N1 (*b*) S_N2
(*c*) Both (*a*) and (*b*) (*d*) None.

22. An optically active alkyl halide of specific rotation – 34.9° undergoes S_N1 reaction, the specific rotation of the product will be
(*a*) + 34.9° (*b*) less than + 34.9°
(*c*) zero (*d*) – 34.9°.

23. The correct order for nucleophilic substitution in the following compounds is

ROH	RF	RO^+H_2	$ROSO_2CF_3$	ROTs
I	II	III	IV	V

(*a*) III > I > II > IV > V (*b*) IV > V > III > II > I
(*c*) IV > V > III > I > II (*d*) V > IV > III ≈ I > II.

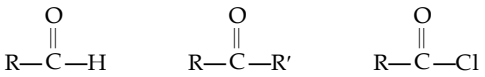
24. Which of the factor increases the rate of following S_N1 reaction; $RX + OH^- \longrightarrow R—OH + X^-$
(*a*) Doubling the concentration of OH^-
(*b*) Doubling the concentration of RX
(*c*) Both of the two
(*d*) None of the two.

25. Consider the following reaction
1-Bromobutene-2 + NaOH ⟶
Which of the following statement is true ?
(*a*) It undergoes S_N2 reaction
(*b*) It undergoes S_N1 reaction and forms one product
(*c*) It undergoes S_N1 reaction and forms two products
(*d*) It can undergo S_N2 as well as S_N1 reaction.

26. The decreasing order of reactivity of the following alkyl bromides towards S_N2 displacement is *n*-Propylmethyl bromide (I), *iso*-propylmethylbromide (II), *sec*-butylmethyl bromide (III), *tert*-butylmethyl bromide (IV)
(*a*) I > II > III > IV (*b*) IV > III > II > I
(*c*) III > IV > II > I (*d*) IV > III > I > II.

27. Which of the following does not involve carbocation as intermediate ?
(*a*) $C_6H_6 + Br_2 \xrightarrow{AlBr_3} C_6H_5Br$
(*b*) $CH_2 = CH_2 + Br_2 \longrightarrow BrCH_2 - CH_2Br$
(*c*) $(CH_3)_3COH + HBr \xrightarrow{H^+} (CH_3)_3CBr + H_2O$
(*d*) None of the above.

28. Although aldehydes and ketones also contain a carbonyl group, like acid halides they do not undergo



nucleophilic substitution reactions because
(*a*) they do not have electronegative chlorine atom
(*b*) carbon atom of carbonyl group in aldehydes and ketones is less electron deficient
(*c*) hydride ion and methylide ion are strong bases and hence are poor leaving groups
(*d*) none of the above is true.

29. Nucleophilic additions on aldehydes and ketones are catalysed by acids because
(*a*) acids dissolve easily both the reactants
(*b*) acids make carbonyl carbon more electron rich
(*c*) acids make carbonyl carbon more electron deficient
(*d*) acids increase the nucleophilicity of the nucleophiles.

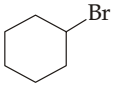
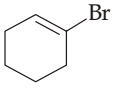
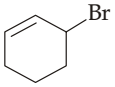
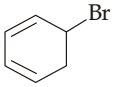
30. During dehydrohalogenation of an alkyl halide, hydrogen of alkyl halide is removed as
(*a*) hydrogen atom (*b*) H^+
(*c*) H^- (*d*) free radical.

31. Two reactions of *tert*-butyl chloride are given below to give products indicated against them
$(CH_3)_3CCl + NaF \xrightarrow{H_2O}$ [A]
$(CH_3)_3CCl + NaF \xrightarrow{(CH_3)_2SO}$ [B]
[A] and [B] are
(*a*) *tert*-Butyl alcohol
(*b*) *iso*-Butene
(*c*) A is *tert*-butyl alcohol, B is *tert*-butyl fluoride
(*d*) A is *tert*-butyl alcohol, B is isobutene.

32. During dehydration of *tert*-butanol, which of the following carbocation is more likely to be formed as an intermediate ?
(*a*) $CH_3CH_2CH_2\overset{+}{C}H_2$ (*b*) $CH_3CH_2\overset{+}{C}HCH_3$
(*c*) Both (*d*) None.

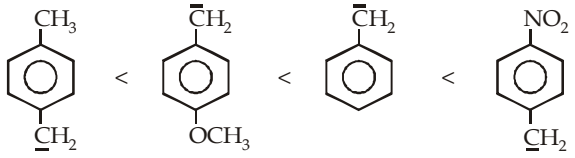
33. A solution of (+)-2-chloro-2-phenylethane in toluene racemises slowly in presence of small amount of $SbCl_5$ due to formation of
(*a*) carbanion (*b*) carbene
(*c*) carbocation (*d*) free radical.

34. Which of the following is least stable ?
(*a*) $C_6H_5\overset{+}{C}H_2$ (*b*) *p*-$OCH_3 . C_6H_4 . \overset{+}{C}H_2$
(*c*) *p*-$NO_2 . C_6H_4 . \overset{+}{C}H_2$ (*d*) *p*-$OH . C_6H_4 . \overset{+}{C}H_2$.

35. Which of the following is fast debrominated ?
(*a*) 
(*b*) 
(*c*) 
(*d*) 

36. Heterolysis of propane gives :
(a) methylium ion and ethyl anion
(b) methyl anion and ethylium ion
(c) either (a) or (b)
(d) methylium and ethylium ions

37. The correct order of decreasing stability of the four carbanions I to IV should be :

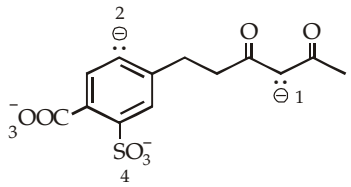


I II III IV

(a) IV > III > II < I (b) IV > III > I > II
(c) I > II > III > IV (d) II > I > IV > III

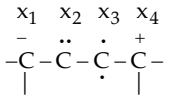
38. Predict the nature of A and B :
$(CH_3)_3C\,CH_2Br + OC_2H_5^- \longrightarrow A$
$(CH_3)_3C\,CH_2Br + CH_3OH \longrightarrow B$
(a) $(CH_3)_3CCH_2O\,C_2H_5$ and $(CH_3)_3CCH_2O\,CH_3$
(b) $(CH_3)_2C(OC_2H_5)CH_2\,CH_3$ and $(CH_3)_2C\,(OCH_3)CH_2\,CH_3$
(c) $(CH_3)_2\overset{OC_2H_5}{\overset{|}{C}}CH_2CH_3$ and $(CH_3)_3C\,CH_2O\,CH_3$
(d) $(CH_3)_2C = CHCH_3$ and $(CH_3)_2C = CH\,CH_3$

39. The structure drawn below has four nucleophilic sites, arrange them in order of decreasing nucleoephilicity.



(a) 3 > 4 > 1 > 2 (b) 4 > 3 > 2 > 1
(c) 4 > 3 > 1 > 2 (d) 3 > 4 > 2 > 1

40. In the following hypothetical structure, which carbon is *sp* hybridised?



(a) x_2 (b) x_3
(c) x_2 and x_3 (d) None

41. In the above structure, which carbon is sp^2 hybridised?
(a) x_1 (b) x_2
(c) x_3 (d) x_4

42. The weakest C – H bond is present in
(a) CH_4 (b) RCH_3
(c) R_2CH_2 (d) R_3CH

43. Heterolysis of propane gives
(a) methylium ions and ethyl anion
(b) methyl anion and ethylium ion
(c) methylium and ethylium ions
(d) both (a) and (b)

44. Which of the following order is (are) correct regarding stability?

(a) $Ph_3\overset{+}{C} > Ph_2\overset{+}{C}H > Ph\overset{+}{C}H_2$

(b) $Ph_3\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}^{-} > Ph_2\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}^{-}H > Ph\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}^{-}H_2$

(c) $p-NO_2C_6H_4-\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}^{-}H_2 > C_6H_5-\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}^{-}H_2 > p-CH_3O-C_6H_4-\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}^{-}H_2$

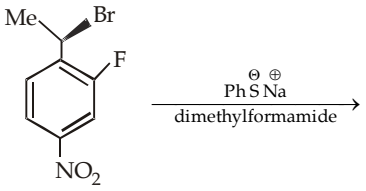
(d) $p\text{-}NO_2-C_6H_4-\overset{+}{C}H_2 > C_6H_5-\overset{+}{C}H_2 > p\,CH_3O-C_6H_4-\overset{+}{C}H_2$

45. Which of the following species have a trigonal planar shape?
(a) $:CH_3^-$ (b) CH_3^+
(c) BF_4^- (d) SiH_4

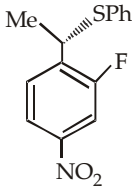
46. A nucleophile must necessarily have
(a) an overall positive charge
(b) an overall negative charge
(c) an unpaired electron
(d) a lone pair of electrons

47. Carbanion is
(a) an electrophile (b) a nucleophile
(c) a Zwitter ion (d) a free radical

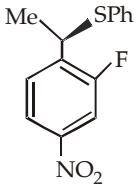
48. The major product of the following reaction is –



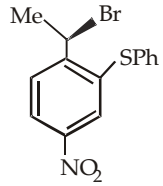
(a)



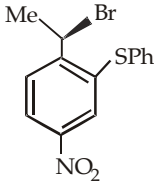
(b)



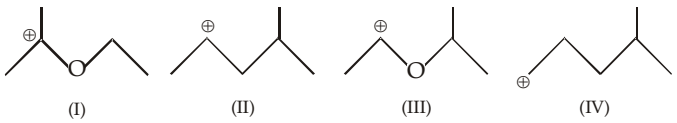
(c)



(d)



49. The correct stability order for the following species is



(I) (II) (III) (IV)

(a) (II) > (IV) > (I) > (III) (b) (I) > (II) > (III) > (IV)
(c) (II) > (I) > (IV) > (III) (d) (I) > (III) > (II) > (IV)

EXERCISE 4.2 (MCQ 1 or >1 option correct, Passage based, Matching, A/R)

DIRECTIONS for Q. 1 to Q. 6 : Multiple choice questions with one or more than one correct option(s).

1. Which of the following statement is true regarding E2 reactions of alkyl halides which follow the following order :

3° > 2° > 1° Alkyl halides

(a) 3° alkyl halides form most stable carbocations
(b) Increased branching (from 1° alkyl halide to 3° halide) successively provides greater number of hydrogens to be eliminated as H^+.
(c) Increased branching leads to the more stable alkene.
(d) Increased branching facilitates the formation of transition state.

2. Which of the following statement is true?
- (a) NH_3 is more basic than PH_3 because N lies in a lower period of the periodic table than P.
- (b) NH_3 is more basic because its bond angle is 90° while the bond angle, H – P – H in PH_3 is 107°.
- (c) NH_3 and PH_3 are equally basic
- (d) NH_3 is less basic than PH_3

3. Pick up the correct statement(s) regarding the hybridisation state of the carbon bearing positive charge.
- (a) All carbocations are sp^2 hybridised
- (b) Vinyl carbocation is *sp* hybridised
- (c) Phenyl carbocation is *sp* hybridised
- (d) Carbocations may be sp^3, sp^2 as well as *sp*

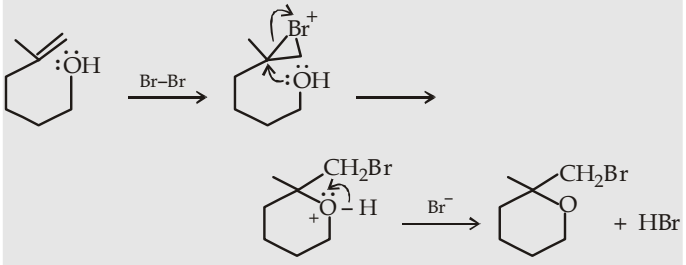
4. A primary carbanion is
- (a) more reactive than a secondary carbanion
- (b) more stable than a secondary carbanion
- (c) less stable than a secondary carbanion
- (d) more stable than a tertiary carbanion

5. Which is/are true statement(s)?
- (a) Protonation increases electrophilic nature of carbonyl group
- (b) $CF_3SO_3^-$ is better leaving group than $CH_3SO_3^-$
- (c) Benzyl carbonium ion is stabilised by resonance
- (d) $CCl_3CH(OH)_2$ is stable

6. The relative order of reactivity of F^-, Cl^-, Br^- and I^- is :
- (a) $F^- > Cl^- > Br^- > I^-$ in non-polar solvents like DMSO (dimethyl sulphoxide)
- (b) $F^- < Cl^- < Br^- < I^-$ in polar solvents like H_2O, alcohol
- (c) $F^- < Cl^- < Br^- < I^-$ in DMSO
- (d) $F^- > Cl^- > Br^- > I^-$ in H_2O

INSTRUCTION for Q. 7 to 15 : Read the passages given below and answer the questions that follow.

PASSAGE 1

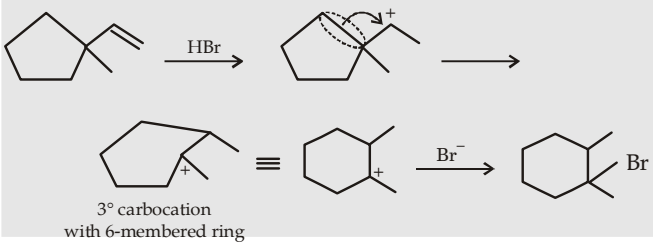


7. The intermediate in the above reaction is
- (a) carbocation (b) carbanion
- (c) free radical (d) none of these

8. Step 2 involves
- (a) elimination of Br^-
- (b) rearrangement (c) cyclization
- (d) cyclization as well as rearrangement

9. Step 3 is
- (a) reaction with the nucleophile Br^-
- (b) an acid–base reaction
- (c) Both (d) none

PASSAGE 2

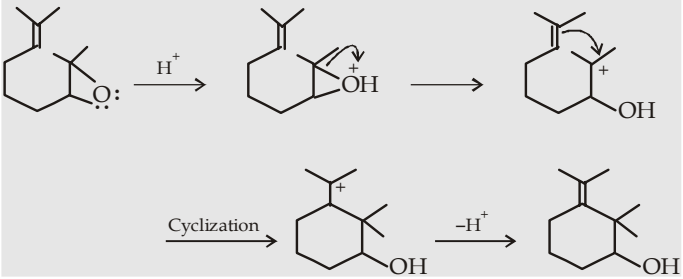


10. Step I involves the formation of
- (a) 1° carbocation (b) 2° carbocation
- (c) 3° carbocation (d) a free radical

11. Step 2 involves
- (a) ring expansion
- (b) conversion of a less stable carbocation to more stable
- (c) Both
- (d) None

12. Step 3 involves
- (a) the addition of a nucleophile
- (b) an acid-base reaction
- (c) both
- (d) elimination of a proton

PASSAGE 3



13. Step 1 involves protonation of oxygen because
- (a) oxygen is most basic
- (b) oxygen is most electronegative
- (c) oxygen can easily accommodate + charge
- (d) resulting protonated epoxide is highly stable

14. Step 2 is due to
- (a) Instability of the epoxide ion
- (b) Formation of more stable 3° carbocation
- (c) Formation of 2° carbocation
- (d) None

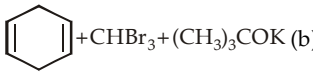
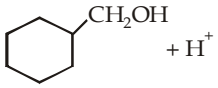
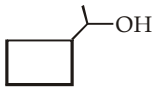
15. The final product having a C = C is
- (a) Hofmann product (b) Saytzeff product
- (c) Cope product (d) None of these

Instructions for Q. 16 to 21 : Following questions are Multiple Matching type Questions :

16.

	Column I		*Column II*
(A)	Carbocations	(a)	E1
(B)	Tetrahedral transition state	(b)	Nucleophilic-addition
(C)	Pentavalent transition state	(c)	S_N2
(D)	Carbonyl compounds	(d)	C = C + HX

17.

	Column I		*Column II*
(A)	$(CH_3)_2C = CH_2 + HBr$	(a)	1° carbocation
(B)		(b)	2° carbocation
(C)		(c)	3° carbocation
(D)		(d)	Carbene

18.

	Column I		*Column II*
(A)	Carbocation	(a)	Reaction with ethylene
(B)	Carbanions	(b)	Reaction with opposite species
(C)	Carbenes	(c)	Rearrangement
(D)	Free radicals	(d)	Disproportionation

19.

	Column I		*Column II*
(A)	S_N1	(a)	$3^o > 2^o$ (stability of intermediate)
(B)	S_N2	(b)	Rearrangement possible
(C)	E1	(c)	A less polar solvent favours
(D)	E2	(d)	Stereospecific

20.

	Column I **(Reaction)**		*Column II* **(Intermediate)**
(A)	Reaction of bromobenzene with sodamide	(a)	Carbocation
(B)	Reaction of 1, 3-butadiene with bromine	(b)	A carbanion
(C)	Alkaline hydrolysis of chloroform	(c)	Benzyne
(D)	Partial reduction of alkynes by Na in liq. NH_3	(d)	Carbene

21. Match the following :

	Column I		*Column II*
(A)	$C_6H_5CH_2CD_2Br$ on reaction with $C_2H_5O^-$ gives $C_6H_5-CH = CD_2$	(a)	E_1
(B)	$PhCHBrCH_2$ and $PhCHBrCD_3$, both react with the same rate	(b)	E_2
(C)	$C_6H_5CH_2CH_2Br$ on treatment with $C_2H_5O^-$ and C_2H_5OD gives $C_6H_5CD=CH_2$	(c)	E_1CB
(D)	$C_6H_5CH_2CH_2Br$ reacts faster than $C_6H_5CD_2CH_2Br$ on reaction with $C_2H_5O^-$ in ethanol	(d)	First order reaction

Instructions for Q. 22 to 26 : Following questions are Assertion and Reasoning Type Questions :

Note : Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 5 choices (a), (b), (c), (d) and (e) out of which ONLY ONE is correct.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.

(c) Statement -1 is True, Statement-2 is False.

(d) Statement -1 is False, Statement-2 is True.

(e) Statement -1 is False, Statement-2 is False.

22. **Statement I :** Addition of singlet carbene to alkene is a stereospecific where as addition of triplet carbene is non-stereo specific.
Statement II : Addition of singlet carbene is proceeds in concerted fashion, where as addition of triplet carbene is a two step process.

23. **Statement I :** 2,4,6 trinitro N, N-diemethylaniline is 40,000 times more basic than 2,4,6-trinitroaniline.
Statement II : In the former steric inhibition or resonance causes the availability of ℓp on N whereas in the later due to H-bonding of NH_2 with NO_2 groups make NH_2 planar with benzene ring, so easy delocalisation of electron pair of N in benzene ring.

24. **Statement I :** Trichloroacetic acid is stronger than acetic acid.
Statement II : Electron withdrawing substituents decrease the activity.

25. **Statement I :** Styrene on reaction with HBr gives 1-bromo-1-phenylethane.
Statement II : Benzyl radical is more stable than alkyl radical.

26. **Statement I:** Rate of hydrolysis of methyl chloride to methanol is higher in DmF than in water.
Statement II : Hydrolysis of methyl chloride follows second order kinetic.

Instructions for Q. 27 to 29 : The following questions are True/False Type Questions :

27. Trimethylmethyl and triphenylmethyl radicals, both being 3° free radical, equally exist in solution.

28. Stability order of carbanions always follows reverse order to that of corresponding carbocations.

29. Among the simple alkyl carbocations, the most stable one is $\overset{+}{C}H_3$ because here the positive charge is dispersed only to small extent.

EXERCISE 4.3 (Subjective Problems)

1. Pick up the stronger nucleophile and stronger base in the following pairs of compounds ?

(*i*) $NH_2^{\ominus}$ and NH_3 (*ii*) OH^- and SH^-

(*iii*) H_2O and H_3O^+ (*iv*) $CH_3CH_2O^-$ and CH_3COO^-

(*v*) Br^- and Cl^- (*vi*) OH^- and F^-.

2. Which of the following behaves as (*a*) a nucleophile, (*b*) an electrophile, (*c*) both or (*d*) neither ?

Cl^-, NO^+, H_2O, CH_3OH, CH_4, CH_2O, CH_3CN, $CH_3CH=CH_2$, $AlCl_3$, $BeCl_2$, Cr^{3+}, H_2 and $SnCl_4$.

3. What are ambident nucleophiles ; give two examples.

4. Compare the (rate of S_N2 reactivity) nucleophilicity of

(*a*) H_2O, OH^-, CH_3O^- and CH_3COO^-

(*b*) NH_3 and PH_3.

5. Compare the effectiveness of the following anions as leaving groups

CH_3COO^-, $C_6H_5O^-$ and $C_6H_5SO_3^-$, pK_a value of their conjugate acids are 4.5, 10.0 and 2.6 respectively.

6. Account for the decreasing stability of the following carbocations :

$Me_3C^+ > Me_2\overset{+}{C}H > Me\overset{+}{C}H_2 > \overset{+}{C}H_3$.

7. Comment on the role played by the adjacent atom or group on the stability/destability of the following carbocations :

(*a*) $-\overset{+}{\underset{|}{C}}-CF_3$ (*b*) $\overset{+}{C}F_3$

(*c*) $-\overset{+}{\underset{|}{C}}-NH_2$ (*d*) $-\overset{+}{\underset{|}{C}}-\overset{+}{N}H_3$.

8. Give the organic product(s) in the following reactions :

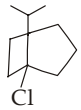
(*i*) $CH_3CHBrCH_3 + HS^- \xrightarrow[\text{as solvent}]{CH_3OH}$

(*ii*) $(CH_3)_3CBr + I^- \xrightarrow[\text{as solvent}]{HCOOH}$

(*iii*) $CH_3CH_2Br + AgCN \longrightarrow$

(*iv*) $CH_3CH_2Br + S_2O_3^{2-} \longrightarrow$

(*v*) $CHCl_3 + Me_3COK + CH_2=CH_2 \longrightarrow$

(*vi*)  + *aq*. KOH $\longrightarrow$.

9. List the following alkyl bromides in order of decreasing (*a*) S_N2 reactivity, and (*b*) reaction with alcoholic $AgNO_3$.

$(CH_3)_2C(Br)C_2H_5$, $CH_3(CH_2)_3CH_2Br$, $(C_2H_5)_2CHBr$

10. Explain the following :

(*i*) Ethanol does not react with NaBr, but reacts in presence of sulphuric acid.

(*ii*) Although neopentyl chloride, Me_3CCH_2Cl is a primary alkyl halide it does not undergo S_{N^2} reaction.

(*iii*) *tert*-Butyl chloride undergoes solvolysis slowly than allyl chloride.

(*iv*) Rate of solvolysis of $(CH_3)_2CHBr$ in presence of 80% water and 20% alcohol is very less than CH_3CH_2Br as well as $(CH_3)_3CBr$.

(*v*) In aqueous solution, an alkyl halide (RCl) undergoes slow hydrolysis to form alcohol, but the hydrolysis becomes fast on the addition of catalytic amount of potassium iodide.

(*vi*) On treatment with a strong base, CH_3CH_2I forms ethylene readily than CD_3CH_2I.

(*vii*) Although primary alkyl halides are the least reactive towards S_{N^1} solvolysis, $CH_3CH_2OCH_2Cl$ undergoes S_{N^1} solvolysis easily in ethanol.

11. Which of the following reactions is primarily displacement or elimination ?

(*a*) $CH_3CH_2CH_2Cl + I^- \longrightarrow$

(*b*) $(CH_3)_3CBr + CN^-$ (ethanol) $\longrightarrow$

(*c*) $CH_3CHBrCH_3 + OH^-(H_2O) \longrightarrow$

(*d*) $CH_3CHBrCH_3 + OH^-$ (ethanol) $\longrightarrow$

(*e*) $(CH_3)_3CBr + H_2O \longrightarrow$.

12. Complete the following reactions and point out the mechanism as S_N1, S_N2, E1 or E2

(*a*) $(CH_3)_3CBr + C_2H_5OH \xrightarrow{60°C}$

(*b*) $CH_3CH=CHCl + NaNH_2 \longrightarrow$

(*c*) $(CH_3)_3CI + H_2O \longrightarrow$

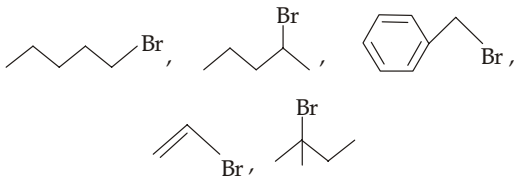
(*d*) $(CH_3)_3CI + OH^- \longrightarrow$.

13. Arrange the following in increasing order of reactivity towards aqueous HBr

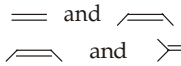
Benzyl alcohol, *p*-chlorobenzyl alcohol, *p*-hydroxybenzyl alcohol, and *p*-nitrobenzyl alcohol

14. Arrange different primary isomeric pentyl alcohols in order of increasing reactivity towards aqueous HBr.

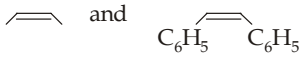
15. Arrange the following in increasing order of their reactivity towards S_{N^1} reaction



16. Among following pairs of alkenes, pick up the alkene which is expected to add HCl readily, assuming that addition is an ionic reaction

(*i*) 

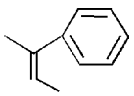
(*ii*) 

(*iii*) 

(*iv*) 

17. Predict the preferred regiochemistry for the addition of HCl to each of the following :

(*i*)  (*ii*) 

(*iii*)  (*iv*) 

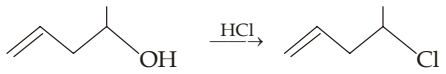
18. Arrange the following in increasing order of reactivity towards the addition of HBr.

Styrene, *p*-methylstyrene, *p*-chlorostyrene, *p*-nitrostyrene.

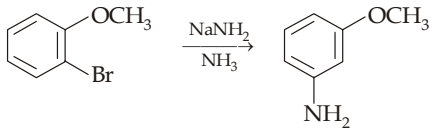
19. Give the mechanism involved in free radical addition of $CBrCl_3$ to 1, 3-butadiene.

20. Explain briefly the formation of products giving structures of the intermediates.

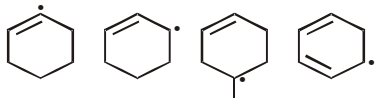
(*i*) 

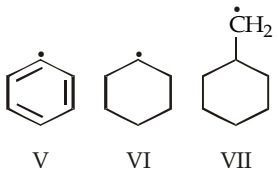
(*ii*) 

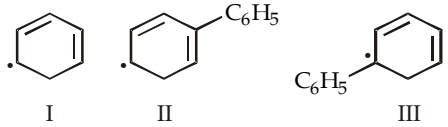
(only)

(*iii*) 

21. Arrange the following in decreasing stability order :

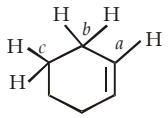
(a) 



(b) 

(c) $:\underset{\text{I}}{CH_2}, \underset{\text{II}}{C_6H_5\ddot{C}H}, \underset{\text{III}}{CH_3\ddot{C}H}, \underset{\text{IV}}{(C_6H_5)_2\ddot{C}}$

(d) Is there any relation betwen the bond energy and stability of a free radical? Cyclohexene has three types of C – H bonds, (marked *a*, *b* and *c*), which C – H bond is strongest and which one is weakest?



22. Complete the following by giving structure of the product :

(a) $CH_3 - N \equiv N \xrightarrow{\text{heat}} N_2 + ...$

(b) $C_6H_5N_3 \xrightarrow{h\nu} N_2 + ...$

(c) $CH_3CON_3 \xrightarrow{h\nu} N_2 + ...$

(d) $HN_3 \xrightarrow{h\nu} N_2 + ...$

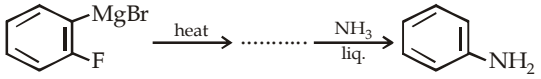
(e) $CH_3NCO \xrightarrow{h\nu} CO + ...$

23. Write the structure of the missing reactant/product

(a) $CH_3CH_2CH_3 + ... \longrightarrow CH_3CH_2CH_2CH_3 + ...$

(b) $CH_3CH = CHCH_3 + ... \longrightarrow$

$CH_3 - \underset{\displaystyle N \atop \displaystyle COCH_3}{CH} - CHCH_3 + ...$

(c) 

SOLUTIONS

TEST YOUR UNDERSTANDING - 4.1

1. (*a*) **Electrophiles.** H^+, Cl^+, Cr^{3+}, NO_2^+ (all have positive charge), $\overset{*}{B}eCl_2$, $\overset{*}{S}nCl_4$ (electron deficient atom, marked by * is present), SiF_4 (although every atom has octet, Si can have 10 electrons in its *d*-orbitals).

(*b*) **Nucleophiles.** Cl^- (negative charge), $CH_3CH = CH_2$ (presence of π electrons), $H_2\ddot{O}:$ (presence of lone pair of electrons)

(*c*) **Both (Ambiphile).** $CH_2 = \ddot{O}:$, $CH_3C \equiv N:$ (In these, C is electrophilic ; while O/N is nucleophilic).

(*d*) **None.** H_2, CH_4 (absence of charge, π electrons, lone pair of electrons or δ+ and δ– charges).

2. The part bearing δ+ will act as an electrophile

$\overset{\delta+}{Cl}—\overset{\delta-}{Cl}$ $\quad$ $\overset{\delta-}{HO}—\overset{\delta+}{H}$ $\quad$ $\overset{\delta+}{H}—\overset{\delta-}{Br}$ $\quad$ $\overset{\delta-}{HO}—\overset{\delta+}{Cl}$

$CH_3\overset{\displaystyle O}{\overset{\|}{C}}—\overset{\delta-}{O}—\overset{\delta+}{H}$ $\quad$ $CH_3—\overset{\displaystyle O}{\overset{\|}{\overset{\delta+}{C}}}—\overset{\delta-}{Cl}$ $\quad$ $C_6H_5\overset{\displaystyle O}{\overset{\|}{S}}—\overset{\delta-}{O}—\overset{\delta+}{H}$
$\quad\quad\quad

(*ii*) Positive. The rigid ring is converted into an acyclic compound which due to free rotation about C—C single bond will have more randomness (less order). Thus here $S_P > S_R$.

(*iii*) Positive. The ions (present in reactants) are solvated by more H_2O molecules than the CH_3COOH (present in product) ; hence when ions form molecules, several water molecules are set free and hence they will have more randomness, *i.e.* $S_P > S_R$.

2. (*i*) Both values increase rate of reaction.

(*ii*) Both values decrease rate of reaction.

(*iii*) Increase in $\Delta H^{\neq}$ will tend to decrease the rate while increase in $\Delta S^{\neq}$ will tend to increase the rate. Hence the net effect is unpredictable.

(*iv*) The trends will be opposite to those in part (*iii*) ; hence here also the net effect will be unpredictable.

3. $\Delta H^{\neq}$ can be decreased by (*a*) raising H_R, (*b*) lowering H_{TS} or (*c*) both of these.

4. (*i*) $A + B \longrightarrow C + D$; rate = $k[A][B]$.

Here both reactants are involved in the rate expression, so the reaction must be biomolecular. Further, the balanced given reaction involves one molecule of A and one molecule of B, the reaction must have a single (concerted) step.

(*ii*) $r = k[A]$. The rate-determining step is unimolecular and involves only one molecule of A. There can be no prior fast step. Molecule B reacts in the second step, which is fast. A possible two-step mechanism is

$$A \xrightarrow{\text{slow}} C + I \text{ (Intermediate)}$$

$$B + I \xrightarrow{\text{fast}} D$$

(*iii*) $r = k[B]$. On the basis of similar explanation, reaction occurs in the following way :

$$B \xrightarrow{\text{slow}} C + I$$

$$A + I \xrightarrow{\text{fast}} D$$

5. The rate expression indicates that one molecule of B and two molecules of A are needed to give the species for the slow step. Since no step is termoloecular, there must be some number of prior fast steps to give at least intermediate needed for the slow step. The second B molecule (given in the reaction equation) must be consumed in a fast step following the slow step to give final products. Two different mechanisms are possible.

Mechanism I *Mechanism II*

$A + B \xrightarrow{\text{fast}} AB$ (Intermediate) $\qquad A + A \longrightarrow A_2$ (Intermediate)

$AB + A \xrightarrow{\text{slow}} ABA \qquad A_2 + B \longrightarrow A_2B$

$ABA + B \xrightarrow{\text{fast}} C + D \qquad A_2B + B \longrightarrow C + D$

6. The slow unimolecular step should involve decomposition of the intermediate AB_2 or B_2A. Further all the given number of molecules of the reaction are accounted for in the rate determining step, this should be the final step. Two possible mechanisms can be given.

Mechanism I *Mechanism II*

$B + B \xrightarrow{\text{fast}} B_2 \qquad A + B \xrightarrow{\text{fast}} AB$

$B_2 + A \xrightarrow{\text{fast}} B_2A \qquad AB + B \xrightarrow{\text{fast}} AB_2$

$B_2A \xrightarrow{\text{slow}} C + D \qquad AB_2 \xrightarrow{\text{slow}} C + D$

TEST YOUR UNDERSTANDING - 4.3

1. According to given statement + 39.6° is the specific rotation for 100% optically pure (+)-2-bromooctane.

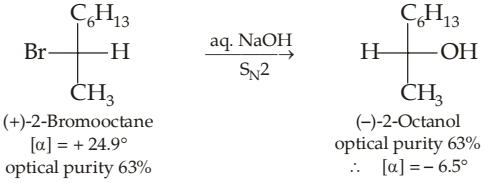
$$\therefore [\alpha] + 24.9° \text{ corresponds to } = \frac{24.9}{39.6} \times 100 = 63\% \text{ optical purity}$$

Since S_{N^2} reactions proceed with 100% inversion, the product, (–)-2-octanol, will also be 63% optically pure.

Thus, 100% optically pure (–)-2-octanol has [α] – 10.3°.

$$\therefore \text{ 63\% optically pure (–)-2-octanol will have } = \frac{-10.3}{100} \times 63$$
$$= -6.5°$$

$\therefore$ Specific rotation of (–)-2-octanol = **– 6.5°.**



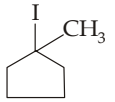
(+)-2-Bromooctane [α] = + 24.9° optical purity 63%

(–)-2-Octanol optical purity 63% ∴ [α] = – 6.5°

TEST YOUR UNDERSTANDING - 4.4

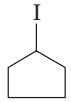
1. (*a*) S_N1 reactions involve formation of carbocation, hence alkyl halide capable of forming carbocation easily (3° > 2° > 1°) will react faster toward S_N1.

(*i*)



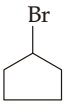
1-Methylcyclopentyl iodide (3° halide)

will react faster than



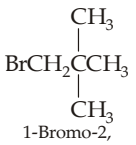
Cyclopentyl iodide (2°)

(*ii*)



Cyclopentyl bromide (2°)

>

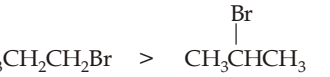


1-Bromo-2, 2-dimethylpropane (1°)

(*iii*) *tert*-Butyl iodide > *tert*-Butyl chloride, C—I bond is weaker than the C—Cl bond.

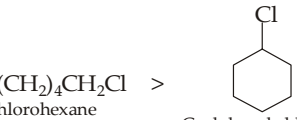
(*b*) S_N2 Reactions involve back-side attack of the nucleophile on the alkyl halide, hence alkyl halide more crowded at the site of substitution will react slowly than the other by S_N2 mechanism.

(*i*)



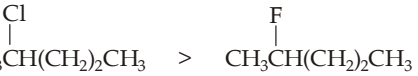
1-Bromopropane, 1° (less crowded) > 2-Bromopropane, 2° (more crowded)

(*ii*)



1-Chlorohexane (1°, less crowded) > Cyclohexyl chloride (2°, more crowded)

(*iii*)



2-Chloropentane > 2-Fluoropentane

Among halogens, fluorine has the strongest bond to carbon, and fluoride is the poorest leaving group, hence it is least reactive toward S_N2 as well as S_N1 reactions.

(*iv*) $CH_3(CH_2)_8CH_2Br$ < $CH_3CH(Br)CH_3$

1-Bromodecane (1°) (although 1°, it is more crowded due to bulky C_9H_{19}— group)

2-Bromopropane (2°) (although 2°, it is having smaller —CH_3 groups)

(*v*) $CH_3C(Br)(CH_3)CH_2CH_2CH_2CH_3$ < $CH_3CH(Br)CH_2CH_2CH(CH_3)CH_3$

2-Bromo-2-methylethane (3°, more crowded)

2-Bromo-5-methylhexane (2°, less crowded)

2. A hydride shift produces tertiary, a more stable carbocation ; while a methyl shift produces a secondary carbocation.

$CH_3-\overset{\oplus}{C}H(CH_3)-CHCH_3$ ← methyl shift — $CH_3-CH(CH_3)-\overset{+}{C}HCH_3$ — hydride shift →

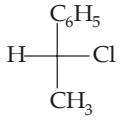
2° Carbocation

1° Carbocation

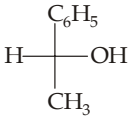
$CH_3-\overset{+}{C}(CH_3)-CH_2CH_3$

3° Carbocation

3. (*a*) According to statement, specific rotations of optically pure (100%) chloride and alcohol are

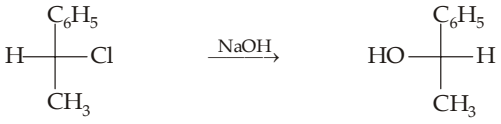


(R)-(–)-α-Phenylethyl chloride, [α] = – 109°



(R)-(–)-α-Phenylethyl alcohol, [α] = – 42.3°

However, according to the reaction the actual specific rotations of the reactant and products are – 34° and + 1.7° respectively, different value of specific rotation and opposite sign of [α] of the product indicates that during reaction inversion as well as retention in configuration occurs and the amount of inverted configuration is more than that of retained configuration.



[α] = – 34° (*optical purity* = 31%) — NaOH → — [α] = + 1.7° (*optical purity* = 4%)

% of optical purity of the reactant with [α] – 34°

$= \frac{34}{109} \times 100 = \mathbf{31\%}$

Similarly, % of optical purity of the product with [α]+ 1.7°

$= \frac{1.7}{42.3} \times 100 = \mathbf{4.0\%}$

(*b*) Determination of net (after subtracting amount utilised in racemic modification) inverted configuration in the

product $= \frac{4}{31} \times 100 = 13\%$

$\therefore$% of racemic modification = 100 – 13 = 87%

Hence % of total inverted configuration = $13 + \frac{87}{2}$

$= \mathbf{56.5\%}$

and % of retained configuration = $\frac{87}{2} = \mathbf{43.5}$

4. Remember wherever rearranged products are formed, carbocations must be formed as intermediates which indicate S_N1 reaction. Carbocation formation in alkyl halides is favoured by bulky alkyl groups and by weak electrophiles like ROH. S_N2 reaction is favoured by alkyl halides having primary alkyl halides and/or by strong nucleophiles like RO^-.

In (*i*), (*ii*) and (*iv*), rearranged products are formed, thus the mechanism will be S_N1. In (*iii*) usual product is formed, reaction is S_N2. However, remember that neopentyl bromide is having Br on primary carbon atom, so its corresponding cation, being primary, is not formed easily. Hence it undergoes S_N1 reaction as in (*iv*) very slowly and in presence of weak nucleophile, in presence of strong nucleophile it undergoes S_N2 reaction as in (*iii*).

5. In neopentyl halides, $(CH_3)_3CCH_2X$, S_N1 reaction is slow because neopentyl cation is primary $(CH_3)_3C\overset{+}{C}H_2$, and hence its formation is slow. The S_N2 reaction is slow because of steric factor, *i.e.* a very large, $(CH_3)_3C$— group, is present on —CH_2X.

TEST YOUR UNDERSTANDING - 4.5

1. $CH_3(CH_2)_{16}CH_2-OH + ClO_2S-C_6H_4-CH_3$ —pyridine→

Octadecyl alcohol — *p*-Toluenesulphonyl chloride

$CH_3(CH_2)_{16}CH_2-O-SO_2-C_6H_4-CH_3$ or $CH_3(CH_2)_{16}CH_2OTs$

Octadecyl-*p*-toluenesulphonate

Note that in the preparation of tosylates, C—O bond of alcohol is not cleaved, hence the configuration of the alcohol and tosylate will be same (difference from alkyl halides : R—OH + HCl $\xrightarrow{H^+}$ R—Cl, where configuration of product will not be similar to that of alcohol). Since *p*-toluenesulphonate is a very good leaving group, it will be displaced by nucleophiles very easily.

(*a*) $CH_3(CH_2)_{16}CH_2-\overset{\curvearrowright}{O}Ts + CH_3COOK \longrightarrow$

Octadecyl tosylate

$CH_3(CH_2)_{16}CH_2-O-C(=O)CH_3$

Octadecyl acetate

(*b*) $CH_3(CH_2)_{16}CH_2-OTs + C_3H_7CH_2SNa \longrightarrow CH_3(CH_2)_{16}CH_2SCH_2C_3H_7$

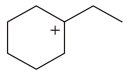
TEST YOUR UNDERSTANDING - 4.6

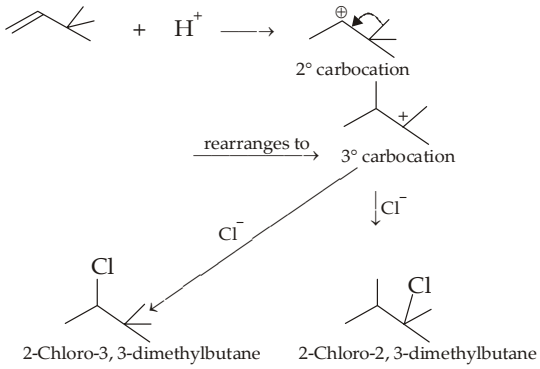
1. (*i*) CH_3COCl, (*ii*) CH_3CONH_2, (*iii*) $CH_3COOC_2H_5$

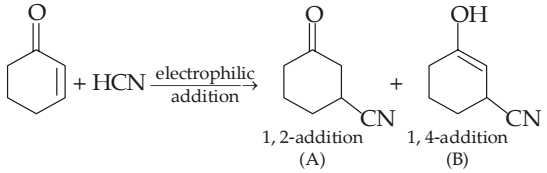
Oxygen atom of the carbonyl group makes carbon more electrophilic in nature and hence compounds having R—C(=O)— group are more susceptible to attack by a nucleophilic than the carbon atom of the alkyl group (—CH_3).

TEST YOUR UNDERSTANDING - 4.7

1. (*i*) $H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{(3°)}{+}}{C}}-CH_2CH_3$ (*ii*) $CH_3CH_2\overset{+}{C}HCH_3$

(*iii*) 

2. 

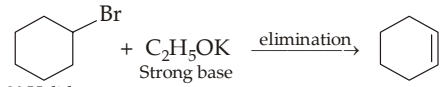
3. (*i*) 

(*ii*) $CH_3CH=CH_2 + CCl_4 \xrightarrow{\text{peroxide}} CH_3-\underset{\underset{Cl}{|}}{CH}CH_2CCl_3$ (C)

(*iii*) $CH_3CH=CH_2 + CBrCl_3 \xrightarrow{\text{peroxide}} CH_3CH(Br)CH_2CCl_3$ (D)

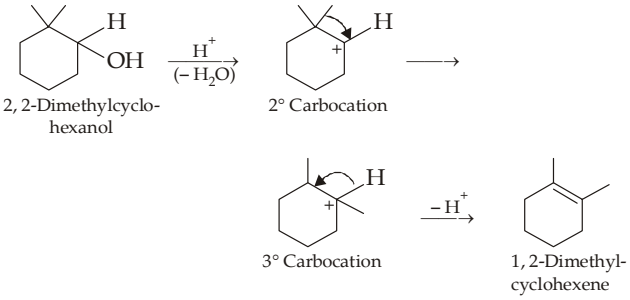
(*iv*) $CH_3CH=CH_2 + CHCl_3 \xrightarrow{\text{peroxide}} CH_3CH_2CH_2CCl_3$ (E)

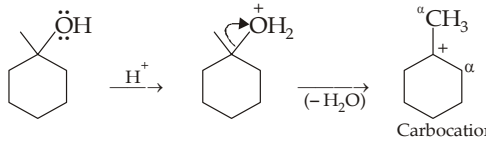
TEST YOUR UNDERSTANDING - 4.8

1. (*i*) 

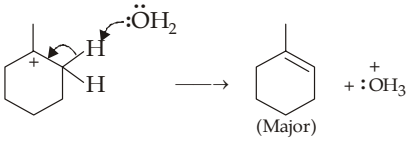
(*ii*) $\underset{\text{2° Halide}}{CH_3\overset{\overset{Br}{|}}{C}HCH_2CH_3} + \underset{\text{Weak base}}{CH_3OH} \xrightarrow{\text{Substitution}} CH_3\overset{\overset{OCH_3}{|}}{C}HCH_2CH_3$

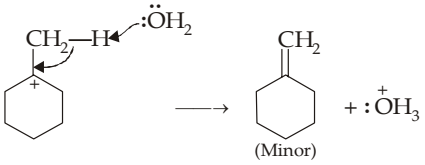
(*iii*) $\underset{\text{2° Halide}}{CH_3\overset{\overset{Br}{|}}{C}HCH_2CH_3} + \underset{\text{Strong base}}{C_2H_5ONa} \xrightarrow{\text{elimination}} CH_3CH=CHCH_3$
cis- and *trans-* (Major)

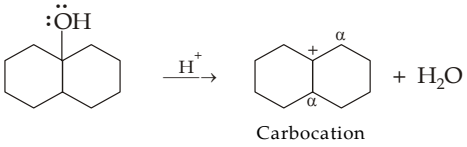
2. 

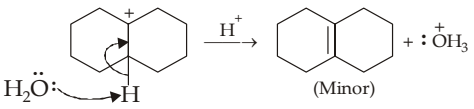
3. (*a*) (i) 

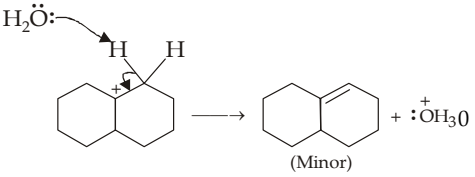
Carbocation can undergo elimination to form 1-methylcyclohexene and methylenecyclohexane.

(*ii*) 

(*iii*) 

(*b*) (i) 

(*ii*) 

(*iii*) 

EXERCISE 4.1

1	(d)	**6**	(d)	**11**	(d)	**16**	(d)	**21**	(c)	**26**	(a)	**31**	(d)	**36**	(b)	**41**	(b)	**46**	(d)
2	(c)	**7**	(b)	**12**	(c)	**17**	(d)	**22**	(b)	**27**	(b)	**32**	(d)	**37**	(b)	**42**	(d)	**47**	(b)
3	(b)	**8**	(d)	**13**	(b)	**18**	(d)	**23**	(b)	**28**	(c)	**33**	(c)	**38**	(c)	**43**	(b)	**48**	(a)
4	(c)	**9**	(d)	**14**	(b)	**19**	(c)	**24**	(b)	**29**	(c)	**34**	(c)	**39**	(c)	**44**	(c)	**49**	(d)
5	(b)	**10**	(c)	**15**	(c)	**20**	(a)	**25**	(c)	**30**	(b)	**35**	(d)	**40**	(b)	**45**	(b)		

1. Ag^+ has positive charge, hence electron deficient, in H_2C:, C has only 6 electrons ; in SiF_4, Si can acquire more than 8 electrons by utilizing its *d*-orbitals.

2. In the reaction, A and C are reactants, B and E are intermediates; and D and F are products. This can be observed by addition of the three steps to get the following net reaction

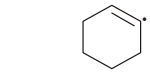
$$2A + C \longrightarrow D + 2F$$

3. The reaction occurs in two steps, in the first step $CH_2 = CH_2$ is nucleophile, while in the second step Br^- is nucleophile

(*i*) $\underset{\text{Nucleophile}_1}{H_2\overset{\delta+}{C} = \overset{\delta-}{C}H_2} + \underset{\text{Electrophile}_2}{\overset{\delta+}{Br}—\overset{\delta-}{Br}} \longrightarrow \underset{\text{Electrophile}_1}{\overset{+}{C}H_2CH_2Br} + \underset{\text{Nucleophile}_2}{Br^-}$

(*ii*) $\underset{\text{Electrophile}_1}{\overset{+}{C}H_2CH_2Br} + \underset{\text{Nucleophile}_2}{Br^-} \longrightarrow CH_2BrCH_2Br$

4. Let us study the free radical formed by the removal of three H·'s



Least stable because H· is to be removed from sp^2 C



Most stable due to allylic nature



More stable because H· is to be removed from sp^3C

5. Isobutane has two types of carbon atoms (1° and 3°) ; hence it will form two products

$\underset{\text{Isobutane}}{CH_3CH(CH_3)CH_3} + :CH_2 \longrightarrow \underset{\text{Insertion on 1°C}}{CH_3CH_2CH(CH_3)CH_3} + \underset{\text{Insertion on 3°C}}{CH_3C(CH_3)(CH_3)CH_3}$

6. In the formation of carbocation (as well as free radical) sp^3 hybridised carbon atom changes to sp^2. This is of special importance in formation of *tert*-carbocation (or free radical) where steric relief is observed. In the parent compound the three bulkyl groups are pushed together due to tetrahedral nature of the carbon atom having bond angle of 109.5° (steric strain) which is greatly relieved in formation of carbocation (or free radical) due to planar structure (120°) of the product, where the three bulky groups are separated from each other by an angle of 120° **(steric relief).**

7. In carbanion, sp^3 hybridised carbon atom has three pairs of bonding electrons and one pair of non-bonding electrons. Thus here two types of repulsions are observed : *lp-bp* and *bp-bp* ; since *lp-bp* > *bp-bp* repulsions, angle between two bonding pairs is slightly reduced than the normal tetrahedral value of 109.5°. Thus the geometry of simple carbanions is not exactly tetrahedral, but pyramidal.

8. Carbocations are sp^2 hybridised, simple (unconjugated) carbanions are sp^3 hybridised but conjugated carbanions are sp^2 hybridised because here delocalization of electrons results in the formation of a double bond which requires all involved atoms to lie in the same plane (coplanar), *i.e.* the molecule becomes flat.

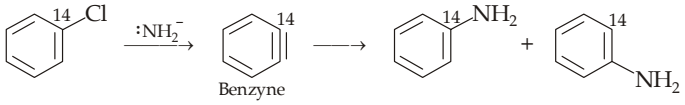
$H_2\ddot{C}—C(CH_3)=O \longleftrightarrow H_2C=C(CH_3)—\ddot{O}$

$H_2C=CH—\ddot{C}H_2 \longleftrightarrow H_2\ddot{C}—CH=CH_2$ or $\left[H_2C^{-\delta}\cdots CH\cdots CH_2^{-\delta}\right]$

9. Carbanion from CH_3CHO and cyclopentadiene is stabilised due to resonance and aromatic sextet respectively.

10. Carbanion is formed as an intermediate which being flat can be attacked by Br_2 on either face forming racemic mixture.

11. Cationoid (cation-like) are those species which are either cations or behave as cations *i.e.* electron deficient.



13. Rate of a multi-step reaction is determined by the slowest step. Thus transition state of such step will require more energy of activation, and thus the corresponding transition state will have highest enthalpy.

14. In multistep reactions, the step with the highest enthalpy transition state (*i.e.* with highest $\Delta H^{\neq}$) is the slowest (rate determining) step.

15. The nucleophilicity of species whose nucleophilic atoms neither lie in the same period nor in the same group of the periodic table should be compared by considering their basic strength or the relative acidic character of their conjugate acids. The decreasing basic character of the species is

$$HS^- > RCOO^- > ROH > RCOOH$$

Conjugate acids $H_2S < RCOOH < ROH_2^+ < RCOOH_2^+$

16. $CH_3C(CH_3)(CH_3)OH \xrightarrow{H^+} CH_3C^{\oplus}(CH_3)(CH_3)$

tert-Butanol — *tert*-Butyl carbocation

tert-Butyl carbocation is formed as an intermediate, which being stable, does not rearrange to the less stable 2° or 1° carbocation.

17. Oxygen, being an electronegative element, can best accommodate negative charge.

18. More the difference between the electronegativities of two concerned atoms, higher will be the chance for dissociation into ions.

19. More the stability of a species greater is the ease of its formation and hence lesser will be the dissociation energy of the bond to be cleaved. Benzyl radical is highly stable due to delocalisation of its odd electron while methyl radical is quite unstable.

20. Free radical substitution leads to complete racemization because the intermediate free radical is coplanar and can be attacked on either of the face equally forming two enantiomers in equal amounts (complete racemization). S_N2 reaction involves the formation of transition state in which attack of nucleophile and removal of the leaving group take place simultaneously, hence the nucleophile can attack back-side from that the leaving group. Consequently, compound having inverted configuration is formed (100% inversion of configuration). In S_{N^1} reaction, the nucleophile attacks the ion pair (R^+X^-), hence back-side attack of the nucleophile predominates although attack from the side of the leaving group (front-side attack) also takes place. Thus the product will be having both enantiomers, and the enantiomer with the inverted configuration predominates. In short, S_N1 reaction leads to partial racemization along with some amount of inverted configuration.

21. Discussed in the above answer.

22. Since S_N1 reaction yields racemic modification along with some amount of the enantiomer of inverted configuration ; as far as specific rotation is concerned, the product will be having opposite specific rotation. Further, its value will be less because *optical purity* of the product will be less than that of reactant.

23. The weaker the base, better will be the leaving group. Further, basic character of the groups can be easily judged by acidic character of its conjugate acid (recall that weak bases have stronger conjugate acids). Thus

Base	^-OH	F^-	OH_2^-	OTs	$^-OSO_2CF_3$
Conjugate acid	H_2O	HF	H_3O^+	HOTs	$HOSO_2CF_3$

The acidic order of the various conjugate acids is

$$CF_3SO_2OH > TsOH > H_3O^+ > HF > H_2O$$

24. S_N1 reactions follow first-order kinetics ; rate = *k*[RX], hence concentration of the nucleophile does not effect its rate.

25. $CH_3CH=CHCH_2Br \longrightarrow [CH_3\overset{+}{C}H-CH=CH_2 \longleftrightarrow CH_3CH=CH\overset{+}{C}H_2] \xrightarrow{OH^-} CH_3CH=CHCH_2OH + CH_3CH(OH)CH=CH_2$

1-Bromobutene-2; Allylic cation; Normal product (S_N1); Rearranged product (S_N1')

Since allylic cation stabilise easily due to resonance, its formation is easy and hence, the compound undergoes S_N1 reaction ; the product formed by rearranged carbocation is known as S_N1, product (unimolecular nucleophilic substitution with rearrangement). It is an example of *allylic rearrangement*.

26. All are primary alkyl bromides and undergo S_N2 reactions in which nucleophile attacks on the carbon from back side. Thus more the branching on the alkyl group attached to C having Br, lesser will be its reactivity towards S_N2 reactions. Thus

$$\underset{(I)}{n\text{-}C_3H_7—CH_2Br} > \underset{(II)}{(CH_3)_2CH—CH_2Br} > \underset{(III)}{\begin{matrix}CH_3\\ \diagdown\\ C_2H_5\end{matrix}\!\!>\!CH—CH_2Br} > \underset{(IV)}{(CH_3)_3C—CH_2Br}$$

27. Addition of halogens to alkenes, involve formation of cyclic halogenonium ion, and not a carbonium ion.

28. Stronger a base, poor will be the leaving group.

29. In nucleophilic additions on carbonyl groups, nucleophile adds on the electron deficient carbon. Thus any factor which can increase electron deficiency of carbonyl carbon will increase rate of nucleophilic addition on carbonyl compounds. Acids perform this function by protonating carbonyl oxygen which thus becomes more electronegative.

$$\begin{matrix}R\\ \diagdown\\ R'\end{matrix}\!\!>\!C=\ddot{O}: + H^+ \rightleftharpoons \begin{matrix}R\\ \diagdown\\ R'\end{matrix}\!\!>\!C=\overset{+}{\ddot{O}}H$$

30. Reaction takes place in presence of a base (:B) which removes hydrogen as proton.

31. F^- is a strong base and causes elimination reaction with *tert*-alkyl halides ; hence the expected product in both should be *isobutene*. However, in presence of H_2O, F^- ion is solvated *via* hydrogen bonding and thus can't exert its influence, the weak base H_2O causes substitution reaction. On the other hand, F^- is not solvated in presence of $(CH_3)_2SO$ (DMSO) causing elimination reaction to form isobutene.

32. $(CH_3)_3COH \longrightarrow (CH_3)_3\overset{+}{C}$.

33. Acid ($SbCl_5$)–catalysed reactions generally involve carbocation as intermediates which here is further confirmed by racemization, since carbocations are flat and can be attacked on either side of the face forming both enantiomers.

34. Electron-withdrawing group like —NO_2 enhances positive charge on the carbon, thus destabilises the carbonium ion, while electron-pushing group like —OH, —OCH_3 disperses positive charge, hence stabilises the carbonium ion.

35. More the stability of the product, faster is debromination of the parent compound.

EXERCISE 4.2

>1 CORRECT OPTION	**1**	(b,c)	**2**	(a, b)	**3**	(b,c)	**4**	(b, d)	**5**	(a, b, c, d)	**6**	(a, b)
PASSAGE 1	**7**	(d)	**8**	(c)	**9**	(b)						
PASSAGE 2	**10**	(b)	**11**	(c)	**12**	(a)						
PASSAGE 3	**13**	(b)	**14**	(b)	**15**	(b)						
MATCHING TYPE QUESTIONS	**16**	(A) - a, d ; (B) - b ; (C) - c, (D) - b					**19**	(A)-a, b ; (B)-c, d ; (C)-a, b ; (D)-a, d				
	17	(A)-a, c ; (B)-d ; (C)-a, c ; (D)-b, c					**20**	(A) – c; (B) – a; (C) – d; (D) – b				
	18	(A) – b,c; (B) – b; (C) – a; (D) – d					**21**	(A) – b; (B) – a, d; (C) – c, d; (D) – b				
A/R	**22**	(a)	**23**	(a)	**24**	(c)	**25**	(a)	**26**	(a)		
TRUE / FALSE	**27**	False;	**28**	False;	**29**	False;						

EXERCISE 4.3

1. (*i*) NH_2^- and NH_3. Here nucleophilic site is same (N), hence nucleophilicity and basicity should be of same order. Since the conjugate acid NH_4^+ is stronger than NH_3, therefore **NH_3 should be weaker base and weaker nucleophile than NH_2^-.**

(*ii*) OH^- is a stronger base than SH^- because the O—H bond is stronger than the S—H bond ; while SH^- is a stronger nucleophile than OH^- because S is less electronegative than O.

(*iii*) H_2O is better nucleophile and stronger base than H_3O^+ (Explanation as that of (*i*)).

(*iv*) On the same line as that of (*i*), $CH_3CH_2O^-$ is a stronger base and better nucleophile than CH_3COO^-.

(*v*) Since the bond dissociation energy of the H—Br is less than that of H—Cl, Br^- will be a weaker base than Cl^-. However, electronegativity of Cl is more than Br, Cl^- will be weaker nucleophile than Br^-.

(*vi*) In OH^- and F^-, the two nucleophilic atoms belong to same period, hence the basicity and nucleophilicity both decrease with the increase in electronegativity. **Thus F^- should be weaker base and weaker nucleophile than OH^- .**

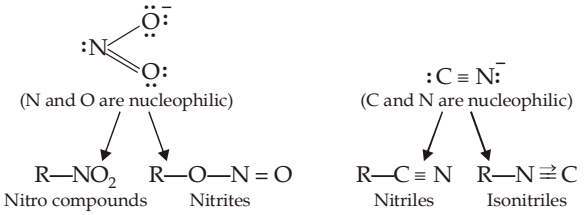
2. (*a*) Nucleophiles (*electron-rich species*) Cl^-, $H_2\ddot{O}$, $CH_3\ddot{O}H$, $CH_3CH=CH_2$,

(*b*) Electrophiles (*electron-deficient species*) : NO^+, $AlCl_3$, $BeCl_2$, Cr^{+3}, $SnCl_4$

(*c*) Both : $CH_2=\ddot{O}$ (electron-rich site O, electron-deficient site C), $CH_3C\equiv\ddot{N}$ (electron-rich site N, electron-deficient site C).

(*d*) None (*neither nucleophilic nor electrophilic*) : CH_4, H_2.

3. Species having two different nucleophilic sites are known as **ambident nucleophiles**, *e.g.* NO_2^- and CN^-



4. (*a*) When the nucleophilic site is the same atom (here O), nucleophilicity parallels basicity. Therefore,

$$CH_3O^- > OH^- > CH_3COO^- > H_2O$$

(*b*) When the attacking (reacting) atoms are different but in the same periodic family, the one with the largest atomic weight is the most reactive. Therefore, $PH_3 > NH_3$. This order is the reverse of basicity.

5. We know that weaker a base better will be the leaving group. Further we know that weaker a base, stronger will be its conjugate acid and hence lower will be its pK_a value. Thus acid strength of the three conjugate acids is

	C_6H_5OH	<	CH_3COOH	<	$C_6H_5SO_3H$
pK_a value	10.0		4.5		2.6
Hence,	$C_6H_5SO_3^-$,		CH_3COO^-,		$C_6H_5O^-$

Basic character increases →
Leaving property decreases

Thus best leaving group is the weakest base ($C_6H_5SO_3^-$) ; and the poorest leaving group is the strongest base ($C_6H_5O^-$).

6. Greater the dispersal of the positive charge, higher will be the stability of the carbocation. Electron-releasing inductive effect and hyperconjugation is maximum in $(CH_3)_3C^+$ and minimum in CH_3^+.

Further stability of these carbocations can be explained on the basis of steric acceleration. Bulkier the group on the carbon bearing positive charge (sp^2 hybridised), more will be steric acceleration (steric relief) in their formation due to conversion of bond angle from 109° present in parent compound (sp^3 hybridised) to 120° in carbocation (steric relief). In short,

	$Me_3C—Br$	>	$Me_2CH—Br$	>	$MeCH_2—Br$	>	$CH_3—Br$
Steric strain and hence unstability	Maximum						Minimum
	Me_3C^+	>	$Me_2\overset{+}{C}H$	>	$Me\overset{+}{C}H_2$	>	$\overset{+}{C}H_3$
Steric relief and hence formation	Maximum						Minimum

7. (*a*) Due to strong electron-withdrawing fluorines, a δ+ develops on the atom adjacent to C^+. Due to positive charges on adjacent atoms, the species is destabilised.

(*b*) Unshared electron pair on fluorine can be shifted to vacant *p*-orbital of $\overset{+}{C}$ (*p*-*p*-overlap). Hence positive charge is dispersed leading to stability of the carbocation.

(*c*) Same explanation as in (*b*).

(*d*) Positive charge is present on the two adjacent atoms, leading to destability of the carbocation.

8. Remember a weak base favours substitution, while a strong base favours elimination.

(*i*) HS^- is a powerful nucleophile which reacts rapidly with the alkyl halide to form mercaptan

$$CH_3CHBrCH_3 + HS^- \xrightarrow{CH_3OH} CH_3CHSHCH_3$$

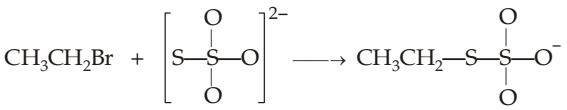
(*ii*) I^- is a powerful nucleophile but weaker base and reacts by S_{N^1} mechanism to form Me_3CI, but again iodide is a better leaving group than Br^-, it reacts with the nucleophilic solvent HCOOH to form formate

$$(CH_3)_3CBr + I^- \xrightarrow[(-Br^-)]{} (CH_3)_3CI \xrightarrow{HCOOH} (CH_3)_3C—O—\overset{O}{\overset{\|}{C}}—H$$

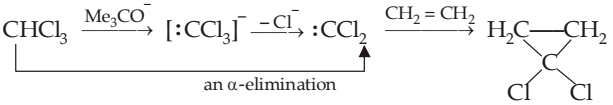
(*iii*) AgCN is an ambident nucleophile and hence, it will form two products.

$$CH_3CH_2Br + AgCN \longrightarrow CH_3CH_2CN + CH_3CH_2NC$$

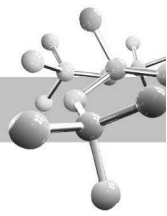
(*iv*) Since S provides a more powerful nucleophilic site than O, alkyl group will be linked to S.



(*v*)



(*vi*) No reaction. Although this is a 3° RCl, it does not undergo an S_{N^1} reaction because the bridgehead C bonded to Cl is part of a rigid structure and therefore cannot form a planar R^+. The bicyclic ring structure does not permit a backside nucleophilic attack on C, ruling out the S_{N^2} mechanism.



9. (*a*) S_{N^2} Reactivity follows the order

$$\underset{1^\circ}{CH_3(CH_2)_3CH_2Br} > \underset{2^\circ}{(C_2H_5)_2CHBr} > \underset{3^\circ}{(CH_3)_2C(Br)C_2H_5}$$

(*b*) Ag^+ catalyzes S_{N^1} reactivity and thus the order is

$$\underset{3^\circ}{(CH_3)_2C(Br)C_2H_5} > \underset{2^\circ}{(C_2H_5)_2CHBr} > \underset{1^\circ}{CH_3(CH_2)_3CH_2Br}$$

10. (*i*) Br^- is an extremely weak Bronsted base, hence it can't displace the strong base OH^-. However, in presence of acid, $R\overset{+}{O}H_2$ is first formed. Now Br^- displaces H_2O which is a very weak base and a good leaving group.

(*ii*) The bulky $(CH_3)_3C$ group sterically hinders backside attack by a nucleophile.

(*iii*) Solvolysis goes by an S_N1 mechanism. Thus relative rates of different reactants in S_{N^1} reactions depend on the stabilities of the intermediate carbonium ions. $CH_2 = CH_2CH_2Cl$ is more reactive because $CH_2 = CH—\overset{+}{C}H_2$ is more stable than $(CH_3)_3\overset{+}{C}$.

(*iv*) CH_3CH_2Br and $(CH_3)_2CHBr$ react by S_N2 pathway in which reactivity of the latter halide is very less because of steric hindrance. However, $(CH_3)_3CBr$ reacts by S_N1 pathway which involves formation of carbocation, $(CH_3)_3\overset{+}{C}$ formation is very rapid because of steric acceleration as well as inductive effect.

(*v*) $ROH + Cl^- \xleftarrow{KI,\ fast} RCl + H_2O \xrightarrow{slow} ROH + Cl^-$

I^- is a powerful nucleophile which reacts rapidly with RCl to form RI. Further, I^- is also a better leaving group than Cl^-, and RI is therefore hydrolysed rapidly to form ROH and regenerate I^-, which recycles in the reaction

$$RCl + H_2O \xrightarrow{Slow} ROH$$
$$\downarrow I^- \ (fast) \qquad RI \xrightarrow[-I]{H_2O,\ fast} \uparrow$$

(*vi*) This is an E2 reaction which involves the cleavage of C—H (or C—D) bond in the rate determining step. Since C—H bond is broken at a higher rate than the stronger C—D bond, formation of ethylene is easy in CH_3CH_2I than in CD_3CH_2I. This ratio of the rate constants, K_H/K_D is called **isotope effect.**

(*vii*) Since S_N1 reactions involve the formation of carbocations and primary carbocations (from primary alkyl halides) are least stable, 1° RCl are least reactive towards S_N1 solvolysis. However, in case of $CH_3CH_2OCH_2Cl$, the carbocation formed has a lone pair of electrons on an atom (O) adjacent to C^+, hence delocalisation (by *p-p* overlap) of the positive charge stabilises the carbocation. Therefore, the compound shows S_N1 reactivity

$$CH_3CH_2OCH_2Cl \xrightarrow[(-Cl^-)]{} \underset{\text{Delocalisation of positive charge possible}}{CH_3CH_2—\ddot{O}=\overset{+}{C}H_2} \xrightarrow{C_2H_5OH} CH_3CH_2—O—CH_2OC_2H_5$$

11. (*a*) S_N2 displacement, I^- is a good nucleophile and a poor base.

(*b*) E2 elimination, a 3° halide and a fairly strong base.

(*c*) Mainly S_N2 displacement.

(*d*) Mainly E2. A less polar solvent than H_2O (in *c*) favours E2.

(*e*) S_N1 displacement ; H_2O is not basic enough to remove a proton to cause elimination.

12. (*a*) $(CH_3)_3CBr \longrightarrow (CH_3)_3\overset{+}{C} \xrightarrow{C_2H_5OH} \underset{\text{Major } (S_N1)}{(CH_3)_3COC_2H_5} + \underset{\text{Very minor (E1) in absence of a strong base}}{(CH_3)_2C = CH_2}$

(*b*) $CH_3CH = CHCl \xrightarrow{NaNH_2} \underset{E2}{CH_3C \equiv CH}$

Vinyl halides are quite inert toward S_N2 reactions.

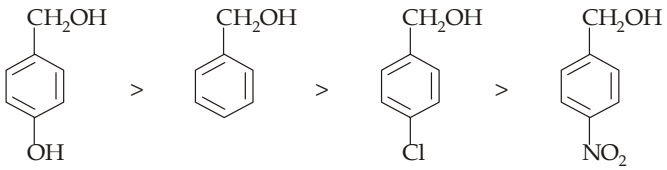
(*c*) $(CH_3)_3CI + H_2O \longrightarrow \underset{(S_N2)}{(CH_3)_3COH} + HI$

In presence of a nucleophilic solvent and in absence of a strong base, 3° RX undergoes S_{N^1} solvolysis.

(*d*) $(CH_3)_3CI + OH^- \longrightarrow \underset{(E2)}{(CH_3)_2C = CH_2} + H_2O + I^-$

In presence of a strong base (OH^-), 3° RX undergoes mainly E2 reaction.

13.

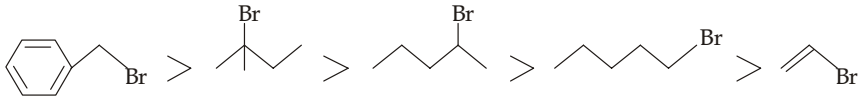


This is an example of S_N1 reaction because benzyl cation is quite stable. Further, presence of electron-pushing group (*e.g.* —OH) increases stability of the carbocation by dispersing positive charge, while electron-withdrawing groups (—Cl and —NO_2) destabilise the carbocation by intensifying the positive charge.

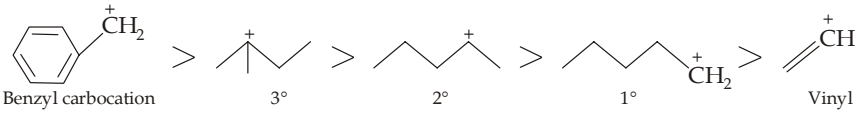
14. There are seven isomeric pentyl alcohols, $C_5H_{11}OH$, of which four are primary, two secondary and one tertiary. Primary alcohols follow S_N2 pathway and hence isomer having bulky alkyl group will be less reactive. Thus

$$CH_3CH_2CH_2CH_2—CH_2OH > (CH_3)_2CHCH_2—CH_2OH > \begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>\!CH—CH_2OH > (CH_3)_3C—CH_2OH$$

15. More the stability of the carbocation, higher will be S_N1 reactivity of the parent compound.



Corresponding cations are

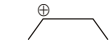
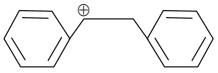


Benzyl carbocation 3° 2° 1° Vinyl

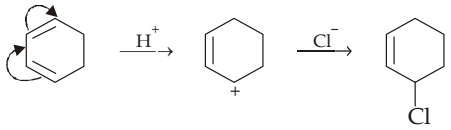
16. Stability of carbocation (Intermediate) determines the reactivity of alkene towards addition of HCl ; more stable the carbocation more will be the reactivity of alkene. Here carbocations of both alkenes are given along with their stability.

(*i*) $CH_3—\overset{\oplus}{C}H_2$ (1° Carbocation) and  (2° Carbocation) More stable

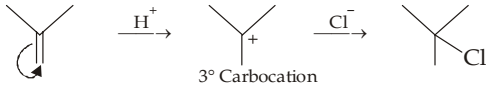
(*ii*)  2° Carbocation and  3° Carbocation (More stable)

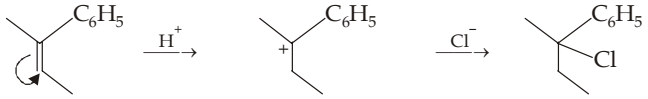
(*iii*)  (2° Carbocation) and  2° Carbocation, with conjugation (More stable)

(*iv*)  (2° Carbocation) and  2° Carbocation, having conjugated double bond (More stable)

17. (*i*) 

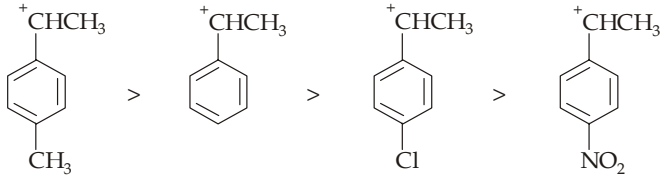
(*ii*) 

(*iii*) 

(*iv*) 

Benzylic carbocation

18. This is an example of electrophilic addition and involves the formation of carbocation, so more is the stability of the carbocation intermediate higher will be the reactivity of the parent compound. Carbocation stability order, and hence reactivity towards HCl of the parent compound follows the order.



19. $CH_2=CH—CH=CH_2 \xrightarrow{\cdot CCl_3} \left[Cl_3C—CH_2—\dot{C}H—CH=CH_2 \longleftrightarrow Cl_3C—CH_2—CH=CH—\dot{C}H_2\right]$

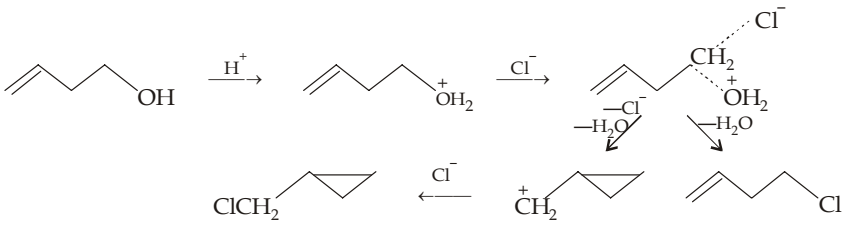
(2° free radical)

$\downarrow Br^{\cdot}$

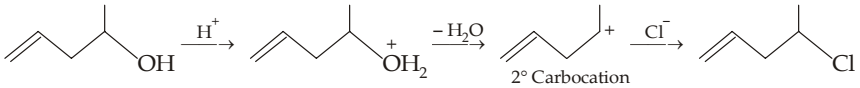
$Cl_3C—CH_2—CHBr—CH=CH_2$ + $Cl_3C—CH_2—CH=CH—CH_2Br$

1, 2-addition 1, 4-addition

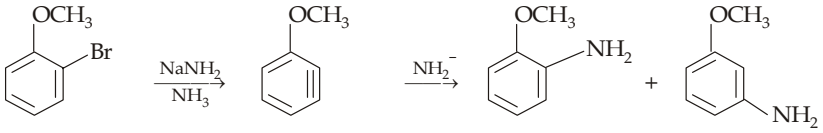
20. (*i*) Primary alcohols mainly undergo S_{N^2} reactions *via* the formation of a transition state which can form two products.



(*ii*) Secondary alcohols undergo S_N1 mechanism.



(*iii*)



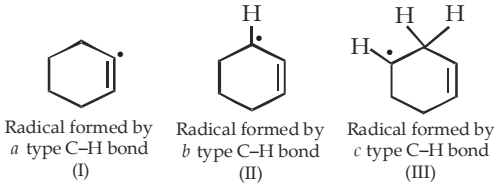
Benzyne

21. (a) $\underset{\text{conjugated allylic}}{\text{IV}} > \underset{\text{allylic}}{\text{II}} > \underset{3^\circ}{\text{III}} > \underset{2^\circ}{\text{VI}} > \underset{1^\circ}{\text{VII}} > \underset{\text{vinylic}}{\text{I}} > \text{V}$

(b) $\underset{\substack{3^\circ \text{ allylic, highly} \\ \text{conjugated}}}{\text{III}} > \underset{\substack{2^\circ \text{ allylic, highly} \\ \text{conjugated}}}{\text{II}} > \underset{2^\circ \text{ allylic}}{\text{I}}$

(c) $(C_6H_5)_2\ddot{C} > C_6H_5\ddot{C}H > CH_3\ddot{C}H > :CH_2$

(d) Yes, more is the stability of a free radical, weaker will be the parent bond. Thus write down the structures of the corresponding free radical formed and observe the relative stability of the free radical.



Radical formed by *a* type C–H bond (I)

Radical formed by *b* type C–H bond (II)

Radical formed by *c* type C–H bond (III)

Relative stability of the free radical :

$$\underset{\text{allylic}}{\text{II}} > \underset{2^\circ}{\text{III}} > \underset{\text{vinylic}}{\text{I}}$$

Thus bond energy of the *a*, *b* and *c* C – H bonds :

$$\text{I} > \text{III} > \text{II}$$

22. (a) CH_3^+ (b) $C_6H_5\ddot{N}:$ (c) $CH_3CO\ddot{N}:$ (d) $H\ddot{N}:$ (e) $CH_3\ddot{N}:$

23. (a) $:CH_2,\ CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

(b) $CH_3CO\ddot{N}:$ (c)



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PREFACE

REVISED EDITION

It gives us immense pleasure and satisfaction to bring out the thoroughly revised first edition of the book **"Disha's Hydrocarbons and Halogen Derivatives"** The book has been designed to give a better look & feel and to make the text more lucid. The new pattern of JEE Main & Advanced has been kept in mind throughout.

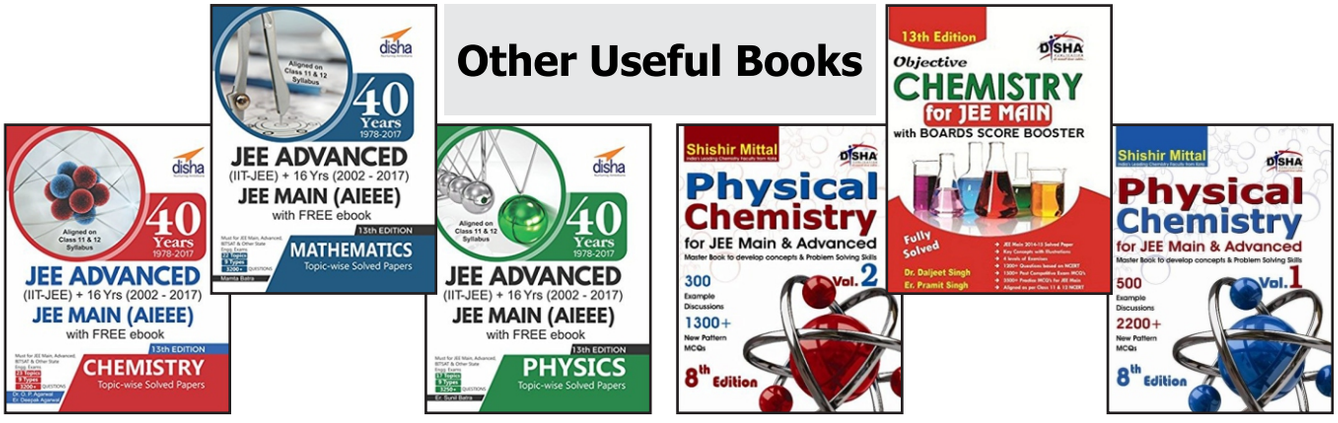
The exercises at the end of each chapter have been designed in the flavour of the new pattern of JEE Main & Advanced. The questions from the previous JEE papers have been incorporated in the different exercises. A separate section having past JEE questions is also provided at the end.

1. **Exercise 1 - MCQ with One correct option :** This exercise contains a collection of question, which has been very carefully selected and it is ensured that there is no repetition. The exercise contains a collection of questions, which has been very carefully selected and it is ensured that there is no repetition. The exercise has been designed so as to cover all the concepts involved in the chapter.
2. **Exercise 2 :** This exercise contains all the four new variety of questions which have been asked in the last 3-4 JEE examinations. These variety of questions are-
   - **(i) MCQ's with one or more than one correct answers :** Around 20-30 well selected problems introduced in each chapter.
   - **(ii) Comprehension based questions :** More than 50 passages which tests the student's comprehension and analytical ability have been added. All these are newly framed problems.
   - **(iii) Matching type question :** Match the following type of question with multiple matching have been introduced in each chapter. These are unique and newly framed problems which will definitely pose a big challenge to the student. I feel that this type of problem is the best way to check a student's concepts.
   - **(iv) Assertion & Reason type questions :** Assertion and Reason type of questions have been incorporated in each and every chapter.
3. **Exercise 3 - Subjective Problems :** This exercise contains a unique collection of subjective problems which will not only give practice to the students but will also help in revising the complete chapter.

In the end, We would like to request all readers to highlight the printing errors and come forward with suggestions for further improvement of the book.

DR. O.P. AGARWAL

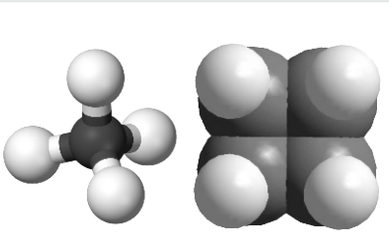
Other Useful Books

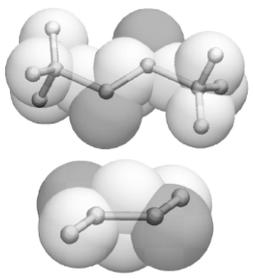


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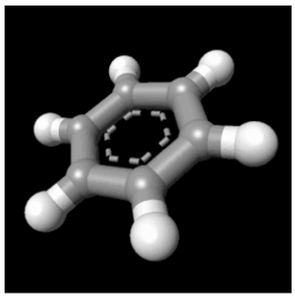


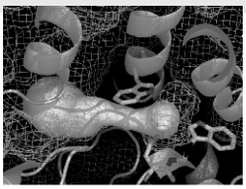
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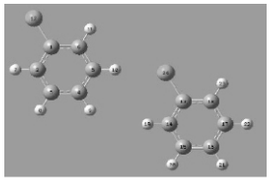


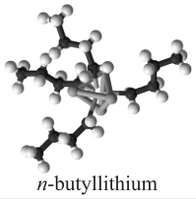
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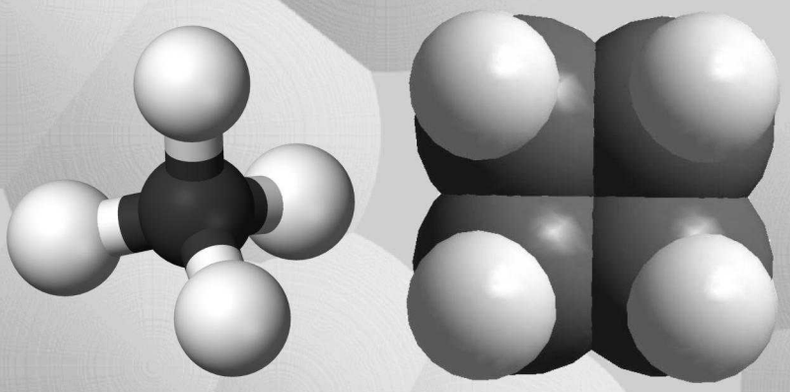


n-butyllithium

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5

Aliphatic Hydrocarbons I : Alkanes and Cycloalkanes

CHAPTER HIGHLIGHTS

5.1 Nomenclature and Isomerism
5.2 Industrial Sources of Alkanes
5.3 Preparation of Alkanes
5.4 Physical Properties
5.5 Chemical Properties
5.6 Nomenclature of Cycloalkanes
5.7 Geometrical Isomerism in Alicyclic Compounds
5.8 Chemical Properties of Cycloalkanes
EXERCISES
SOLUTIONS

Compounds containing *only two elements*, carbon and hydrogens, are known as **hydrocarbons**. On the basis of structure and properties, hydrocarbons are divided in two main classes, *viz*. **aliphatic** and **aromatic**. Aliphatic hydrocarbons are further divided into different families, namely alkanes, alkenes, alkynes and their cyclic analogs (cycloalkanes, cycloalkenes and cycloalkynes). The last type of hydrocarbons are also known as **cyclic aliphatic** or **alicyclic compounds.**

ALKANES

Alkanes are open-chain (acyclic) hydrocarbons comprising the homologous series with the general formula C_nH_{2n+2} where n is an integer. They have only single bonds and therefore said to be **saturated**. Because of their low chemical activity, alkanes are also known as **paraffins**.

5.1 Nomenclature and Isomerism

According to IUPAC system of nomenclature, open chain aliphatic compounds are named as **alkanes**. The first three members do not exhibit isomerism, all other members show **chain** or **nuclear isomerism**. The number of isomers increases with the increase in the number of carbon atoms, *e.g. butane has 2 isomers, pentane 3, hexane 5, heptane 9, octane 18 and decane 75.*

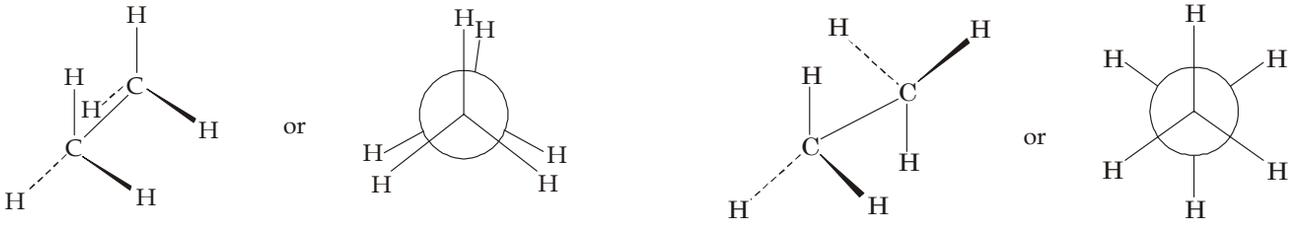
Conformations : Each carbon atom of alkanes is in sp^3 state of hybridisation and all C – H and C – C bonds are strong **sigma** (σ) **bonds**. Since sigma bonded carbon atoms can rotate about the C – C bond, a chain of singly bonded carbon atoms can be arranged in any zig-zag shape. Two such arrangements are shown for four consecutive carbon atoms.



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Such *different arrangements of atoms that can be converted into one another by rotation about single bonds are called conformations*. **Since conformations cannot be isolated, they are not isomers.** Ethane can have infinite number of conformations, the two extreme conformations are **eclipsed*** (with highest energy, hence least stable) and **staggered*** (with lowest energy, hence most stable). The infinite number of intermediate conformations are called **skew** conformations.

To represent such conformations, we shall often use two kinds of three dimensional formulas : *andiron* or sawhorse *formulas (i) and Newman projections (ii)*.



(*i*) (*ii*) (*i*) (*ii*)

(a) Eclipsed (b) Staggered

The energy required to rotate the ethane molecule about the carbon-carbon bonds is called *torsional energy* and thus the instability of the eclipsed conformation or any of the skew conformations is said to be due to *torsional strain*.

REMEMBER THAT

(i) like ethane, two extreme conformations of propane are eclipsed and staggered.

(ii) The relative stability order of the six important conformations of *n*-butane is

Anti > Gauche ≡ Gauche > Eclipsed ≡ Eclipsed > Fully eclipsed

(iii) The two conformations of cyclohexane are the boat or C-form and the chair or Z-form; the latter form is more stable than the boat form by 44 kJ mol^{-1}.

TEST YOUR UNDERSTANDING - 5.1

1. How many types of carbon atoms are present in the hydrocarbon 3, 3, 5-trimethylhexane?

2. Write down the IUPAC name of the compound $(CH_3)_2C\ (C_2H_5).C(CH_3)(C_2H_5).CH(C_2H_5).CH_3$.

3. Draw the structures of the following groups, and give their more common names.

(a) the (1-methylethyl) group (b) the (2-methylpropyl) group

(c) the (1-methylpropyl) group (d) the (1,1-dimethylethyl) group

4. Draw the structures of the following compounds.

(a) 1,1-Dimethyl-2-(1,1,3-trimethylbutyl)cyclooctane. (b) 5-(1,2,2-trimethylpropyl)nonane

5. Comment on the calculated and experimental values of entropy of ethane.

5.2 Industrial Sources of Alkanes

The principal industrial source of alkanes is **petroleum** which is accompanied by *natural gas*. Natural gas consists mainly of methane and progressively small amounts of ethane, propane and higher alkanes. The propane-butane fraction obtained from natural gas is used as domestic fuel under the name of **LPG** (*Liquefied Petroleum Gas*). Petroleum is separated by fractional distillation into various fractions. The use of each fraction chiefly depends upon its volatility or viscosity. The non-volatile fraction, residue or coke obtained from paraffin-base petroleum consists of complex hydrocarbons having a high carbon-to-hydrogen ratio, it is used as a fuel or in the manufacture of *carbon electrodes* for the electrochemical industries.

The second potential source of alkanes is coal which is converted into useful petroleum products through hydrogenation.

* There is an energy barrier of 2.8 kcal/mol for the interconversion of staggered and eclipsed conformations. This value is not high, even at room temperature the fraction of collisions with sufficient energy is large enough to overcome the energy barrier of 2.8 kcal/mol.

5.3 Preparation of Alkanes

5.3.1 Hydrogenation of Alkenes and Alkynes

(For details, consult chapter on alkenes)

$$\underset{\text{Propene}}{CH_3CH=CH_2} + H_2 \xrightarrow{\text{Pt, Pd or Ni}} \underset{\text{Propane}}{CH_3CH_2CH_3}$$

$$CH \equiv CH + 2H_2 \xrightarrow{Ni} CH_3 - CH_3$$

REMEMBER THAT

(i) The reaction temperature varies from room temperature to 200–300°. Hydrogenation of alkene using Ni catalyst at 200–300°C is known as **Sabatier-Senderens reduction.**

(ii) Raney nickel* is highly active and can be used at ordinary temperatures.

(iii) Other catalysts used during hydrogenation are PtO_2 (Adam's catalyst) and $[(Ph_3P)_3RhCl]$ – Wilkinson's catalyst.

5.3.2 Reduction of Alkyl Halides

(a) *Reduction of alkyl halides by electron-transfer from metal (Zn).*

$$RX \xrightarrow[\text{or Zn–Cu couple} + C_2H_5OH]{Zn + H^+,\ Zn + OH^-} RH$$

Remember, here reduction is not done by nascent hydrogen. The metal transfers the electron to the alkyl halide generating *carbanion* which, being a very strong base, abstracts a proton from the acid or any potential proton donor including solvent like ethanol.

$$Zn: \longrightarrow Zn^{2+} + 2e^-$$

$$R - X + e^- \longrightarrow R^{\cdot} + X^{\ominus}$$

$$R^{\cdot} + e^- \longrightarrow R:^{\ominus}$$

$$R:^{\ominus} + H^+ \longrightarrow R - H$$

(b) *Reduction with hydride donors like lithium aluminium hydride ($LiAlH_4$) or sodium borohydride ($NaBH_4$).*

$$4RX + LiAlH_4 \longrightarrow 4RX + LiX + AlX_3\ (X \neq F)$$

REMEMBER THAT

(i) Reduction takes place in four independent steps, each involving a nucleophilic displacement by hydride ions ($H:^{\ominus}$) given by $LiAlH_4$.

(ii) $LiAlH_4$ reduces 1° and 2° alkyl halides, while $NaBH_4$ reduces only 2° and 3° alkyl halides.

(c) *Reduction by tri-n-butyl tinhydride or triphenyl tinhydride.*

$$RX + (n\text{-}C_4H_9)_3\ SnH \longrightarrow RH + (n\text{-}C_4H_9)_3\ SnX$$

(d) *Reduction via organometallic compounds.*

(i) $$RX + 2Li \xrightarrow[(-LiX)]{\text{dry ether}} \underset{\text{Alkyllithium}}{R^-Li^+} \xrightarrow{H_2O} RH + LiOH$$

(ii) $$RX + Mg \xrightarrow{\text{dry ether}} \underset{\text{Grignard reagent}}{R^-(Mg^+X)} \xrightarrow{H_2O} RH + Mg(X)OH$$

* Raney nickel is prepared by treating Ni–Al alloy with NaOH, Al dissolves in NaOH leaving behind nickel in finely divided form.

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Note that organometallics have basic carbanionic site and hence can easily abstract proton from water, dil. acid or alcohol.

Due to carbanionic character of the alkyl group of the Grignard reagent, latter may be considered as a magnesium salt of the extremely weak acid, R–H. Thus the reaction of RMgX with water is simply the displacement of the weaker acid, R–H from its salt by the stronger acid (HOH).

$$RMgX + \underset{\text{Stronger acid}}{HOH} \longrightarrow \underset{\text{Weaker acid}}{RH} + Mg(OH)X$$

TEST YOUR UNDERSTANDING - 5.2

1. How will you prepare C_2H_5D from C_2H_5Br?

2. $CH_3CH_2CH_2Cl + Mg \xrightarrow{\text{dry ether}} CH_3CH_2CH_2MgCl$ or $(CH_3)_2CHMgCl$

3. Pick up the stronger and weaker acids in the following reaction :

$$C_2H_5MgBr + NH_3 \longrightarrow C_2H_6 + Mg(NH_2)X$$

(e) Alkyl iodides undergo reduction on heating with hydriodic acid at high temperature in presence of red phosphorus.

$$RI + HI \xrightarrow{\text{red P, 150°C}} RH + I_2$$

Iodine is removed as PI_3 ($2P + 3I_2 \longrightarrow 2PI_3$).

5.3.3 Reduction of functional groups containing oxygen with HI and red phosphorus

e.g. ROH to RH, RCHO to RCH_3, R_2CO to R_2CH_2, RCOOH to RCH_3.

$$CH_3OH + 2HI \xrightarrow[150°C]{\text{red P}} CH_4 + H_2O + I_2$$

$$CH_3CHO + 4HI \xrightarrow[150°C]{\text{red P}} CH_3CH_3 + H_2O + I_2$$

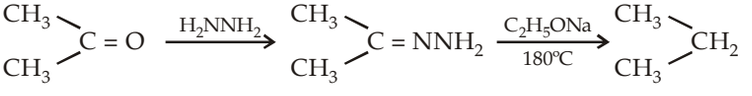
$$CH_3COOH + 6HI \xrightarrow[200°C]{\text{red P}} CH_3CH_3 + 2H_2O + I_2$$

$$CH_3COCl + 6HI \longrightarrow CH_3CH_3 + H_2O + HCl + 3I_2$$

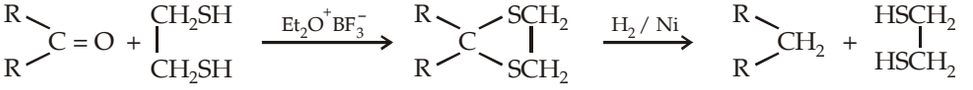
Phosphorus and iodine react to form PI_3 which again produces hydriodic acid.

Aldehydes and ketones can also be reduced to hydrocarbons by **Clemmensen reduction** (reagent : Zn-Hg/conc. HCl) and **Wolf-Kishner reduction** (reagent : NH_2NH_2/C_2H_5ONa at 180°).

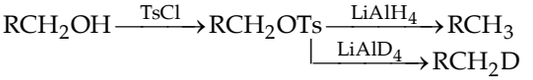
$$CH_3CHO \xrightarrow[HCl]{Zn-Hg} CH_3CH_3 + H_2O$$



In Mozingo reduction : The carbonyl group is converted into its dithioacetal using ethanedithiol which is then hydrogenated over Raney nickel.



Primary and secondary alcohols can also be converted to alkanes through fosylates.



5.3.4 Hydroboration of Alkanes

$$RCH=CH_2 \xrightarrow{B_2H_6} \underset{\text{Trialkylborane}}{(R-CH_2-CH_2-)_3\,B} \xrightarrow[CH_3CH_2COOH]{CH_3COOH\text{ or}} 3RCH_2CH_3$$

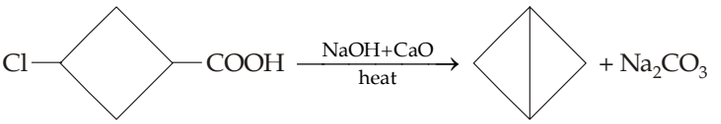
5.3.5 Decarboxylation of carboxylic acids

$$RCOONa + \underset{\text{Soda lime}}{NaOH(CaO)} \xrightarrow{heat} RH + Na_2CO_3$$

Yield of alkanes is low in case of higher alkanes, e.g.

$$C_2H_5COONa + NaOH(CaO) \xrightarrow{heat} C_2H_6 + CH_4 + H_2$$

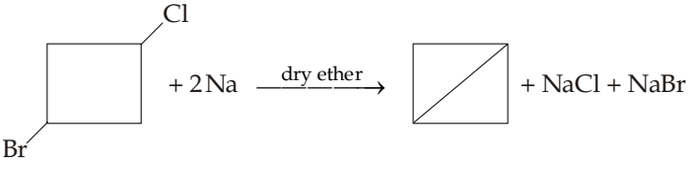
This reaction involves carbanion as the intermediate, hence nucleophilic substitution is also possible during decaroxylation.



5.3.6 Coupling of alkyl halides with organometallic compounds

(*i*) *Wurtz reaction*. The two alkyl groups can be coupled by reacting an ethereal solution of RBr, RCl or RI with Na or K. Yields of product are best for 1° (60%) and poorest for 3° (10%) alkyl halides.

$$2C_2H_5Cl + 2Na \xrightarrow{\text{dry ether}} C_2H_5C_2H_5 + 2NaCl$$



$$BrCH_2CH_2CH_2Br + 2Na \xrightarrow{\text{dry ether}} \text{(cyclopropane)} + 2NaBr$$

(a) The yield is good in case of symmetrical alkanes (*alkanes having even number of carbon atoms*) i.e. when the two alkyl halides are same, otherwise cross products will be formed.

$$CH_3Br + C_2H_5Br \xrightarrow[\text{dry ether}]{Na} CH_3CH_3 + C_2H_5C_2H_5 + CH_3C_2H_5$$

It is very difficult to separate the mixture of hydrocarbons.

(b) Other hydrocarbons are also formed as by-products, e.g.

$$2C_2H_5Br \xrightarrow{Na,\text{ dry ether}} C_2H_5C_2H_5 + C_2H_6 + C_2H_4$$

Mechanism of Wurtz reaction

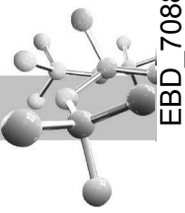
Ionic mechanism. It operates when the reaction is carried out in solution.

$$RX + 2Na^{\bullet} \longrightarrow R^-Na^+ + NaX$$

$$R^- + RX \xrightarrow{S_N2} R-R + X^-$$

Formation of by-products, *viz.* alkene is due to **disporportionation reaction,** *i.e. one molecule gains hydrogen at the expense of the other.*

$$CH_3-\overset{\ominus}{C}H_2 + H-CH_2-CH_2-X \longrightarrow CH_3-CH_3 + CH_2=CH_2 + X^-$$



Free radical mechanism. It operates when the reaction is carried out in vapour phase.

$$RX + Na^{\bullet} \longrightarrow R^{\bullet} + NaX$$

$$R^{\bullet} + R^{\bullet} \longrightarrow R - R$$

Disproportionation in free radicals, *e.g.* $C_2H_5^{\bullet}$

$$C_2H_5^{\bullet} + C_2H_5^{\bullet} \longrightarrow C_2H_6 + C_2H_4$$

(*ii*) *Frankland reaction*

$$R - I + Zn + I - R \xrightarrow{\text{heat}} R - R + ZnI_2$$

(*iii*) *Corey-House synthesis*

$$\underset{(1^{\circ}, 2^{\circ} \text{ or } 3^{\circ})}{R - X} \xrightarrow{Li} \underset{\text{Alkyllithium}}{R - Li} \xrightarrow{CuX} \underset{\substack{\text{Lithium} \\ \text{dialkylcuprate*}}}{R - \underset{|}{\overset{R}{C}}uLi} \xrightarrow[(\textbf{only } 1^{\circ})]{R'X} R - R'$$

$$(CH_3)_2CHCl \xrightarrow{Li} (CH_3)_2CH - Li \xrightarrow{CuI} (CH_3)_2CH - \underset{|}{\overset{CH(CH_3)_2}{C}}uLi \xrightarrow{CH_3CH_2Cl} \underset{\text{2–Methylbutane}}{(CH_3)_2CH - CH_2 - CH_3}$$

(a) Grignard reagents can be used in place of alkyllithium.

(b) R' can be same or different from R, but the former should be primary.

5.3.7 Kolbe's electrolytic method

$$RCOO^-Na^+ \xrightarrow{\text{electrolysis}} \underbrace{R - R + CO_2}_{\text{At anode}} + \underbrace{NaOH + H_2}_{\text{At cathode}}$$

At cathode : $Na^+ + e^- \longrightarrow Na^{\bullet}$; $Na^{\bullet} + H_2O \longrightarrow NaOH + \frac{1}{2}H_2$

At anode : $RCO\ddot{O}:^- \xrightarrow{-e} RC\dot{O}: \longrightarrow R^{\bullet} + CO_2$

$$R^{\bullet} + R^{\bullet} \xrightarrow{\text{Coupling}} R - R$$

5.3.8 Methane can be prepared from aluminium carbide

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

5.4 Physical Properties

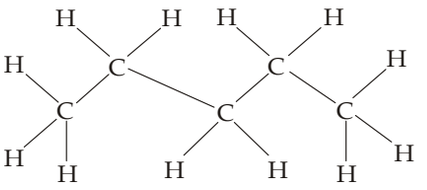
(*i*) C_1–C_4 are gases, C_5–C_{17} are liquids and higher are solids.

(*ii*) As in other homologous series, boiling points of *n*-alkanes increase nearly 20-30° with the increase of each CH_2 unit. In case of isomeric alkanes, boiling points decrease with the increase in the branching of the chain. The higher boiling points of *n*-alkanes among isomeric alkanes is because of their large surface area which leads to large vander Waals attractive forces. With the increase in branch, the molecule tends to become spherical due to which surface area decreases and thus the vander Waals forces become weaker.

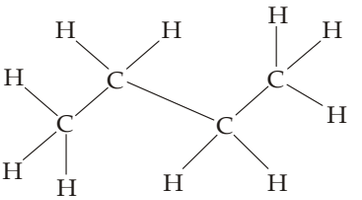
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* Lithium dialkylcuprate is also known as **Gilman reagent.**

(*iii*) The increase in melting point is not regular, an alkane with even number of carbon atoms melts at a higher temperature than that with the higher homologue having an odd number of carbon atoms. This is because of the zig-zag shape of the chains due to which the terminal carbon atoms of the alkane with odd number of carbon atoms will lie on the same side while the terminal carbon atoms of the alkane with even number of carbon atoms will be on the opposite sides. Thus alkanes with even number of carbon atoms pack better into a solid structure, hence they melt at higher temperatures than the odd numbered alkanes which do not pack so well.



Structure of *n*-pentane (an odd numbered alkane). Note the two end C atoms are lying on the same side leading to loose packing



Structure of *n*-butane (an even numbered alkane). Note the two end C atoms are lying on the opposite ends allowing closer packing

Branching of the chain also affects the alkanes' melting point. A branched alkane generally melts at a higher temperature than the *n*-alkane with the same number of carbon atoms. Branching of an alkane gives it a more compact three-dimensional structure which packs more easily into a solid structure and thus increases the melting point.

(*iv*) The relative density increases with the size of the alkanes and tends to approach a constant value of 0.8 with $C_{16}H_{34}$. Remember that nearly all organic compounds are less dense than water, as they consist mainly of C and H. In general, for a compound to be denser than water, it must contain a heavy atom like Br or I or several atoms like Cl.

TEST YOUR UNDERSTANDING - 5.3

1. Arrange the following compounds in order of decreasing boiling point.

(a) Octane, hexane, and decane

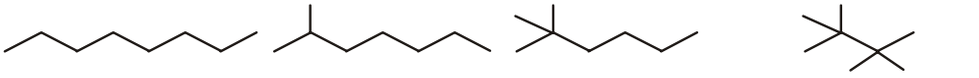
(b) *n*-Octane, 3,3-dimethylhexane, and 2,2,3,3-tetramethylbutane

2. Arrange the above compounds in order of decreasing melting point.

Relative stabilities of isomeric alkanes : Like most other organic compounds, alkanes burn readily in air. This combination with oxygen is known as **combustion** and is quite exothermic. All hydrocarbons yield carbon dioxide and water as the final products, e.g.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \qquad \Delta H^0 = -212.8 \text{ kcal. } (-890 \text{ kJ})$$

The heat released on complete combustion of one mole of a substance is called its **heat of combustion**. A low value of heat of combustion indicates the low heat content or **enthalpy** and thus higher stability of the molecule. Heat of combustion is used for assessing the relative stability of isomeric alkanes. For example,



	Octane	2-Methylheptane	2,2-Dimethylhexane	2,2,3,3-Tetramethylbutane
ΔH^0 (kJ/mol.)	5471	5466	5458	5452
(kcal/mol.)	1307.5	1306.3	1304.6	1303

Thus here, 2,2,3,3-tetramethylbutane, the most highly branched isomer, is the most stable and octane, the unbranched isomer is the least stable. The small differences in stability between branched and unbranched alkanes depend on induced dipole-induced dipole attractive forces. We know that branching causes spherical shape which leads to **decreased** forces of attraction between molecules (*intermolecular forces*).

Simultaneously, **branching** causes induced dipole-induced dipole attractions within a molecule which leads to **increased** *intramolecular attractive forces* causing stability of the molecule. Thus branching increases intramolecular attractive forces leading to increased stability.



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5.5 Chemical Properties

Since alkanes have completely non-polar C–C bonds and nearly non-polar C–H bonds, these are highly stable to most of the common reagents at room temperature. However, they undergo substitution reactions involving *free radical chain mechanism* in the presence of UV, at higher temperature or in the presence of certain free-radical initiators such as peroxides etc.

5.5.1 Substitution reactions

(*i*) **Halogenation.**

$$R-H + X_2 \xrightarrow[\text{or heat}]{UV} R-X + HX$$

For example, $\underset{\text{Methane}}{CH_4} \xrightarrow{Cl_2} \underset{\text{Methyl chloride}}{CH_3Cl} \xrightarrow{Cl_2} \underset{\text{Methylene chloride}}{CH_2Cl_2} \xrightarrow{Cl_2} \underset{\text{Chloroform}}{CHCl_3} \xrightarrow{Cl_2} \underset{\text{Carbon tetrachloride}}{CCl_4}$

REMEMBER :

(i) When equimolar amounts of CH_4 and chlorine are taken, a mixture of the four possible products is formed.

(ii) The yield of methyl chloride can highly be improved by using a large excess of methane. Due to great difference between the boiling points of methane (–161.5°C) and methyl chloride (–24°C), the two can be separated easily.

(iii) **Reactivity of X_2 :** $F_2 > Cl_2 > Br_2 > I_2$.

(iv) Bromination takes place somewhat less readily than chlorination.

(v) Iodination is a reversible reaction, since HI, formed as a by-product, is a strong reducing agent and reduces alkyl iodides back to alkane. Hence, iodination can be done only in presence of a strong oxidising agent like iodic acid, nitric acid or HgO which destroys the hydriodic acid.

$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$

Iodides are more conveniently prepared by treating the chloro- or bromo-derivative with sodium iodide dissolved in methanol or acetone **(Conant Finkelstein reaction)**.

$$RCl + \underset{\text{Soluble in acetone}}{NaI} \xrightarrow{\text{acetone}} RI + \underset{\text{Insoluble in acetone}}{NaCl\downarrow}$$

(vi) Fluorine, being the most reactive, reacts so viogorously even in the dark and at room temperature that it may lead to explosion and cleavage of the C–C as well as C–H bonds. Thus fluorination when required, is carried out by

(a) using fluorine diluted with an inert gas.

(b) or by using inorganic fluorides (e.g. HgF_2) on bromo or iodo derivatives.

$$2C_2H_5Br + HgF_2 \longrightarrow 2C_2H_5F + HgBr_2$$

(vii) **Reactivity of hydrogen atoms :** $3° > 2° > 1° > CH_4$.

Halogenation of higher alkanes : Consider the following examples.

(i) $\underset{\text{Propane}}{CH_3CH_2CH_3} \xrightarrow[\text{light, 25°C}]{Cl_2} \underset{n\text{–Propyl chloride (45\%)}}{CH_3CH_2CH_2Cl} + \underset{\text{Isopropyl chloride (55\%)}}{CH_3CH(Cl)CH_3}$

(ii) $\underset{n\text{–Butane}}{CH_3CH_2CH_2CH_3} \xrightarrow[\text{light, 25°C}]{Cl_2} \underset{\text{1–Chlorobutane (28\%)}}{CH_3CH_2CH_2CH_2Cl} + \underset{\text{2–Chlorobutane (72\%)}}{CH_3CH_2CH(Cl)CH_3}$

(iii) $\underset{\substack{\text{2–Methylpropane}\\\text{(Isobutane)}}}{CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_3} \xrightarrow[\text{light, 25°C}]{Cl_2} \underset{\substack{\text{1–Chloro–2–methyl–}\\\text{propane (Isobutyl}\\\text{chloride) 64\%}}}{CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2Cl} + \underset{\substack{\text{2–Chloro–2–methylpropane}\\\text{(}tert\text{–Butyl chloride) 36\%}}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_3}$

(iv) $\underset{\text{Propane}}{CH_3CH_2CH_3} \xrightarrow[\text{light, 127°C}]{Br_2} \underset{n\text{–Propyl bromide (3\%)}}{CH_3CH_2CH_2Br} + \underset{\text{Isopropyl bromide (97\%)}}{CH_3CH(Br)CH_3}$

(v) $\underset{n-\text{Butane}}{CH_3CH_2CH_2CH_3} \xrightarrow[\text{light, 127°C}]{Br_2} \underset{\text{1–Bromobutane (2\%)}}{CH_3CH_2CH_2CH_2Br} + \underset{\text{2–Bromobutane (98\%)}}{CH_3CH_2CH(Br)CH_3}$

(vi) $\underset{\text{Isobutane}}{CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_3} \xrightarrow[\text{light, 127°C}]{Br_2} \underset{\textit{trace}}{CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2Br} + \underset{>99\%}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}-CH_3}$

From the above reactions, it is observed that chlorination gives mixture in which no isomer greatly predominates, while bromination gives mixture in which one isomer predominates greatly (97-99%). Three factors determine the relative yields of the isomeric products.

(*i*) *Probability factor*. This factor is based on the number of each kind of H atom in the molecule. For example, in $CH_3CH_2CH_2CH_3$ there are *six* equivalent 1° H's and *four* equivalent 2° H's. The probability of abstracting 1° H's to 2° H's is 6 to 4 *i.e.* 3 to 2.

(*ii*) *Reactivity of hydrogen*. The order of reactivity of H is 3° > 2° > 1°.

For example, the relative rates per hydrogen atom is found to be

3° (5.0) > 2° (3.8) > 1° (1.0) For chlorination at 25°C

3° (1600) > 2° (82) > 1° (1) For bromination at 127°C

(*iii*) *Reactivity of halogen free radical*. The more reactive chlorine free radical is less selective and more influenced by the probability factor. On the other hand, the less reactive Br is more selective and less influenced by the probability factor **(Reactivity-selectivity principle)**.

TEST YOUR UNDERSTANDING - 5.4

1. Predict the porportions for bromination at 127° of the following compounds; relative reactivity ratio for 3°, 2° and 1° hydrogens during bromination is 1600 : 82 : 1.

(a) isobutane (b) 2-methylbutane

(c) 2,3-dimethylbutane (d) n-pentane

Mechanism of halogenation : Halogenation takes place *via* free radical formation according to following steps :

(i) $Cl_2 \xrightarrow{\text{heat or light}} 2Cl^{\bullet}$ } **Chain initiation**

(ii) $Cl^{\bullet} + CH_4 \longrightarrow CH_3^{\bullet} + HCl$

(iii) $CH_3^{\bullet} + Cl_2 \longrightarrow CH_3Cl + Cl^{\bullet}$ } **Chain-propagation**

Steps (ii) and (iii) are repeated again and again until finally chain is terminated by either of the reactions.

(iv) $Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$

or $CH_3^{\bullet} + CH_3^{\bullet} \longrightarrow CH_3CH_3$ } **Chain-termination**

or $CH_3^{\bullet} + Cl^{\bullet} \longrightarrow CH_3Cl$

NOTE THAT

(i) Each photon of light cleaves one chlorine molecule to two chlorine atoms.

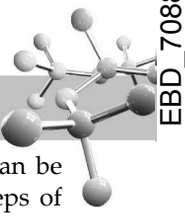
(ii) Each chloride atom (or free radical) starts a chain and on an average, each chain consists of 5000 repititions of chain-propagating cycle.

(iii) Under one set of conditions, nearly 10000 molecules of CH_3Cl are formed for every quantum (photon) of light absorbed.

(iv) Presence of even a small amount of **inhibitors** (*e.g.* oxygen) slows down or stops a reaction by reacting with the intermediate free radicals, *e.g.*

$$CH_3^{\bullet} + O_2 \longrightarrow CH_3-O-O^{\bullet}$$

The $CH_3OO^{\bullet}$ radical is mch reactive than the $CH_3^{\bullet}$ radical and hence can't propagate the chain. When all the oxygen molecules present have reacted with methyl radicals, the reaction takes its usual path.



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Relative reactivities of halogens towards methane : The observed relative order ($F_2 > Cl_2 > Br_2 > I_2$) can be explained with the values of ΔH (since E_{act} has been measured only for a few of these reactions) for the three steps of halogenation for the four halogens.

Three steps of halogenation	Value of ΔH for each step with the four halogens			
	F	Cl	Br	I
(i) $X_2 \longrightarrow 2X^{\bullet}$	+38	+58	+46	+36
(ii) $X^{\bullet} + CH_4 \longrightarrow CH_3^{\bullet} + HX$	−32	+1	+16	+33
(iii) $CH_3^{\bullet} + X_2 \longrightarrow CH_3X + X^{\bullet}$	−70	−26	−24	−20

Recall that in case of diatomic molecules (X_2), E_{act} = ΔH. Thus chlorine with the largest E_{act} should dissociate most slowly, while iodine having smallest E_{act} should dissociate most rapidly. Since this does not agree with the observed order of reactivity ($F_2 > Cl_2 > Br_2 > I_2$), *dissociation step (i) can't be the rate-determining step of halogenation.*

Now consider, step (*iii*) which is exothermic in all cases. Further, the value of ΔH with chlorine, bromine and iodine has nearly the same value, their E_{act} should be small and these should react faster and nearly with the same rate. Hence this step also cannot be the cause of the observed relative reactivities.

Now consider, step (*ii*), note that the values of ΔH is spread over a wide range.

(a) The value of ΔH for bromine (+16 kCal) indicates that the E_{act} of their reaction must be at least 16 kCal which in practice is found to be 18 kCal.

(b) The smaller value of ΔH (+1 kCal) for chlorine indicates that the E_{act} of this reaction could have a smaller value, which is found to be 4 kCal. The large difference in E_{act} values with chlorine and bromine indicates that *fraction of collisions* of chlorine and methane *possessing sufficient energy* is much larger than that of bromine and methane. In other words, fruitless collisions are very high in case of bromine and methane as compared to chlorine and methane and thus the chain in bromination becomes much shorter than in clorination. Thus, it can be concluded that although at a given temperature, bromine atoms are formed more rapidly than chlorine atoms because of lower E_{act} of step **(*i*)**, **overall bromination is slower than chlorination because of the shorter chain length which in turn is due to larger E_{act} of step (*ii*) with bromine.**

(c) For an endothermic reaction of an iodine atoms, E_{act} should be atleast 33 kCal. To achieve this large value, iodine atoms should collide with an enormous number of methane molecules (nearly 10^{13} at 275°C). However, no iodine atom lasts this long, but it recombines with another iodine atom to form iodine molecules. Thus iodination proceeds at a negligible rate. Thus although iodine atoms are easily formed, their inability to abstract hydrogen from CH_4 prevents iodination.

(d) The E_{act} for the highly exothermic fluorination, step (ii), is not expected to be larger than for the endothermic chlorination step (ii), in practice the value is found to be 1 kCal thus permitting *longer chains* than for chlorination. Further, due to weak F–F bond, fluorine atoms are formed faster than chlorine atoms, leading to *more chains*. Thus due to more chains and longer chains, fluorination is extremely endothermic with a ΔH of –102 kCal.

In short, we have observed that of the two propagating steps (ii) and (iii), step (ii) is more difficult than (iii). Thus, it is the rate of the formation of methyl radical [step (ii)] that determines the rate of halogenation. The relative reactivity of X_2 towards CH_4 is due to difference in the value of ΔH in step (ii) which in turn is due to difference in the bond energy of the H–X bond. In other words, reactivity of a halogen towards CH_4 depends upon the strength of the bond which that halogen forms with hydrogen.

Reactivity of alkanes (Ease of abstraction of hydrogen atom) Snce the rate determining step in halogenation is abstraction of hydrogen by a halogen atom, *i.e.* the formation of alkyl radical, halogenation of alkanes follows order of stability of free radicals, *i.e.*

$$3° > 2° > 1° > \dot{C}H_3 \qquad (\textit{Order of stability of radicals})$$

The above order of stability of radicals is due to ease of their formation from the corresponding alkane which in turn is due to difference in the avlue of ΔH.

$$CH_3 - H \longrightarrow \underset{\text{Methyl}}{CH_3^{\bullet}} + H^{\bullet} \qquad \Delta H = 104 \text{ kcal}$$

$$CH_3CH_2 - H \longrightarrow \underset{\text{Ethyl (1°)}}{CH_3\dot{C}H_2} + H^{\bullet} \qquad \Delta H = 98 \text{ kcal}$$

$$CH_3CH_2CH_2 - H \longrightarrow \underset{\text{Propyl (1°)}}{CH_3CH_2\dot{C}H_2} + H^{\bullet} \qquad \Delta H = 98 \text{ kcal}$$

$$CH_3\underset{\underset{H}{|}}{CH}CH_3 \longrightarrow \underset{\text{Isopropyl (2°)}}{CH_3\dot{C}HCH_3} + H^{\bullet} \qquad \Delta H = 95 \text{ kcal}$$

$$CH_3\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_3 \longrightarrow \underset{\textit{tert}-\text{Butyl}}{CH_3\overset{\overset{CH_3}{|}}{\dot{C}}CH_3} + H^{\bullet} \qquad \Delta H = 92 \text{ kcal}$$

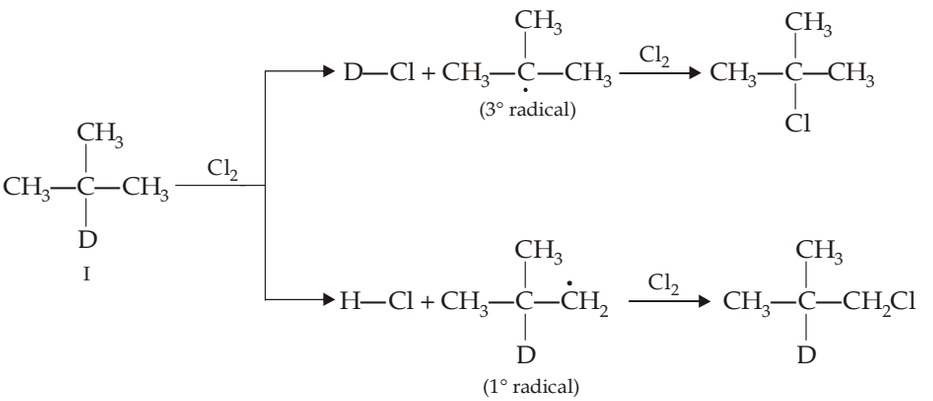
Thus the amount of energy required to form the various classes of radicals decreases in the order : $CH_3^{\bullet} > 1° > 2° > 3°$, *i.e.* it is easiest to form 3° radical and it is most difficult to form $CH_3^{\bullet}$. We can also interpret this in an alternative way "the ease of abstraction of hydrogen atoms from hydrocarbons follows the sequence $3° > 2° > 1° > CH_4$ which should also be the ease of formation of free radicals." Now we know that *the more stable the free radical, the more easily it is formed*. Thus the order of stability and ease of formation of free radicals is

$$3° > 2° > 1° > CH_3^{\bullet}$$

The above order of stability is in accordance with the stability of free radicals on the basis of delocalisation of odd electron.

Allyl, benzyl > 3° > 2° > 1° > methyl, vinyl (*Order of stability of various free radicals*)

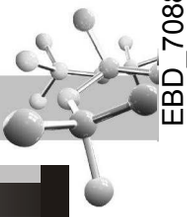
No rearrangement in free radicals. Unlike carbocation, a less stable free radical does not rearrange to the more stable free radical. This can be proved by the photochemical chlorination of the deuterium-labelled isobutane, I. In this experiment, the DCl : HCl ratio was found to be equal to the *tert*-butyl chloride : deuterated isobutyl chloride, clearly indicating that every abstraction of a *tert*-hydrogen (deuterium) gave a molecule of *tert*-butyl chloride, and every abstraction of a primary hydrogen gave a molecule of deuterated isobutyl chloride.



This leads to the conclusion that the 1° radical formed in the second reaction does not rearrange to the more stable 3° radical by migration of hydrogen atom or alkyl group. However, *less stable radical carrying halogen atom can rearrange to the more stable radical by migration of halogen, e.g.*

$$CH_3 - \underset{\text{(1° radical)}}{\underset{\underset{Br}{|}}{CH} - \dot{C}H_2} \longrightarrow \underset{\text{(2° radical)}}{CH_3 - \dot{C}H - CH_2Br}$$

$$CH_3 - \underset{\text{(1° radical)}}{\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}} - \dot{C}H_2} \longrightarrow \underset{\text{(3° radical)}}{CH_3 - \overset{\overset{CH_3}{|}}{\dot{C}} - CH_2Cl}$$



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TEST YOUR UNDERSTANDING - 5.5

1. Account for the fact that the chain-initiating step in thermal chlorination of CH_4 is

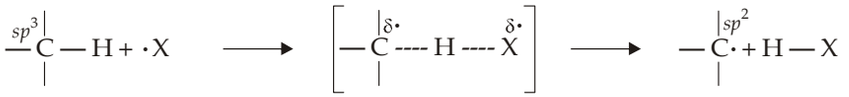
$$Cl_2 \xrightarrow{heat} 2Cl^{\bullet} \text{ and not } CH_4 \xrightarrow{heat} CH_3^{\bullet} + H^{\bullet}$$

2. Draw the reactants, transition state and products for the following reaction, indicating state of hybridisation at each stage.

$$Cl^{\bullet} + CH_4 \longrightarrow {}^{\bullet}CH_3 + HCl$$

3. Predict the product obtained by chlorination of *tert*- butyl bromide.

(i) **Transition state for halogenation.** The rate determining step of halogenation of alkanes proceeds in the following way :



Reactants — Transition state (C and X both have partial radical character) — Products

We have observed that the differences in reactivity towards halogen atoms are mainly due to differences in E_{act}, the lower is the E_{act} of formation of a free radical, the more stable it is. This in turn means that the more stable the radical, the more stable is the transition state leading to its formation. The transition states formed during chlorination and bromination differ from each other.

1. Amount of cleavage of the C—H bond of alkanes is less in chlorination.
2. Free radical character of carbon is less in chlorination and more in bromination. More* fully developed is the radical character in the transition state, more effective with be the delocalization of the odd electon and more will be the stability of the radical. Thus difference in stability between 1°, 2° and 3° radicals and hence reactivity of H's (3° > 2° > 1°) becomes more important in bromination than in chlorination.
3. It is formed earlier in chlorination than in bromination.
4. Transition state of chlorination resembles more with reactants, while that of bromination resembles more with products.

(ii) **Nitration.**

$$CH_3CH_2CH_3 + HNO_3 \xrightarrow[\text{(vapour phase)}]{400-500^{\circ}C} \underset{\text{1–Nitorpropane}}{CH_3CH_2CH_2NO_2} + \underset{\text{2–Nitropropane}}{CH_3\overset{NO_2}{\overset{|}{C}}HCH_3} + \underset{\text{Nitroethane}}{CH_3CH_2NO_2} + \underset{\text{Nitromethane}}{CH_3NO_2}$$

Vapour phase nitration causes chain fission. *Liquid phase nitration* is possible for alkanes having 6 or more carbon atoms

(iii) **Sulphonation.** in case of *n*-alkanes, sulphonation is possible in alkanes having 6 or more carbon atoms, while branched chain alkanes having less than 6 carbon atoms can also be sulphonated.

$$\underset{\text{Isobutane}}{(CH_3)_3CH} + \underset{\text{(fuming)}}{H_2SO_4} \xrightarrow{\text{or Oleum}} \underset{\textit{tert}\text{–Butyl sulphonic acid}}{(CH_3)_3CSO_3H}$$

5.5.2 Combustion or Complete oxidation

$$CH_4 + 2O_2(\text{excess}) \longrightarrow CO_2 + 2H_2O + 212.8 \text{ kcal}$$

In general, $$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O + \text{Heat}$$

* In short, the declocalization of an odd electron, or accommodation of a positve or negative charage will take place more effectively when the transition state is more fully developed, *i.e.* when the reagent is less reactive.

The value of n and thus the nature of alkane can be ascertained by the following relation.

$$\frac{\text{Volume of hydrocarbon}}{\text{Volume of oxygen}} = \frac{2}{3n+1}$$

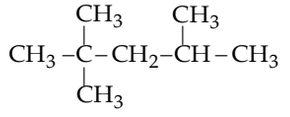
Complete combustion of alkanes is the source of energy for the internal combustion engine. Although the complete mechanism of combustion of alkanes is not fully developed, the reaction is a *free radical chain raction.*

To make gasoline engine more efficient, compression ratio of the fuel -air mixture was made higher, which, sometimes produced *knocking* (objectionable metallic sound) instead of smooth explosion; knocking in turn reduces the power of engine. Knocking depends upon the nature of the hydrocarbon and it falls off in the following order.

n-Alkanes > branched alkanes > alkenes > arenes

The relative antiknock tendency of a fuel is indicated by its **octane number.** An arbitraty scale has been set up with *n*-heptane which knocks very badly, being given an octane number of zero, and 2, 2, 4- *trimethylpentane* **(iso-octane),** being given the octane number of 100.

$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
n–Heptane
(Octane number = 0)


2,2,4–Trimethylpentane
(Octane number =100)

Thus **octane number** *of a gasoline is defined as the percentage of iso-octane present in a mixture of iso-octane and n-heptane which matches the fuel (gasoline) in knocking;* **higher the octane number of a gasoline better is its quality. Regular gasolines** have an octane number of 74, gasolines having lower value than 74 are known as **third grade gasoline,** while those having more than 74 octane number are known as **premium gasolines.** Compounds having more than 100 and even less than 0 octane numbers are known ; e.g. *n*-nonane has an octane number of -45, while triptane (2, 2, 3-trimethylbutane) has an octane number of 125. Gasoline with 100 or more octane number are used as fuel in aeroplanes (*aviation gasoline*).

Octane number of *straight -run gasoline* (gasoline, obtained by direct distillation of petroleum) can be improved by the addition of compounds having higher octane number, viz. arenes, alkenes and branched chain alkanes. These compounds in turn are produced from petroleum hydrocarbons by *catalytic cracking, catalytic reforming* and *alkylation* of alkanes by alkenes. Octane number of a fuel is greatly improved by adding a small amount of tetraethyl lead, $(C_2H_5)_4Pb$. Gasoline, so obtained is known as *ethyl gasolne* or *loaded gasoline*. Tetraethyl lead (TEL) is believed to produce tiny particles of lead oxides on whose surface certain reaction chains are broken.

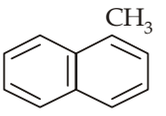
In addition to CO_2 and H_2O, gasoline engine discharges include certain pollution-causing substances like carbon monoxide, unburnt hydrocarbons, oxides of nitrogen and various lead compounds. This problem has been solved by installing **converters** in automobile engines. Converters clean up exhaust emissions by catalytic oxidation of hydrocarbons and carbon monoxide and by breaking oxides of nitrogen into nitrogen and oxygen. However, oxidation catalysts used in converters contain platinum which is poisoned by lead. For overcoming this problem, use of **unleaded petrol is made compulsory.** Absence of TEL in gasoline brought back the problem of knocking, which is solved in two ways.

(i) By lowering the compression ratio in the newly built automobile engines.

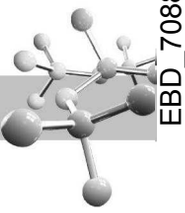
(ii) By increasing octane number by the addition of arenes, alkenes and branched alkanes.

As octane number is used to describe the knocking property of gasoline, **cetane number** is used for measuring the knocking character of diesel, used as fuel in diesel engines, Cetane (*n*-hexadecane) ignites very readily and is given a cetane number of 100, while a-methylnaphthalene which ignites very sluggishly is given cetane number zero.

$CH_3(CH_2)_{14}CH_3$
Hexadecane (Cetane)
(Cetane number = 100)


α-Methylnaphthalene
(Cetane number = 0)

It must be noted that the discharge of CO_2 from gasoline engines is also one of the compounds responsible for causing *green house effect.* Gases accumulated in the atmosphere absorb and trap infrared light radiated outward from the earth and convert it into heat, increasing temperature of the earth which in due course of time could cause drastic climatic changes. Principal green house gases are carbon dioxide, chlorofluorocarbons (commonly known as CFCs) and methane.



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Other oxidation reactions of alkanes are

(i) $2CH_4 + 3O_2(\text{limited}) \longrightarrow 2CO + 4H_2O$

$CH_4 + O_2(\text{limited}) \longrightarrow \underset{\text{(Carbon black)}}{C} + 2H_2O$

(ii) $\underbrace{CH_4 + O_2}_{1:1} \xrightarrow[100\text{ atm, }200^\circ C]{\text{Cu tubes}} CH_3OH$

(iii) $CH_4 + O_2 \xrightarrow{\text{heated MoO}} HCHO + H_2O$

(iv) $\underset{\text{Alkane with 3°C}}{(CH_3)_3CH} + [O] \xrightarrow{\text{alk.}KMnO_4} \underset{\textit{tert}\text{-Butanol}}{(CH_3)_3COH}$

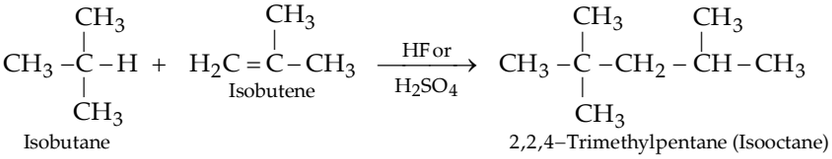
5.5.3 Pyrolysis

Decomposition of a compound by heat in absence of oxygen is known as pyrolysis. Pyrolysis of alkanes, especially when applied to petroleum, is known as *cracking*, Here larger alkanes are converted into smaller alkanes, alkenes and some hydrogen.

$$\underset{\text{Ethene}}{CH_2=CH_2} + \underset{\text{Methane}}{CH_4} \xleftarrow{400-600^\circ C} \underset{\text{Propane}}{CH_3CH_2CH_3} \xrightarrow{400-600^\circ C} \underset{\text{Propene}}{CH_3CH=CH_2} + H_2$$

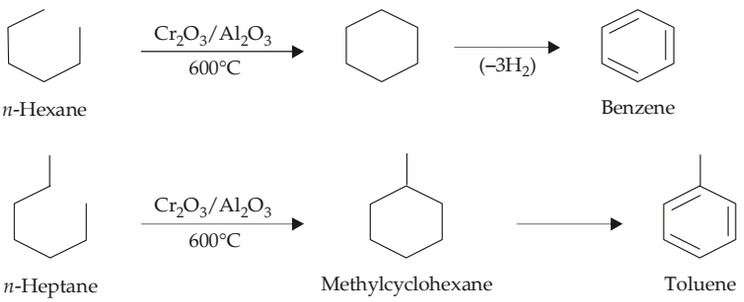
Of the four types of cracking (thermal cracking, steam cracking, hydrocracking and catalytic cracking), the last one is most important. Here higher boiling petroleum fractions (gas oil) are heated in presence of finely divided silica-alumina catalyst at 450-550°C and under slight pressure. Catalytic cracking not only converts larger molecules into smaller ones thus increases the yield of gasoline, but it also improves the quality of gasoline by forming highly branched alkanes and alkenes.

5.5.4 Alkylation



5.5.5 Reforming, catalytic reforming or aromatisation

(*Conversion of alkanes and cycloalkanes into aromatic compounds*)



Reforming, carried out in presence of hydrogen, is known as **hydroforming** and in presence of platinum as **platforming.**

5.5.6 Isomeration

$$\underset{n-\text{Butane}}{CH_3CH_2CH_2CH_3} \xrightarrow[200^\circ C/35\text{ atm}]{\text{anhy. }AlCl_3, HCl} \underset{\text{Isobutane}}{CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_3}$$

Pyrolysis, alkylation, isomerisation and reforming are usd for increasing the octane number of gasoline

5.5.7 Insertion of methylene (carbene)

Singlet carbene (generated by the irradiation of ketene) can insert randomly into a σ C–H bond of an alkane ; e.g.

$$\underset{n-\text{ Pentane}}{CH_3CH_2CH_2CH_2CH_3} + H_2C: \longrightarrow \underset{n\text{-Hexane(48\%)}}{H\mathbf{CH_2}CH_2CH_2CH_2CH_2CH_3} + \underset{\text{2-Methylpentane(35\%)}}{CH_3CH(\mathbf{CH_2}H)CH_2CH_2CH_3} + \underset{\text{3-Methylpentane (17\%)}}{CH_3CH_2CH(\mathbf{CH_2}H)CH_2CH_3}$$

NOTE

CH_2, marked black are coming from carbene.

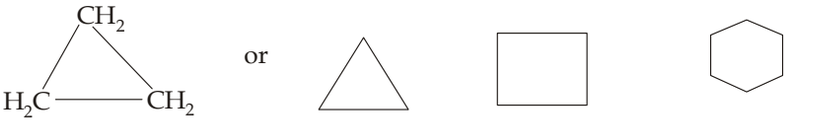
Remember that methylene is one of the most reactive and least selective species in organic chemistry.

CYCLOALKANES

Alicyclic (aliphatic cyclic) are those carbocyclic or homocyclic componds whose chemical properties are similar to that of aliphatic compounds. The saturated hydrocarbons of this family are known as **cycloalkanes** and are designated by the general formula C_nH_{2n}.

5.6 Nomenclature of Cycloalkanes

For convenience, alicyclic compounds are often shown by the topological formulation (line formula) and hence structures of these compounds are drawn as a regular polygon whose each corner depicts a CH_2 (methylene) group unless some other group is indicated. Thus saturated hydrocarbons, *i.e* cycloalkanes are also named as **polymethylenes,** the number of methylene groups is indicted by the prefix *tri- , tetra- penta-* etc. before the word methylene. According to IUPAC system, these are named as **cycloalkanes.** Thus



Common name	Trimethylene		Tetramethylene	Hexamethylene
IUPAC name	Cyclopropane		Cyclobutane	Cyclohexane

Substituents on the ring and unsaturation in the ring are named according to IUPAC formula, For example,



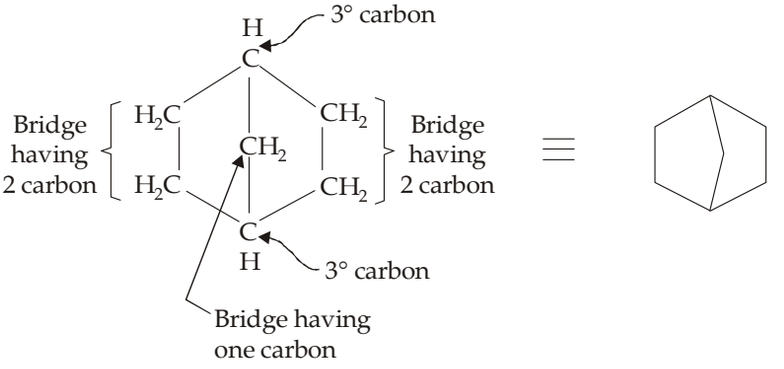
3-Chloromethylcyclohexane | 1, 2-Cyclohexanediol | 1, 3-Cyclopentadiene | 3-Cyclohexenol

Bicyclic compound are named according to following rules :

(i) The compound is named as a bicyclo alkane corresponding to the total number of carbon atoms constituting various rings (side chain carbon atoms should not be considered)

(ii) The number of carbon atoms in each of the three bridges joining the two tertiary carbon atoms, known as *bridge-heads*, is written in brackets in descending order.

Prefix bicyclo indicate two rings, the word heptane indicates that the compound has seven carbon atoms in various rings first numeral 2 indicates that there are two carbon atoms between the two bridge heads, similar is the case with the second numeral 2, while the numeral 1 indicates that there is only one carbon between two bridge heads.



Bicyclo [2.2.1] heptane or Norborane

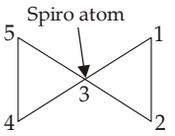
(iii) For substituted bicyclic compounds, numbering is done from a bridge head of the longest bridge, continued to the next longest bridge and then to the shortest bridge. For example,



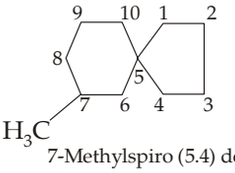
3-Methylbicyclo [3.2.1] octane | 3-Chloro-7-methylibicyclo [4.3.0] non-7-ene

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If two rings are joined by a quaternary carbon at the apex, then they are prefixed by the word *spiro*. The numbering starts from the atom next to the spiro atom and proceeds through the smaller ring first, e.g.



Spiro (2.2) pentane



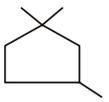
7-Methylspiro (5.4) decane

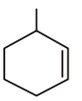
Certain polcyclic hydrocarbons having strange and wonderful shapes have been synthesized. These are generally given common names, sometimes indicating their shapes e.g. **cubane** (having shape of a cube), **basketane (having shape of a basket).**

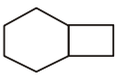
TEST YOUR UNDERSTANDING - 5.6

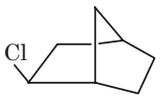
1. Draw tropological structural formula for (i) 3- propylcyclopentene, (ii) cyclopent-3-enol, (iii) bicyclo (3.2.1) octane (iv) bicyclo (3.1.0) hexane, (v) 1-methyl-2-propenylcyclopentane, (vi) cis-1-chloro-2-bromocyclobutane.

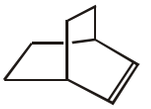
2. Write the IUPAC name of the following compounds :

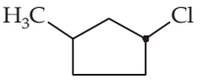
(*i*) 

(*ii*) 

(*iii*) 

(*iv*) 

(*v*) 

(*vi*) 

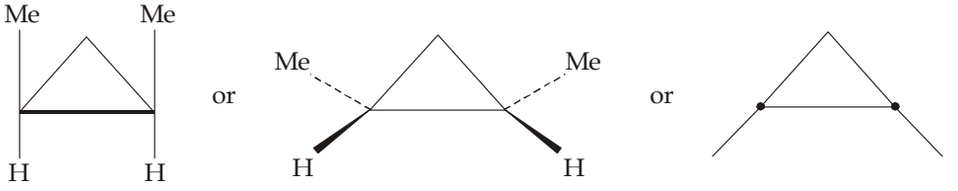
3. Use the solid-dot topological convention to indicate the *cis-trans* isomers for (i) 1,1,2-trimethylcyclopropane, (ii) 1,3-dimethylcyclobutane, (iii) 1,2,4-trimethylcyclohexane, and (iv) 1-methyl-2-propenylcyclopentane.

4. (a) Draw the structural formula and stereochemical designation of the isomeric dimethylcyclohexane.

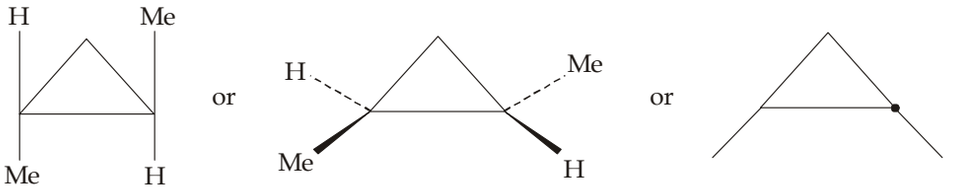
(b) Draw the structure and give the molecular formula for cyclododecane.

5.7 Geometrical Isomerism in Alicyclic Compounds

The inability of atoms in rings to rotate completely about their bonds leads to *cis-trans* (geometrical) isomerism in alicyclic compounds. A cycloalkane has two distinct faces. If two substituents point towards the same face, they are *cis*; if they point towards opposite faces, they are *trans*, e.g. 1, 2 -dimethylcyclopropane.



cis-1, 2-Dimethylcyclopropane



trans-1, 2-Dimethylcyclopropane

In topological notation, the solid dot denotes an H projecting towards the viewer.

5.8 Chemical Properties of Cycloalkanes

Chemically, cycloalkanes behave both like alkanes and alkenes.

All cycloalkanes, except cyclopropane, undergo halogenation in presence of diffused day light; cyclopropane under these conditions undergo addition reactions indicating that the three-membered ring is highly unstable. Actually, tendency of forming addition compounds decreases with increase in size of ring, i.e.

Cyclopropane > Cyclobutane > Cyclopentane > Cyclohexane

Addition reactions of cycloalkanes indicate that the stability of the ring increases as the ring becomes larger, i.e. increasing stability of the various cycloalkanes upto cyclohexane follows the order :

Cyclopropane < Cyclobutane < Cyclopentane

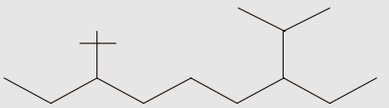
Relative stability of alicyclic compounds is due to different amount of strain in the various rings. Different amount of strain is due to deviation (d) form the normal bond angle of 109°28′

$$d = \frac{109°28' - \alpha}{2}$$

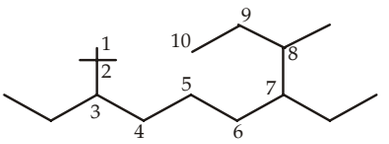
where α is the bond angle which is 60°, 90° and 108° in cyclopropane, cyclobutane and cyclopentane respectively. Thus cyclopropane has the maximum strain and thus it will be least stable while cyclopentane with less strain is the most stable among these three cycloalkanes. Strain theory, commonly known as **Baeyer strain theory**, explains the relative stability of the first three cycloalkanes.

Example 1 :

Give IUPAC name of the following alkane.



Solution :

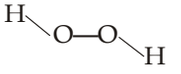


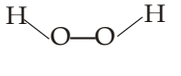
3,7-Diethyl-2,2,8-trimethyldecane

Example 2 :

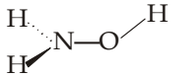
Draw the eclipsed and staggered conformations of H_2O_2, NH_2OH and CH_3OH.

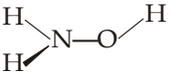
Solution :



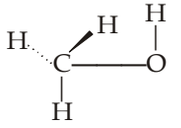


(H_2O_2)

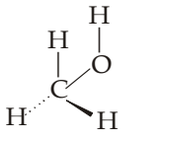




(NH_2OH)



Staggered conformations



Eclipsed conformations

(CH_3OH)

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Example 3 :

Predict the proportions of isomeric products from chlorination at room temperature of (a) isobutane, (b) 2-methylbutane, (c) 2, 3-dimethylbutane and (d) *n*-pentane. Relative reactivities of 3°, 2° and 1° H's for chlorination is 5. 0 : 3. 8 : 1.0.

Solution :

(*a*) $CH_3CH(CH_3)CH_3 \xrightarrow{Cl_2} CH_3CH(CH_2Cl)CH_3 + CH_3C(Cl)(CH_3)CH_3$

Isobutane → Isobutyl chloride (I) + *tert*-Butyl chloride (II)

Relative proportions of the two products can be calculated as below :

Product formed	Type and No. of H atoms involved	Relative reactivity	Weighted reactivity	% Yield
I	1° (9 in No.)	1	9 × 1 = 9	$\left(\frac{9}{14}\right) \times 100$ = **64%**
II	3° (1 in No.)	5.0	1 × 5 = 5	$\left(\frac{5}{14}\right) \times 100$ = **36%**

(*b*) $CH_3CH(CH_3)CH_2CH_3 \xrightarrow{Cl_2}$

2-Methylbutane (It has six 1°, three 1°C and two 2° H's)

→ 1-Chloro-3-methylbutane (I) + 1-Chloro-2-methylbutane (II) + 2-Chloro-3-methylbutane (III) + 2-Chloro-2-methylbutane (IV)

Calculation of % formed of each product.

Name of product	Type and No. of H's involved	Relative reactivity	Weighted reactivity	% Yield
I	1°′ (three in No.)	1	3 × 1 = 3	$\frac{3}{21.6} \times 100$ = **14%**
II	1° (six in No.)	1	6 × 1 = 6	$\frac{6}{21.6} \times 100$ = **28%**
III	2° (two in No.)	3.8	2 × 3.8 = 7.6	$\frac{7.6}{21.6} \times 100$ = **35%**
IV	3° (one in No.)	5.0	1 × 5 = 5	$\frac{5}{21.6} \times 100$ = **23%**

(*c*) $CH_3CH(CH_3)CH(CH_3)CH_3 \xrightarrow{Cl_2} CH_3CH(CH_3)CH(CH_3)CH_2Cl + CH_3C(Cl)(CH_3)CH(CH_3)$

2, 3-Dimethylbutane → (I) + (II)

(It has twelve 1° H's and two 3° H's)

Name of product	Type and No. of H's involved	Relative reactivity	Weighted reactivity	% Yield
I	1° (12 in No.)	1	12 × 1 = 12	$\left(\frac{12}{22}\right)$ × 100 = **55%**
II	3° (2 in No.)	5	2 × 5 = 10	$\left(\frac{10}{22}\right)$ × 100 = **45%**

(*d*) $\underset{n\text{-Pentane}}{CH_3CH_2CH_2CH_2CH_3} \xrightarrow{Cl_2} \underset{I}{CH_3CH_2CH_2CH_2CH_2Cl} + \underset{II}{CH_3CH_2CH_2\overset{\overset{Cl}{|}}{C}HCH_3} + \underset{III}{CH_3CH_2CH_2\overset{\overset{Cl}{|}}{C}HCH_2CH_3}$

(It has six 1° H's. four 2° H's and two 2° H's)

Name of product	Type and No. of H's involved	Weighted reactivity	% Yield
I	1° (Six in No.)	6 × 1 = 6	$\left(\frac{6}{28.8}\right)$ × 100 = **21%**
II	2° (Four in No.)	4 × 3.8 = 15.2	$\left(\frac{15.2}{28.8}\right)$ × 100 = **53%**
III	2°′ (Two in No.)	2 × 3.8 = 7.6	$\left(\frac{7.6}{28.8}\right)$ × 100 = **26%**

Example 4 :

Chlorine atom can react with CH_4 in the following two ways :

$$HCl + CH_3^{\cdot} \longleftarrow CH_4 + Cl^{\cdot} \longrightarrow CH_3Cl + H^{\cdot}$$

Are both steps possible? Explain your answer.

Solution :

Let us write down the two possible reactions with their ΔH and E_{act} values.

$$\underset{(104)}{Cl^{\cdot} + CH_3{-}H} \longrightarrow \underset{(103)}{H{-}Cl + CH_3^{\cdot}} \qquad \Delta H = +1 \text{ kCal}$$

$$E_{act} = 4 \text{ kCal}$$

$$\underset{(104)}{Cl^{\cdot} + CH_3{-}H} \longrightarrow \underset{(84)}{CH_3{-}Cl + H^{\cdot}} \qquad \Delta H = +20 \text{ kCal}$$

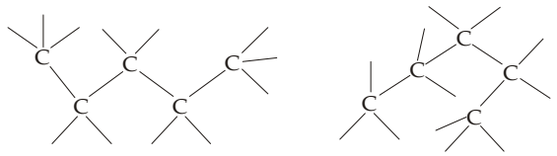
$$Eact \geq 20 \text{ kCal}$$

Thus due to difference in E_{act}, we can say that the first reaction should be the only reaction that takes place.

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EXERCISE 5.1 (MCQ - ONE option correct)

1. Following two structures represent



(a) geometrical isomers (b) chain isomers
(c) enantiomers (d) conformers

2. Which conformation of ethane is more prevalent at high temperature?
(a) staggered (b) eclipsed
(c) skew (d) all are equal.

3. Which of the following can exist in different conformations ?
(a) H_2O_2 (b) CH_3OH
(c) NH_2OH (d) All the three.

4. The possible number of conformations in CH_3OH is
(a) 1 (b) 2
(c) 8 (d) ∞

5. Which is the correct representation for the reduction of alkyl halide by Zn and dil. HCl?

(a) $R-X+Zn+H^+ \longrightarrow R-H+Zn^{2+}+X^-$

(b) $R-X+2[H] \longrightarrow R-H+HX$
(c) Both of the above
(d) None of the two

6. Boiling points of C_2H_6 and C_3H_8 ; C_2H_5OH and C_3H_7OH ; CH_3NH_2 and $C_2H_5NH_2$ generally differ by
(a) 5-10°C (b) 10-20°C
(c) 20-30°C (d) no definite range

7. The strongest known acid is
(a) H_2CrO_4 (b) HNO_3
(c) $HF–SbF_5$ (d) $FSO_3H–SbF_5$

8. Mixture of *n*-alkanes and branched alkanes can be separated by
(a) steam distillation
(b) fractional distillation
(c) urea inclusion complex formation
(d) fractional crystallisation.

9. Pick up the correct statement regarding reactivity of CH_4 and C_2H_6 towards chlorination.
(a) CH_4 is more reactive than C_2H_6
(b) C_2H_6 is more reactive than CH_4
(c) Both are equal reactive
(d) (a) and (b) are correct.

10. Halogenation of alkanes is an example of
(a) substitution (b) oxidation
(c) both (a) and (b) (d) elimination.

11. When isobutane is treated with bromine at 127°C, the product formed is
(a) a mixture of isobutyl bromide and *tert*-butyl bromide
(b) a mixture of *sec*-butyl bromide and *tert*- butyl bromide
(c) a mixture of isobutyl bromide, *sec*- butyl bromide and *tert*-butyl bromide as the major product
(d) almost 100% *tert*-butyl bromide.

12. The relative rate for chlorination of a hydrocarbon per hydrogen atom is found to be 5.0 : 3.8 : 1.0 for *tert*-, *sec*- and *pri*-hydrogen atoms. What changes can be brought about with change in temperature?
(a) The relative rates do not change at all with rise in temperature
(b) The relative rates further widen with increase in temperature
(c) The relative rates can shrink even to 1 : 1 : 1 with rise in temperature
(d) Selectivity of a reagent for its attack on a site does not change with temperature.

13. If the E_{act} for a forward reaction is given

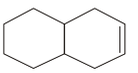
$CH_3-H+Cl^{\bullet} \longrightarrow CH_3^{\bullet}+H-Cl \quad \Delta H=+1\,kCal,\ E_{act}=4\,kCal$

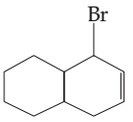
the E_{act} for the backward reaction will be
(a) 1 kcal (b) 4 kcal
(c) –4 kcal (d) 3 kcal

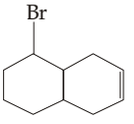
14. Which of the following statement is false?
(a) Energy of activation for an endothermic reaction can't be less than the value of ΔH
(b) Reactions involving the union of two free radicals has no E_{act}
(c) Whole of energy liberated during formation of a bond is available for the cleavage of bond
(d) Energy of activation for the cleavage of Cl–Cl bond to $Cl^{\bullet}$ is equal to the bond energy of the Cl–Cl bond.

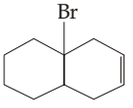
15. Reactivity of chlorine and bromine towards methane at 275°C differ by a factor of nearly
(a) 10^2 (b) 10^3
(c) 10^4 (d) $> 10^5$

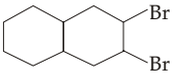
16. Predict the nature of A in the following reaction :



(a) 

(b) 

(c) 

(d) 

17. Chlorination of methane involves following steps :

(i) $Cl-Cl \longrightarrow 2Cl^{\bullet}$

(ii) $CH_4+Cl^{\bullet} \longrightarrow CH_3^{\bullet}+HCl$

(iii) $CH_3^{\bullet}+Cl_2 \longrightarrow CH_3Cl+Cl^{\bullet}$

Which of the following steps is rate determining?
(a) step (i) (b) step (ii)
(c) step (iii) (d) steps (ii) and (iii) both

18. The use of leaded petrol in engines fitted with converters is objectionable mainly because
(a) it is costlier
(b) it gives less mileage
(c) it causes more pollution
(d) its lead content poisons the catalyst used in converters

19. 20 ml of methane are burnt with 50 ml of oxygen, the volume of the gas left after cooling to room temperature will be
(a) 80 ml (b) 60 ml
(c) 30 ml (d) 20 ml

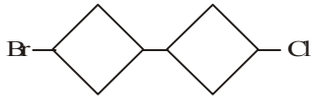
20. The most stable of meso $HOOC-\underset{\underset{Me}{|}}{CH}-\underset{\underset{Me}{|}}{CH}-COOH$ in strong basic medium is
(a) Anti form (b) Gauche form
(c) Fully eclipsed form (d) Partially eclipsed form

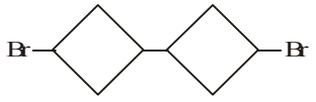
21. $CH_3-CH_2-CH_3 \xrightarrow[(3)\,z]{(1)\,x} CH_3-CH_2-CH_2-Br$

x, y, z are respectively :
(a) $Br_2/h\nu$, conc. H_2SO_4, ThO_2/Δ
(b) $Cl_2/h\nu$, alc. KOH/Δ, HBr/R_2O_2
(c) $Cl_2/h\nu$, ter-$BuO^{\ominus}/\Delta$, HBr (dark)
(d) $F_2/h\nu$, Al_2O_3/Δ, NBS

22. The reaction of 1-bromo-3-chlorocyclobutane with metallic sodiuim in dioxane under refluxed condition gives

(a) 

(b) 

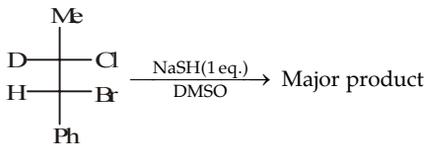
(c) 

(d) 

23. Which of the following compound has twice the number of primary hydrogens as the number of secondary hydrogens?
(a) $(CH_3)_2CClCH(CH_3)_2$
(b) $(CH_3)_3C.CH_2.C(CH_3)_3$
(c) $(C_2H_5)_2C(CH_3)CH_2CH_3$
(d) $(C_2H_5)_2CHCH_2CH_2CH(CH_3)_2$

24. Methane can be chlorinated by
(i) treating with chlorine in presence of UV light
(ii) heating with chlorine in presence of tetraethyl lead
(iii) treating with tert-butyl hypochlorite in presence of UV light
(a) only (i) method (b) only (i) and (ii) methods
(c) (i) and (iii) methods (d) (i), (ii) as well as (iii) method.

25. In the following reaction



Which option has the correct features for reaction mechanism, leaving group & stereochemistry ?
(a) $S_N2/ Cl^{\ominus}$ / inversion (b) $S_N2/ Br^{\ominus}$ / inversion
(c) $S_N1/ Br^{\ominus}$ / racemisation (d) E2/ $Br^{\ominus}$ / anti-elimination

26. An alkyl bromide, RBr of molecular weight 151 is the exclusive product of bromination of which hydrocarbon?
(a) 2, 2,-Dimethylhexane (b) 2, 2, 3-Trimethylheptane
(c) 2, 2-Dimethylpropane (d) Dodecane

27. Chlorination of an equimolar mixture of neopentane and ethane gives neopentyl chloride and ethyl chloride in the ratio of 2.3 : 1. The reactivity ratio of 1° hydrogen atoms of the neopentane and ethane will be
(a) same (b) 1.15 : 1
(c) 2 : 1 (d) 1.70 : 1

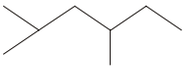
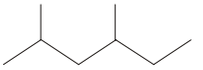
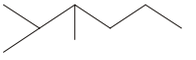
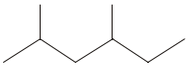
28. During bromination of methane, addition of HBr will
(a) speed up bromination
(b) slow down bromination
(c) produce no effect on bromination
(d) change the mechanism of bromination

29. When *n*-pentane and diazomethane mixture is irradiated with UV light, three compounds are formed

$\underset{\text{I}}{CH_3CH_2CH_2CH_2CH_2CH_3}$ $\underset{\text{II}}{(CH_3)_2CHCH_2CH_2CH_3}$

$\underset{\text{III}}{(C_2H_5)_2CHCH_3}$

Which of the compound given above will be formed as major product?
(a) I (b) II
(c) III (d) all equal

30. Pick up the dissimilar structure
(a) 
(b) 
(c) 
(d) 

31. The simplest chiral alkane will have how many carbon atoms?
(a) 4 (b) 6
(c) 7 (d) 8

32. The highest boiling point is expected for
(a) isooctane
(b) *n*-octane
(c) 2, 2, 3, 3-tetramethylbutane
(d) *n*-Butane

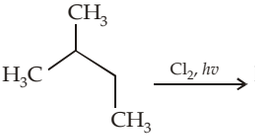
33. The reaction conditions leading to the best yield of C_2H_5Cl are
(a) C_2H_6 (excess) + $Cl_2 \xrightarrow{\text{UV light}}$
(b) $C_2H_6 + Cl_2 \xrightarrow[\text{room temp.}]{\text{dark}}$
(c) $C_2H_6 + Cl_2$ (excess) $\xrightarrow{\text{UV light}}$
(d) $C_2H_6 + Cl_2 \xrightarrow{\text{dark, heat}}$

34. Which of the following will have least hindered rotation about C–C bond?
(a) Ethane (b) Ethylene
(c) Acetylene (d) Hexachloroethane

35. Isomers which can be interconverted through rotation around a single bond are
(a) enantiomers (b) diastereomers
(c) conformers (d) positional isomers

36. When cyclohexane is poured on water, if floats because
(a) cyclohexane is in boat form
(b) cyclohexane is in chair form
(c) cyclohexane is in crown form
(d) cyclohexane is less dense than water.

37. Photobromination of 2-methylpropane gives a mixture of 1-bromo-2-methylpropane and 2-bromo-2-methylpropane in the ratio of 9 : 1. This can be explained on the basis that
(a) bromine is highly reactive
(b) reactivity order for 3°, 2° and 1° hydrogen during bromination is 5.0 : 3.8 : 1 respectively
(c) reactivity of bromine is governed by probability factor
(d) the above statement is false.

38.  N (isomeric products);

$C_5H_{11}Cl \xrightarrow{\text{fractional distillation}}$ M (isomeric products)

Identify N and M
(a) 6, 4 (b) 6, 6
(c) 4, 4 (d) 3, 3

39. When fluorine reacts with 2-methylpropane in presence of light gives 14% tert-butyl fluoride and 86% isobutylfluoride. What will be the ratio of relative reactivity of a tertiary hydrogen to primary hydrogen ?
(a) 0.682 (b) 1.46
(c) 6.14 (d) 0.813

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EXERCISE 5.2 (MCQ 1 or >1 option correct, Passage based, Matching, A/R)

DIRECTIONS for Q. 1 to Q. 12 : Multiple choice questions with one or more than one correct option(s).

1. Which of the following statements are not correct for alkanes?
(a) All C – H and C – C bonds have a length of 1.112Å and 1.54Å respectively
(b) All bond angles are tetrahedral having a value of 109.5'.
(c) The C–C chain is linear and not zigzag
(d) All alkanes exhibit isomerism

2. Which of the following reactions can be used to prepare methane?
(a) Clemmensen reduction
(b) Wurtz reaction
(c) Catalytic hydrogenation of methyl iodine
(d) Reduction of methyl idodide by using a zinc copper couple

3. Methane is obtained when
(a) sodium acetate is heated with soda lime
(b) iodomethane is reduced
(c) aluminium carbide reacts with water
(d) potassium acetate is electrolysed

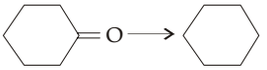
4. Which of the following will give three monobromo derivatives?
(a) $CH_3CH_2CH_2CH_2CH_2CH_3$
(b) $CH_3CH_2CH_2-CH(CH_3)CH_3$
(c) $CH_3-CH_2-C(CH_3)_2CH_3$
(d) $CH_3CH(CH_3)CH(CH_3)CH_3$

5. Alkenes undergo
(a) substitution reactions (b) addition reactions
(c) ozonolysis (d) none of these

6. Methane can be prepared by
(a) Wurtz reaction (b) Decarboxylation
(c) Hydrogenation reaction
(d) Alkyl magnesium bromide

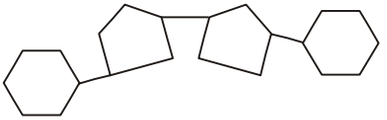
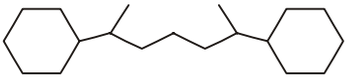
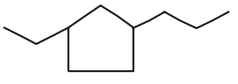
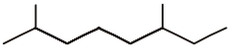
7. Only two isomeric monochloro derivatives are possible for :
(a) n-butane (b) 2, 4-dimethylpentane
(c) benzene (d) 2-methylpropane

8. Which is/are true statements/reactions?
(a) $Al_4C_3 + H_2O \longrightarrow CH_4$ (b) $CaC_2 + H_2O \longrightarrow C_2H_2$
(c) $Mg_2C_3 + H_2O \longrightarrow CH_3C \equiv CH$
(d) Holme signal uses mixture of Ca_3P_2 and CaC_2

9. 
This change can be carried out using :
(a) NH_2NH_2, glycol/OH^- (b) Sn(Hg)/conc. HCl
(c) P/HI (d) NH_3/$LiAlH_4$

10. CH_4 gas is also called/content of :
(a) CNG (b) Marsh gas
(c) water gas (d) producer gas

11. Methane will be produced in which of the following reaction ?
(a) $Be_2C \xrightarrow{H_2O}$ (b) $CH_3OH \xrightarrow{LAH}$
(c) $CH_3-Cl \xrightarrow[EtOH]{Na}$ (d) $Al_4C_3 \xrightarrow{H_2O}$

12. Compound which can not be synthesized by Wurtz reaction using one type of halide only ?
(a) 
(b) 
(c) 
(d) 

DIRECTIONS for Q. 13 to Q. 23 : Read the following passages and answer the questions that follows :

PASSAGE 1

At certain temperature, the % of monochlorinated products obtained for the following reactions are given :

$$CH_3-CH_2-CH_2-CH_3 \xrightarrow{Cl_2/h\nu}$$

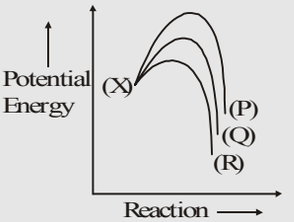
$$\underset{(28.30\%)}{CH_3-CH_2-CH_2-CH_2-Cl} + \underset{\underset{Cl}{|}\ (71.70\%)}{CH_3-CH-CH_2-CH_3}$$

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3 \xrightarrow{Cl_2/h\nu} CH_3-\underset{\underset{Cl}{|}\ (33.33\%)}{\overset{\overset{CH_3}{|}}{C}}-CH_3 + CH_3-\underset{\underset{CH_3}{|}\ (66.66\%)}{CH}-CH_2-Cl$$

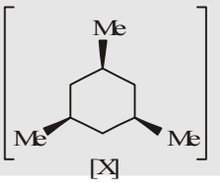
For all questions assume reactivity ratio to be same as in the above reactions.
The propagation step of monochlorination of alkane involves formation of the radical intermediate.

$$R-H + \dot{Cl} \longrightarrow \dot{R} + H-Cl$$

The energy profile for the formation of free radical is described as



for the compound (X)



[X]

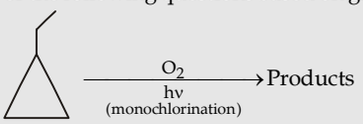
13. For the compound (X), the following statement is true for the monochlorination via intermediate (Q)
(a) 2-different products both optically active.
(b) 2-different products one active and other inactive.
(c) 2-different products and are distereomers of each other.
(d) Only one product is obtained

14. Which of the following is incorrect for the monochlorination of (X)?
(a) Via intermediate (P), only one product is obtained
(b) Via intermediate (R), two products are obtained which are enantiomers
(c) All products obtained are optically inactive
(d) The % distribution of product formed via intermediate (P) is 19.86%

15. Excluding stereochemistry which of the following is false for all the products obtained by monochlorination of (X).
(a) Product obtained by the most stable free radical intermediate is the major product of the reaction.
(b) 50.33% of the product is formed by intermediate Q formed in the reaction.
(c) Three different types of products are obtained.
(d) All three types of products are having prochiral carbon atom.

PASSAGE 2

Answer the following questions based on given reaction.



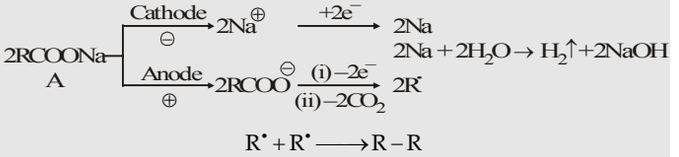
16. Total number of theoretically products (including stereo) are
(a) 4 (b) 5
(c) 8 (d) 10

17. How many products are resolvable ?
(a) 2 (b) 4
(c) 5 (d) 6

18. How many fractions are present on fractional distillation ?
(a) 4 (b) 5
(c) 6 (d) 8

PASSAGE 3

Kolbe's electrolysis can be represented as



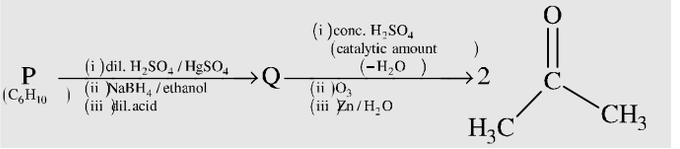
19. During the electrolysis of sodium ethanoate, the gas liberated at cathode is :
(a) H_2 (b) CO_2
(c) CH_4 (d) $CH_3 - CH_3$

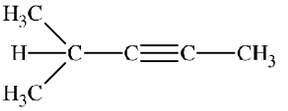
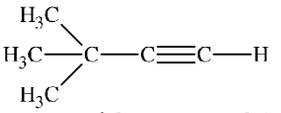
20. During the electrolysis pH of electrolyte ..... progressively
(a) increases (b) decreases
(c) remains same (d) can not be predicted

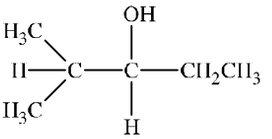
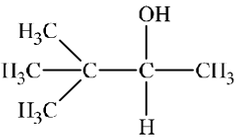
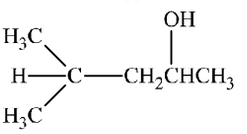
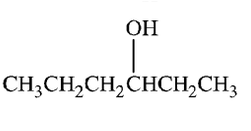
21. In Kolbe's electrolysis, if A is sodium propanoate, then hydrocarbon formed is :
(a) $CH_3 - CH_3$ (b) $CH_2 = CH_2$
(c) $CH_3 - CH_2 - CH_2 - CH_3$ (d) A mixture of 1, 2 and 3

PASSAGE 4

An acyclic hydrocarbon **P**, having molecular formula C_6H_{10}, gave acetone as the only organic product through the following sequence of reaction, in which **Q** is an intermediate organic compound.



22. The structure of compound **P** is
(a) CH CH CH CH C C H
(b) H CH C C C CH CH
(c) 
(d) 

23. The structure of the compound **Q** is
(a) 
(b) 
(c) 
(d) $CH_3CH_2CH_2CHCH_2CH_3$ 

Instructions for Q. 24 & 26 : Following questions are Multiple Matching type Questions :

24.

	Column I	*Column II*
(A)	CH_3CH_3	(a) Wurtz reaction
(B)	$CH_3CH_2CH_3$	(b) Frankland reaction
(C)	$(CH_3)_3CCH_3$	(c) Corey House reaction

25.

	Column I	*Column II*
(A)	Lowest alkane	(a) CNG
(B)	A higher straight chain alkene	(b) Possess lowest octane number
(C)	Gasoline	(c) Aromatic hydrocarbons
(D)	Sodium plumbite	(d) Doctor sweetening solution

26.

	Column-I	**Column-II**
(A)	Decarboxylation of RCOONa	(a) Methane
(B)	Wurtz reaction	(b) Ethyne
(C)	Corey House reaction	(c) *n*-Butane
(D)	Dehydrohalogenation	(d) 2-Methylpropane

Instructions for Q. 27 to 33 : Following questions are Assertion and Reasoning Type Questions :
Note : Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement -1 is True, Statement-2 is False.
(d) Statement -1 is False, Statement-2 is True.
(e) Statement -1 is False, Statement-2 is False.

27. **Statement 1 :** Cyclopropane has the highest heat of combustion per methylene group
Statement 2 : Its potential energy is raised by angle strain.

28. **Statement 1 :** Iodination of alkane is slow and reversible in nature
Statement 2 : Iodination of alkane is performed in the presence of strong an oxidising agent like HIO_3, which consumes the by-product HI and recycles into reactants I_2.

29. **Statement 1 :** When n-butane is heated in the presence of $AlCl_3$/HCl it will be converted into propane
Statement 2 : In the presence of $AlCl_3$/HCl if any alkane having more than four carbon is heated than isomerisation is held to give isomer of reactant alkane.

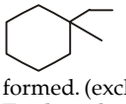
30. **Statement 1 :** Branched alkanes have lower boiling point than their unbranched isomers.
Statement 2 : Branched alkanes has relatively small surface area, so less London's dispersion force act among molecules.

31. **Statement 1 :** Alkanes float on the surface of water.
Statement 2 : Density of alkanes is in the range of 0.6 – 0.9 g/ml, which is lower than water.

32. **Statement 1 :** 2-chlorobutane on dehydrochlorination gives 2-butene (cis + trans) as a major product rather than 1-butene
Statement 2 : 2-Butene is thermodynamically more stable than 1-butane.

33. **Statement 1 :** 2-Bromobutane on reaction with sodium ethoxide in ethanol gives 1-butene as a major product.
Statement 2 : 1-Butene is more stable than 2 -butene.

Instructions for Q. 34 to 41 : Following questions are Integer Type Questions :

34.  $\xrightarrow[h\nu]{Cl_2}$ (A) number of monochloro derivatives formed. (excluding stereoisomers)

35. Total number of trichloroderivatives of the compound (excluding stereoisomers) will be  .

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36. Number of monochloro derivatives (excluding stereoisomers), dichloro derivatives and trichloro derivatives of cyclopentane are n_1, n_2 and n_3 then $(n_1 + n_2)/n_3$ is equal to

37. How many isomers (including geometrical and optical) are possible for bromochlorocyclobutane?

38. How many stereoisomers are possible for dichlorocyclobutane?

39. How many enantiomeric pairs are possible in bromochlorocyclopentane?

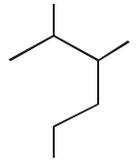
70. How many *meso* isomers are possible in diiodcyclopentane?

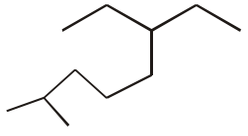
41. On conversion into the Grignard reagent followed by treatment with water, how many alkyl bromides would yield isopentane?

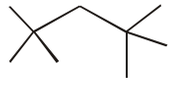
EXERCISE 5.3 (Subjective Problems)

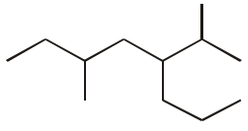
1. Write IUPAC name of the following compounds :

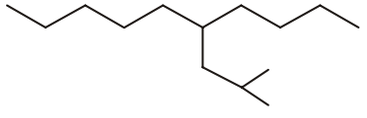
(*a*) 

(*b*) 

(c) 

(d) 

(e) 

(f) 

2. Draw line formula for
(i) 2, 2, 3, 3-Tetramethylpentane
(ii) 2-Chloro-2, 4, 4-trimethylheptane
(iii) 5-(1', 2'-dimethylpropyl)-6-methyldodecane.

3. Write the structural formula and give IUPAC names for the possible monobromo derivatives of isopentane.

4. Give the structure and IUPAC name of alkane or alkanes having molecular weight 86.

5. Derive the structural formula and IUPAC names for all dichloro derivatives of propane.

6. Arrange the following alkanes in order of their increasing boiling points :
(i) *n*-Pentane (ii) *n*-Heptane
(iii) 2-Methylhexane (iv) 2-Methylheptane
(v) 3, 3-Dimethylpentane

7. Write equations for the preparation of *n*-butane from
(i) *n*-butyl bromide (ii) *sec*-butyl bromide
(iii) ethyl chloride

8. Give the simplest and easiest possible way for synthesising
(i) monodeuteratedethane
(ii) 1, 2-dideuteratedethane
(iii) 1, 1-dideuteratedethane

9. How will you carry out following synthesis in the minimum steps?
(i) propane to 2, 3-dimethylbutane
(ii) propane to 2-methylpentane
(iii) propane to neopentane

10. 2-Methylpropane can be synthesised from three-carbon compounds by two alternate ways, which of the two is superior.

11. Arrange the following compounds in order of decreasing ease of abstraction of hydrogen atom :
(a) $CH_2 = CH_2$ (b) $CH_2 = CHCH_3$
(c) $C_6H_5CH_3$

12. Name the first four simplest alkanes that give a single product on methylene insertion.

13. Predict the percentage of isomers formed during monochlorination of
(a) 2, 2-dimethylbutane
(b) isohexane and
(c) 2, 2, 4-trimethylpentane
Relative order of reactivity is 3° (5.0), 2° (3.8) and 1° (1.0)

14. Chlorination of propane gives four products (A, B, C and D) of the formula $C_3H_6Cl_2$. A, B, C and D on further chlorination gives one, two, three and three trichloro derivatives respectively. Assign structures to A, B, C and D.

15. Explain the following :
(a) Alkanes are inert
(b) Pyrolysis of alkanes leads to cleavage of C–C bonds rather than C–H bonds
(c) Although combustion of alkanes is a strongly exothermic process, it occurs only at high temperatures.

16. Identify A to G

(i) $CH_3CH_2CH_2CH_2Br + [(CH_3)_3C-]_2CuLi \longrightarrow A$

(ii) $CH_3.CHBrCH_3 \xrightarrow{Cl^\bullet} B \longrightarrow C \xrightarrow{Cl_2} D$

(iii) $RCl \underset{(E)}{\xrightarrow[ether]{Li}} F \xrightarrow{H_2O} G$, $F \xrightarrow{Na}$ 2,7-Dimethyloctane

17. Draw structural formula of
(i) Cyclopentylacetylene
(ii) 3-Chloro-1, 1-dimethylcycloheptane
(ii) *cis*-1-Bromo-2-methylcyclopentane
(iv) Bicyclo [2.2.1] hepta-2, 5-diene
(v) 1-Chlorobicyclo [2.2.2] octane

18. Two isomeric hydrocarbons, A and B have the molecular formula C_6H_{12}. These do not react with hydrogen but react with chlorine in sunlight to give the monochloro derivatives of the formula $C_6H_{11}Cl$. Compound A gives only one product, while B gives several different products. Assign structures to A and B.

19. A rocket is filled with a petroleum fuel of composition *n*-$C_{14}H_{30}$ and density 0.764 g/mL and liquid oxygen.
(a) Determine the weight of oxygen required for complete combustion of every litre of the petroleum fuel.
(b) Determine the amount of heat evolved in the combustion of one litre of the fuel, assuming that each $-CH_2-$ and each $-CH_3$ group evolve 157 kcal/mol and 186 kcal/mol respectively.
(c) Determine the weight of hydrogen required for producing same heat as one litre of petroleum fuel and the necessary oxygen. Given $\Delta H_{H_2} = -104$ kcal/mol. Assuming that formation of H_2 is the only reaction that takes place in the rocket fuel.

20. A solution containing 4.12 mg of an unknown alcohol (ROH) is added to a solution of methylmagnesium iodide and 1.56 mL of a gas were collected at STP. Determine the molecular weight of ROH.

21. 1.79 mg of an alcohol of mol. wt. 90 gave 1.34 mL of the gas measured at NTP. Determine the number of –OH groups in the compound.

SOLUTIONS

EXERCISE 5.1

1	(d)	**6**	(c)	**11**	(d)	**16**	(c)	**21**	(b)	**26**	(c)	**31**	(c)	**36**	(d)
2	(b)	**7**	(d)	**12**	(c)	**17**	(b)	**22**	(d)	**27**	(b)	**32**	(b)	**37**	(d)
3	(d)	**8**	(c)	**13**	(d)	**18**	(d)	**23**	(c)	**28**	(b)	**33**	(a)	**38**	(a)
4	(d)	**9**	(b)	**14**	(c)	**19**	(c)	**24**	(d)	**29**	(a)	**34**	(a)	**39**	(b)
5	(a)	**10**	(c)	**15**	(d)	**20**	(a)	**25**	(b)	**30**	(c)	**35**	(c)		

1. The two structures are the zig zag structures of a compound having five carbon atoms in a straight chain.

2. The eclipsed-like conformations become more prevalent with increase in temperature.

3. A compound can exist in different conformations only when it has three consecutive single bonds.

4. Due to restricted rotation, about a single bond, infinite number of arrangements are possible ; the two extreme cases are known as eclipsed and staggered.

5. Reduction of alkyl halides by Zn and HCl takes place by electron-transfer mechanism and not through nascent hydrogen, as believed earlier.

6. Boiling points of two lower homologues generally differ by 20–30°C.

7. FSO_3H—SbF_5, also known as magic acid, is the strongest known acid. It easily reacts even with alkanes forming a variety of products.

8. *n*-Alkanes and branched alkanes have close boiling points, hence they can't be separated by fractional distillation. If a mixture of isomeric alkanes is treated with urea preferably in presence of a little CH_3OH, only *n*-alkanes form urea inclusion complexes which crystallise out leaving behind branched chain alkanes. These complexes are decomposed by treating with water when urea dissolves leaving behind *n*-alkane.

9. Hydrogen atoms of methane, fall into a special class, and are less reactive than the 1° hydrogen atoms of other alkanes.

10. Halogenation (a common substitution reaction), is an oxidative process in which C has lost its shared electrons to some extent to the newly introduced halogen (C—X).

11. Bromine is less reactive than chlorine and hence more selective, leading to the formation of the product corresponding to 3° free radical, *i.e. tert*-butyl bromide.

12. At very high temperatures, virtually every collision has enough energy for abstraction of even 1° hydrogens. It is generally true that as the temperature is raised a given reagent becomes less selective in the position of its attack ; conversely, as the temperature is lowered it becomes more selective.

13. $E_{act\ (backward)} = E_{act\ (forward)} - \Delta H_{forward} = 4 - 1 = 3$ kcal.

14. Bond-breaking and bond-making are not perfectly synchronized, and thus the energy liberated by the one process is not completely available for the other.

15. Chlorine atoms are 375000 times as reactive as bromine atoms towards methane under given conditions. This difference is due to difference in E_{act} which is 4 kcal for chlorine and 18 kcal for bromine.

16. Bromine is less reactive and hence highly selective leading to the replacement of *tert*-hydrogen atom hence the product A and B will not formed. In presence of light substitution reaction takes place rather than addition.

17. Of the two propagating steps, E_{act} of the first step is high and hence it is difficult to accomplish.

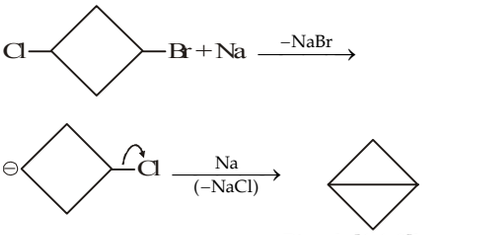
18. Lead poisons the platinum used in converters to oxidise pollutants like hydrocarbons, carbon monoxide and nitrogen oxides and thus these pollutants will be released as such in the atmosphere causing pollution.

20. (a) In strong basic medium $^{\ominus}OOC-\underset{Me}{\underset{|}{CH}}-\underset{Me}{\underset{|}{CH}}-COO^{\ominus}$ will be stable in its anti form to minimise repulsion.

21. (b) $CH_3-CH_2-CH_3 \longrightarrow CH_3-\underset{Cl}{\underset{|}{CH}}-CH_3 \xrightarrow[alc.\Delta KOH]{-HCl}$

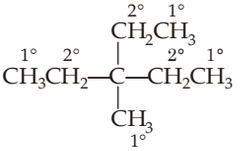
$$CH_3-CH=CH_2 \xrightarrow{HBr,.R_2O_2} CH_3-CH_2-CH_2-Br$$

22. (d) Since bromides are more reactive than chlorides in Wurtz reaction, therefore, Wurtz reaction occurs on the side of Br atom i.e.,



Bicyclo[1.1.0]butane

23.



No. of 1° H's = 12
No. of 2° H's = 6

24. Chlorination of methane is a free radical reaction and hence it can be initiated by any factor that can produce chlorine free radical.

(*a*)
$$Cl—Cl \xrightarrow{UV} Cl^{\bullet} + Cl^{\bullet}$$
$$CH_4 + Cl^{\bullet} \longrightarrow CH_3^{\bullet} + HCl$$
$$CH_3^{\bullet} + Cl—Cl \longrightarrow CH_3Cl + Cl^{\bullet}$$

(*b*)
$$(C_2H_5)_4Pb \xrightarrow{heat} 4CH_3CH_2^{\bullet} + Pb^{\bullet}$$
$$CH_3CH_2^{\bullet} + Cl—Cl \longrightarrow CH_3CH_2Cl + Cl^{\bullet}$$
$$CH_4 + Cl^{\bullet} \longrightarrow CH_3^{\bullet} + HCl$$
$$CH_3^{\bullet} + Cl—Cl \longrightarrow CH_3Cl + Cl^{\bullet}$$

(*c*)
$$(CH_3)_3COCl \xrightarrow{UV} (CH_3)_3CO^{\bullet} + Cl^{\bullet}$$
$$CH_4 + (CH_3)_3CO^{\bullet} \longrightarrow CH_3^{\bullet} + (CH_3)_3COH$$
$$CH_3^{\bullet} + (CH_3)_3COCl \longrightarrow CH_3Cl + (CH_3)_3CO^{\bullet}$$

26. An alkyl bromide (RBr) can be the exclusive bromination product of a hydrocarbon whose all hydrogen atoms are equivalent. The molecular weight of the alkyl group (R–) is 151 – 80 = 71 and thus alkane should have molecular weight of 71 + 1 = 72, thus it should be a pentane, which is found to be neopentane, $(CH_3)_4C$, whose all 12 hydrogen atoms are identical.

27. Neopentane, $(CH_3)_4C$ has 12 primary hydrogen atoms, while ethane, CH_3CH_3 has 6. Further the ratio of products formed is 2.3 : 1 ; thus the reactivity ratio should be 1.15 : 1.

28. Addition of HBr, during bromination of methane will produce following reaction, which is

$$CH_3^{\bullet} + HBr \longrightarrow CH_4 + Br^{\bullet}$$

the reverse of one of the chain-carrying steps, hence, consequently bromination will slow down.

29. Since methylene is highly reactive, here probability factor is important. Thus, *n*-hexane will be the major product because *n*-pentane has six 1° hydrogen atoms.

$$\overset{1^\circ}{C}H_3\overset{2^\circ}{C}H_2\overset{2^\circ}{C}H_2\overset{2^\circ}{C}H_2\overset{1^\circ}{C}H_3 \xrightarrow{:CH_2} HCH_2CH_2CH_2CH_2CH_2CH_3$$

30. Note that all compounds are derivatives of hexane, and in (*a*), (*b*) and (*d*) the two methyl groups are separated by one —CH_2— group, while in (*c*) the two methyl groups are present on adjacent carbon atoms.

31. In a chiral alkane, the four substituents on C should be different, so the simplest alkane will have H, CH_3, C_2H_5 and C_3H_7 as substituents.

32. Branching decreases surface area of the molecule. Thus among normal and branched chain isomers, normal alkane will have highest boiling point.

33. When equimolar amounts of C_2H_6 and Cl_2 react, a mixture of all possible mono- and poly-chloro products will be formed. However, if excess of C_2H_6 is used, the yield of C_2H_5Cl is greatly improved since the chances of a Cl. colliding with C_2H_6 molecule rather than with a chlorinated derivative are enhanced.

34. Ethylene has restricted rotation, acetylene no rotation, hexachloroethane has more rotation than ethylene but less than ethane because of greater size of the substituent (chlorine) than in ethane (substituent is H).

35. Conformers are isomers obtained due to rotation around C—C single bond.

36. A substance lighter than water will float on water.

37. Br. is less reactive, hence it is more selective, and therefore 2-bromo-2-methylpropane will be major product. The relative ratio of the products 1-bromo-2-methylpropane and 2-bromo-2-methylpropane will be 0.56 : 99.4.

39. (b) Suppose relative reactivity for 3° H is x
and suppose relative reactivity for 1° H is y.
So with the given information

$$\frac{9y}{9y+x} = 0.86 \qquad \frac{x}{9y+x} = 0.14$$

$$\text{So } \frac{9y}{0.86} = \frac{x}{0.14}$$

$$\text{Hence, } \frac{x}{y} = \frac{9\times 0.14}{0.86} = 1.46$$

EXERCISE 5.2

>1 CORRECT OPTION	**1**	(c, d)	**2**	(c, d)	**3**	(a, b, c)	**4**	(a, c)
	5	(a, b, c)	**6**	(b, d)	**7**	(a, d)	**8**	(a, b, c, d)
	9	(a, b, c)	**10**	(a, b)	**11**	(a, c, d)	**12**	(b, c, b)
PASSAGE 1	**13**	(c)	**14**	(b)	**15**	(a)		
PASSAGE 2	**16**	(c)	**17**	(d)	**18**	(b)		
PASSAGE 3	**19**	(a)	**20**	(a)	**21**	(d)		
PASSAGE 4	**22**	(d)	**23**	(b)				
MATCHING TYPE QUESTIONS	**24**	(A) - a, b ; (B) - a, b ; (C) -c						
	25	(A) - a ; (B) - b ; (C) - c, d; (D) - d						
	26	(A) - a,c,d; (B) - c,d; (C) - d; (D)-b						
A/R	**27**	(a)	**28**	(b)	**29**	(d)	**30**	(a)
	31	(a)	**32**	(a)	**33**	(e)		
INTEGER	**34**	**6**	**35**	**4**	**36**	**1**	**37**	**7**
	38	**5**	**39**	**4**	**40**	**2**	**41**	**4**

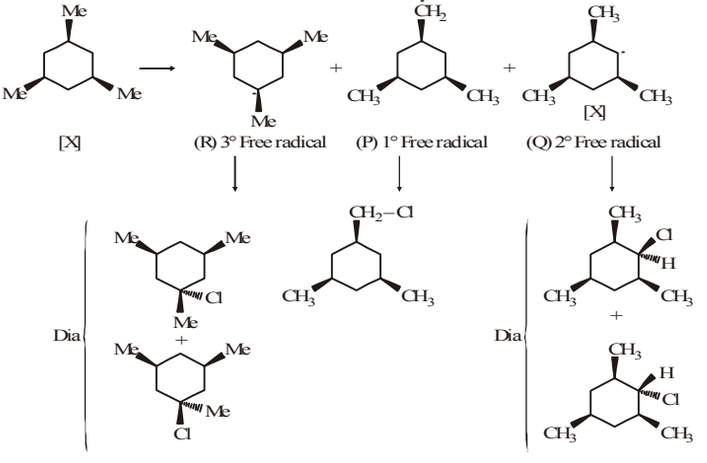
11. (a, c, d) $Be_2C + 4H_2O \rightarrow CH_4 + 2Be(OH)_2$

$$CH_3 - Cl \xrightarrow[EtOH]{Na} CH_4$$

$$Al_4C_3 + 12H_2O \rightarrow 3CH_4 + 4Al(OH)_3$$

12. (b, c, d)

Sol. (13-15)



$9 \times 1 = 9$ 1° product $= \frac{9}{45.3} \times 100 = 19.86\%$

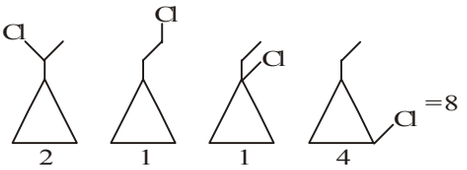
$6 \times 3.8 = 22.8$ 2° product $= \frac{22.8}{45.3} \times 100 = 50.33\%$

$3 \times 4.5 = 13.5$ 3° product $= \frac{13.5}{45.3} \times 100 = 29.80\%$

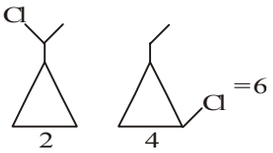
45.3

13. (c) **14.** (b) **15.** (a)

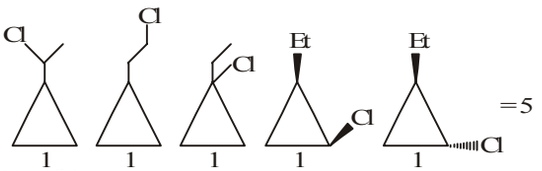
16. (c)



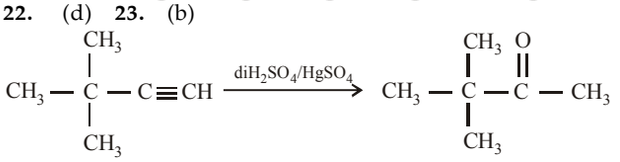
17. (d)



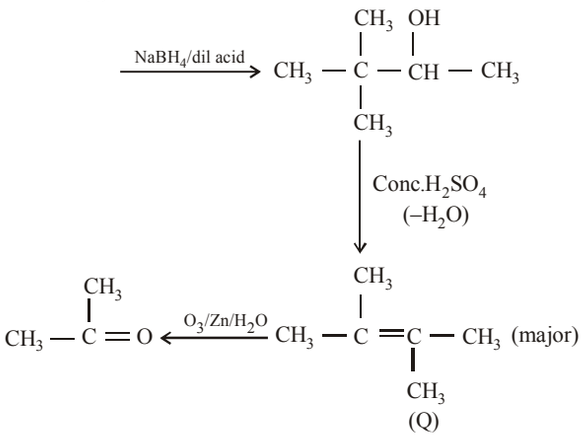
18. (b)



22. (d) **23.** (b)



(P)

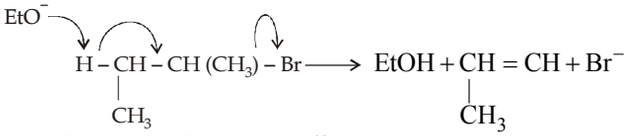


(Q)

26. A - (a, c, d); B - (c, d); C - (d); D - (b)

29. When n-butane is heated in the presence of $AlCl_3/HCl$ it will be converted into isobutane. In the presence of $AlCl_3/HCl$ if any alkane having more than four carbon is heated than isomerisation is held to give isomer of reactant alkane.

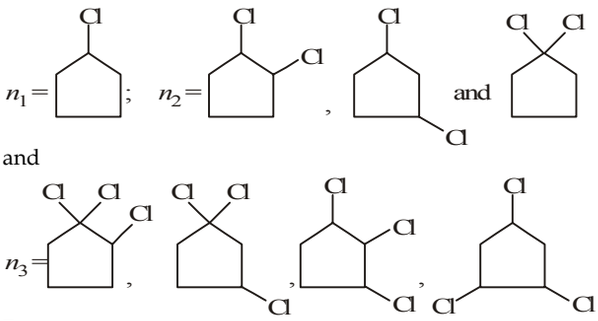
33. 2-bromobutane on reaction with sodium ethoxide in ethanol gives 2-butene as a major product.



This is according to saytzeff's rule i.e. the predominant product is the most substituted alkene, i.e. are carrying the largest number of alkyl substituents of hydrogen is eliminated preferentially from the carbon atom joined to the least number of hydrogen atoms.

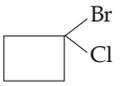
2-butene is more stable than 1-butene due to presence of large number of hyperconjugating structures in 2-butene.

36. 1

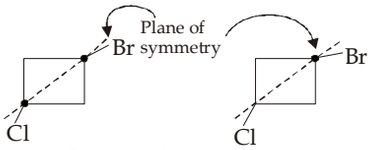


37. 7

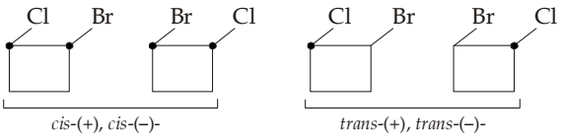
Seven possible isomers are



1-Bromo-1-chlorocyclobutane
(Stereoisomerism not possible)



1-Bromo-3-chlorocyclobutane
(Both are optically inactive)

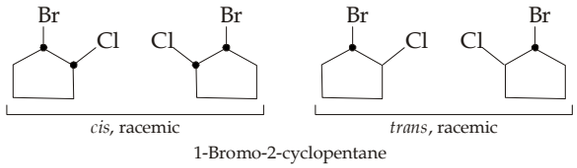


1-Bromo-2-chlorocyclobutane

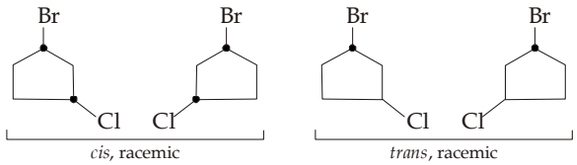
38. 5

1, 3-Dichlorocyclobutane can exist in *cis* and *trans* forms. *trans*-1, 2-Dichlorocyclobutane can exist in (+)– and (–)-forms. However, *cis*-1, 2-Dichlorocyclobutane has a plane of symmetry and hence it can exist as *meso* isomer.

39. 4

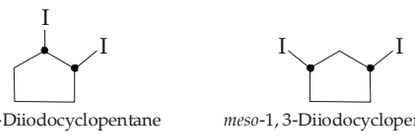


1-Bromo-2-cyclopentane



1-Bromo-3-cyclopentane

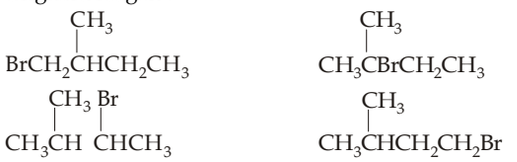
40. 2



meso-1, 2-Diiodocyclopentane *meso*-1, 3-Diiodocyclopentane

41. 4

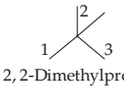
All alkyl bromides having carbon skeleton of isopentane (2-methylbutane $(CH_3)_2CHCH_2CH_3$) will give isopentane via Grignard reagent.



EBD_7088

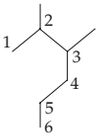
EXERCISE 5.3

1. (*a*)



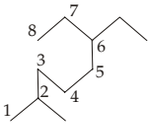
2, 2-Dimethylpropane

(*b*)



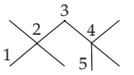
2, 3-Dimethylhexane

(*c*)



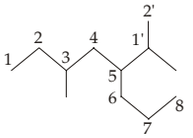
6-Ethyl-2-methyloctane

(*d*)



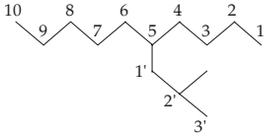
2, 2, 4, 4-Tetramethylpentane

(*e*)



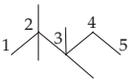
5-(1'-methylethyl)-3-methyloctane

(*f*)

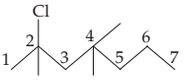


5-(2'-methylpropyl) decane

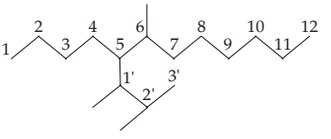
2. (*i*)



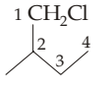
(*ii*)



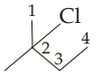
(*iii*)



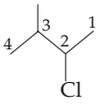
3. Isopentane has four types of hydrogen atoms, so four monobromo derivatives are possible.



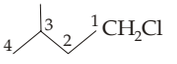
1-Chloro-2-methyl-butane



2-Chloro-2-methyl-butane



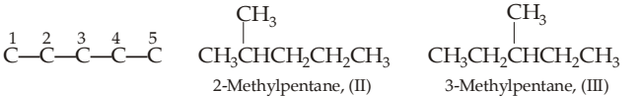
2-Chloro-3-methyl-butane



1-Chloro-3-methyl-butane

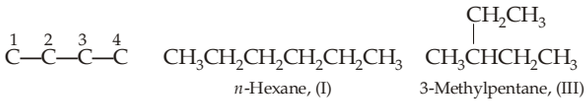
4. An alkane (C_nH_{2n+2}) of molecular weight 86 should have molecular formula of C_6H_{14} ; so one suitable alkane should be *n*-hexane, $CH_3CH_2CH_2CH_2CH_2CH_3$ (I), having a chain of six carbon atoms.

(*i*) Now let us take a chain of 5 carbon atoms, then the CH_3 group may be placed either on C^2 or C^3 to give two different monomethylpentanes.



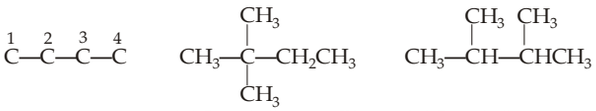
2-Methylpentane, (II) 3-Methylpentane, (III)

(*ii*) Now let us take a chain of 4 carbon atoms, then the two remaining carbon atoms can be present either as a CH_3CH_2 or two CH_3 groups. However, introduction of CH_3CH_2 on any of the four carbon atoms will give either of the above three isomer, *i.e.* no new alkane will be formed.



n-Hexane, (I) 3-Methylpentane, (III)

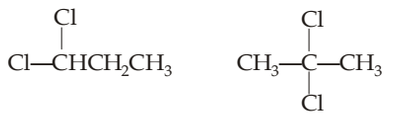
Hence the two carbon atoms should be present as two CH_3 groups ; and that too not on the end carbon atoms. Hence two CH_3 groups can be attached exclusively on C^2 or C^3 to give one dimethylbutane or one CH_3 group on C^2 and other on C^3 to give another dimethylbutane.



2, 2-Dimethylbutane, (IV) 2, 3-Dimethylbutane, (V)

So, on the whole C_6H_{14} can exist in five isomeric forms. Similarly, we can derive the possible number of isomers of any alkane.

5. Two chlorine can be placed on the same carbon atom and also on different carbon atoms, the possible different structures obtained are



1, 1-Dichloropropane 2, 2-Dichloropropane



1, 2-Dichloropropane 1, 3-Dichloropropane

6. Order of increasing boiling points :

$$\underset{(C_5)}{\text{n-Pentane}} < \underset{(C_7)}{\text{3, 3-Dimethylpentane}} < \underset{(C_7)}{\text{2-Methylhexane}} < \underset{(C_7)}{\text{n-Heptane}} < \underset{(C_8)}{\text{2-Methylheptane}}$$

n-Pentane has lowest boiling point because it has least number of carbon atoms, while 2-methylheptane has maximum number of carbon atoms (C_8), so it should have highest boiling point. Of the three hydrocarbons, each having seven carbon atoms, *n*-heptane has the longest chain and thus has the highest boiling point, 3, 3-dimethylpentane is more branched, hence has the smallest surface area and so the lowest boiling point among the three C_7 compounds.

7. (*i*) $\underset{\text{n-Butyl bromide}}{CH_3CH_2CH_2CH_2Br} \xrightarrow{Mg} CH_3CH_2CH_2CH_2MgBr$

$$\xrightarrow{H_2O} \underset{\text{n-Butane}}{CH_3CH_2CH_2CH_3}$$

(*ii*) $CH_3CH_2\underset{\text{sec-Butyl bromide}}{\underset{|}{\overset{CH_3}{|}}CHBr} \xrightarrow{Mg} CH_3CH_2\overset{CH_3}{\underset{|}{CH}}MgBr \xrightarrow{H_2O} \underset{n\text{-Butane}}{CH_3CH_2CH_2CH_3}$

(*iii*) $\underset{\text{Ethyl chloride}}{CH_3CH_2Cl} \xrightarrow{Li} CH_3CH_2Li \xrightarrow{CuCl} (CH_3CH_2)_2CuLi \xrightarrow{CH_3CH_2Cl} \underset{n\text{-Butane}}{CH_3CH_2CH_2CH_3}$

8. (*i*) $CH_3CH_2Br \xrightarrow[ether]{Mg} CH_3CH_2MgBr \xrightarrow{D_2O} CH_3CH_2D$

(*ii*) $CH_2 = CH_2 + D_2 \xrightarrow{Pt} CH_2DCH_2D$

(*iii*) $CH_4 + CD_2N_2 \xrightarrow{UV} CH_3CD_2H + N_2$

9. (*i*) $CH_3CH_2CH_3$ to $(CH_3)_2CHCH(CH_3)_2$.

syn-Alkanes can be easily prepared by Wurtz reaction

$$CH_3CH_2CH_3 \xrightarrow{Br_2,\ 127°C} (CH_3)_2CHBr \xrightarrow[ether]{Na} (CH_3)_2CHCH(CH_3)_2$$

Note : Bromination of propane is preferred over chlorination because the ratio of isopropyl to *n*-propyl halide is 96 : 4 in bromination and 56 : 44 in chlorination.

(*ii*) $CH_3CH_2CH_3$ to $(CH_3)_2CHCH_2CH_2CH_3$

Unsymmetrical higher alkanes are best prepared by Corey-House synthesis.

$$CH_3CH_2CH_3 \xrightarrow{Cl_2,\ UV} CH_3CH_2CH_2Cl + (CH_3)_2CHCl$$

$$(CH_3)_2CHCl \xrightarrow{Li,\ ether} (CH_3)_2CHLi \xrightarrow{CuI} (CH_3)_2CH\underset{|}{\overset{CH(CH_3)_2}{|}}CuLi \xrightarrow{CH_3CH_2CH_2Cl} (CH_3)_2CHCH_2CH_2CH_3$$

(*iii*) Propane to neopentane, $(CH_3)_2C(CH_3)_2$. Note that two more methyl groups are introduced which can easily be done by Corey synthesis.

$$CH_3CH_2CH_3 \xrightarrow{Br_2} CH_3CHBrCH_3 \xrightarrow[(iii)\ CH_3I]{(i)\ Li\ (ii)\ CuI} (CH_3)_2CHCH_3 \xrightarrow[(iii)\ CH_3I]{(i)\ Li,\ (ii)\ CuI} (CH_3)_2C(CH_3)_2$$

10. (*a*) $CH_3CH_2CH_2X + [(CH_3)_2CH-]_2-CuLi \longrightarrow (CH_3)_2CHCH_2CH_2CH_3$

(*b*) $(CH_3)_2CHX + [CH_3CH_2CH_2-]_2-CuLi \longrightarrow CH_3CH_2CH_2CH(CH_3)_2$

Dialkylcopper lithium in two cases is prepared from $(CH_3)_2CHLi$ and $CH_3CH_2CH_2Li$ respectively ; however method (*a*) is superior as it uses 1° halide (Corey-House synthesis).

11. More is the stability of a free radical formed, more will be the ease of its formation (or abstraction of hydrogen to give free radical) ; thus the ease of abstraction of hydrogen follows the order

$CH_2 = CHCH_2\text{—}\mathbf{H}$, $C_6H_5CH_2\text{—}\mathbf{H}$ > $CH_2 = CH\text{—}\mathbf{H}$

Allylic hydrogen Benzylic hydrogen Vinylic hydrogen

12. An alkane having identical hydrogen atoms will give only one product on methylene insertion. The first four such alkanes are CH_4, CH_3CH_3 , $(CH_3)_4C$ and $(CH_3)_3C\text{—}C(CH_3)_3$.

13. (*a*) 2, 2-Dimethylbutane has nine 1°, two 2° and three 1°′ hydrogen atoms. So it will form three products.

Name of product	Weight reactivity No. of H's × Relative reactivity	% Yield (Weighted react. × 100)
1-Chloro	9 × 1 = 9	$\frac{9}{19.6} \times 100 = 46$
3-Chloro	2 × 3.8 = 7.6	$\frac{7.6}{19.6} \times 100 = 39$
4-Chloro	3 × 1 = 3	$\frac{3}{19.6} \times 100 = 15$

(*b*) Isohexane, $\overset{1°}{CH_3}\text{—}\underset{3°}{\overset{1°}{\overset{|}{\overset{CH_3}{|}}CH}}\text{—}\overset{2°}{CH_2}\text{—}\overset{2°'}{CH_2}\text{—}\overset{1°'}{CH_3}$ has five types of hydrogen atoms, namely six 1°, one 3°, two 2°, two 2°′ and three 1°′. Thus the corresponding monochloro derivative will be in the ratio of 21, 17, 26, 26 and 10% respectively.

(*c*) 2, 2, 4-Trimethylpentane has four types of hydrogen atoms, the % product corresponding will be 33, 28, 18 and 22%.

$$\overset{1°}{CH_3}\text{—}\underset{1°}{\overset{1°}{\overset{|}{\overset{CH_3}{|}}C}}\text{—}\overset{2°}{CH_2}\text{—}\underset{3°}{\overset{1°'}{\overset{|}{\overset{CH_3}{|}}CH}}\text{—}\overset{1°'}{CH_3}$$

14. The four dichloro derivatives are

$\overset{1°}{CH_3}\overset{1°}{CCl_2}CH_3$ (*i*), A

$\overset{1°}{Cl}\overset{2°}{CH_2}CH_2CH_2Cl$ (*ii*), B

$\overset{1°}{CH_3}\overset{2°}{CH_2}\overset{1°'}{CHCl_2}$ (*iii*), C

$\overset{1°}{CH_3}\overset{2°}{CHCl}\overset{1°'}{CH_2}Cl$ (*iv*), D

15. (*a*) A reactive site in a molecule generally has at least one of the following features : (*i*) one or more unshared pair of electrons, (*ii*) a polar bond, (*iii*) an electron deficient atom, (*iv*) an atom with an expandable octet. Alkanes have none of these features, hence these are inert.

(*b*) The C—C bond has a lower average bond energy (ΔH = + 347 kJ mol^{-1}) than the C—H bond (ΔH = + 415 kJ mol^{-1}).

(*c*) The reaction is very slow at moderate temperatures because of a very high activation energy.

16. (*i*) $(CH_3)_3CCH_2CH_2CH_2CH_3$ (A)

(*ii*) $CH_3CHBrCH_3 \xrightarrow{Cl^{\bullet}} \underset{\text{(B) 1° radical}}{CH_3CHBr\dot{C}H_2} \xrightarrow[\text{(migration of Br)}]{\text{rearrangement}} CH_3\dot{C}HCH_2Br \xrightarrow{Cl_2} CH_3CHClCH_2Br$

2° radical (c) (D)

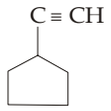
Note that although alkyl free radicals do not rearrange by migration of hydrogen or alkyl, they rearrange by migration of halogen.

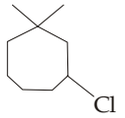
(*iii*) Since 2, 7-dimethyloctane is formed by Wurtz reaction, the RCl must be symmetrical molecule *i.e.* $(CH_3)_2CHCH_2CH_2Cl$. Thus compounds E to (G) may be as below :

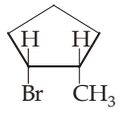
$$(CH_3)_2CHCH_2CH_2X \xrightarrow{Li} (CH_3)_2CHCH_2CH_2Li \xrightarrow{H_2O} \underset{\text{Isopentane (G)}}{(CH_3)_2CHCH_2CH_3}$$

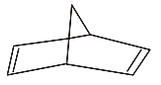
(E) (F)

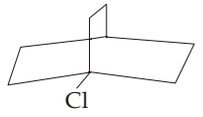
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17. (*i*) 

(*ii*) 

(*iii*) 

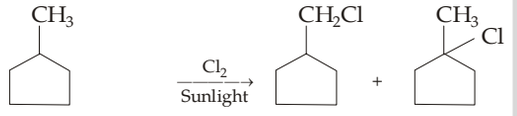
(*iv*) 

(*v*) 

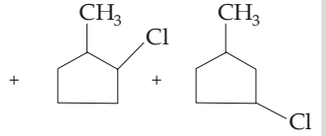
A thickened line indicates a bond coming out of the plane of the paper.

18. 

Cyclohexane, A



Methylcyclopentane



19. (*a*) Density of the petroleum fuel = 0.764 g/mL

∴ Weight of 1 litre of petroleum fuel = 764 g

∴ No. of moles of the fuel $= \frac{764\text{ g}}{198\text{ g/mol}}$

(Mol. wt. of fuel = 198)

Now writing the combustion reaction

$$n\text{-}C_{14}H_{30} + \frac{43}{2}O_2 \longrightarrow 14CO_2 + 15H_2O$$

∴ Amount of O_2 required by 1 litre of fuel $= \frac{764}{198} \times \frac{43}{2}$

or Wt. of O_2 required by 1 litre of fuel $= \frac{764}{198} \times \frac{43}{2} \times 32$

$= \mathbf{2650\ g}$

(*b*) The molecular formula of the fuel n–$C_{14}H_{30}$ indicates that it has twelve —CH_2— and two CH_3— groups, thus the total amount of heat evolved on the combustion of 1 mol of the fuel

$= (12 \times 157) + (2 \times 186) = 2256$ kcal/mol

∴ Heat evolved by 1 litre or $\frac{764}{198}$ moles of fuel

$= \frac{764}{198} \times 2256 = \mathbf{8710\ kcal}$

(*c*) Given, $H + H \longrightarrow H_2$, $\Delta H = -104$ kcal/mol

Thus 104 kcal of heat is evolved by 1 mole of H_2

8710 kcal of heat will be evolved by $\frac{1 \times 8710}{104}$

$= 84$ mol of $H_2 = \mathbf{168\ g\ H_2}$

20. We know that

$$\text{No. of mmol} = \frac{\text{Vol. of gas in mL}}{22.4\text{ mL/mmol}} = \frac{\text{Wt. of substance in mg}}{\text{Mol. wt. in mg/mmol}}$$

Here, $\text{No. of mmol of alcohol} = \frac{1.56\text{ mL}}{22.4\text{ mL/mmol}}$

∴ $\text{Mol. wt. of ROH in mg/mmol} = \frac{\text{Wt. of ROH in mg}}{\text{No. of mmol}}$

$= \frac{4.12\text{ mg}}{(1.56/22.4)\text{ mmol}} = 59$ mg/mmol

Since, alcohol (ROH) contains one —OH group

∴ $C_nH_{2n+1(OH)} = 59$

$12n + (2n + 1)\ 1 + 16 + 1 = 59$

$14n + 18 = 59$

$n \approx 3$

∴ ROH is $\mathbf{C_3H_7OH}$.

21. $\text{No. of mmol of alcohol} = \frac{1.79\text{ mg}}{90\text{ mg/mmol}} \approx 0.02$

$\text{No. of mmol of alcohol} = \frac{1.34\text{ mL}}{22.4\text{ mL/mmol}} \approx 0.06$ m mol

0.02 mmol of an alcohol gives 0.06 mmol of H_2

1 mmol of alcohol gives 3 mmol of H_2

or 1 mole of alcohol gives 3 moles of H_2

∴ Alcohol contains 3 —OH groups which is further confirmed by its molecular weight.

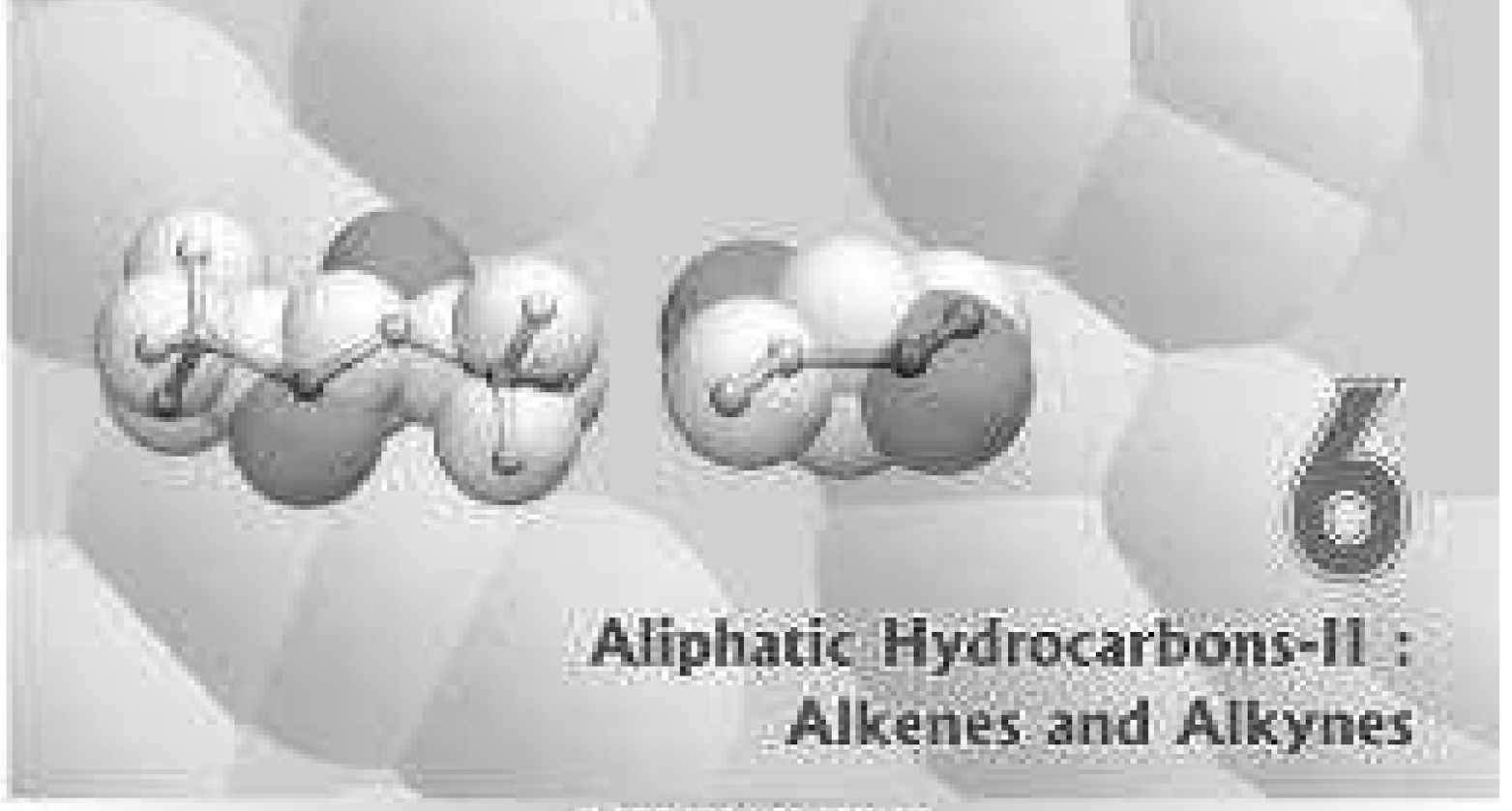
For trihydric alcohol,

$C_nH_{2n-1}(OH)_3 = 90$

$12n + (2n - 1)(1) + 51 = 90$

$14n + 50 = 90$

$n \approx \mathbf{3}$



6

Aliphatic Hydrocarbons-II : Alkenes and Alkynes

CHAPTER HIGHLIGHTS

ALKENES

6.1 Relative Stability of Alkenes
6.2 Stability of Cycloalkenes
6.3 Preparation of Alkenes
6.4 Physical Properties
6.5 Chemical properties

DIENES

6.6 1,3-Butadiene
6.7 Degree of Unsaturation
6.8 Illustrative Examples on Alkenes

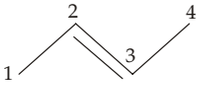
ALKYNES OR ACETYLENES

6.9 Preparation of Alkynes
6.10 Physical Properties
6.11 Chemical Properties
6.12 Illustrative Examples on Alkynes
6.13 Characteristics of Alkanes, Alkenes and Alkynes

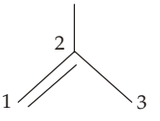
EXERCISES
SOLUTIONS

ALKENES

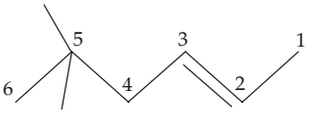
Alkenes are open-chain hydrocarbons having carbon-carbon double bonds, C=C. They have the general formula C_nH_{2n} and are also called **alkylenes** or **olefins.** The fist three members are commonly named by their common names, namely *ethylene, propylene* and *butylenes;* higher alkenes are named by their IUPAC names, *viz.*



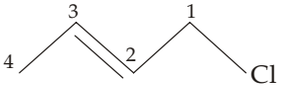
2-Butene



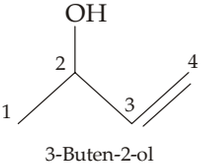
2-Methylpropene



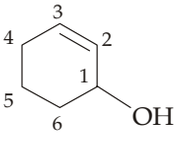
5, 5-Dimethyl-2-hexene



1-Chloro-2-butene



3-Buten-2-ol
(Note that *-ol* takes priority over *-ene*)



2-Cyclohexenol

Alkenyl groups : Like alkyl groups (alkane – H), there are three commonly encountered alkenyl groups which are given special (trivial) names.

$CH_2=CH-$
Vinyl

$\overset{3}{C}H_2=\overset{2}{C}H-\overset{1}{C}H_2-$
Allyl

$\overset{3}{C}H_3-\overset{2}{C}H=\overset{1}{C}H-$
Propenyl

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Isomerism : Alkenes show *chain* (1-butene and isobutene), *position* (butene –1 and butene-2), functional (propene and cyclopropane) and *geometrical isomerism.*

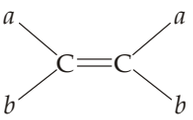
$CH_3CH_2CH = CH_2$ and $(CH_3)_2C = CH_2$; $CH_3CH_2CH = CH_2$ and $CH_3CH = CHCH_3$; $CH_3CH = CH_2$

Butene-1 Isobutene — Chain isomers

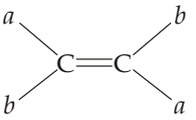
Butene-1 Butene-2 — Position isomers

Propene Cyclopropane — Functional isomers

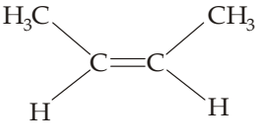
Geometrical isomerism : The π bond of alkenes prevents free rotation, i.e there is hindered rotation about the carbon-carbon bond, therefore an alkene having two different substituents on each doubly bonded carbon, i.e. alkenes of the type *ab*C = C*ab* can exist in two different geometric isomers. For example,



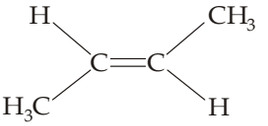
cis



trans



cis-2-Butene



trans-2-Butene

NOTE :

(i) In the cycloalkenes the *trans* isomers are unstable unless the ring contains at least eight carbon atoms

(ii) Geometric (*cis-trans)* isomers are stereoisomers because they differ only in the spatial arrangement of the groups.

(iii) Geometrical isomers are diastereomers (stereoisomers which are not enantiomers are called **diastereomers)** and thus have different physical properties (m. p., b.p. etc.).

(iv) In modern nomenclature the terms *cis* and *trans* are being replaced by the letters Z (when the higher-priority substituents on each carbon are on the same side of the double bond) and E (when the higher-priority substituents are on opposite sides).

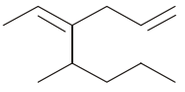
(v) The priority orders among some common atoms and groups are given below :

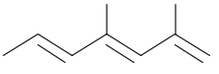
(a) I, Br, Cl, S, F, O, N, C, D, H

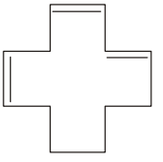
(b) I, Br, Cl, SO_3H, F, OCOR, OR, OH, NO_2, NR_2, NHCOR, NHR, NH_2, CCl_3, COCl, COOR, COOH, $CONH_2$, COR, CHO, CH_2OH, CN, C_6H_5, CR_3, CHR_2, CH_2R, CH_3, D and H.

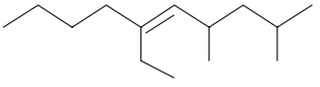
TEST YOUR UNDERSTANDING - 6.1

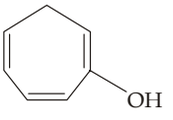
1. Give IUPAC name of the following compounds:

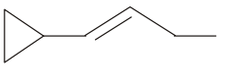
(i) 

(ii) 

(iii) 

(iv) 

(v) 

(vi) 

2. Draw structural formula of

(*i*) *trans*-2-methyl-3-heptene (*ii*) Z-2-chloro-2-butene

(iii) E-1-Iodo-2-pentene (*iv*) Z-1, 3-pentadiene.

3. Write structural formulas for trisubstituted alkenes of the formula C_6H_{12}.

6.1 Relative Stability of Alkenes

Stabilities of a compund can be compared by converting different compounds to a common product and comparing the amounts of heat given off. The smaller value of heat given off indicates smaller heat content (enthalpy) and hence larger stability of the molecule. Two types of heat of reactions are used for comparing the stability of alkenes.

1. **Heat of combustion :** It is the amount of heat evolved during the complete burning of one mole of the alkene with oxygen to form CO_2 and H_2O. However, heats of combustion are large numbers, and there is a small difference in values of the two or more isomers, which is measured with difficulty.
2. **Heat of hydrogenation :** It is the amount of heat evolved when one molecule of an alkene is hydrogenated in presenc eof a platinum catalyst forming corresponding alkane. Hydrogenation is mildly exothermic, evolving about 20 to 30 kcal (80 to 120 kJ) of heat per mole of hydrogen consumed.

$$\underset{\text{3–Methyl–1–butene}}{CH_3CH(CH_3)CH=CH_2} + H_2 \xrightarrow{Pt} CH_3CH(CH_3)CH_2CH_3 \quad \Delta H^0 = -30.3 \text{ kcal / mol. } (-127 \text{ kj/mol.})$$

$$\underset{\text{2–Methyl–1–butene}}{CH_3CH_2C(CH_3)=CH_2} + H_2 \xrightarrow{Pt} CH_3CH_2CH(CH_3)CH_3 \quad \Delta H^0 = -28.5 \text{ kcal / mol. } (-119 \text{ kj/mol.})$$

$$\underset{\text{2–Methyl–2–butene}}{CH_3C(CH_3)=CHCH_3} + H_2 \xrightarrow{Pt} CH_3CH(CH_3)CH_2CH_3 \quad \Delta H^0 = -26.9 \text{ kcal / mol. } (-113 \text{ kj/mol.})$$

Since all the three compounds form the same alkane (2-methylbutane), so the energy of the product for each of the three reactions is same. Hence different heats of hydrogenation for the three reactions must be due to different heat contents of the three reactants. The reactant having least heat of hydrogenation is the most stable because it has least energy (enthalpy), while the reactant having maximum heat of hydrogenation is the least stable because it has greatest energy (enthlpy). Thus the stability order of the above three alkenes is

$$CH_3C(CH_3)=CHCH_3 \;>\; CH_3CH_2C(CH_3)=CH_2 \;>\; CH_3CH(CH_3)CH=CH_2$$

Heat of hydrogenation can't be used for measuring relative stabilities of isomeric alkenes which yields different products on hydrogenation. For example, 2-methylpropene can't be compared directly with the isomeric butenes like 1-butene, *cis*- and *trans*-2-butene because hydrogenation of 2-methylpropene gives 2-methylpropane (isobutane) while the three isomeric butenes give *n*-butane.

$$\underset{\text{2–Methylpropene}}{CH_3C(CH_3)=CH_2} + H_2 \xrightarrow{Pt} \underset{\text{Isobutane}}{CH_3CH(CH_3)CH_3}$$

$$\underset{\text{1–butene}}{CH_3CH_2CH=CH_2},\ \underset{\text{2–butenes}}{CH_3CH=CHCH_3} \xrightarrow[Pt]{H_2} \underset{n\text{-Butane}}{CH_3CH_2CH_2CH_3}$$

Since butane and isobutane do not have the same enthalpy, a direct comparison of heat of hydrogenation is not possible.

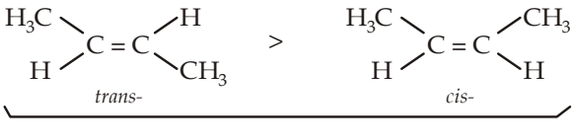
Studies of numerous alkenes reveal that the stabilities of alkenes is related to the number of alkyl groups bonded to the two sp^2 carbons. *The greater the number of alkyl groups attached to the two sp^2 carbon atoms* (i.e. the more highly substituted the carbon atoms of the double bond), *the greater is the stability of the alkene*. In other words, fewer the number of H's present on the sp^2 carbons, more is the stability of the alkene.

Thus the relative order of stabilities of the different alkenes is

$$R_2C=CR_2 \;>\; R_2C=CHR \;>\; RCH=CHR \;>\; RCH=CH_2$$

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Further in dialkylsubstituted alkenes, the *trans*-isomer is more stable than the *cis*-isomer because in the *trans*-isomer, the large substituents are farther apart and thus exert less steric strain than in the correspond *cis*-isomer.



Two alkyl groups are on different sp^2 C's

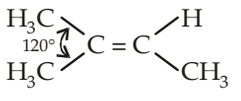
Three factors are responsible for the stabilizing effect of alkyl groups on a double bond.

(i) **Hyperconjugation :** More the possibility of hyperconjugation in an alkene, higher will be its stability.

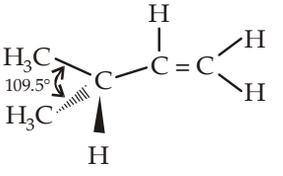
(ii) Steric repulsion between bulky groups makes the isomer relatively less stable than the other.

(iii) In highly substituted alkene, bulky alkyl groups are more away from each other (120° separation) than in the isomer which have fewer alkyl groups on the sp^2 carbon because here two alkyl groups are separated by the tetrahedral bond angle of about 109.5°. For example

$$(CH_3)_2C = CHCH_3 \quad > \quad (CH_3)_2CHCH = CH_2$$

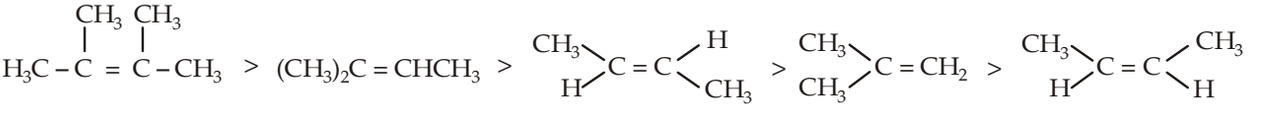


The two methyl groups are separated by 120°, less steric strain



The two methyl groups are separated by 109.5°

Thus the relative stability of the following alkenes can be summed up as below.



(12 H-C hyper-conjugated bonds)

(9 H-C hyper-conjugated bonds)

(*trans*-least steric strain)

(*cis*-steric strain)

(all the three have 6 H-C hyperconjugative bonds)

$$> \quad CH_3CH = CH_2$$

(3 H-C hyper. bonds)

In general, the stability order of substituted ethylenes is :

Tetrasubstituted > Trisubstituted > *trans*-Disubstituted > *gem*-Disubstituted > *cis*-Disubstituted.

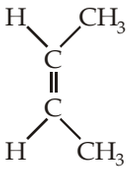
Actually, there are contradictory views regarding the relative stability of *cis*-disubstituted and *gem*-disubstituted ethylenes.

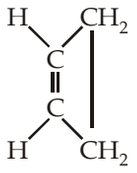
6.2 Stability of Cycloalkenes

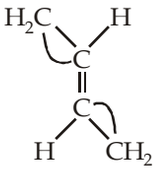
The presence of a ring system in cycloalkene affects in two ways : (i) a small ring produces ring strain and thus imparts unstability, and (ii) presence of a *trans*-double bond is not possible in smaller rings, while in larger rings although the *trans*- double bond exists, yet it is less stable than the *cis*- isomer (difference from open chain alkenes).

Cyclopropene is not stable because here a great strain is created when the usual angle of 120° (in alkenes) is converted (compressed) to 60° (present in cycloalkenes).

Alkenes with fewer than eight carbon atoms do not form *trans*-isomer at room temperature because the two alkyl groups on a *trans* double bond are so far apart that several carbon atoms are needed to complete the ring.


cis- Butene-2


cis- Cyclobutene


trans- Cyclobutene
(not possible)
The two connecting –CH_2
moieties are very far away

Although *trans*- cycloheptene can be isolated at room temperature, it is not quite stable. *trans*-Cyclooctene is stable at room temperature and the higher homologues containing at least 10 carbon atoms are quite stable in their *trans*- form. The stability of the *trans*- cycloalkenes can be summed up in the form of **Bredt rule** "a bridged bicyclic compound can't have a double bond at a bridge-head position unless one of the rings contains at least eight carbon atoms."

TEST YOUR UNDERSTANDING - 6.2

1. Tell which member of each pair is more stable?
   (a) 2-methyl-1-butene or 3-methyl-1-butene (b) 2-methyl-1-butene or 2-methyl-2-butene
   (c) 2, 3-dimethyl-1-butene or 2, 3-dimethyl-2-butene (d) *cis*- cyclooctene or *trans*- cyclooctene
2. Which of the following compounds is most stable?
   3, 4-dimethyl-2-hexene, 2, 3-dimethyl-2-hexene, 4, 5-dimethyl-2-hexene.
3. (a) How many alkenes could you treat with H_2/Pt in order to prepare methylcyclopentane?
   (b) Which alkene is the most stable?
   (c) Which alkene has the smallest heat of hydrogenation?
4. Give three alkenes containing six carbon atoms that form the same product whether they react with HBr in the presence of peroxides or with HBr in the absence of peroxides.
5. Arrange the following alkenes in order of decreasing stability:
   1-pentene, (E)-2-pentene, (Z)-2-pentene and 2-methyl-2-butene

6.3 Preparation of Alkenes

Common methods used for preparing alkenes involve elimination of atoms or groups from two adjacent carbons (β- *elimination*)

6.3.1 By Dehydrohalogenation of Alkyl Halides

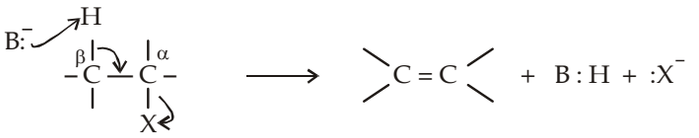
Dehydrohalogenation, elimination of a hydrogen and a halogen atom from an alkyl halide, can take place by the E2 and E1 mechanisms. The second-order elimination (E2) is almost always better for synthetic purposes because the E1 has many competing reactions, one being rearrangement of the carbon skeleton.

E2 Mechanism

An E2 reaction gives excellent yield when bulky secondary and tertiary alkyl halides that are poor S_N2 substrates (in case of primary alkyl halide, a bulky base must be used to get good result) are treated with a strong base, like C_2H_5ONa in C_2H_5OH, potassium *tert*-butoxide in *tert*-butyl alcohol or dimethyl sulphoxide, or potassium hydroxide in ethanol. In the last case the reactive base is the ethoxide ion formed by the following equilibrium :

$$OH^- + C_2H_5OH \rightleftharpoons H_2O + C_2H_5O^-$$

The E2 reaction is a concerted, one-step reaction, i.e. the proton and the halide ion are removed in the same step without forming any intermediate



Mechanism of E2 reaction

Since the **E2 reaction** is initiated by removing the proton from a β-carbon, it is sometimes called **β-elimination**. Further since the atoms (H and X) are removed from the two adjacent carbons, E2 reaction is also called **1,2-elimination** reaction.

Orientation of the double bond in the product : When the alkyl halide has two structurally different β-carbons from which a proton can be removed, two elimination products are possible. For example,

$$CH_3-\underset{|}{\overset{Br}{CH}}-CH_2CH_3 + Base \longrightarrow \underset{But-2-ene}{CH_3CH=CHCH_3} + \underset{But-1-ene}{CH_2=CHCH_2CH_3}$$

which one is the major product, depends upon several factors.

(i) **Nature of base :** If we use a small base, such as ethoxide ion or hydroxide ion, the major product of the reaction will be the **more stable**, i.e. more highly substituted alkene (**Zaitsev rule**). This product is known as **Zaistev or Saytzeff product.**

$$CH_3CH_2-\underset{CH_3}{\overset{Br}{\underset{|}{\overset{|}{C}}}}-CH_3 \xrightarrow[C_2H_5OH]{C_2H_5O^-} \underset{(71\%)}{CH_3CH=\underset{CH_3}{\overset{|}{C}}-CH_3} + \underset{(29\%)}{CH_3CH_2-\underset{CH_3}{\overset{|}{C}}=CH_2}$$

If we use a bulky base, such as *tert*-butoxide, triethylamine, diisopropylamine, 2,6-dimethylpyridine, etc., the major product will be the least highly substituted product, called the **Hofmann product**.

$$CH_3CH_2-\underset{CH_3}{\overset{Br}{\underset{|}{\overset{|}{C}}}}-CH_3 \xrightarrow[(CH_3)_3COH]{(CH_3)_3CO^-} \underset{\text{Saytzeff product (28\%)}}{CH_3CH=\underset{CH_3}{\overset{|}{C}}-CH_3} + \underset{\text{Hofmann product (72\%)}}{CH_3CH_2-\underset{CH_3}{\overset{|}{C}}=CH_2}$$

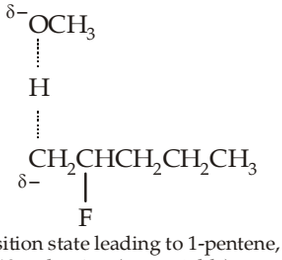
(Least hindered H)

Here the bulky *tert*-butoxide ion easily abstracts the less hindered proton forming less substituted alkene as the major product.

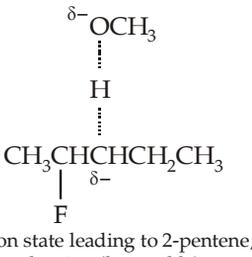
(ii) **Nature of halogen in alkyl halides :** Although the major product of the E2 dehydrohalogenation of RCl, RBr, and RI is normally the more substituted alkene, the major product of the E2 dehydrohalogenation of RF is the less substituted alkene.

$$CH_3-\underset{|}{\overset{F}{C}}HCH_2CH_2CH_3 + CH_3O^- \xrightarrow{CH_3OH} \underset{\text{2–Pentene (E and Z) (30\%)}}{CH_3CH=CHCH_2CH_3} + \underset{\text{1–Pentene (70\%)}}{CH_2=CHCH_2CH_2CH_3}$$

This is due to the fact that among halide ions the fluoride ion is the strongest base and thus the poorest leaving group. So when the base begins to remove a proton from the alkyl fluoride, the poor leaving character of the fluoride ion delays its removal with the result a transition state resembling to a carbanion is formed (which is not the case in other halides because Cl^-, Br^- and I^- are good leaving groups). Thus when a carbanion type of situation arises, naturally a stable carbanion will be formed easily (1° > 2° > 3°). Thus now let us study the two possible transition states during above reaction.



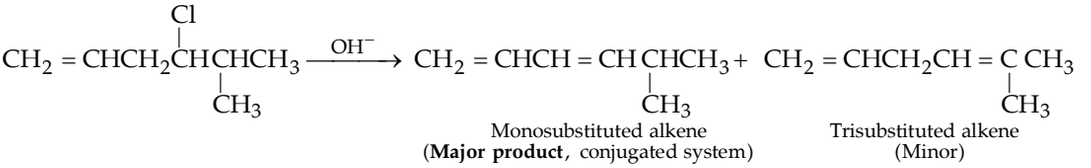
Transition state leading to 1-pentene, 1° carbanion (more stable)



Transition state leading to 2-pentene, 2° carbanion (less stable)

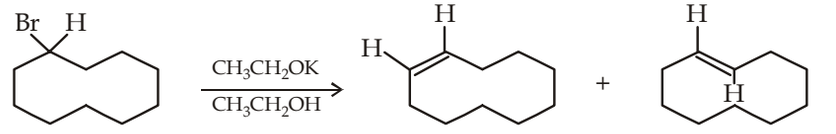
Because the transition state leading to 1-pentene is more stable, 1-pentene is formed more rapidly and thus constitutes the major product.

(iii) Alkyl halide containing double bond. In case the alkyl halide has a double bond or a benzene ring, a conjugated alkene will be the major product which may or may not be the Saytzeff product.



Thus an E2 reaction is said to be **regioselective** because one of the constitutional isomers is formed in major amount than the other.

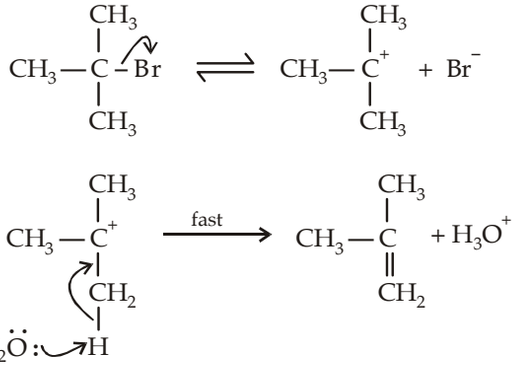
In addition to being regioselective, dehydrohalogenation of alkyl halides is stereoselective and favours the formation of the more stable stereoisomer. Usually, the *trans* (or *E*) alkene is formed in greater amounts than its *cis* (or *Z*) stereoisomer. Elimination reactions of cycloalkyl halides lead to *cis* cycloalkenes when the ring has fewer than 11 carbons. As the ring becomes larger, it can accommodate either a *cis* or a *trans* double bond, and thus large - ring cycloalkyl halides give mixtures of *cis* and *trans* cycloalkenes.



Bromocyclodecene — *cis*-Cyclodecene (85%) + *trans* -cyclodecene (15%)

E1 Mechanism

First order dehydrohalogenation usually takes place in a good ionizing solvent (such as an alcohol or water), without a strong nucleophile or base. The substrate is usually a secondary or tertiary alkyl halide. The reaction involves two steps, the first step is rate determining and hence the increase in concentration of the base which is involved in the second fast step has no effect on the rate of the reaction.



(i) When two products are possible, the major product is the Saytzeff product.

(ii) Because the rate determining step involves the removal of halide ion and formation of a carbocation, the rate of E1 reaction depends on both the ease with which the leaving group leaves and the stability of the carbocation formed. Stability of the common carbocations is:

3° benzylic > 3° allylic > 2° benzylic > 2° allylic > 3° > 1° benzylic ≈ 1° allylic ≈ 2° > 1° > vinyl

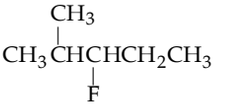
(iii) Since carbocations are formed as intermediates, E1 dehydrohalogenations are prone to rearrangement.

TEST YOUR UNDERSTANDING - 6.3

1. Give the major elimination product obtained from an E2 reaction of each of the following alkyl halides with OH^-.

(a) 

(b) 

(c) 

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2. Which alkyl halide should be more reactive in an E2 reaction?

(a) $CH_3CH_2CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$ or $CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_2CH_3$ (b) $CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH_2CH_3$ or $CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH_2CH_3$

CH_3 CH_3

3. For each of the following reactions, indicate whether elimination will occur via an E2 or and E1 reaction. Give the major product in each case.

(a) $CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 \xrightarrow[DMSO]{OCH_3^-}$ (b) $CH_3\underset{\displaystyle Cl}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}CH_3 \xrightarrow{H_2O}$

(c) $CH_3CH_2\underset{\displaystyle F}{\underset{|}{C}}HCH_3 \xrightarrow{CH_3OH}$ (d) $(CH_3)_3C\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 \xrightarrow{CH_3CH_2OH}$

(e) $(CH_3)_3C\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 \xrightarrow[DMSO]{CH_3CH_2OH}$

6.3.2 By Dehydration of Alcohols

Dehydration of alcohols is done with Bronsted acids (proton donors) like sulphuric acid and phosphoric acid in the laboratory, and with Lewis acids such as alumina in industries.

$$CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3 + H_2SO_4 \overset{heat}{\rightleftharpoons} CH_3CH=CHCH_3 + H_3O^+ + HSO_4^-$$

Dehydration is reversible and in most cases the equilibrium constant is not large. In fact the reverse reaction (hydration of alkenes) is a method for converting alkenes to alcohols. The reversibility of the reaction can be prevented by removing the alkene by distillation as soon as it is formed (recall that alkenes have much lower boiling point than the corresponding alcohol because the alcohol is hydrogen bonded). Like dehydrohalogenation of alkyl halides, alcohols undergo dehydration in two ways E1 and E2 reactions.

Acid catalysed dehydration of secondary or tertiary alcohols : An E1 reaction : The first step in the dehydration of alcohols is protonation which converts OH^- (a poor leaving group) to H_2O (a good leaving group).

Step 1 : $CH_3\underset{\displaystyle :\ddot{O}H}{\underset{|}{C}}HCH_3 + H-OSO_3H \overset{fast}{\rightleftharpoons} CH_3\underset{\displaystyle :\overset{+}{O}H_2}{\underset{|}{C}}HCH_3 + {}^-OSO_3H$

Step 2 : $CH_3-\overset{\displaystyle :\overset{+}{O}H_2}{\overset{|}{C}}H-CH_3 \overset{slow}{\rightleftharpoons} CH_3-\overset{+}{C}H-CH_3 + H_2\ddot{O}:$

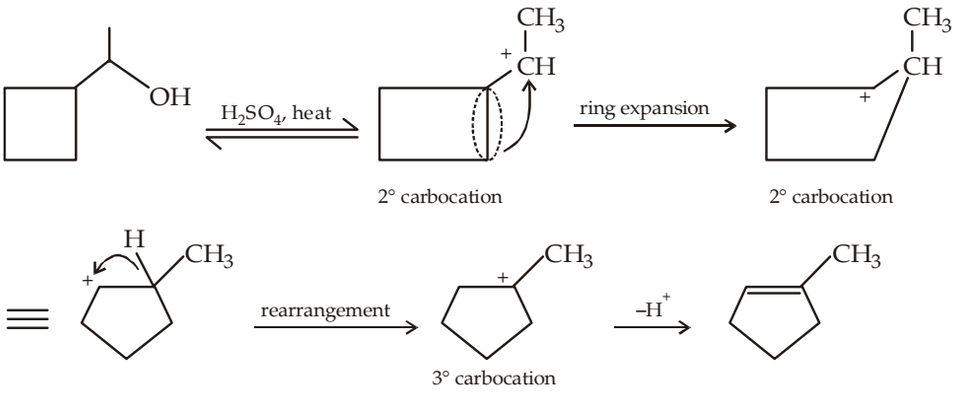
Step 3 : $CH_3-\overset{+}{C}H-\underset{\displaystyle H}{\underset{|}{C}}H_2 \overset{fast}{\rightleftharpoons} CH_3CH=CH_2 + B:H$

$B:$

(i) Note that the overall role of the acid (H_2SO_4) is catalytic as it is regenerated in the reaction. The reaction is exothermic.

(ii) The base B: used for removing proton may be any base present in the reaction mixture, i.e. ${}^-OSO_3H$, H_2O or $(CH_3)_2CHOH$ in the present case.

(iii) The carbocation may rearrange to the more stable one to form rearranged final product. Sometimes, ring expansion may occur (relief of strain) and thus higher cyclic compound will be formed. **Ring expansion** is observed when positive charge is on carbon next to ring; and ring contraction is observed when positive charge is on ring carbon atom.



(iv) Since 3° carbocations are formed most easily, followed by 2° carbocation and then 1°, the ease of dehydration follows the order :

Type of alcohol	R_3COH	>	R_2CHOH	>	RCH_2OH
Dehydration condition	5% H_2SO_4 at 50°C		75% H_2SO_4 at 100°C		95% H_2SO_4 at 170°C

(v) Dehydration of secondary and tertiary alcohols is an E1 reaction.

Acid-catalysed dehydration of primary alcohols : An E2 reaction. Since primary carbocations are not highly stable, they are believed to undergo dehydration in an E2 manner. Here also the first step is protonation which loses H_2O (a good leaving group) with the simultaneous attack by a Lewis base, present in the reaction mixture, at the β-hydrogen atom.

Step I : $CH_3CH_2\ddot{O}H + H-OSO_3H \rightleftharpoons CH_3CH_2\overset{H}{\overset{\cdot\cdot}{O}}H^+ + {}^-OSO_3H$

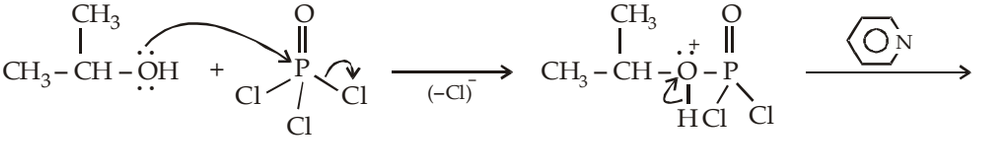
Step II : $B: \rightarrow H-\overset{\beta}{C}H_2-\overset{\alpha}{C}H_2-\overset{H}{\overset{+}{O}}H \xrightarrow[\text{of } :B, \text{ and removal of } H^+]{\text{Simultaneous attack}} CH_2=CH_2 + H_2O + \overset{+}{B}H$

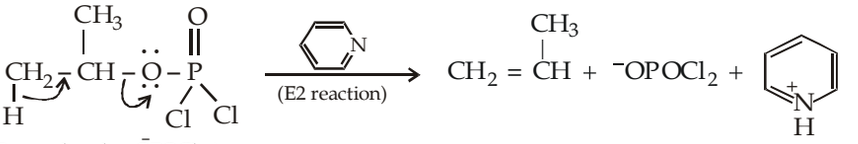
In case of dehydration of primary alcohols, ether is also obtained due to a competing reaction.

$$CH_3CH_2\ddot{O}H + CH_3CH_2-\overset{H}{\overset{+}{O}}H \longrightarrow CH_3CH_2\overset{+}{\underset{H}{O}}CH_2CH_3 + H_2O \xrightarrow{-H^+} CH_3CH_2OCH_2CH_3$$

Dehydration of alcohols by phosphoryl oxychloride in presence of pyridine : Dehydration of alcohols with acids involves relatively harsh conditions (acid and heat) and gives low yield of the desired product due to formation of carbocation as intermediate. These shortcomings can be avoided by carrying dehydration of alcohol in the presence of phosphoryl oxychloride ($POCl_3$) and pyridine.

$$CH_3CH_2\overset{OH}{\overset{|}{C}}HCH_3 \xrightarrow[\text{pyridine, } 0°C]{POCl_3} CH_3CH=CHCH_3$$





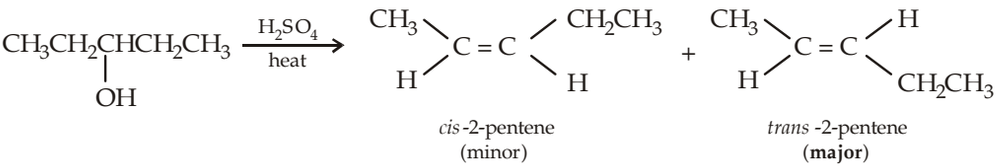
Remember that $\bar{O}POCl_2$ is a good leaving group

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(i) The mildly basic reaction conditions prevailing during the reaction favours E2 reaction, and hence no carbocation is formed.

(ii) Formation of HCl is avoided by using pyridine.

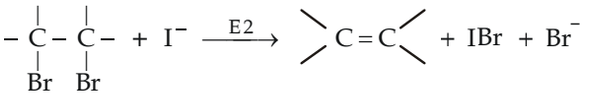
Alcohol dehydration, like alkyl halides, are **regioselective** (formation of one constitutional isomer in major amount than the other) as well as **stereoselective** (formation of one stereoisomer in major amount than the other).

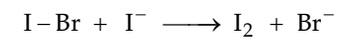


cis-2-pentene (minor) *trans*-2-pentene (**major**)

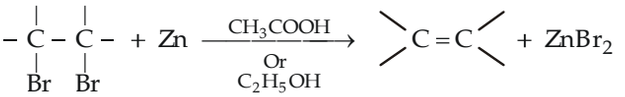
6.3.3 By Dehalogenation of vicinal Dihalides

(a) By treating *vic*-dibromide with a solution of NaI in acetone.





(b) By treating *vic*-dibromide with a mixture of zinc dust in acetic acid (or ethanol)



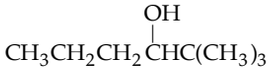
Other electropositive metals like Na, Ca and Mg can also cause debromination of *vic*-dibromides. The reaction follows E2 path and it is stereoselective as well as stereospecific meso form gives *trans*- alkene and *d*- and *e*-forms give *cis*-alkene.

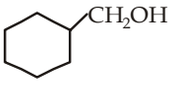
Since *vic*-dihalides are themselves generally prepared from alkenes, the method is of little use as a general preparative reaction. However, halogen addition on alkene followed by dehalogenation is useful (i) *for the purification of alkenes* and (ii) *in protecting the double bond.*

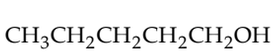
TEST YOUR UNDERSTANDING - 6.4

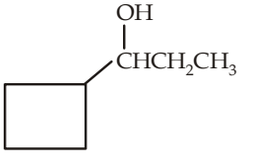
1. Like dehydration of a primary alcohol, *n*-butanol when treated with conc. H_2SO_4 undergoes dehydration by E2 reaction, and expected to form butene-1, yet butene-2 (expected product due to E1 reaction) is the main product in this reaction. Explain.

2. Give the major product formed when each of the following alcohol is heated in presence of conc. H_2SO_4.

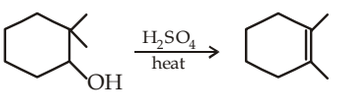
(a) 

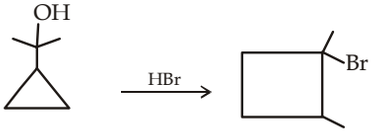
(b) 

(c) 

(d) 

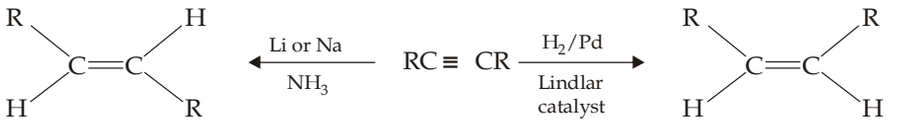
3. Propose mechanism for each of the following reactions.

(a) 

(b) 

4. Predict the order of reactivity of dehydrohalogenation of ethyl bormide, n- propyl bromide, isobutyl bromide and neopentyl bromide.
5. Give structures of alknenes likely to be formed from dehydrobromination, by a strong base, of
   (i) 2-bromo-2-methylbutane (ii) 2-bromo-2, 3-dimethylbutane
   (iii) 1-bromo-2, 2-dimethylpropane (iv) 3-Bromo-2, 3-dimethylpentane.
6. Name the alkyl halide that would yield each of the following pure alkene upon dehydrohalogenation by a strong base
   (i) 2-pentene (ii) 2-methyl-2-butene (iii) 2-methyl-1-butene.
7. Arrange the following in their decreasing dipole moment
   $CH_3CH = CH_2$, $CH_2 = CHCl$, $CH_3CH=CHCl$
8. Predict the products formed by the dehydration of
   (i) $(CH_3)_2C(OH)CH(CH_3)_2$ (ii) $CH_3CH_2CH_2CH_2OH$ (iii) $(CH_3)_3C.CHOH.CH_3$
   (iv) $(CH_3)_3C.\ CH_2OH$

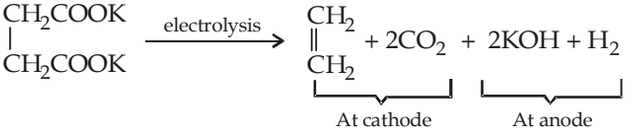
6.3.4 Partial Reduction of Alkynes



anti-(*trans*-) Alkene syn-(*cis*-) Alkene

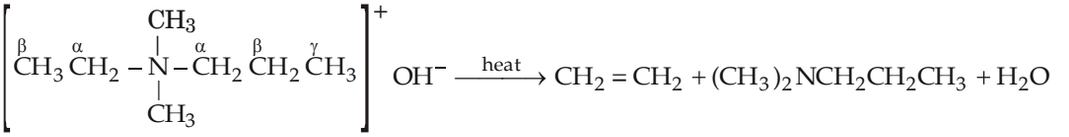
Detailed discussion of reduction of alkynes is given in the chapter on alkynes.

6.3.5 Electrolysis of Aqueous Solution of Sodium or Potassium Salts of the Saturated Carboxylic Acids (*Kolbe method*)



6.3.6 Pyrolysis of Quaternary Ammonium Hydroxide (Hofmann elimination)

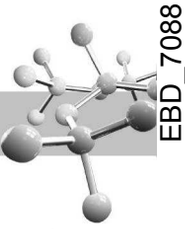
When tetralkyl ammonium hydroxides are heated, an alkene is formed along with a tertiary amine.



NOTE THAT :

(i) Here proton is abstracted from the β-carbon atom.

(ii) Here the least substituted alkene is the main product (*Hofmann rule*) which is opposite to that of *Saytzeff rule.* Note that in the above example, ethylene is the main product instead of propene. This is due to the fact that the strongly electronegative ($-N^+R_3$) group induces positive charge on all the neighbouring atoms which render β-hydrogen atom acidic. Now if electron releasing alkyl group is present on the β-carbon atom, it will reduce its acidic character and hence its abstraction, as in the case of $\overset{+}{N}-\overset{\alpha}{C}H_2-\overset{\beta}{C}H_2 \leftarrow CH_3$ group, become less prominent.



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6.3.7 Cope Elimination

Amine oxides are obtained in good yield by the oxidation of tertiary amines either with H_2O_2 or a peroxyacid. Because of positive charge on nitrogen, the amine oxides when heated undergo **cope elimination** to form alkenes (similarity with Hofmann elimination of quarternary ammonium salts).

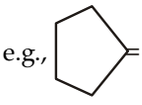
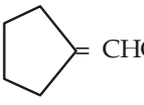
$$CH_3CH_2\underset{\displaystyle CH_3}{\overset{|}{C}}HN(CH_3)_2 \xrightarrow{H_2O_2} CH_3CH_2\underset{\displaystyle CH_3}{\overset{|}{C}}H\,\underset{\displaystyle O^-}{\overset{|}{N^+}}(CH_3)_2 \xrightarrow{\text{heat}} CH_3CH=CHCH_3 + (CH_3)_2NOH$$

Cope elimination occurs under milder conditions than Hofmann elimination. Cope elimination generally gives the same orientation as Hofmann elimination (i.e. Hofmann product). The reaction occurs with *syn*-stereochemistry.

6.3.8 Wittig Reaction

For details, consult reactions of aldehydes and ketones.

$$\begin{matrix}R\\R\end{matrix}\!\!>\!C=O + Ph_3P=CHR' \longrightarrow \begin{matrix}R\\R\end{matrix}\!\!>\!C=CHR' + Ph_3P=O$$

e.g.,  $= O + Ph_3P=CHCH_3 \longrightarrow$  $= CHCH_3 + Ph_3P=O$

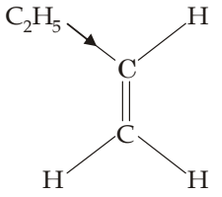
6.4 Physical Properties

(i) The first four members (C_1–C_4) are gases, C_5–C_{17} are liquids while the higher ones are solids.

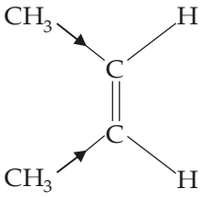
(ii) They are insoluble in water, but quite soluble in non-polar solvents. They are less dense than water.

(iii) Like alkanes, the boiling points rise with increasing carbon number (20 –30° per CH_2 added) and again branching lowers the boiling point.

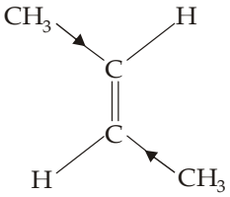
(iv) **Dipole moment.** Since the loosely held π electrons of the double bond are easily displaced, alkenes are weakly polar and hence have larger dipole moments than alkanes (non-polar), *e.g.* dipole moments of propene and butene-1 are 0.35 D and 0.37 D respectively. In case of geometrical isomers, *cis*-isomer has relatively higher dipole moment than the corresponding *trans*-isomer which may have zero dipole moment in case of symmetrical compound, *viz.* *trans*-2-butene.



1-Butene (μ = 0.37 D)
(Note that polarity is developed only in one bond)



cis-2-Butene
(μ = A small value)



trans-2-Butene
(μ = 0)

NOTE THAT :

(a) In *cis*- 2- butene, polarity and hence dipole moment in the two bonds are equal and in the same direction while in the *trans*-2-butene dipole moments of the two groups are equal in magnitude but opposite in direction, hence they cancel each other giving net zero dipole moment.

(b) Permanent dipole moment in *cis*- but-2-ene causes dipole-dipole attractions (which is absent in the trans-but-2-ene) which leads to increased intermolecular attractions and hence higher boiling point than the trans, although both isomers have similar vander Waals attractive forces.

(c) Melting points of the *cis*- and *trans*-alkenes do follow opposite trend, *i.e.* *cis*-isomer has lower m.p. than the *trans*- because in *trans*-isomer molecules are held tightly in crystal lattice due to its molecular symmetry.

6.5 Chemical properties

Due to the presence of loosely held π electrons, alkens undergo addition reactions.

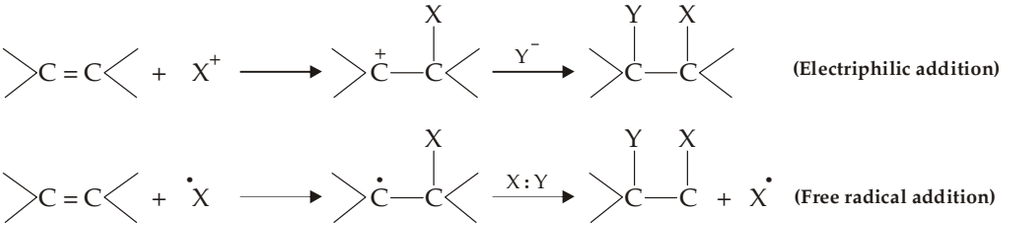


NOTE THAT

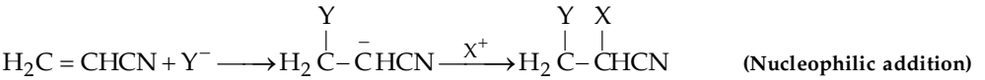
(i) π-bond (a reactive bond) is converted into σ bond (relatively less reactive bond).

(ii) During addition reactions, strain is relieved, i.e. bond angle (120°) is converted into tetrahedral bond angle of 109°28′

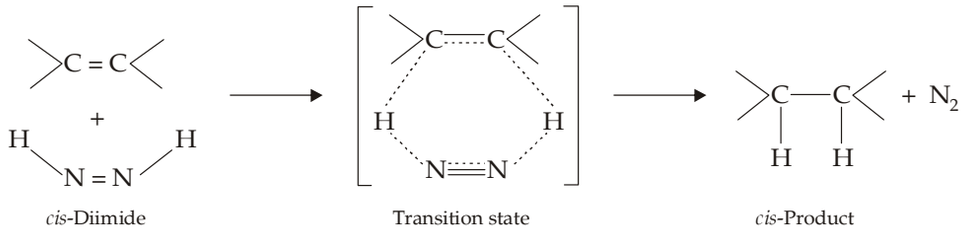
Addition on alkenes may be initiated by an electrophile or a free radical, both of which remain in search of electrons or electron respectively.



Alkenes having strongly electron-withdrawing group on one of the doubly bonded carbon atoms polarize the electrons in such a way that the β-carbon becomes electron deficient and hence react with the nucleophile (**nucleophilic addition**), *e.g.*



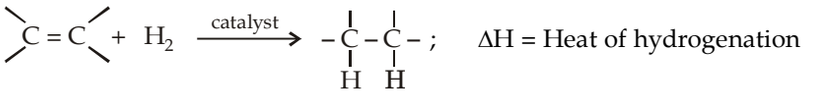
Although most of addition reactions of alkenes follow two-step path, certain (rare) addition reactions take place *via* one-step path. For example, hydrogenation of alkenes using hydrazine in conjunction with H_2O_2, O_2 or $[K_3Fe(CN)_6]$. Here the active reducing agent is *cis*-diimide.



However, the most common addition reactions of alkenes are electrophilic.

6.5.1 Addition of Hydrogen (*Catalytic hydrogenation*)

Alkenes react with hydrogen in the presence of a catalyst to yield the corresponding saturated alkane.



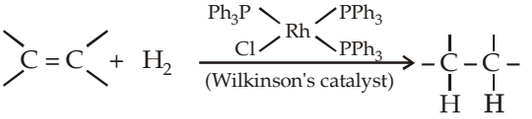
Hydrogenation is, although, an exothermic proces, it proceeds at a negligible rate in the absence of a catalyst, even at elevated temperatures. Thus it is evident that the function of a catalyst is to lower the energy of activation and the reaction can proceed rapidly at room temperature. A catalyst lowers the E_{act} by causing the reaction to take place by a different mechanism.Platinum and palladium are the most common catalysts, palladium is normally used as a very fine powder supported on an inert material like charcoal (Pd/C) to maximise surface area. Platinum is normally used as PtO_2; commonly known as Adam's catalyst. Other catalysts used during catalytic hydrogenation are nickel, rhodium and ruthenium. Unlike most other organic reactions, catalytic hydrogenation is a **heterogeneous process**, i.e. the reaction does not occur in a

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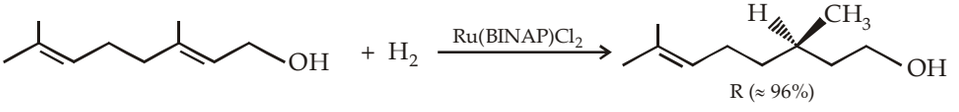
homogeneous solution but takes place on the surface of insoluble catalyst particles. In practice the alkene is dissolved in an alcohol, an alkane, or acetic acid; a small amount of the metal catalyst (insoluble in any solvent) is added and the container is shaken or sitrred. Hydrogenation takes place at the surface of the metal catalyst, where the liquid solution of the alkene comes into contact with hydrogen and the catalyst. The adsorption of H_2 over a catalyst is a chemical reaction in which unpaired electrons on the surface of the metal pair with the electrons of hydrogen and bind the hydrogen to the surface. The collision of an alkene with the surface bearing absorbed hydrogen causes adsorption of the alkene as well. A stepwise transfer of hydrogen atoms takes place producing an alkane which leaves the catalyst surface. As a consequence both hydrogen atoms usually add from the same side of the double bond that is complexed with the catalyst (*syn* addition).

If H_2 and D_2 are mixed in the presence of a catalyst, the two isotopes quickly scramble to produce a random mixture of HD, H_2 and D_2 (no scrambling occurs in the absence of the catalyst).

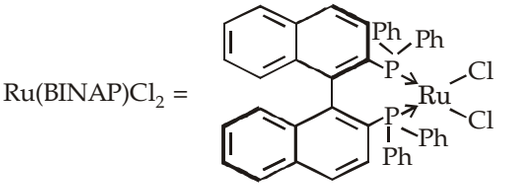
Soluble homogeneous catalysts, such as **Wilkinson's catalsyt**.



Wilkinson's catalyst is not chiral, but its triphenylphosphine (PPh_3) ligands can be replaced by chiral ligands to give chiral catalysts that are capable of converting optically inactive starting materials to optically active products **(chirally catalyzed hydrogenation reactions)**. Such a process is called **asymmetric induction or enantioselective synthesis.** For example,



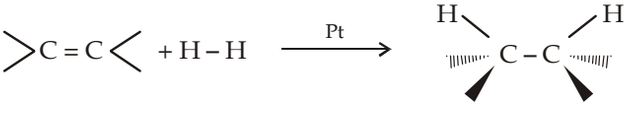
R (≈ 96%)



Here the catalyst is chiral because of sterically hindered restricted rotation around the carbon-carbon single bond.

Enantioselective synthesis is particularly important in the pharmaceutical industry, because in several drugs only one enantiomer of a chiral drug is found to have the desired effect.

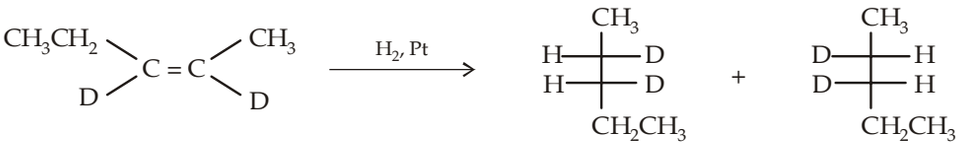
Stereochemistry of hydrogen addition : When hydrogen adds to an alkene, both hydrogen atoms add to the same side of the double bond which makes the addition of H_2 a *syn* addition reaction.



Syn - addition of H_2

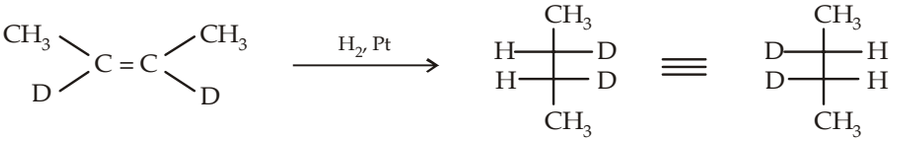
If addition of hydrogen to an alkene forms a product with two chirality centers, only two of the four possible stereoisomers are obtained because only *syn* addition can occur. The particular pair of stereoisomers that is formed depends on whether the reactant is *cis* or *trans* alkene. *Syn* addition of hydrogen to a *cis* alkene forms only the erythro pair of enantiomers.

In case the two chirality centers have the same set of substituents, the two structures obtained will be same and hence a single compound (*meso* isomer) will be formed instead of the pair of erythro enantiomers.



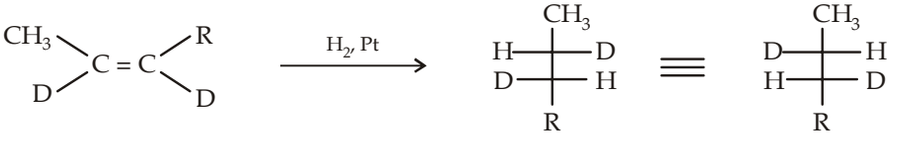
cis-2,3-Dideuteriopent-2-ene

erythro enantiomers



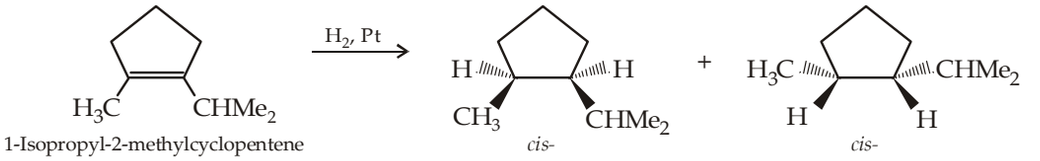
cis-2,3-Dideuteriobut-2-ene erythro *meso* isomer

Syn addition of hydrogen to a *trans* alkene forms only the threo pair of enantiomers.



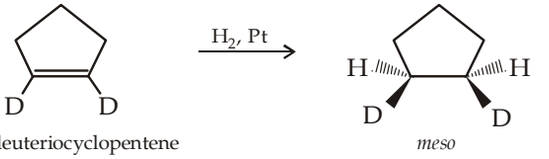
tran-Alkene threo isomers (R = CH_3 or other alkyl)

Addition of hydrogen on cycloalkene



1-Isopropyl-2-methylcyclopentene *cis*- *cis*-

Enantiomers



1,2-Dideuteriocyclopentene *meso*

Recall that cycloalkenes with fewer than eight carbon atoms can exist only in the *cis* configuration because they do not have enough carbons to incorporate a *trans* double bond. Therefore, it is not necessary to use the '*cis*' designation with their names.

Another interesting stereochemical feature of catalytic hydrogenation is its **stereoselectivity** (a reaction in which a single starting material can give two or more stereoisomeric products, one of which is either exclusive or major product than the other). Catalytic hydrogenation of α-pinene is a stereoselective reaction. *syn*- Addition of hydrogen can theoretically lead to either *cis*- pinane or *trans*- pinane depending on which face of the double bond accepts the hydrogen atoms. However, the actual product is only *cis*- pinane, no *trans*- isomer is formed.

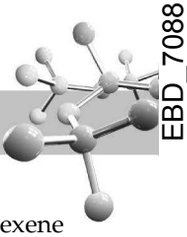
Thus addition of hydrogen on α-pinene is 100 percent stereoselective. The reason being the fact that catalytic hydrogenation is extremely sensitive to the steric environment around the double bond and often approaches only the less hindered face of the double bond forming a single product.

TEST YOUR UNDERSTANDING - 6.5

1. Indicate the direction of the net dipole moments for *cis*-2, 3-dichloro-2-butene and *cis*-1, 2-dibromo-1, 2-dichloroethene. Compare their dipole moments with that of *cis*-1, 2-dichloroethene.

2. Predict the nature of products formed by the catalytic hydrogenation of each of the following reactions.

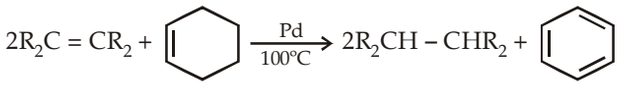
(a) *cis*-Pent-2-ene (b) *cis*-Hex-2-ene (c) *trans*-Pent-2-ene (d) *trans*-Hex-2-ene



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Transfer hydrogenation

Here hydrogen required for hydrogenation is supplied by some well-known stable compounds like cyclohexene or hydrazine.



$$2R_2C = CR_2 + \text{(cyclohexene)} \xrightarrow[100°C]{Pd} 2R_2CH - CHR_2 + \text{(benzene)}$$

$$2R_2C = CR_2 + H_2N - NH_2 \xrightarrow[100°C]{Pd} 2R_2CH - CH\,R_2 + N_2$$

The driving force in such cases is higher stability of the compound formed after transferring hydrogen. For example, benzene is more stable than cyclohexene due to aromatic ring and N_2 is more stable than hydrazine due to strongly bonded nitrogen atoms in N_2.

6.5.2 Addition of Halogens

Treatment of alkenes with chlorine or bromine yields 1, 2- dihalogenated alkanes (vicinal dihalides).

$$CH_3CH = CH_2 + Br_2 \longrightarrow \underset{\text{1,2–Dibromopropane}}{CH_3CHBrCH_2Br}$$

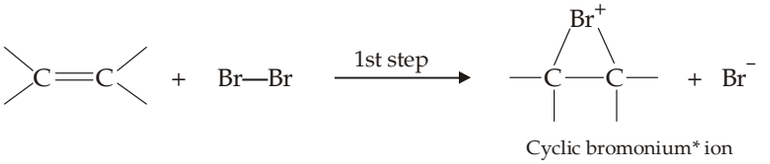
The reaction is carried out simply by mixing the two reactants usually in an inert solvent like CCl_4, $CHCl_3$ and dichloromethane which dissolve both reactants. The reaction takes place rapidly at room temperature or below; in fact high temperature, exposure to light and presence of excess of halogens should be avoided because these conditions may lead to substitution reaction.

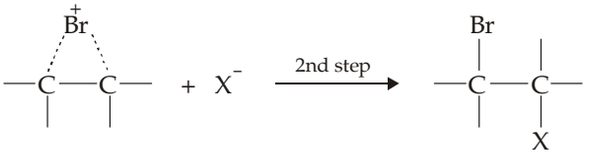
(i) Addition of bromine is extremely useful for detecting the presence of carbon-carbon multiple bond. Rapid decolorization of a bromine solution (red) is characteristic of compounds containing C–C multiple bonds. Use of bromine is preferred over chlorine owing to its ease of handling (as it is a liquid while chlorine is a gas) and coloured nature. F_2 and I_2 are not used as reagents, because fluorine reacts explosively with alkenes, while addition of I_2 to form vicinal diiodide is thermodynamically unfavourable because vicinal diiodides are unstable at room temperature, decomposing back to alkene and I_2.

(ii) The least reactive iodine ($F_2 > Cl_2 > Br_2 > I_2$) can be added by the use of its compounds like ICl, IBr etc.

Mechanism of addition of halogens

It is similar to mechanism involving addition of protic acids. However, here a **cyclic halonium ion** is formed in the first step instead of the usual carbocation.

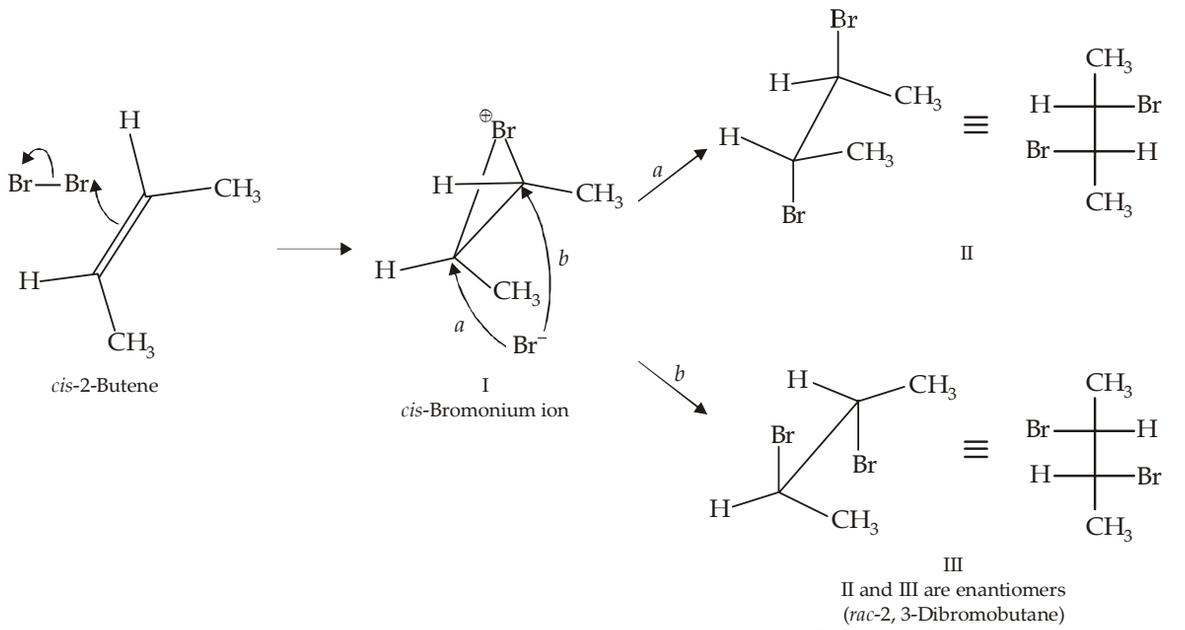




Here X^- = Br^- (from Br_2), OH^- (from H_2O) or other nucleophile added from outside.

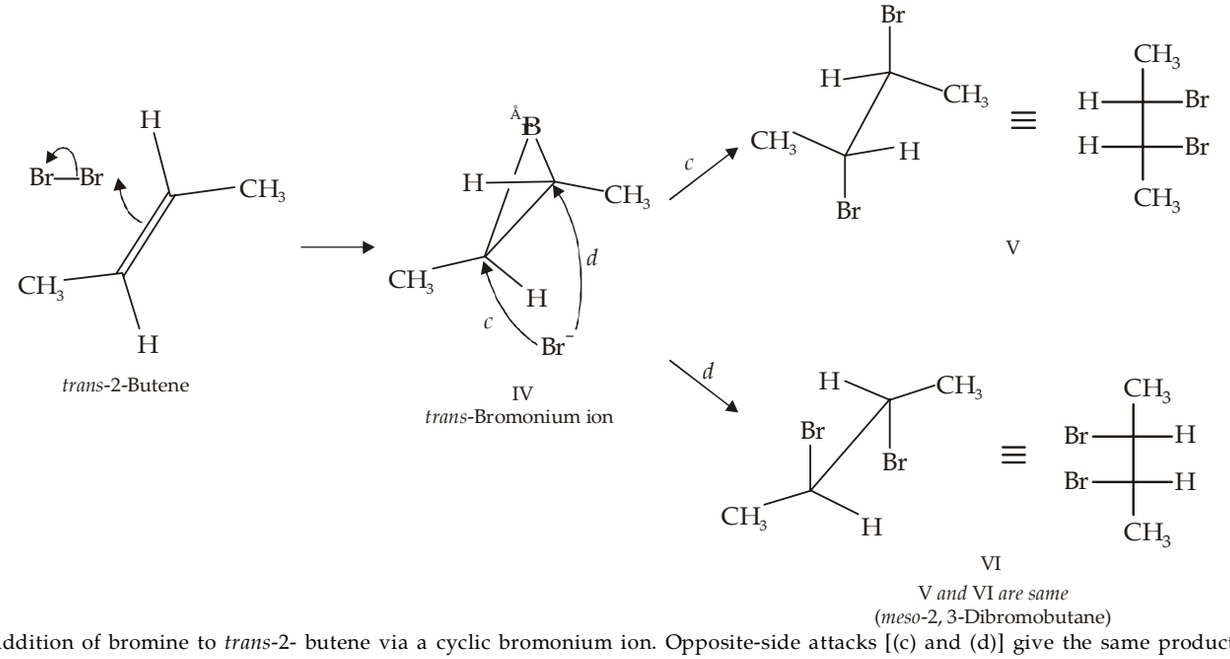
Evidence for the formation of bromonium ion comes from the **stereospecific addition** of bromine to isomeric 2-butenes. Thus *cis*-2-butene exclusively forms racemic -2, 3-dibromobutane and the *trans*-2-butene results in the exclusive formation of *meso-2,* 3-dibromobutane. This leads to the conclusion that addition of bromine to 2-butenes involves (*anti*)-addition, *i.e.* the two bromine atoms are attached to opposite faces (*anti*) of the double bond. This is possible only when cyclic bromonium ion is formed as an intermediate.

* Unlike a normal carbocation, all atoms in a cyclic halonium ion have filled octets. High reactivity of the ion is due to three membered ring and presence of positive charge on an electronegative halogen atom.



Addition of bromine to *cis*-2-butene *via* a cyclic bromonium ion. Opposite-side attacks [(a) and (b)] are equally likely, and give enantiomers in equal amounts.

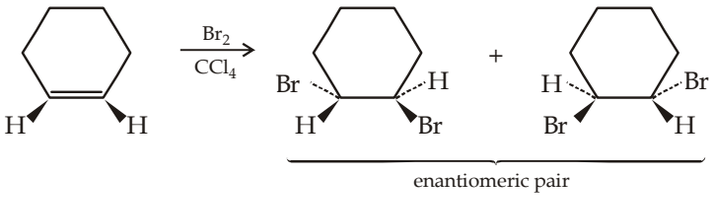
Since addition of Br_2 to the *cis*-alkene forms a pair of *threo* isomers, the two isomers II and III represent enantiomeric pair.



Addition of bromine to *trans*-2- butene via a cyclic bromonium ion. Opposite-side attacks [(c) and (d)] give the same product.

In case of erythro isomers, if the four substituents are same, the two isomers (V and VI) are identical and constitute meso compound.

Addition of Br_2 to a cyclic alkene results in the formation of only the pair of enantiomers in which two bromine atoms are added on opposite sides of the ring.



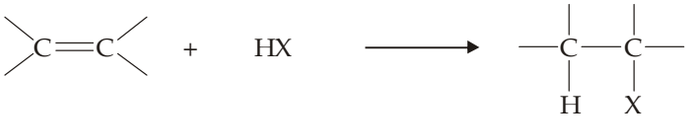
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TEST YOUR UNDERSTANDING - 6.6

1. Write the product of 1-butene with I–Cl.
2. Write down the major product obtained from the reaction of bromine with 1-butene if the reaction were carried out in each of the following solvents separately.
   (a) Dichloromethane (b) water (c) Methanol (d) Ethanol

6.5.3 Addition of Hydrogen Halides

Hydrogen halides add on carbon-carbon double bond forming alkyl halides, e.g.



(HCl, HBr or HI) Alkyl halide

Reaction is carried out by passing dry hydrogen halide directly into the alkene or by treating the two reactants in presence of moderately polar solvent like acetic acid which will dissolve both the polar HX and the non-polar alkene. *Aqueous solutions of hydrogen halides are not generally used because it may lead to addition of water on alkene.* Order of reactivity among hydrogen halides is

$$HI^{*} > HBr > HCl > HF \quad \textbf{(Relative reactivity of HX)}$$

Addition of hydrogen halides on unsymmetrical alkenes(*e.g.* $CH_3CH{=}CH_2$, $CH_2{=}CHCl$, $CH_3CH_2CH{=}CH_2$ etc.) may led to two products, but actually only one product is exclusively or predominantly formed. For example,

$$\underset{\text{Propene}}{CH_3CH=CH_2} \xrightarrow{HI} \underset{\text{Isopropyl iodide}}{CH_3.CHICH_3} + \underset{n\text{–Propyl iodide (Not formed)}}{CH_3CH_2CH_2I}$$

$$\underset{\text{Isobutene}}{(CH_3)_2C=CH_2} \xrightarrow[H_3PO_4]{KI} \underset{\text{tert–Butyl iodide}}{(CH_3)_2CICH_3} + \underset{\text{(Not formed)}}{(CH_3)_2CH.CH_2I}$$

Such *reactions which, from the standard point of orientation, give exclusively or nearly exclusively one of several possible isomeric products are called* **regioselective** (Latin *regio-direction*).

In such cases, addition is governed by Markownikoff's rule. "In the addition of HX to an alkene, the H attaches to the carbon with fewer alkyl substituents and th X attaches to the carbon with more alkyl substituents." When both ends of the double bond have the same degree of substitution, a mixture of two products is formed.

$$\underset{\text{2–Pentene}}{CH_3CH_2CH=CHCH_3} + HI \longrightarrow \underset{\text{3–Iodopentane (}\approx 50\%\text{)}}{CH_3CH_2CHICH_2CH_3} + \underset{\text{2–iodopentane (}\approx 50\%\text{)}}{CH_3CH_2CH_2CHICH_3}$$

Mechanism of addition of hydrogen halides on carbon-carbon double bond. It is similar to the general mechanism of electrophilic addition of acidic reagents to carbon-carbon double bonds.

(i) $\underset{\substack{\text{Br}\\ \text{Isopropyl bromide}}}{CH_3-\overset{|}{CH}-CH_3} \xleftarrow{Br^-} \underset{\substack{\text{A 2° carbocation}\\ \text{(More stable)}}}{CH_3-\overset{\oplus}{C}H-CH_3} \longleftarrow CH_3-CH=CH_2 + H^+ \longrightarrow \underset{\substack{\text{Less stable 1° carbocation}\\ \text{(Not formed)}}}{CH_3-CH_2-\overset{\oplus}{C}H_2}$

(ii) Similarly, for the addition of HBr on isobutene.

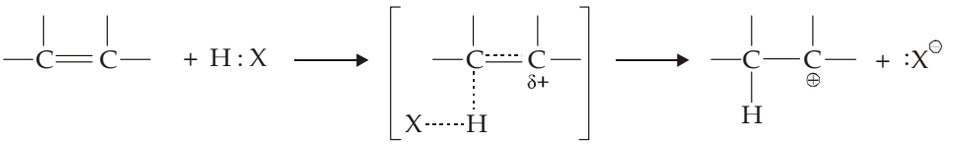
$$\underset{\substack{tert\text{- Butyl bromide}}}{(CH_3)_2CBr.CH_3} \xleftarrow{Br^-} \underset{\substack{\text{3° carbocation}\\ \text{(More stable)}}}{(CH_3)_2\overset{\oplus}{C}CH_3} \longleftarrow (CH_3)_2C=CH_2 \xrightarrow{H^+} \underset{\substack{\text{1° carbocation}\\ \text{(Less stable)}}}{(CH_3)_2CH\overset{\oplus}{C}H_2}$$

Thus, orientation in electrophilic addition in determined by the relative rates of formation of the carbocation which is same as their relative order of stability

$$3° > 2° > 1° > CH_3^+ \quad \textbf{(Rate of formation of carbocations)}$$

Thus now Markownikoffs rule can be defined as " *electrophilic addition to a carbon-carbon double bond involves the intermediate formation of the more stable carbocation* (reaction intermediate)". The rate of formation of a carbocation in electrophilic addition depends upon its stability can be proved by the stability of the transition state leading to carbocation.

* HI is usually generated in the reaction mixture by treating potassium iodide with phosphoric acid.



Transition state

Presence of electron-releasing groups tend to disperse the partial positive charge developing on carbon of the transition state leading to its greater stability. Recall that stabilization of transition state lowers E_{act} and permits a faster reaction.

Thus the sability of a carbocation determines not only the orientation of addition to an alkene (i.e the nature of the product), but also the *relative reactivities* of different alkenes.

Reactivity of alkenes towards HX

$$\underset{\text{I}}{(CH_3)_2C=CH_2} > \underset{\text{II}}{CH_3CH=CHCH_3}, \underset{\text{III}}{CH_3CH_2CH=CH_2} > \underset{\text{IV}}{CH_3CH=CH_2} > \underset{\text{V}}{CH_2=CH_2} > \underset{\text{VI}}{CH_2=CHCl}$$

(a) Alkene I is most reactive because here the most stable (3°) carbocation is formed as an intermediate.

(b) Alkenes II, III and IV form 2° carbocations, hence they have intermediate reactivity.

(c) Alkenes V and VI form 1° carbocation but the carbocation from VI will be less stable due to the presence of electron-attracting Cl which intensifies the positive charge on the carbon atom of the transition state.

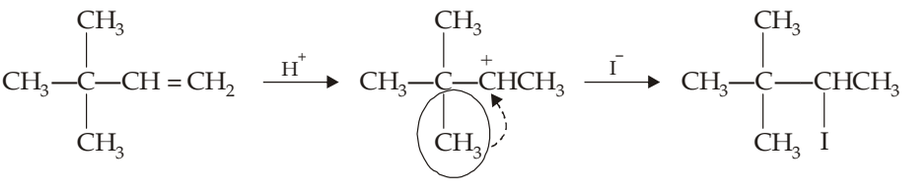
$\overset{+}{C}H_2CH_3$ (more stable) $\qquad$ $\overset{+}{C}H_2CH_2Cl$ (less stable)

$$F_3CCH=CH_2 \xrightarrow{HBr} \underset{\substack{\textit{anti}\text{-Markovnikov's product}\\ \textbf{(Major)}}}{F_3CCH_2CH_2Br} + \underset{\substack{|\\ Br\\ \text{(Minor)}}}{F_3CCHCH_3}$$

This is due to the presence of electron-withdrawing nature of the $-CF_3$ group which causes the 2° carbocation I to be less stable than II (a 1° carbocation)

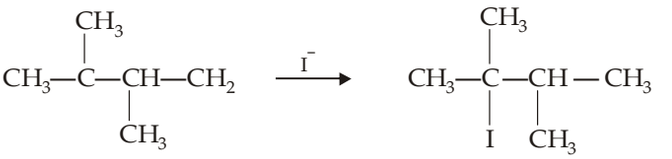
$F_3C \leftarrow \overset{+}{C}H-CH_3$ I (2°) $\qquad$ $F_3C \leftarrow CH_2-\overset{+}{C}H_2$ II (1°), more stable

In certain reactions, Markownikoff's addition product is also accompanied by unexpected product, rather the latter product predominates. This is found in those alkenes where the structure of carbocation, formed at the first step, permits rearrangement to the more stable carbocation. For example, addition of HI on 3, 3-dimethyl-1- butene gives not only the expected Markownikoff's product (3-iodo-2, 2-dimethylbutane), but also unexpected product, 2-iodo-2, 3-dimethylbutane.



3, 3-Dimethyl-1-butene $\qquad$ 2° Carbocation $\qquad$ 3-Iodo-2, 2-dimethylbutane

1, 2-CH_3^- shift



3° Carbocation (More stable) $\qquad$ 2-Iodo-2, 3-dimethylbutane **(Unexpected but major product)**

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Addition of hydrogen bromide on C=C in presence of peroxide, *anti* Markownikoff's addition or Peroxide effect. Addition of hydrogen bromide (not HCl and HI) in presence of peroxides takes place contrary to Markownikoff's rule. For instance, addition of hydrogen bromide to propene in presence of peroxide gives 1-bromopropane (*n*-propyl bromide) rather than 2-bromopropane (isopropyl bromide).

$$\underset{\text{(Not formed)}}{CH_3-\overset{\overset{Br}{|}}{CH}-CH_3} \xleftarrow[\text{peroxide}]{HBr} CH_3CH=CH_2 \xrightarrow[\text{peroxide}]{HBr} \underset{\text{1–Bromopropane}}{CH_3-CH_2CH_2Br}$$

This *reversal of the orientation of addition caused by the presence of peroxides* is known as **peroxide effect.**

Further, Kharasch and Mayo found that if peroxide formation is carefylly excluded during the reaction or certain *inhibitors* (*e.g* hydroquinone, diphenylamine, etc.) are added, the addition of HBr to alkenes follows Markownikoffs rule.

$$\underset{\text{2–Bromopropane}}{CH_3\overset{\overset{Br}{|}}{C}HCH_3} \xleftarrow[\text{no peroxide}]{HBr} CH_3CH=CH_2 \xrightarrow[\text{hydroquinone}]{HBr,\ \text{peroxide},} \underset{\text{2–Bromopropane}}{CH_3\overset{\overset{Br}{|}}{C}HCH_3}$$

Mechanism of peroxide effect. The *anti*-Markownikoffs addition (peroxide effect) is explained on the basis of the fact that in the presence of peroxides *addition takes place via free radical mechanism* rather than ionic mechanism in Markownikoff's addition. Peroxides are compounds containing the weak –O–O– linkage; they initiate the free radical formation and thus addition of HBr involves the following general steps of free radical reactions.

Step 1.

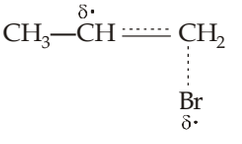
$$\left.\begin{aligned} RO-OR &\longrightarrow 2RO^{\bullet} \\ RO^{\bullet}+H:Br &\longrightarrow ROH+Br^{\bullet} \end{aligned}\right\} \text{Chain – initiating steps} \qquad \Delta H^0 = -15 \text{ kcal}$$

Step 2.

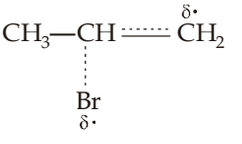
$$Br^{\bullet}+CH_3CH=CH_2 \longrightarrow \underset{\substack{\text{A2°radical}\\ \textbf{(more stable)}}}{CH_3\dot{C}HCH_2Br} \text{ or } \underset{\substack{\text{A1°radical}\\ \text{(less stable, not formed)}}}{CH_3CHBrCH_2} \Big\} \text{Chain – propagation steps} \qquad \Delta H^0 = -3 \text{ kcal}$$

$$\underset{\text{More stable 2° radical}}{CH_3\dot{C}HCH_2Br} + H:Br \longrightarrow \underset{\text{1–Bromopropane}}{CH_3CH_2CH_2Br} + Br^{\bullet} \qquad \Delta H^0 = -6 \text{ kcal}$$

Formation of the more stable 2° free radical ($CH_3\dot{C}HCH_2Br$) rather 1° free radical $CH_3CHBr\dot{C}H_2$ can again be explained on the basis of sability of their corresponding transition states.



Transition state leading to 2° radical, less crowded and hence more favourable



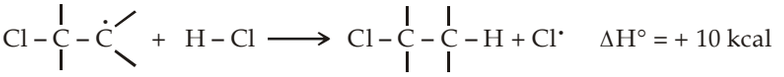
Transition state leading to 1° radical, more crowded and hence less favourable

NOTE THAT

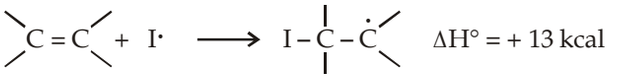
(i) *anti*-Markownikoffs addition is caused not only by the presence of peroxides but also by irradiation with light of a Wavelength known to dissociate HBr into $H^{\bullet}$ and $Br^{\bullet}$ atoms (radicals).

(ii) HF, HCl and HI do not exhibit peroxide effect because of their relative bond strength (HF > HCl > HBr > HI). Thus H—F and H—Cl bonds are too strong to break into free radicals, while H—I bond although dissociates easily into iodine radicals, they being bigger in size are not much reactive but recombine together to form iodine molecule.

Alternatively, the reaction of an alkyl radical with HCl is strongly endothermic, so the free-radical chain reaction is not effective for the addition of HCl.



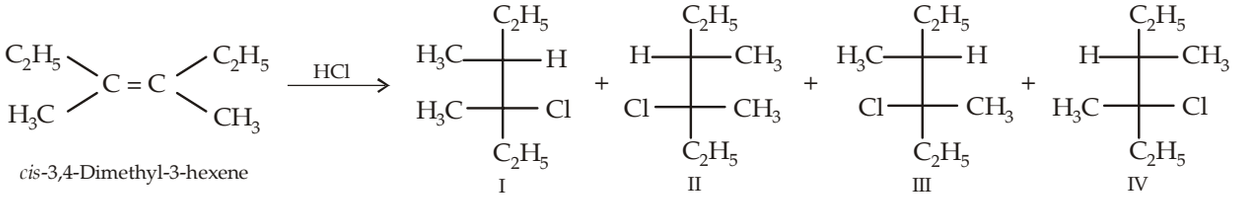
Similarly, the reaction of an iodine atom with an alkene is strongly endothermic and the free-radical addition of HI is not observed.



Thus only HBr has just the right reactivity for each step of the free-radical chain reaction to take place.

Stereochemistry of addition of hydrogen halides (Additions involving a carbocation or a free radical intermediate)

If two chirality centers are created as the result of an addition reaction through a carbocation or a radical intermediate, four stereoisomers can be obtained as products.



cis-3,4-Dimethyl-3-hexene

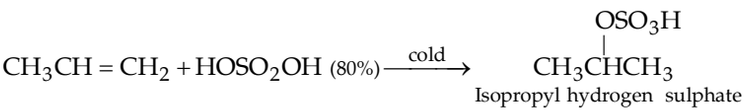
3-Chloro-3,4-dimethylhexane (Four stereoisomeric products)

However, I and II are identical and represent *meso* compound.

The four stereoisomers are obtained due to attack of Cl^- ion on the carbocation (formed in the first step by the addition of H^+ on alkene) from above or below. In short, the two atoms of the reagent (H and Cl) can add from **above-above, above-below, below-above, or below-below**. When the two atoms add to the same side or opposite sides of the double bond, the addition is called **syn addition** and **anti addition** respectively. Because the four stereoisomers obtained by the *cis* or *trans* alkene are identical, **the reaction is not stereospecific.**

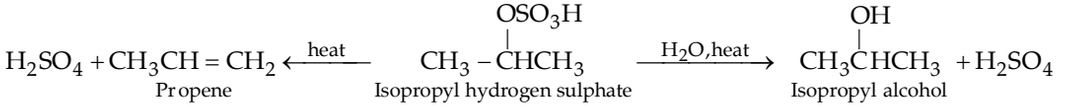
6.5.4 Addition of Sulphuric Acid

This is also proton initiated electrophilic addition and takes place in accordance with Markownikoff's rule forming **alkyl hydrogen sulphate** ($ROSO_3H$)



Since alkyl hydrogen sulphates are soluble in sulphuric acid, a clear solution is obtained.

Like alkyl sulphonates which are esters of sulphonic acids, alkyl hydrogen sulphates are esters of sulphuric acid and hence undergo hydrolysis when heated with water leading to the formation of alcohol and sulphuric acid. Alkyl hydrogen sulphates, when heated alone, regenerate alkenes.



Thus reaction of alkene with sulphuric acid is used in the preparation of alcohols but since the addition of sulphuric acid follows Markownikoff's rule, certain alcohols can't be prepared by this method, for example, **isopropyl alcohol can be prepared but not *n*-propyl ; *tert*-butyl alcohol can be prepared but isobutyl alcohol not.**

The fact that alkenes dissolve in cold concentrated alcohol to form alkyl hydrogen sulphate, which on heating regenerates the parent alkene, is used in the purification and separation of alkenes from alkane (alkanes are insoluble in sulphuric acid).

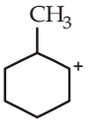
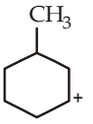
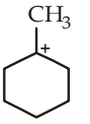
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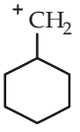
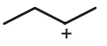
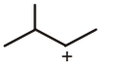
TEST YOUR UNDERSTANDING - 6.7

1. Predict the possible products formed by the addition of HBr on
(i) 3– methyl-1-butene (ii) 3, 3-dimethyl -1-butene

2. Convert propene to (i) CH_3CHDCH_2D and (ii) CH_3CHDCH_3

3. Which of the following carbocations would you expect to rearrange?

(a)  (b)  (c) 

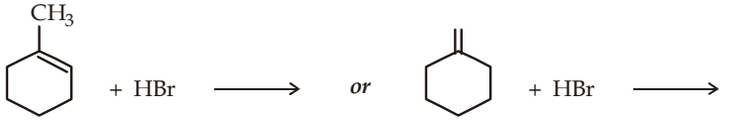
(d)  (e)  (f) 

4. What will be the major product in each of the following reaction?

(a) $CH_3CH = CH_2 + 2NaI + HBr \longrightarrow$ (b) $CH_3CH = CHCH_3 + HCl \xrightarrow{H_2O}$

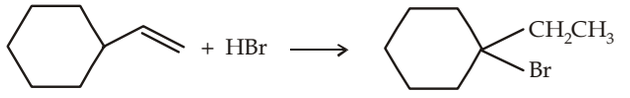
(c) $CH_3CH = CHCH_3 + HBr \xrightarrow{CH_3OH}$

5. Which of the following reaction is highly regioselective?



6. Which member of each pair is more reactive toward addition of HBr?
(a) 1-Propene or 2-methylpropene (b) Cyclohexene of 1-methylcyclohexene (c) 1-Butene or 1,3-butadiene

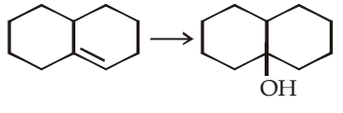
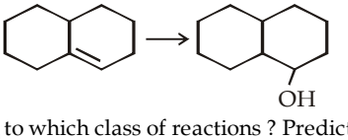
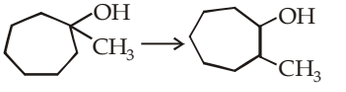
7. Propose mechanism for the following transformation.



8. (a) When Z-3-methyl-3-hexene undergoes hydroboration-oxidation, two isomeric products are formed. What is the relationship between these isomers?
(b) Write the hydroboration-oxidation product(s) of the E-isomer of the above problem. Give the relationship between the products formed from the Z- and E-isomers.

9. When HBr adds across the double bond of 1, 2-dimethylcyclopentene, the product is a mixture of the *cis*- and *trans*- isomers. Explain why this addition is not stereospecific?

10. Show how the following transformations are accomplished?

(a)  (b)  (c) 

11. Hydrolysis of alkyl hydrogen sulphates belong to which class of reactions ? Predict the mechanism or mechanisms for hydrolysis of ethyl hydrogen sulphate and *tert*-butyl hydrogen sulphate.

6.5.5 Addition of Water (Acid -catalyzed hydration)

Water adds directly to the more reactive alkenes in presence of a strongly acidic catalyst forming alcohols. Addition occurs according to Markownikoff's rule.

$$CH_3CH = CH_2 \xrightarrow{H^+} CH_3\overset{+}{C}HCH_3 \xrightarrow{H_2\ddot{O}:} CH_3\underset{|}{\overset{OH_2^{\oplus}}{C}}HCH_3 \xrightarrow{-H^+} CH_3\underset{|}{\overset{OH}{C}}HCH_3 + H^+$$

For dehydrating alcohols, a conc. dehydrating acid like H_2SO_4 or H_3PO_4 is used to drive the equilibrium in favour of alkene. Hydration of an alkene, on the other hand, is done by adding excess water to drive the equilibrium in favour of alcohol.

6.5.6 Addition of Hypohalous Acids (HOCl, HOBr or halogen + H_2O)

This reaction is similar to that of the addition of halogen in the presence of water, where we get haloalcohols (also known as *halohydrins).*

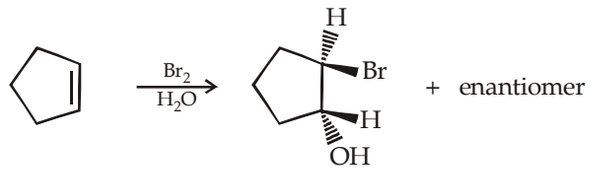
Halohydrin formation does not take place by direct reaction of an alkene with HOCl or HOBr; rather the addition is done indirectly by reaction of the alkene with either Cl_2 or Br_2 in presence of water.

$$CH_2 = CH_2 \xrightarrow[H_2O]{Cl_2} CH_2OHCH_2Cl$$

When halogenation is done with no solvent or with an inert solvent like CCl_4 or $CHCl_3$, only the halide ion (from halogen) is available as a nucleophile to attack the halonium ion forming dihalide as the final product. But when an alkene reacts with a halogen in presence of a nucleophilic solvent like water, although there are two nucleophiles X^- and H_2O, but H_2O being the solvent is present in large amount than Br^-, hence it will preferentially attack the halonium ion forming halohydrin as the final product.

$$CH_2(Cl^+) - CH_2 \xrightarrow{H_2O} ClCH_2CH_2\overset{+}{O}H_2 \xrightarrow{H_2O} ClCH_2CH_2OH + H_3O^+$$

Since the mechanism involves a halonium ion, the stereochemistry of addition is *anti*. For example, addition of bromine water to cyclopentene gives *trans*-2-bromocyclopentanol.

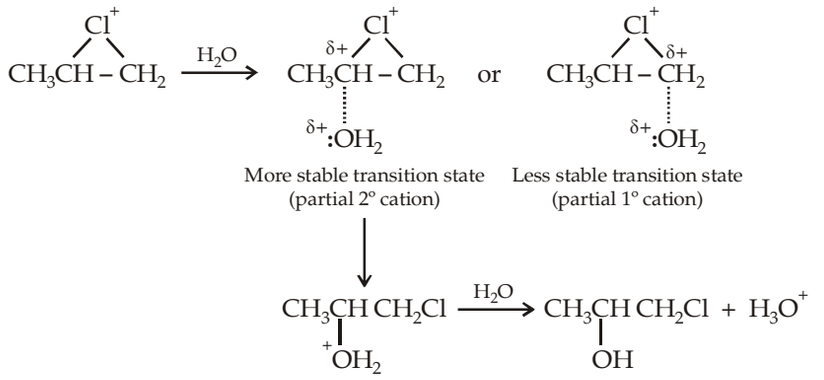


Cyclopentene *trans*-2-Bromocyclopentanol

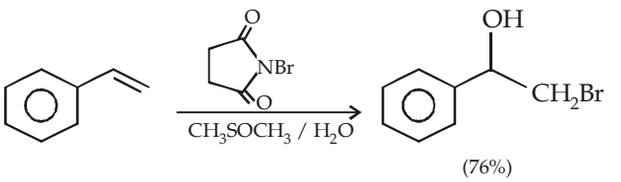
Further, halohydrin formation follows Markownikov's rule (the electrophilic end, the chlorine atom, adds to the less highly substituted carbon of the double bond and nucleophilic end, the hydroxyl group, adds to the more highly substituted carbon of the double bond.

$$CH_3CH = CH_2 + Cl_2 + H_2O \longrightarrow CH_3\underset{|}{\overset{OH}{C}}HCH_2Cl + HCl$$

The Markovnikov orientation is explained by the stability of the transition state, formed by the attack of nucleophile on the halonium ion.



However, only few alkenes are soluble in water and thus bromohydrin formation is often carried out in a solvent such as aqueous dimethyl sulphoxide, CH_3SOCH_3 (DMSO), using N-bromosuccinimide (NBS) as a source of bromine. NBS is a stable, easily handled compound that decomposes slowly in water to yield Br_2 at a controlled rate.

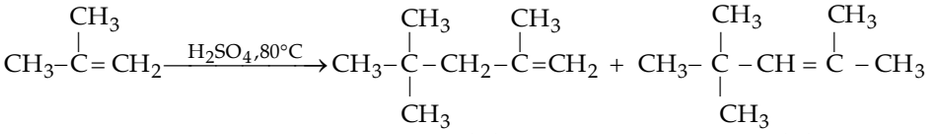


(76%)

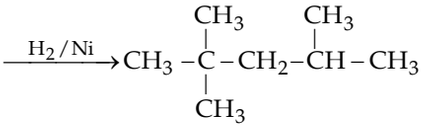
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6.5.7 Dimerization

Isobutene, when heated with sulphuric acid, phosphoric acid or HF undergoes dimerization forming a mixture of two alkenes each having 8 carbon atoms. Hydrogenation of either of these alkenes produces the same alkane, 2, 2, 4-trimethylpentane, commonly known as **iso-octane.**



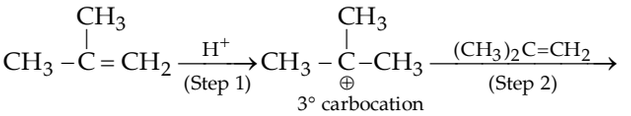
2, 4, 4 - Trimethyl -1-pentene 2, 4, 4-Trimthyl-2-pentene **(major)**



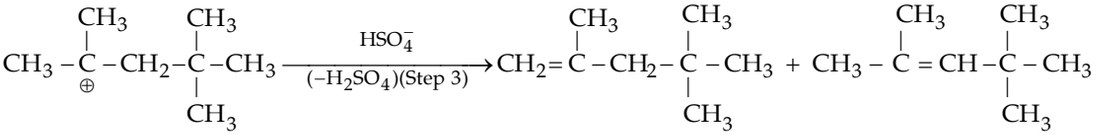
2,2,4–Trimethylpentane (Isooctane)

Note that this is in not an industrial method for the preparation of isooctane.

Mechanism : Since reaction is catalysted by acids, it is on electrophilic addition and proceeds as below :



3° carbocation



Dimeric 3° carbocation (major) A (minor) B

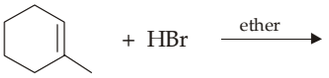
Under suitable conditions, the dimeric 3° carbocation may further take a fresh molecule of isobutene to form trimeric 3° carbocation and so on, leading to the formation of a polymer.

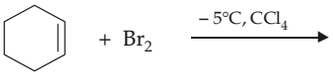
The unexpected product ratio, i.e. formation of A as major product is because of less steric hindrance. The expected Saytzeff product B is sterically hindered because the bulky *tert*-butyl group is *cis* to a methyl group.

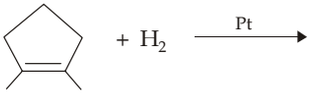
Dimerization of alkenes can't be carried out by acid catalysts like HCl, HBr, or HI because the conjugate bases of these acids i.e. Cl^-, Br^-, and I^- are good nucleophiles and hence will attack the carbocation in preference to the alkene leading to addition of HX on the alkene instead of dimerisation.

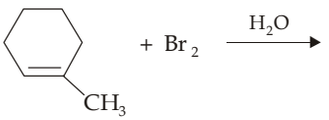
TEST YOUR UNDERSTANDING - 6.8

1. Predict the nature of the products :

(i) 

(ii) 

(iii) 

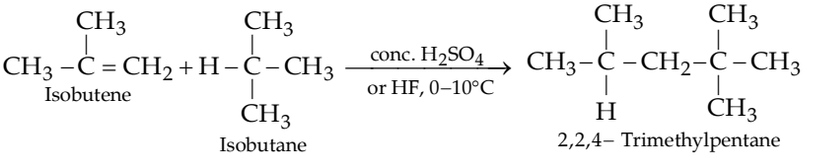
(iv) 

2. (a) Write down the intermediate dimeric carbocation formed during dimerization of propene.

(b) Write the structural formula for the major trimeric alkene formed from iosbutene.

6.5.8 Alkylation

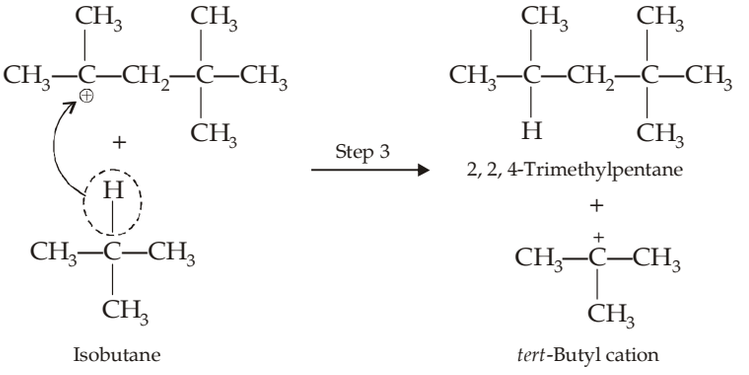
Branched chain alkanes (especially those which contain 3° hydrogen atom) add across a double bond in the presence of an acidic catalyst to form higher alkanes, *e.g.*



This reaction is used to prepare isooctane on industrial scale.

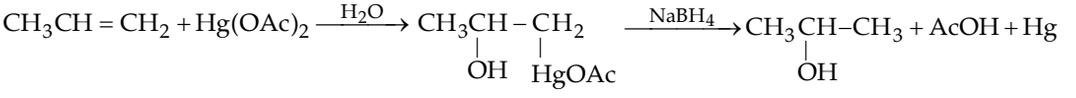
Mechanism : Mechanism is similar to that of dimerization upto step -2 leading to the formation of a carbocation having eight carbon atoms. In step 3, the carbocation abstracts a hydrogen atom with its pair of electrons (*i. e.* **a hydride ion)** from alkane molecule to form isooctane and a stable (3°) *tert* - butyl cation. This reaction shows that

(i) **a carbocation is extremely acidic in nature,** and (*ii)* inertness of alkanes is greatly exaggerated since alkanes can react quite readily, with a strong acid, and that too in a heterolytic manner. Remember that 1, 2-shift accompanying the rearrangement of carbocations is commonly encountered, however, this type of hydride transfer was *intramolecular* (within a molecule), here it is intermolecular (between two molecules).



6.5.9 Hydration by Oxymercuration - Demercuration

Many alkenes do not easily undergo hydration in aqueous acid. Some alkenes are nearly insoluble in aqueous acid, and others undergo side reactions like polymerization or charring under these strongly acidic conditions. In some cases, the overall equilibrium favours the alkene rather than the alcohol. Oxymercuration - demercuration works with many alkenes that do not easily undergo direct hydration. Alkenes react with mercuric acetate in presence of water to form hydroxymercurial compounds (*oxymercuration*) which on reduction give alcohols (*demercuration*).



This way of hydration has following advantages over direct hydration.

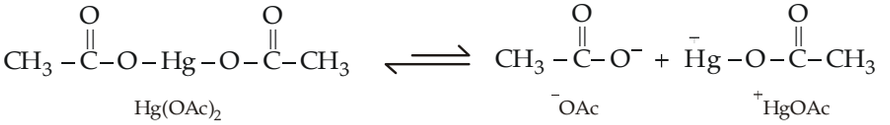
(a) The process is fast (completed within minutes) and convenient (the alkene is added at room temperature to an aqueous solution of mercuric acetate diluted with the solvent, tetrahydrofuran).

(b) The reaction takes place under mild conditions and gives excellent results (> 90%).

(c) The organomercurial intermediate compound is not isolated but is simply reduced in *situ* by sodium borohydride.

(d) No free carbocation is formed, so no question of rearrangement.

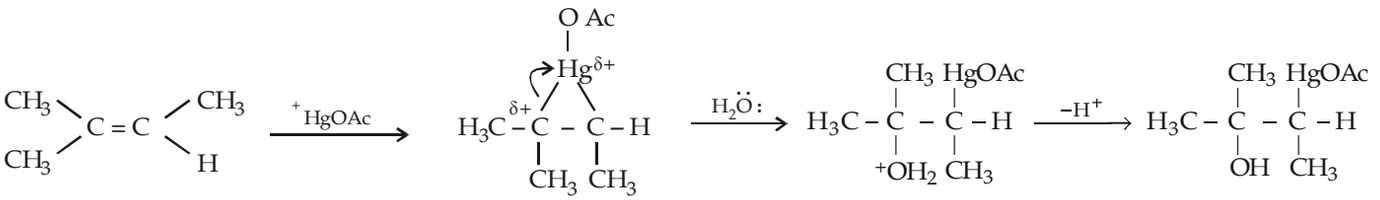
Mechanism : Oxymercuration-demercuration is highly regioselective and yields alcohols corresponding to Markovnikoff's addition of water. The first step (**oxymercuration**) is initiated by the dissociation of mercuric acetate to form the electrophile, $\overset{+}{H}gOAc$.



Mercuric acetate may act as an electrophile as such because of presence of electrons in 5 *d* orbital of Hg. The electrophile attacks on the double bond to form a cyclic mercurium ion as intermediate which is indicated by the absence of formation of products corresponding to rearranged carbocation. The cyclic mercurium ion reacts with water (solvent) to give an organomercurial alcohol.

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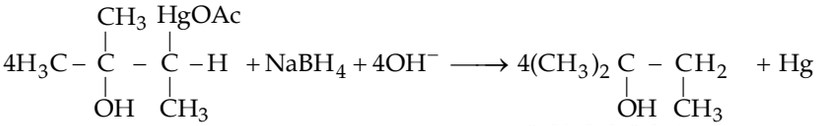
Attack by water on the mercurinium ion comes from the opposite side of the ring, and at the more highly substituted carbon, thus the hydroxyl group and the mercury atoms are added on opposite sides (***anti* addition**).



2-Methyl-2-butene

In unsymmetrical mercurinium ion more substituted C has positive charge (3° carbocation)

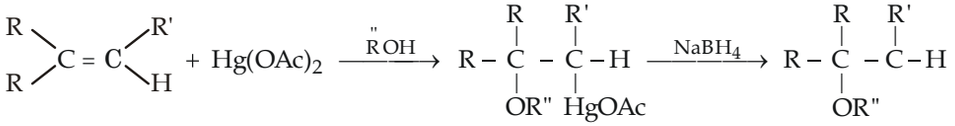
Mercury is removed in the second step (**demercuration**) by sodium borohydride, a reducing agent.



2–Methyl–2–butanol (Markovnikov product)

Alkoxymercuration-demercuration

When mercuration take place in presence of alcohol (solvent), the alcohol serves as a nucleophile to form alkoxymercurial compound (*alkoxymercuration*) which as in the above reaction can be reduced (*deoxymercuration*) with $NaBH_4$ to form ether as the final product.



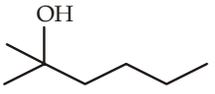
TEST YOUR UNDERSTANDING - 6.9

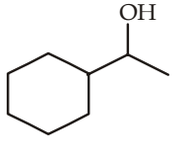
1. Predict the major products in each of the following reactions :

(a) 1-Methylcyclohexane + aqueous mercuric acetate (b) 1-Methylcyclohexene + mercuric acetate in presence of ethanol

(c) the product from part (b) is treated with $NaBH_4$

2. From which alkenes the following alcohols have been prepared?

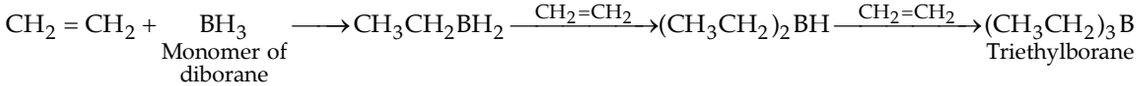
(a) 

(b) 

3. Give steps involved in the conversion of 1-iodo-2-methylcyclopentane to 1-methylcyclopentanol.

6.5.10 Hydroboration or Hydroboronation

Hydroboration involves addition of a B – H bond of borane (BH_3) to an alkene to yield organoborane intermediates, RBH_2, R_2BH and R_3B. Since BH_3 has three hydrogens, addition occurs in three steps forming R_3B as the final product.

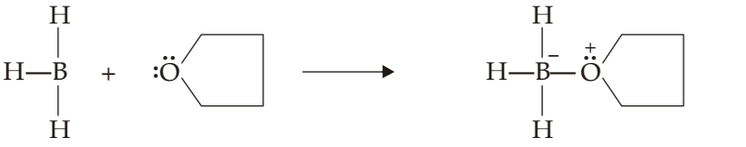


Monomer of diborane

Triethylborane

(i) The reaction procedure is simple and convenient leading to excellent yield.

(ii) Hydroboration is carried out in ether, *viz.* tetrahydrofuran or diglyme (diethylene glycol methyl ether). Commercially diborane is available in tetrahydrofuran solution, where it exists as the monomer in the form of acid-base complex with the solvent.



Borane (Acid) Tetrahydrofuran (Base) Borane-tetrahydrofuran complex

(iii) Alkylboranes are important intermediates for the synthesis of alcohols and alkanes. These are not isolated and converted in *situ* to the corresponding product.

Preparation of alcohols : Alkylboranes formed by hydroboration of alkenes can be easily oxidised by alkaline hydrogen peroxide in which boron is replaced by –OH forming alcohol as the final product

$$3CH_2=CH_2+BH_3 \xrightarrow{THF} \underset{\text{Triethylborane}}{(CH_3CH_2)_3B} + 3H_2O_2 \xrightarrow{OH^-} \underset{\text{Ethyl alcohol}}{3CH_3CH_2OH} + \underset{\text{Boric acid}}{B(OH)_3}$$

Thus in *hydroboration-oxidation* reaction three moles of alkene react with one mole of BH_3 to form three moles of alcohol. (hydration of alkenes) Hydration of alkenes through hydroboration is highly regioselective as we will observe in the following examples that the alcohol formed correponds to ***anti*-Markownikoff's addition of water (opposite to oxymercuration-demercuration and by direct acid-catalysed hydration).**

$$CH_3CH=CH_2 \xrightarrow[(ii)\,H_2O_2,\,OH^-]{(i)\,(BH_3)_2} \underset{n-\text{Propyl alcohol}}{CH_3CH_2CH_2OH} \quad \lim_{\delta x \to 0}$$

$$\underset{\text{2–Methyl–2–butene}}{CH_3-CH=C(CH_3)_2} \longrightarrow \underset{\text{3–Methyl–2–butanol}}{CH_3CH(OH)-CH(CH_3)_2}$$

$$CH_3-\overset{CH_3}{\overset{|}{C}}-CH=CH_2 \xrightarrow[(ii)\,H_2O_2/OH^-]{(i)\,(BH_3)_2} CH_3-\overset{CH_3}{\overset{|}{C}}-CH_2-CH_2OH$$

3, 3–Dimethyl–1–butanol (1°)

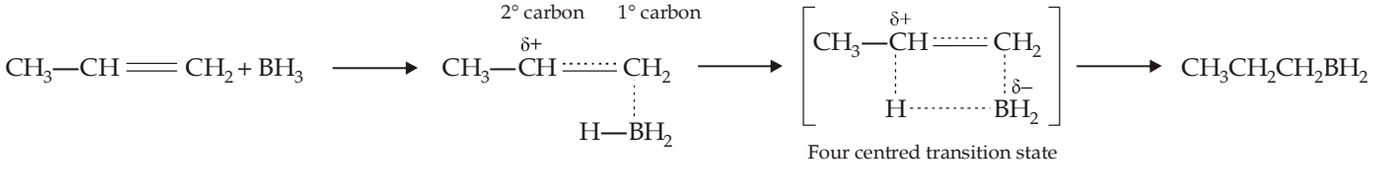
Formation of 1° alcohol indicates that **rearrangement does not occur in hydroboration** leading to the fact that carbocations are not formed as intermediates.

Preparation of alkanes : Alkylboranes are readily cleaved to alkanes on boiling with acetic or propanoic acid.

$$(CH_3CH_2CH_2)_3B \xrightarrow{C_2H_5COOH} \underset{\text{Propane}}{3CH_3CH_2CH_3}$$

Thus **hydroboration-acid hydrolysis** provides a valuable method for reducing a double bond.

Mechanism of hydroboration : Because of vacant orbital on boron, borane may be regarded as an electrophile and thus attacks π electrons of the alkene; positive charge on the alkene develops on that carbon atom which is best able to support it. Moreover, steric hindrance favours addition of boron to the less hindered carbon of the double bond.



2° carbon 1° carbon

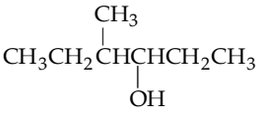
Four centred transition state

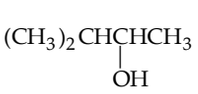
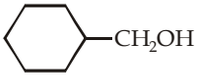
Because of the four-centre mechanism, hydroboration is a *cis*-addition i.e., boron and hydrogen add across the double bond on the same side of the molecule. During the oxidation step, the boron is replaced by an –OH with the same stereochemistry, overall resulting in *syn* non-Markovnikov addition of water. Thus 1-methylcyclopentene on hydroboration-oxidation yields *trans*-2-methylcyclopentanol. Further, a racemic mixture is expected because a chiral product is formed from achiral reagents. Alkylboranes behave like borane and react further with excess of alkene forming di-and tri-alkylboranes. The rate of hydroboration decreases with the increase in the number of alkyl substituents on the double bond.

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TEST YOUR UNDERSTANDING - 6.10

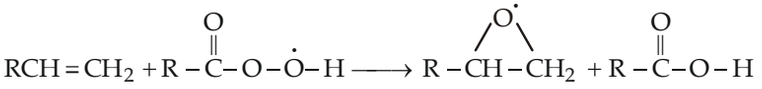
1. Convert $CH_3CH = CH_2$ to $CH_3CH_2CH_2D$.
2. What product would you obtain from the reaction of 1-ethylcyclopentene with
   (a) BH_3 followed by H_2O_2, OH^- (b) $Hg(OAc)_2$ followed by $NaBH_4$
3. Predict the starting material for preparing following alcohol by hydration method so that a quantitative yield can be obtained.



4. What product will be formed from hydroboration-oxidation of 1-methylcyclopentene with deuterated borane, BD_3? Show both the stereochemistry and regiochemistry of the product.
5. What alkenes might be used for preparing the following alcohols by hydroboration-oxidation?
   (a) $(CH_3)_2CH\ CH_2CH_2OH$ (b)  (c) 

6.5.11 Epioxidation and *anti*-Hydroxylation of Alkenes

Alkenes when treated with a peroxyacid form **epoxides**, also called **oxiranes**; commonly used peroxyacids are peroxyacetic acid, peroxybenzoic acid, and *m*-chloroperoxybenzoic acid.



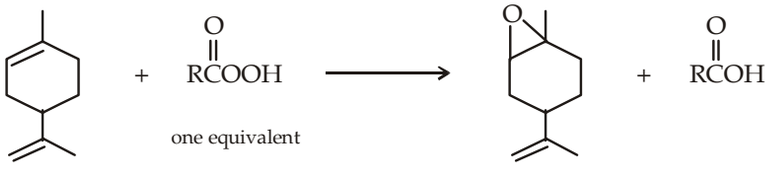
Recall that an oxygen-oxygen bond is weak and easily broken. The oxygen atom of the OH group (marked by asterisk) accepts a pair of electrons from the π bond of the alkene. Thus epoxidation is an example of electrophilic addition, where peroxy acid act as an electrophile and alkene acts as a nucleophile. The mechanism is analogous to the mechanism for the addition of bromine to a double bond. In short, epoxidation is a concerted process where several bonds are broken and several are formed at the same time through a cyclic transition state.

(i) Since the epoxidation takes place in one step, the epoxide retains the stereochemistry of the alkene (an example of **stereospecific reaction**).

(ii) If the solution is not too acidic, epoxides are easily isolated as stable products, if the acid used is strong, epoxides are converted to glycols.

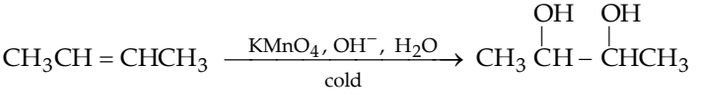
(iii) If the acid used is weakly acidic (e.g. peroxybenzoic acid in CCl_4), epoxides are the final products. However, if peracetic acid in strongly acidic water solution is used, epoxides are protonated and finally converted to *trans*-glycol.

(iv) Presence of electron-releasing groups on the doubly bonded carbon atom increases the electron density of the double bond and hence increases the rate of epoxidation. Thus, if a diene is treated with limited amount of peroxy acid, the most substituted double bond will be epoxidized.



6.5.12 *syn*-Hydroxylation of Alkenes

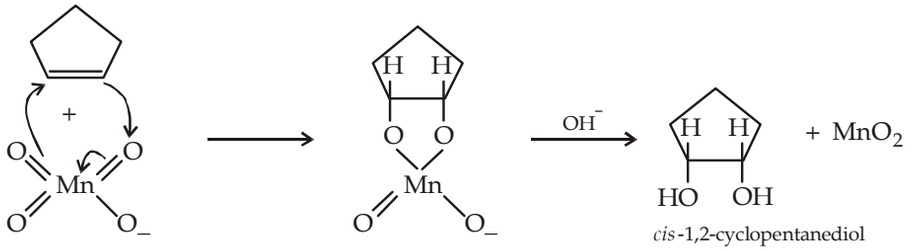
An alkene can be oxidised to *cis*-1,2-glycols either by potassium permanganate in a cold basic solution or by osmium tetroxide, also called *osmic acid*.



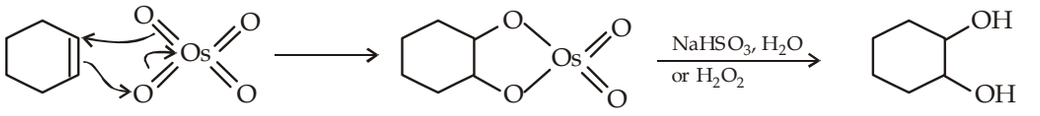
The solution must be basic and reaction must be carried out at room temperature or below, in case the solution is acidic or it is heated, the diol will be further oxidised.

$$CH_3CH=CHCH_3 \xrightarrow[\text{or } OsO_4,\ H_2O_2]{OsO_4\ /\ NaHSO_3\ (\text{or } Na_2SO_3),\ H_2O} CH_3\overset{OH}{\underset{|}{C}}H-\overset{OH}{\underset{|}{C}}HCH_3$$

Since both Mn and Os are in highly positive oxidation state (+7 and +8, respectively), they attract electrons and the reactions occur to form cyclic intermediates. Further since the two carbon-oxygen bonds are formed simultaneously with the cyclic ester, the hydroxyl groups appear to the same face of the double bond (*syn*-**hydroxylation**). Therefore, such oxidations are highly *stereoselective*.



cis-1,2-cyclopentanediol



cis-1,2-cyclohexanediol

Hydrogen peroxide hydrolyzes the osmate ester and reoxidizes osmium to osmium tetroxide

Of the two reagents used for *syn*-hydroxylation, osmium tetroxide gives the higher yields. However, the reagent is expensive, highly toxic and volatile.

6.5.13 Oxidative Cleavage of Alkenes.

(i) *Oxidation with hot alkaline permanganate, acidic permanganate or acidic dichromate or potassium periodate ($NaIO_4$) in presence of catalytic amounts of $KMnO_4$.* Aldehydes, ketones, carboxylic acids and carbon dioxide are formed.

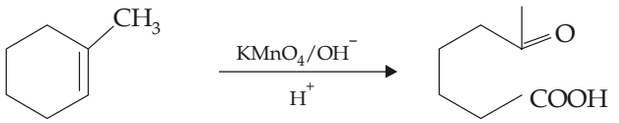
(a) The terminal CH_2 group ($=CH_2$) of alkenes is completely oxidised to CO_2 and H_2O.

(b) A doubly bonded carbon atom having an alkyl group ($=CHCH_3$) is oxidised to aldehyde which is further oxidised to carboxylic acid.

(c) A doubly bonded carbon atom having two alkyl groups ($=CR_2$) is oxidised to ketone.

$$CH_3CH_2CH=CH_2 \xrightarrow[(ii)\ H^+]{(i)KMnO_4,OH^-} CH_3CH_2\overset{CH_3CH_2COOH}{\underset{\uparrow}{C}}HO + CO_2 + H_2O$$

$$(CH_3)_2C=CHCH_3 \xrightarrow[(ii)H^+]{(i)KMnO_4,\ OH^-} (CH_3)_2C=O + CH_3COOH$$



1-Methylcyclohexene

(ii) *Oxidation with potassium periodate or lead tetra-acetate (mild oxidising agents).* This is similar to the above oxidation except that here aldehyde, if formed, is not further oxidised to acid.

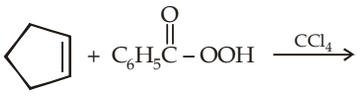
$$CH_3CH=CH_2 \xrightarrow[\text{or } Pb(OAc)_4]{NaIO_4} CH_3CHO + CH_2O$$

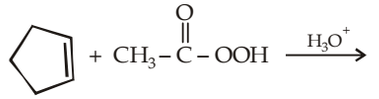
$$CH_3CH=C(CH_3)_2 \xrightarrow{NaIO_4} CH_3CHO + O=C(CH_3)_2$$

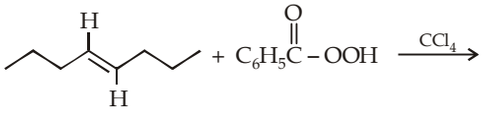
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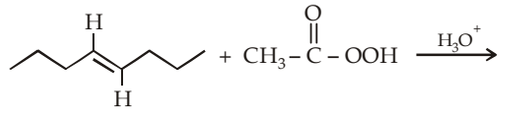
TEST YOUR UNDERSTANDING - 6.11

1. Write down the products in each of the following reactions; mentioning the stereochemistry in each case.

(a) 

(b) 

(c) 

(d) 

2. Predict the major product of the following reactions, including stereochemistry.

(a) Cyclohexene + peroxyacetic acid in water

(b) Methylenecyclohexane + OsO_4, $NaHSO_3$

(c) *cis*-2-Pentene + OsO_4 / H_2O_2

(d) *cis*-2-Pentene + peroxyacetic acid in water

(e) *trans*-2-Pentene + OsO_4 / H_2O_2

(f) *trans*-2-Pentene + peroxyacetic acid in water

3. *Z*-2-Pentene when treated with OsO_4 in pyridine followed by treatment with $NaHSO_3$ in water gives a diol that is optically inactive and can't be resolved, while similar reaction with *E*-2-butene gives a diol that is optically inactive but can be resolved into enantiomers. Explain.

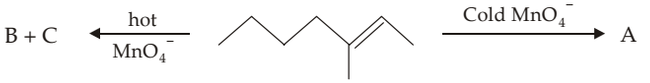
4. Give the products formed in each case :

(a) Cyclopentene is oxidised with osmium tetroxide.

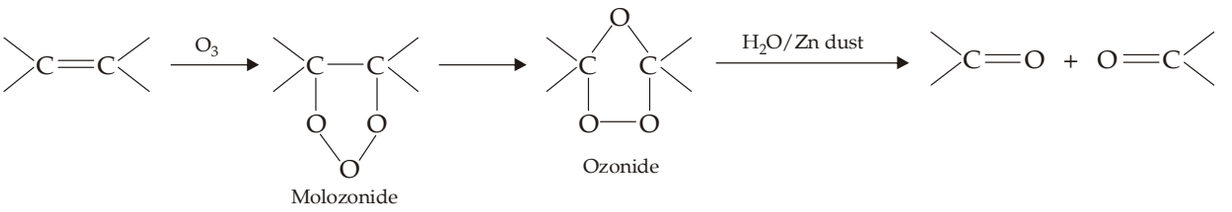
(b) *trans*-Butene-2 is oxidised with dilute alkaline cold $KMnO_4$ solution

(c) Maleic acid is oxidised with performic acid

5. Identify A, B and C in the following set :



(iii) *Oxidative cleavage by ozone (ozonolysis).* Ozonolysis is carried out in two stages. At first stage ozone is added by passing ozone gas into a solution of the alkene in some inert solvent like CCl_4 to form unstable compound called initial ozonide (**Primary ozonide or molozonide**) which rearranges spontaneously to stable ozonide. In the second stage, highly explosive ozonide is hydrolysed in situ with water in presence of a reducing agent such as zinc or dimethyl sulphide to form carbonyl compounds (**reductive ozonolysis**).



In short, $CH_3CH_2CH=C(CH_3)_2 \xrightarrow[(ii)H_2O/Zn]{(i)O_3} CH_3CH_2CHO + O=C(CH_3)_2$

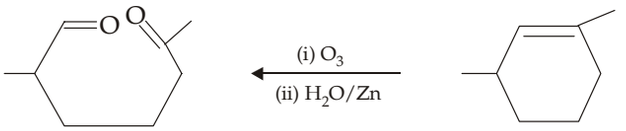
The function of a reducing agent is to prevent the oxidation of aldehydes to carboxylic acids.

If the ozonide is cleaved in the presence of an oxidizing agent (e.g. H_2O_2), the products formed will be ketones and/or carboxylic acids (**oxidative ozonolysis**).

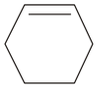
Knowing the number and structure of carbonyl compouns, the structure of the parent alkene can be easily worked out. For this first write down the structural formulae of the products. Remove oxygen atoms of the ketonic or aldehydic groups and then join the two carbonyl carbon atoms of the two products by a double bond. These can be judged by the following examples :

(a) $\underset{\text{Butanal}}{CH_3CH_2CH_2CHO} + \underset{\text{Ethanal}}{OHC.CH_3} \xleftarrow[(ii)\ H_2O/Zn]{(i)O_3} \underset{\text{2–Hexene}}{CH_3CH_2CH_2CH=CHCH_3}$

(b) $\underset{\text{Propanal}}{CH_3CH_2CHO} + \underset{\text{Propanone}}{OC(CH_3)_2} \xleftarrow[(ii)\ H_2O/Zn]{O_3} \underset{\text{2– Methyl-2-pentene}}{CH_3CH_2CH=C(CH_3)_2}$

(c) 

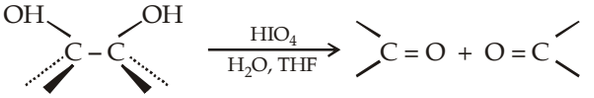
(d) $2CH_3COCH_3 + OHC.CH_2COCH_3 \longleftarrow (CH_3)_2C = CH.CH_2.\overset{CH_3}{\overset{|}{C}} = C(CH_3)_2$

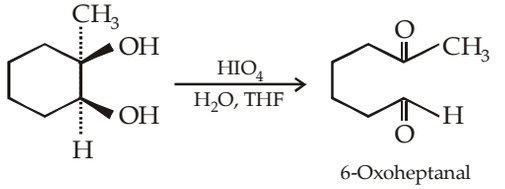
(e) $OHC\,.\,(CH_2)_4CHO \longleftarrow$ 

(f) $CH_3COCH_2CHO + 2HCHO \longleftarrow H_2C = CH.CH_2\overset{CH_3}{\overset{|}{C}} = CH_2$

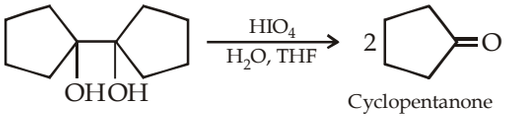
6.5.14 1, 2-Diol Cleavage

1, 2-Diols are oxidatively cleaved by reaction with periodic acid to yield carbonyl compounds.





6-Oxoheptanal



Cyclopentanone

Cleavage of alkenes through hydroxylation with OsO_4 followed by diol cleavage with HIO_4 is an excellent alternative to direct alkene cleavage with $KMnO_4$ or ozone.

6.5.15 Substitution Reactions

Due to the presence of alkyl group in higher alkenes, higher alkenes undergo substitution reactions, under suitable conditions, at allylic position. For example, propene when heated with chlorine at high temperatures (500 – 600°C) gives 3-choro-1-propene commonly known as **allyl chloride** (bromine behaves similarly), recall that addition of halogens to alkenes takes place at low temperature and in presence of inert solvent like carbon tetrachloride.

$$\underset{\text{1,2–Dichloropropane}}{CH_3\overset{Cl}{\overset{|}{C}}H-\overset{Cl}{\overset{|}{C}}H_2} \xleftarrow[\text{low temp.}]{Cl_2/CCl_4} CH_3CH = CH_2 \xrightarrow[500-600°C]{Cl_2} \underset{\text{3–chloro-1-propene}}{CH_2ClCH = CH_2}$$

Halogenations of alkenes similar to like *free-radical substitution* of alkanes, in alkenes halogenation always takes place at the allylic position, $(-*CH_2-CH=CH_2)$ marked by asterisk. This is due to ease of abstraction of allylic hydrogen atom. The *relative ease of abstraction of hydrogen atoms* corresponds to the following order :

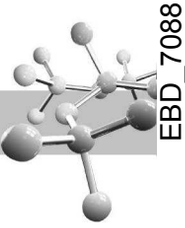
Allylic H atom > 3° > 2° >1°>CH_4 > Vinylic

The same order is also found to be the *relative order of stability of the various free radicals.*

Allylic free radical > 3° > 2° >1°>$CH_3^{\bullet}$> Vinylic

Higher stability of ally radical is due to resonance.

Mechanism of allylic chlorination.



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$$CH_3-CH=CH_2 \xrightarrow{Cl^\bullet} {}^\bullet CH_2-CH=CH_2 \xrightarrow{Cl_2} \underset{\text{Allyl chloride}}{ClCH_2-CH=CH_2} + Cl^\bullet$$
(Allyl radical)

Note that due to resonance the two terminal carbon atoms may have radical character

$$\dot{C}H_2-CH=CH_2 \longleftrightarrow CH_2=CH-\dot{C}H_2 \text{ or } \underset{\dot{}}{CH_2\cdots CH\cdots CH_2}$$

This becomes important in unsymmetrically substituted allylic radical because in such cases two products are formed in the final product

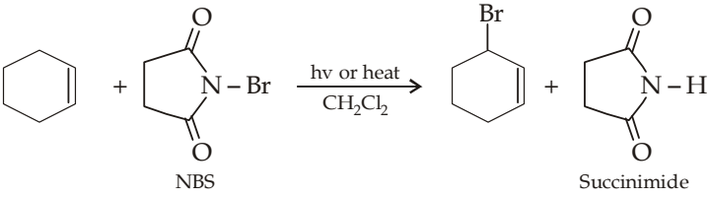
$$RCH_2CH=CH_2 \xrightarrow{Cl^\bullet} \left[R\dot{C}H-CH=CH_2 \longleftrightarrow RCH=CH-\dot{C}H_2\right] \xrightarrow{Cl^\bullet} \underset{\text{Allylic product}}{RCH(Cl)-CH=CH_2} + \underset{\text{Rearranged product}}{RCH=CHCH_2Cl}$$

The question arises why chlorine radical only abstracts hydrogen, when it can also add to double bond to form new free radical which can give addition product in the following way.

$$CH_3-CH=CH_2 \underset{\text{high temp.}}{\overset{Cl^\bullet}{\rightleftharpoons}} \underset{\text{I}}{CH_3-\dot{C}H-CH_2Cl} \xrightarrow{Cl_2} CH_3CHClCH_2Cl$$

However, the above reaction does not take place at high temperature because at high temperature the radical I is reconverted into the starting material. Moreover, the radical I relatively being less stable than the allyl radical will require halogen molecule immediately; while the allyl radical, being more stable, can wait for the halogen molecule to react. Thus allylic halogenation can take place at higher temperature and in low halogen concentration.

Allylic bromination is best carried out by N-bromosuccinimide (NBS) because it allows a radical substitution reaction to be carried out without using a relatively high concentration of Br_2 that could add to the double bond. Homolytic cleavage of the N–Br bond generates the bromine radical needed to initiate the radical reaction. Light or heat can be used to promote the reaction. The solvent used is generally CH_2Cl_2.



NBS Succinimide

$$CH_3CH_2CH=CH_2 \xrightarrow{NBS} [CH_3\dot{C}HCH=CH_2 \longleftrightarrow CH_3CH=CH\dot{C}H_2]$$

$$\xrightarrow{Br_2} \underset{\text{3–Bromo–1–butene}}{CH_3\underset{Br}{\underset{|}{C}}HCH=CH_2} + \underset{\text{1–Bromo–2–butene}}{CH_3CH=CHCH_2Br}$$

Allylic bromination by means of N-bromosuccinimide is known as **Wohl-Ziegler reaction.**

6.5.16 Polymerization

The process of joining together of many small molecules to form very large molecule is known as **polymerization,** the comound formed is known as **polymer** and the simple compound from which polymer is made is called **monomer.**

Formation of polyethylene is a simple and most common example of polymerization. Ethylene when heated under pressue in presence of oxygen undergoes polymerization to form **polyethylene,** a common plastic material used in packaging.

$$nCH_2=CH_2 \xrightarrow[\text{pressure}]{O_2,\text{ heat}} -(-CH_2-CH_2-CH_2-CH_2-)-_n$$

Polymerization of substituted ethylenes gives plastics of widely differing physical properties

$$n\underset{X}{\underset{|}{CH_2=CH}} \xrightarrow{\text{peroxide}} \left[-CH_2-\underset{X}{\underset{|}{CH}}-\right]_n$$

where X = Cl, CN, $COOCH_3$, CH_3, C_6H_5 etc. depending upon the nature of the group X. For example, vinyl chloride (when X = Cl, i.e. $CH_2 = CHCl$) polymerizes to polyvinyl chloride (PVC) used in industry for making plastics, pipes, records etc.

Most of the polymerization of alkenes occurs by chain mechanism and, depnding upon the reaction conditions, may be classified into three categories free-radical, cationic and anionic.

Cationic polymerization

Alkenes that easily form carbocations are good candidates for cationic polymerization. The reaction is similar to electrophilic additions on an alkene. It is initiated by acidic catalysts like H_2SO_4, BF_3, $AlCl_3$, HF, etc. Polymerization of isobutylene in presence of H_2SO_4, and styrene in presence of BF_3 are common examples.

Free-radical polymerization

Many alkenes undergo free-radical polymerization, when they are heated with radical initiators. For example, styrene polymerizes to polystyrene when it is heated to 100°C in presence of a peroxide.

$$RO-OR \xrightarrow{\text{heat}} 2RO^{\bullet}$$

$$H_2C=\underset{\displaystyle C_6H_5}{\underset{|}{CH}} \xrightarrow{\overset{\bullet}{O}R} RO-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{\overset{\bullet}{C}H}} \xrightarrow{C_6H_5CH=CH_2} RO-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{\overset{\bullet}{C}H}}$$

The chain reaction stops, either by coupling of two chains or by reaction with an impurity (e.g. O_2).

Ethylene also polymerizes by free-radical polymerization. Because, the free radical intermediates are less stable, so stronger reaction conditions are required, i.e. by heating to about 200°C under a pressure of about 3000 atm. The product formed is called *low-density* polyethylene, and is the material used in polyethylene bags.

Anionic polymerization

Like cationic polymerisation, anionic polymerization depends on the presence of a stabilizing group. Thus the presence of a strong electron-withdrawing group (e.g. carbonyl, cyano, nitro, etc.) on one of the doubly bonded carbon atom increases the stability of the carbanion. Hence methyl α-cyanoacrylate (containing two powerful electron-withdrawing groups) undergoes anionic polymerization in presence of a trace of a base because the intermediate carbanion is very stable.

$$CH_2=\overset{\displaystyle CN}{\overset{|}{\overset{\curvearrowright}{C}}}-COOC_2H_5 \xrightarrow{OH^-} HOCH_2-\overset{\displaystyle CN}{\overset{|}{\overset{-}{C}}}-COOC_2H_5 \xrightarrow{H_2C=\overset{\displaystyle CN}{\overset{|}{\overset{\curvearrowright}{C}}}-COOC_2H_5}$$

Methyl α - cyanoacrylate
(Acts as super glue)

$$HOCH_2-\underset{\displaystyle CN}{\underset{|}{\overset{\displaystyle COOC_2H_5}{\overset{|}{C}}}}-CH_2-\overset{\displaystyle CN}{\overset{|}{C}}-COOC_2H_5 \longrightarrow \text{Polymer (Solid)}$$

TEST YOUR UNDERSTANDING - 6.12

1. An alkene undergoes ozonolysis to form two moles of 1, 4-butandial. Deduce its structure.

2. Complete the following :

(a)  $+ Br_2 \xrightarrow{\text{high temperature}}$ (b) $CH_3(CH_2)_3CH_2CH_2CH=CH_2 + NBS \longrightarrow$

(c) Designate different types of hydrogen atoms present in the compound $CH_3CH=CHCH_2CH_2CH(CH_3)_2$, and arrange them in the decreasing order of their reactivity with bromine atom (Br.).

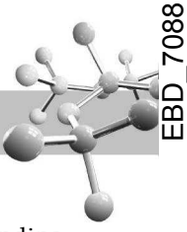
3. Predict the nature of all possible products formed in the following reaction :

$$^{14}CH_3-CH=CH_2 \xrightarrow[(ii)\ O_3,\ (iii)\ H_2O/Zn]{(i)\ NBS}$$

4. *tert*-Butyl hypochlorite (*tert*-BuOCl) causes allylic chlorination. What products are formed by treating butene-1 and butene-2 with this reagent ?

5. When cyclohexanol is dehydrated to cyclohexene, a gummy green substance forms on the bottom of the flask. Explain.

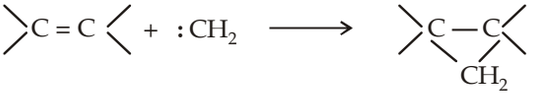
6. When a thin film of methyl α-cyanoacrylate is applied between two metal pieces of a metal, they become non-detachable. Explain.



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6.5.17 Addition of Carbenes

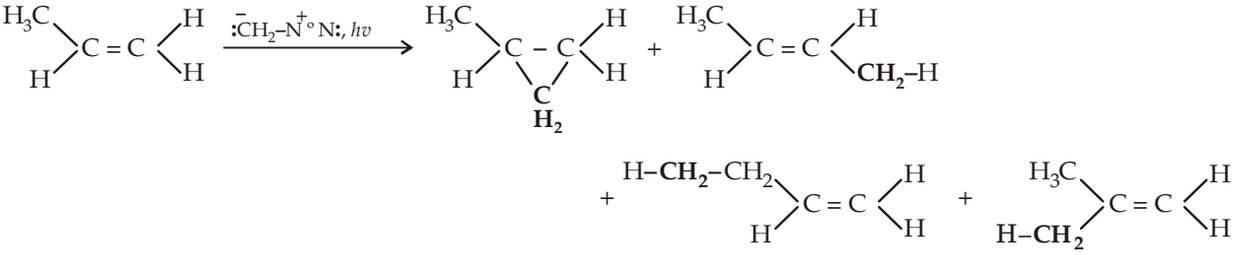
Carbenes are uncharged, reactive intermediates that have a carbon atom with two bonds and two nonbonding electrons. Like borane (BH_3), methylene (the simplest member of carbenes) is a potent electrophile because it has an unfilled octet. It adds to the electron rich π bond of an alkene to form a cyclopropane.



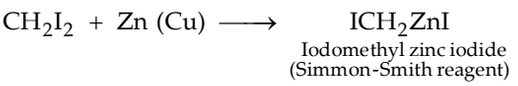
Methylene is obtained by heating dizaomethane (thermolysis) or by irradiating it with light of a wavelength that it can absorb (photolysis). However, use of diazomethane for preparing cyclopropane derivatives has two difficulties.

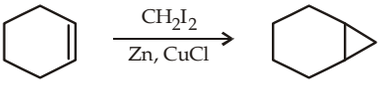
(a) It is extremely toxic and explosive.

(b) Methylene (obtained from diazomethane) is so reactive that it inserts into C=C bonds as well as C–H bonds, thus forming several side products.



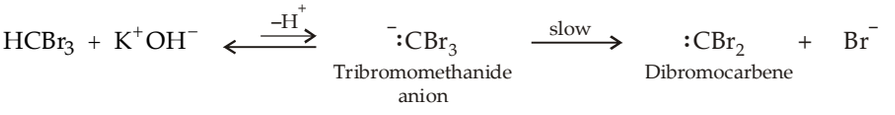
However, cyclopropanes can best be prepared by **Simmons-Smith reaction** which involves the use of iodomethyl zinc iodide. Iodomethyl zinc iodide is prepared by adding methylene iodide to the zinc-copper couple. This type of reagent is called a **carbenoid** because it reacts much like a carbene, but it does not actually contain a divalent carbon.



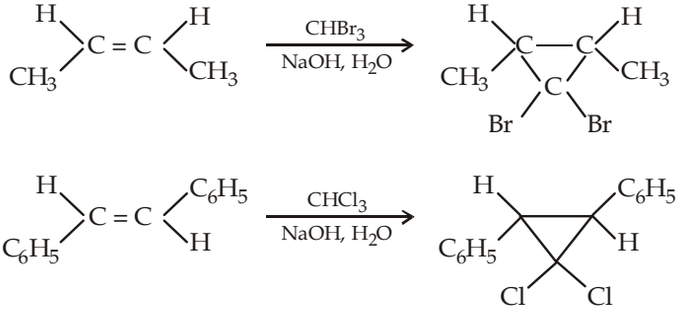


Addition of dihalocarbenes

Dihalocarbenes can be synthesized by the α-elimination of HX from haloform. Note that the H atom of HCX_3 is acidic due to the presence of three electronegative elements on carbon; hence haloform when treated with a base undergoes α-elimination (removal of H and halogen from the same carbon atom) to form dihalocarbenes.*



The cycloaddition products of dihalocarbenes retain the geometry of the alkene.



Since only a single stereoisomer (*cis-* or *trans-*) is formed as product, reaction is said to be **stereospecific**.

* Dihalocarbene carbon atom is sp^2 hybridised (similarity to carbocations).

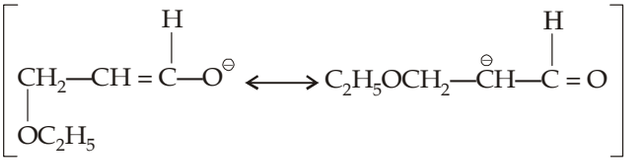
6.5.18 Nucleophilic Additions

Alkenes having electron withdrawing group easily undergo nucleophilic additions rather than electrophilic. Actually, electron-withdrawing group deactivates the carbon-carbon double bond towards electrophilic additions but at the same time makes it more susceptible to nucleophilic attack by stabilizing the intermediate carbanion by dispersing the negative charge. Common examples are the additions on α, β-unsaturated nitriles, aldehydes, ketones and esters.

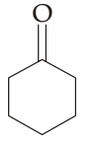
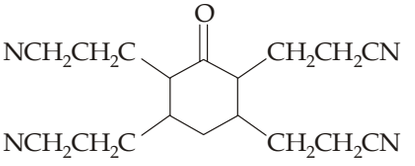
$$CH_2=CH-C\equiv N \xrightarrow{C_2H_5O^{\ominus}} [C_2H_5OCH_2-\overset{\ominus}{C}H-C\equiv N \longleftrightarrow C_2H_5OCH_2-CH=C=N^{\ominus}] \xrightarrow{C_2H_5OH} C_2H_5OCH_2-CH_2-C\equiv N$$

Other examples of nucleophilic additions are

(i) $R_2\ddot{N}H + CH_2=CHCN \longrightarrow R_2NCH_2CH_2CN$

(ii) $CH_2=CH-CH=O \xrightarrow{OC_2H_5^-}$ 

$$\xrightarrow{C_2H_5OH} C_2H_5OCH_2CH=CHOH + C_2H_5OCH_2CH_2CHO$$

(iii)  $+ CH_2=CHCN \xrightarrow{NaOH}$ 

6.5.19 Isomerization

An alkene may be converted into other by heating at high temperature or preferably at a low temperature in the presence of a catalyst like anhydrous aluminium chloride. Either of the following occurs during isomerization.

(i) A double bond migrates from the terminal position forming more substituted alkene, *e.g.*

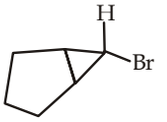
$$\underset{\text{Pentene-1}}{CH_3CH_2CH_2CH=CH_2} \xrightarrow[AlCl_3]{heat} \underset{\text{Pentene-2}}{CH_3CH_2CH=CHCH_3}$$

(ii) A methyl group may shift from an allylic position, again forming more substituted alkene, e.g

$$\underset{\text{Butene-1}}{CH_3CH_2CH=CH_2} \xrightarrow[AlCl_3]{heat} \underset{\text{Isobutene}}{(CH_3)_2CH=CH_2}$$

TEST YOUR UNDERSTANDING - 6.13

1. Give reaction(s) involved in the conversion of each of the following reactions.

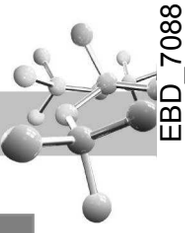
(a) *trans*-2-Butene to *trans*-1,2-dimethylcyclopropane (b) Cyclopentene to 

2. What products would you expect from each of the following reactions?

(a) *trans*-2-Butene $\xrightarrow[Me_3COK]{CHCl_3}$ (b) *cis*-2-Butene $\xrightarrow[Zn(Cu)]{CH_2I_2}$

3. Give various steps involved in the following reactions,

(a) $CH_3CH_2CH_2CH=CH_2 \xrightarrow[200-300^\circ]{AlCl_3} CH_3CH_2CH=CHCH_3$ (b) $CH_3CH_2CH=CH_2 \longrightarrow CH_2=\overset{CH_3}{\overset{|}{C}}-CH_3$



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Summary for stereochemical aspect of additions on alkenes

	Reagent	*Name of alkene*	*Stereochemical addition*	*Product formed*
1.	H_2/Catalyst	*cis*-alkene *trans*-alkene	*syn*	*meso*- *racemic*-
2.	X_2	*cis*-Butene-2 *trans*-Butene-2	*anti*	*racemic*-2,3-Dibromobutane *meso*-2,3-Dibromobutane
3.	HOCl	*cis*-Butene-2 *trans*-Butene-2	*anti*	*racemic*-3-Chlorobutanol-2 *meso*-3-Chlorobutanol-2
4.	Cold alk. $KMnO_4$ or OsO_4	Maleic acid (*cis*-isomer) Fumaric acid (*trans*-isomer)	*syn*	*meso*-Tartaric acid *racemic*-Tartaric acid
5.	Peracids	Maleic acid Fumaric acid	*anti*	*racemic*-Tartaric acid *meso*-Tartaric acid
6.	Singlet carbene	*cis*-Butene-2 *trans*-Butene-2	*syn*	*cis*-1,2-Dimethylcyclopropane *trans*-1,2-Dimethylcyclopropane
7.	Triplet carbene	*cis*-Butene-2 or *trans*-Butene-2	Non-stereoselective	Mixture of *cis*- and *trans*- 1,2-Dimethylcyclopropane

DIENES

Hydrocarbons containing two, three, four and several double bonds in a molecule are called *dienes, trienes, tetraenes* and *polyenes* respectively. Dienes have the general formula, C_nH_{2n-2} and are isomeric with alkynes. Depending upon the relative positions of double bonds, dienes are divided into three classes.

(i) Dienes having two double bonds on the same carbon atom are known as **cumulative dienes.** Such system is found in allenes, cumulenes, ketenes etc.

$CH_2 = CH = CH_2$
1,2–propadiene
(Allene)

$CH_3 - CH = C = CH - CH_3$
2, 3–Pentadiene
(*sym*–Dimethylallene)

(ii) Dienes having alternate arragement of sngle and double bonds are called **conjugated dienes**, *e.g.*

$CH_2 = CH - CH = CH_2$
1, 3–Butadiene

$CH_2 = \overset{CH_3}{\overset{|}{C}} - CH = CH_2$
2–Methyl–1, 3–butadiene (Isoprene)

(iii) Dienes having isolated double bonds, *i.e.* two double bonds separated by at least one sp^3 hybridised carbon, are known as **isolated double bonds.**

$CH_2 = CH - CH_2 - CH_2 - CH = CH_2$
1, 5–Hexadiene (diallyl)

$CH_2 = CH - \overset{CH_3}{\overset{|}{C}}H - CH = CH_2$
3–methyl–1, 4–pentadiene

Among the three types, conjugated dienes are the most important. They differ from simple alkenes in three ways.

(a) They are more stable and hence the preferred products of elimination.
(b) They undergo *1, 4-addition*, both electrophilic and free radical.
(c) They are more reactive toward free-radical additions.

6.6 1, 3-Butadiene

1,3-Butadiene (a conjugated diene) is the most important diene. Commercially, it is prepared by the cracking of hydrocarbons. It is purely a synthetic compound and has several worth-noting features.

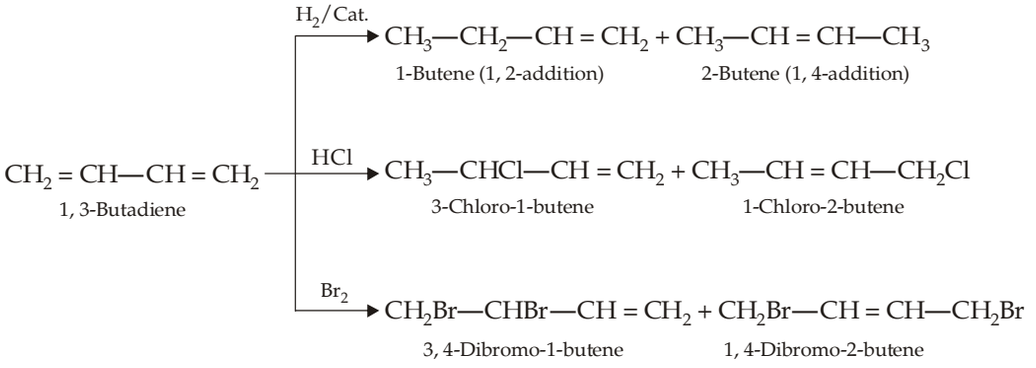
(i) Its all carbon atoms are sp^2 hybridised.

(ii) It is highly stable as compared to compound having two isolated or two cumulative double bonds. High stability is indicated by its low heat of hydrogenation (57.1 kCal) than the isolated diene (60 kCal). Difference of 60 kCal and 57.1 kCal represents resonance energy (2.9 kCal) of the molecule; the three resonating structures are drawn below.

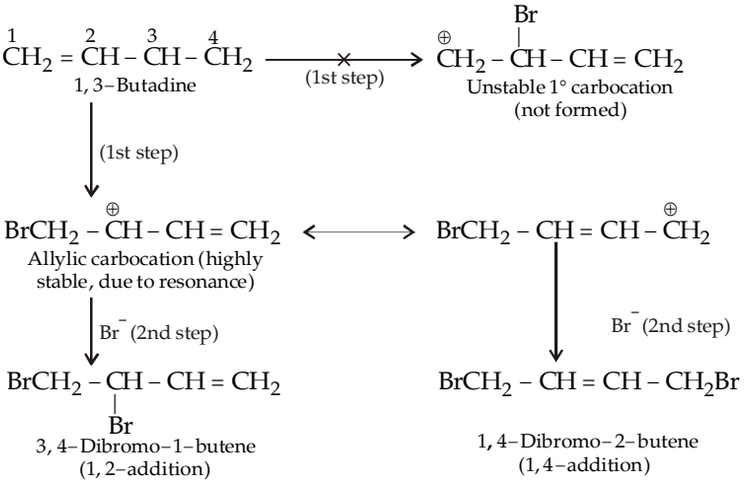
$$CH_2 = CH - CH = CH_2 \longleftrightarrow \overset{+}{C}H_2 - \overset{-}{C}H - CH = CH_2 \longleftrightarrow \overset{+}{C}H_2 - CH = CH - \overset{-}{C}H_2$$

(iii) 1, 3-Butadiene is thermodynamically more stable than isolated alkenes but its chemical reactivity is more than that of alkenes because it involves the formation of highly stable allylic type of intermediate.

1. **Electrophilic additions :** 1, 3-Butadiene readily undergoes catalytic hydrogenation and electrophilic addition reactions with halogens (*e.g.* Br_2) and hydrogen halides (*e.g.* HCl) to form two types of products : in one the two atoms of the reagent add on C_1 and C_2 (**1, 2-addition**), while in other the two atoms add on C_1 and C_4 (**1, 4-addition**); usually the 1, 4-addition product predominates.



The formation of two products, *viz.* 1, 2-addition and 1, 4-addition product is explained on the basis of the stability of the intermediate carbocation.



Relative proportion of 1, 2- and 1, 4-addition products depends upon reaction temperature. Reaction at a low temperature (–80°C) gives a mixture contaning 80% of the 1, 2-product and 20% of the 1,4-product; while reaction at a higher temperature (40°C) gives a mixture containing 20% 1, 2- and 80% 1, 4-product. The fact that the 1, 4-compound predominates at room temperature indicates that it is more stable than the 1, 2-product. Stability of the 1, 4-product is due to more substituted alkene.

Predominance of the 1, 2-product at –80°C indicates that this compound is formed faster than the 1, 4-product (*i.e.* its predominance is due to its faster rate of formation, hence the 1, 2-product can said to be a *kinetically or rate controlled product*). With increase in temperature, although the proportion of the two products formed at initial stage remains the same, conversion of the 1, 2-product to 1, 4-product takes place faster to reach an equilibrium state whose exact composition depends upon the value of temperature. Since at high temperatures, more stable 1, 4-product predominates which is actually due to conversion of the 1, 2-product to the 1, 4-product, we can say that the 1, 4-product is *thermodynamically* or *equilibrium controlled product.*

2. **Free radical additions :** Conjugated dienes also undergo free radical addition reactions forming a mixture of 1, 2- and 1, 4-addition products. It is interesting to note that conjugated dienes are more stable than isolated alkenes, even then they are more reactive to free-radical attack than the isolated alkenes. This is because of the fact that the allyl radical formed in the first propagation step is more stable and requires a lower activation energy than the alkyl free radical from the isolated alkenes.

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For example, addition of $BrCCl_3$ to 1, 3-butadiene in presence of peroxides takes place in the following way :

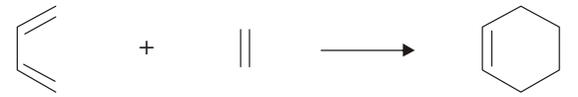
$$\text{Peroxide} \longrightarrow \text{Free radical (Rad}^{\bullet}\text{)}$$

$$\text{Rad}^{\bullet} + BrCCl_3 \longrightarrow \text{Rad} - Br + {}^{\bullet}CCl_3$$

$$CH_2 = CH—CH = CH_2 \xrightarrow{{}^{\bullet}CCl_3} Cl_3C—CH_2—\underbrace{CH\cdots CH\cdots CH_2}_{\text{Allylic free radical}}$$

$$\xrightarrow{BrCCl_3} Cl_3C—CH_2—\underset{\text{1, 2-Addition product}}{\overset{Br}{\overset{|}{CH}}—CH = CH_2} + \underset{\text{1, 4-Addition product}}{Cl_3C—CH_2—CH = CH—CH_2Br}$$

3. **[4 + 2] Cycloaddition :** Addition of two unsaturated compounds, one havng four carbon atoms and other two, to form cyclic products are known as [4 + 2] cycloadditions. Best known example is addition of 1, 3-butadiene (a 4-carbon unit) to ethylene (a 2-C unit) to form cyclohexene (**Diel's-Alder reaction**).



Butadiene (a diene) + Ethylene (a dienophile) → Cyclohexene (an adduct)

It should be noted that in Diel's-Alder reaction, 1, 3-butadiene reacts only in the *s*-cis form.

4. **Chemical reduction :** The enhanced chemical reactivity of conjugated alkenes relative to isolated double bonds is reflected in the reduction of butadiene with sodium and alcohol to form butene-2 (1, 4-addition product) which although has a double bond is not reduced further.

$$H_2C = CH - CH = CH_2 \xrightarrow{Na/C_2H_5OH} \underset{\text{Butene–2}}{H_3C - CH = CH - CH_3} \xrightarrow{Na/C_2H_5OH} \text{No reduction}$$

$$2Na \longrightarrow 2Na^{\bullet} + 2e;\ H_2C = CH - CH = CH_2 \xrightarrow{2e}$$

$$\left[H_2C = CH—\overset{\ominus}{C}H—\overset{\ominus}{C}H_2 \longleftrightarrow H_2\overset{\ominus}{C}—CH = CH—\overset{\ominus}{C}H_2\right] \equiv H_2\overset{\ominus}{C}\cdots CH\cdots \overset{\ominus}{C}H—CH_2$$

$$\xrightarrow{2H^+} \underset{\text{Butene-2}}{H_3C—CH = CH—CH_3} \xrightarrow{2e} \underset{\text{highly unstable (hence not formed)}}{H_3C—\overset{\ominus}{C}H—\overset{\ominus}{C}H—CH_3}$$

The enhanced reactivity of conjugated alkenes is again due to the formation of resonance stabilized allylic carbanion as intermediate.

5. **Polymerization :** Like substituted ethylenes, conjugated dienes also undergo polymerization. For example, 1, 3-butadiene when heated with metallic sodium under the influence of heat, light or peroxide forms a rubber like polymer known as *buna-N*.

$$n CH_2 = CH - CH = CH_2 \xrightarrow{Na} -(-CH_2 - \underset{\text{Buna N}}{CH = CH} - CH_2-)-_n$$

Monomers are joined largely by 1, 4-linkages and to some extent by 1, 2-linkages.

6.7 Degree of Unsaturation

The number of pairs of hydrogen atoms required by the molecular formula of an unsaturated compound to be converted into corresponding alkane is called **degree of unsaturation**. Mathematically,

$$\text{Degree of unsaturation} = \frac{2n_1 + 2 - n_2}{2}$$

where, n_1 is the number of carbon atoms and n_2 is the number of hydrogen atoms.

1° unsaturation indicates the presence of one C=C bond or one ring.

2° unsaturation indicates the presence of two C=C bonds, or one C≡C bond, or one C=C bond and one ring, or two rings.

Degree of unsaturation with hetero atoms

Heteroatoms are any atoms other than carbon and hydrogen. The rules for calculating elements of unsaturation in hydrocarbons can be extended to include heteroatoms.

Halogens : A halogen simply substitutes for a hydrogen atom in the molecular formula. Thus in calculating the degree of unsaturation, simply count halogens as hydrogen atoms. Thus $C_4H_5Br_3$ is equal to C_4H_8 it means the halogen derivative has *two degree of unsaturation.*

Oxygen : An oxygen atom can be added to the chain without changing the number of hydrogen atoms or carbon atoms. Thus in calculating the degree of unsaturation, *ignore the oxygen atoms.*

Nitrogen : A nitrogen atom can take the place of carbon atom in the chain. However, nitrogen is trivalent, having only one additional hydrogen atom, compared with two hydrogens for each additional carbon atom. Thus in computing the degree of unsaturation, count nitrogen as half a carbon atom. For example, in a compound of the formula C_4H_9N means $C_{4.5}H_9$ whose corresponding alkene would be $C_{4.5}H_{(4.5\times 2)+2}$ or $C_{4.5}H_{9+2}$; thus the formula C_4H_9N has one degree of unsaturation.

TEST YOUR UNDERSTANDING - 6.14

1. Predict the product of the reaction :

(i) $(CH_3)_2CH-CHCl-CH_2-CH=CH_2 \xrightarrow{\text{alc. KOH}}$ (ii) $CH_3-CH=CH-CH=CH-CH_3 + HCl \longrightarrow$

2. Determine the number of elements of unsaturation in each of the following molecular formula.

(a) C_4H_8O (b) $C_4H_4O_2$ (c) $C_5H_5NO_2$ (d) C_6H_3NClBr

3. Determine the degree of unsaturation in the following compounds and write down the structure of the isomeric cyclic compounds in each case. (a) C_6H_{12} (b) C_4H_6.

4. Assuming that unsaturation in the following compounds is present in the form of ring and C=C bonds only, *i.e.*, no C≡C bond is present, determine the number of C=C bonds in the following compounds :

(a) α-Pinene ($C_{10}H_{16}$) containing two rings (b) Anthracene ($C_{14}H_{10}$) containing three rings

(c) Pyrene ($C_{16}H_{10}$) containing 4 rings.

6.8 Illustrative Examples on Alkenes :

Example 1 :

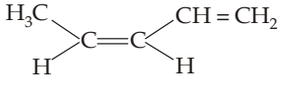
Draw and name the possible geometrical isomers of the following

(i) $CH_3CH=CH-CH=CH_2$ **(ii)** $CH_3CH=CH-CH=CHCH_2CH_3$

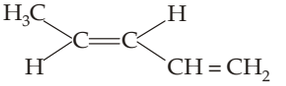
(iii) $CH_3CH=CH-CH=CHCH_3$

Solutions :

(*i*) Only two geometrical isomers are possible, because each carbon atom of one of the double bonds has two different substituents, while one of the carbon atoms of the other double bond has two hydrogen.

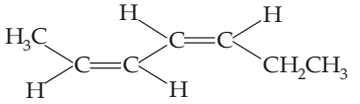


Z-1, 3-Pentadiene (*cis*)

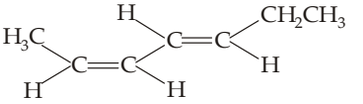


E-1, 3-Pentadiene (*trans*)

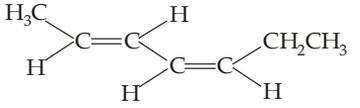
(*ii*) Both double bonds meet the conditions of geometrical isomers and hence 4 diastereomers are possible.



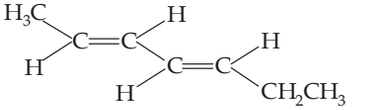
cis, *cis* or (*Z*, *Z*)-2, 4-Heptadiene



cis, *trans* or (*Z*, *E*)-2, 4-Heptadiene



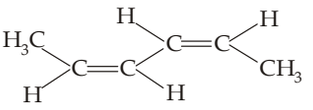
trans, *cis* or (*E*, *Z*)-2, 4-Heptadiene



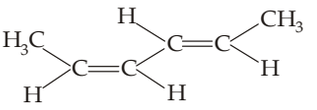
trans, *cis* or (*E*, *E*)-2, 4-Heptadiene

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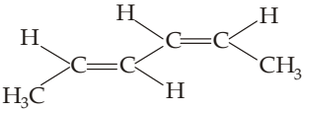
(*iii*) The four possible structures are



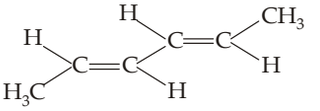
cis, *cis*-2, 4-Hexadiene



cis, *trans*-2, 4-Hexadiene



trans, *cis* or (*Z*, *E*)-2, 4-Hexadiene

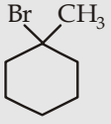
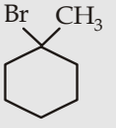


trans, *trans* or (*E*, *E*)-2, 4-Hexadiene

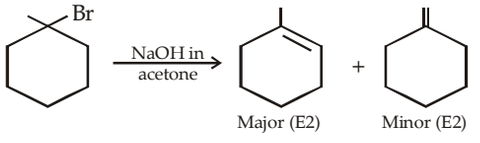
Note that *cis*, *trans*- and *trans*, *cis* are identical and hence only **three geometrical isomers** are possible in case of 2, 4-hexadiene.

Example 2 :

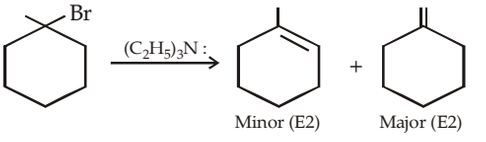
Give the major product formed in each of the following reaction :

(a)  + NaOH $\xrightarrow{(CH_3)_2CO}$ **(b)**  + $(C_2H_5)_3N$ $\longrightarrow$

Solutions :

(a) 

Major (E2) Minor (E2)

(b) 

Minor (E2) Major (E2)

Hindered base, as Et_3N:, gives Hofmann product as major isomer.

Example 3 :

1-Octene when treated with NBS gives unexpected primary bromide as the major product rather than 2° bromide.

Solution :

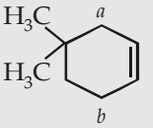
$$CH_3(CH_2)_4CH_2CH=CH_2 \xrightarrow[CCl_4]{NBS} \left[\underset{2^\circ \text{ allylic}}{CH_3(CH_2)_4\dot{C}HCH=CH_2} \longleftrightarrow \underset{1^\circ \text{ allylic}}{CH_3(CH_2)_4CH=CH\dot{C}H_2} \right]$$

$$\longrightarrow \underset{\text{3–Bromo–1–octene (17\%)}}{CH_3(CH_2)_4\underset{\displaystyle Br}{\underset{|}{C}}H.CH=CH_2} + \underset{\text{1–Bromo–2–octene (87\%)}}{CH_3(CH_2)_4CH=CH\,CH_2Br}$$

Primary bromide is favoured because it involves reaction at the less hindred radical.

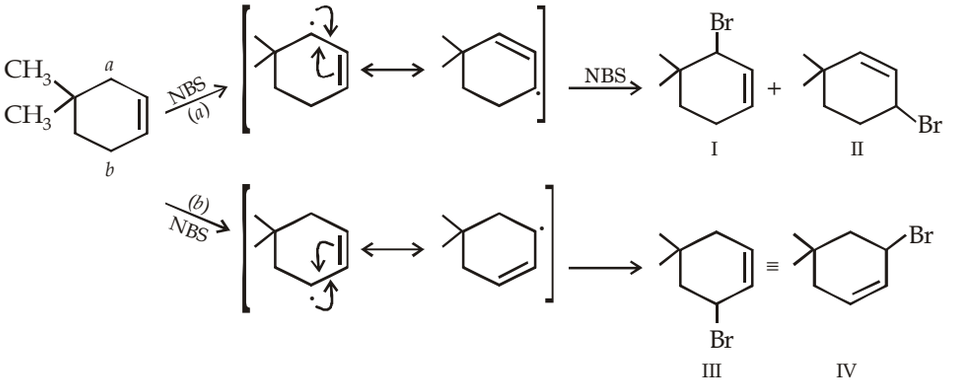
Example 4 :

What product would you expect from reaction of 4, 4-dimethylcyclohexene with NBS?



Solution :

The compound has two allylic positions, marked *a* and *b*. Further, the free-radical formed from each of the allylic positions is resonance hybrid of two structures. Thus, in all four bromo products will be formed.



However, structures III and IV are identical, so in all three products are formed.

Example 5 :

Give the configuration of the products obtained from the following reactions.

(a) **1-Butene + HCl**

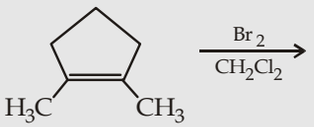
(b) **1-Butene + HBr + peroxide**

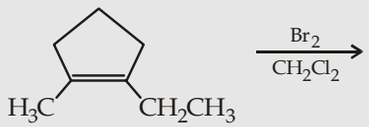
(c) **3-Methyl-3-hexene + HBr + peroxide**

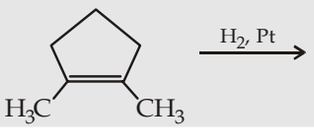
(d) ***cis*-3-Hpetene + Br_2**

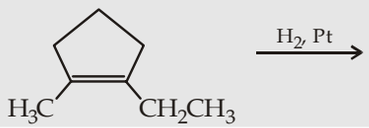
(e) ***trans*-3-Heptene + Br_2**

(f) ***trans*-3-Hexene + Br_2**

(g) 

(h) 

(i) 

(j) 

Solution :

(a) $CH_3CH_2\overset{*}{C}H(Cl)CH_3$. The product has one chirality center, so equal amounts of the *R* and *S* enantiomers will be formed.

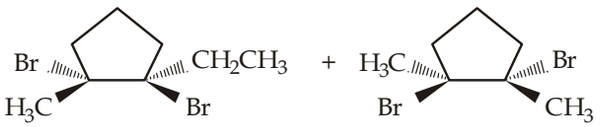
(b) $CH_3CH_2CH_2CH_2Br$. The product does not have a chirality center, hence there are no stereoisomers.

(c) $CH_3CH_2\overset{*}{C}H(CH_3)\overset{*}{C}H(Br)CH_2CH_3$. Two chirality centers are present in the product. The reaction involves radical intermediate, two pairs (erythro and threo) of enantiomers are formed.

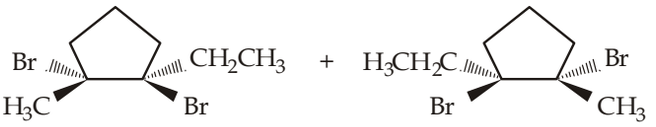
(d) $CH_3CH_2\overset{*}{C}H(Br)\overset{*}{C}H(Br)CH_2CH_2CH_3$. Two chirality centers are created in the product. Because the reactant is *cis* and addition of Br_2 is *anti*, the threo pair of enantiomers is formed.

(e) $CH_3CH_2\overset{*}{C}H(Br)\overset{*}{C}H(Br)CH_2CH_2CH_3$. Because the reactant is *trans* and additon of Br_2 is *anti*, the erythro pair of enantiomers is formed.

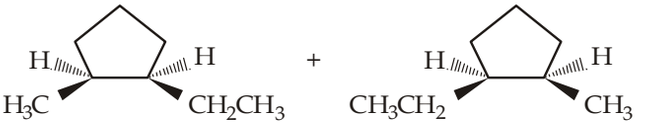
(f) $CH_3CH_2\overset{*}{C}H(Br)\overset{*}{C}H(Br)CH_2CH_3$. Because the reatant is *trans* and addition of Br_2 is *anti*, erythro pair of enantiomers is expected. However, the two chirality centers are identical the erythro product will be a single *meso* compound.

(g) 

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(h) 

(i) 
(No enantiomer)

(j) 

Example 6 :

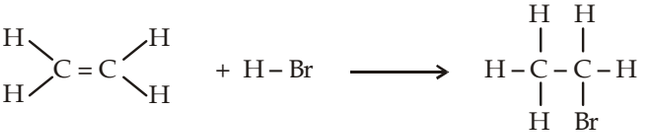
(a) Calculate the ΔH^0 for the addition of HBr on ethene, the ΔH^o (bond dissociation energy) for the various bonds are given below.

C = C	**152 kcal/mol**	**C – Br**	**69 kcal/mol**
C – C	**91 kcal/mol**	**H – Br**	**87 kcal/mol**
C – H	**101 kcal/mol**		

(b) Tell whether the reaction is

(i) exothermic or endorthermic, (ii) exergonic or endergonic

Solution :

(a) 

ΔH^o involved in bond breaking

π bond* = 61 kcal/mol.

H – Br = 87 kcal/mol.

ΔH^o_{total} = 148 kcal/mol

ΔH^o involved in bond forming

C – H = 101 kcal/mol.

C – Br = 69 kcal/mol.

ΔH^o_{total} = 170 kcal/mol.

*ΔH^o for carbon-carbon π bond = ΔH^o for carbon-carbon double bond (i.e. $\sigma + \pi$ bonds) – (ΔH^0 for carbon-carbon σ bond)

= 152 kcal/mol – 91 kcal/mol = 61 kcal/mol.

ΔH^o for the reaction = ΔH^o for bonds being broken – ΔH^0 for bonds being formed

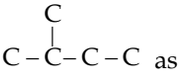
= 148 kcal/mol – 170 kcal/mol. = – 22 kcal/mol.

(b) The negative value for ΔH^o indicates that the reaction is **exothermic.** Since ΔH^o has a significant negative value (–22 kcal/mol.), it can be said that ΔG^o is also negative, i.e. the reaction is **exergonic.** In case the value of ΔH^o were close to 0, it can't be said that the sign of ΔG^o is the same as ΔH^o.

Example 7 :

Three isomeric alkenes A, B and C, C_5H_{10}, are hydrogenated to give 2-methylbutane. A and B give the same 3° alcohol on oxymercuration-demercuration, while B and C give the different 1° alcohols on hydroboration-oxidation. Deduce the structures of A, B and C.

Solution :

(i) The three isomers must have  as the skeleton, indicated by the formation of 2-methylbutane by all the three.

(ii) Since A and B give a 3° alcohol, both must have the $=C(CH_3)_2$ or $H_2C=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-$ grouping.

(iii) Since B and C give 1° alcohols, both must have $H_2C=$ grouping. Thus A, B, and C should be

$$\underset{\textbf{[A]}}{H_3C-\overset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=CH-CH_3} \qquad \underset{\textbf{[B]}}{H_2C=\overset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-CH_2-CH_3} \qquad \underset{\textbf{[C]}}{H_3C-\overset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}-CH=CH_2}$$

Example 8 :

A hydrocarbon (A) of the molecular formula $C_{10}H_{10}$, on oxidation, gives a tricarboxylic acid (B) with the structure given below as the main product. Deduce the structure of A.

$$\underset{\text{(B)}}{HOOCCH_2\overset{\displaystyle CH_2COOH}{\overset{\displaystyle |}{C}}HCH_2COOH}$$

Solution :

(i) Degree of unsaturation in A $= \dfrac{20+2-10}{2} = 6$

(ii) Appearance of three —COOH groups in B by the oxidation of A indicates that the latter has three acetylenic bonds which is in agreement with the 6 degree of unsaturation.

(iii) Oxidative product (B) has three carbon atoms less indicating the presence of three $\equiv CH$ groupings which are lost as HCOOH or CO_2 during oxidation.

(iv) Hence strucutre of A should be

$$\underset{\text{(A)}}{HC\equiv C.CH_2.\overset{\displaystyle CH_2C\equiv CH}{\overset{\displaystyle |}{C}}H.CH_2.C\equiv CH} \xrightarrow{\text{Oxidation}} \underset{\text{(B)}}{HOOC.CH_2.\overset{\displaystyle CH_2.COOH}{\overset{\displaystyle |}{C}}H.CH_2.COOH} + 3CO_2$$

Example 9 :

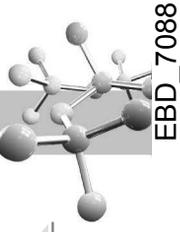
An organic compound *A* reacts with HI to form two products *B* and *C*. On reaction with alcoholic KOH, *B* regenerates *A*, while *C* gives an alkene which on reductive ozonolysis gives acetone as the exclusive product. Give the structure of A and explain the reactions.

Solution :

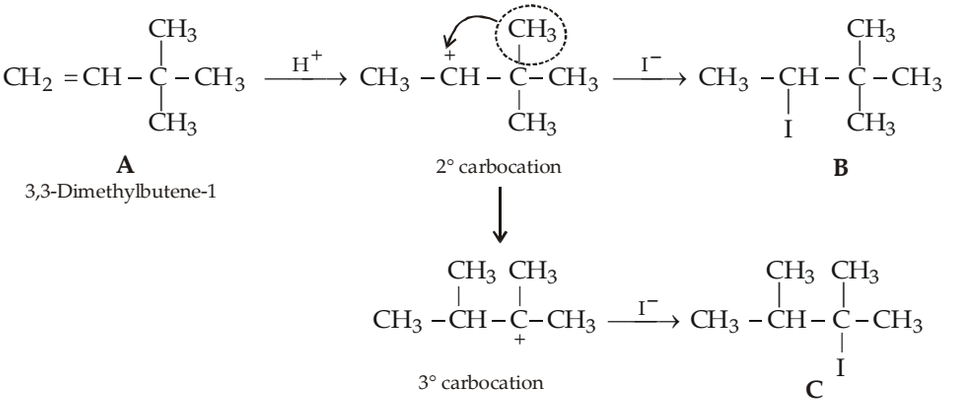
Formation of acetone indicates that **C** is a symmetrical alkene of the formula $Me_2C=CMe_2$ (2,3-dimethylbutene) thus its precursor **B** should be the corresponding alkyl halide.

$$CH_3-\overset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=\overset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-CH_3 \xleftarrow{-HI} \underset{\textbf{C}}{CH_3-\overset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-\overset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-CH_3} \xleftarrow{HI} \underset{\textbf{A}}{\text{Alkene}} \xrightarrow{HI} \textbf{B}$$

Since the alkene **A** forms two isomeric products with HI, it should be unsymmetrical dimethylbutene, i.e. 2,3-dimethylbutene-1 or 3,3-dimethylbutene-1. However, only the latter explains the formation of the products with HI.

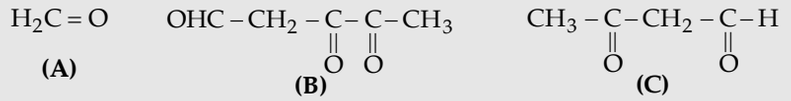


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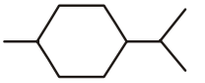
Example 10 :

Deduce the structure of the compound X, $C_{10}H_{14}$ that is hydrogenerated with three eq. of H_2/Pd to give 1-isopropyl-4-methylcyclohexane, and, on reductive ozonolysis gives the following products.



Solution :

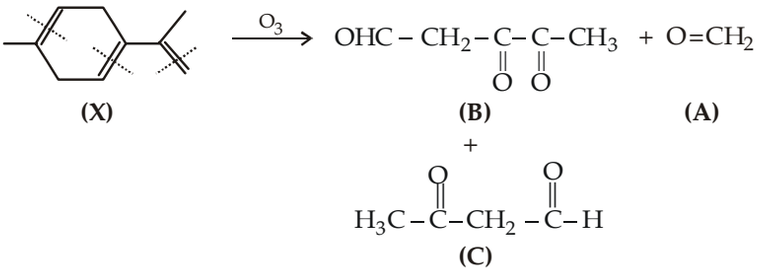
(i) The given compound has 4° of unsaturation coming from three C=C's (indicated by uptake of 3 eq. of H_2) and one cyclohexane ring (indicated by the formation of 1-isopropyl-4-methylcyclohexane).

(ii) Formation of 1-isopropyl-4-methylcyclohexane, by hydrogenation of **X**, indicates the presence of  as the carbon-framework of **X**. So now we must introduce three double bonds in the above mentioned frame-work.

(iii) Formation of $CH_2 = O$ (**A**) on reductive ozonolysis indicates the presence of $= CH_2$ grouping and that too outside the ring.

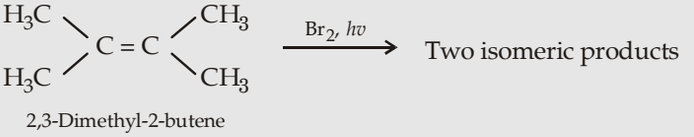
(iv) In compounds (**B**) and (**C**), two methyl groups are present, hence these must also be present in **X**, hence the $=CH_2$ group can be present only in the isopropyl group.

(v) Since both compounds (**B**) and (**C**) have one $–CH_2$ in between the two carbonyl groups, the two double bonds (responsible for the creation of carbonyl groups) in the ring must be separated by one $–CH_2$. Hence X should have following structure which explains all the ozonolysis products.



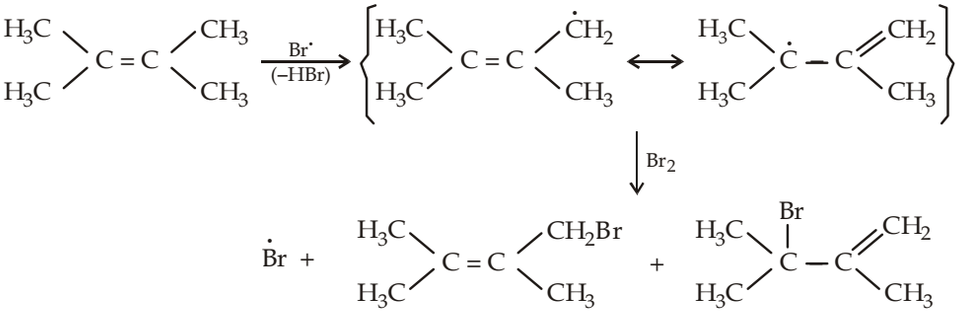
Example 11 :

Write down the structure of the two products formed in the following reaction.



Give proper mechanism for this reaction.

Solution :



Example 12 :

Predict the different possible products in the dehydrobromination of 1,2-dibromopropane with alc. KOH. Which product you expect to be the major?

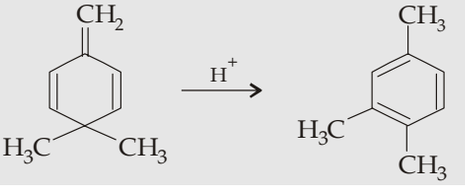
Solution:

$$\overset{1}{\mathrm{Br}}\mathrm{CH_2}-\overset{2}{\mathrm{C}}\mathrm{HBr}\overset{3}{\mathrm{C}}\mathrm{H_3} \xrightarrow[\text{KOH}]{\text{alc.}} \underset{\text{I}}{\mathrm{CH_2=CBrCH_3}} + \underset{\textbf{(Major) II}}{\mathrm{BrCH=CHCH_3}} + \underset{\text{III}}{\mathrm{BrCH_2CH=CH_2}}$$

The C_1, being 1°H is more acidic than the C_2, it is more easily removed by OH^- than the 2°H of –CHBr. Further, the C_1–H is less sterically hindered and moreover the C_1 has 2 H's while C_2 has 1 H so there are two times more chances for the H of C_1 to be removed leading to II as the major product. Allyl bromide (III) is also formed in small amount because 1°H of CH_3 is less acidic than the 1°H of CH_2Br, and the vinyl bromide (I and II) is more stable by virtue of delocalization of electrons from Br to C = C.

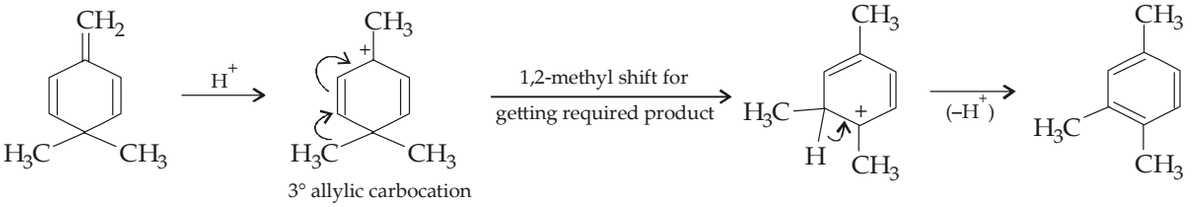
Example 13 :

Propose a mechanism for the following reaction.



Solution :

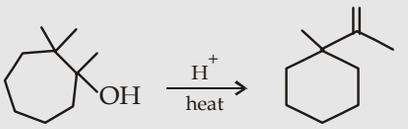
For solving such problems, keep in mind about the relative stability of the species and **structure of the required product**.



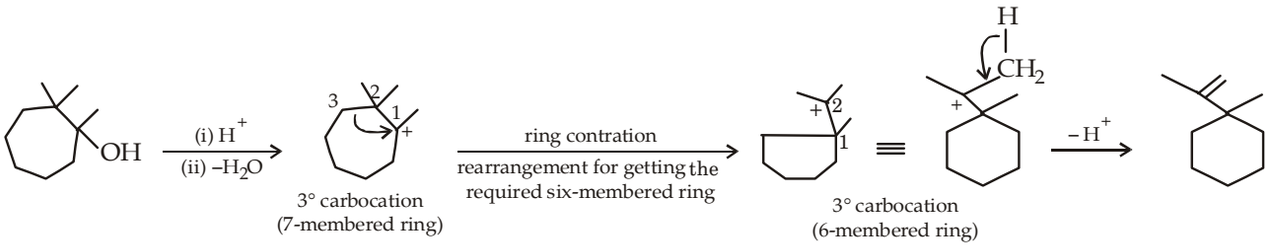
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Example 14 :

Propose a mechanism for the following reaction

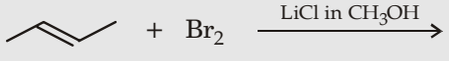


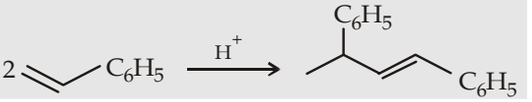
Solution :



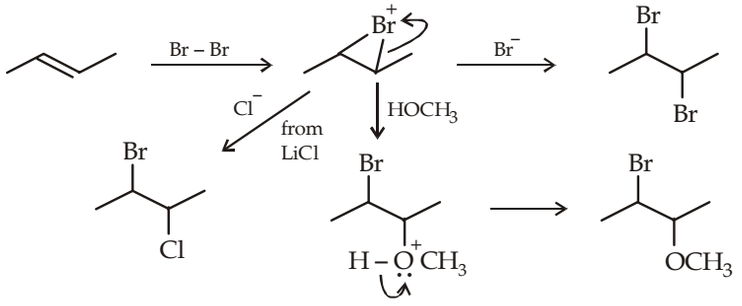
Example 15 :

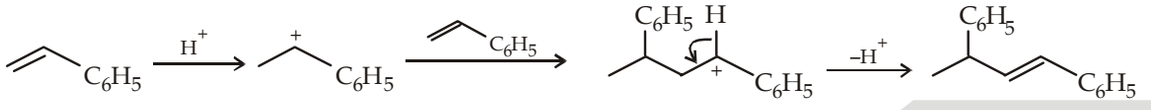
Propose mechanism for the following reactions

(a) 

(b) 

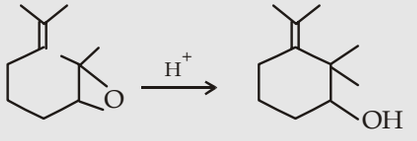
Solution :

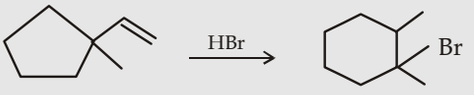
(a) 

(b) 

Example 16 :

Propose a mechanism for the following reactions :

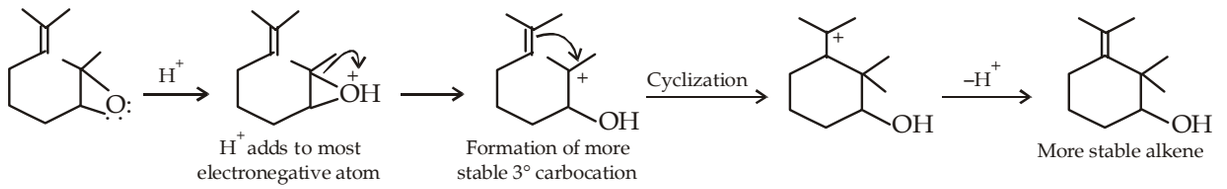
(a) 

(b) 

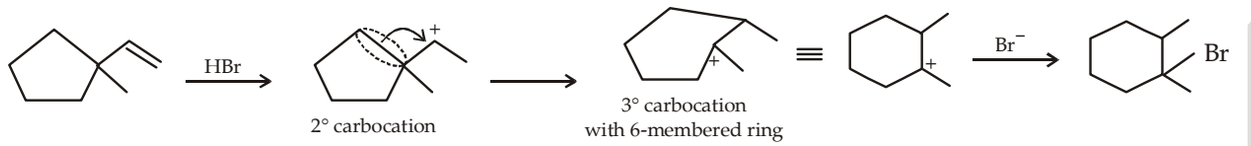
(c) 

Solution :

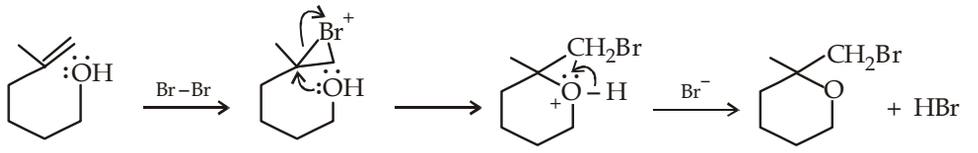
(a)



(b)



(c)



Example 17 :

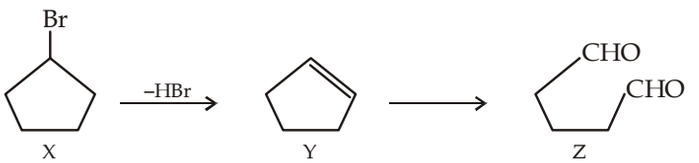
An organic compound (X), C_5H_9Br, does not react with bromine or with dilute $KMnO_4$. However, its product (Y) due to dehydrobromination, decolorises bromine as well as $KMnO_4$ colour. Compound Y on ozonolysis gives another compound Z, $C_5H_8O_2$. Assign the most probable structure(s) to X and explain the reactions.

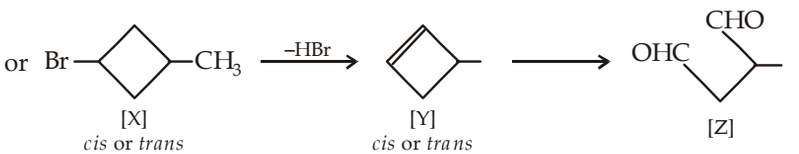
Solution :

(i) Degree of unsaturation in X is one.

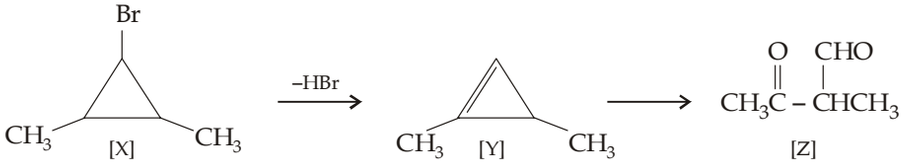
(ii) Since the compound reacts neither with bromine nor with $KMnO_4$, the degree of unsaturation must be due to ring.

(iii) Ozonylysis product of Y has same number of carbon atoms as the compound X, so unsaturation must be in the ring which may be five membered or 4-membered.





[X] may also be a cyclopropane derivative.



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Example 18 :

(a) A hydrocarbon (*A*) of the molecular formula $C_{10}H_{16}$ undergoes oxidative or reductive ozonolysis to form two moles of the same compound (*B*). (*A*) takes up three eq. of H_2/Pd at 120°C. Deduce all possible structures for the compounds (*A*) and (*B*) if neither (*A*) nor (*B*) is resolvable.

(b) What would have been the structures of *A* and *B* if each of them were resolvable?

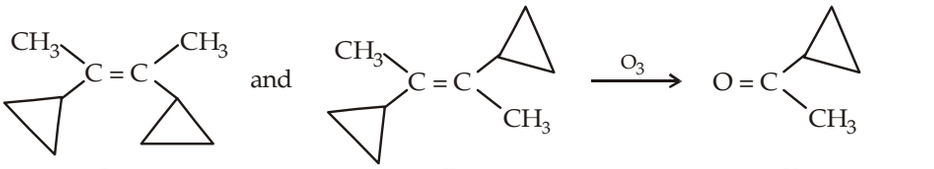
(c) What would have been the structure of (*A*) under following assumptions.

(i) It is nonresolvable, but gives same hydrogenation properties as the original compound *A*.

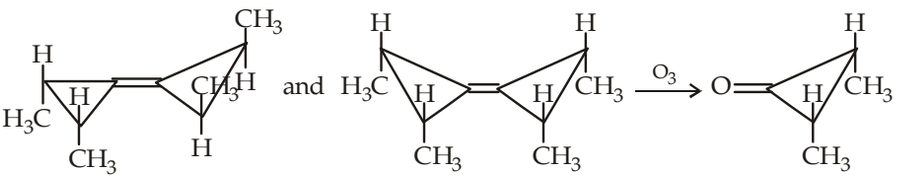
(ii) It gives single product on oxidative ozonolysis, and a *different* but single compound on reductive ozonolysis product, neither of the ozonolysis product is resolvable.

Solution :

(a) Compound **A** has 3° of unsaturation. Since compound **A** on ozonolysis gives two moles of the same compound **B, A** must be symmetrical and should have only one C=C bond. The 2° of unsaturation must be in the form of two rings. Reaction with three eq. of H_2 at elevated temperatures indicates that **A** has two cyclopropyl ring (recall that among cycloalkanes, only cyclopropyl ring reacts with H_2 and that too at elevated temperatures). Thus the alkene **A** belongs to RR'C = CRR' type. Inability to be resolved means an absence of chiral atom in **A** and **B**. The possible structures for **A** (I to IV) and **B** (V and VI) are



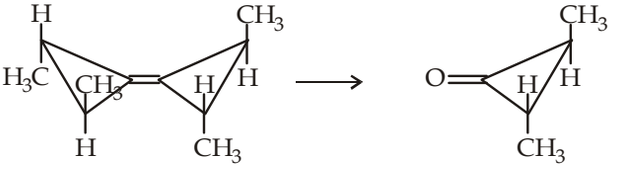
I (A) II V (B)



III (A) IV VI (B)

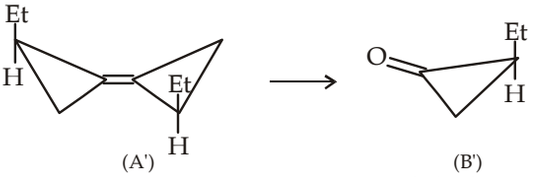
(b) For both (A) and (B) to be resolvable, each cyclopropyl ring must be substituted and the double bond must be exocyclic to each ring. Further, the substituents are either two *trans* CH_3 groups or one C_2H_5 and one H, *cis* or *gem*-dimethyls would give achiral molecules.

Arrange the *trans* methyls to avoid planes and points of symmetry to preclude the possibility of *meso* isomer. Thus the possible structures for (A) and (B) under these conditions are



(A') (B')

rac, trans- Dimethylcyclopropanone



(A') (B')

rac - Ethylcyclopropanone

(c) To expalin different products on oxidative and reductive ozzonolysis, the alkene should be of RCH = CHR type (where R is a cyclopropyl group).

$$2RCHO \xleftarrow[\text{ozonolysis}]{\text{reductive}} RCH = CHR \xrightarrow[\text{ozonolysis}]{\text{oxidative}} [2RCHO \longrightarrow 2RCOOH]$$

However, note that the R's can't be methylcyclopropyl groups because then the ozonolysis products would be a resolvable racemate of chiral enantiomers.

Hence R is either *cis*- or *trans*- cyclopropyl-$CH_2CH = CHCH_2$-cyclopropyl.

ALKYNES OR ACETYLENES

Alkynes or **acetylenes** (C_nH_{2n-2}) have a —C ≡ C— moiety and are isomeric with alkadienes, which have two double bonds. Thus the degree of unsaturation of an alkyne having one—C ≡ C— moiety is 2. For acetylene (C_2H_2),

$$\text{Degree of unsaturation} = \frac{2 \times \text{No. of C atoms} + 2 - \text{No. of H atoms}}{2} = \frac{2 \times 2 + 2 - 2}{2} = 2$$

In IUPAC system, acetylenes are called **alkynes** and their corresponding groups obtained by the removal of one hydrogen atom are called **alkynyl**.

$HC \equiv CH$ Ethyne and $HC \equiv C-$ Ethynyl

$CH_3.C \equiv CH$ Propyne and $CH_3C \equiv C-$ Propynyl

Alkynes are isomeric with alkadienes, cycloalkenes and bicycloalkanes. Thus $CH_3C{\equiv}CCH_3$, butyne-2 (C_4H_6) is isomeric with

$H_2C = CH—CH = CH_2$
1, 3-Butadiene



Cyclobutene

and



The triple bond, characteristic of acetylenes (—C ≡ C—), is formed by *sp* hybridisation. Thus only two of the four *p* orbitals of C are *sp* hybridised. The two unhybridised *p* orbitals (p_y and p_z) are at right angles to each other and also to the axis of the *sp* hybrid orbitals. Sidewise overlap of the p_y and p_z orbitals on each carbon forms the π_y and π_z bonds respectively.

TEST YOUR UNDERSTANDING - 6.15

1. Give IUPAC names of the following :

(i) $HC \equiv C–CH_2–CH=CH_2$ (ii) $CH_3–CH=CH–C \equiv C–C \equiv CH$ (iii) $CH_3C \equiv CCH_2^-$

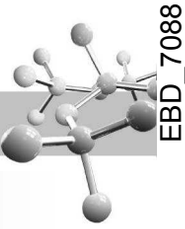
2. Give structures and IUPAC names for all alkynes with the formula C_6H_{10}.

3. Why is the C ≡ C distance shorter (124 pm) than the C=C (134 pm) and C–C (154 pm)?

4. Why geometrical isomerism is not possible in $CH_3C \equiv CC_2H_5$?

5. Is optical isomerism possible in alkynes? If yes, give the structure of the lowest alkyne that can exhibit optical isomerism.

6. An alkyne of the formula C_6H_8 has three degree of unsaturation and shows geometrical isomerism. Give the probable structure of the alkyne.



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6.9 Preparation of Alkynes

6.9.1 Synthesis of Alkynes by Elimination Reactions :

Alkynes can be prepared by double dehydrohalogenation of a geminal or vicinal dihalide. The two dehydrohalogenation steps in the base-promoted reaction occur sequentially, alkenyl halides (vinyl halides) are formed as intermediates.

$$R-\underset{|}{\overset{X}{CH}}-\underset{|}{\overset{X}{CH}}-R' \xrightarrow[\text{fast}]{\text{base, (-HX)}} R-CH=\underset{|}{\overset{X}{C}}-R' \xrightarrow[\text{slow}]{\text{base, (-HX)}} RC\equiv CR'$$

The second dehydrohalogenation step (dehydrohalogenation of vinyl halides) is more difficult than the first, so rather strongly basic conditions or high temperatures are required to eliminate second molecule of HX. When weaker bases like alcoholic KOH and low temperatures are used, the intermediate alkenyl halide may be isolated. Thus double dehydrohalogenation of alkyl dihalides is carried out by under extremely basic conditions, viz.,

(i) heating with fused (molten) KOH at about 200°C

(ii) heating with alcoholic KOH at about 200°C

(iii) heating with potassium *tert*-butoxide or sodium amide at a lower temperature.

Heating an alkyl dihalide either with fused KOH or alcoholic KOH at about 200°C yields an internal alkyne, while heating with sodium amide gives terminal alkyne as the final product. Thus any of several isomers of dibromopentane give mostly 2-pentyne on heating with fused KOH at 200°C. Actually in each case, the alkyne initially formed rearranges to the most stable isomer, 2-pentyne.

$CH_3-\underset{|}{\overset{Br}{CH}}-\underset{|}{\overset{Br}{CH}}-CH_2CH_3$ (2,3-Dibromopentane) *or* $\underset{|}{\overset{Br}{CH_2}}-\underset{|}{\overset{Br}{CH}}-CH_2CH_2CH_3$ (1,2-Dibromopentane) *or*

$Br\underset{|}{\overset{Br}{CH}}-CH_2CH_2CH_2CH_3$ (1,1-Dibromopentane) *or* $CH_3\underset{|}{\overset{Br}{C}}(Br)CH_2CH_2CH_3$ (2,2-Dibromopentane)

$\xrightarrow[200°C]{KOH} CH_3-C\equiv C-CH_2CH_3$ (2-Pentyne)

Formation of internal alkyne (non-terminal alkyne) as the final product is due to rearrangement of the less stable terminal alkyne (e.g. 1-pentyne) to the more stable highly substituted alkyne (as in alkenes) in presence of weak base like KOH. However, this rearrangement (i.e. terminal to internal alkyne) is not possible in presence of very strong base ($NaNH_2$) because the strong base converts the terminal alkyne to alkynide salt which, being very strong base, cannot rearrange.

$$CH_3CH_2CH_2C\equiv CH \xrightarrow{NH_2^-} CH_3CH_2CH_2C\equiv C:^-$$

On the other hand, strongly basic $NaNH_2$ converts the internal alkyne to the terminal alkyne on heating to 150°C.

$$\underset{\text{Pentyne–2}}{CH_3C\equiv CCH_2CH_3} \xrightarrow{NaNH_2,\ 150°C} CH_3CH_2CH_2C\equiv C:^-\ Na^+ \xrightarrow{H_2O} \underset{\text{Pentyne–1}}{CH_3CH_2CH_2C\equiv CH}$$

In short,

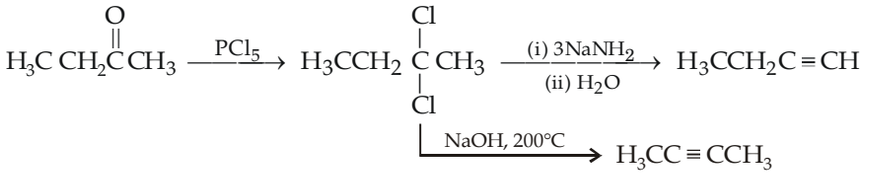
$$\text{Terminal alkyne} \xleftarrow[\text{(ii) } H_2O]{\text{(i) } NaNH_2,\ 150°C} \underset{H}{\overset{R}{\diagdown}}C=C\underset{R'}{\overset{X}{\diagup}} \xrightarrow[200°C]{KOH} \text{More stable internal alkyne}$$

Recall that the vicinal dihalides and geminal dihalides are easily prepared from alkenes and aldehydes (or ketones) respectively.

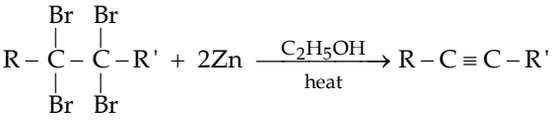
$$\underset{\text{Butene–1}}{CH_3CH_2CH=CH_2} \xrightarrow[CCl_4]{Br_2} CH_3CH_2\underset{|}{\overset{Br}{CH}}-\underset{|}{\overset{Br}{CH_2}} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } 3NaNH_2} \underset{\text{Butyne–1}}{CH_3CH_2C\equiv CH}$$

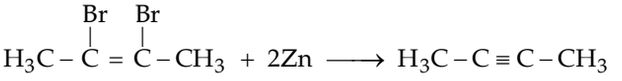
$$\downarrow NaOH,\ 200°C$$

$$\underset{\text{Butyne–2}}{CH_3C\equiv CCH_3}$$



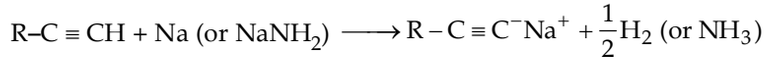
vicinal-Tetrahalogen compounds and *vicinal*-alkenyl dihalides can be converted to alkynes by heating with Zn or Mg.

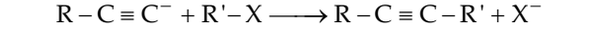




6.9.2 By Alkylation of Acetylide Ions

As we shall see later, alkynes with a terminal triple bond (R–C ≡ C–H) are acidic and react readily with sodium (or sodium amide) forming salts called *acetylides*. These **acetylides are good nucleophiles** and react with primary alkyl halides (not *sec* or *tert*) to form higher alkyl alkynes (S_N2 reaction).



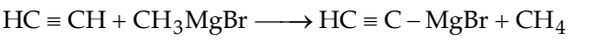


NOTE :

(i) This method is used to prepare higher alkynes.

(ii) Alkyl halides, used for alkylation should be 1° with no bulky substituents or branches close to the reaction center., 2° and 3° alkyl halides will also undergo elimination reaction (E2 elimination) in presence of acetylides, strongly basic compounds.

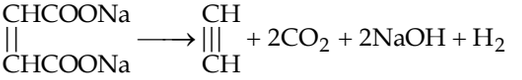
Acetylenes having at least one terminal hydrogen atom can also be alkylated by means of Grignard reagents.





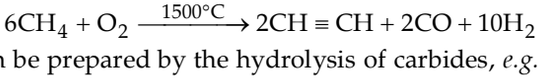
6.9.3 Kolbe's method

Electrolysis of a solution of sodium or potassium salt of maleic or fumaric acid gives acetylene at anode.

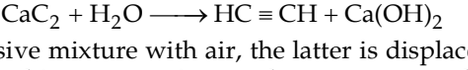


6.9.4 Industrial Methods

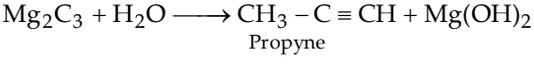
(i) Acetylene and propyne can be prepared by the controlled, high-temperature partial oxidation of methane.



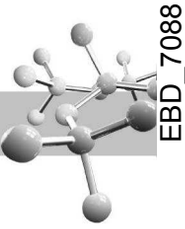
(ii) Acetylene and propyne can be prepared by the hydrolysis of carbides, *e.g.*



Since acetylene forms an explosive mixture with air, the latter is displaced from the flask by oil gas. Impurities like H_2S, NH_3, arsine and phosphine present in acetylene are removed by passing the gas through an acidic copper sulphate solution. The pure gas is collected over water.



Propyne



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6.9.5 Acetylene can be prepared by heating iodoform or chloroform with silver powder or zinc.

$$CHI_3 + 6Ag + I_3CH \longrightarrow HC \equiv CH + 6AgI$$

TEST YOUR UNDERSTANDING - 6.16

1. Explain the formation of A as the major product in the following reaction :

$$CH_3\overset{\overset{Br}{|}}{C}HCH_2Br \xrightarrow{1\text{ alc. KOH}} \underset{(A)}{CH_3CH=CHBr} + \underset{(B)}{CH_2=CHCH_2Br} + \underset{(C)}{CH_3\overset{\overset{Br}{|}}{C}=CH_2}$$

2. Give the product formed in each case :

(a) $HC \equiv C:^- Na^+ + Br_2 \longrightarrow$ (b) $HC \equiv C:^- Na + CH_3CH_2CH_2Br \longrightarrow$

(c) $HC \equiv C:^- Na^+ + CH_3CH_2CH_2Cl \longrightarrow$ (d) $CH_3C \equiv C:^- + (CH_3)_2CHCH_2Br \longrightarrow$

3. Give steps involved in the synthesis of the following compounds :

(a) 2-Hexyne from acetylene (b) 5-Methyl-2-hexyne from acetylene

(c) 3-Octyne from 1-bromobutane (d) Ethylcyclohexylacetylene by alkylation process

4. Formulate the reaction between calcium carbide and water to form acetylene as a Bronsted acid-base reaction.

5. Give reactions for the following conversions :

(i) Propene to propyne (ii) 2-butene to 2-butyne (iii) Ethyne to 2-hexyne

6.10 Physical Properties

Being compounds of low polarity, physical properties of alkynes are nearly same as that of alkenes and alkanes. These are insoluble in water but quite soluble in usual organic solvents of low polarity, *viz*. ether, benzene and CCl_4. These are less dense than water.

Alkynes are colourless and odourless; however, the garlic like odour associated with common acetylene is due to the presence of impurities like H_2S, PH_3 etc. Acetylene liquefies at –84°C under ordinary pressure. However, since liquid acetylene is dangerously explosive, use or storage of acetylene in the form of liquid is prohibited and hence it is stored and transported in acetone solution, soaked on porous solid like asbestose kept in steel cylinders under high pressure.

6.11 Chemical Properties

Chemical properties of alkynes are mainly due to two factors.

(i) *Presence of π-electrons*. Due to the presence of π bonds, alkynes (—C ≡ C—) have loosely held π electrons; hence, like alkenes, they undergo electrophilic additions very easily. However, additions on alkynes differ from that of alkenes in the following two respects.

(a) A carbon-carbon triple bond is less reactive than a carbon-carbon double bond towards electrophilic addition reactions. This is because of the fact that the *sp* hybridised carbon of alkynes has more *s* character than that of the sp^2 hybridised carbon of alkenes. Now since greater is the *s* character of a carbon atom, more strongly will be the attraction for π electrons and hence lesser will be their availability for reaction.

(b) In addition to electrophilic additions, alkynes also undergo nucleophilic additions with electron rich reagents (nucleophiles), like water, HCN, RCOOH and ROH.

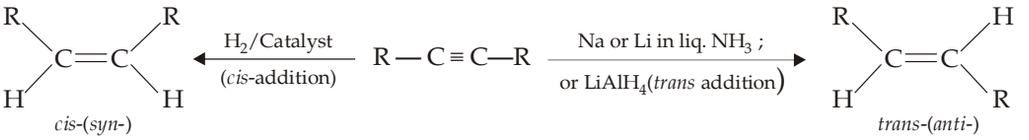
(ii) *Presence of acidic hydrogen atoms.* Hydrogen atom attached to the triply bonded carbon atom can be easily removed by a strong base, hence acetylenes or 1-alkynes are considered as **weak acids**.

6.11.1 Addition of Hydrogen

Catalytic hydrogenation of alkynes takes place in two stages first forming an alkene and then alkane.

$$R-C\equiv C-R' \xrightarrow{H_2/Cat.} R-CH=CH-R' \xrightarrow{H_2/Cat.} R-CH_2-CH_2-R'$$

However, hydrogenation can be stopped at the alkene stage by using calculated amount of hydrogen and choosing suitable reaction conditions. Further, if the triple bond is not present at the terminal carbon atom, the alkene formed may be *cis* or *trans* depending upon the nature of the reducing agent.



***syn*-Addition of hydrogen (Synthesis of *cis*-alkenes)**

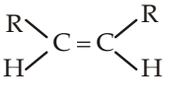
Hydrogenation of an alkyne can be stopped at the alkene stage by using a partially deactivated (poisoned) catalyst. The most common partially deactivated metal catalyst is **Lindlar's catalyst** (metallic palladium, deposited on calcium carbonate, or barium sulphate, poisoned with lead acetate and quinoline). The catalytic hydrogenation of alkynes is similar to the hydrogenation of alkenes. The reaction takes place on the surface of the catalyst leading to *syn* addition in both cases.

A number of other catalysts for semihydrogenation of alkynes have been developed. These include Pd supported on barium sulphate, and a **nickel boride** also known as **P-2 catalyst.** Nickel boride can be prepared by the reduction of nickel acetate with sodium borohydride.

$$(CH_3\overset{O}{\overset{\|}{C}}O)_2Ni \xrightarrow[C_2H_5OH]{NaBH_4} Ni_2B$$

Hydrogenation of alkynes in the presence of P-2 catalyst also causes syn addition of hydrogen.

$$RC\equiv CR \xrightarrow[\text{or } H_2, Pd/CaCO_3, \text{ quinoline}]{H_2/Ni_2B}$$

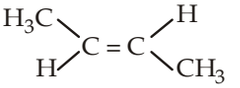


cis-2-Butene

***anti*-Addition of hydrogen (Synthesis of *trans*- alkenes)**

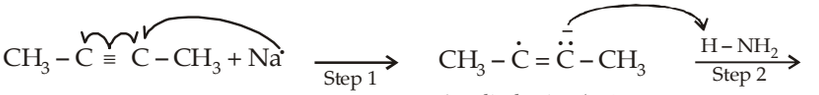
Anti addition of hydrogen atoms to the triple bond occurs when alkynes are reduced with sodium (or lithium) metal in amonia, ethylamine, or alcohol at low temperatures. This reaction called, a **dissolving metal reduction**, produces an (*E*)- or *trans*- alkene.

$$CH_3-C\equiv C-CH_3 \xrightarrow[liq.\ NH_3]{Na/Li}$$

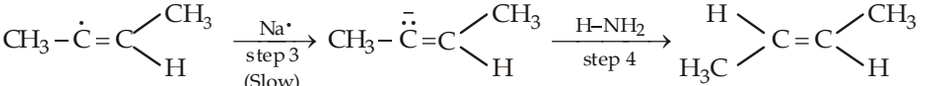


2-Butyne *trans* -2-Butene

The mechanism for this reduction involves successive electron transfer from sodium (or lithium) atoms (steps 1 and 3) and proton transfer from ammonia, or amines, or alcohol (steps 2 and 4) used as a cosolvent.



A radical anion (a strong base) species with a – charge and an unpaired electron)



A vinylic radical **A vinylic anion** (base)

Since *trans*-vinylic anion is more stable (bulky alkyl groups are farther apart) than the *cis*-, the former is formed faster leading to *tans*-alkene as the final product.

Note that sodium amide and sodium in liquid ammonia are different, sodium amide is a strong base, used for removing a proton from a terminal alkyne. On the other hand, sodium in liq. NH_3 is used as a source of electrons in the reduction of an alkyne to a *trans* alkene.

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TEST YOUR UNDERSTANDING - 6.17

1. Give steps involved in each of the following conversions.

(a) *trans*-2-Pentene to *cis*-2-pentene (b) *cis*-2-Pentene to *trans*-2-pentene

(c) *cis*-Cyclodecene to *trans*-cyclodecene (d) Propyne to 2-methyl-1-penten-3-yne, $CH_3C \equiv C\overset{CH_3}{\overset{|}{C}} = CH_2$

2. Can you convert a mixutre of 60% *trans*-2-pentene and 40% *cis*-2-pentene to a pure *cis*-2-pentene?

6.11.2 Electrophilic Addition to alkynes takes place in two stages.

$$-C \equiv C- + XY \longrightarrow -\overset{X}{\underset{|}{C}} = \overset{Y}{\underset{|}{C}}- \xrightarrow{XY} -\overset{X}{\underset{|}{C}}-\overset{Y}{\underset{|}{C}}-$$

As mentioned earlier, addition of an electrophile to alkynes takes place slowly than that on alkenes as evidenced by the fact that in some reactions, a catalyst (generally a metal salt is needed.) The low reactivity of alkynes is belived to be due to following two factors.

(i) The bridged intermediate carbocation formed by the initial attack of an electrophile on the triple bond is a highly strained system, and hence less stable.

$$-C \equiv C- + E^{\oplus} \longrightarrow \underset{\text{Highly strained bridged carbocation}}{-C \overset{E^{\oplus}}{\equiv} C-}$$

The formation of cyclic carbocation as an intermediate is borne out by the fact that the olefinic intermediate is always *trans*.

(ii) Due to *sp* hybridization of acetylenic carbon atom, π-electrons are more tightly held by the carbon nuclei and hence they are less easily available for combination with electrophiles.

(a) **Addition of halogens (Br_2, Cl_2).** Addition of halogens takes place in two stages, first forming a *trans*-1, 2-dihaloalkene and then 1, 1, 2, 2-tetrahaloalkane.

$$R-C \equiv C-R' \xrightarrow{X_2} \underset{X}{\overset{R}{}}C=C\underset{R'}{\overset{X}{}} \xrightarrow{X_2} R-CX_2-X_2-R'$$

However, the reaction may be limited to the formation of halogenated alkene stage by choosing proper conditions like use of bromine water instead of bromine alone which will form tetrabromo derivative.

Addition of Cl_2 on ethyne is important as it leads to the formation of industrially important compounds.

$$\underset{\text{Ethyne}}{\overset{CH}{\overset{|||}{CH}}} \xrightarrow{Cl_2} \underset{\text{1, 2–Dichloroethene}}{\overset{CHCl}{\overset{||}{CHCl}}} \xrightarrow{Cl_2} \underset{\substack{\text{1, 1, 2, 2–Tetrachloroethane}\\(\text{Westron})}}{\overset{CHCl_2}{\overset{|}{CHCl_2}}} \xrightarrow[(-HCl)]{BaCl_2} \underset{\substack{\text{Trichloroethylene}\\(\text{Westrosol})}}{\overset{CCl_2}{\overset{||}{CHCl}}}$$

Westron and westrosol are used as industrial solvents for rubber, fats and varnishes.

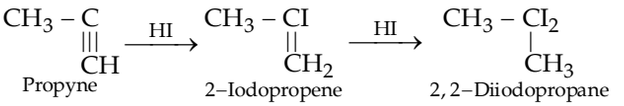
(b) **Addition of halogen acids (HCl, HBr, HI)** takes place according to Markownikoff's rule.

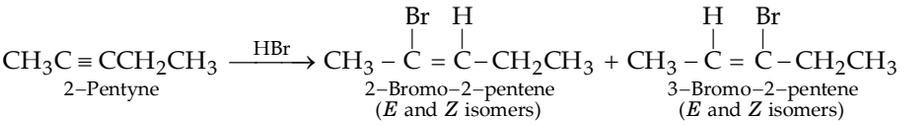
$$\underset{\text{Ethyne}}{\overset{CH}{\overset{|||}{CH}}} + HCl \longrightarrow \underset{\text{Vinyl chloride}}{\overset{CH_2}{\overset{||}{CHCl}}} \xrightarrow{HCl} \overset{CH_3}{\overset{|}{CHCl_2}}$$

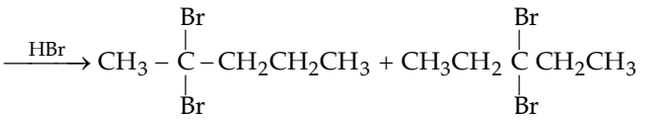
The order of reactivity of halogen acids is HI > HBr > HCl > HF; HF adds only under pressure.

Addition of HCl on ethyne can be limited to vinyl chloride in presence of mercuric ions (catalyst).

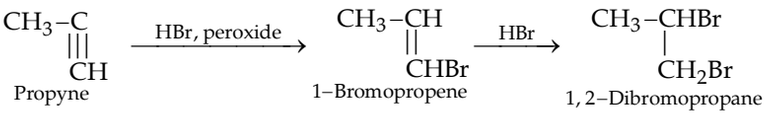
In case of unsymmetrical alkynes, addition takes place according to Markownikoff's rule.







In presence of peroxides, *anti*-Markownikoff's product is obtained.

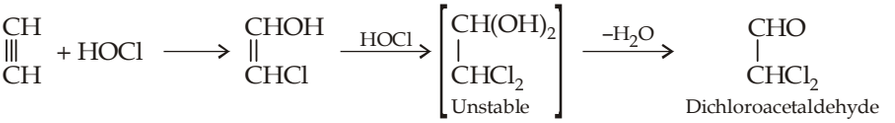


(c) **Addition of other acids** *e.g.* CH_3COOH, HOCl, conc. H_2SO_4.

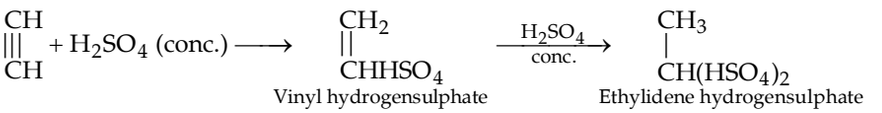
(i)



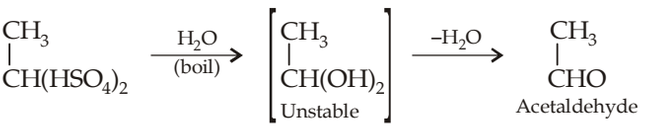
(ii)



(iii)

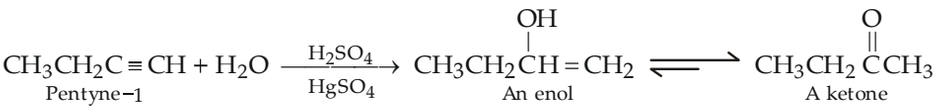


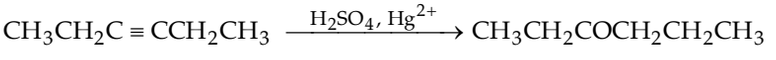
Ethylidene hydrogensulphate on boiling with water produces acetaldehyde.

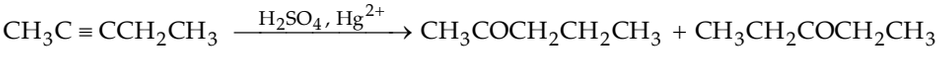


(d) **Hydration of alkynes by addition of water :** Like alkenes, alkynes undergo acid-catalyzed addition of water in the presence of mercuric ion as a catalyst. A mixture of mercuric sulphate in aqueous sulphuric acid is commonly used as the reagent.

The reaction follows Markovnikov's rule leading to the formation of an enol which immediately rearranges to the more stable carbonyl compound (**keto-enol tautomerization**). Since alkynes possess only limited solubility in aqueous sulphuric acid, methanol or acetic acid is often added as a co-solvent.

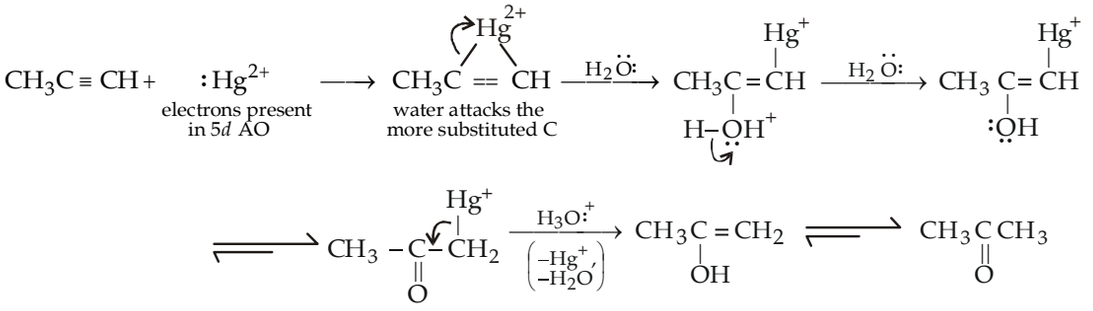






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Mechanism :



The mechanism of the mercury (II) - catalyzed alkyne hydration is analogous to the oxymercuration reaction of alkenes. In the former case, vinylic carbocation containing mercury loses proton to water to form a mercury-containing enol intermediate. Now mercury is lost due to acidic conditions (H_3O^+), thus requiring no $NaBH_4$ as in case of alkenes.

TEST YOUR UNDERSTANDING - 6.18

1. One mole of Br_2 and 1 mole of butyne-1 are reacted to form corresponding dibromide, which should be the better choice for adding one compound to another?

(i) Bromine solution added to butyne-1. (ii) Butyne-1 added to bromine solution.

2. Alkenes are more reactive than alkynes toward addition of electrophilic reagents (e.g. Br_2, HBr, etc.) yet it is easy to stop the reaction at the alkene stage when 1 molar equivalent of the reagent is used. Explain.

3. Give the product in the following reaction.

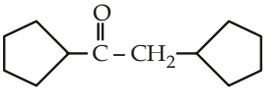
$$CH_2 = CHCH_2C \equiv CH \xrightarrow{1\ eq.\ HBr}$$

4. Alkynes are less reactive than alkene toward addition of Br_2. Explain on the basis of stability of bromonium ion.

5. Although alkenes are more reactive than alkynes toward addition reaction, reverse is true regarding catalytic hydrogenation. Explain.

6. Acetylene does not dissolve in conc. H_2SO_4, while ethylene and other alkynes dissolve. Explain.

7. List the alkynes needed to synthesize the following ketones in the best possible yields.

(a) $Me_2CH\overset{O}{\overset{\|}{C}}CH_3$ (b) $CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3$ (c) 

(e) **Hydration of alkynes by addition of borane (hydroboration - oxidation) :** Borane adds to alkynes in the same way as in alkenes to form enol which rearranges to the more stable carbonyl compound.

$$3CH_3C \equiv CCH_3 + BH_3 \xrightarrow{THF} CH_3CH = \underset{\displaystyle BH_2}{\underset{|}{C}}CH_3 \xrightarrow[H_2O]{OH^-,\ H_2O_2}$$

$$3CH_3CH = \underset{\displaystyle OH}{\underset{|}{C}}CH_3 \rightleftharpoons 3CH_3CH_2\overset{O}{\overset{\|}{C}}CH_3$$

(i) The reaction stops at the alkene stage in the internal alkynes because the bulky groups on the boron-substituted alkene prevent further addition of borane. However, in case of terminal alkynes, hindered dailkylborane must be used to prevent the addition of the two molecules of borane across the triple bond. One such borane is **disecondary-isoamylborane**, also called as *disiamyl*borane (siamyl *stands for* secondaryisoamyl), and abbreviated as Sia_2BH.

$$\left[(CH_3)_2CH - \underset{\displaystyle CH_3}{\underset{|}{C}}H - \right]_2 BH \quad \textit{or} \quad Sia_2BH$$

In case unhindered dialkylborane is used, terminal alkynes add two molecules of diborane to form aldehyde as the final product.

$$CH_3CH_2 \equiv CH \xrightarrow{HBR_2} \left[CH_3CH_2CH_2\overset{\displaystyle BR_2}{\overset{|}{C}}H \right] \xrightarrow[H_2O]{H_2O_2} CH_3CH_2CH_2CHO$$

Thus hydroboration / oxidation sequence is complementary to the direct, mercury (II)-catalyzed hydration reaction of a terminal alkyne because different products are obtained.

$$\underset{\text{An aldehyde}}{R-CH_2-\overset{O}{\overset{\|}{C}}-H} \xleftarrow[(ii)\ H_2O_2]{(i)\ BH_3,\ THF} R-C\equiv CH \xrightarrow[HgSO_4]{H_2O,\ H_2SO_4} \underset{\text{A ketone}}{R-\overset{O}{\overset{\|}{C}}-CH_3}$$

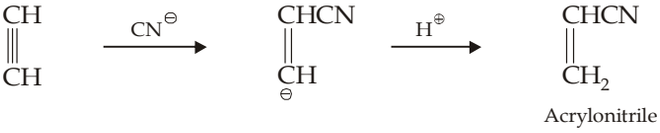
(ii) In case of unsymmetrical alkynes, boron adds on the less substituted carbon, thus *anti*-Markovnikov addition of water takes place.

Alkenylboranes are readily cleaved to alkenes on boiling with acetic acid or propanoic acid (similarity with alkylboranes which give alkanes on similar treatment).

$$CH_3C\equiv CH \xrightarrow[THF]{BH_3} [CH_3CH=CH]_3B \xrightarrow{CH_3COOH} CH_3CH=CH_2$$

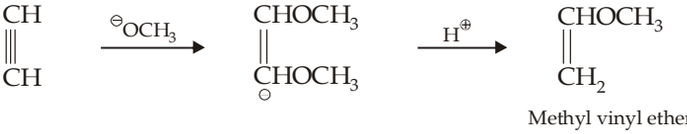
6.11.3 Nucleophilic Addition Reactions

Due to decreased reactivity of a carbon-carbon triple bond towards electrophilic additions, alkynes are found to be susceptible to nucleophilic attack. Addition of hydrogen cyanide, methanol and carbonyl compounds in presence of sodium ethoxide are important examples.

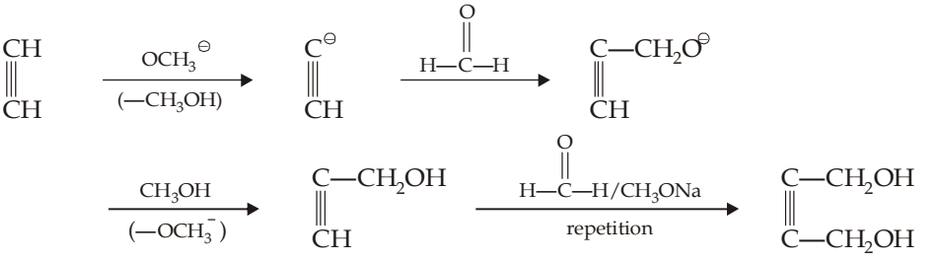
(a)


Acrylonitrile

Acrylonitrile is extensively used for the manufacture of **buna N**.

(b)


Methyl vinyl ether

(c)


Thus the net result is the replacement of the acetylenic hydrogen atom(s) by CR_2OH group.

6.11.4 Oxidation of Alkynes with Permanganate

(i) Using aq. $KMnO_4$ in nearly neutral conditions.

$$R-C\equiv C-R' \xrightarrow[H_2O,\ \text{neutral}]{KMnO_4} \left[R-\overset{OH}{\overset{|}{C}}-\overset{OH}{\overset{|}{C}}-R' \right] \xrightarrow{-2H_2O} R-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R'$$

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(ii) Using warm, basic permanganate, diketone formed above undergoes further oxidation forming salts of carboxylic acids.

$$R-C\equiv C-R' \xrightarrow[H_2O,\ heat]{KMnO_4,\ KOH} R-\overset{O}{\overset{\|}{C}}-O^- + R'-\overset{O}{\overset{\|}{C}}-O^-$$

Alkynes are not affected by peroxyformic acid and chronic acid.

6.11.5 Ozonolysis

Ozonolysis requires neither oxidative nor reductive work up, it is followed only by hydrolysis. Carbon dioxide is obtained from the CH group of a terminal alkyne.

$$CH_3C\equiv CH \xrightarrow[(ii)\ H_2O]{(i)\ O_3} CH_3COOH + CO_2$$

$$CH_3CH_2C\equiv CCH_3 \xrightarrow[(ii)\ H_2O]{(i)\ O_3} CH_3CH_2COOH + CH_3COOH$$

Since a triple bond is less reactive than a double bond, yields of oxidation products are sometimes low.

TEST YOUR UNDERSTANDING - 6.19

1. Give the product when 2-butyne is treated with BH_3.THF.

2. Complete the following

$$CH_3C\equiv CCH_3 \xrightarrow{BD_3.THF} [A] \xrightarrow{CH_3COOD} [B]$$

3. Give the products of

(i) Mercuric-ion catalyzed addition of water, and

(ii) Hydroboration oxidation for each of the following

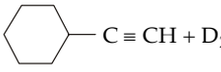
(a) 1-Butyne (b) 2-Butyne (c) 2-Pentyne

4. Complete the following :

(a) $CH\equiv CH + Br_2 \longrightarrow$ (A)

(b) $CH\equiv CH + 2HBr \longrightarrow$ (B)

(c) $CH_3 - C\equiv CH + CCl_3Br \longrightarrow$ (C)

(d)  $\xrightarrow{H_2SO_4/HgSO_4}$ (D)

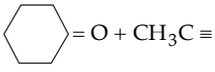
(e) $CH_2=CHCH_2C\equiv CH + HBr \longrightarrow$ (E)

(f) $CH\equiv CCH=CH_2 + HBr \longrightarrow$ (F)

5. Alkynes undergo nucleophilic addition, such as addition of CN^-, while alkenes do not undergo such reactions. Explain.

6. Complete the following reaction :

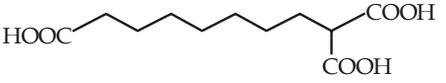
(i) $CH_3CHO + HC\equiv CD \xrightarrow{CH_3ONa}$

(ii)  $\xrightarrow{CH_3ONa}$

7. Give the product expected by the oxidation of cyclodecyne with

(i) dilute, neutral $KMnO_4$, and (ii) warm basic $KMnO_4$.

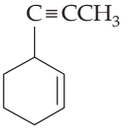
8. An alkyne undergoes oxidative cleavage to give following compounds.

 + CH_3CH_2COOH

Propose a structure for the alkyne.

9. Deduce the structural formula of a compound, $C_{10}H_{10}$ that gives $HOOCCH_2CH(CH_2COOH)_2$ as the organic compound on oxidative cleavage.

10. Complete the following :

(i) C + D $\xleftarrow{O_3/H_2O}$  $\xrightarrow[heat]{KMnO_4}$ A + B

(ii) $CH_3CH_2C\equiv CH \xrightarrow{BH_3} E \xrightarrow{CH_3COOD} F$

6.11.6 Acidic Nature

Hydrogen atom or atoms attached to the triply bonded carbon atoms can be easily removed by a strong base, thus 1-alkynes are considered as **weak acids**.

$$R-C\equiv C:H + Base \longrightarrow R-C\equiv C^{-} + H-Base$$

The acidity of acetylene or 1-alkynes can be explained on the basis of molecular orbital concept according to which formation of C–H bonds in acetylene involves *sp*-hybridised carbon atom. Now since *s* electrons are closer to the nucleus than *p* electrons, the electrons present in a bond having more *s* character will be correspondingly more closer to the nucleus. The amount of *s* character in various types of C–H bonds is as follows.

Type of C–H bond	≡ C–H	= C–H	–C–H
% of *s* character in C	50%	33.3%	25%

Thus owing to high *s* character of the C–H bond in alkynes (*s* = 50%), the electrons constituting this bond are most strongly held by the carbn nucleus (*i.e.* the acetylenic carbon atom or the *sp* orbital acts as more electronegative species than the sp^2 and sp^3) with the result the hydrogen present on such a carbon atom (≡ C–H) can be easily removed as a proton. The acidic nature of the three types of C–H bonds follows the following order.

$$\equiv C-H > = C-H > -C-H$$
$$sp \qquad sp^2 \qquad sp^3$$

Being most electronegative*, the carbon of acetylene is best able to accommodate the electron pair in the anion left after the porton is lost. In other words, anion of acetylene is the most stable and hence most acidic, while anion of ethane is the least stable (because sp^3 carbon is the least electronegative) and hence least acidic.

$$CH\equiv CH + :B^{-} \rightleftharpoons HB + HC\equiv C:^{-} \quad \textbf{(Most stable)}$$

$$H_3C-CH_3 + :B^{-} \rightleftharpoons HB + H_3C-CH_2:^{-} \quad \textbf{(Least stable)}$$

Relative acidities $HOH \simeq HOR > CH\equiv CR > HNH_2 > H_2C=CH_2 > CH_3-CH_3$

Relative basicities $^{-}OH \simeq {}^{-}OR < {}^{-}C\equiv CR < {}^{-}NH_2 < {}^{-}CH=CH_2 < {}^{-}CH_2-CH_3$

Because of acidic nature, acetylenic hydrogen atom can be easily replaced by certain metals to give the metallic derivative called **acetylides** or **alkynides**. Acetylene has two such hydrogen atoms, 1-alkynes have one such hydrogen atom and the other alkynes nil.

$$\underset{\substack{\text{Acetylene}\\\text{(having two acidic hydrogen)}}}{H-C\equiv C-H} \quad , \quad \underset{\substack{\text{1–Butyne}\\\text{(one acidic hydrogen)}}}{CH_3CH_2-C\equiv C-H} \quad , \quad \underset{\substack{\text{2–Butyne}\\\text{(no acidic hydrogen)}}}{H_3C-C\equiv C-CH_3}$$

Alkynides (dry) are generaelly unstable and explosive. These are easily converted into original alkynes when heated with dilute acids.

$$NaC\equiv CNa + 2HNO_3 \longrightarrow HC\equiv CH + 2NaNO_3$$

Hence *this reaction can be used for the purification, separation and identification of alkynes.*

(*i*) **Formation of sodium acetylides :** Acetylenes and monoalkylacetylenes react with sodium in liquid ammonia or sodamide to form acetylides.

$$H-C\equiv C-H + Na \xrightarrow[NH_3]{liq.} \underset{\text{Monosodium acetylide}}{H-C\equiv C-Na} \xrightarrow[120^\circ]{NaNH_2} \underset{\text{Disodium acetylide}}{NaC\equiv CNa}$$

$$CH_3-C\equiv C-H \xrightarrow{NaNH_2} \underset{\text{Sodium propynide}}{CH_3-C\equiv CNa}$$

Similarly, $$HC\equiv CH + CH_3MgI \longrightarrow \underset{\text{Acetylenicmagnesium iodide}}{HC\equiv CMgI} + CH_4$$

These alkynides are ionic in nature.

As discussed earlier the sodium alkynides react with primary alkyl halides to form higher alkynes.

$$CH_3-C\equiv CNa + ICH_3 \xrightarrow{S_N2} CH_3-C\equiv C-CH_3 + NaI$$

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* Remember that higher the electronegativity of an atom, greater is its ability to hold bonding electrons close to it. The order of electronegativity of the three type of carbon atoms is $sp > sp^2 > sp^3$.

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(ii) **Addition of acetylide ions to carbonyl groups :** Like other carbanions, acetylide ions are strong nucleophiles and strong bases. Thus in addition to displacing halide ions in S_N2 reactions, they can add to carbonyl groups, to form alkoxide ions which again being strong bases react with water or a dilute acid to give corresponding alcohol.

$$RC\equiv C^{-}: + \begin{matrix} R \\ \diagdown \\ R' \end{matrix}\!\!>C=O \longrightarrow RC\equiv C-\underset{\displaystyle R'}{\overset{\displaystyle R}{\underset{|}{\overset{|}{C}}}}-O^{-} \xrightarrow{H_3O^{+}} RC\equiv C-\underset{\displaystyle R'}{\overset{\displaystyle R}{\underset{|}{\overset{|}{C}}}}-OH$$

Alcohol (1°, 2° or 3°)

where, R and R' may be H or any alkyl group

Note that these reactions are similar to those of Grignard reagents.

(*iii*) **Formation of copper and silver acetylides :** Copper and silver alkynides are obtained by passing alkynes in the ammonical solution of cuprous chloride and silver nitrate respectively.

$$HC\equiv CH + \underbrace{Cu_2Cl_2 + 2NH_4OH}_{\text{Ammonical cuprous chloride}} \longrightarrow \underbrace{CuC\equiv CCu\downarrow}_{\text{Copper acetylide (red ppt.)}} + 2NH_4Cl + 2H_2O$$

$$HC\equiv CH + \underbrace{2AgNO_3 + 2NH_4OH}_{\text{Amm. silver nitrate}} \longrightarrow \underbrace{AgC\equiv CAg\downarrow}_{\text{Silver acetylide (white ppt.)}} + 2NH_4NO_3 + 2H_2O$$

Silver and copper acetylides are bonded more covalently than other acetylides. These are not very soluble and form characteristic precipitates. These are much less basic and less nucleophilic.

These reactions are used for *detecting the presence of acetylenic hydrogen atom.* For example, butyne-1 having acetylenic hydrogen atom gives red and white precipitate with ammonical cuprous chloride and ammonical silver nitrate solution, respectively, while butyne-2 does not give such precipitate.

$$\underset{\text{Butyne–1}}{CH_3CH_2C\equiv CH} \qquad \underset{\text{Butyne–2}}{CH_3C\equiv CCH_3}$$

It is important to note that these heavy metal acetylides are likely to explode. Hence they should be destroyed while still wet by warming with nitric acid; the strong mineral acid regenerates the weak acid, acetylene.

$$CH_3C\equiv CAg \xrightarrow{HNO_3} CH_3C\equiv CH + Ag^{+}$$

(*iv*) Reaction with Grignard reagents :

$$HC\equiv CH + CH_3MgI \longrightarrow CH_4 + HC\equiv CMgI$$

$$HC\equiv CMgI \xrightarrow{RI} HC\equiv CR$$

TEST YOUR UNDERSTANDING - 6.20

1. Is there any inconsistency between the facts that the C–H bond in acetylene has the greatest bond energy of all C–H bonds and hence it is the most acidic?

2. Comment on the feasibility of the following reactions :

(i) $CH_3C\equiv CH + \text{aq. NaOH} \longrightarrow$ (ii) $CH_3CH_2C\equiv CMgI + CH_3OH \longrightarrow$ (iii) $CH_3C\equiv C^{-} + NH_4^{+} \longrightarrow$

3. Butyne-1 reacts with ethyl magnesium bromide to form gas A which does not decolourise Br_2 water or alkaline $KMnO_4$. Identify gas A.

4. Complete the following :

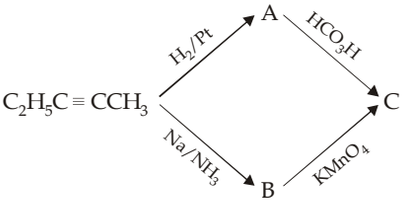
(i) $CH\equiv CH + Br_2 \longrightarrow A \xrightarrow{KMnO_4} B$ (ii) $CH_3CHBrCHBrCH_2CH_3 \xrightarrow{KNH_2} C$

(iii) $HC\equiv CCH_2CH_3 \xrightarrow{Ag(NH_3)_2^{+}} D \xrightarrow{HNO_3} E$ (iv) $CH_3C\equiv CH \xrightarrow{BH_3} F \xrightarrow{CH_3COOH} G \xrightarrow{\text{dil. aq } KMnO_4} H$

(v) $ClCH_2CH(CH_3).CHCl.CH_3 \xrightarrow{\text{Alc. KOH}} I \xrightarrow[KMnO_4]{BrCCl_3} J + K$

5. Give all steps used for the conversion of 2-bromobutane to *trans*-2-butene.

6. Identify (A) to (C) in the following reactions :



7. Name the product and give mechanism for the reaction of propyne with Br_2 + NaOH.

6.11.7 Rearrangement of alkynes

(i) When heated with ethanolic potassium hydroxide, the triple bond of an alkyne migrates towards the centre of the chain, *e.g.*

$$\underset{\text{1–Butyne}}{CH_3CH_2C \equiv CH} \xrightarrow[KOH]{\text{ethanolic}} \underset{\text{2–Butyne}}{CH_3C \equiv CCH_3}$$

(ii) When heated with sodamide in an inert solvent (paraffin), the triple bond of an alkyne shifts towards the end of the chain, *e.g.*

$$\underset{\text{2–Butyne}}{CH_3C \equiv CCH_3} \xrightarrow[\text{paraffin}]{NaNH_2} CH_3CH_2 \equiv C^-Na^+$$

6.11.8 Polymerisation

Alkynes undergo polymerisation to give linear or cyclic products depending upon the temperature and catalyst used.

Linear polymerisation

Acetylene when passed into cuprous chloride solution containing ammonium chloride, its two molecules combine together to form vinylacetylene; since two molecules are involved, the reaction is more correctly known as **dimerisation**.

$$HC \equiv CH + HC \equiv CH \xrightarrow[NH_4Cl]{Cu_2Cl_2} \underset{\text{Vinylacetylene}}{CH_2 = CH - C \equiv CH}$$

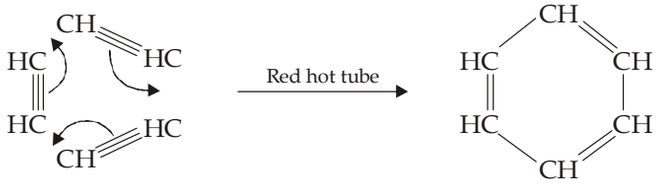
The dimer product may further be converted into trimer.

$$\underset{\text{Vinylacetylene}}{CH_2 = CH - C \equiv CH} + CH \equiv CH \xrightarrow{Cu_2Cl_2} \underset{\text{Divinylacetylene}}{CH_2 = CH - C \equiv C - CH = CH_2}$$

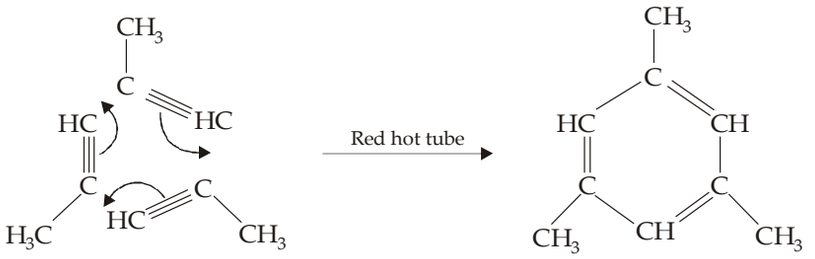
The dimer of acetylene, *i.e.*, vinylacetylene is a very important compound since it reacts with HCl to form 2-chloro-1, 3-butadiene, commonly known as **chloroprene** which is used in the manufacture of a synthetic rubber, **neoprene**.

$$\underset{\text{Vinylacetylene}}{CH_2 = CH - C \equiv CH} + HCl \longrightarrow \underset{\text{Chloroprene}}{CH_2 = CH - \overset{\overset{Cl}{|}}{C} = CH_2}$$

Alkynes, when passed through a red hot iron tube, undergo cyclic polymerisation to form aromatic hydrocarbons.



Acetylene (3 molecules) Benzene



Propyne (3 molecules) — 1, 3, 5-Trimethylbenzene (Mesitylene)

Acetylene, when treated with nickel cyanide under pressure, forms cyclo-octatetraene

$$4CH \equiv CH \xrightarrow[\text{pressure}]{Ni(CN)_2}$$ 

Cyclo-octatetraene

6.11.9 Combustion

Acetylenes burn in air or oxygen to form CO_2 and water with the evolution of large amount of heat.

$$C_nH_{2n-2} + \frac{3n-1}{2}O_2 \longrightarrow nCO_2 + \frac{2n-2}{2}H_2O + \text{Heat}$$

e.g. $$2CH \equiv CH + 5O_2 \longrightarrow 4CO_2 + 2H_2O + 312\ \text{kCal}$$

The combustion of acetylene is used industrially for welding and cutting of metals in which oxy-acetylene flame having high temperature (3000°C) is produced.

6.11.10 Other Reactions of Acetylene

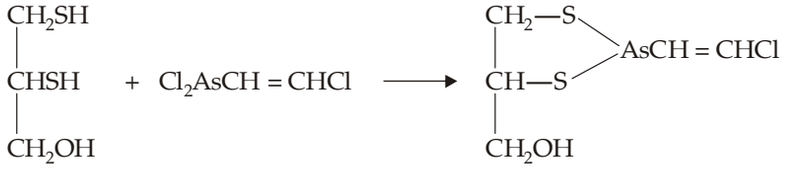
(*i*) **Addition of arsenic trichloride :** Acetaldehyde adds on arsenic chloride in presence of $AlCl_3$, Cu_2Cl_2 or $HgCl_2$ to form 2-chlorovinyldichloroarsine, commonly known as **Lewisite**.

$$\begin{matrix}CH\\ \|\\ CH\end{matrix} + ClAsCl_2 \longrightarrow \begin{matrix}CHCl\\ \|\\ CHAsCl_2\end{matrix}$$

2–Chlorovinyldichloroarsine (**Lewisite**)

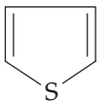
Lewisite is a powerful poisonous gas. It is four times active than the mustard gas. It causes immediate casualities since it readily penetrates clothing and body tissues.

Its toxic nature is found to be due to its reaction with —SH groups of enzymes. However, the action of lewisite may be checked by its antidote developed by Britain in World War II under the name of BAL (**British Anti-Lewisite**). Actually, BAL combines with the lewisite to form a cyclic, non-toxic compound.

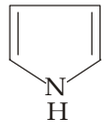


BAL — Lewisite — Non-toxic cyclic compound

(*ii*) $$2HC \equiv CH + N_2 \xrightarrow{\text{electric spark}} 2HCN$$

(*iii*) $$2\ \begin{matrix}CH\\ \|\\ CH\end{matrix} + S \longrightarrow$$ 

Thiophene

(*iv*) $$2\ \begin{matrix}CH\\ \|\\ CH\end{matrix} + NH_3 \longrightarrow$$ 

Pyrrole

Applications of acetylene and its derivatives

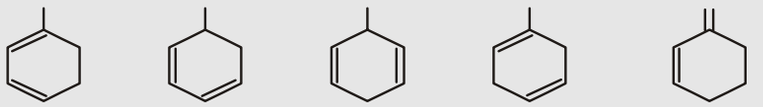
1. Acetylene is used (*a*) for illuminating purposes in hawker's lamps and light houses, (*b*) for artificial ripening of fruits, (*c*) in the form of oxyacetylene flame for welding, cutting and cleaning iron and steel; and (*d*) for producing several chemicals like acetaldehyde, acetic acid, ethyl alcohol, acetone, benzene etc.
2. Westron (acetylene tetrachloride) and westrosol (trichloroethylene) are used as industrial solvents.
3. Vinyl chloride, vinyl acetate and vinyl ethers are used in the production of plastics (*e.g.* polyvinyl chloride commonly known as PVC) and artificial rubber.
4. Vinyl cyanide, also known as acrylonitrile (CH_2 = CHCN) is used for the production of synthetic rubber (**buna N**) and synthetic fibre (**orlon**).
5. *Chloroprene* (2-chloro-1, 3-butadiene) is used in the manufacture of **neoprene** (a synthetic rubber).
6. Lewisite (ClCH = $CHAsCl_2$) is a powerful poisonous gas.

6.12 Illustrative Examples on Alkynes / Dienes

Example 19 :

Arrange each of the following in order of decreasing heat of hydrogenation.

(a) 1,2-hexadiene, 1,3-hexadiene, 1,4-hexadiene, 1,5-hexadiene, 2,4-hexadiene, and 1,3,5-hexatriene.

(b) 

(c) 1-Pentyne, 2-pentyne, 1,4-pentadiene, 1,2-pentadiene, *trans*-1,4-hexadiene, *trans*-1,3-pentadiene.

Solution :

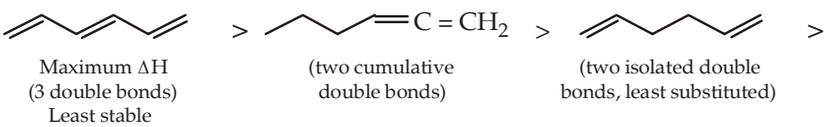
Observe following points carefully in the given structures in the following order for decreasing heat of hydrogenation or increasing order of stability :

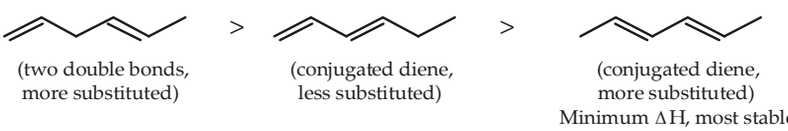
(i) Number of double bonds

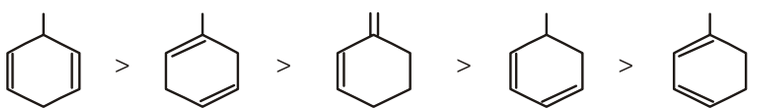
(ii) Presence of conjugation

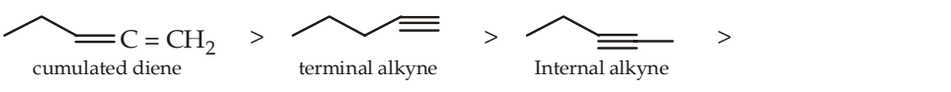
(iii) Possibility of *cis-trans* isomerism

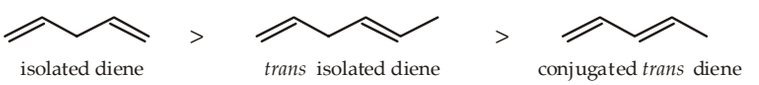
(iv) Degree of substitution of the alkene or alkyne decreasing ΔH

(a) 



(b) 

(c) 



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Example 20 :

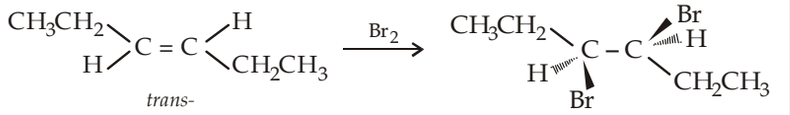
Give steps involved in the conversion of acetylene to (a) *rac*-3,4-dibromohexane, (b) *meso*-3,4-dibromohexane.

Solution :

(a) $HC \equiv CH \xrightarrow[(ii)\ 2CH_3CH_2Br]{(i)\ 2NaNH_2} CH_3CH_2C \equiv CCH_2CH_3 \xrightarrow[\text{catalyst}]{H_2,\ \text{Lindlar}}$

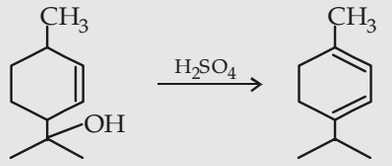


(b) $CH_3CH_2C \equiv CCH_2CH_3 \xrightarrow{Na,\ liq.\ NH_3}$

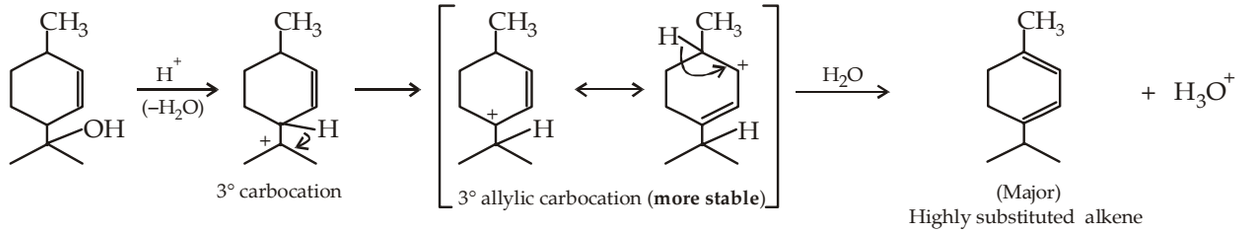


Example 21 :

Give mechanism involved in the following conversion :



Solution :



Example 22 :

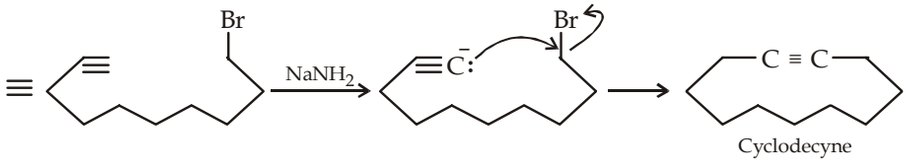
Give steps involved in the preparation of each of the following compounds.

(a) Cyclodecyne from acetylene and 1,8-dibromooctane.

(b) 3-Methylpent-1-yne from 1-pentyne

Solution :

(a) $HC \equiv CH \xrightarrow{NaNH_2} HC \equiv C:^- Na^+ + Br(CH_2)_8Br \longrightarrow HC \equiv C(CH_2)_8Br$



Intramolecular cyclization leading to rings with more than six carbons are difficult, and intermolecular reactions predominate. However, **intramolecular cyclization may be forced by using very dilute solutions,** which makes intermolecular alkylation difficult.

(b) Here 1-pentyne must be converted to dianion by using two moles of a very strong base such as butyllithium per mole of 1-pentyne.

$$CH_3CH_2CH_2C\equiv CH \xrightarrow[\text{step 1}]{2BuLi} CH_3CH_2\ddot{C}HC\equiv C:^- \xrightarrow[\text{step 2}]{CH_3I} CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HC\equiv C:^- \xrightarrow{H_3O^+} CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HC\equiv CH$$

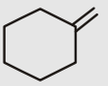
Step 1 : Remember that propargylic H's (H present on C atom attached to acetylenic carbon) are acidic enough, hence it is easily removed as proton by a strong base. It is because such C is attached to *sp* (acetylenic) C which is electronegative. Further the corresponding anion stabilizes due to resonance.

$$-\underset{|}{\overset{\cdot\cdot}{C}}-C\equiv C- \longleftrightarrow -C=C=\overset{\cdot\cdot}{C}-$$

Step 2 : The propargylic carbanion is more basic than the acetylenic carbanion, hence RX preferrentially attacks the former carbanion.

Example 23 :

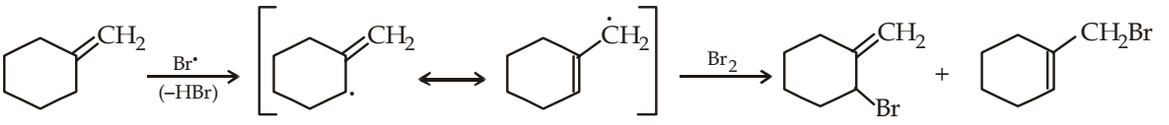
Predict the product(s) in the following reaction.



$$+ Br_2 \text{ (low conc.)} \xrightarrow[\text{lamp}]{\text{sun or}}$$

Solution :

Two products are formed due to the formation of allylic free radical.



Example 24 :

Give steps involved in the synthesis of 1-hexen-5-yne from $CH_3CHOHCH_3$.

Solution :

The two three-carbon fragments (CH_2=$CHCH_2$ – and – $CH_2C\equiv CH$) of $CH_2 = CHCH_2CH_2C\equiv CH$ are first synthesised separately and then they are joined by Corey-House reaction.

(a) $$CH_3CHOHCH_3 \xrightarrow{H_2SO_4,\ heat} CH_3CH=CH_2 \xrightarrow{Br_2}$$

$$CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH_2Br \xrightarrow[(ii)\ H_2O]{(i)\ NaNH_2} CH_3C\equiv CH \xrightarrow{Cl_2,\ heat} \underset{\textbf{A}}{ClCH_2C\equiv CH}$$

(b) $$CH_3CH=CH_2 \xrightarrow{Cl_2,\ heat} \underset{\textbf{B}}{ClCH_2CH=CH_2}$$

(c) $$ClCH_2CH=CH_2 \xrightarrow[(ii)\ CuI]{(i)\ Li} (CH_2=CHCH_2)_2CuLi \xrightarrow{ClCH_2C\equiv CH} \underset{\text{1–Hexen–5–yne}}{CH_2=CHCH_2CH_2C\equiv CH}$$

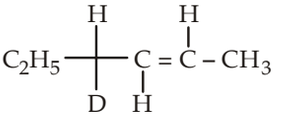
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Example 25 :

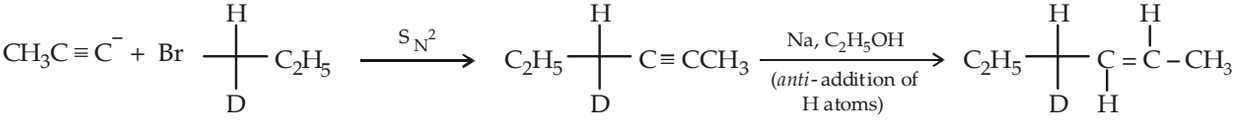
How will you prepare (*S*)-(*E*)-4-deuterio-2-hexene from an alkyne and an alkyl halide.

Solution :

The structure of the required product

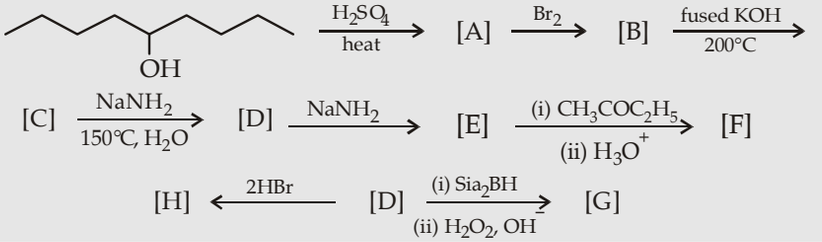


indicates that the required alkyl halide is $C_2H_5C(H)(D)X$ and the alkyne should be $CH_3C \equiv CH$. However, the stereochemical aspect should be noted carefully. The alkyl halide and the product has same priority among groups, but this particular reaction being S_N2 proceeds with inversion so the alkyl halide used should be the *R* enantiomer because the product is *S* enantiomer. Thus

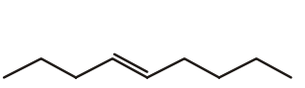


Example 26 :

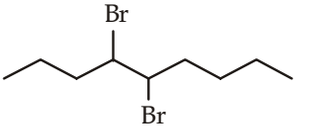
Complete the following by supplying structure to the bracketed compounds.



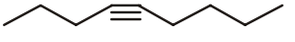
Solution :



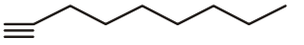
[A]



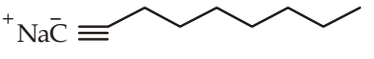
[B] *anti*-addition of Br_2



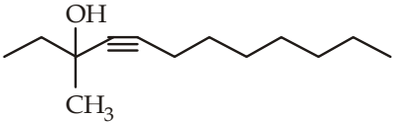
[C], internal alkyne formed during heating with fused KOH at high temp.



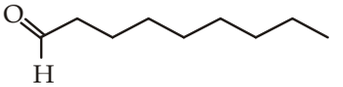
[D], heating with $NaNH_2$ gives terminal alkyne



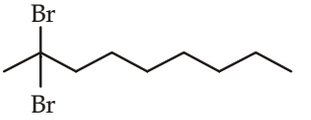
[E]



[F], Alkynides give 3° alcohols with ketones



[G], Alkynides react with Sia_2BH to form aldehydes (*anti*-Markovnikof, addition)



[H]

Example 27 :

Hydrocarbon(X), C_7H_{12}, on reaction with boron hydride followed by treatment with acetic acid yields(A). On reductive ozonolysis (A) yields a mixture of two aldehydes (B) and (C). Of these only (B) can undergo Cannizzaro reaction. (A) exists in two geometric isomers A-1 and A-2, of which A-2 is more stable. Give structure of (X), (A), (B), (C), (A-1) and (A-2) with proper reasoning.

Solution :

$$C_7H_{12}(X) \xrightarrow[(ii)\ CH_3COOH]{(i)\ BH_3} \underset{\substack{\text{(two geometric}\\ \text{isomers)}}}{(A)} \xrightarrow[(ii)\ Zn/CH_3COOH]{(i)\ O_3} \underset{\substack{\text{(responds Cannizzaro}\\ \text{reaction)}}}{(B)} + (C)$$

Above set of reactions leads to following conclusions :

(i) Compound (X) has 2° of unsaturation; however since compound (X) gives compound (A) which in turn undergoes ozonolysis indicating that (A) is still unsaturated and hence 2° of unsaturation in (X) must be in the form of a carbon-carbon triple bond.

$$\underset{[X]}{-C\equiv C-} \xrightarrow{BH_3} \left\{CH=C\right\}_3B \xrightarrow{CH_3COOH} \underset{[A]}{\left\{CH=CH\right\}}$$

(ii) The ozonolysis product (B) undergoes Cannizzaro reaction, while (C) does not. It shows that (B) has $CH_3-\overset{O}{\overset{\|}{C}}-$ group while (C) has a quaternary carbon at α-position.

$$[A] \longrightarrow \underset{(B)}{CH_3-\overset{O}{\overset{\|}{C}}-} + \underset{(C)}{R-\overset{R}{\underset{R}{C}}-\overset{O}{\overset{\|}{C}}-}$$

Thus the parent alkene [A] and [X] should be

$$\underset{C_7}{R-\overset{R}{\underset{R}{C}}-C=C-CH_3} \quad \text{or} \quad \underset{\text{Alkene (A)}}{CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{H}{C}=\overset{H}{C}-CH_3} \qquad \underset{(C_7H_{12}),\ X}{CH_3-\overset{CH_3}{\underset{CH_3}{C}}-C\equiv C-CH_3}$$

$$\underset{[X]}{CH_3-\overset{CH_3}{\underset{CH_3}{C}}-C\equiv C-CH_3} \xrightarrow[(ii)\ CH_3COOH]{(i)\ BH_3} \underset{\substack{[A]\\ cis- \text{ and } trans-}}{CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH=CHCH_3} \xrightarrow[(ii)\ Zn/CH_3COOH]{(i)\ O_3} \underset{[C]}{CH_3-\overset{CH_3H}{\underset{CH_3}{C}}-C=O} + \underset{[B]}{O=\overset{H}{C}-CH_3}$$

Example 28 :

An alkyne, when treated with ozone followed by dimethyl sulphide gives methanoic acid, hexanal and 3-oxobutanoic acid. Can you assign the structure to the alkyne on the basis of this information only?

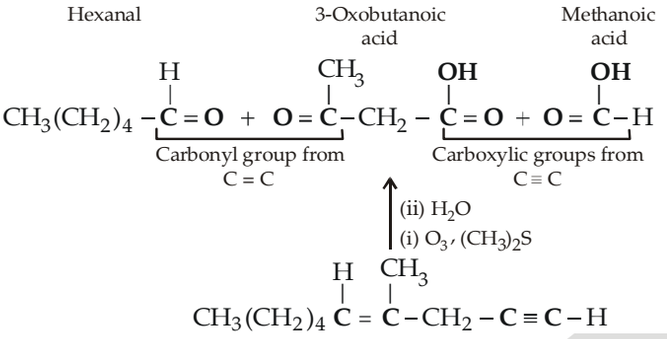
Solution :

Yes. Remember that alkynes on ozonolysis gives carboxylic acids, while reductive ozonolysis (as in the present case) of alkenes gives aldehydes and ketones. Further remember that formation of methanoic acid as one of the products indicates that the alkyne is terminal, i.e. it has –C ≡ CH type of grouping.

To get the structure of the parent compound, arrange the ozonolysis products in such a way that when they are joined by replacing the carboxyl groups (derived from C ≡ C linkage) or carbonyl group (derived from C = C linkage in reductive ozonolysis) by the corresponding linkage (C ≡ C, or C = C), the structure of the parent compound is obtained.

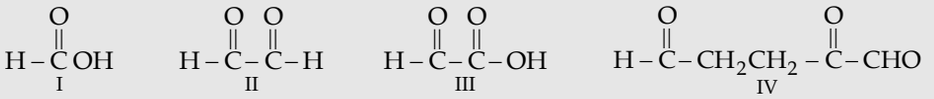
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Thus here,



Example 29 :

An organic compound *Z*, when treated with ethanolic silver nitrate gives a white precipitate which is soluble in dilute acid. The compound absorbs five equivalents of hydrogen in presence of Pt to form *n*-butylcyclohexane. The compound when treated with sufficient amount of ozone, followed by dimethyl sulphide and water gives following four well-known compounds.

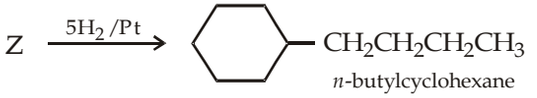


Prepare a structure for the compound *Z*.

Solution :

(i) Reaction with ethanolic $AgNO_3$ to form white precipitate soluble in dil. acid, indicates the presence of –C ≡ CH grouping.

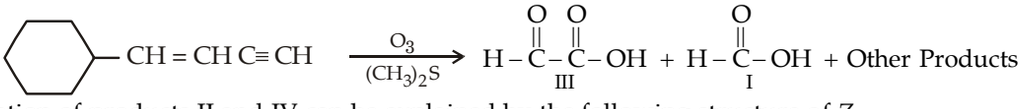
(ii) Intake of 5 equivalents of H_2 indicates the presence of 5π bonds. Now we are to assign the position of these π bonds in the skeleton of *n*-butylcyclohexane.



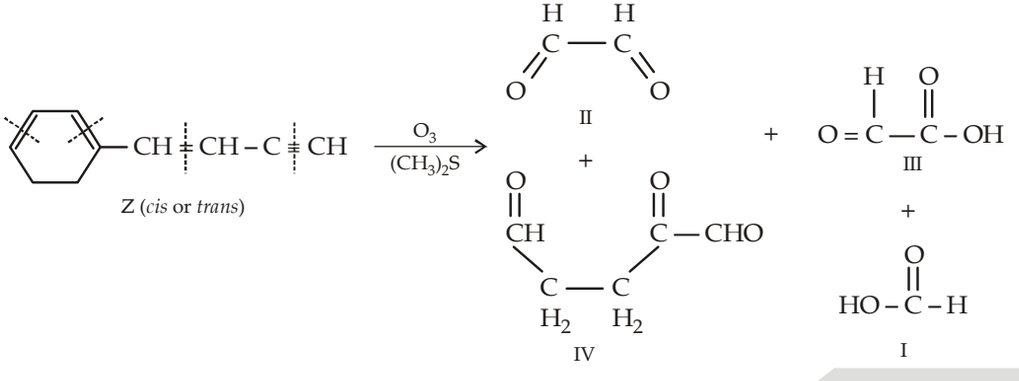
(iii) Since the compound has C ≡ CH group, the triple bond must be present at the end carbon atom of the side chain.

(iv) Note that the ozonolysis is reductive one, so aldehydic and ketonic functional groups developed in the products must be coming from the double bonds; while the –COOH groups in the product must be coming from carbon-carbon triple bond. Since only two –COOH groups are present in the products, the compound should have only one triple bond. Further the presence of six carbonyl groups in the products indicates the presence of three double bonds.

Now join the two carbons of the –COOH groups through a carbon-carbon triple bond. Further formation of III indicates the position of one of the double bonds too.



Formation of products II and IV can be explained by the following structure of *Z*.

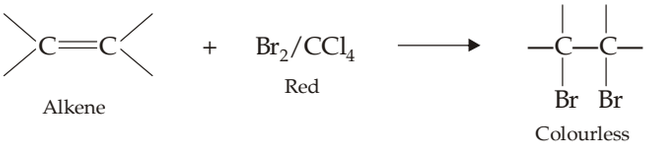


6.13 Characteristics of Alkanes, Alkenes and Alkynes

1. An **alkane** shows negative tests to all functional groups. These are insoluble in water, dilute acids, dilute base and concentrated sulphuric acid.

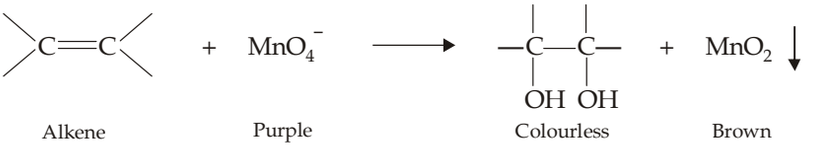
2. **Alkenes** are characterised by the following tests :

(a) Rapid decolorization of bromine in carbon tetrachloride without evolution of HBr.



This test is also given by alkynes.

(b) Alkenes decolourise a cold, dilute, neutral, aqueous permanganate solution (**Baeyer test**) and forms brown precipitate of MnO_2.



Remember that this test is also given by alkynes and aldehydes.

(c) Alkenes are soluble in cold concentrated sulphuric acid (difference from alkanes). However, remember that other compounds like those containing oxygen and those which are readily sulphonated are also soluble in cold conc. H_2SO_4.

3. **Alkynes** can be detected by combination of the following tests :

(a) Like alkenes, alkynes (*i*) decolourise bromine in CCl_4 without evolution of HBr, (*ii*) decolourise cold, neutral, dilute permanganate solution, (*iii*) are not oxidised by chromic anhydride.

(b) On ozonolysis, alkynes yield carboxylic acids, whereas alkenes yield aldehydes and ketones, *e.g.*

$$CH_3C \equiv CCH_2CH_3 \xrightarrow[(ii)\,H_2O]{(i)\,O_3} CH_3COOH + HOOCCH_2CH_3$$

$$CH_3CH = CHCH_2CH_3 \xrightarrow[(ii)\,H_2O]{(i)\,O_3} CH_3CHO + OHC.CH_2CH_3$$

(c) Acidic alkynes, also known as terminal alkynes ($\equiv CH$), react with certain heavy metal ions, chiefly Ag^+ and Cu^+, to form insoluble alkynides. Formation of a precipitate upon addition of an alkyne to either of the following solutions :

(i) a solution of $AgNO_3$ in alcohol,

(ii) an ammonical solution of $AgNO_3$,

(iii) an ammonical solution of cuprous chloride

indicate an acidic alkyne. This reaction can be used to differentiate terminal alkynes (acidic alkynes) from non-terminal alkynes (non-acidic alkynes)

$R-C\equiv CH$ — A terminal alkyne

$R-C\equiv C-R$ — A non–terminal alkyne

TEST YOUR UNDERSTANDING - 6.21

1. Give a simple test to distinguish between

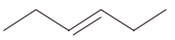
(a) 1-butene and 2-butene

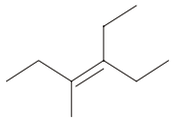
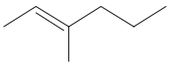
(b) 1,3-dibromopropane and 1,2-dibromopropane

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EXERCISE 6.1 (MCQ - ONE option correct)

1. Which of the following alkenes exhibit *cis-trans* isomerism?

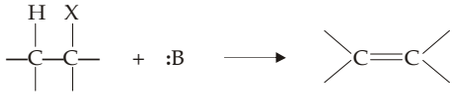
(i)  (ii) 

(iii)  (iv) 

(a) (ii) and (iii) (b) (iii)
(c) (ii) and (iv) (d) All the four

2. The number of isomers possible for amylene is
(a) 3 (b) 4
(c) 5 (d) 6

3. In 1, 2-elimination of HX



The electron pair of the newly formed π-bond is provided by
(a) the lone pair of electrons present on the base B (b) the pair of electrons forming C–X bond
(c) the pair of electrons forming C–H bond
(d) either of the three

4. Which of the following chloride will exclusively give 2-methyl-2-butene on dehydrohalogenation by a strong base?
(a) 2-chloro-2-methylbutane
(b) 2-chloro-3-methylbutane
(c) 1-chloro-2-methylbutane
(d) None of the three

5. Isobutene can be prepared from *tert*-butanol by
(i) heating it in the presence of acid
(ii) treating it with HCl followed by reaction with alcoholic potash
(iii) treating it with *p*-tosyl chloride followed by reaction with potassium *tert*-butoxide.
(a) method (i) only (b) methods (i) and (ii) only
(c) all above methods (d) method (ii) only

6. Isobutene is the exclusive product of dehydrohalogenation (by a strong base) of
(a) isobutyl chloride (b) *tert*-butyl bromide (c) both (a) and (b) (d) none of the two

7. Dehydration of *tert*-butyl alcohol and *sec*-butyl alcohol is carried out by heating with 20% H_2SO_4 at 90°C and 60% H_2SO_4 at 100°C, *n*-butyl alcohol can best be dehydrated by heating with
(a) 50% H_2SO_4 at 130°C (b) 20% at 150°C
(c) 75% H_2SO_4 at 140°C (d) 60% at 95°C

8. 2-Butene can be obtained by the electrolysis of an aqueous solution of
(a) 1, 2-Dimethylmaleic acid
(b) 2, 2-Dimethylbutandioic acid
(c) 3, 3-Dimethylbutandioic acid
(d) 2, 3-Dimethylbutandioic acid

9. *cis*-2-Butene has higher boiling point than the *trans*-analog. It is because of
(a) hydrogen bonding in the *cis*-isomer
(b) higher molecular mass of the *cis*-isomer
(c) vander Waal forces in the *cis*-isomer
(d) polarity in the *cis*-isomer.

10. Melting point of the *cis*-ethylene bromide is –53°C, the expected melting point for the *trans*-isomer should be
(a) –53°C (b) –68°C
(c) –6°C (d) can't be predicted.

11. If the photochemical chlorination of excess of deuterated toluene ($C_6H_5CH_2D$) with 0.1 mol of Cl_2 forms 0.0868 mol of HCl and 0.0212 mol of DCl, the relative amounts of DCl and HCl formed from $C_6H_5CHD_2$ will be
(a) 0.0414 : 0.0462 (b) 0.0212 : 0.0868
(c) 0.0462 : 0.0414 (d) 2 : 2.05.

12. How many types of hydrogen are present in 6-methyl-2-heptene?
(a) 4 (b) 5
(c) 6 (d) 7

13. Which of the following can undergo nucleophilic addition?
(a) $CH_2 = CH_2$ (b) $CH_2 = CHCN$
(c) $CH_2 = CH–CH = CH_2$ (d) None.

14. Addition of Br_2 on butene-2 is a
(a) stereoelective reaction (b) stereospecific reaction
(c) both (a) as well as (b) (d) neither (a) nor (b).

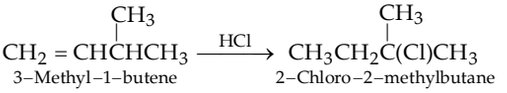
15. The decreasing order of hydrogen bromide on the following alkenes is

$CH_2 = CH_2$, $CH_3CH_2CH = CH_2$, $CH_2 = CHCl$, $(CH_3)_2C = CH_2$
I II III IV

(a) I > III > II > IV (b) IV > II > I >III
(c) III > I > II > IV (d) II > IV > I > III

16. In the reaction of propene with HBr in presence of light, first step involves the
(a) addition of H atom
(b) addition of H^+ ion
(c) addition of bromine atom
(d) none of the three.

17. Which of the following is involved in the following reaction?



3–Methyl–1–butene 2–Chloro–2–methylbutane

(a) Shifting of H^+ from position 1 to 2
(b) Shifting of H^- from position 1 to 2
(c) Shifting of CH_3^+ from position 1 to 2
(d) Shifting of CH_3^- from position 1 to 2.

18. Which of the following is true during electrophilic addition of HBr to alkenes?
(i) In aqueous solution of HBr, electrophile is H_3O^+
(ii) Aqueous solution of HBr is a better electrophile than dry HBr.
(a) (i) is true (b) (ii) is true
(c) (i) & (ii) both are true (d) None is true.

19. Addition of D_2O in presence of D^+ to 2-methyl-2-butene gives
(a) $(CH_3)_2C(OD).CH_2CH_3$
(b) $(CH_3)_2C(OH)CD_2CH_3$
(c) $(CH_3)_2$ C(OD).CHD.CH_3
(d) all the above

20. Reaction of alkene with cold concentrated sulphuric acid followed by heating with water is one of the important methods for the preparation of alcohols. Which of the following fact is not in accordance with this method?
(a) It can be used for the preparation of *tert*-butanol
(b) It can be used for the preparation of isopropanol
(c) It can be used for the preparation of isobutanol
(d) All the above statements are correct

21. The favourable conditions for the hydration of water are
(a) low water concentration and high temperature
(b) low water concentration and low temperature
(c) high water concentration and high temperature
(d) high water concentration and low temperature

22. $CH_2 = CH_2 \xrightarrow{98\%\ H_2SO_4} CH_3CH_2OSO_3H$

$\xrightarrow{H_2O,\ heat} CH_3CH_2OH + H_2SO_4$

The two consecutive steps in the above set involves
(a) electrophilic addition and elimination
(b) electrophilic addition and S_N1
(c) electrophilic addition and S_N2
(d) nucleophilic addition and elimination

23. The rate-determining step in the following reaction is

$$CH_2 = CH_2 + HOCl \longrightarrow CH_2OHCH_2Cl$$

(a) addition of OH^- (b) addition of OH^+
(c) addition of Cl^+ (d) addition of Cl^-

24. Reaction between isobutene and isobutane in presence of acid to form isoctane involves
(a) methyl shift
(b) intramolecular hydride shift
(c) intermolecular hydride shift
(d) none of the three

25. Propene is treated with mercuric acetate in methanol solution, followed by reduction with sodium borohydride. The product formed is
(a) $CH_3CH_2CH_2OH$ (b) $CH_3CHOHCH_3$
(c) $CH_3CH_2CH_2OCH_3$ (d) $CH_3CH(OCH_3).CH_3$

26. Which of the following is true regarding free radical addition of HBr on propene?
(a) It is faster than that of ethylene and form isopropyl bromide
(b) It is slower than that of ethylene and forms isopropyl bromide
(c) It is faster than that of ethylene and forms *n*-propyl bromide
(d) It is slower than that of ethylene and forms *n*-propyl bromide.

27. The probability factor for bromination of cylcohexane to cyclohexene is
(a) 12 : 2 (b) 12 : 4
(c) 12 : 18 (d) 12 : 10.

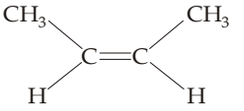
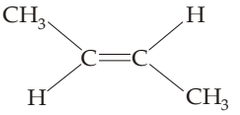
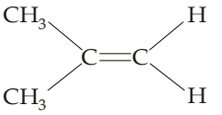
28. Addition of bromine on *cis*- and *trans*-2-butenes exclusively give *racemic*- and *meso*-2, 3-dibromobutane respectively. What does these reactions indicate?
(a) A free carbonium ion is formed as an intermediate
(b) A free carbonium ion is not formed as an intermediate
(c) Bromine adds in *syn* manner in case of *cis*-2-butene and in an *anti* manner in case of *trans*-2-butene
(d) Bromine adds in *anti* manner on *cis*-2-butene and in *syn* manner on *trans*-2-butene.

29. Like bromination of butene-2, hydroxylation of butene-2 by alkaline permanganate also involves the formation of a cyclic intermediate, hydroxylation of *trans*-2-butene will give
(a) *meso*-glycol
(b) *racemic*-glycol
(c) the reaction is not stereospecific
(d) no product.

30. Predict the product P. $CH_3CH = CH_2 \xrightarrow[(ii)\ H_2O_2/OH^-]{(i)\ (BH_3)_2} P$
(a) $CH_3CH_2CH_2OH$
(b) $CH_3CHOHCH_3$
(c) *a* and *b* in equal amounts
(d) neither of the two.

31. Which of the following is identical in *cis*-3-hexene and *trans*-3-hexene?
(a) Rate of hydrogenation
(b) Product of hydrogenation
(c) Adsorption of alumina
(d) None of the three is identical

32. Baeyer's reagent is
(a) alkaline permanganate solution
(b) acidified permanganate solution
(c) neutral permanganate
(d) aqueous bromine solution

33. Markownikoff's rule provides guidance of HBr on
(a) $CH_2 = CH_2$ (b) 
(c)  (d) 

34. Of the following compounds, which will have a zero dipole moment?
(a) 1, 1-Dichloroethylene
(b) *cis*-1, 2-Dichloroethylene
(c) *trans*-1, 2-Dichloroethylene
(d) None of the three.

35. The molecule(s) that will have dipole moment is/are
(i) 2, 2-dimethylpropane (ii) *trans*-2-pentene
(iii) *cis*-2-hexene (iv) 2, 2, 3, 3-tetramethylbutene
(a) only (ii) (b) only (iii)
(c) (ii) and (iii) (d) (iii) and (iv)

36. Which of the following has smallest heat of hydrogenation per mole?
(a) 1-Butene (b) *trans*-2-Butene
(c) *cis*-2-Butene (d) 1, 3-Butadiene

37. Anit-Markownikoff's addition of HBr is not observed in
(a) propene (b) butene
(c) but-2-ene (d) pent-2-ene

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38. The reaction of $CH_3CH = CH$–C$_6$H$_4$–OH with HBr gives

(a) $CH_3CHBrCH_2$–C$_6$H$_4$–OH

(b) CH_3CH_2CHBr–C$_6$H$_4$–OH

(c) $CH_3CHBrCH_2$–C$_6$H$_4$–Br

(d) CH_3CH_2CHBr–C$_6$H$_4$–Br

39. If heat of hydrogenation of 1, 3-pentadiene and 1, 4-pentadiene are X and Y kCal respectively, heat of hydrogenation of 2, 3-pentadiene will be

(a) between X and Y

(b) less than X as well as Y

(c) greater than X as well as Y

(d) It can't be predicted.

40. Which of the following statement is true regarding 1, 3-butadiene?

(a) It can exist in *cis* and *trans* forms

(b) It can exist in transoid and cisoid conformations (c) Both (a) and (b) are correct

(d) Neither (a) nor (b) in correct.

41. Observe the resonating structures of 1, 3-butadiene

$$\underset{\text{I}}{CH_2 = CH - CH = CH_2} \longleftrightarrow \underset{\text{II}}{\overset{+}{C}H_2 - \overset{-}{C}H - CH = CH_2}$$

$$\longleftrightarrow \underset{\text{III}}{\overset{+}{C}H_2 - CH = CH - \overset{-}{C}H_2}$$

(i) Among the three structures, structure I contributes more than the other two structures.

(ii) All the three structures contribute equally.

(iii) Resonance energy of 1, 3-butadiene is quite high.

(iv) Resonance energy of 1, 3-butadiene is small.

Which of the above statement(s) is(are) true?

(a) (i) and (iii) (b) (ii) and (iii)

(c) (i) and (iv) (d) (ii) and (iv)

42. Isopropene, $CH_2 = \overset{CH_3}{\overset{|}{C}} - CH = CH_2$ is treated with HCl, the products formed will be a mixture of

(i) $CH_3 - \overset{CH_3}{\overset{|}{\underset{Cl}{\underset{|}{C}}}} - CH = CH_2$ (ii) $CH_2 = \overset{CH_3}{\overset{|}{C}} - \underset{Cl}{\underset{|}{CH}} = CH_3$

(iii) $CH_3 - \overset{CH_3}{\overset{|}{C}} = CH - CH_2Cl$ (iv) $ClCH_2 - \overset{CH_3}{\overset{|}{C}} = CH - CH_3$

(a) (i) and (iii) (b) (ii) and (iii)

(c) (ii) and (iv) (d) All the four.

43. Which of the following is (are) feasible?

(a) $CH_2 = CH_2 \xrightarrow{Na/\text{alcohol}} CH_3 - CH_3$

(b) $CH_2 = CH - CH = CH_2 \xrightarrow{Na/\text{alcohol}}$

$CH_3 - CH = CH - CH_3$

(c) $CH_2 = CH - CH = CH_2 \xrightarrow{Na/\text{alcohol}}$

$CH_3CH_2CH_2CH_3$

(d) All are feasible.

44. $CH_2 = CH–CH = CH–CH_3 + HI \longrightarrow$

$CH_3–CHI–CH = CH–CH_3$

Above product may be regarded as

(a) 1, 2-adduct

(b) 1, 4-adduct

(c) both 1, 2-as well as 1, 4-adduct

(d) none of the two

45. 1, 3-Butadiene is treated with hot $KMnO_4/NaIO_4$, the product(s) formed is(are)

(a) 2HCHO + OHC – CHO

(b) 2HCOOH + HOOC–COOH

(c) $2CO_2$ + HOOC–COOH

(d) $4CO_2$

46. Reaction of propylene bromide with the equivalent amount of alcoholic KOH gives mainly

(a) $CH_3CH = CHBr$ (b) $CH_2 = CHCH_2Br$

(c) $CH_3C(Br) = CH_2$ (d) all the three compounds.

47. Ethyne when treated with bromine water gives

(a) only 1, 2-dibromoethene

(b) only 1, 1, 2, 2-tetrabromoethane

(c) both (a) and (b)

(d) none of the two

48. $\underset{CH}{\overset{CH}{|||}} + Br_2 \longrightarrow \underset{\text{I}}{\overset{CHBr}{\underset{CHBr}{||}}} \xrightarrow{Br_2} \underset{\text{II}}{\overset{BrCHBr}{\underset{BrCHBr}{|}}}$

The compound I will predominate under which conditions?

(i) By using excess of ethyne.

(ii) By driping the bromine water into a solution of ethyne.

(iii) By bubbling ethyne into a solution of bromine in carbon tetrachloride.

(a) (i) (b) (ii)

(c) (i) and (ii) (d) (i) and (iii)

49. Formation of acetylene from calcium acetylide can be represented as

$$Ca^{2+}C \equiv C^{2-} + 2HOH \longrightarrow H - C \equiv C - H + 2OH^- + Ca^{2+}$$

In the above reaction, which one is correct?

(a) The stronger acid (acetylene) is displaced from its salt by a weaker acid (water)

(b) The weaker acid (acetylene) is displaced from its salt by a stronger acid (water)

(c) The weak acid (acetylene) is displaced from its salt by another weak acid (water)

(d) The weaker acid (acetylene) is displaced from its salt by neutral substance (water).

50. Which of the following alkyne will form 2-butanone on hydration?

(a) $CH_3CH_2C \equiv CH$ (b) $CH_3C \equiv CCH_3$

(c) Both (d) None

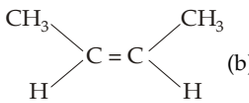
51. If addition of HBr on $CH_2 = CHCH_2C \equiv CH$ gives $CH_3CHBrCH_2C \equiv CH$, addition of HBr on $CH \equiv CCH = CH_2$ would give
(a) $CH_2 = CBrCH = CH_2$ (b) $CH \equiv CCHBrCH_3$
(c) Both (d) $CH_2 = CBrCHBrCH_3$

52. $CH_3C \equiv CCH_3 \xrightarrow{H_2/Pt} A \xrightarrow{D_2/Pt} B$
The compounds A and B, respectively are
(a) *cis*-butene-2 and *rac*-2, 3-dideuterobutane
(b) *trans*-butene-2 and *rac*-2, 3-dideuterobutane
(c) *cis*-butene-2 and *meso*-2, 3-dideuterobutane
(d) *trans*-butene-2 and *meso*-2, 3-dideuterobutane

53. The compound X in the following reaction is $CH_3C \equiv CCH_3 \xrightarrow[(ii)\ Br_2]{(i)\ H_2/Pt} X$
(a) *d*-2, 3-Dibromobutane
(b) *l*-2, 3-Dibromobutane
(c) *dl*-2, 3-Dibromobutane
(d) *meso*-2, 3-Dibromobutane.

54. Identify Y in the following :
$CH_3C \equiv CC_2H_5 \xrightarrow{H_2/Catalyst} X \xrightarrow[Zn(Cu)]{CH_2I_2} Y$
(a) *meso*-2, 3-diiodobutane
(b) *racemic*-2, 3-diiodobutane
(c) *cis*-1-ethyl-2-methylcyclopropane
(d) *trans*-1-ethyl-2-methylcyclopropane

55. Identify the reagent from the following list which can easily distinguish between 1-butyne and 2-butyne
(a) bromine, CCl_4 (b) H_2, Lindlar catalyst
(c) dilute H_2SO_4, $HgSO_4$ (d) ammonical Cu_2Cl_2 solution.

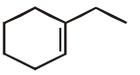
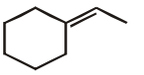
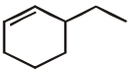
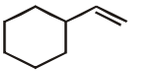
56. Which of the following hydrocarbons has the lowest dipole moment?
(a)  (b) $CH_3C \equiv CCH_3$
(c) $CH_3CH_2C \equiv CH$ (d) $CH_2 = CH–C \equiv CH$

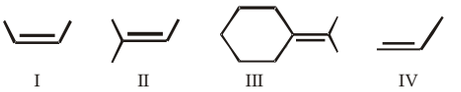
57. The compound having both *sp* and sp^2 hybridised carbon atom is
(a) propene (b) propyne
(c) propadiene (d) butadiene

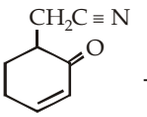
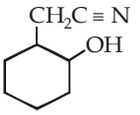
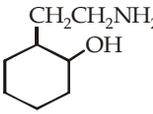
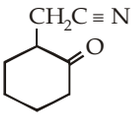
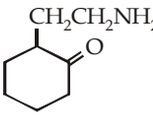
58. The number of sigma and pi bonds in 1-buten-3-yne are
(a) 5σ and 5π (b) 7σ and 3π
(c) 8σ and 2π (d) 6σ and 4π

59. Which of the following reaction will yield 2, 2-dibromopropane?
(a) $HC \equiv CH + 2HBr \longrightarrow$
(b) $CH_3C \equiv CH + 2HBr \longrightarrow$
(c) $CH_3CH = CH_2 + HBr \longrightarrow$
(d) $CH_3CH = CHBr + HBr \longrightarrow$

60. The product(s) obtained via oxymercuration ($HgSO_4 + H_2SO_4$) of 1-butyne would be
(a) $CH_3CH_2COCH_3$
(b) $CH_3CH_2CH_2CHO$
(c) $CH_3CH_2CHO + HCHO$
(d) $CH_3CH_2COOH + HCOOH$.

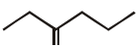
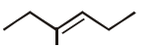
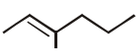
61. Catalytic hydrogenation of which of the following is most exothermic?
(a)  (b) 
(c)  (d) 

62. The relative rate of catalytic hydrogenation of the following alkenes is:

I II III IV
(a) I > II > III > IV (b) III > II > I > IV
(c) IV > I > II > III (d) IV > I > II = III

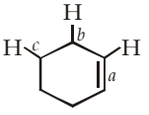
63.  $\xrightarrow{H_2, Pd/C}$ product P is :
(a)  (b) 
(c)  (d) 

64. Which of the following statement is true regarding the addition reaction of an alkene?
(a) Stereoselectivity of a reaction may vary from 1 to 50%
(b) Stereoselectivity of a reaction is always 50%
(c) Stereospecificity of a reaction is always 100%
(d) Stereospecificity of a reaction may vary from 1 to 75%

65. An organic compound takes up one molar equivalent of hydrogen and gives methylcyclohexane. The original compound can exist in ..... isomeric forms.
(a) 1 (b) 2
(c) 3 (d) 4

66. 3-Chloro-3-methylhexane is formed by the addition of HCl on :
(a)  (b) 
(c)  (d) Any of the three

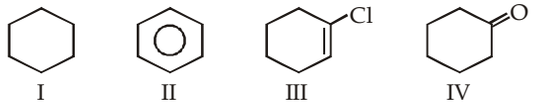
67. How many types of C–H bonds are present in cyclohexene?
(a) 2 (b) 3
(c) 4 (d) 5

68. Which of the C–H bond in the structure drawn below is strongest?


(a) *a* (b) *b*
(c) *c* (d) all are equal

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69. Arrange the following compounds in order of increasing oxidation level.



(a) I < II < IV < III (b) I < II < III < IV
(c) I < II < III ≈ IV (d) I < IV ≈ III < II

70. The reactivities of ethane, ethylene and acetylene are of the order
(a) ethane < ethylene < acetylene
(b) ethane < acetylene < ethylene
(c) acetylene < ethylene < ethane
(d) acetylene = ethylene > ethane

71. Ozonolysis of 2-methylbutene-2-yields
(a) Only aldehyde (b) Only ketone
(c) Both aldehyde and ketone
(d) None

72. Which one of the following has the smallest heat of hydrogenation per mole?
(a) 1-butene (b) trans-2-butene
(c) cis -2-butene (d) 1,3-butadiene

73. Propyne and propene can be distinguished by
(a) conc. H_2SO_4 (b) Br_2 in CCl_4
(c) dil. $KMnO_4$ (d) $AgNO_3$ in ammonia

74. In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markovnikov addition to alkenes because
(a) both are highly ionic
(b) one is oxidizing and the other is reducing
(c) one of the steps is endothermic in both the cases
(d) all the steps are exothermic in both the cases

75. The nodal plane in the π-bond of ethene is located in
(a) the molecular plane
(b) a plane parallel to the molecular plane
(c) a plane perpendicular to the molecular plane which bisects the carbon - carbon σ -bond at right angle
(d) a plane perpendicular to the molecular plane which contains the carbon - carbon σ -bond.

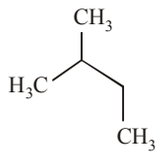
76. Which of the following is used for the conversion of 2-hexyne into *trans*-2-hexene?
(a) $H_2/Pd/BaSO_4$ (b) H_2, PtO_2
(c) $NaBH_4$ (d) Li-NH_3/C_2H_5OH

77. $CH_3 - CH = CH_2 + NOCl \longrightarrow P$

Identify the product P.

(a) $CH_3 - \underset{\underset{NO}{|}}{CH} - \underset{\underset{Cl}{|}}{CH_2}$ (b) $CH_3 - \underset{\underset{Cl}{|}}{CH} - \underset{\underset{NO}{|}}{CH_2}$

(c) $\underset{\underset{NO}{|}}{CH_2} - CH_2 - \underset{\underset{Cl}{|}}{CH_2}$ (d) $CH_3 - CH_2 - \underset{\underset{Cl}{|}}{\overset{\overset{NO}{|}}{CH}}$

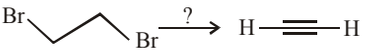
78. 

$\xrightarrow{Cl_2,\ hv}$ N (isomeric products)

$C_5H_{11}Cl \xrightarrow{\text{fractional distillation}} M$ (isomeric products)

Identify N and M
(a) 6, 4 (b) 6, 6
(c) 4, 4 (d) 3, 3

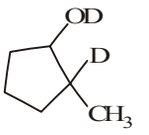
79. The reagent(s) for the following conversion,



is/are
(a) alcoholic KOH
(b) alcoholic KOH followed by $NaNH_2$
(c) aqueous KOH followed by $NaNH_2$
(d) Zn/CH_3OH

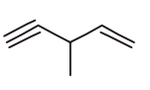
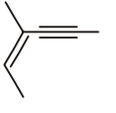
80. The number of stereoisomers obtained by bromination of *trans-2-butene* is
(a) 1 (b) 2
(c) 3 (d) 4

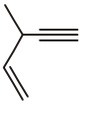
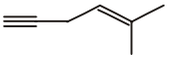
81. 1-Methylcyclopentene can be converted into the given compound

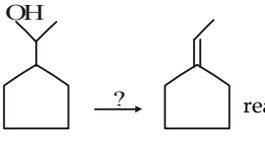


by the use of which of the following reagents ?
(a) dil. D_2SO_4
(b) $Hg(OAc)_2 + D_2O$ followed by $NaBD_4$
(c) B_2D_6 followed by D_2O, AcOD
(d) B_2D_6 followed by D_2O_2, NaOD

82. Which of the following produces chiral molecule after treatment with H_2 in the presence of Lindlar's catalyst ?

(a)  (b) 

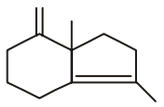
(c)  (d) 

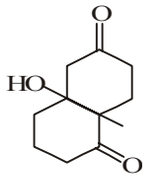
83. 

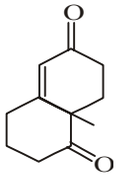
reagent which can be used is

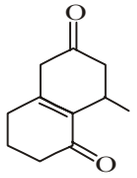
(a) conc. H_2SO_4, Δ (b) Al_2O_3, Δ
(c) ThO_2, Δ (d) All

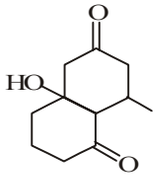
84. Two C_4H_6 isomers give the same C_4H_8O product with $HgSO_4$ and dil. H_2SO_4. However, these isomers give different $C_4H_6Br_4$ products with excess bromine. What are these isomeric hydrocarbons ?
(a) cyclobutene and 1-butyne
(b) 1, 2-butadiene and 1, 3-butadiene
(c) 3-butyne and cyclobutene
(d) 2-butyne and 1-butyne

85.  $\xrightarrow[\Delta]{H^{\oplus}/KMnO_4}$ Product $\xrightarrow[\Delta]{KOH}$ Product.

(a) 

(b) 

(c) 

(d) 

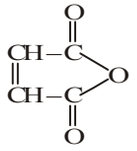
86. $HC \equiv CH \xrightarrow{2CH_3MgBr} (A) \xrightarrow[(ii)\,KOH/H^{\oplus}]{(i)\,2CO_2} (B)$

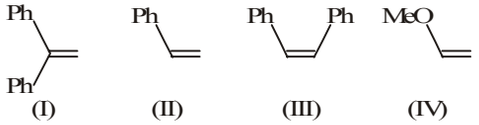
$\xrightarrow[HgSO_4]{H_2SO_4} (C) \xrightarrow{\Delta} (D)$

(a) $CH_3-\overset{\overset{O}{\|}}{C}-COOH$

(b) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

(c) $HOOC-\overset{\overset{O}{\|}}{C}-CH_2-COOH$

(d) 

87. 

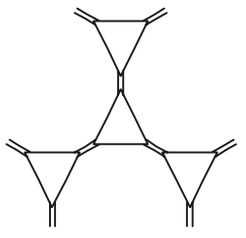
(I) (II) (III) (IV)

Order of rate of electrophilic addition reaction with HBr will be

(a) IV > I > III > II (b) I > II > III > IV

(c) I > III > II > IV (d) IV > I > II > III

88. The ozonolysis reaction of the given compound gives products in the ratio :



(a) 6 : 3 : 1 (b) 9 : 3 : 1

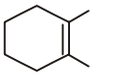
(c) 6 : 4 (d) 8 : 4

89. Which of the following compounds form single product in each of the following reactions ?

I. Ozonolysis

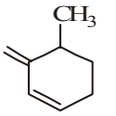
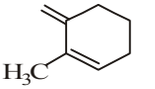
II. Catalytic hydrogenation

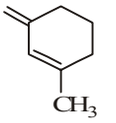
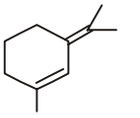
III. Hydrogenation followed by monochlorination

(a)  (b) 

(c)  (d) 

90. The correct stability/order of following is :

I.  II. 

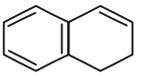
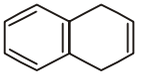
III.  IV. 

(a) I > II > III > IV (b) III > IV > II > I

(c) II > IV > III > I (d) IV > III > II > I

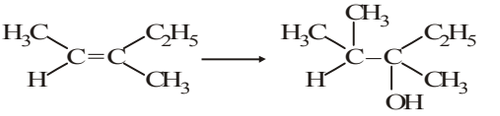
91. The correct order of rate of acid catalyzed hydration of following compounds is :

I. $CH_3-C \equiv CH$ II. $CH_2 = CH_2$

III.  IV. 

(a) II > I > IV > III (b) III > I > IV > II

(c) I > III > IV > II (d) III > IV > II > I

92. 

(P) (Q)

The transformation of P to Q can be carried out by using the reagents

(a) Dil. H_2SO_4, CH_3MgCl, H^+

(b) $HOCl/H^+$, CH_3MgCl(1 eq.), H^+

(c) CH_3CO_3H/Δ, CH_3MgCl, H^+

(d) $Cl_2/HClO_4$, CH_3MgCl(1 eq.), H^+

93. *cis*-But-2-ene $\longrightarrow$ *trans*-But-2-ene

This conversion is best carried out by using the sequence of reagents

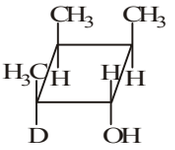
(a) Br_2/CCl_4, $NaNH_2$, Na/NH_3 (l)

(b) H_2O/H^+, Al_2O_3/Δ

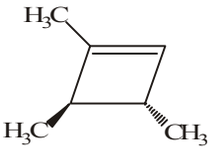
(c) $Hg(OAc)_2/H_2O$, $NaBH_4$, ThO_2

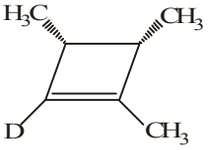
(d) Br_2/H_2O, alc. KOH, $Na/NH_3(l)$

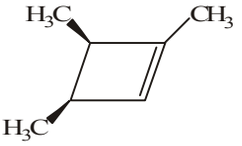
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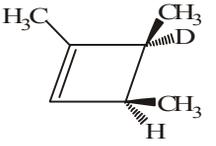
94. (X) $\xrightarrow[(2)\ H_2O_2/\ OH^{\ominus}]{(1)\ BD_3-THF}$  (major)

The reactant (X) is

(a) 

(b) 

(c) 

(d) 

95. From the following reactions,

$$HC\equiv CH + LiNH_2 \rightleftharpoons NH_3 + HC\equiv CLi$$

$$NH_3 + R^- \rightleftharpoons NH_2^- + RH$$

predict which of the following orders regarding acid strength is correct ?

(a) $RH < NH_3 < HC\equiv CH$ (b) $RH > NH_3 > HC\equiv CH$

(c) $RH > NH_3 < HC\equiv CH$ (d) $RH < NH_3 > HC\equiv CH$

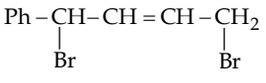
96. Ethylene combines with sulphur monochloride to form

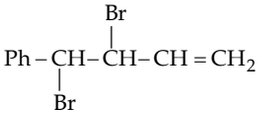
(a) Phosgene (b) Mustard gas

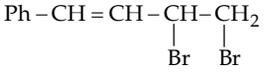
(c) Methyl isocyanate (MIC) (d) Lewisite

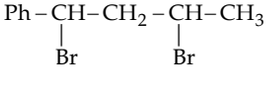
97. $Ph-CH=CH-CH=CH_2 \xrightarrow[CCl_4]{Br_2}$ Major product (Formed by more stable carbocation)

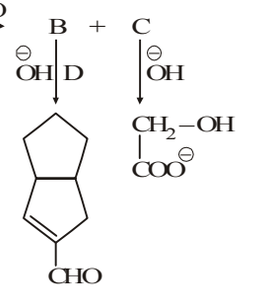
Major product is ?

(a) 

(b) 

(c) 

(d) 

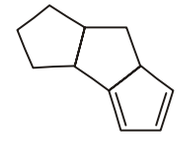
98. A $\xrightarrow[Zn/\ H_2O]{O_3/}$ 

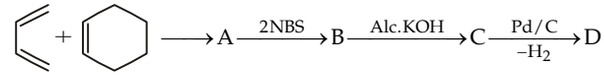
Reactant A is :

(a) 

(b) 

(c) 

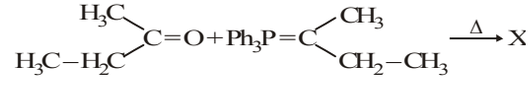
(d) 

99. 

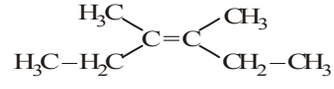
The final product D in the above sequence of reactions is

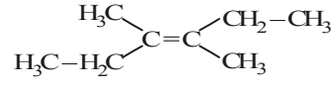
(a) Benzene (b) Tetralin

(c) Decalin (d) Naphthalene

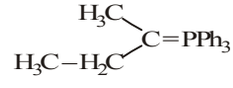
100. 

Product X will be :

(a) 

(b) 

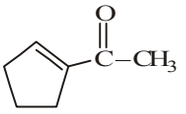
(c) Both (a) and (b)

(d) 

101. How many alkene structures are possible for C_5H_{10} ?

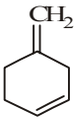
(a) 4 (b) 10

(c) 6 (d) 5

102. (1) $\xrightarrow{O_3/Zn/H_2O}$ (2) $\xrightarrow{NaOH}$ 

The reactant (1) will be :

(a)  (b) 

(c)  (d) 

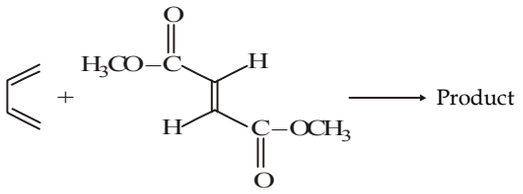
103. Which of the following on treatment with $CH \equiv CH$ produce gas(es) :

I. NH_2^- II. CH_3

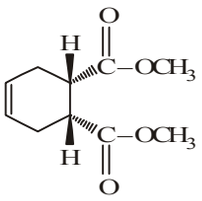
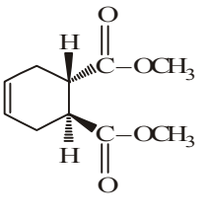
III. OH^- IV. Na in liq. NH_3

(a) II, III and IV (b) I, II and III

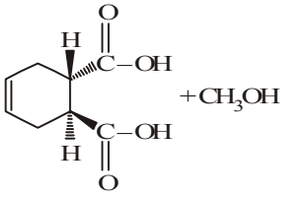
(c) I, II and IV (d) I, III and IV

104. 

Here, the product will be :

(a)  (b) 

(c) Both (a) and (b) in equimolar ratio

(d) 

105. A C_8H_{14} hydrocarbon (X) is reduced by sodium in liquid ammonia to a single C_8H_{15} product (Y). Both of these compounds undergo hydrogenation (Pt catalyst) to give 2, 5-dimethylhexane. Ozonolysis of Y with an oxidative workup produces a single $C_4H_8O_2$ carboxylic acid. Reaction of Y with perbenzoic acid ($C_6H_5CO_3H$) gives a chiral $C_8H_{14}O$ product, but reaction with bromine gives an achiral $C_8H_{14}Br_2$ product. What are X and Y ?

(a) X is 2, 5-dimethyl-3-hexyne; Y is *cis*-2, 5-dimethyl-3-hexene

(b) X is 2, 5-dimethyl-3-hexyne; Y is *trans*-2, 5-dimethyl-3-hexene

(c) X is 2, 5-dimethyl-1, 5-hexadiene; Y is 2, 5-dimethyl-3-hexyne

(d) X is 2, 5-dimethyl-2, 4-hexadiene; Y is *cis*-2, 5-dimethyl-3-hexene

106. Which of the following statements is correct ?

(a) Alkynes are more reactive than alkenes towards halogen additions

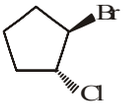
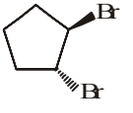
(b) Alkynes are less reactive than alkenes towards halogen addition

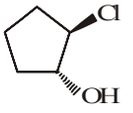
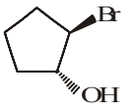
(c) Both alkynes and alkenes are equally reactive towards halogen additions

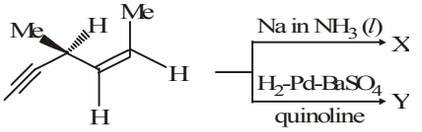
(d) Primary vinylic cation is more reactive than secondary vinylic cation

107.  $\xrightarrow[NaCl]{Br_2-H_2O}$ Product(s)

The product(s) in the above reaction that cannot be formed is :

(a)  (b) 

(c)  (d) 

108. 

The correct statements regarding X and Y is/are

(a) Both X and Y are optically inactive

(b) Both X and Y are optically active

(c) X is optically inactive whereas Y is active

(d) X is optically active whereas Y is inactive.

109. The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromoalkane and alkyne respectively are

(a) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_2CH_2C \equiv CH$

(b) $BrCH_2CH_2CH_3$ and $CH_3CH_2CH_2C \equiv CH$

(c) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3C \equiv CH$

(d) $BrCH_2CH_2CH_2CH_3$ and $CH_3CH_2C \equiv CH$

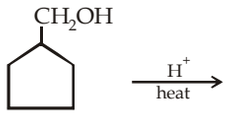
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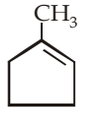
EXERCISE 6.2 (MCQ 1 or >1 option correct, Passage based, Matching, A/R)

DIRECTIONS for Q. 1 to Q. 24 : Multiple choice questions with one or more than one correct option(s).

1. Which of the following statement is true?
(a) Catalytic hydrogenation can't convert an optically inactive compound to optically active product
(b) Catalytic hydrogenation may convert an optically inactive compound to optically active product
(c) Catalytic hydrogenation may be heterogeneous as well as homogeneous
(d) Hydrogenation of ethylene by a mixture of H_2 and D_2 in absence of catalyst forms three products, CH_3CH_3, CH_2DCH_2D and CH_2DCH_3

2. Which product is formed when the following alcohol is heated with sulphuric acid?



(a)  (b) 

(c)  (d) All the three

3. Monobromination of butene-1 with NBS gies
(a) $CH_2BrCH_2CH = CH_2$ (b) $CH_3CHBrCH = CH_2$
(c) $CH_3CH = CHCH_2Br$ (d) $CH_3CH_2CHBrCH_2Br$

4. C_4H_6 may contain
(a) only single bonds (b) a double bond
(c) a triple bond (d) two double bonds

5. Which of the following contains acidic hydrogen?
(a) ethene (b) ethane
(c) ethyne (d) butyne-1

6. Which of the following will react with sodium metal?
(a) ethyne (b) butyne-1
(c) butyne-2 (d) ethane

7. Markownikoff's rule provides guidance of addition of HBr on
(a) $CH_2 = CH_2$ (b) $CH_3.CH=CH_2$
(c) $CH_3.CH=CH.CH_3$ (d) $CH_2 = CHBr$

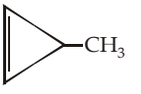
8. Ammonical silver nitrate reacts with
(a) Ethyne (b) Ethylene
(c) Butyne-1 (d) Butyne-2

9. Chlorination can be done on
(a) $CH_3–CH_3$ (b) $CH_2 = CH_2$
(c) $CH_3–CH=CH_2$ (d) $CH \equiv CH$

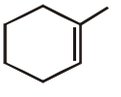
10. Kolbe's electrolytic method can be applied on
(a) $CH_3.CH_2.COOK$ (b) $\begin{matrix}CH_2.COOK\\|\\CH_2.COOK\end{matrix}$
(c) $\begin{matrix}CH.COOK\\\|\\CH.COOK\end{matrix}$ (d) $\begin{matrix}CH_2.COOK\\|\\CH_2.COONa\end{matrix}$

11. Acetylene is
(a) Red coloured gas (b) Garlic in colour
(c) Soluble in acetone (d) Useful in polymer industry

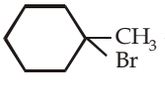
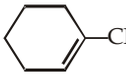
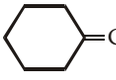
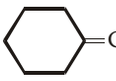
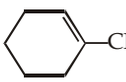
12. Reaction of Br_2 on ethylene in presence of NaCl gives
(a) $BrCH_2 – CH_2Br$ (b) $ClCH_2 – CH_2Br$
(c) $ClCH_2 – CH_2Cl$ (d) $NaCH = CHNa$

13. $A(C_4H_6) \xrightarrow{H_2/Pt} B(C_4H_8) \xrightarrow{O_3/H_2O/Zn} C \xrightarrow{HCN} D$
D has chiral carbon and can be hydrolysed to lactic acid. Hence A is :
(a) $CH_3 – C \equiv C – CH_3$ (b) $CH_2 = CH – CH = CH_2$
(c)  (d) 

14. $\underset{(A)}{C_4H_6} \xrightarrow{H_2/Pt} \underset{(B)}{C_4H_8} \xrightarrow{O_3/H_2O} CH_3COOH$
Hence A and B are :
(a) $CH_3C = CCH_3$, $CH_3CH = CHCH_3$
(b) $CH_2 = CHCH = CH_2$, $CH_3CH = CHCH_3$
(c)  , $CH_3CH = CHCH_3$
(d) none

15. Hydroboration oxidation and acid hydration will yield the same product in case of :
(a)  (b) 
(c) $CH_2 = CH_2$ (d) $CH_3 – CH = CH – CH_3$

16. Following are used as anaesthetics in surgical operations :
(a) C_2H_4 (b) N_2O
(c) $CHCl_3$ (d) solid CO_2

17.  $\xrightarrow{\text{t-BuOK}}$ Product
Which is/are correct statements about the product :
(a)  is an endocyclic Saytzeff product
(b)  is an exocyclic Saytzeff product
(c)  is an exocyclic Hofmann product
(d)  is an endocyclic Hofmann product

18. Baeyer test is for :

(a) testing alkenes (b) testing alkynes

(c) testing alkanes (d) testing aromatic compounds

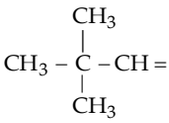
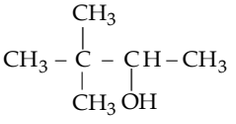
19. $A \xrightarrow{HgSO_4 / H_2SO_4} B \xrightarrow[H_2O_2 / OH^-]{BH_3 / THF}$

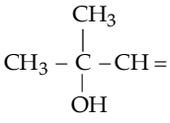
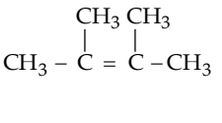
B is identical when A is :

(a) $CH \equiv CH$ (b) $CH_3 - C \equiv CH$

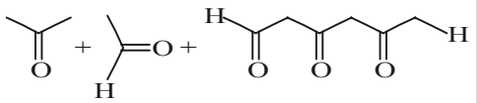
(c) $CH_3 - C \equiv C - CH_3$ (d) $CH_3 - CH_2 - C \equiv CH$

20. $A + HCl \longrightarrow 2 - chloro - 2, 3 - dimethyl - butane$. Hence A can be

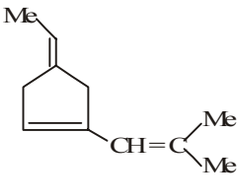
(a)  (b) 

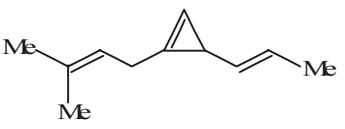
(c)  (d) 

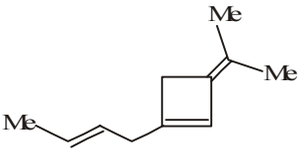
21. $\underset{\text{(Hydrocarbon)}}{A} \xrightarrow[(ii)\ Zn / H_2O]{(i)\ O_3}$

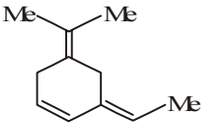


Structure of A can be :

(a) 

(b) 

(c) 

(d) 

22. $CH_3 - C \equiv CCH_3 \xrightarrow{D_2, Li / NH_3(l)} (X) \xrightarrow{H_2 / Ni} (Y) \xrightarrow{Cl_2 / hv} (Z)$

The correct statements are :

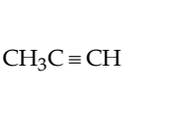
(a) (X) is single stereoisomer formed as Z-but-2-ene.

(b) (Y) is a mixture of two enantiomers obtained by *syn*-addition of hydrogen atoms.

(c) (Z) is a mixture of four structural isomers.

(d) All monochloro isomers are chiral.

23. Outline the best synthesis of 4, 4-dimethyl-2-pentyne using $NaNH_2$ in liquid NH_3 and following compounds.

I. $CH_3C \equiv CH$ II. 

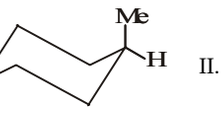
III.  IV. CH_3I

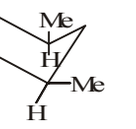
V. $CH_3 - C \equiv CBr$

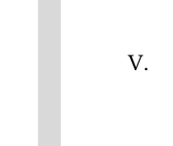
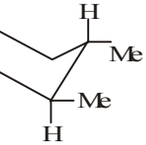
(a) I + II (b) III + V

(c) III +IV (d) II + V

24. Consider the following molecules :

I.  II. 

III.  IV. 

V.  VI. 

and select the correct options given below :

(a) I and II are diastereomers

(b) IV and V are chiral molecules

(c) I, II and III are achiral molecules

(d) At normal temperature, there are three isolable stereo-isomers of V and VI

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INSTRUCTION for Q. 25 to 75 : Read the passages given below and answer the questions that follow.

PASSAGE 1

One of the common methods for the preparation of alkenes is dehydrohalogenation of alkyl halides.

$$CH_3\underset{|}{\overset{Br}{C}}HCH_2CH_3 + \text{Base} \longrightarrow CH_3CH=CHCH_3 + CH_2=CHCH_2CH_3$$

Nature of major product (alkene) depends upon the stability of alkene and size of the base used. Use of a small base gives mainly highly substituted alkene **(Saytzeff product)**, while a bulky base gives the least substituted as the major product **(Hofmann product)**.

Dehydrohalogenation of alkyl halides follows E2 or E1 mechanism. E2 mechanism occurs in a single step reaction; while E1 mechanism is a two step process involving carbocation formation. Nature of the major product, i.e. which alkene is formed in greater amount depends upon the nature (especially size) of the base and stability of the alkene formed. Where geometrical isomerism is possible, *cis*- or *trans*- isomer may be formed in greater amount depending upon the nature of alkyl halide.

Another common method for the preparation of alkenes is dehydration of alcohols with conc. H_2SO_4 or conc. phosphoric acid. Mechanism of dehydration of alcohols resembles the E1 mechanism.

25. An alkyl halide can undergo dehydrohalogenation by E2 as well as E1 mechanism. Which of the two mechanisms will give good result for the required alkene?

(a) E2 mechanism (b) E1 mechanism

(c) Both (d) E1 $\geq$ E2

26. $CH_3CH_2\underset{|}{\overset{Br}{C}}HCH_3 \xrightarrow{Et_3N} CH_3CH=\underset{|}{C}HCH_3$ + $CH_3CH_2\underset{|}{C}=CH_2$

(A) (B) (C)

The main product is

(a) B (b) C

(c) both in equal amounts (d) None

27. $CH_2=CHCH_2\underset{|}{\overset{Cl}{C}}HCH(CH_3)_2 \xrightarrow{OH^-}$

(D)

$CH_2=CHCH=\underset{|}{C}HCH + CH_2=CHCH_2CH=\underset{|}{C}CH_3$

CH_3 CH_3

(E) (F)

Here the major product is :

(a) E (b) F

(c) E = F (d) Reaction not possible

28. Which of the following statement is true?

(a) Reactions in Q. 2 and 3 are stereoselective

(b) Reactions in Q. 2 and 3 are stereospecific

(c) Reactions in Q. 2 and 3 are regioselective

(d) Reaction in Q. 2 is regioselective, while in 3 it is regiospecific.

29. Dehydrohalogenation of alkyl halides is (one or more may be correct) :

(a) regioselective (b) regiospecific

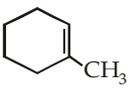
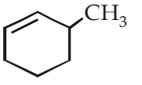
(c) stereoselective (d) stereospecific

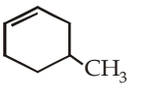
30. Which of the above mentioned compounds does not show geometrical isomerism as well as enantiomerism but either of the two? (one or more may be correct).

(a) B (b) D

(c) E (d) F

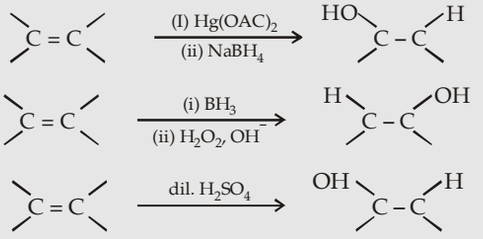
31. 2-Methylcyclohexanol is heated with conc. sulphuric acid, the product formed is (one or more may be correct).

(a)  (b) 

(c)  (d) 

PASSAGE 2

The most usual properties of alkenes are the electrophilic addition. The reaction generally occurs in two steps : addition of electrophile followed by addition of nucleophile. The intermediate formed is an ordinary carbocation, cyclic cation or a transition state. One of the important addition reactions is hydration of alkenes to alcohols.



Additions on alkenes may be *syn*- or *anti*-depending upon the nature of the reagent.

32. *anti*-Stereochemistry is observed during

(a) addition of Br_2 (b) hydroboration-oxidation

(c) addition of HOCl (d) none of the three

33. Hydration of propene to form *n*-propyl alcohol through hydroboration-oxidation reaction suggests the formation of :

$$CH_3CH=CH_2 \xrightarrow[(ii)\ H_2O_2,\ OH^-]{(i)\ (BH_3)_2} CH_3CH_2CH_2OH$$

(a) 1° carbocation as an intermediate

(b) 2° carbocation as an intermediate

(c) carbocation is not formed as an intermediate

(d) nothing about formation of intermediate

34. Reaction of alkene with Br_2, HOCl, alk. $KMnO_4$, OsO_4 and per acids involves formation of cyclic cation as intermediate. Which of the above reaction involves *syn* addition?

(a) reaction of HOCl (b) reaction of alk. $KMnO_4$

(c) reaction of peracids (d) reaction of OsO_4

35. Non-Markownikoff's *syn*-hydration of propene is possible in
(a) hydroboration/oxidation
(b) oxymercuration-demercuration
(c) aq. acid
(d) reaction with HCl in presence of peroxide followed by treatment with aq. KOH

PASSAGE 3

Acidic properties of terminal alkynes plays a central role in alkyne chemistry. The acidity of hydrocarbons increases with the increasing *s*-character of the orbitals. i.e. $sp^3 < sp^2 < sp$.

Alkynide ions are strong nucleophiles and thus like other nucleophiles they react with alkyl halides especially primary. Alkynide ions are also sufficiently strong bases and cause dehydrohalogenation of 2° and 3° alkyl halides. Heavy metal alkynides are not very soluble and form characteristic precipitates. However, like other alkynides, these alkynides are converted back to the parent alkyne on treatment with dilute acids.

36. The charge separation is maximum in
(a) $CH \equiv C^-$ (b) $CH_2 = CH^-$
(c) $CH_3CH_2^-$ (d) $^-C \equiv C^-$

37. $CH_3CH_2C \equiv CH$ can be converted into $CH_3CH_2C \equiv C:^{\ominus}$ by reaction with
(a) sodium hydroxide (b) sodamide
(c) sodium ethoxide (d) sodium *ter*- butoxide

38. Which of the following reaction is not possible? (one or more may be correct)
(a) $HC \equiv CH + CH_3Li$
(b) $CH \equiv C:^- Na^+ + CH_3OH$
(c) $HC \equiv C:^- Na^+ + CH_2 = CH_2$
(d) $CH_2 = CH_2 + NaNH_2$

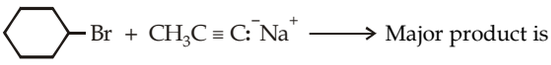
39. 1-Hexene (b.p. 64°C) and 1-hexyne (b.p. 71°C) can't be separated from each other by distillation. However, the two can be separated completely by reacting the mixture with sodamide followed by :
(a) distillation
(b) reaction with ammonical silver nitrate
(c) both (d) none of the two

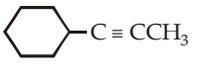
40. Which of the following is a strong nucleophile?
(a) $CH_3CH_2C \equiv CNa$ (b) $CH_3CH_2C \equiv CAg$
(c) Both (d) None

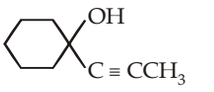
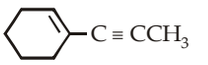
41. $CH_3CH_2C \equiv CH \xrightarrow[(ii)\ CH_3CH(Br)CH_3]{(i)\ NaNH_2} CH_3CH = CH_2 + \text{Product}$

If the above reaction occurs through E2 mechanism, the other main product should be
(a) $CH_3CH_2C \equiv CCH(CH_3)_2$
(b) $CH_3CH_2C \equiv CH$
(c) Both (d) $CH_3CH_2CH = CH_2$

42. Sodium acetylide can cause (one or more may be correct) :
(a) nucleophilic substitution
(b) nucleophilic addition
(c) electrophilic substitution
(d) elimination.

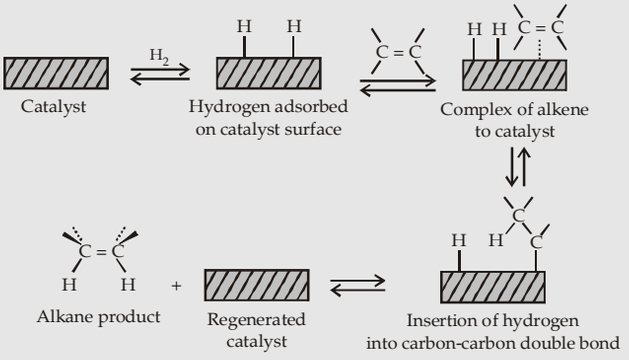
43.  Major product is

(a)  (b) 

(c)  (d) 

PASSAGE 4

Catalytic hydrogenation of a carbon-carbon double bond follows following path :



Mechanism of alkene hydrogenation. The reaction takes place with syn stereochemistry on the surface of insoluble catalyst particles.

On the basis of the above mechanism, answer the following questions :

44. Which of the following statement is true regarding adsorption of hydrogen over the catalyst?
(a) It is a physical process
(b) It is a chemical reaction
(c) It involves pairing of electrons between metal and hydrogen
(d) The metal used should belong to transition series

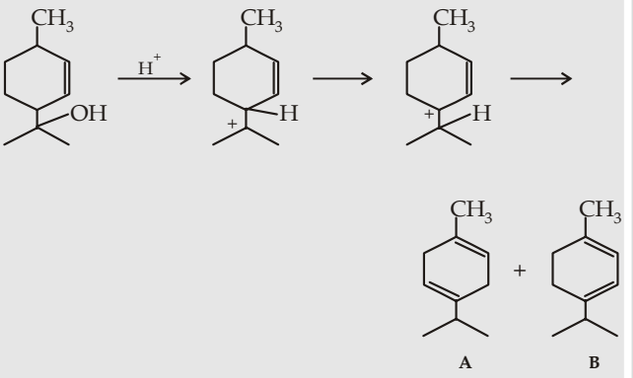
45. The complex between alkene and hydrogen-adsorbed catalyst is formed by
(a) overlapping of *p*-orbital of carbon with the *d*-orbital of the metal
(b) overlapping of *s*-orbital of carbon with the *d*-orbital of the metal
(c) overlapping of *s*-orbital of hydrogen with the *p*-orbital of carbon
(d) no overlapping occurs

46. Which of the following statement is/are true?
(a) Hydrogenation does not occur at all in absence of catalyst
(b) The two hydrogen atoms are added stepwise
(c) Both hydrogen atoms are added in one step
(d) Catalyst decreases the activation energy of the reaction

47. If a mixture of H_2 and D_2 is used in place of H_2, the product formed by ethylene will be
(a) CH_3CH_3 (b) $CH_2D\ CH_2D$
(c) $CH_2D\ CH_3$ (d) all the three

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PASSAGE 5



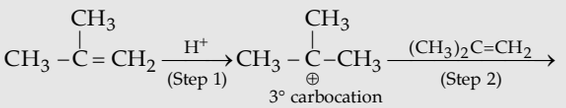
48. Step 2 of reaction involves conversion of
(a) a 2° carbocation to a 3° carbocation
(b) a 3° carbocation to a cyclic carbocation
(c) a 3° carbocation to a 2° allylic carbocation.
(d) a 3° carbocation to a 3° allylic carbocation

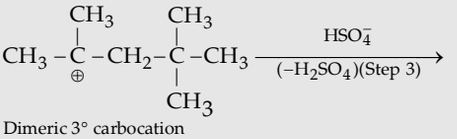
49. The final product is a mixture of A and B in which
(a) A is major (b) B is major
(c) Both in equal amounts (d) Nothing is certain

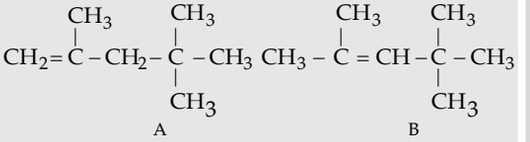
50. The final product will behave like an
(a) aliphatic compound (b) aromatic compound
(c) both (d) none

PASSAGE 6

Isobutene, when heated with sulphuric acid, phosphoric acid or HF undergoes dimerization forming a mixture of two alkenes each having 8 carbon atoms. Since reaction is catalysted by acids, it is an electrophilic addition and proceeds as below :







Less sterically hindered alkene is the major product

51. Which of the two alkenes is major product
(a) A (b) B
(c) both in equal amount (d) can't be predicted

52. Both (A) and (B) can be converted into identical product by
(a) oxidation (b) reduction
(c) chlorination (d) heating to high temperature

53. Dimerization of isobutene can be performed by
(a) HCl (b) HF
(c) Both (d) None

PASSAGE 7

Three isomeric alkenes A, B and C, C_5H_{10}, are hydrogenated to give 2-methylbutane. A and B give the same 3° alcohol on oxymercuration-demercuration, while B and C give the different 1° alcohols on hydroboration-oxidation.

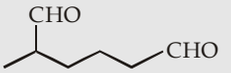
54. The alkene (A) is
(a) $(CH_3)_2CHCH=CH_2$ (b) $CH_2=C(CH_3)CH_2CH_3$
(c) $(CH_3)_2C=CHCH_3$ (d) $(CH_3)_2C=C=CH_3$

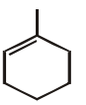
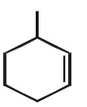
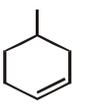
55. The alkene (B) is
(a) $(CH_3)_2CHCH=CH_2$ (b) $CH_2=C(CH_3)CH_2CH_3$
(c) $(CH_3)_2C=CHCH_3$ (d) $(CH_3)_2C=C=CH_3$

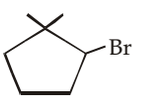
56. The alkene (C) is
(a) $(CH_3)_2CHCH=CH_2$ (b) $CH_2=C(CH_3)CH_2CH_3$
(c) $(CH_3)_2C=CHCH_3$ (d) $(CH_3)_2C=C=CH_3$

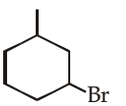
PASSAGE 8

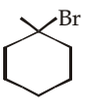
Hydrocarbon A(C_7H_{12}) was treated with HBr / peroxide to provide B($C_7H_{13}Br$) as the only product. Reaction of B with *tert*-butoxide ion / base gives C (isomeric with A) in addition to other olefin(s). Treatment of C with ozone, followed by Zn/H_2O produces only following compound.

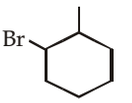


57. What is the correct structure for A?
(a) 
(b) 
(c) 
(d) 

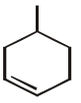
58. What is the correct structure for B?
(a) 

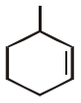
(b) 

(c) 

(d) 

59. The correct structure for C is

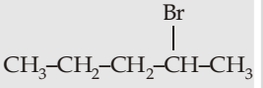
(a)  (b) 

(c)  (d) None of these

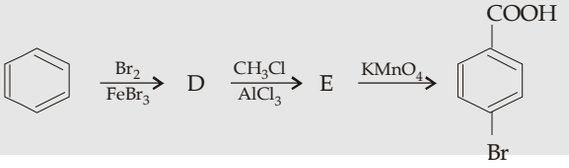
PASSAGE 9

Synthesis I :

$$HC\equiv CH \xrightarrow[NaNH_2,\ NH_3]{} A \xrightarrow[C_3H_7Br]{} B \xrightarrow[\text{Lindlar catalyst}]{H_2} C \xrightarrow[HBr,\ \text{ether}]{}$$



Synthesis II :



60. In synthesis I, compound A is

(a) ethene (b) ethane

(c) 1,3-butadiene (d) acetylide ion

61. In synthesis I, compound B is

(a) 1-pentyne (b) 2-pentyne

(c) 1-pentene (d) 2-pentene

62. In synthesis I, compound C is

(a) trans-2-pentene (b) cis-2-pentene

(c) 1-pentene (d) 2-pentene

63. In synthesis II, compound E is

(a) p-bromomethylbenzene

(b) m-bromomethylbenzene

(c) p-bromophenol

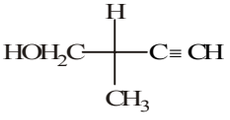
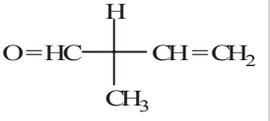
(d) p-bromobenzaldehyde.

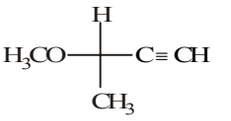
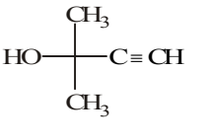
PASSAGE 10

Compound X (C_5H_8O) on reaction with H_2/Ni gives Y ($C_5H_{12}O$). Y on monchlorination gives Z ($C_6H_{11}ClO$), which is a mixture of 5 products of different structural formula (although some of these have stereoisomers also). Oxidative ozonolysis of X produces W ($C_4H_8O_3$) along with one more product.

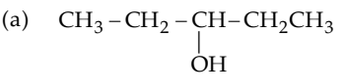
X, Y and W are chiral compounds. Lucas and 2, 4-DNP tests are negative for X.

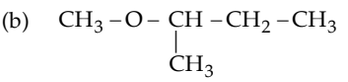
64. The compound X can be

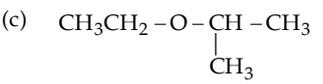
(a)  (b) 

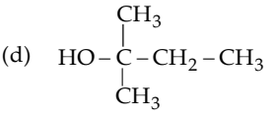
(c)  (d) 

65. The compound Y can be

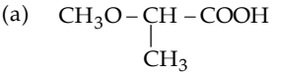
(a) 

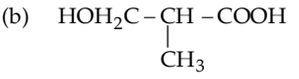
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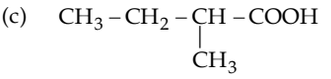
(c) 

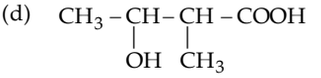
(d) 

66. The compound W can be :

(a) 

(b) 

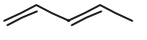
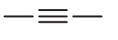
(c) 

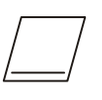
(d) 

PASSAGE 11

'X'(C_4H_6) on catalytic hydrogenation by H_2/Ni produces 'Y' (C_4H_8). 'Y' on dichlorination by Cl_2/hv forms 'Z' ($C_4H_6Cl_2$), mixture of total six isomers (all dichloro isomers). Reductive ozonolysis of X produces a single compound W ($C_4H_6O_2$).

67. The compound X can be

(a)  (b) 

(c)  (d) 

68. The compound of fractions obtained by fractional distillation of mixture Z is

(a) 3 (b) 4

(c) 5 (d) 6

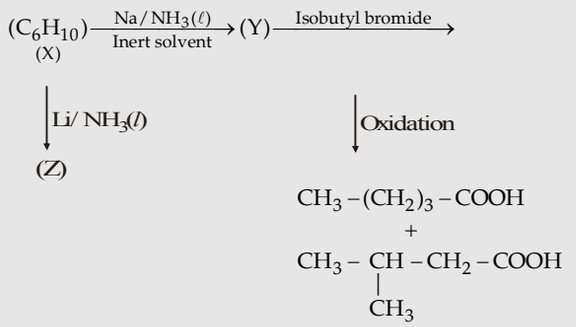
69. The number of dioxime isomers formed by 'W' on reaction with NH_2OH.

(a) 1 (b) 2

(c) 3 (d) 4

EBD_7088

PASSAGE 12



70. The compound (X) is

(a) $CH_3-(CH_2)_3-C\equiv CH$

(b) $CH_3-(CH_2)_2-C\equiv C-CH_3$

(c) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-C\equiv CH$

(d) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-C\equiv C-CH_3$

71. The compound (Z) is

(a) (Z)-Hex-2-ene (b) (E)-Hex-2-ene

(c) (Z)-2-Methylpent-2-ene (d) (E)-2-Methylpent-3-ene

72. The compound (Y) is

(a) $CH_3-(CH_2)_3C\equiv \overset{\ominus\oplus}{C}Na$

(b) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-C\equiv \overset{\ominus\oplus}{C}Na$

(c) $CH_3-(CH_2)_3-CH=CH-CH_3$ (*Trans*)

(d) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH=CH-CH_3$ (*Trans*)

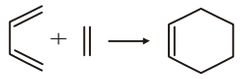
PASSAGE 13

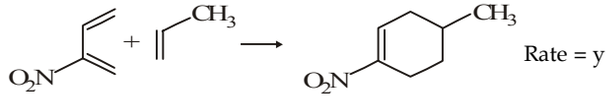
Diels-Alder reaction involves the 1, 4-addition of an alkene to a conjugated diene to form an adduct of six-membered ring. The double bond compound is called the dienophile.

Electron withdrawing substituents in the dienophile such as >C = O, –CHO, –CN, $–NO_2$, etc. promote the reaction.

The reaction rate is also accelerated by the presence of electron – releasing groups in the dienes. Triply bonded compounds, allenes and benzyne may also function as dienophiles. Beside the acyclic hydrocarbons, dienes may be alicyclic hydrocarbon, in which the conjugated double bonds may be wholly or partly inside the ring, some heterocyclic and some aromatic hydrocarbon. These reactions are highly stereospecific.

73.



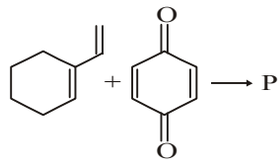


The correct order is :

(a) x > y (b) x < y

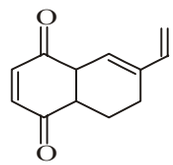
(c) x = y (d) can't predict

74.

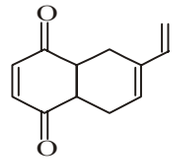


Product P in the above reaction will be :

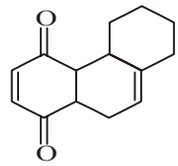
(a)



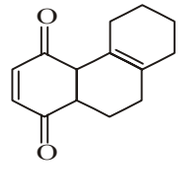
(b)



(c)



(d)



75.



(a) Product is a mixture of two geometrical isomers in unequal concentration

(b) Product is exclusively cis, cyclic and unsaturated dicarboxylic acid

(c) Product is exclusively trans, cyclic and unsaturated dicarboxylic acid

(d) Product is a mixture of two geometrical isomers but in equal concentration

Instructions for Q. 76 to 80 : Following questions are Multiple Matching type Questions :

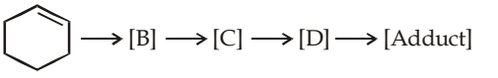
76.

	Column I		*Column II*
(A)	$CH_2CH_2\underset{\displaystyle Br}{\underset{\vert}{C}}HCH_3$ $\xrightarrow[E2]{CH_3CH_2O^-Na^+}$	(a)	Stereoselective
(B)	$CH_3CH_2\underset{\displaystyle N^+Me_3}{\underset{\vert}{C}}HCH_3$ $\xrightarrow[E2]{heat}$	(b)	Stereospecific
(C)	*cis*-2-Butene + Br_2	(c)	Hofmann product
(D)	*trans*-2-Butene + Br_2	(d)	Saytzeff product

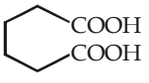
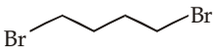
77.

	***Column I* (Reaction on C = C)**		***Column II* (Nature of reactant / product)**
(A)	OsO_4	(a)	Toxic
(B)	Acidic $KMnO_4$	(b)	Aldehydes
(C)	O_3 / $(CH_3)_2S$	(c)	Alcohols
(D)	O_3 / H_2O_2	(d)	Carboxylic acids

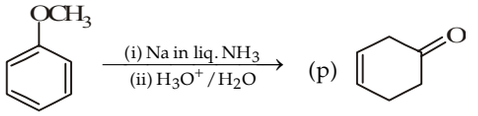
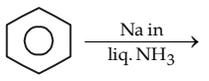
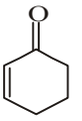
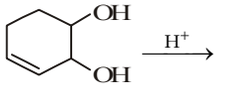
78. A series of reactions is given below :



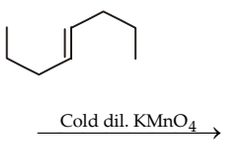
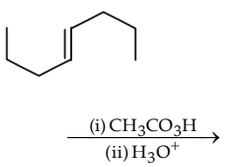
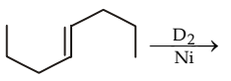
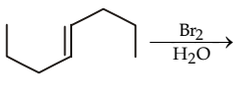
Pick up the appropriate reagent and corresponding product pair from the respective column X and Y :

	***Column I* - X (Reagent)**		***Column II* - Y (Product)**
(A)	alcoholic potash	(a)	
(B)	Ag^+/Br_2, heat	(b)	
(C)	acidic $KMnO_4$	(c)	
(D)	Ethylene	(d)	

79. Match the following column I with column II :

	Column-I (Reaction)		**Column-II (Products)**
A.		(p)	
B.		(q)	
C.	$H_2C=CH-CH=CH_2$ $\xrightarrow[\Delta, aq.KOH]{CH_2=CBr_2}$	(r)	(4 + 2)-addition reaction
D.		(s)	Birch reduction
		(t)	CH_3OH

80. Match the following questions :

	Column-I		**Column-II**
A.		(p)	Optically inactive due to internal compensation
B.		(q)	Optically inactive due to external compensation
C.		(r)	Product has two chiral centres
D.		(s)	Diastereomers will be formed
		(t)	Overall syn addition

Instructions for Q.81 to 91 : Following questions are Assertion and Reasoning Type Questions :

Note : Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 5 choices (A), (B), (C), (D) and (E) out of which ONLY ONE is correct.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.

(c) Statement -1 is True, Statement-2 is False.

(d) Statement -1 is False, Statement-2 is True.

(e) Statement -1 is False, Statement-2 is False.

81. **Statement 1 :** Addition of HBr to 1, 3 – Butadiene gives 1,2 product at low temperature and 1, 4 product at high temperature.

Statement 2 : For 1, 2 product to be formed the activation energy requirements are less.

82. **Statement-1 :** With respect to alkenes, the electrophilic addition reaction and elimination reaction are reversible

Statement-2 : because, the direction of the reaction is controlled by decrease in free energy of the reaction

83. **Statement 1 :** $CH_2 = CH_2 > R - CH = CH_2 > R - CH = CH - R$ decreasing order of addition of H_2

Statement 2 : Addition of H_2 takes place by the formation of transition state therefore least substituted alkene will be more reactive.

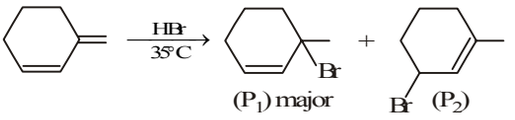
84. **Statement 1 :** 1-Butene on reaction with HBr in the presence of a peroxide produces 1-bromo-butane.

Statement 2 : It involves the free radical mechanism.

85. **Statement 1 :** Trans-2-butene on reaction with Br_2 gives meso-2, 3-dibromobutane.

Statement 2 : The reaction involves syn-addition of bromine.

86. **Statement-1 :** In the reaction



(P_1) major (P_2)

Statement-2 : P_1 is formed by more stable carbocation intermediate.

87. $CH_3 - CH = CH - CH_3 + HX \xrightarrow{\text{Peroxide}}$

$$CH_3 - \underset{\underset{X}{|}}{CH} - CH_2 - CH_3$$

Statement-1 : The stereochemistry of product is same whether HCl or HBr is used as reactant.

Statement-2 : The reaction mechanism with HCl and HBr are same in above conditions.

88. **Statement-1 :** Alcoholic KOH converts $CH_3 - CH_2 - Br$ into $CH_2 = CH_2$, whereas aqueous KOH converts $CH_3 - CH_2 - Br$ into $CH_3 - CH_2 - OH$.

Statement-2 : Alcoholic KOH is more basic than aqueous KOH.

89. **Statement-1 :** 1-Chloro-2-methylbutane may rotate the plane of polarised light anti-clockwise.

Statement-2 : Two counter-rotating circularly polarized beams travel with different velocities through the chiral medium.

90. **Statement-1 :** A mixture of *cis*-2-butene and *trans*-2-butene on addition with ozone produces three stable ozonides.

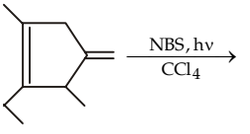
Statement-2 : Formation of ozonide is an example of addition reaction.

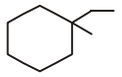
91. **Statement-1 :** In presence of an organic peroxide, when HCl is added to propene, 1-chloropropane is the major product.

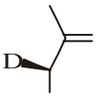
Statement-2 : Peroxide facilitates free radical mechanism.

Instructions for Q. 92 to 100 : Following questions are Integer Type Questions :

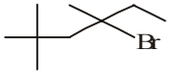
92. How many free radicals can be produced during following reaction (ignoring resonating structure) ?

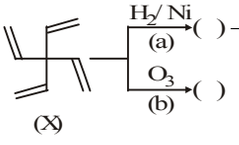


93. (a)  $\xrightarrow[h\nu]{Cl_2}$ (A) number of monochloro derivatives formed.

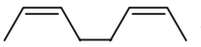
(b)  $\xrightarrow[brine]{Br_2}$ (B) number of fractions obtained after fractional distillation of product mixture.

Give the sum of the products obtained in above two reactions.

94.  $\xrightarrow{alc.KOH}$ Number of alkenes produced.

95. 

Calculate sum of number of products formed in the reaction a, b and c.

96.  $\xrightarrow{D_2/Ni} C_8H_{14}D_4$

Find the total number of isomers formed in the end product.

97. How many alkenes, alkynes, alkadienes can be hydrogenated to form isopentane (include all isomers).

98. For the given reaction write the correct code :

$$CH_3-CH_2-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3 \xrightarrow{alc.KOH/\Delta}$$

Code :

(01) If the reaction is regioselective but not stereoselective.

(02) If the reaction is stereoselective but not regioselective.

(03) If the reaction is both regioselective and stereoselective.

(04) If the reaction is none of regioselective and stereoselective.

99. Total no. of alkynes that on catalytic reduction gives 3-ethyl-4-methylheptane.

100. The total number of cyclic isomers possible for a hydrocarbon with the molecular formula C_4H_6 is 5.

EBD_7088

EXERCISE 6.3 (Subjective Problems)

1. How a symmetrical molecule like bromine acts as an electrophile during addition on alkenes?

2. Define Saytzeff rule for orientation of elimination in terms of number of hydrogen atoms on carbon atoms of the substrate (*i.e.* in terms of Markownikoff's rule).

3. Compare the relative rates of addition of HCl, HBr and HI to alkenes.

4. Solubility of alkenes in water increases in presence of Ag^+ salts. Explain.

5. Dehydrohalogenation of isopropyl alcohol by alcoholic KOH requires several hours of refluxing, while it can be carried out immediately at room temperature by potassium *t*-BuO^- in dimethyl sulphoxide (DMSO). Explain.

6. Write the structures for the products of the following addition reactions :

(a) $(CH_3)_2C = CHCH_3 + ICl \longrightarrow$

(b) $(CH_3)_2C = CH_2 + HSCH_3 \longrightarrow$

(c) $CH_2 = CHCF_3 + HCl \longrightarrow$

(d) $Me_3\overset{+}{N}CH = CH_2 + HI \longrightarrow$

7. Give the structure of the alkene and reagent used for the preparation of

(a) $(CH_3)_3CI$, (b) CH_3CHBr_2,

(c) $CH_2(Br)CH(Cl)CH_3$, (d) $CH_2(Cl)CH(OH)CH_2Br$.

8. Predict the product(s) and give mechanism to explain the following :

(a) $CH_3CHOH.\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}.CH_3 \xrightarrow{\text{conc. } H_2SO_4}$ Product(s)

(b) $CH_2 = CH_2 + (CH_3)_3CH \xrightarrow{HF}$ Product(s)

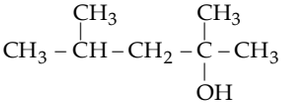
(c) $CH_2 = CH - C(CH_3)_3 + HCl \longrightarrow$ Product(s)

(d) $CH_3 - \underset{\displaystyle OTs}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{CH}}}} - CH - CH_2CH_3 \xrightarrow[\text{(no base)}]{n\text{-}C_4H_9OH,\ \text{heat}}$ Product(s)

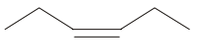
(e) $^{14}CH_3CH = CH_2 + Br_2 \xrightarrow{300°C}$ Product(s)

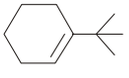
9. Complete the following :

(i) Alkene (A) + Reagent(B) $\longrightarrow$

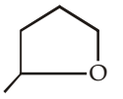


(ii)  + HOBr $\longrightarrow$ C

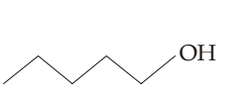
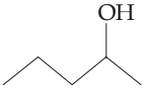
(iii) E $\xleftarrow[\text{heat}]{KMnO_4}$  $\xrightarrow[\text{(cold)}]{KMnO_4}$ D

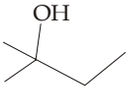
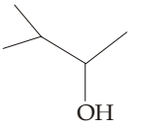
(iv)  $\xrightarrow[\text{dark}]{HBr}$ F

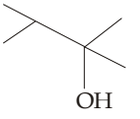
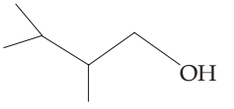
(v) $CH_2 = CHCH_2CH_2CH_2OH \xrightarrow{Hg(OAc)_2}$

G $\xrightarrow{-H^+}$ H $\xrightarrow{NaBH_4}$ 

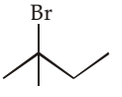
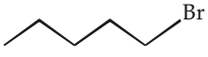
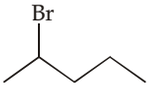
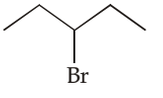
10. Which alcohol of each pair would you expect to me more easily dehydrated?

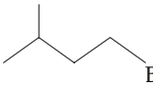
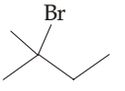
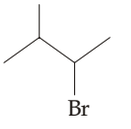
(a)  and 

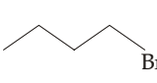
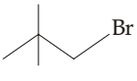
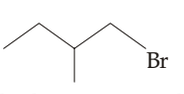
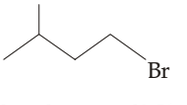
(b)  and 

(c)  and 

11. Arrange the compounds of each set in order of reactivity towards dehydrohalogenation by strong base

(a)  ,  ,  and 

(b)  ,  and 

(c)  ,  ,  and 

12. Is it possible to dehydrate neopentyl alcohol with an acid? If yes, give the possible product(s).

13. Heat of combustion of three alkenes (1-pentene, *cis*-2-pentene and *trans*-2-pentene) were found to be 804.3, 805.3 and 806.9 kCal/mole. Can you get any concrete result from these data?

14. Addition of an electrophile to 2, 4-hexadiene gives two intermediates. Write their structures and tell which one is more stable?

15. Dehydration of butanol-1 gives expected product butene-1 and rearranged product butene-2. Can we convert 1-butanol to 2-butene without involving any rearrangement?

16. What will happen when a solution of chlorine in tetrachloroethylene ($Cl_2C = CCl_2$) is kept in dark at room temperature?

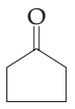
17. In a polymer having regularly alternating groups, the monomer units are always linked in a head-to-tail manner. Comment.

18. Which alkene of each pair is expected to be more reactive towards addition of sulphuric acid?
(a) Ethylene and propylene
(b) Propylene and 2-butene
(c) 2-Butene and isobutene
(d) 1-Pentene and 2-methyl-1-butene
(e) Ethylene and vinyl chloride
(f) Vinyl chloride and 1, 2-dichloroethylene
(g) Ethylene and acrylic acid
(h) Propylene and 3, 3, 3-trifluoropropene.

19. Reaction of 2-butene with HCl in presence of alcohol forms a compound of molecular formula $C_6H_{14}O$ as one of the products. How will you explain its formation?

20. Deduce the structures of alkenes A to F which on ozonolysis gave products mentioned against them

$A \longrightarrow CH_3CH_2CHO$

B ⟶  + HCHO

$C \longrightarrow CH_3CO.CHO + 2CH_3.CO.CH_3$;

$D \longrightarrow CH_3COCH_2CH_2CH_2CH_2CHO$

$E \longrightarrow CH_3CHO + HCHO + CHO.CH_2.CHO$;

$F \longrightarrow CHO.CH_2CH_2CH_2.CHO$

21. Predict the stereochemistry of the product formed by the addition of Br_2 on (a) *cis*-1, 2-dideuterioethene and (b) *trans*-1, 2-dideuterioethene.

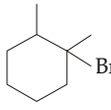
22. Predict the products formed by the addition of one mode of bromine to $C_6H_5CH = CH–CH = CH_2$. Which one of them is expected to be most stable?

23. When isobutene is treated with chlorine in dark at 0°C in the absence of peroxide, a substitution (methallyl chloride) rather than addition is the main product. Explain.

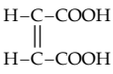
24. Propene ($CH_3CH = CH_2$) when treated with bromine and water gives $CH_3CHOHCH_2Br$ (a secondary alcohol), on the other hand allyl bromide ($CH_2BrCH = CH_2$), on similar treatment mainly gives $CH_2Br.CHBr.CH_2OH$, a primary alcohol. Explain.

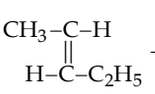
25. *n*-Butyl-*tert*-butyl ether dissolves in cold concentrated H_2SO_4, however on standing, an acid insoluble layer having a polymer separates out. Explain.

26. Complete the following :

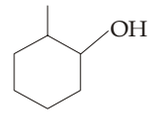
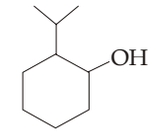
(i)  $\xrightarrow{\text{alc. KOH}}$ Products

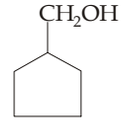
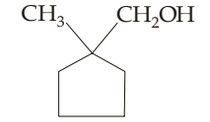
(ii)  + Br_2 $\xrightarrow{300°C}$ Main product

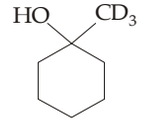
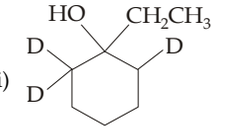
(iii)  + D_2 ⟶ Product(s)

(iv) B $\xleftarrow{\text{dil. KMnO}_4}$  $\xrightarrow{HCOOOH}$ A

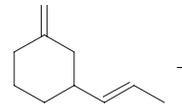
27. Predict the product(s) of dehydration of the following alcohols :
(i) $(CH_3)_2CH.CHOH.CH_3$ (ii) $(CH_3)_2C(OH).CH(CH_3)_2$

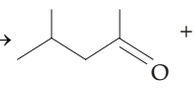
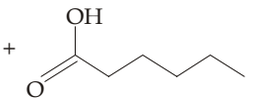
(iii)  (iv) 

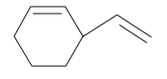
(v)  (vi) 

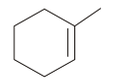
(vii)  (viii) 

28. Complete the following :

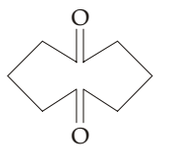
(i)  $\xrightarrow[\text{heat}]{\text{hot KMnO}_4}$ All possible products

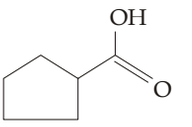
(ii) [A] $\xrightarrow[\text{heat}]{KMnO_4}$  + 

(iii)  $\xrightarrow[CHCl_3 \text{ at } 25°C]{C_6H_5CO_3H}$ [B]

(iv)  $\xrightarrow[(ii)\ H_2O_2/OH^-]{(i)\ BD_3,\ THF}$ [C]

(v)  + : CBrCl ⟶ Two Products

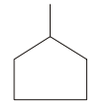
(vi) [D] $\xrightarrow{\text{Ozonolysis}}$ 

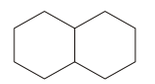
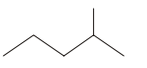
(vii) E $\xrightarrow[(ii)\ H_2O]{(i)\ O_3}$ 2 

29. (a) Write down structures of the isomeric dimers obtained by the dimerisation of isobutene.
(b) Write down the ozonolysis products of *cis*- and *trans*-2-butenes.

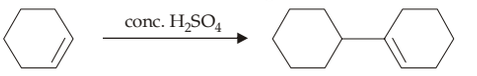
30. Which of the following isomeric compound will have lower heat of combustion in each of the following pairs?
(i) *cis*-2-Butene and *trans*-2-Butene
(ii) *trans*-2-Hexene and 2-methyl-2-pentene
(iii) Octane and 2, 5-dimethylhexane.

31. Predict the major monochloro products in the following :

(i)  (ii) 

(iii)  (iv) 

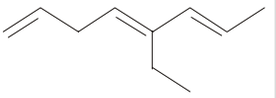
32. Give mechanism of the following reaction.



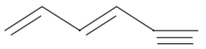
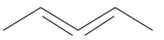
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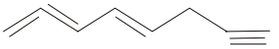
33. Tetrachloroethylene adds chloride only in presence of $AlCl_3$. Comment.

34. (a) Give IUPAC name of the following :

(i)  (ii) 

(b) Give the state of hybridisation of each carbon in the following compounds :

(i)  (ii) 

(iii) 

35. Give the products obtained from the acid-catalysed dehydration of $CH_2 = CH.CH_2.CH(OH).CH_3$. Predict which will be major product, if any.

36. Give the products obtained from the reaction of 2-methyl-1, 3-butadiene with bromine.

37. (a) Give the various possible products formed by the addition of one mole of Br_2 to one mole of 1, 3, 5-hexatriene.

(b) Which products will be obtained under thermodynamic controlled conditions?

38. (a) Write down the different resonating structures of the following carbocation having + charge on different carbon atoms.

$$CH_2 = CH - CH = CH - CH = CH - \overset{\oplus}{C}H_2$$

(b) Which of the canonical structure will react with the nucleophile (Nu^-) to give the thermodynamic controlled product?

39. Arrange the following alkenes in the order of decreasing reactivity towards HBr :

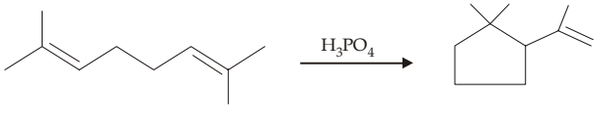
$$\underset{I}{CH_3 - CH = CH - CH_3}, \quad \underset{II}{CH_2 = CH - CH_2 - CH_3},$$

$$\underset{III}{CH_2 = CH - CH = CH_2}, \quad \underset{IV}{CH_2 = \overset{CH_3}{\overset{|}{C}} - \overset{CH_3}{\overset{|}{C}} = CH_2},$$

$$\underset{V}{CH_3 - CH = CH - CH = CH_2}$$

40. Give structures of the products expected from the reaction of 1, 3-butadiene with (a) 1 mol of HCl, and (b) 2 mole of HCl.

41. Suggest a mechanism for the following reaction :



42. Draw the orbital picture of 1, 2-propadiene and 1, 3-butadiene.

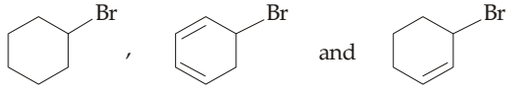
43. Is the fact that conjugated dienes are more stable and more reactive than isolated dienes is an incongruity?

44. What products are formed in the following reaction?

$$CH_2 = CH - CH = CH - CH = CH_2 + Br \longrightarrow$$

Name the type of intermediate formed in the reaction.

45. Arrange the following in the increasing order of dehydrobromination :



46. Addition of HCl to 3, 3-dimethyl-1-butyne gives a mixture 2, 2-dichloro-3, 3-dimethylbutane (44%), 1, 3-dichloro-2, 3-dimethylbutane (34%) and 2, 3-dichloro-2, 3 dimethylbutane (18%). Explain.

47. Predict the relative C–C bond lengths in CH_3CH_3, $CH_2 = CH–CH = CH_2$ and $HC \equiv C–C \equiv CH$.

48. What happens when 1-butyne is (i) ozonolysed, (ii) treated with hot $KMnO_4$.

49. Give reaction involved in the conversion of 2-butyne to

(i) *meso*-2, 3-dibromobutane

(ii) *racemic*-3-chloro-2-butanol

(iii) *meso*-2, 3-butanediol

(iv) *racemic*-2, 3-butanediol.

50. Mention the chemical methods that would distinguish between

(i) 2-pentyne and 2-pentene

(ii) 2-pentyne and 1-pentyne

(iii) 1, 3-pentadiene and 2-pentyne

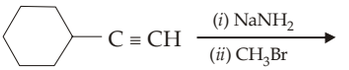
(iv) 2-hexyne and isopropyl alcohol.

51. Identify A to H in the following :

(i) $B \xleftarrow[(ii)\ CH_3COOD]{(i)\ BH_3,\ THF} RC \equiv CR \xrightarrow[(ii)\ CH_3COOH]{(i)\ BD_3,\ THF} A$

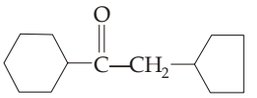
(ii) $O{=}\langle\rangle{=}O + CH_3C \equiv CH \xrightarrow{CH_3ONa} C$

(iii) $HC \equiv CH \xrightarrow[(ii)\ 2CH_3Br]{(i)\ 2NaNH_2} D \xrightarrow{Na + C_2H_5OH} E \xrightarrow{Br_2} F$

(iv) 

(v) $J \xleftarrow[(ii)\ H_2O]{(i)\ O_3} CH_3CH_2C \equiv CCOOH \xrightarrow[heat]{KMnO_4} I$

52. (a) Name the alkyne used for the synthesis of the following ketone :



(b) Name the smallest stable cycloalkyne. Why cyclohexyne is not stable?

53. An alkyne an oxidation gives two moles of CH_3COOH and one mole of glutaric acid, draw its probable structure.

54. A hydrocarbon gives red precipitate with ammonical silver nitrate and forms following compounds on ozonolysis :

(a) methanoic acid,

(b) pentanal and 4-oxopentanoic acid

Suggest the structure of the hydrocarbon.

55. (a) Name the smallest alkynes that can show geometrical/ optical isomerism.

(b) Partial reduction of alkynes is always stereospecific, comment on the statement.

(c) Which type of alkynes will give same product on oxidative hydroboration and hydration.

56. Explain the following :

(i) Although acetylene is acidic in nature, it does not react with NaOH or KOH.

(ii) The C ≡ C distance is shorter than the C = C and C–C distances.

(iii) Although the C–H bond in acetylene has the greatest bond energy of all the C–H bonds, yet it is most acidic.

(iv) The $CH_2 = CH^-$ is more basic than $HC \equiv C^-$.

(v) The C ≡ C bond although has two π bonds, it is less reactive than the C = C towards electrophilic addition reactions.

57. Draw the stereochemical structure of the product in the following reactions :

$$R - C \equiv C - R \xrightarrow{H_2,\ Lindlar\ catalyst}$$

58. Deduce the structural formula of a compound of molecular formula C_6H_{10} which (i) adds 2 moles of hydrogen to form 2-methylpentane, (ii) forms a carbonyl compound in aqueous H_2SO_4 –$HgSO_4$ solution, and (iii) does not react with ammonical $AgNO_3$ solution.

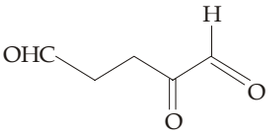
59. An unsaturated optically active compound (A) of the molecular formula C_6H_{12} absorbs a mole of hydrogen to form unresolvable compound (B). Write structures of A and B. How will you prepare (A) from its corresponding alkyl bromide?

60. An aqueous solution of potassium salt of a dibasic acid liberated a hydrocarbon at anode. The hydrocarbon took up one molecule of hydrogen to form *n*-butane. Assign structure to the salt of dicarboxylic acid.

61. A hydrocarbon of the molecular formula $C_{10}H_{16}$ absorbs three moles of hydrogen to form $C_{10}H_{22}$. On ozonolysis it yields following compounds :

(i) 

(ii) CH_2O

(iii) 

Assign structure to the hydrocarbon.

62. A 10.02 mg sample of a hydrocarbon (mol. wt. in the range of 80–85) absorbs 8.40 ml of hydrogen gas at 0°C and 760 mm pressure. Ozonolysis of the hydrocarbon gave methanal and glyoxal. Assign the probable structure to the hydrocarbon.

63. An unsaturated hydrocarbon A, having 87.2% C, takes up hydrogen and yields another hydrocarbon B with 84.1% C. Compound A on ozonolysis gives acetic acid, acetone and pyruvic acid. Assign structures to A and B.

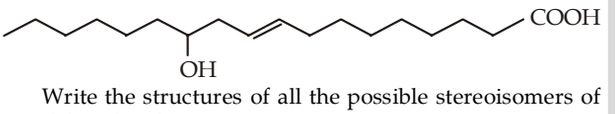
64. An organic compound A, having carbon and hydrogen, adds one mole of hydrogen in the presence of platinum as catalyst to form *n*-hexane. On vigorous oxidation with $KMnO_4$ it gives a single carboxylic acid containing three carbon atoms. Assign structure to the compound A.

65. One mole of a hydrocarbon (A) reacts with one mole of Br_2 giving a dibromo compound $C_5H_{10}Br_2$. Substance (A) on treatment with cold, dilute alkaline $KMnO_4$ solution forms a compound $C_5H_{12}O_2$. On ozonolysis, (A) gives equimolar quantities of propanone and ethanal. Deduce the structural formula of (A).

66. A hydrocarbon A (molecular formula C_5H_{10}) yields 2-methylbutane on catalytic hydrogenation. A adds HBr (in accordance with Markownikoff's rule) to form a compound B which on reaction with silver hydroxide forms an alcohol C, $C_5H_{12}O$. Alcohol C on oxidation gives a ketone D. Deduce the structures of A to D and show the reactions involved.

67. There are six different alkenes A, B, C, D, E and F. Each on addition of one mole of hydrogen gives G which is the lowest molecular weight hydrocarbon containing each one asymmetric carbon atom. None of the above alkenes gives acetone as a product on ozonolysis. Give the structures of A, B, C, D, E and F. Identify the alkene which is likely to give a ketone containing more than five carbon atoms on treatment with a warm concentrated solution of alkaline $KMnO_4$. Show various configurations of G in Fischer projection.

68. (a) Ricinoleic acid, an unsaturated fatty acid isolated from castor oil, was assigned following structure.



Write the structures of all the possible stereoisomers of ricinoleic acid.

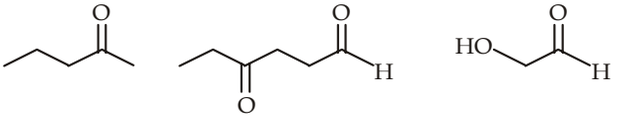
(b) Mycomycin, a naturally occurring antibiotic is found to have following structure.

$HC \equiv C - C \equiv C - CH = C = CH - (CH = CH)_2CH_2COOH$

What will be the action of plane polarized light on the solution of this compound. Explain your answer.

69. An optically active hydrocarbon A (C_6H_{10}) on catalytic hydrogenation gives optically inactive hydrocarbon B(C_6H_{14}). Propose structures to A and B.

70. The sex attractant pheromone of the codling moth of the molecular formula $C_{13}H_{24}O$ absorbs two molar equivalents of hydrogen to form 3-ethyl-7-methyl-1-decanol. On reductive ozonolysis, it forms following three products



Assign structure to the pheromone.

71. Four isomeric hydrocarbons A, B, C and D of the molecular formula C_6H_{10} show following characteristics.

(i) All the four are soluble in cold concentrated sulphuric acid and decolorize colour of bromine in carbon tetrachloride.

(ii) A reacts with ammonical silver nitrate to give red precipitate.

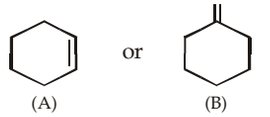
(iii) Oxidation with hot alkaline permanganate solution gives different products; A gives only pentanoic acid, B gives only propanoic acid, C gives only adipic acid; and D gives a mixture of acetic acid and oxalic acid in 2 : 1 molar ratio.

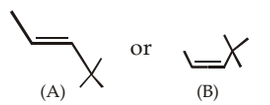
Assign structures from A to D.

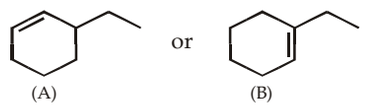
72. An optically active compound A ($C_7H_{11}Br$) reacts with hydrogen bromide, in the absence of peroxide, to form two isomeric products B and C ($C_7H_{12}Br_2$). Compound B is optically active, while C is not. Reaction of B with one mol of potassium *tert*-butoxide regenerated A, while similar reaction with C gives racemic mixture of A.

When A is treated with potassium *tert*-butoxide, a new compound D (C_7H_{10}) is formed which on reductive ozonolysis gives 2 mol of formaldehyde and 1 mol of 1,3-cyclopentanedione. Propose structures from A to D, keeping stereochemistry in mind.

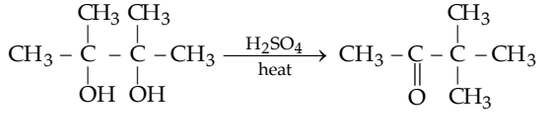
73. Which member of the following pairs is more stable than the other in each case?

(a) 
(A) (B)

(b) 
(A) (B)

(c) 
(A) (B)

74. Write down the structure(s) of the intermediate(s) formed in the following reaction, commonly known as pinacolone rearrangement.



75. (a) Draw and name all possible isomers of formula C_3H_5Cl.

(b) Cholesterol, $C_{27}H_{46}O$, has only one pi bond. What other information can be drawn regarding its structure?

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SOLUTIONS

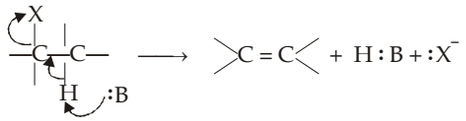
EXERCISE 6.1

1	(c)	**11**	(d)	**21**	(d)	**31**	(b)	**41**	(c)	**51**	(a)	**61**	(d)	**71**	(c)	**81**	(d)	**91**	(d)	**101**	(d)
2	(d)	**12**	(c)	**22**	(c)	**32**	(a)	**42**	(a)	**52**	(c)	**62**	(c)	**72**	(b)	**82**	(a)	**92**	(c)	**102**	(b)
3	(c)	**13**	(b)	**23**	(c)	**33**	(d)	**43**	(b)	**53**	(c)	**63**	(c)	**73**	(d)	**83**	(b)	**93**	(a)	**103**	(c)
4	(d)	**14**	(c)	**24**	(c)	**34**	(c)	**44**	(c)	**54**	(c)	**64**	(c)	**74**	(c)	**84**	(d)	**94**	(c)	**104**	(c)
5	(c)	**15**	(b)	**25**	(d)	**35**	(c)	**45**	(c)	**55**	(d)	**65**	(d)	**75**	(a)	**85**	(b)	**95**	(a)	**105**	(b)
6	(c)	**16**	(c)	**26**	(c)	**36**	(b)	**46**	(a)	**56**	(b)	**66**	(d)	**76**	(d)	**86**	(a)	**96**	(b)	**106**	(b)
7	(c)	**17**	(b)	**27**	(b)	**37**	(c)	**47**	(a)	**57**	(c)	**67**	(b)	**77**	(b)	**87**	(d)	**97**	(b)	**107**	(c)
8	(d)	**18**	(a)	**28**	(b)	**38**	(b)	**48**	(c)	**58**	(b)	**68**	(a)	**78**	(a)	**88**	(c)	**98**	(c)	**108**	(c)
9	(d)	**19**	(c)	**29**	(b)	**39**	(c)	**49**	(b)	**59**	(b)	**69**	(d)	**79**	(b)	**89**	(a)	**99**	(d)	**109**	(d)
10	(c)	**20**	(c)	**30**	(a)	**40**	(b)	**50**	(c)	**60**	(a)	**70**	(b)	**80**	(a)	**90**	(d)	**100**	(c)		

1. In (*i*), one doubly bonded carbon atom has two 2H's while in (*iii*) one doubly bonded carbon atom has two C_2H_5's.

2. Amylene (C_5H_{10}) can exist in five structural isomeric forms among which one can show *cis-trans* isomerism.

$CH_3CH_2CH_2CH = CH_2$ $CH_3CH_2CH = CHCH_3$ (*cis-trans*) $(CH_3)_2CH—CH = CH_2$ $CH_3CH_2\overset{\displaystyle CH_3}{\overset{|}{C}} = CH_2$ $CH_3CH = C(CH_3)_2$

3. 

4. The first two compounds will give a mixture of two alkenes, while the third will exclusively form 2-methyl-1-butene.

5. (*i*) $CH_3—\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}—CH_3 \xrightarrow{H^+,\ heat} CH_3—\overset{\displaystyle CH_3}{\overset{|}{C}} = CH_2$

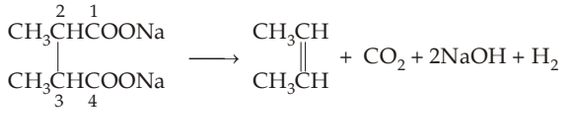
(*ii*) $CH_3—\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}—CH_3 \xrightarrow{Hcl} CH_3—\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle Cl}{\underset{|}{C}}}}—CH_3 \xrightarrow[KOH]{alc.} CH_3—\overset{\displaystyle CH_3}{\overset{|}{C}} = CH_2$

(*iii*) $CH_3—\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}—CH_3 \xrightarrow{TsCl} CH_3—\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OTs}{\underset{|}{C}}}}—CH_3 \xrightarrow{tert\text{-}BuOK} CH_3—\overset{\displaystyle CH_3}{\overset{|}{C}} = CH_2 + TsOH$

6. $CH_3—\overset{\displaystyle CH_3}{\overset{|}{C}}H—CH_2Cl \xrightarrow{(-HCl)} CH_3—\overset{\displaystyle CH_3}{\overset{|}{C}} = CH_2 \xleftarrow{(-HBr)} CH_3—\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C}}}}—CH_3$

Isobutyl chloride — 2-Methylpropene (Isobutene) — *tert*-Butyl bromide

7. The order of reactivity of alcohols towards dehydration is 3° > 2° > 1°. Hence for dehydration of primary alcohols more concentrated H_2SO_4 and high temperature must be used.

8. 

9. In *trans*-isomer polarity developed by one —CH_3 group is cancelled by polarity of the order —CH_3 group placed in opposite direction while the *cis*-isomer is polar although weak causing high boiling point than the *trans*-isomer.

10. Melting point of the *trans*-isomer is higher than that of *cis*-isomer due to molecular symmetry in the former case.

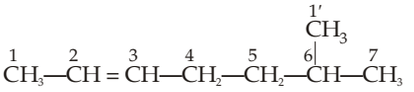
11. First calculate the value of isotopic effect (K^H/K^D) per hydrogen atom from the chlorination of $C_6H_5CH_2D$.

$$\frac{K^H}{K^D} = \frac{\text{Moles of HCl formed/No. of available H atoms}}{\text{Moles of DCl formed/No. of available D atoms}} = \frac{0.0868/2}{0.0212/1} = 2.05$$

Similarly, for $C_6H_5CHD_2$

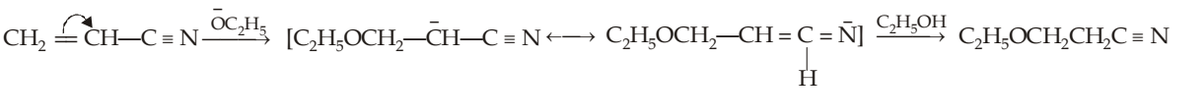
$$\frac{K^H}{K^D} = \frac{\text{Moles of HCl formed/No. of H atoms}}{\text{Moles of DCl formed/No. of available D atoms}}$$

$$2.05 = \frac{\text{Moles of HCl}}{\text{Moles of DCl}} \times \frac{2}{1} \text{ or } \frac{\text{Moles of HCl}}{\text{Moles of DCl}} = \frac{2.05}{2}$$

12. 

(i) C^1 is 1° allylic ; (ii) C^2 and C^3 are vinylic ; (iii) C^4 is 2° allylic ; (iv) C^5 is 2° ; (v) C^6 is 3° ; (vi) $C^{1'}$ and C^7 are 1°.
The order of reactivity of these H's is 2° allylic > 1° allylic > 3° > 2° > 1° > vinylic

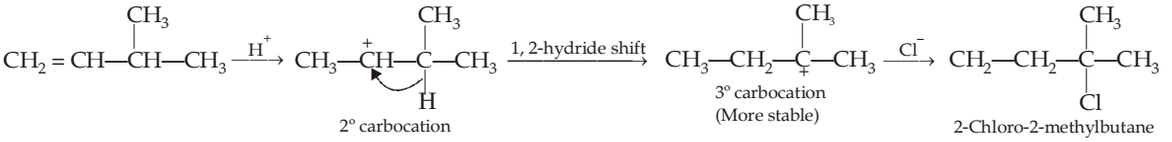
13. Alkenes having strong electron-withdrawing group on one of the doubly bonded carbon atom undergo polarization in such a manner that the β-carbon becomes electron deficient and thus becomes the site for an electron rich reagent (nucleophile).



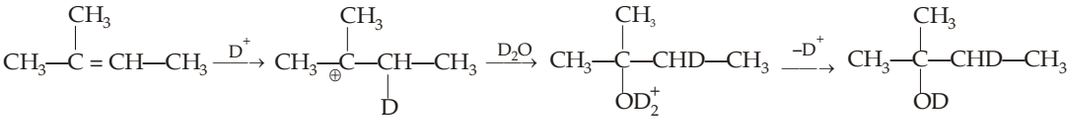
14. Addition of bromine to alkenes is both stereoselective as well as stereospecific. It is stereospecific as stereoisomeric alkenes react differently, *i.e.* they give stereochemically different products. It is stereoselective since a given isomer gives only one diastereomer (or one pair of enantiomers).

15. The relative reactivities of alkenes towards HX are directly related to the stabilities of the intermediate carbocations. Isobutene (IV) forms the most stable 3° carbocation followed by butene-1 (II) which forms 2° carbocation. Ethylene (I) and vinyl chloride (III), both form 1° carbocation, but the carbocation from vinyl chloride will be less stable because electron-withdrawing halogen intensifies the positive charge and thus destabilizes the carbocation. Hence vinyl chloride will be less reactive than ethylene.

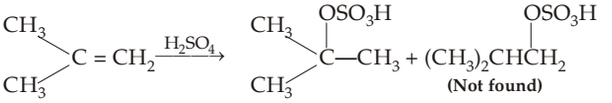
16. In presence of light addition of HBr takes place through free radical mechanism where addition of bromine atom (bromine radical, Br·) is the first step.

17. 

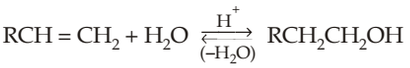
18. In aqueous solution, HBr reacts with water to form H_3O^+, a weaker acid. Dry HBr is a stronger acid than H_3O^+, former can better transfer H^+ to an alkene. Further, H_2O is a nucleophile and can react with R^+ to give an alcohol.

19. 

20. Addition of H_2SO_4 to alkenes takes place according to Markownikoff's rule, so isobutanol $(CH_3)_2CHCH_2OH$, can't be prepared by this method ; isobutene will be forming *tert*-butanol.



21. Hydration of alkenes to form alcohols and dehydration of alcohols to form alkenes are reversible.

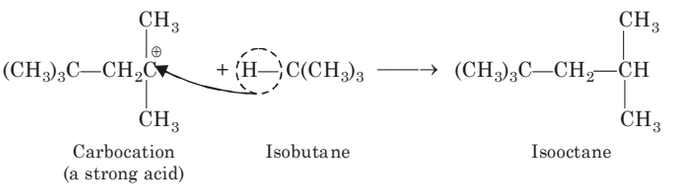


Low H_2O concentration and high temperature favour alkene formation because the volatile alkene distills out of the reaction mixture and shifts the equilibrium toward alkene. On the other hand, hydration of alkenes occurs at low temperature and with dil. acid which provides a high concentration of H_2O as reactant.

22. First step involves addition of H^+ (from acid) forming ethyl hydrogen sulphate as the final product. Ethyl hydrogen sulphate, being 1°, undergoes S_N2 mechanism.

23. Addition of hypochlorous acid $(\overset{\delta-}{HO}—\overset{\delta+}{Cl})$ to alkenes is an electrophilic addition, so Cl^+ will be adding at the first (rate determining) step to the π bond.

24. Reaction of an alkene in presence of acid forms a carbocation. Carbocation is a strong acid and hence can abstract *tert*-hydride ion from isobutane to form isooctane



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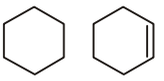
25. $CH_3CH = CH_2 \xrightarrow{Hg(OAc)_2^+} CH_3—CH(Hg)—CH_2(OAc)(AcO) \xrightarrow{CH_3OH} [CH_3—CH(HOCH_3)—CH_2(Hg)(AcO)(OAc)] \xrightarrow{-H^+} CH_3—CH(OCH_3)—CH_2HgOAc \xrightarrow{NaBH_4}$

$CH_3—CH(OCH_3)—CH_3 + Hg + AcOH$

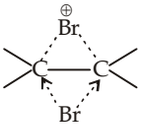
This method of formation of ethers is preferred to Williamson synthesis where elimination reaction competes substitution reaction, provided appropriate alkene is readily available.

26. Due to the formation of more stable 2° free radical $CH_3\dot{C}HCH_2Br$, the final product will be *n*-propyl bromide, $CH_3CH_2CH_2Br$. Due to the presence of electron repelling methyl group, the transition state will be more stable than that of the $CH_2 = CH_2$, hence addition of HBr on propene will be faster.

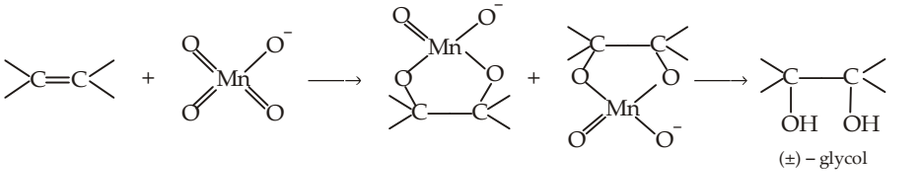
27. In cyclohexane either of the 12H atoms can be brominated, while in cyclohexene, only 4H atoms at the allylic position can be brominated. However, cyclohexene is brominated faster than cyclohexane because in the former an allyl radical is formed.



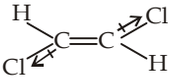
28. A cyclic bridged ion **(bromonium ion)** is formed as an intermediate. In this way configuration of the parent alkene is retained in the intermediate. In the second step, the nucleophile attacks the side opposite the bridging group to yield the *anti* addition product.



29. Note that here the electrophile is MnO_4^- which has more than one electrophilic oxygen atoms. Thus here both the carbon atoms are linked separately to two oxygen atoms and thus the configuration of the intermediate will be the configuration of the product, *i.e.* the addition takes place in *syn*-manner although a cyclic intermediate is formed.



30. The hydroboration-oxidation process gives products corresponding to *anti*-Markownikoff's addition of water. Remember that carbocations are not intermediates in these reactions, hence rearrangement does not occur in hydroboration.



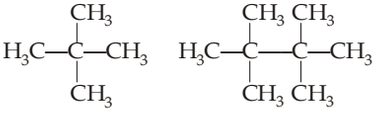
31. *cis*-3-Hexene and *trans*-3-hexene will form same product on hydrogenation.

32. Baeyer's reagent is dilute (nearly 1%) alkaline $KMnO_4$ solution.

33. Only in isobutene, $Me_2C = CH_2$, the two doubly bonded carbon atoms are different in terms of number of hydrogen atoms attached.

34. *trans*-1, 2-Dichloroethylene is symmetrically substituted, dipole moment due to one C—Cl bond is cancelled by equal but opposite dipole moment due to other C—Cl bond.

35. 2, 2-Dimethylpropane and 2, 2, 3, 3-tetramethylbutane are symmetrical molecules



36. More the number of double bonds in an alkene, higher will be the heat of hydrogenation. Among molecules having one double bond, more substituted, *viz*-2-butene will be more stable (Saytzeff rule). Further, among isomeric alkenes *trans*-isomer is more stable because bulky groups are far apart from each other and thus its heat of hydrogenation will be less than the *cis*-isomer.

37. In but-2-ene ($CH_3CH = CHCH_3$), both of the doubly bonded carbon atoms are similar.

38. The intermediate carbocation is more stable, because positive charge is in conjugation with the benzene nucleus, due to possibility of resonance.

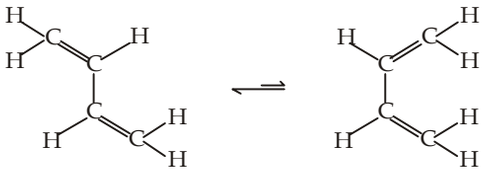
39. Heat of hydrogenation is a measure of stability, more stable an alkene, less is its heat of hydrogenation and vice-versa. Stability of alkadiene follows the order.

Conjugated diene	>	Isolated diene	>	Cumulative diene
(1, 3-pentadiene)		(1, 4-pentadiene)		(2, 3-pentadiene)

Thus the order of heat of hydrogenation is

Cumulative diene > Isolated diene > Conjugated diene.

40. Due to rotation about C_2—C_3 single bond, two conformations of 1, 3-butadiene are possible, namely *s-trans* (transoid) and *s-cis* (*cisoid*), the symbol *s*-refers to the fact that the isomerism is with respect to single bond.

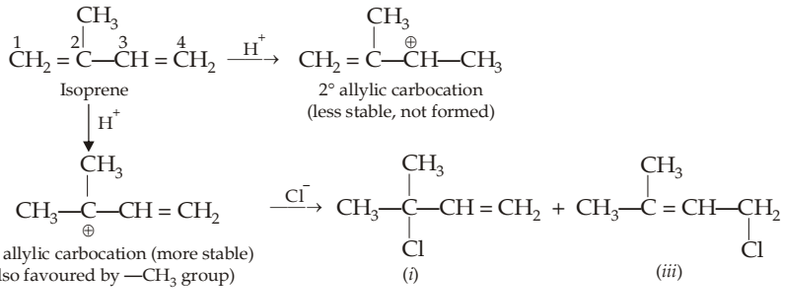


s-trans (More stable) *s-cis* (Less stable)

However, it should be noted that the energy barrier for conversion of *s-trans* to *s-cis* form is quite low (5 kCal/mole).

41. Structure (I) is non-polar and has more (11) bonds than the polar structures (II) and (III), each having 10 bonds. Thus structure (I) should contribute more. Since the contributing structures are not equivalent, the resonance energy of 1, 3-butadiene is small.

42. H^+ adds to C^1 to form a more stable allylic 3° carbocation rather than to C^2 or C^3 to form a nonallylic 1° carbocation ($\overset{+}{C}H_2—CH(CH_3)CH = CH_2$ and $H_2C = C(CH_3)CH_2—\overset{+}{C}H_2$, respectively) or to C^4 to yield to a 2° allylic carbocation.



Isoprene — 2° allylic carbocation (less stable, not formed)

3° allylic carbocation (more stable) (also favoured by —CH_3 group) → (*i*) + (*iii*)

43. Intermediate in the reduction of isolated double bond would give a high-energy dianions having localized charge on two adjacent carbon atoms, a highly unstable feature

$$RHC = CHR \xrightarrow{2e^-} R\overset{\ominus}{C}H = \overset{\ominus}{C}HR$$

On the other hand, reduction of one of the double bonds of butadiene would give a resonance stabilized allylic carbanion, a highly stable intemediate.

$$H_2C = CH—CH = CH_2 \xrightarrow{2e^-} H_2\bar{C}—\bar{C}H—CH = CH_2 \longleftrightarrow H_2\bar{C}—CH = CH—\bar{C}H_2$$

allylic carbanion

44. Addition of HI on C^1 and C^2

$\overset{1}{C}H_2 = \overset{2}{C}H—\overset{3}{C}H = \overset{4}{C}H—\overset{5}{C}H_3 \xrightarrow{HI} CH_3—CHI—CH = CH—CH_3$ (1, 2-adduct)

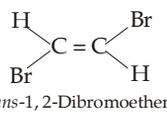
Addition of HI on C^1 and C^4

$\overset{5}{C}H_3—\overset{4}{C}H = \overset{3}{C}H—\overset{2}{C}H = \overset{1}{C}H_2 \longrightarrow CH_3—CHI—CH = CH—CH_3$

45. Hot $KMnO_4/NaIO_4$ are strong oxidising agents which will give CO_2 and COOH–COOH.

46. Due to – I effect of Br, the terminal carbon, atom bearing Br group becomes more acidic, hence one equivalent of alcoholic KOH reacts with its hydrogen rapidly while removal of less acidic hydrogen becomes difficult.

47. $HC \equiv CH + Br_2$ water $\longrightarrow$



trans-1, 2-Dibromoethene

Addition of second molecule of Br_2 is prevented partly by the low concentration of Br_2 in the form of bromine water and partly by the fact that the – I effect of bromine groups decreases the nucleophilic reactivity of the double bond.

48. Additon of Br_2 on the triple bond can be restricted by using excess of alkyne and by using bromine water rather than bromine itself.

49. Acetylene is a weaker acid than water.

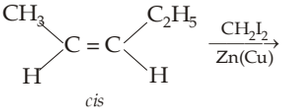
50. $CH_3CH_2C \equiv CH + H_2O \xrightarrow[Hg^{2+}]{H_2SO_4} \underset{\text{2-Butanone}}{CH_3CH_2\overset{\overset{O}{\|}}{C}CH_3} \longleftarrow CH_3C \equiv CCH_3$

51. An isolated double bond is more reactive than an isolated triple bond. However, in case of $HC \equiv CCH = CH_2$, addition of HBr will preferentially take place on triple bond as it leads to formation of conjugated diene.

52. Catalytic hydrogenation of alkynes gives *cis-alkene* which in turn adds deuterium atoms in presence of H_2 again in *cis*-manner forming *meso*-2, 3-dideuterobutane.

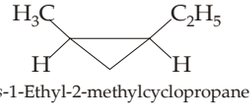
53. Alkynes add hydrogen in *cis*-manner ; the *cis*-alkene adds bromine in *anti* manner forming racemic product.

54. $CH_3C \equiv CC_2H_5 \xrightarrow{H_2/\text{Cat}}$



cis

$\xrightarrow[Zn(Cu)]{CH_2I_2}$



cis-1-Ethyl-2-methylcyclopropane

55. Terminal alkynes, (having $\equiv CH$ *e.g.* 1-butyne), react with ammonical Cu_2Cl_2 giving red precipitate.

56. $CH_3C \equiv CCH_3$, being linear and having symmetrical structure, has lowest dipole moment.

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57. $\overset{sp^2}{H_2C} = \overset{sp}{C} = \overset{sp^2}{CH_2}$ Propadiene $\overset{sp^2}{CH_2} = \overset{sp^2}{CH}—\overset{sp^2}{CH} = \overset{sp^2}{CH_2}$ Butadiene

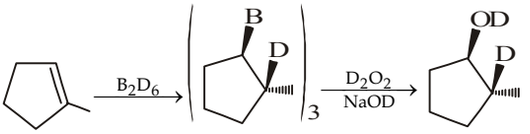
58. $CH_2 = CH—C \equiv CH$ No. of σ bonds = 7 ; No. of π bonds = 3

59. $CH_3C \equiv CH \xrightarrow{HBr} CH_3C(Br) = CH_2 \xrightarrow{HBr} CH_3CBr_2CH_3$

60. $CH_3CH_2C \equiv CH \xrightarrow{H_2SO_4/Hg^{2+}} CH_3CH_2COCH_3$.

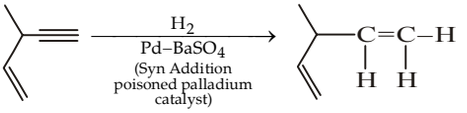
69. The oxidation level in compounds having same number of carbon atoms can be calculated as below :
Oxidation level = (sum of number of C – O, C – N and C – X bonds – sum of C – H bonds)
In I oxidation level = 0 – 12 = –12; In II, oxidation level = 0 – 6 = –6
In III oxidation level = 1 – 9 = –8;
In IV, oxidation level = 2 – 10 = –8
Thus oxidation level is : I < IV = III < II

81. (d)

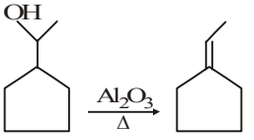


Syn addition

82. (a)

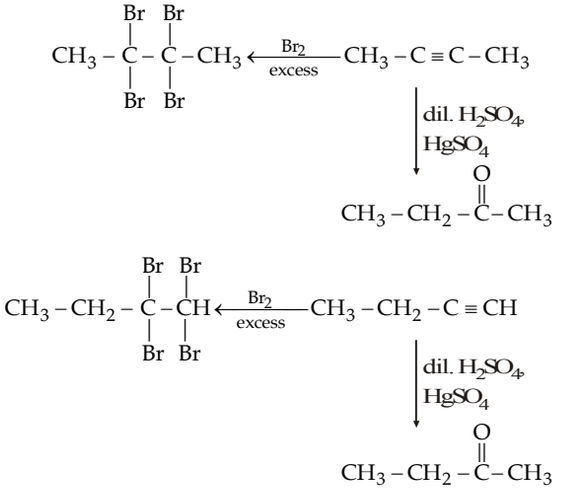


83. (b)

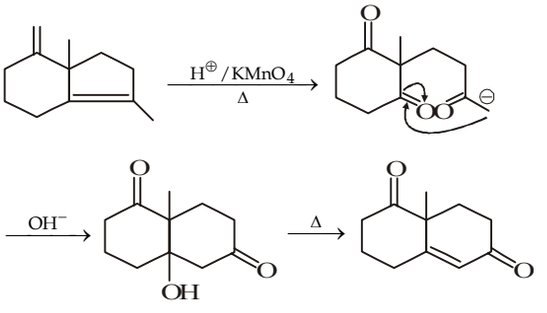


E2 (Bimolecular elimination without rearrangement)

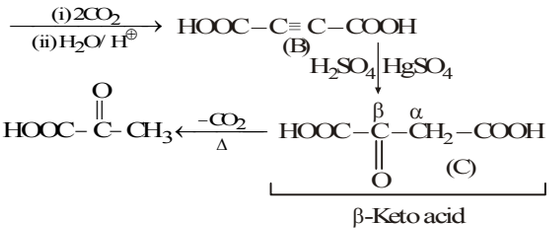
84. (d) $C_4H_6 \longrightarrow C_4H_8O$



85. (b)



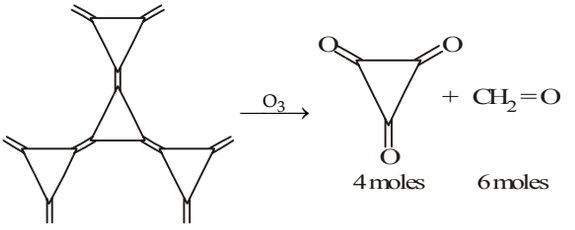
86. (a $HC \equiv CH \xrightarrow[-2CH_4]{2CH_3MgBr} BrMg - C \equiv C - MgBr$



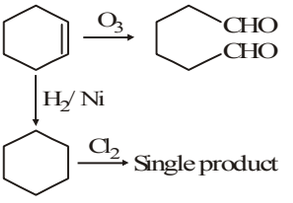
β-Keto acid

87. (d) Rate of electrophilic addition ∝ Nucleophilicity of alkene ∝ stability of carbocation, so order IV > I > II > III.

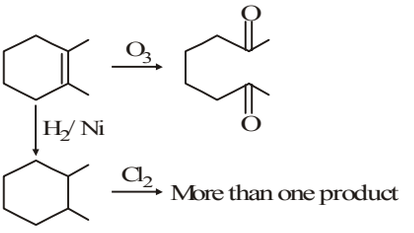
88. (c)



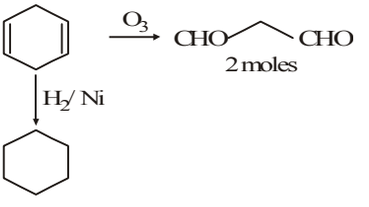
89. (a)



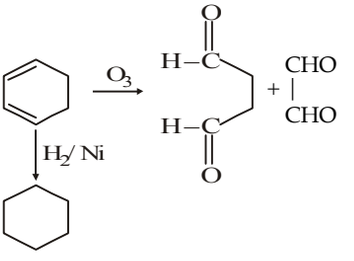
(b)



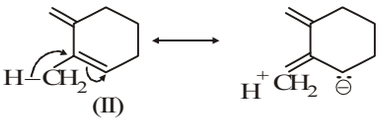
(c)



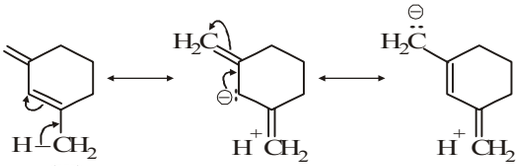
(d)



90. (d) Stability ∝ Resonance
∝ Hyperconjugation
Length of conjugation is equal in all I, II, III and IV.
But hyperconjugation is IV > III = II > I and hyperconjugation in structure III is more and hence more stable than II.

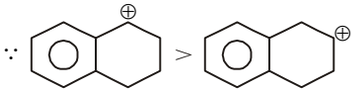


(II)



(III)

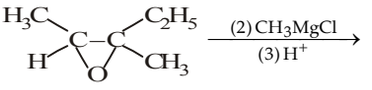
91. (d) Rate of acid catalysed hydration of alkenes $\propto$ Stability of carbocation produced

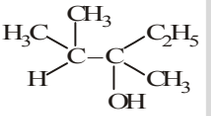


$> \overset{\oplus}{C}H_2-CH_3 > CH_3-\overset{\oplus}{C}=CH_2$ (stability)

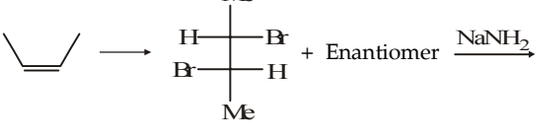
$\therefore$ correct answer is III > IV > II > I.

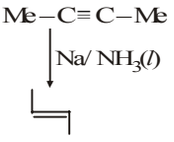
92. (c)



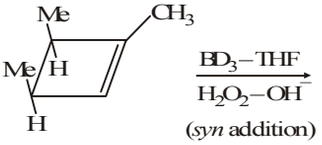


93. (a)

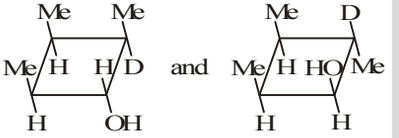




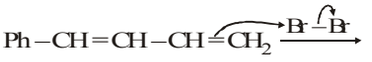
94. (c)

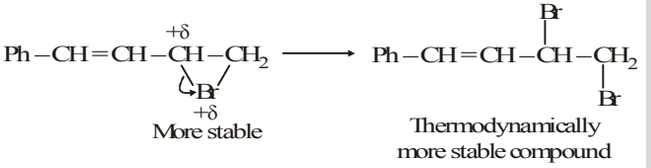


(*syn* addition)



97. (b)

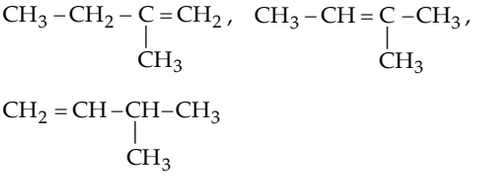




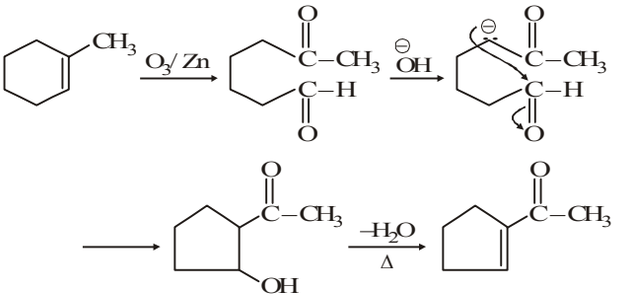
100. (c) It is Wittig reaction

101. (d) $CH_3-CH_2-CH_2-CH=CH_2$,

$CH_3-CH_2-CH=CH-CH_3$,



102. (b)



103. (c) $CH\equiv C-H+N\bar{H}_2 \longrightarrow CH\equiv C^- + NH_3$

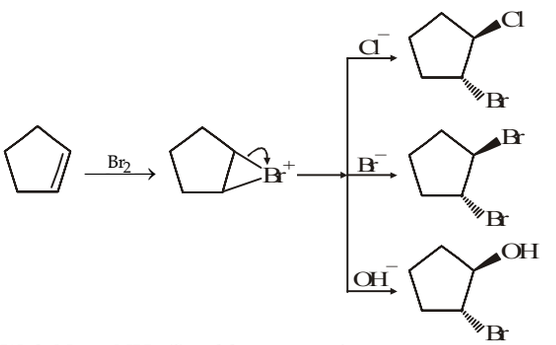
$CH\equiv C-H+CH_3^- \longrightarrow CH\equiv C^- + CH_4$

$CH\equiv CH + Na \text{ in liq. } NH_3 \longrightarrow CH_2=CH_2$

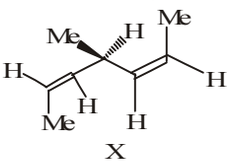
104. (b) Diels-Alder reaction is highly stereospecific and it is *syn* addition where the configuration of dienophile is retained.

106. (b) Alkynes are less reactive due to unstable intermediate formed.

107. (c) It is a case of *anti*-addition in which cyclic bromonium ion is formed.



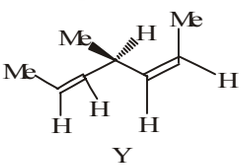
108. (c) With Na in NH_3 (*l*), addition is *anti*.



Optically inactive

X

But with Pd-$BaSO_4$ – quinoline, hydrogen addition is *cis* and the product is



Optically active

Y

109. (d) Only (d) can form 3-Octyne

$CH_3CH_2C\equiv CH \xrightarrow[-NH_3]{NaNH_2} CH_3CH_2C\equiv C^-Na^+$

$\xrightarrow[(S_N2)]{CH_3CH_2CH_2CH_2Br}$

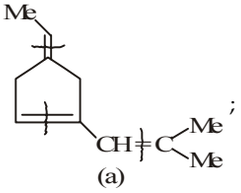
$CH_3CH_2C\equiv CCH_2CH_2CH_2CH_3 + NaBr$

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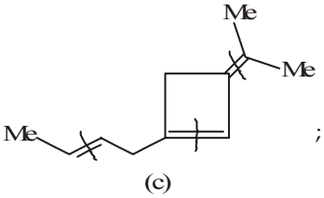
EXERCISE 6.2

MCQ > 1 CORRECT OPTION	1	(b,c)	2	(b,c)	3	(b,c)	4	(c, d)	5	(c, d)
	6	(a, b)	7	(b, d)	8	(a, c)	9	(a, c)	10	(a, b, c, d)
	11	(b, c, d)	12	(a, b)	13	(a, b)	14	(a, b)	15	(b, c, d)
	16	(a, b, c)	17	(a, c)	18	(a, b)	19	(a, c)	20	(a,b,d)
	21	(a, c, d)	22	(b, d)	23	(c)	24	(a,b,c,d)		
PASSAGE 1	25	(a)	26	(c)	27	(a)	28	(c)	29	(a,c)
	30	(b,c)	31	(b,c)						
PASSAGE 2	32	(a,c)	33	(c)	34	(b,d)	35	(a)		
PASSAGE 3	36	(c)	37	(b)	38	(c,d)	39	(a)	40	(a)
	41	(b)	42	(a,b,d)	43	(b)				
PASSAGE 4	44	(b,c,d)	45	(a)	46	(b,d)	47	(d)		
PASSAGE 5	48	(d)	49	(b)	50	(a)				
PASSAGE 6	51	(a)	52	(b)	53	(b)				
PASSAGE 7	54	(c)	55	(b)	56	(a)				
PASSAGE 8	57	(a)	58	(d)	59	(c)				
PASSAGE 9	60	(d)	61	(a)	62	(c)	63	(a)		
PASSAGE 10	64	(c)	65	(b)	66	(a)				
PASSAGE 11	67	(d)	68	(c)	69	(c)				
PASSAGE 12	70	(b)	71	(b)	72	(a)				
PASSAGE 13	73	(a)	74	(c)	75	(b)				
MATCH THE FOLLOWING	76	(A) – d; (B) – c; (C) – a,b; (D) – a,b								
	77	(A)-a, c ; (B)-b, d ; (C)-a, b ; (D)-a, d								
	78	(A)-d ; (B)-c ; (C)-b ; (D)-a								
	79	(A)-a, d, e ; (B)-d ; (C)-a, c ; (D)-a, b								
	80	(A)-b, c, e; (B)-a, c; (C)-b, c, e; (D)-c, d								
A/R	81	(a)	82	(a)	83	(a)	84	(a)	85	(c)
	86	(d)	87	(c)	88	(a)	89	(a)	90	(b)
	91	(d)								
INTEGER	92	4	93	1	94	5	95	6	96	3
	97	6	98	3	99	3	100	5		

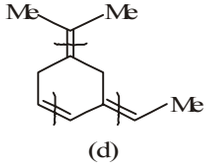
21. (a, c, d)



(a) ;

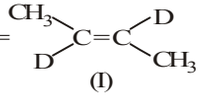


(c) ;

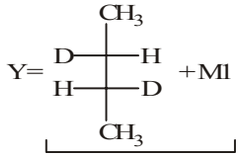


(d)

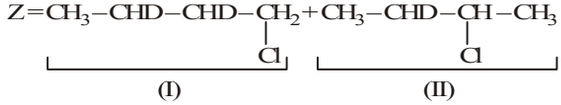
22. (b, d)



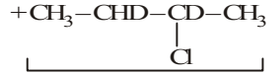
(I)



Total = 2

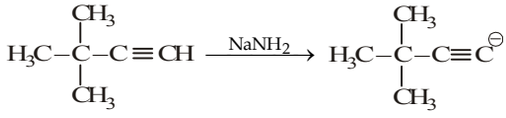


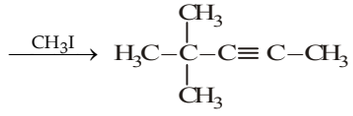
(I) (II)



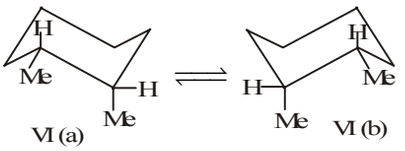
(III)

23. (c)

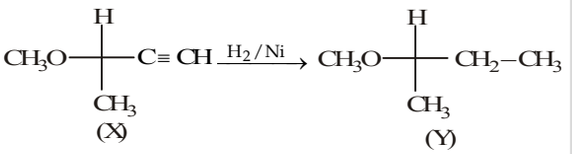


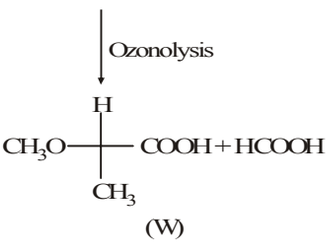


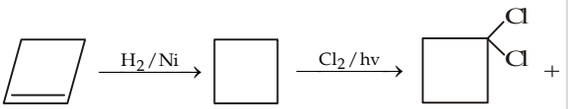
24. (a, b, c, d) (I) and (II) represent *cis* and *trans*-1, 4-dimethylcyclohexane and both posses a plane of symmetry.
(III) represents *cis*-1, 3-dimethylcyclohexane and it also possesses a plane of symmetry.
(IV) represents *trans*-1, 3-dimethylcyclohexane and do not possess a plane of symmetry.
(V) represents *trans*-1, 2-dimethylcyclohexane and has no plane of symmetry.
(VI) represents *cis*-1, 2-dimethylcyclohexane.

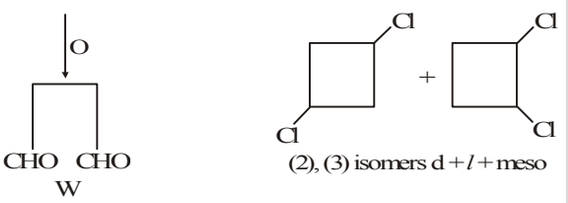


Each structure [VI (a) and VI (b)] is chiral molecule, but they are interconvertible by a ring flip. Therefore although, the two structures represent enantiomers, they cannot be separated because they are interconvertible readily. So these simply represent different conformations of the same compound. So, VI (a) and VI (b) are not configurational stereoisomers, they are conformational stereoisomers. This means that at normal temperature, there are only three isolable stereoisomers of 1, 2-dimethylcyclohexane.

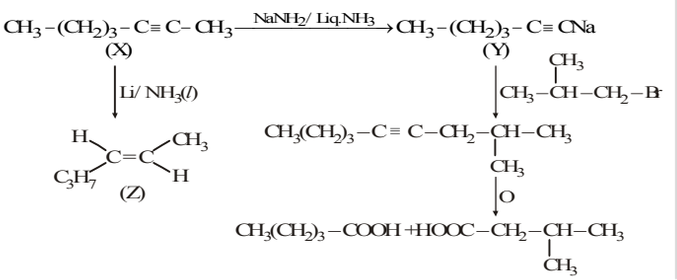
64. (c) 



67. (d) 

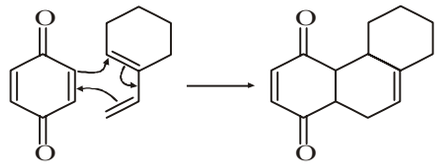


Sol. 70-72

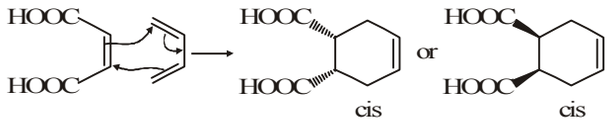


70. (b) **71.** (b) **72.** (a)

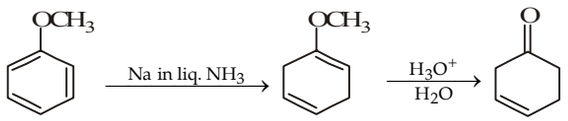
73. (a) The rate is accelerated when diene is attached with electron releasing and dienophile with electron withdrawing but here in second case it is reserved. So, x > y.

74. (c) 

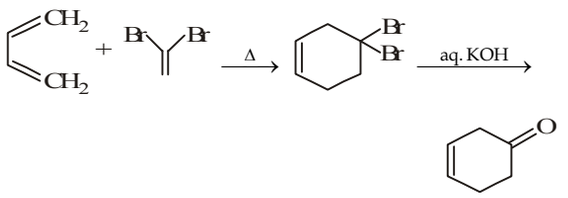
75. (b) Diels-Alder's reaction is stereospecific because it takes place through concerted process.

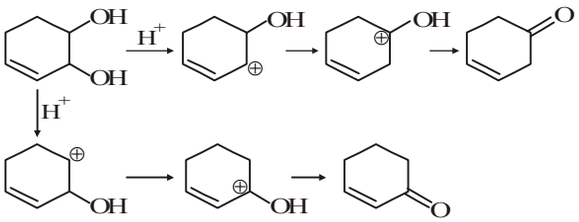


79. A - (p, s, t); B - (s); C - (p, r); D - (p, q)

(A) 

(B) Birch reduction

(C) 

(D) 

80. A - (q, r, t); B - (p, r); C - (q, r, t); D - (r, s)

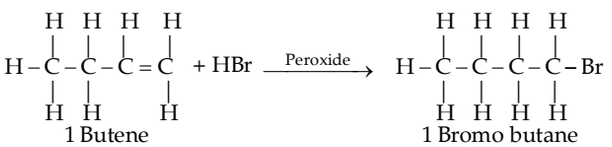
(A) *trans*-alkene (symmetrical + syn-hydroxylation) → Racemic mix. of 1, 2-diol, having two chiral carbon.

(B) *trans*-alkene (symmetrical) $\xrightarrow[\text{anti hydroxylation}]{}$ meso-compound

(C) *trans*-alkene (symmetrical) $\xrightarrow[\text{syn addition}]{}$ Racemic mixture

(D) Bromohydrin formation having two chiral centres and so mixture of products are diastereomers.

84. This reaction is followed by anti Markonikoff rule

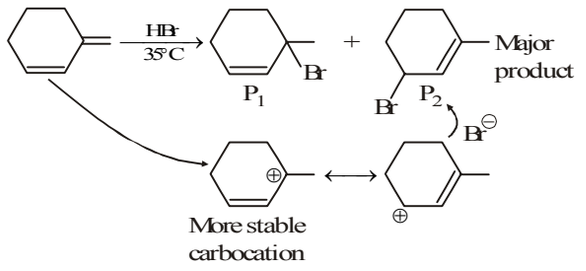


In this reaction anti Markonikoff's addition is explained on the basis of the fact that is in the presence of peroxide the addition takes place via a free radical mechanism.

85. The statement 1 that *trans*-2 butene reacts with Br_2 to produce *meso*-2, 3-dibromobutane is correct but it does not involve *syn*-addition of Br_2.

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86. (d)



87. (c) $CH_3-CH=CH-CH_3+HBr \xrightarrow[\text{free radical mechanism}]{\text{Peroxide}}$

$CH_3-\underset{\underset{Br}{|}}{CH}-CH_2-CH_3$ (±)

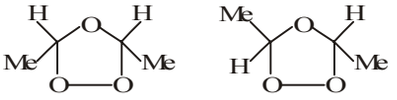
$CH_3-CH=CH-CH_3+HCl \xrightarrow[\text{Ionic mechanism}]{\text{Peroxide}}$

$CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2-CH_3$ (±)

88. (a) Alcoholic KOH causes E2 with CH_3-CH_2-Br whereas aqueous KOH cause S_N2.

89. (a) There is no necessary co-relation between the (R) and (S) designation and the direction of rotation of plane polarised light. Hence R-1-chloro-2-methylbutane may rotate the plane clockwise or anticlockwise.

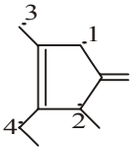
90. (b)



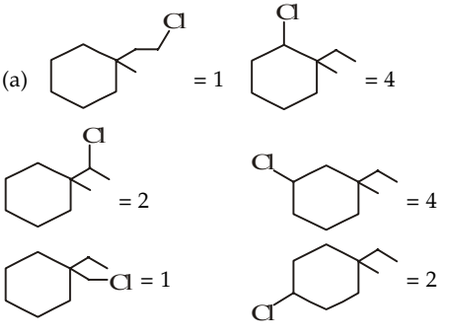
(I) (II) and its enantiomer

91. (d) Peroxide effect is observed only with HBr not with HCl and HI.

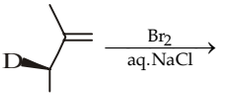
92. **4**



93. **1** (a)



(b)

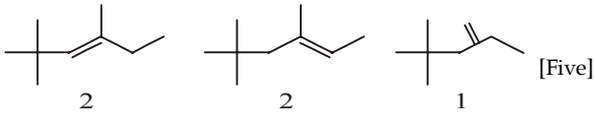




Diastereomeric pair Diastereomeric pair Diastereomeric pair

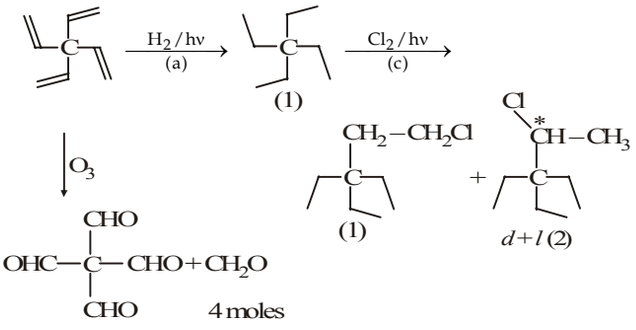
Boiling points of diastereomers are different.
Now (A) = 14 (B) = 6
Then, (A + B) = 14 + 6 = 20

94. **5**



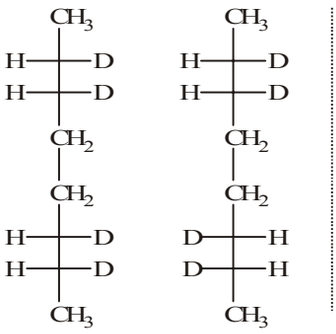
2 2 1 [Five]

95. **6**



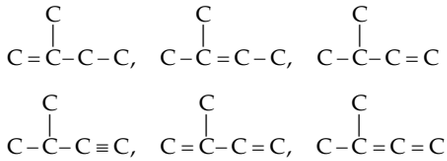
a = 1; b = 2; c = 3 Sum =1 2 3 = 6

96. **3**



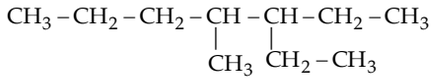
Mirror image

97. **6**

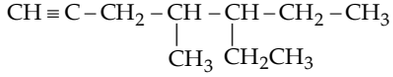


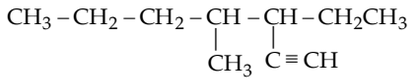
98. **03**

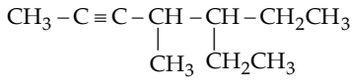
99. **3**



3-Ethyl-4-methylheptane



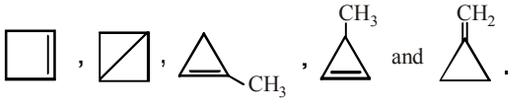




100. **5.**

The number of cyclic isomers for a hydrocarbon with molecular formula C_4H_6 is **5**.

The structures are



EXERCISE 6.3

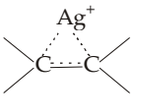
1. As the bromine molecule comes near π electron cloud of alkene, the unshared pair of electrons on the bromine atom near the double bond is repelled because of *electron-electron repulsion* making this end of bromine molecule partially positive and the other end partially negative.

2. Removal of hydrogen takes place from the carbon carrying the fewer hydrogens. (*i.e.* poor becomes poorer).

3. The relative reactivity depends on the ability of HX to donate an H^+ (*i.e.* acidity) to form R^+ in the rate-controlling first step. The acidity and reactivity order is HI > HBr > HCl.

4. Ag^+ coordinates with the alkene by p–$d\pi$ bonding to give an ion similar to a bromonium ion, but more soluble.

5. *t*-BuO^- in dimethylsulphoxide is not solvated via hydrogen bonding and hence it is a much stronger base than the highly solvated OH^- in alcohol.



6. (*a*) $(CH_3)_2C = CHCH_3 + ICl \longrightarrow (CH_3)_2C(Cl)CH(I)CH_3$

Since Cl is more electronegative than I ; in $\overset{\delta+}{I} - \overset{\delta-}{Cl}$, I will add to the carbon that has more hydrogens.

(*b*) $(CH_3)_2C = CH_2 + HSCH_3 \longrightarrow (CH_3)_2C(SCH_3)CH_3$

Here H is less electronegative than S $\left(\overset{\delta+}{H}—\overset{\delta-}{S}CH_3\right)$, thus it will add on the carbon atom having more hydrogen atoms.

(*c*) $CH_2 = CHCF_3 + HCl \longrightarrow CH_2Cl\,.\,CH_2\,.\,CF_3$

Note that the addition is *anti*-Markownikoff. This is due to the presence of strong electron-attracting, CF_3 group which destabilizes positive charge present on adjacent carbon in $CH_3\overset{+}{C}HCF_3$, hence $^+CH_2CH_2CF_3$ (a 1° carbocation) is the intermediate rather than $CH_3\overset{+}{C}HCF_3$ (a 2° carbocation).

(*d*) $Me_3\overset{+}{N}CH = CH_2 + HI \longrightarrow Me_3\overset{+}{N}CH_2CH_2I$

Here *anti*-Markovnikov's addition is due to the presence of positive charge on N which destabilizes the carbocation having positive charge on an adjacent carbon. [Thus a more stable carbocation, $Me_3\overset{+}{N}CH_2\overset{+}{C}H_2$ will be formed than $Me_3\overset{+}{N}\overset{+}{C}HCH_3$.]

7. (*a*) Here the reagent added seems to be HI, thus alkene should be $(CH_3)_2C = CH_2$

$$(CH_3)_2C = CH_2 + HI \longrightarrow (CH_3)_3CI$$

(*b*) Here the reagent added seems to be HBr and thus alkene is $CH_2 = CHBr$

$$CH_2 = CHBr + HBr \longrightarrow CH_3CHBr_2$$

(*c*) Here the reagent added may be BrCl and thus the alkene will be $CH_2 = CHCH_3$

$$CH_2 = CHCH_3 + \overset{\delta+}{Br}\overset{\delta-}{Cl} \longrightarrow CH_2BrCHClCH_3$$

Alternatively, the reagent added may be HBr and thus the alkene will be $CH_2 = CClCH_3$.

$$CH_2BrCHClCH_3 \xleftarrow[\text{anti-Mark.}]{\text{peroxide}} CH_2 = CClCH_3 + HBr \xrightarrow[\text{addition}]{\text{Mark.}} CH_3C(Cl)(Br)CH_3$$

Alternatively, the reagent added may be HCl and thus the alkene will be $CH_2BrCH = CH_2$

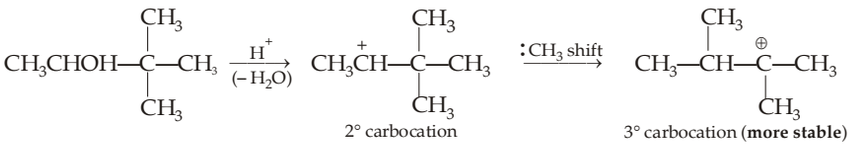
$$CH_2BrCH = CH_2 + HCl \longrightarrow CH_2Br\,.\,CHCl\,.\,CH_3$$

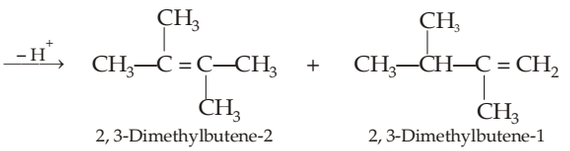
However, this possibility is discarded because in this case, the intermediate carbocation will be $Br\overset{\delta+}{C}H_2\overset{+}{C}HCH_3$ which is less stable than $Br\overset{\delta+}{C}H_2CH_2\overset{+}{C}H_2$ and thus here the reaction will lead to the formation of $BrCH_2CH_2Cl$ rather than $CH_2Br.CHCl.CH_3$.

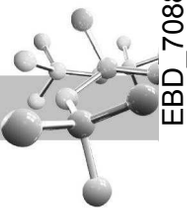
(*d*) Here the reagent may be HOCl and thus the alkene is $BrCH_2CH = CH_2$. Alternatively, the reagent may be HOBr and thus the alkene will be $CH_2 = CHCH_2Cl$.

$$BrCH_2CH = CH_2 + HOCl \longrightarrow CH_2Br\,.\,CHOH\,.\,CH_2Cl$$
$$CH_2 = CHCH_2Cl + HOBr \longrightarrow CH_2Br\,.\,CHOH\,.\,CH_2Cl$$

8. (*a*)







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(*b*) $H_2C=CH_2 \xrightarrow{HF} H_3C-\overset{\oplus}{C}H_2 \xrightarrow{(CH_3)_3CH} CH_3CH_3 + (CH_3)_3\overset{+}{C}$

$CH_2=CH_2 + \overset{+}{C}(CH_3)_3 \longrightarrow \overset{+}{C}H_2-\underset{\text{1° carbocation}}{\underset{|}{\overset{H}{CH}}}-C(CH_3)_3 \xrightarrow{:H\ shift} CH_3-\underset{\text{2° carbocation}}{\overset{+}{C}H-\underset{CH_3}{\overset{CH_3}{C}}-CH_3} \xrightarrow{:CH_3\ shift}$

$CH_3-\underset{\text{3° carbocation}}{\overset{CH_3}{\underset{|}{CH}}-\overset{+}{\underset{Ch_3}{\underset{|}{C}}}-CH_3} \xrightarrow{(CH_3)_3CH} CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{CH}}}-\underset{CH_3}{\underset{|}{CH}}-CH_3 + (CH_3)_3\overset{+}{C}$

(*c*) $CH_2=CH-\underset{CH_3}{\overset{CH_3}{\underset{|}{C}}}-CH_3 \xrightarrow{H^+} \left[CH_3\overset{\oplus}{C}H-\underset{CH_3}{\overset{CH_3}{\underset{|}{C}}}-CH_3 \underset{\text{2° carbocation}}{\overset{:CH_3\ shift}{\longleftrightarrow}} CH_3CH-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{\oplus}{C}}}}-CH_3\ \text{3°carbocation}\right] \xrightarrow{Cl^-}$

$CH_3-\underset{\text{3-Chloro-2, 2-dimethylbutane}}{\underset{|}{\overset{Cl}{CH}}-C(CH_3)_3} + \underset{\text{2-Chloro-2, 3-dimethylbutane}}{(CH_3)_2\underset{|}{\overset{Cl}{CH}}-C(CH_3)_2}$

(*d*) $CH_3-\underset{|}{\overset{CH_3}{CH}}-\underset{|}{\overset{OTs}{CH}}-CH_2CH_3 \xrightarrow{-Ots} CH_3-\underset{\text{2° carbocation}}{\underset{|}{\overset{CH_3}{CH}}-\overset{\oplus}{CH}-CH_2CH_3} \xrightarrow[:H\ shift]{rearranges} CH_3-\underset{\text{3° carbocation}}{\underset{|}{\overset{CH_3}{C}}-\overset{\oplus}{}-CH_2-CH_2CH_3}$

$\xrightarrow{-H^\oplus}$ $CH_3-\underset{\text{4-Methyl-2-pentene, I (Disubstituted alkene)}}{\underset{|}{\overset{CH_3}{CH}}-CH=CHCH_3}$; $\xrightarrow{-H^\oplus}$ $CH_3-\underset{\text{2-Methyl-2-pentene, II (Trisubstituted alkene)}}{\overset{CH_3}{\underset{|}{C}}=CHCH_2CH_3}$; $\underset{\text{2-Methyl-1-pentene, III (Disubstituted alkene)}}{CH_2=\overset{CH_3}{\underset{|}{C}}-CH_2-CH_2CH_3}$

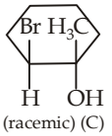
The relative amount formed is in the order II > I > III

(*e*) $^{14}CH_3CH=CH_2 + Br^\cdot \longrightarrow [^{14}\dot{C}H_2CH=CH_2 \longleftrightarrow {}^{14}CH_2=CH\dot{C}H_2] \xrightarrow{Br_2} Br\,{}^{14}CH_2CH=CH_2 + {}^{14}CH_2=CHCH_2Br$

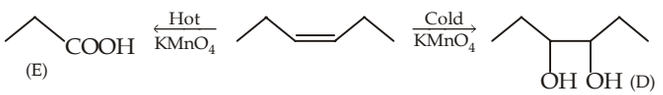
9. (*i*) **The 3° alcohol is formed by acid-catalysed hydration (by dil. aq. H_2SO_4) of alkene A.**

$CH_3-\underset{|}{\overset{CH_3}{CH}}-CH=\overset{CH_3}{\underset{|}{C}}-CH_3$ (A) or $CH_3-\underset{|}{\overset{CH_3}{CH}}-CH_2-\overset{CH_3}{\underset{|}{C}}=CH_2$ (B) + dil. Aq $H_2SO_4 \longrightarrow CH_3-\underset{|}{\overset{CH_3}{CH}}-CH_2-\underset{OH}{\overset{CH_3}{\underset{|}{C}}}-CH_3$

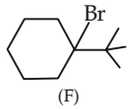
(*ii*) Addition of HOBr takes place by Markownikoff rule, *i.e.* the positive Br adds to the carbon having more hydrogen. Further, addition is *anti*, hence Br will be *trans* to OH but *cis* to CH_3.



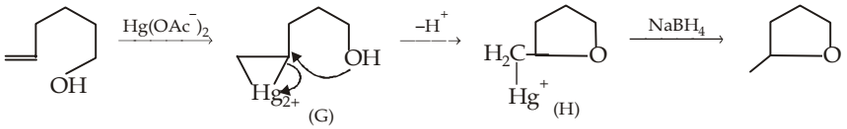
(racemic) (C)

(*iii*) 

(E) (D)

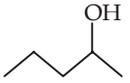
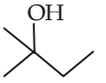
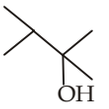
(*iv*) 

(F)

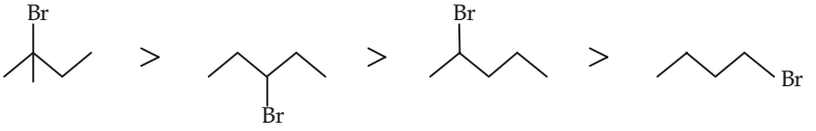
(*v*) 

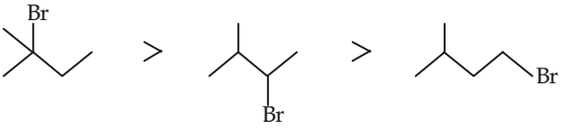
(G) (H)

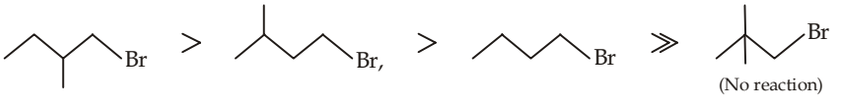
10. The order of dehydration of alcohols is 3° > 2° > 1°.

(*a*)  (*b*)  (*c*) 

11. Reactivity of alkyl halide towards dehydrohalogenation depends upon the stability of the alkene formed (more substituted is an alkene, more will be its stability).

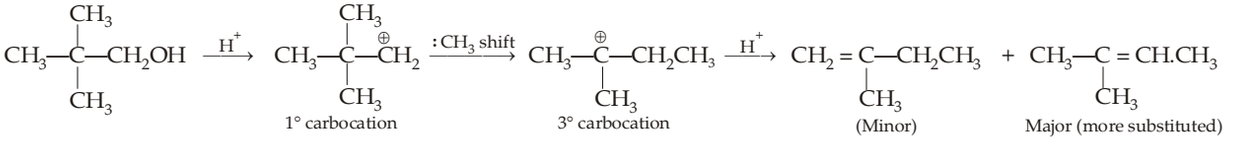
(*a*) 

(*b*) 

(*c*) 

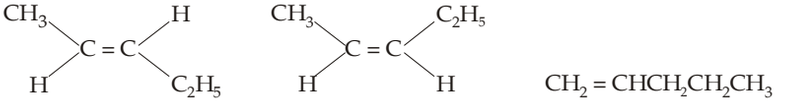
(No reaction)

12. Although neopentyl alcohol has no α—H atom, yet it easily undergoes dehydration because 1° carbocation formed rearranges to the more stable 3° carbocation which has α—H atom(s), hence undergoes dehydration.



1° carbocation — 3° carbocation — (Minor) — Major (more substituted)

13. Yes, heat of combustion of an alkene provides a direct measure of the stability of an alkene. More stable an alkene is, less will be its energy content and thus heat of combustion. Now we know that more highly branched alkene is more stable (Saytzeff rule), further among *cis*, *trans*-isomers, latter is more stable because of less crowding and less vander Waals strain. Thus the value of heat of combustion corresponds with the three alkenes as below :



trans-2-Pentene (804.3 kcal) — *cis*-2-Pentene (805.3 kcal) — Pentene-1 (806.9 kcal)

14. $CH_3CH=CH-CH=CHCH_3 \xrightarrow{E^+} CH_3\overset{+}{C}H-CH-CH=CHCH_3 + CH_3-CH-\overset{+}{C}H-CH=CHCH_3$ (E on the first carbon; E on the second carbon)

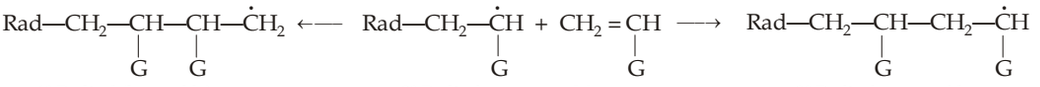
(More stable allylic type)

15. Yes. $CH_3CH_2CH_2CH_2OH \xrightarrow{H^+} CH_3CH_2CH=CH_2 \xrightarrow[(dil.\ H_2SO_4)]{H_2O} CH_3CH_2\underset{OH}{C}HCH_3 \xrightarrow{H^+} CH_3CH=CHCH_3$

Butanol-1 — 2-Butene

16. No reaction will take place : (*a*) dichloroethylene in deactivated towards electrophilic addition due to presence of four chlorine atoms, (*b*) free radicals are not formed in dark and thus free radical addition reaction does not occur.

17. Head-to-tail arrangement of the monomer units is due to the fact that 2° radicals are formed faster in every step rather than a 1° radical. For example,



1° Radical (less stable) (leading tail-to-tail arrangement) — 2° Radical — Monomer — 2° Radical more stable (leading to head-to-tail arrangement)

18. Addition of H_2SO_4 on alkenes is an electrophilic addition reaction. Reactivity of alkenes towards addition of acids is governed by the following facts.

(*i*) Alkene capable of forming 3° carbocation will be more reactive than that which forms 2° carbocation which in turn will be more reactive than that which forms 1°carbocation.

(*ii*) An electron-withdrawing group intensifies the positive charge on the carbocation and will thus destabilise it. Hence its presence will slow down the formation of carbocation and will thus decrease the reactivity of alkenes towards electrophilic additions. On the other hand, presence of electron-pushing group will facilitate electrophilic additions. Therefore,

(*a*) $CH_3CH=CH_2$ > $CH_2=CH_2$

Propylene (2° carbocation) — Ethylene (1° carbocation)

(*b*) $CH_3CH=CHCH_3$ > $CH_3CH=CH_2$

2-Butene (two + I groups) — Propylene (one + I group)

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(*c*) $(CH_3)_2C=CH_2$ > $CH_3CH=CHCH_3$

Isobutene (3° carbocation) — 2-Butene (2° carbocation)

(*d*) $CH_2=C(CH_3)CH_2CH_3$ > $CH_2=CHCH_2CH_2CH_3$

2-Methyl-1-butene (3° carbocation) — 1-Pentene (2° carbocation)

(*e*) $CH_2=CH_2$ > $CH_2=CHCl$

Ethylene — Vinyl chloride (– I group)

(*f*) $CH_2=CHCl$ > $CHCl=CHCl$

Vinyl chloride (one –I group) — 1, 2-Dichloroethylene (two – I groups)

(*g*) $CH_2=CH_2$ > $CH_2=CHCOOH$

Ethylene — Acrylic acid (– I group)

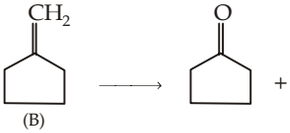
(*h*) $CH_3CH=CH_2$ > $F_3CCH=CH_2$

Propylene (+ I group) — 3, 3, 3-Trifluoropropene (– I group)

19. $CH_3CH=CHCH_3 \xrightarrow{H^+} CH_3\overset{+}{C}HCH_2CH_3 \xrightarrow{Cl^-} CH_3CH(Cl)CH_2CH_3$

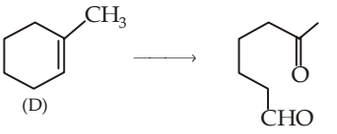
$CH_3CH(C_2H_5OH)CH_2CH_3 \xrightarrow{-H^+} CH_3CH(OC_2H_5)CH_2CH_3$ ($C_6H_{14}O$)

20. $CH_3CH_2CH=CHCH_2CH_3 \xrightarrow{\text{ozonolysis}} 2CH_3CH_2CHO$; (A)


(B)

$+ CH_2O$

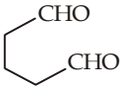
$(CH_3)_2C=C(CH_3)-CH=C(CH_3)_2 \longrightarrow 2(CH_3)_2CO + CH_3COCHO$; (C)


(D)

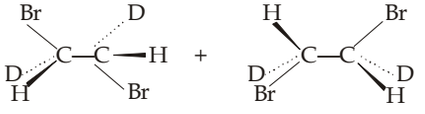
$\equiv CH_3COCH_2CH_2CH_2CH_2CHO$

$CH_3CH=CHCH_2CH=CH_2 \longrightarrow CH_3CHO + OHCCH_2CHO + CH_2O$; (E)

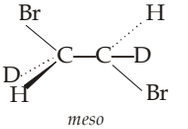

(F)



21. (*a*)


racemic mixture

(*b*)


meso

22. $C_6H_5CH=CH-CH=CH_2 + Br_2 \longrightarrow C_6H_5CH(Br)-CH(Br)-CH=CH_2$ (A) + $C_6H_5CH(Br)-CH=CH-CH_2Br$ (B) + $C_6H_5CH=CH-CH(Br)-CH_2Br$ (C) (Most stable)

23. Reaction of chlorine in dark, at low temperature and in absence of peroxides should be ionic. This reaction involves electrophilic addition followed by E_1 elimination.

$CH_3-C(CH_3)=CH_2 + Cl_2 \longrightarrow CH_3-C^{\oplus}(CH_3)-CH_2Cl \xrightarrow{-H^+} CH_2=C(CH_3)-CH_2Cl$

3° carbocation (Open carbocation is shown only for simplicity) — Methallyl chloride

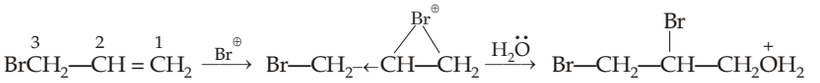
Note that here the second step is elimination rather than addition. It is due to high stability of 3° carbocation which is less reactive towards Cl^-, and more prone to lose one of six hydrogens to form the branched alkene.

24. Let us take the case of propene

$\overset{3}{C}H_3\overset{2}{C}H=\overset{1}{C}H_2 \xrightarrow{Br^{\ominus}} CH_3-\overset{\oplus}{C}H-CH_2 \xrightarrow{:OH_2} CH_3CH(\overset{\oplus}{O}H_2)-CH_2Br$

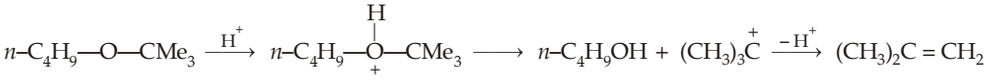
Note the possibility of the dispersal of positive charge on C_2 due to presence of electron-pushing $-CH_3$ group on the adjacent carbon atom.

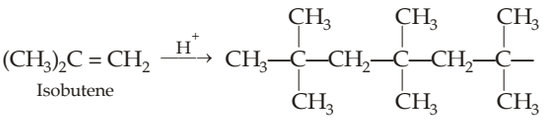
Now let us take the case of allyl bromide



Note that here positive charge on C_2 will be intensified due to the presence of electron-withdrawing —CH_2Br group on the adjacent carbon atom and hence the corresponding intermediate will be less stable. Thus positive charge is more likely to be developed on C_1 and the product formed will be $BrCH_2CHBr\,.\,CH_2OH$.

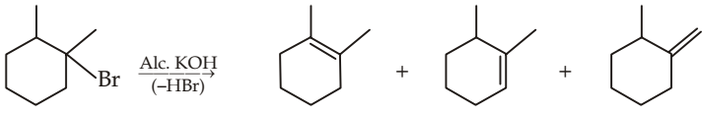
25. *n*-Butyl-*tert*-butyl ether dissolves in cold conc. H_2SO_4 due to the formation of oxonium salt. However, on standing it decomposes to form isobutene which undergoes polymerisation in presence of acid forming polyisobutene.





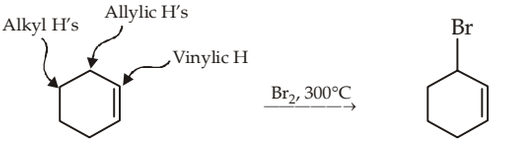
Isobutene — Polyisobutene

26. (*i*)

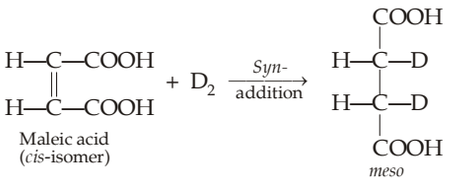


Major (More substituted) — (Minor) — (Minor)

(*ii*) Reaction of Br_2 with cyclohexene at 300°C proceeds through free radical bromination. However, cyclohexene has three types of hydrogen atoms (allylic, alkyl a vinylic type), whose order of reactivity is allylic > alkyl > vinylic. Thus allylic bromination will be the main reaction.

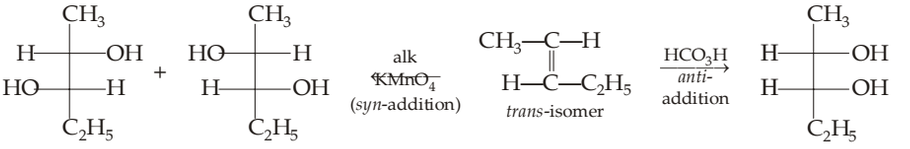


(*iii*)



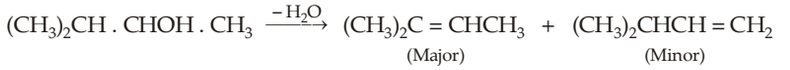
Maleic acid (*cis*-isomer) — *meso*

(*iv*) Hydroxylation by alk. $KMnO_4$ and HCO_3H takes place in *syn* and *anti* manner respectively. Thus



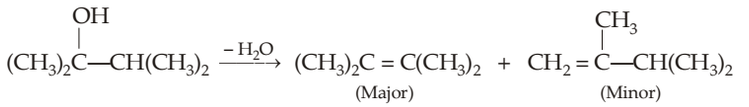
(B) racemic mixture — (*syn*-addition) — *trans*-isomer — (A) *meso*

27. (*i*)



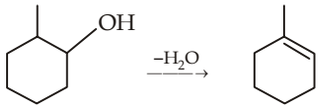
(Major) — (Minor)

(*ii*)



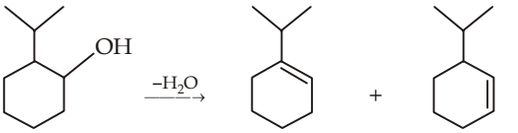
(Major) — (Minor)

(*iii*)



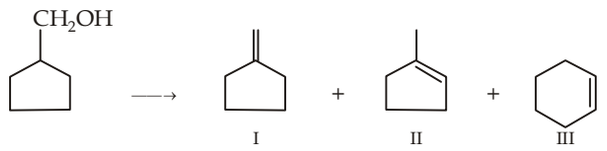
(Major)

; (*iv*)

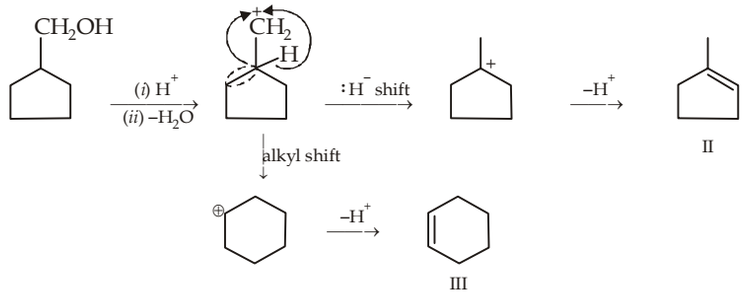


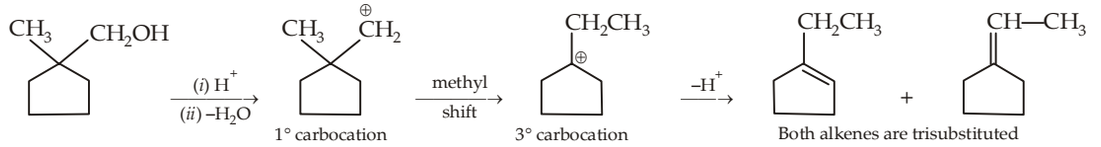
(Major)

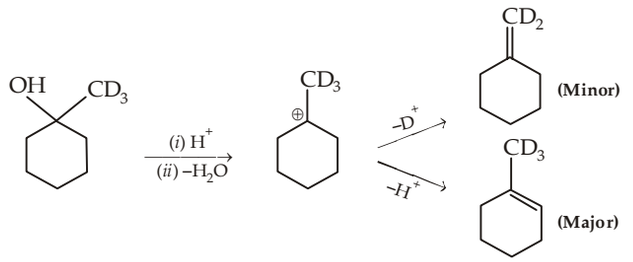
EBD_7088

(*v*) 

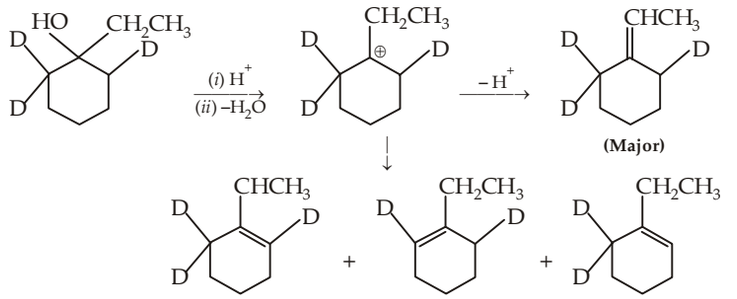
Formation of II and III



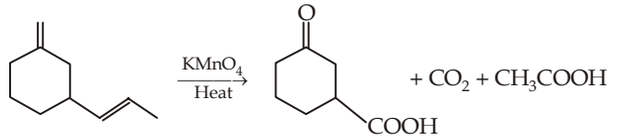
(*vi*) 

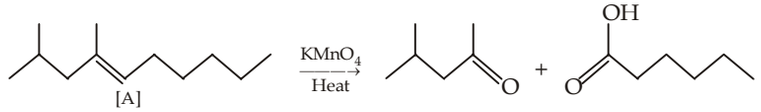
(*vii*) 

Remember that the C—H cleavage is nearly seven times faster than the C—D cleavage, hence product corresponding to elimination of H^+ will predominate than that which involves elimination of D^+.

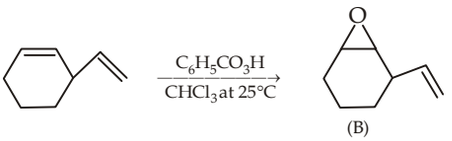
(*viii*) 

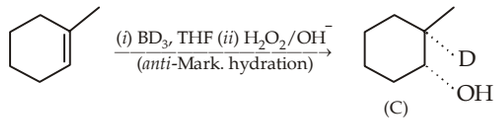
28. Hot $KMnO_4$ oxidises $=CH_2$ to CO_2

(*i*) 

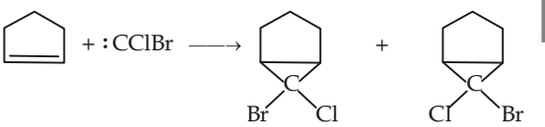
(*ii*) 

(*iii*) The more substituted double bond is more nucleophilic and hence it will react faster with peroxy acids than the less substituted double bond.

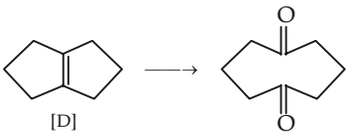


(*iv*) 

(C)

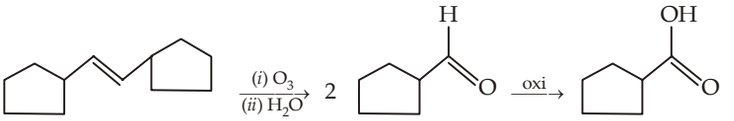
(*v*) 

(*vi*) Join the two carbon atoms of the >CO group.

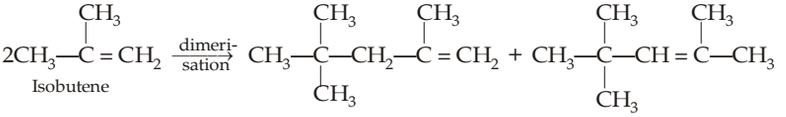


[D]

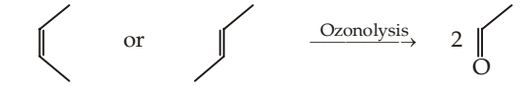
(*vii*) Ozonolysis is done in absence of zinc dust, hence the aldehyde formed will be oxidised to acids.



(E)
1, 2-Dicyclopentyl ethylene

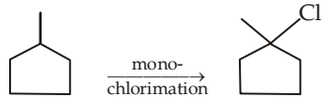
29. (*a*) 

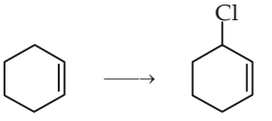
Isobutene

(*b*) 

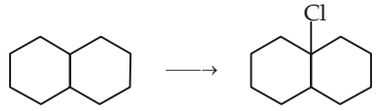
cis-2-Butane *trans*-2-Butene Ethanal

30. We know that lesser is the heat of combustion of a compound, more will be its stability. Thus the more stable isomer in the various pairs will have less heat of combustion.
(*i*) *trans*-2-Butene (*ii*) *trans*-2-hexene (*iii*) 2, 5-Dimethylhexane.

31. (*i*) 

(Abstraction of 3° H) (*ii*) 

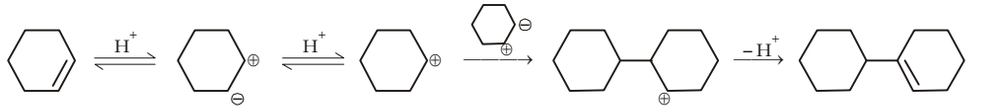
(Abstraction of allylic H)

(*iii*) 

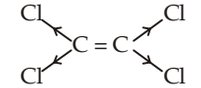
(Abstraction of 3° H)

(*iv*) 

(Abstraction of 3° H)

32. 

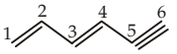
33. Presence of four chlorine atoms decreases considerably the electron density of the two olefinic carbon atoms ; hence weak electrophile (Cl_2) can add only when it can produce Cl^+ ion easily which happens in presence of $AlCl_3$.



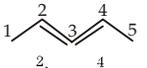
$$AlCl_3 + Cl_2 \longrightarrow AlCl_4^- + Cl^+$$

$$Cl_2C = CCl_2 + Cl^+ \longrightarrow Cl_2\overset{+}{C}—CCl_3 \xrightarrow{AlCl_4^-} Cl_3C—CCl_3$$

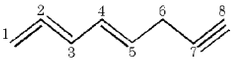
34. (*a*) (*i*) 1, 2-Propadiene (*ii*) 5-Ethyl-1, 4, 6-octatriene

(*b*) (*i*) 

C_1 to $C_4 = sp^2$; C_5 and $C_6 = sp$

(*ii*) 

C_1 and $C_5 = sp^3$; C_2 and $C_4 = sp^2$, $C_3 = sp$

(*iii*) 

C_1, C_3, C_4 and $C_5 = sp^2$, C_2, C_7 and $C_8 = sp$; $C_6 = sp^3$.

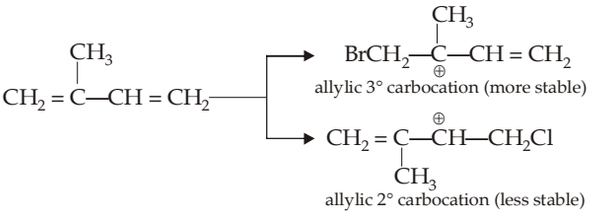
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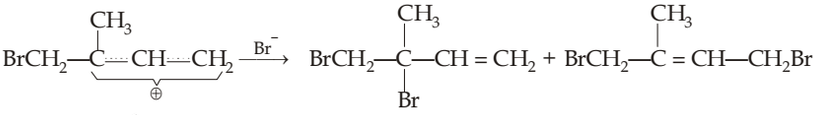
35. $CH_2=CH—CH_2—CHOH—CH_3 \xrightarrow[(-H_2O)]{H^+} CH_2=CH—CH=CH—CH_3 + CH_2=CH—CH_2—CH=CH_2$

1, 3-Pentadiene (major) 1, 4-Pentadiene (minor)

Although 1, 3-pentadiene is less substituted, it will be major product because it is a conjugated diene (possibility of resonance). 1, 4-Pentadiene is although more substituted, it is an isolated diene, hence resonance is not possible.

36.





37. (*a*) In the first step, Br^+ adds at C^1 to form a 2° allylic type of carbocation, whose positive charge can delocalize on C^2, C^4 and C^6 forming three corresponding products (I, II and III) during attack of Br^- at the second stage. However, a fourth product (IV) is also possible due to addition of Br_2 on C^3 and C^4.

$$\overset{1}{CH_2}=\overset{2}{CH}—\overset{3}{CH}=\overset{4}{CH}—\overset{5}{CH}=\overset{6}{CH_2} \xrightarrow{Br^\oplus} [BrCH_2—\overset{+}{C}H—CH=CH—CH=CH_2$$

$$\longleftrightarrow BrCH_2—CH=CH—\overset{+}{C}H—CH=CH_2 \longleftrightarrow BrCH_2—CH=CH—CH=CH—\overset{+}{C}H_2]$$

$$\xrightarrow{Br^-} \underset{Br}{\underset{|}{CH_2}}—\underset{Br}{\underset{|}{CH}}—CH=CH—CH=CH_2 + \underset{Br}{\underset{|}{CH_2}}—CH=CH—\underset{Br}{\underset{|}{CH}}—CH=CH_2$$

I II

$$+ \underset{Br}{\underset{|}{CH_2}}—CH=CH—CH=CH—\underset{Br}{\underset{|}{CH_2}} \; ; \; CH_2=\underset{Br}{\underset{|}{CH}}—\underset{Br}{\underset{|}{CH}}—CH=CH—CH=CH_2$$

III IV

(*b*) Thermodynamic-controlled conditions favour the most stable product. Among the four products, I and III are conjugated dienes and hence more stable than the isolated dienes II and III. Further, III is more stable than I because its doubly bonded carbon atoms are more substituted.

38. (*a*) $\underset{I}{CH_2=CH—CH=CH—CH=CH—\overset{+}{C}H_2} \longleftrightarrow \underset{II}{CH_2=CH—CH=CH—\overset{+}{C}H—CH=CH_2}$

$$\longleftrightarrow \underset{III}{\overset{+}{C}H_2—CH=CH—CH=CH—CH=CH_2}$$

(*b*) Thermodynamically-controlled product is the more stable product, which will be formed by the attack of Nu^- on III or I (same).

$$\underset{III}{\overset{\oplus}{C}H_2—CH=CH—CH=CH—CH=CH_2} \xrightarrow{Nu^-} \underset{Nu}{\underset{|}{CH_2}}—CH=CH—CH=CH—CH=CH_2$$

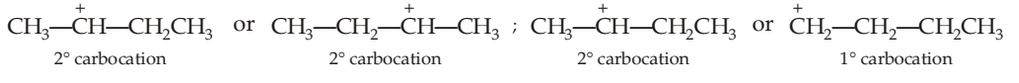
Conjugated triene

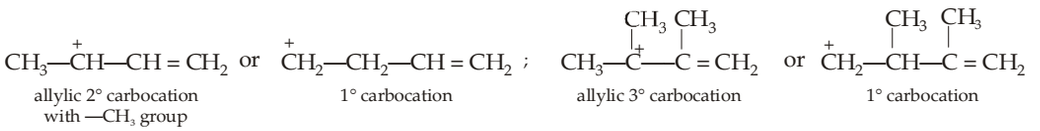
Products from canonical structure II will be a triene with 2 conjugated double bonds.

39. Reactivity of alkenes towards HBr is determined on the basis of relative stability of the intermediate carbocation. The more stable a carbocation, more easily it is formed and hence more will be the reactivity of the alkene from which it is derived.

Conjugated dienes form the more stable allyl carbonium ions and hence they are more reactive than alkenes. Further, presence of alkyl group(s) on the unsaturated carbons increases reactivity because of the formation of the more stable (3° > 2° > 1°) carbocation and/or because of charge dispersal by + I alkyl groups.

Structures of the intermediate carbocations formed by different alkenes are drawn below.





$CH_3—CH_2—\overset{+}{C}H—CH=CH_2$ or $\overset{+}{C}H_3—CH—CH_2—CH=CH_2$

allylic 2° carbocation with $—C_2H_5$ group (more + I effect) — 2° carbocation

From V

We know that order of stability of the carbocations is allylic 3° > allylic 2° with $—C_2H_5$ group > allylic 2° with $—CH_3$ group > 2° carbocation > 1° carbocation. Thus the reactivity of alkenes is

IV > V > III > I > II

40. (*a*) $CH_2=CH—CH=CH_2 \xrightarrow{HCl} CH_3.CHCl.CH=CH_2$ (1, 2-Adduct) + $CH_3.CH=CH.CH_2Cl$ (1, 4-Adduct)

(*b*) (*i*) $CH_3CHClCH=CH_2 \xrightarrow{H^+} CH_3CHCl\overset{\oplus}{C}HCH_3 \xrightarrow{Cl^-} CH_3CHClCHClCH_3$

2° carbocation

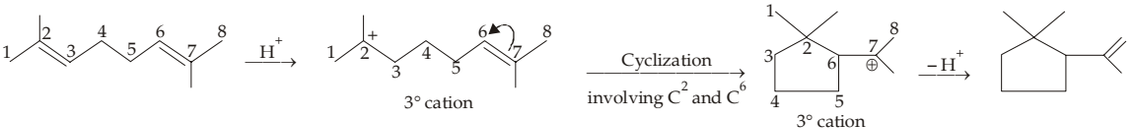
(*ii*) $CH_3CH=CHCH_2Cl \xrightarrow{H^+} CH_3—\overset{+}{C}HCH_2CH_2Cl \xrightarrow{Cl^-} CH_3CHClCH_2CH_2Cl$

2° carbocation I

$CH_3CH=CHCH_2Cl \xrightarrow{H^+} CH_3CH_2\overset{+}{C}HCH_2Cl$

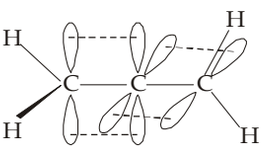
2° carbocation II (unstable)

In (*ii*) case, carbocation I is more likely to be formed because the positive charge is farther from the electron-withdrawing —Cl ; while in carbocation II the positive charge is present near to carbon having —Cl leading to *intensification* of the positive charge which leads to unstability of the carbocation.

41. 

This reaction is analogous to acid-catalysed dimerization of alkenes. Since both of the double bonds (of two alkene molecules in dimerization) are present in the same molecule, reaction leads to *cyclization.*

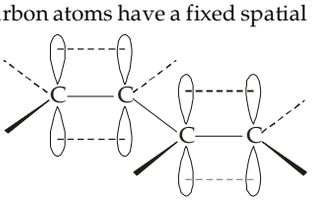
42. In the molecule of 1, 2-propadiene (allene), the central carbon atom is *sp* hybridised while the terminal carbon atoms are sp^2 hybridized. The central carbon atom forms a σ-bond with each of the terminal sp^2 hybridized carbon atom. The remaining two *p*-orbitals of the central carbon atom form two π-bonds by sideways overlapping with the *p*-orbitals of the terminal carbons.



Since the two *p* orbtials of the central carbon are directed at right angles to each other, the two MO's (or the two π bonds) will be at right angles to each other. The two hydrogens on C^1 are in a plane at right angles to the plane of the two hydrogens on C^3.

Because there is no free rotation about the two π bonds, the two hydrogens on each of the two terminal carbon atoms have a fixed spatial relationship.

Thus when the two substituents on each of the two terminal carbon atoms of allene are different as in 2, 3-pentadiene ($CH_3CH=C=CHCH_3$), the molecule lacks symmetry and will be chiral.



Molecular orbital picture of 1, 3-butadiene. Each carbon in butadiene is sp^2 hybridized and forms three sigma bonds. The terminal carbons forming two sp^2-*s* bonds with hydrogen and sp^2-sp^2 bond with carbon ; while the middle carbon atoms form two sp^2-sp^2 bonds with adjacent carbons and one sp^2-*s* bond with hydrogen. Thus each carbon atom of butadiene has one unhybridized *p* orbital, each containing one electron. Thus the four *p*-orbitals of butadiene are adjacent and parallel and overlap to form an extended π system involving all the four carbon atoms. This results in greater stability and decreased energy.

43. No. Reactivity depends on the relative values of energy of activation. Although the ground state enthalpy for the conjugated diene is lower than that of the isolated dienes, the transition-state enthalpy for conjugated system is lower by a greater amount.

E_{act} for conjugated < E_{act} for isolated and $rate_{conjugated} > rate_{isolated}$

44. $CH_2=CH—CH=CH—CH=CH_2 \xrightarrow{Br^+} \left[CH_2—\overset{\oplus}{C}H—CH=CH—CH=CH_2 \longleftrightarrow CH_2—CH=CH—\overset{\oplus}{C}H—CH=CH_2 \longleftrightarrow CH_2—CH=CH—CH=CH—\overset{\oplus}{C}H_2\right]$

(Br on the first carbon of each resonance form)

$\equiv CH_2—CH\cdots CH\cdots CH\cdots CH=CH_2 \xrightarrow{Br^-} CH_2—CH—CH=CH—CH=CH_2$

(Br on the first carbon; Br on the second carbon)

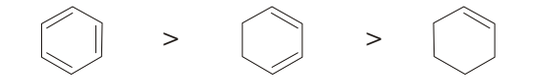
Resonance hybrid of doubly allylic cation — 5, 6-Dibromo-1, 3-hexadiene (conjugated diene)

+ $CH_2—CH=CH—CH—CH=CH_2$ (Br on the second and fifth carbons) — 3, 6-Dibromo-1, 4-hexadiene (*Not formed*, Isolated diene)

+ $CH_2—CH=CH—CH=CH—CH_2$ (Br on the first and fifth carbons) — 1, 6-Dibromo-2, 4-hexadiene (conjugated diene)

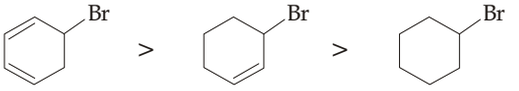
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45. Increasing order of stability of the dehydrobrominated products will be



Conjugated triene > Conjugated diene > Simple alkene

∴ Order of the dehydrobromination of the parent compounds will be



46. $(CH_3)_3C—C \equiv CH \xrightarrow{H^+} (CH_3)_3C—\overset{\oplus}{C} = CH_2 \xrightarrow{Cl^-} (CH_3)_3C—\underset{Cl}{C} = CH_2 \xrightarrow{HCl} (CH_3)_3C—\underset{Cl}{\overset{Cl}{C}}—CH_3$

3, 3-Dimethyl-1-butyne; Vinylic cation; 2, 2-Dichloro-3, 3-dimethylbutane

↓ methyl shift

$CH_3—\underset{\oplus}{C}(CH_3)—CH_2 \xrightarrow{Cl^-} CH_3—C(CH_3) = C—CH_2Cl \xrightarrow{HCl} CH_3—\underset{Cl}{C}(CH_3)—C—CH_2Cl$

Allylic cation; 1, 3-Dichloro-2, 3-dimethylbutane (The addition of HCl is controlled by the – I effect of chlorine, already present in the molecule)

↓ Cl^-

$CH_3—\underset{Cl}{C}(CH_3)—C = CH_2 \xrightarrow{HCl} CH_3—\underset{Cl}{C}(CH_3)—\underset{Cl}{C}H—CH_3$

2, 3-Dichloro-2, 3-dimethylbutane

47. Bond length becomes shorter with the increase in *s* character of the carbon involved in bond formation, thus relative C—C bond lengths should decrease in the order

$$\underset{sp^3}{H_3C}—\underset{sp^3}{CH_3} > \underset{sp^2}{H_2C} = \underset{sp^2}{CH}—\underset{sp^2}{CH} = \underset{sp^2}{CH_2} > \underset{sp}{HC} \equiv \underset{sp}{C}—\underset{sp}{C} \equiv \underset{sp}{CH}$$

48. (*i*) $CH_3CH_2C \equiv CH + O_3 \xrightarrow{H_2O} CH_3CH_2COOH + HCOOH$

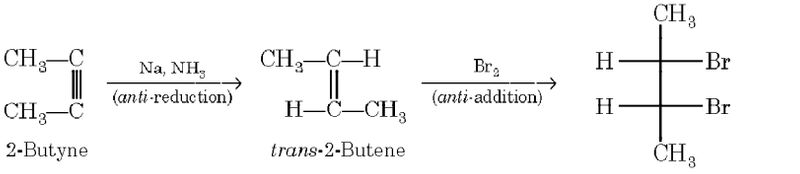
(*ii*) $CH_3CH_2C \equiv CH \xrightarrow{\text{hot } KMnO_4} CH_3CH_2COOH + CO_2$

49. (*i*) *2-Butyne to meso-2, 3-dibromobutane.* The principle reactions involved are

$$CH_3C \equiv CCH_3 \xrightarrow[\text{reduction}]{\text{Partial}} CH_3CH = CHCH_3 \xrightarrow{Br_2} CH_3CH(Br)CHBrCH_3$$

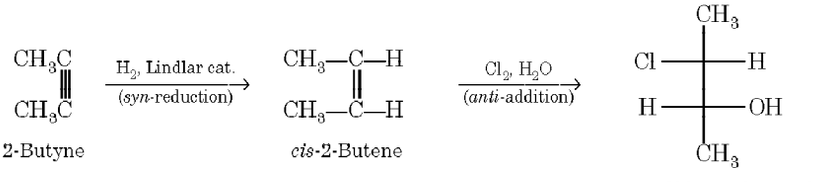
2-Butyne; 2-Butene; 2, 3-Dibromobutane

Since addition of Br_2 to alkenes is anti, for obtaining *meso*-2, 3-dibromobutane we must take *trans*-alkene which in turn can be obtained by the reduction of alkyne with sodium in liquid ammonia.



2-Butyne; *trans*-2-Butene; *meso*-2, 3-Dirbromobutane

(*ii*) *2-Butyne to racemic-3-chloro-2-butanol.* Since halohydrin formation is *anti*, for obtaining racemic product we must take *cis*-alkene which in turn is obtained by the partial reduction of alkyne with hydrogen in presence of Lindlar catalyst. Thus the necessary reactions will be



2-Butyne; *cis*-2-Butene; *rac*-3-Chloro-2-butanol

(*iii*) *2-Butyne to meso-2, 3-butanediol.* It can be achieved in two ways.

(*a*) $CH_3C{\equiv}CCH_3 \xrightarrow[(syn\text{-reduction})]{H_2/\text{Lindlar catalyst}} \underset{cis\text{-2-Butene}}{CH_3CH{=}CHCH_3} \xrightarrow[(syn\text{-Hydroxylation})]{KMnO_4} \underset{meso\text{-2, 3-Butanediol}}{\begin{matrix}CH_3\\ H\text{—}C\text{—}OH\\ H\text{—}C\text{—}OH\\ CH_3\end{matrix}}$

(*b*) $\underset{2\text{-Butyne}}{CH_3C{\equiv}CCH_3} \xrightarrow[(anti\text{-reduction})]{Na,\ NH_3} \underset{trans\text{-2-Butene}}{CH_3CH{=}CHCH_3} \xrightarrow[(anti\text{-Hydroxylation})]{HCO_3H} \underset{meso\text{-2, 3-Butanediol}}{\begin{matrix}CH_3\\ H\text{—}C\text{—}OH\\ H\text{—}C\text{—}OH\\ CH_3\end{matrix}}$

(*iv*) *2-Butyne to racemic-2, 3-butanediol.* It can also be achieved in two ways.

(*a*) $\underset{2\text{-Butyne}}{CH_3C{\equiv}CCH_3} \xrightarrow[(syn\text{-reduction})]{H_2,\ \text{Lindlar cat.}} \underset{cis\text{-2-Butene}}{CH_3CH{=}CHCH_3} \xrightarrow[anti\text{-Hydroxylation}]{HCO_3H} \underset{racemic\text{-2, 3-Butanediol}}{\begin{matrix}CH_3\\ HO\text{—}C\text{—}H\\ H\text{—}C\text{—}OH\\ CH_3\end{matrix}}$

(*b*) $\underset{2\text{-Butyne}}{CH_3C{\equiv}CCH_3} \xrightarrow[anti\text{-reduction}]{Na,\ NH_3} \underset{trans\text{-2-Butene}}{CH_3CH{=}CHCH_3} \xrightarrow[syn\text{-Hydroxylation}]{KMnO_4} \underset{racemic\text{-2, 3-Butanediol}}{\begin{matrix}CH_3\\ HO\text{—}C\text{—}H\\ H\text{—}C\text{—}OH\\ CH_3\end{matrix}}$

50. (*i*) **2-Pentyne** takes up two moles of H_2, while **2-pentene** takes only one mole to form fully saturated compound.

(*ii*) Only 1-pentyne (a terminal alkyne) gives precipitate with ammonical silver nitrate, while 2-pentyne (a non-terminal alkyne) does not do so.

(*iii*) 1, 3-Pentadiene and 2-pentyne can be distinguished by their ozonolysis followed by identification of products :

$$\underset{\text{1, 3-Pentadiene}}{H_2C{=}CH{-}CH{=}CHCH_3} \xrightarrow[(ii)\ H_2O]{(i)\ O_3} \underset{\text{Formaldehyde}}{H_2CO} + \underset{\text{Glyoxal}}{OHC{-}CHO} + \underset{\text{Ethanal}}{OHCCH_3}$$

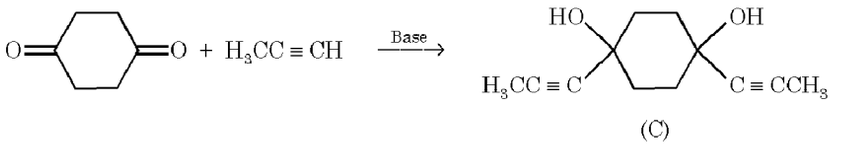
$$\underset{\text{2-Pentyne}}{CH_3C{\equiv}CCH_2CH_3} \xrightarrow[(ii)\ H_2O]{(i)\ O_3} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Propanoic acid}}{CH_3CH_2COOH}$$

(*iv*) 2-Hexyne gives positive test with Br_2—CCl_4 solution and Baeyer's test ; isopropyl alcohol is oxidised by chromic anhydride CrO_3, in aqueous sulphuric acid within two seconds (clear orange solution turns blue-green and finally becomes opaque).

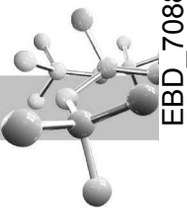
$$\underset{1^\circ \text{ or } 2^\circ}{ROH} + \underset{\text{Clear, orange}}{HCrO_4^-} \longrightarrow \underset{\text{blue green}}{\text{Opaque}}$$

51. (*i*) Remember that addition of BH_3 to alkynes takes place in *syn* manner to form *cis*-isomer (*cis*-trivinylborane) which on hydrolysis with CH_3COOH gives *cis*-alkenes. Further, one hydrogen (or deuterium) is added at each step so in both cases product will be same, *i.e.*

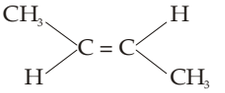
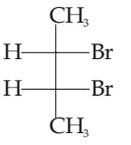
$$A = B = \begin{matrix}R & & R\\ & C = C & \\ H & & D\end{matrix}$$

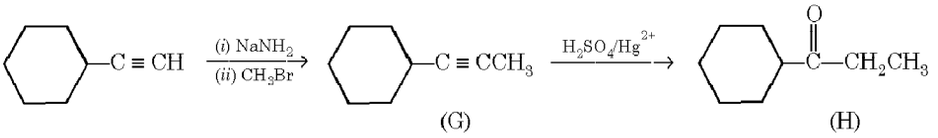
(*ii*) 

(C)



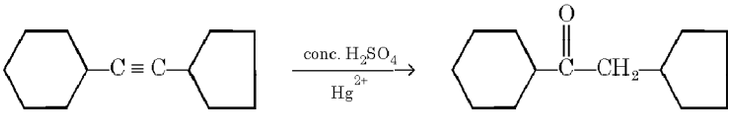
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(*iii*) $HC \equiv CH \xrightarrow[(ii)\ 2CH_3Br]{(i)\ 2NaNH_2} \underset{(D)}{CH_3C \equiv CCH_3} \xrightarrow[(anti\text{-reduction})]{Na/C_2H_5OH}$  *trans*-(E) $\xrightarrow[anti\text{-addition}]{Br_2}$  *meso*-(F)

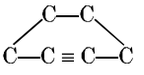
(*iv*) 

(G) (H)

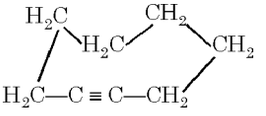
(*v*) I and J are mixtures of CH_3CH_2COOH and $(COOH)_2$.

52. (*a*) 

(*b*) The linear structural unit with *sp* hybridised carbon atoms can't be bridged with only two carbon atoms, *i.e.* —C—C ≡ C—C— group can't form cyclic compound having a bridge of two carbon atoms and hence following structure is not feasible.



The lowest stable cycloalkyne is cyclooctyne.



53. Formation of 2 moles of CH_3COOH indicates the presence of two $\equiv CCH_3$ groupings, while formation of glutaric acid indicates the presence of $\equiv C—(CH_2)_3—C \equiv$ grouping. Thus the alkyne is

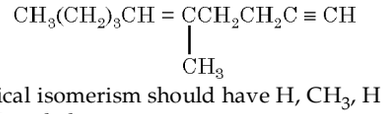
$$CH_3C \equiv C(CH_2)_3C \equiv CCH_3 \xrightarrow{\text{oxidation}} CH_3COOH + HOOC(CH_2)_3COOH + CH_3COOH$$

54. (*i*) Formation of methanoic acid (HCOOH) suggests the presence of ≡CH grouping.

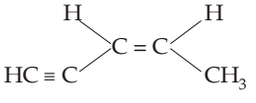
(*ii*) Formation of an aldehyde (pentanal, $CH_3(CH_2)_3CHO$) indicates the presence of an olefinic linkage having $CH_3(CH_2)_3CH =$ grouping.

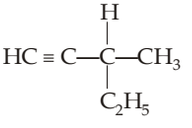
(*iii*) Formation of 4-oxopentanoic acid indicates the presence of a grouping having C = C as well as C ≡ C ; the grouping should be $= C(CH_3)CH_2CH_2C \equiv$.

Thus the hydrocarbon should have the following structure



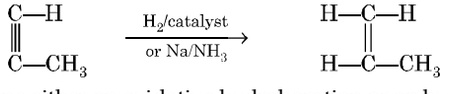
55. (*a*) Smallest alkyne that can show geometrical isomerism should have H, CH_3, H and HC ≡ C— groups on the two doubly bonded carbon atoms, arranged in the manner given below.





The smallest alkyne than can show optical isomerism should have H, CH_3, C_2H_5 and C ≡ CH groupings around the central carbon atom.

(*b*) Non-terminal alkynes (RC ≡ CR) give stereospecific products on reduction, alkynes having acetylenic hydrogen on reduction gives only one product.



(*c*) Symmetrical alkynes give same ketone either on oxidative hydroboration or on hydration.

$$H_3CCOCH_2CH_3 \xleftarrow[Hg^{2+}]{\text{conc. } H_2SO_4} H_3CC \equiv CCH_3 \xrightarrow[(ii)\ H_2O_2/OH^-]{(i)\ BH_3} CH_3COCH_2CH_3$$

56. (*i*) Acetylene is a very weak acid (pK_a = 25) and hence only on extremely strong base like amide ion (NH_2^-) can successfully remove a proton. Alternatively,

$$\underset{\text{Weaker acid}}{HC \equiv CH} + \underset{\text{Stronger base}}{\text{aq. NaOH}} \longrightarrow \underset{\text{Stronger base}}{HC \equiv C^-Na^+} + \underset{\text{Stronger acid}}{H_2O}$$

As the products are stronger base and stronger acid, the reaction is not feasible.

(*ii*) The carbon nuclei in C ≡ C are shielded by 6 electrons (from 3 bonds) rather than by 4 or 2 electrons as in C = C and C—C, respectively. With more shielding electrons present, the carbon atoms of –C ≡ C— can get closer, thereby affording more orbital overlap and stronger bonds. Alternatively, this can be explained on the basis of hybrid orbitals.

(*iii*) Bond energy is a measure of homolytic cleavage, $\equiv C—H \longrightarrow \equiv C^{\bullet} + {}^{\bullet}H$

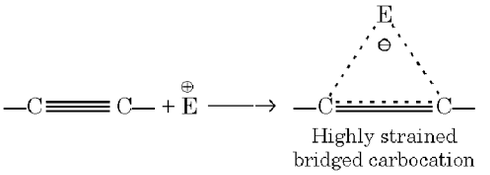
Acidity is do to heterolytic cleavage, $\equiv C—H \longrightarrow \equiv C:^{-} + H^{+}$

(*iv*) $HC \equiv C^{-}$ is the conjugate base of the acid HC ≡ CH, while $H_2C = CH^{-}$ is the conjugate base of the acid $CH_2 = CH_2$. Since HC ≡ CH is stronger acid (due to *sp* hybridised carbon) than $H_2C = CH_2$ (due to sp^2 hybridised carbon), a stronger acid always has weak base and *vice-versa.*

(*v*) The low reactivity of alkynes towards electrophilic addition reactions is believed to be due to following two factors.

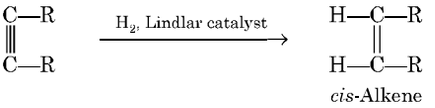
(*a*) The bridged intermediate cation formed by the initial attack of electrophile on the triple bond is less stable because it is a highly strained system.

Due to formation of cyclic intermediate carbocation, the olefinic intermediate products would invariably be *trans.*



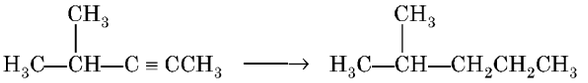
(*b*) In acetylenic carbon atoms, the π electrons are more tightly held by the carbon nuclei and hence they are less easily available for reaction with electrophiles.

57. Catalytic hydrogenation of alkynes takes place in *cis* manner.



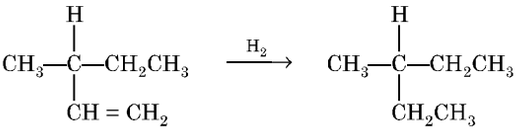
cis-Alkene

58. Molecular formula C_6H_{10} corresponds to alkynes (C_nH_{2n-2}). C ≡ C is confirmed by the fact that it takes 2 moles of hydrogen to form fully saturated compound. Its non reactivity towards ammonical silver nitrate indicates that the alkyne is non-terminal, *i.e.* no acetylenic hydrogen is present. Formation of 2-methylpentane on hydrogenation suggests the following carbon-framework.



4-Methyl-2-pentyne 2-Methylpentane

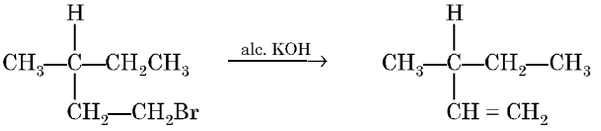
59. Since the compound A with molecular formula C_6H_{12} is optically active, its four substituents should be different. Further, compound A on hydrogenation absorbs a molecule of hydrogen to form optically inactive compound B, one of the substituents of A should be unsaturated analogue of the other fully saturated, *viz.* —CH = CH_2 and —CH_2—CH_3. Thus the four substituents in A should be H, CH_3, —CH_2CH_3 and —CH = CH_2. Hence structure A and B will be as below :



[A] [B]

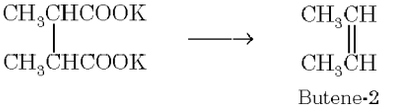
(C_6H_{12}, optically active) (C_6H_{14}, optically inactive)

Preparation of A from its corresponding bromide.



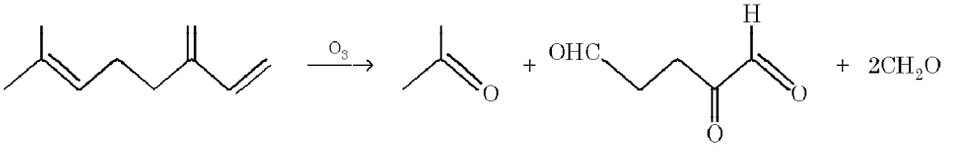
[B]

60. Since the hydrocarbon takes up a molecule of hydrogen to form *n*-butane, it should be butene-1 or butene-2. However, only butene-2, being symmetric, can be obtained by the electrolysis of the potassium salt of a dicarboxylic acid.



Butene-2

61. The hydrocarbon, $C_{10}H_{16}$ contains 10 carbon atoms, but the total number of carbon atoms in the three products is only nine, the missing carbon atom must be found in a second molecule of HCHO. Hence number of molecules of ozonolysis products must be four which agrees with the presence of three double bonds (cleavage at three places gives four products). Hence hydrocarbon must have following structure.



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62. m moles of H_2 absorbed $= \dfrac{8.40 \text{ ml}}{22.4 \text{ ml/m mole}}$ m moles of compound $\approx \dfrac{10.02 \text{ mg}}{80 \text{ mg/m mole}}$

Degree of unsaturation $= \dfrac{\text{m moles of } H_2 \text{ absorbed}}{\text{m moles of the compound}} = \dfrac{8.40/22.4}{10.02/80} = 3$

Thus the hydrocarbon contains either three double bonds or one double bond and one triple bond. It is interesting to note that the ozonolysis products (HCHO and OHCCHO) contains only *three carbon atoms* which can't account the molecular weight (80—85) of the compound, it indicates that the original compound should have six carbon atoms ($6 \times 12 = 72$) which in turn indicates that two moles of each ozonolysis product are obtained per mole of hydrocarbon. Thus the hydrocarbon should have following structure (recall that formation of HCHO indicates the presence of terminal $=CH_2$ grouping).

$$H_2C = CH—CH = CH—CH = CH_2$$

1, 3, 5-Hexatriene

63. Determination of empirical formula of A and B.

	For A		For B	
Element	**C**	**H**	**C**	**H**
Percentage	87.2	12.8	84.1	15.9
Mole %	$\frac{87.2}{12} = 7.27$	$\frac{12.8}{1} = 12.8$	$\frac{84.1}{12} = 7$	$\frac{15.9}{1} = 15.9$
Ratio	$\frac{7.27}{7.27} = 1$	$\frac{12.8}{7.27} = 1.76$	$\frac{7}{7} = 1$	$\frac{15.9}{7} = 2.27$
Simple ratio	$1 \times 4 = 4$	$1.76 \times 4 = 7$	$1 \times 4 = 4$	$2.27 \times 4 = 9$
Empirical formula	$\mathbf{C_4H_7}$		$\mathbf{C_4H_9}$	

$$A \xrightarrow{\text{ozonolysis}} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Acetone}}{CH_3COCH_3} + \underset{\text{Pyruvic acid}}{CH_3COCOOH}$$

Note that the ozonolysis products have $2 + 3 + 3 = 8$ carbon atoms, so the molecular formula of A should be $(C_4H_7)_2 = C_8H_{14}$ and hence for B, it should be C_8H_{18}. The difference in the molecular formulae of A and B indicates the presence of two C = C double bonds in A. We know that the precursor of the carboxylic acids is aldehydes, so the three initial ozonolysis products of A should be

CH_3CHO, (precursor of CH_3COOH) CH_3COCH_3 and CH_3COCHO (precursor of pyruvic acid)

Hence, compound A which can explain the formation of the above compounds on ozonolysis should be

$$\underset{\text{[A]}}{(CH_3)_2C{=}CH—C(CH_3){=}CHCH_3} \xrightarrow{\text{ozonolysis}} (CH_3)_2C{=}O + OHC—C(CH_3){=}O + OHCCH_3$$

$$\downarrow$$

$$\underset{\text{Pyruvic acid}}{HOOC—COCH_3} + \underset{\text{Acetic acid}}{HOOCCH_3}$$

64. Since the compound A (hydrocarbon) absorbs only one mole of hydrogen to form *n*-hexane it must be *n*-hexene. The position of double bond in *n*-hexene is established by its oxidation to a single C_3 carboxylic acid which is possible only when the double bond is present in the middle of the chain to give two moles of the same C_3 carboxylic acid. Thus *n*-hexene must be hexene-3.

$$\underset{\text{Propanoic acid}}{2CH_3CH_2COOH} \xleftarrow[[O]]{KMnO_4} \underset{\text{Hexene-3}}{CH_3CH_2CH = CHCH_2CH_3} \xrightarrow{H_2—Pt} \underset{n\text{-Hexane}}{CH_3(CH_2)_4CH_3}$$

65. Since the hydrocarbon (A) adds one mole of bromine to form dibromo compound $C_5H_{10}Br_2$, it has one double bond which is further confirmed by its reaction with dilute alkaline $KMnO_4$ (Baeyer's reagent) to form $C_5H_{12}O_2$ (hydroxylation, introduction of two —OH groups).
Since the hydrocarbon C_5H_{10} (A) on ozonolysis gives equal amounts of propanone (CH_3COCH_3) and ethanal (CH_3CHO), it must have following structure.

$$\underset{\text{2-Methyl-2-butene}}{CH_3CH = C(CH_3)_2} \xrightarrow[(ii)\ H_2O/Zn\ dust]{(i)\ O_3} \underset{\text{Ethanal}}{CH_3CHO} + \underset{\text{Propanone}}{O = C(CH_3)_2}$$

66. For this type of problem, students are advised to summarise the whole problem in the form of reaction

$$\underset{\text{2-Methylbutane}}{H_3CCH(CH_3)CH_2CH_3} \xleftarrow{H_2} \underset{(C_5H_{10})}{A} \xrightarrow[\text{Markow addition}]{HBr} \underset{\text{(having Br)}}{B} \xrightarrow{AgOH} \underset{\text{(alcohol)}}{C} \xrightarrow{\text{Oxidation}} \underset{\text{(ketone)}}{D}$$

Let us draw some conclusions from the above set of reactions.

(*i*) The molecular formula C_5H_{10} (C_nH_{2n}) for A indicates that it is an alkene having one double bond.

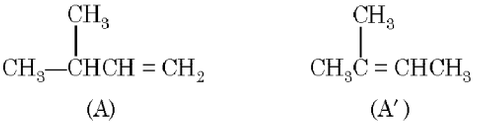
(*ii*) Since the alcohol C on oxidiation gives a ketone D, C must be a secondary alcohol and henceB must be a secondary bromide.

(*iii*) The structure of 2-methylbutane, the hydrogenated product of A, indicates that the secondary bromide must have following structure.

$$CH_3—\underset{Br}{\underset{|}{CH}}—\underset{CH_3}{\underset{|}{CH}}—CH_3$$

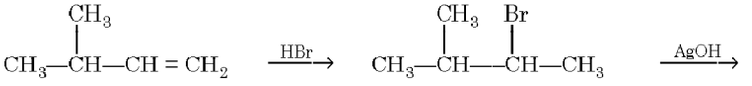
(B)

(*iv*) Thus the corresponding olefin A must have structure A which on Markownikoff addition of HBr gives the bromide B, the other possible alkene A′ will not give B when HBr is added on it according to Markownikoff rule.

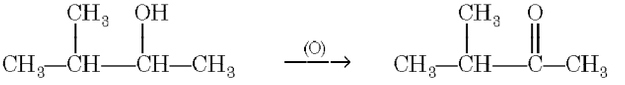


(A) (A′)

Thus the reactions involved can be represented as below :

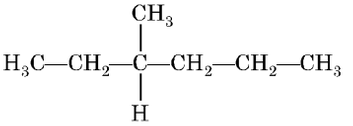


3-Methylbutene-1, A 2-Bromo-3-methylbutane, B



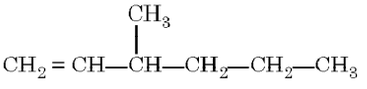
3-Methylbutanol-2, C 3-Methylbutanone-2, D

67. Possible structure for (G), the lowest molecular weight hydrocarbon containing only 1 chiral carbon atom will be that in which the central (chiral) carbon atom has one H, one CH_3, one C_2H_5 and one C_3H_7 group, *i.e.*,

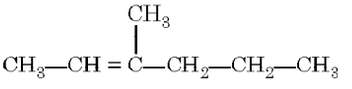


3-Methylhexane (G)

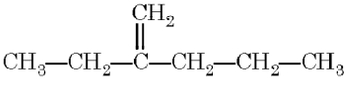
Note that none of the alkenes gives acetone on ozonolysis. So the possibility of isopropyl group in (G) in place of *n*-propyl is discarded. The possible six different alkenes capable of giving (G) on addition of one mole of hydrogen may thus be written by inserting one double in the structure of (G) at different positions.



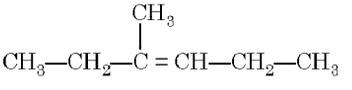
3-Methylhexene-1 (A)



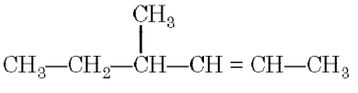
3-Methyl-2-hexene (B)



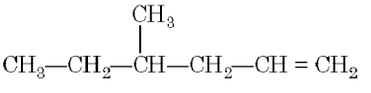
2-Ethylpentene-1 (C)



3-Methyl-3-hexene (D)

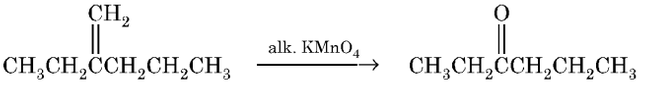


4-Methyl-2-hexene (E)



4-Methylhexene (F)

Alkene capable of giving a ketone containing more than five carbon atoms on treatment with a warm conc. alkaline $KMnO_4$ solution is (C).

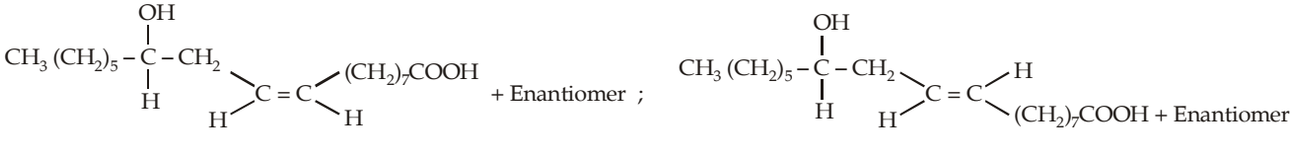


2-Ethylpentene-1 (C) Hexanone-3

The possible Fisher projection of (G) are

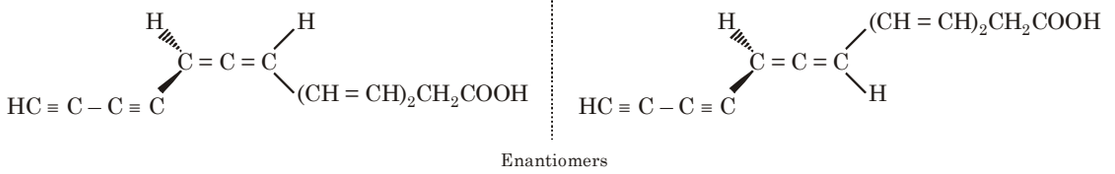


68. (a) Four stereoisomers are possible

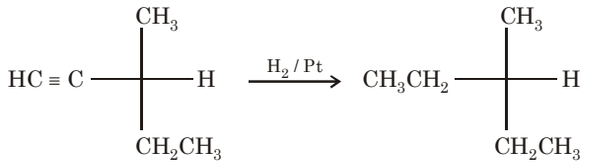


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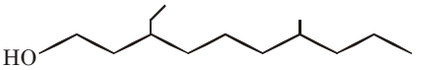
(b) It will rotate the plane polarized light because the molecule although does not have any chiral center, it is chiral.

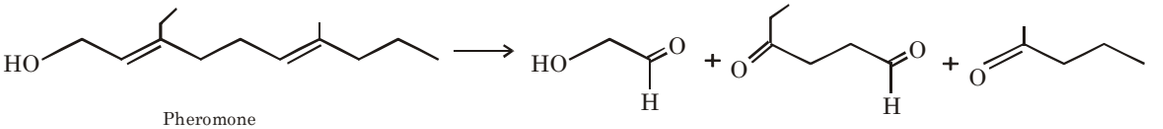


Enantiomers

69. 

or its enantiomer [A] optically inactive [B]

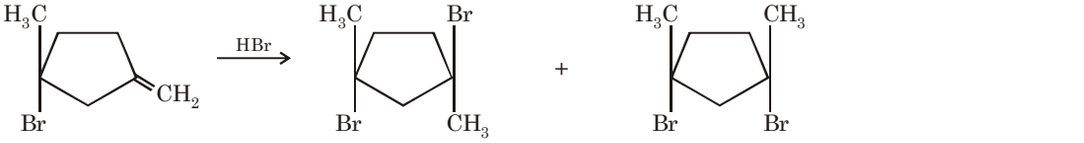
70. Pheromone, $C_{13}H_{24}O$ $\xrightarrow[Pt]{2H_2}$ 



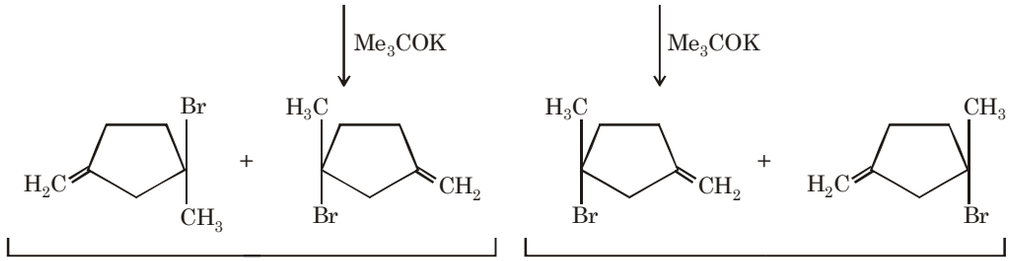
Pheromone

71. 

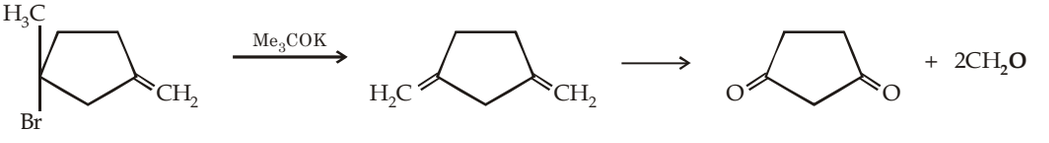
[A] [B] [C] [D]

72. 

(+) - or (–) - [A] Optically active [B] meso (optically inactive) [C]

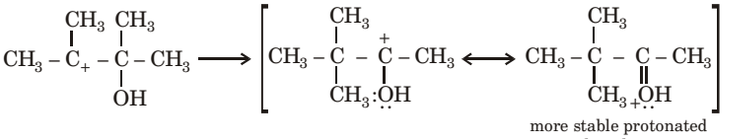


Both are same, [A] Different (±) – A

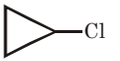


(+) - or (–) - [A] [D]

73. (a) - (A) endo; (b)- (A) - *trans*; (c) - (B) - Tetrasubstituted.

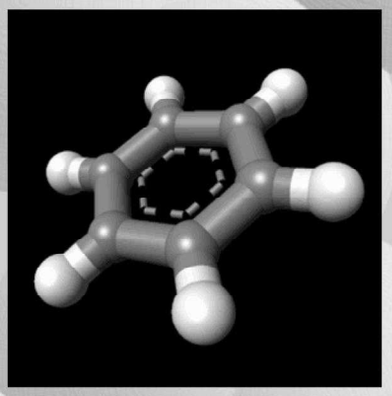
74. 

more stable protonated carbonyl group

75. (a) $CH_3CH = CHCl$ $CH_3C(Cl) = CH_2$ $CH_2Cl\,CH = CH_2$ 

cis-l-trans-

(b) It has 5 of saturation, one π bond is present, so four rings must be present.



7

Aromatic Hydrocarbons

CHAPTER HIGHLIGHTS

7.1 Introduction
7.2 Methods of Preparation of Benzene
7.3 Reactions of Benzene
7.4 Structure of Benzene
7.5 Concept of Aromatic Character (Aromaticity)
7.7 Role of Inductive and Hyperconjugative Effects in Aromatic Substitution of the Substituted Benzenes
7.8 Orientation of Some Special Groups
7.9 Theory of Reactivity and Orientation Based on Carbocation (σ-complex) Stability
7.10 Theory of Orientation and Carbocation Stability
7.11 Methods of Preparation of Alkylbenzenes
7.12 Reactions of Alkylbenzenes
7.13 Alkenylbenzenes
7.14 Tests of Arenes
7.15 Predicting Orientation in Disubstituted Benzenes
7.16 Nucleophilic and Free-Radical Substitutions
Illustrative Examples (Aromatic Hydrocarbons)
EXERCISES
SOLUTIONS

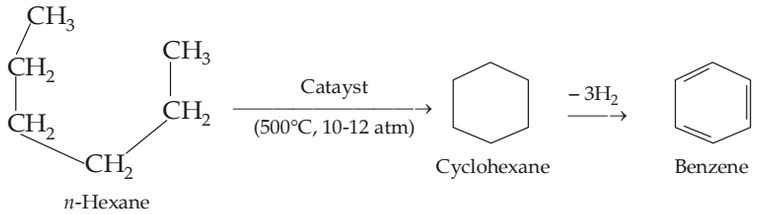
7.1 Introduction

Aromatic compounds are benzene and compounds that resemble benzene in chemical behaviour, which will be discussed at length later on.

Benzene was first isolated by Faraday in 1825 from the gas obtained by pyrolysis of whale oil. The major source of benzene and its derivatives is coal-tar followed by petroleum. Coal-tar is the distillation product obtained by dry distillation of **coal** at 1000—1300°C in absence of air, after removing the gaseous product (*coal gas*, a mixture of CH_4 and H_2) and leaving behind the residual portion, known as *coke*. Chemically, coal-tar is a mixture of aromatic hydrocarbons, their oxygenated derivatives and some heterocyclic compounds.

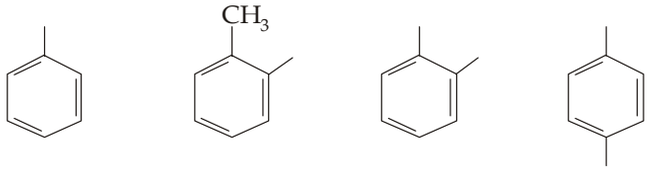
Coal-tar on fractional distillation gives various fractions, *viz*. light or crude naphtha, middle oil or carbolic acid, heavy oil or creosote oil, green oil or anthracene oil and pitch as residue. Benzene, toluene and xylenes are obtained from the light oil fraction.

Coal-tar cannot meet the demand of large quantities of aromatic hydrocarbons needed for industrial purposes, hence many of aromatic hydrocarbons are synthesised from alkanes (**obtained from petroleum**) by *catalytic reforming* which involves, cyclization, aromatization (dehydrogenation) and sometimes isomerization. For example,



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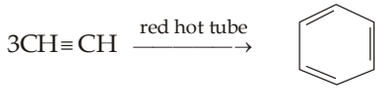
The aryl group. In general the univalent group obtained by removing a hydrogen atom from the nucleus of the aromatic compound is known as *aryl group* (Ar—). The univalent group obtained by the removal of one hydrogen atom from benzene nucleus is named as phenyl (C_6H_5—, Ph—, or ϕ) group. Removal of two hydrogen atoms from the benzene nucleus gives rise to bivalent *phenylene* group. Some of the common aryl groups are



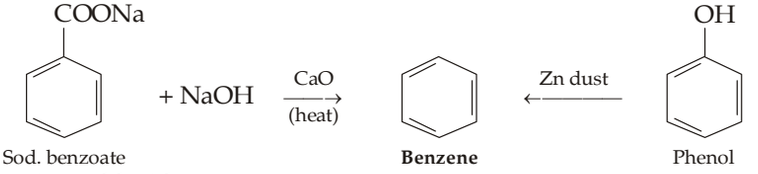
Phenyl *o*-Toluyl *o*-Phenylene *p*-Phenylene

7.2 Methods of Preparation of Benzene

1. From acetylene (Berthelot).



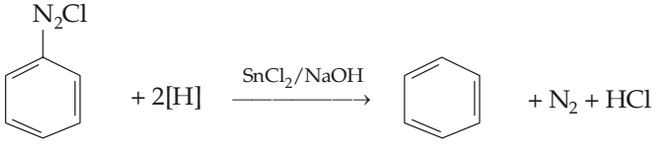
2. From sodium benzoate and phenol (*Laboratory methods*).



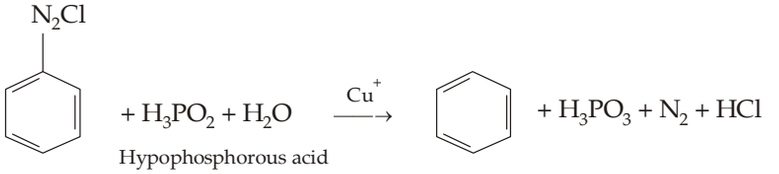
Sod. benzoate **Benzene** Phenol

3. From benzenediazonium chloride.

(a)

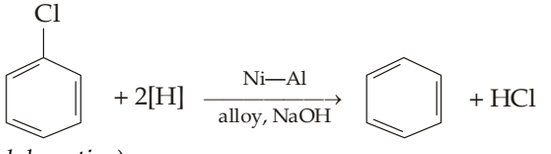


(b)

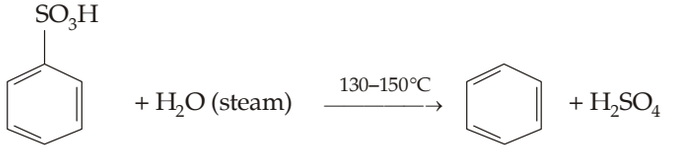


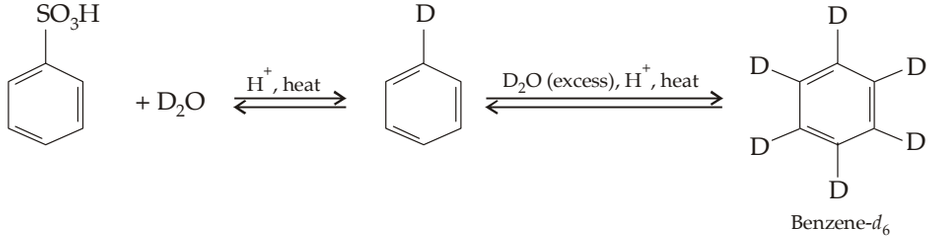
Hypophosphorous acid

4. From chlorobenzene (*Reduction*).



5. From sulphonic acids (*Desulphonation*)





Benzene-d_6

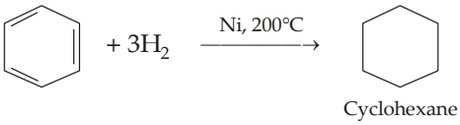
Benzene-d_6 (C_6D_6) is a common solvent used in NMR studies.

7.3 Reactions of Benzene

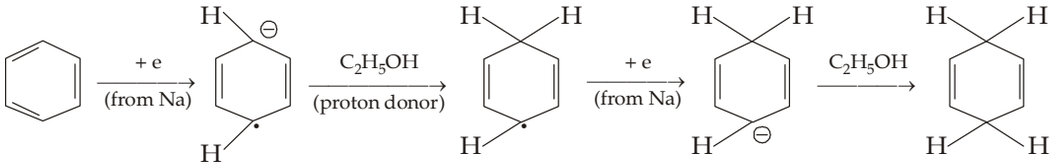
Benzene is a quite stable compound. Although it has three double bonds, it is resistant to oxidation and usual reagents which add to the carbon-carbon multiple bonds under ordinary conditions. However, it gives certain addition reactions under vigorous conditions. On the other side, benzene undergoes electrophilic substitution reactions readily, actually these are considered to be the characteristic reactions of benzene nucleus.

7.3.1 Addition Reactions

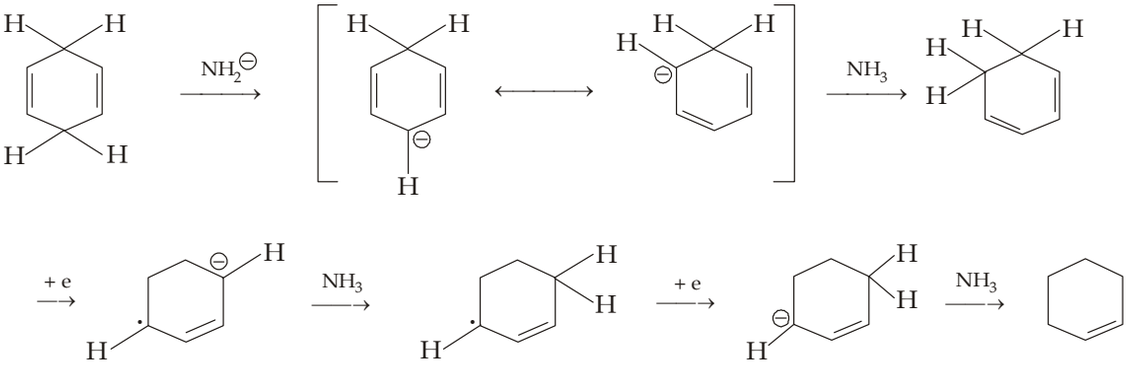
(*i*) *Addition of hydrogen (Reduction of benzene*).



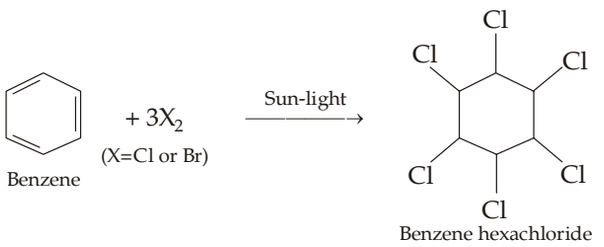
Benzene can also be reduced to cyclohexa-1,4-diene on treatment with Na in liquid ammonia and a proton source usually ethanol (**Birch reduction**). Reaction is possible only in conjugated compounds and involves following steps.



If Birch reduction is carried out with Na in liquid NH_3 in presence of primary alkylamine, (solvent) at 60—130°C, 1, 4-cyclohexadiene is further reduced to cyclohexene. It is because here ammonia acts as proton donor to form strongly basic NH_2^- ion which rearranges 1, 4-cyclohexadiene (non-conjugated) to conjugated 1, 3-cyclohexadiene liable to be reduced by Birch reduction.



(*ii*) *Addition of chlorine or bromine (not iodine).*

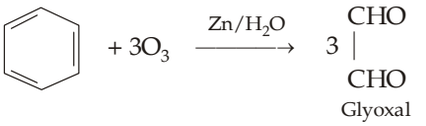


Note that this is an example of halogen addition and not halogenation. Halogen addition is a free radical reaction and occurs in presence of sunlight and without evolution of HX, while halogenation is an electrophilic substitution that takes place in presence of Lewis acid (halogen carrier) and with evolution of HX.

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Benzene hexachloride (BHC) can exist in nine stereoisomeric forms ; five of them have actually been isolated. They are called α, β, γ, δ and ε forms. This mixture of stereoisomeric hexachlorides is valuable insecticide commonly known as **BHC or 666.** The insecticidal properties are due to the γ-isomer called **gammexene** or **lindane.**

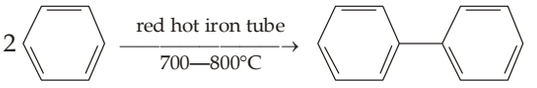
(*iii*) **Ozonolysis.** Benzene adds three molecules of ozone to form a triozonide which on decomposition with water gives three molecules of glyoxal, OHC—CHO.



Glyoxal

7.3.2 Coupling Reaction

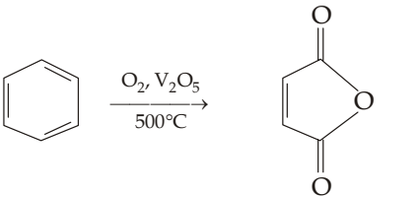
Benzene when passed through a red hot iron tube at 700—800°C forms diphenyl.



Biphenyl

7.3.3 Oxidation

Although benzene ring is resistant to oxidation under ordinary conditions, drastic conditions may rupture the ring. For example, benzene is oxidised to maleic anhydride when its vapours mixed with air are passed over heated V_2O_5 catalyst.



Maleic anhydride

On strong heating with chromic acid or potassium permanganate, it is oxidised to form carbon dioxide and water as the final products.

7.3.4 Combustion

Like other aromatic compounds arenes are inflammable and burn with a sooty flame to form CO_2 and water.

$$2C_6H_6 + 15O_2 \longrightarrow 12CO_2 + 6H_2O$$

7.3.5 Substitution in Benzene Nucleus (Aromatic Substitution)

The replacement of an atom, generally hydrogen, or a group attached to carbon of benzene ring by another group is known as aromatic substitution. Like substitution at aliphatic system, aromatic compounds may also undergo three types of substitutions.

(*i*) *Electrophilic substitution,* S_E. These reactions involve attack by an electrophile or electron-seeking reagent.

(*ii*) *Nucleophilic substitution,* S_N. These involve attack by a nucleophile or electron-donating reagent.

(*iii*) *Free-radical substitution.* These involve attack by a free radical.

However, unlike aliphatic system[1], electrophilic substitution reactions are most common in aromatic compounds and all the common and well known substitution reactions like nitration, halogenation, sulphonation and Friedel-Craft reactions (alkylation and acylation) are examples of electrophilic substitution.

Why aromatic compounds undergo electrophilic substitution reactions? Due to the presence of π-electron clouds above and below the plane of benzene ring (or any other aromatic ring), the ring serves as a source of electrons and is easily attacked by electrophiles (electron loving reagents). Further substitution reactions in benzene rather than addition are due to the fact that in the former reactions resonance-stabilised benzene ring system is retained while the addition reactions lead to the destruction of benzene system. For example, addition of one molecule of hydrogen on benzene would destroy benzene ring and forms cyclohexadiene which is less stable than benzene. Hence *electrophilic substitution reactions are the characteristic reactions of aromatic compounds.*

(*a*) **Electrophilic aromatic substitution**

The electrophilic aromatic substitution reactions proceed by a common mechanism. Therefore, we will first deal the mechanism, in general, and then apply it to specific substitution reactions like nitration, halogenation, etc.

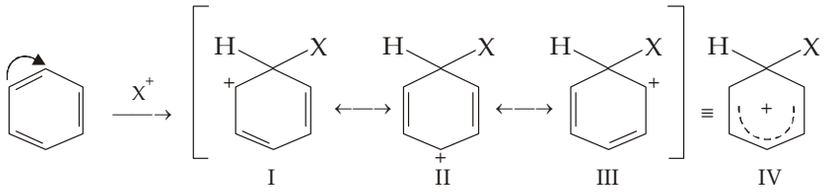
General mechanism. Electrophilic aromatic substitution reactions are believed to proceed by bimolecular (S_E2) mechanism which involves three steps.

1. In aliphatic system, nucleophilic substitution reactions are the most common followed by free radical substitution.

(*i*) *Generation of an electrophile (electrophilic reagent).* First of all the attacking electrophile, say X^+, is generated from the reagent, say XY.

$$X:Y \longrightarrow \underset{\text{Electrophile}}{X^+} + :Y^-$$

(*ii*) *Formation of the intermediate carbocation.* On the approach of the electrophile X^+, benzene undergoes electromeric effect (as shown by the curved arrow) with the result one carbon atom of the benzene ring gets positively charged and the other gets negatively charged. The electrophile then attacks on the negative centre resulting in the formation of an intermediate known as **aronium cation, carbocation, σ-complex[1]** or **the pentadienyl cation[2], I.**



Electromeric effect in benzene — Resonating structures of the benzenonium ion[3] — Resonance hybrid[4] of the benzenonium ion

Where $X^+ = NO_2^+$ (nitronium ion) in nitration

$= Cl^+$ (chloronium ion) in chlorination

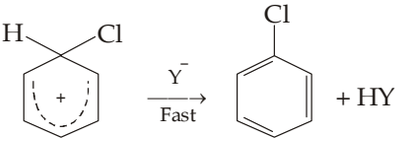
$= SO_3$ (sulphur trioxide) in sulphonation

$= CH_3^+$ (methyl cation) in alkylation

$= \overset{+}{C}OCH_3$ (acetyl cation) in acetylation

The carbocation I is stabilised by resonating structures I, II and III ; and the resonance hybrid can be represented by the structure IV. Thus note the positive charge on the intermediate carbocation is not confined to one carbon but is dispersed over the entire molecule especially on the *o*- and *p*-positions with respect to the carbon carrying the attacking reagent. Since formation of intermediate carbocation is a slow step, it constitutes the rate determining step of the complete reaction.

(*iii*) *Formation of the product.* The reaction is completed by abstraction of a proton from the carbon atom bearing electrophile by an anionic species (: Y^-) present in the reaction mixture to form a substituted product.



We will apply this general mechanism on nitration, halogenation, sulphonation and Friedel-Craft's alkylation and acylation at a later stage.

(*b*) **Evidence in support of electrophilic character of substitution**

Electrophilic nature of aromatic substitution reactions is proved by the following facts.

1. Such substitutions can be accomplished by reagents containing pre-formed electrophilic species. For example, benzene can be easily nitrated by salts like nitronium nitrate ($NO_2^+NO_3^-$) and nitronium perchlorate ($NO_2^+ ClO_4^-$) clearly indicating that NO_2^+ (an electrophile) is the real nitrating agent.
2. In certain Friedel-Craft's alkylation reactions, rearranged alkyl groups are found to be present in the substituted product. For example, Friedel-Craft's reaction of benzene with *n*-propyl chloride gives isopropylbenzene rather than *n*-propylbenzene. This can be explained on the basis of formation of *n*-propyl cation (an electrophile) which rearranges to the more stable isopropyl cation (another electrophile) which then attacks on benzene forming isopropylbenzene.

$$\underset{\text{n-Propyl bromide}}{CH_3CH_2CH_2Br} \longrightarrow \underset{\substack{\text{n-Propyl cation}\\ \text{(primary carbocation)}}}{CH_3CH_2\overset{+}{C}H_2} \xrightarrow{\text{rearrangement}} \underset{\substack{\text{Isopropyl cation}\\ \text{(sec. carbocation)}}}{CH_3\overset{+}{C}HCH_3}$$

3. The observed reactivity and orientation (discussed later on) in aromatic compounds are in accord with the electrophilic character of these reactions.

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1. Since a discrete σ-bond has been formed.
2. Since the intermediate has no longer a benzene structure but an unstable cation with four π electrons delocalized over five carbon nuclei (the sixth carbon atom is a saturated carbon and forms sp^3 hybrid bond), it is known as pentadienyl cation.
3. Note that benzenonium ion is not flat because the carbon bonded to Cl and H is tetrahedral.
4. For the sake of simplicity we will write only one of the resonating structures of the resonance hybrid in our further discussion, and not the hybrid itself.

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(*c*) **Evidence in favour of two step mechanism**

Theoretically, an electrophilic aromatic substitution reaction can proceed *via* one step or two step mechanism. However, before discussing the evidence in favour of actual two step mechanism, let us summarise both the mechanisms.

One step mechanism. $C_6H_5—H + X^{\oplus} \longrightarrow \left[X- - - C_6H_5- - -\overset{\oplus}{H}\right] \longrightarrow C_6H_5—X + \overset{\oplus}{H}$

Two step mechanism. (*i*) $C_6H_5—H + X^{\oplus} \xrightarrow{\text{slow}} C_6H_5\overset{+}{\underset{X}{\overset{H}{<}}}$

(*ii*) $C_6H_5\overset{+}{\underset{X}{\overset{H}{<}}} + :Y^{\Theta} \xrightarrow{\text{fast}} C_6H_5—X + H:Y$

However, all electrophilic aromatic substitution reactions proceed *via* two steps which has been proved by **isotope tracer technique.** Benzene (or other aromatic compound) labelled with deuterium (the heavier isotope of hydrogen having a mass of 2 amu) was nitrated (or halogenated, sulphonated, etc.) and its rate of nitration was determined. It was observed that the rate of nitration of deuterated benzene and ordinary benzene (*i.e.* the rate of replacement of deuterium or protium by —NO_2 group) was same

$$\underset{\text{Deuterated benzene}}{C_6H_5—D} + HONO_2 \xrightarrow{K} C_6H_5—NO_2 + HOD$$

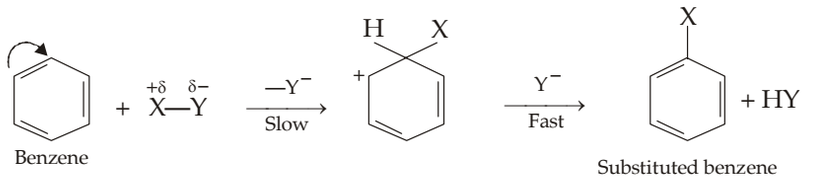
$$\underset{\text{Ordinary benzene}}{C_6H_5—H} + HONO_2 \xrightarrow{K'} C_6H_5—NO_2 + H_2O\ ;\ K = K'$$

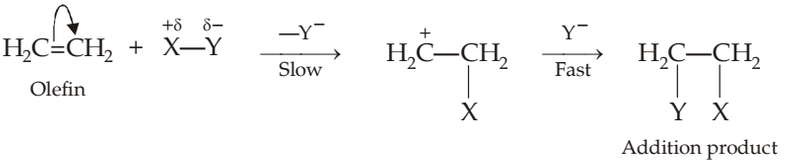
Hence we can safely conclude that there is no **isotopic effect**[1] in aromatic substitution.

Now since a carbon-deuterium bond is broken more slowly than a carbon-hydrogen (protium) bond, had the mechanism of the above reaction been one step (involving breaking of carbon-hydrogen bond), the rate of replacement of deuterium and hydrogen must have been different. The same rate of nitration can easily be explained on the basis of two-step mechanism. In the two-step mechanism, since the rate determining step (first step) does not involve the cleavage of C—H or C—D bond, it does not effect the rate of replacement of H or D. Cleavage of C—H bond actually takes place in the second step (fast step) of the reaction which, being fast, does not affect the rate of reaction. Thus *absence of isotopic effect established the two-step mechanism for electrophilic aromatic substitution reaction in which formation of carbocation (first step) is the rate determining step.*

(*d*) **Electrophilic aromatic substitution reactions versus electrophilic addition reactions of alkenes**

There are certain similarities between the electrophilic aromatic substitution reactions of benzene and electrophilic addition reactions of olefins. But before we summarise the various points of similarities, let us rewrite the mechanism of both the reactions.





Now let us summarize the similarities between the two reactions.

(*i*) Both types of reactions are polar, two-step processes and involve the attack of electrophilic reagent on the sp^2 hybridised carbon.

(*ii*) In both cases the rate determining step is the attack of an electrophile at carbon (first step) to form carbocation.

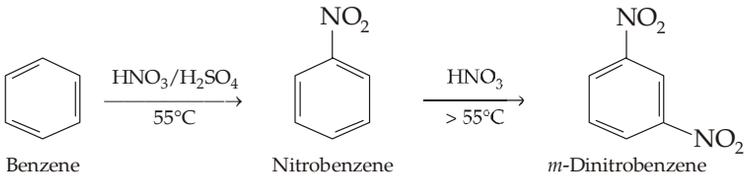
1. A difference in reaction rate due to a difference in the isotope present in a reaction system is called as isotope effect.

So we see that the two reactions are quite similar upto the formation of carbocation but after this the two reactions differ very much as one regenerates the original structure with a substituent, *i.e.* a substituted product is formed, while the other (addition on olefins) gives an addition product and thus the original structure (presence of double bond) is destroyed. The difference is due to the fact that in substitution reactions the regenerated benzene nucleus, obtained by the loss of proton from the carbocation, stabilizes itself by resonance while there is no such comparable large resonance stabilisation in case of addition reactions on alkenes which thus tend to add the nucleophile.

Now let us discuss important examples of electrophilic substitution reactions of benzene.

1. Nitration

Nitration is brought about by treating the aromatic compound with *nitrating mixture* (a mixture of concentrated nitric acid and conc. sulphuric acid). Remember that the —NO_2 group is electron-withdrawing group, so its presence deactivates benzene ring for further nitration. Hence *nitration of benzene* (not having —NO_2) *is easier than nitrobenzene* (having —NO_2 group).



Benzene Nitrobenzene *m*-Dinitrobenzene

Mechanism.

The three steps of the reaction are given below.

(*i*) *Generation of electrophile.* In nitration, **nitronium ion,** NO_2^+ is the active nitrating agent (*electrophile*). It is produced by the reaction of nitric acid and sulphuric acid.

$$HO—NO_2 + H_2SO_4 \rightleftharpoons H_2O^+ — NO_2 + HSO_4^-$$
$$H_2O^+ —NO_2 \rightleftharpoons H_2O + NO_2^+$$
$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^-$$

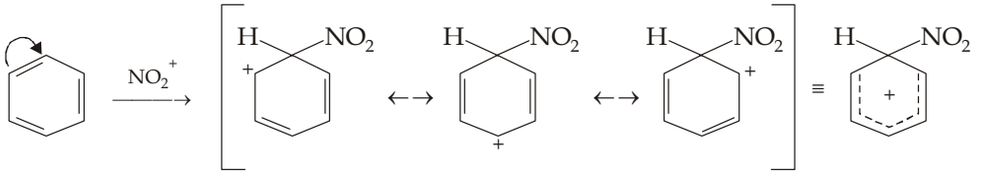
On adding, $$HONO_2 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$$

Thus note that here sulphuric acid acts as an acid and protonates nitric acid (which thus acts as a base) to form protonated nitric acid. The latter decomposes into **nitronium ion** (electrophile) and water. Water, so formed, is absorbed by another molecule of sulphuric acid.

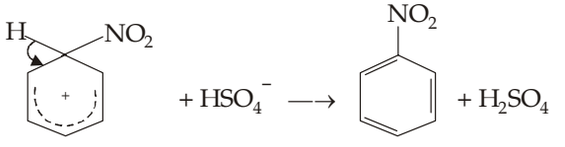
N_2O_5 in CCl_4 in presence of P_2O_5 is used as nitrating agent when anhydrous conditions are used.

$$N_2O_5 \rightleftharpoons NO_2^+ + NO_3^-$$

(*ii*) *Formation of carbocation.*



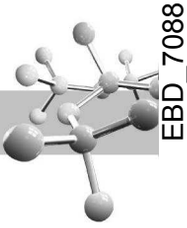
(*iii*) *Formation of the final product.*



2. Halogenation

Aromatic *halogenation* (e.g. chlorination and bromination) *is generally brought about by treating the aromatic compound with halogen in cold, dark and in the presence of a strong Lewis acid (halogen carrier)* like Fe, I_2, ferric halide or aluminium halide. The usual practice is to add to the reaction mixture (aromatic compound + halogen), some iron fillings which are converted by the halogen into the corresponding ferric halide.

$$\underset{\text{Benzene}}{C_6H_6} + Cl_2 \xrightarrow{AlCl_3} \underset{\text{Chlorobenzene}}{C_6H_5Cl} + HCl$$



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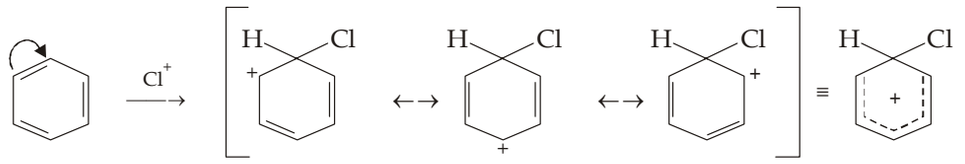
Mechanism.

The common three steps of the reaction are as below.

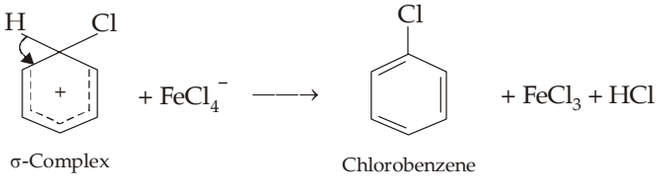
(*i*) *Formation of electrophile.* The metallic halide (Lewis acid) polarises the halogen molecule to yield the electrophile, X^+ (halonium ion). For example,

$$FeCl_3 + Cl_2 \longrightarrow FeCl_4^- + Cl^+$$

(*ii*) *Formation of carbocation.*



(*iii*) *Formation of final product.*



Halogenation can also be effected by other reagents like hypochlorous or hypobromous acid in presence of strong acids like HCl which protonates the hypohalous acids thus making them powerful electrophiles.

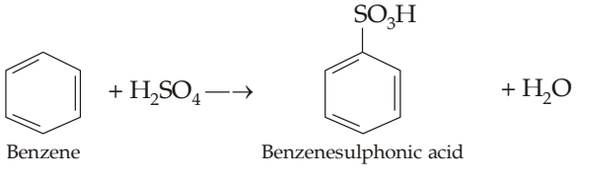
$$HOCl + H^+ \rightleftharpoons H_2O^+—Cl \rightleftharpoons H_2O + Cl^+$$

Since the reaction between benzene and fluorine is very vigorous, direct fluorination of arenes is not possible. Now since hydroiodic acid (HI) is a strong reducing agent it will reduce iodobenzene (formed by the iodination of benzene) to benzene back, iodination should be carried out in presence of an oxidising agent like iodic acid, nitric acid or mercuric oxide.

$$C_6H_6 + I_2 \longrightarrow C_6H_5I + HI$$
$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$
$$\text{or} \quad 5C_6H_6 + 5I_2 + HIO_3 \longrightarrow 5C_6H_5I + 3I_2 + 3H_2O$$

3. Sulphonation

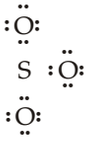
Sulphonation is brought about by the action of sulphuric acid containing an excess of SO_3 (oleum).



Mechanism

The reaction mechanism involves the following steps.

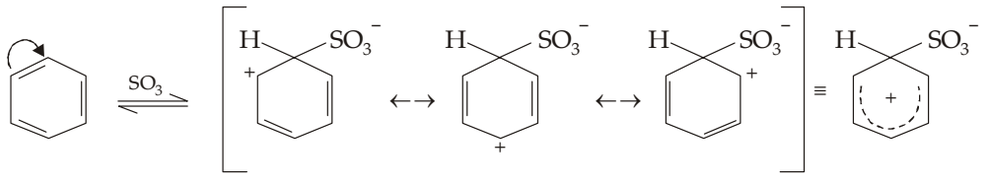
(*i*) *Formation of electrophile.* Here the electrophile is free sulphur trioxide which is present as such in oleum (conc. $H_2SO_4 + SO_3$) or may be produced by the dissociation of sulphuric acid.



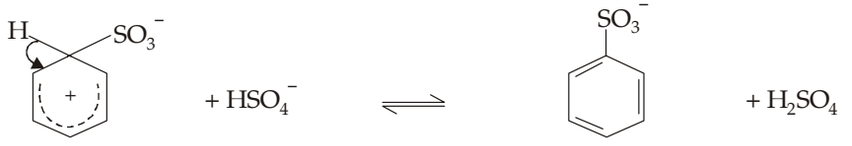
$$\underset{\text{Sulphuric acid (2 moles)}}{HO—SO_2OH + H_2SO_4} \rightleftharpoons SO_3 + H_3O^+ + HSO_4^-$$

The electrophilic character of SO_3 is due to the presence of electron deficient sulphur atom as is obvious from the structure of its molecule (Note that sulphur has 6 electrons).

(*ii*) *Formation of carbocation.*



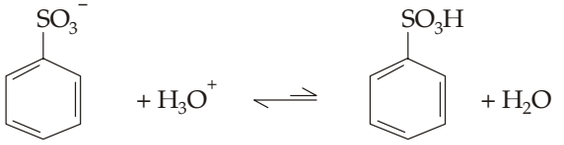
(*iii*) Transfer of proton to form the resonance-stabilised sulphonic acid anion.



σ-Complex Benzenesulphonic acid anion

Note that all steps of sulphonation reaction are reversible.

(*iv*) *Reaction between sulphonic acid anion and hydronium ion to form the final product.*



The equilibrium of this reaction lies to left.

With some aromatic compounds and at certain acidities, the electrophile may be HSO_3^+ or molecule that can readily transfer SO_3 or HSO_3^+ to the aromatic ring.

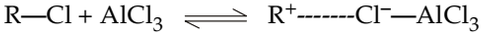
4. Friedel-Craft's alkylation

This reaction involves *the action of an alkyl halide on aromatic compound in the presence of anhydrous aluminium chloride* (catalyst).*

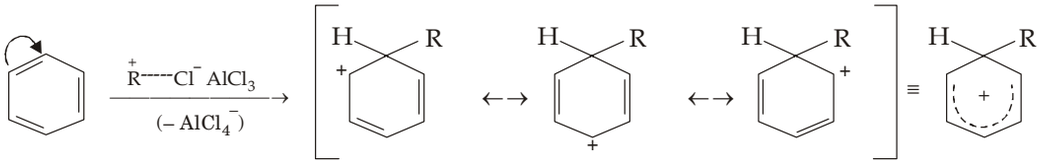
Mechanism

The reaction mechanism involves the following steps.

(*i*) *Generation of electrophile.* Here the electrophile is alkyl carbocation.

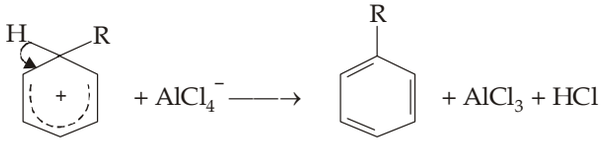


(*ii*) *Formation of carbocation.*



Note that complex formation with AlX_3 is observed in case of only primary alkyl halides ; in case of secondary and tertiary alkyl halides Lewis acid acts as electron deficient species and alkyl carbocation is produced directly.

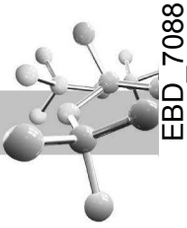
(*iii*) *Transfer of proton from the carbocation to form the final product.*



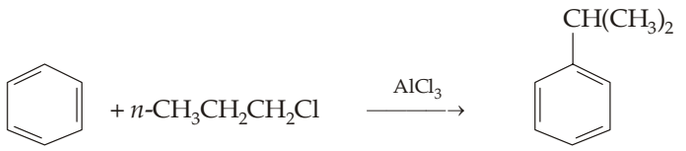
It is important to note that in higher alkyl halides, the alkyl carbocation, formed at the initial stage may undergo rearrangement to form the more stable (2° or 3°) rearranged carbocation and thus the unexpected alkylbenzene is formed as the product. For example, benzene when treated with *n*-propyl chloride gives isopropylbenzene rather than *n*-propylbenzene.

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* Since the function of $AlCl_3$ is to generate the carbocation by abstracting the halogen from the alkyl halide, other Lewis acids like BF_3, $FeCl_3$, HF etc. can be used in place of $AlCl_3$.



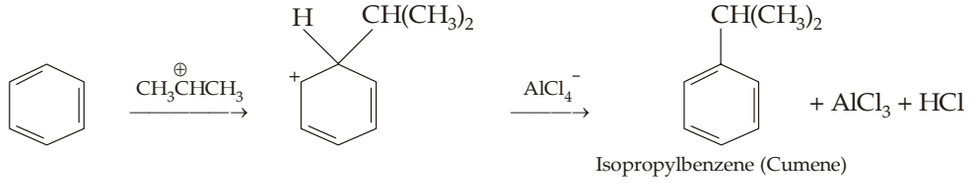
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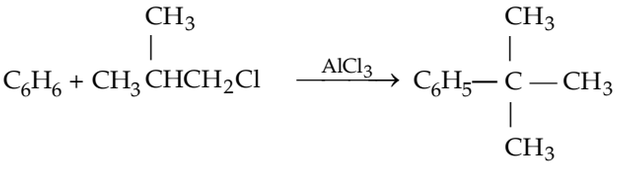
It is due to the rearrangement of the *n*-propyl cation (1°) to the more stable *iso*-propyl cation (2°).



Now it is the more stable isopropyl cation that attacks the benzene molecule to form isopropylbenzene.

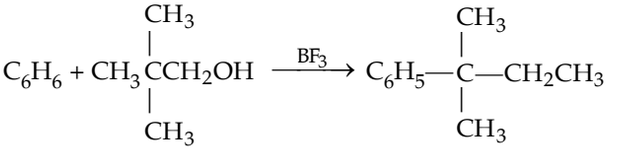


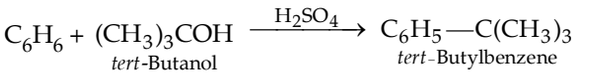
Similarly,

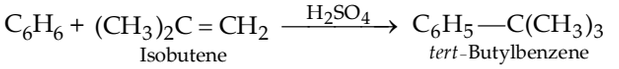


Modifications of Friedel-Craft's alkylation

Like alkyl halides, alcohols and alkenes can also provide carbocations in presence of acids like BF_3, mineral acids etc. hence alcohols and alkenes can also be used as alkylating agent for aromatic rings.





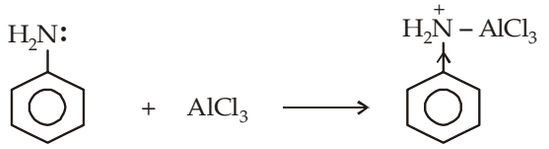


Limitations of the Friedel-Craft's alkylation :

(i) Friedel-Craft reactions (both alkylation as well as acylation) either fail or give poor yields when any of the following powerful electron-withdrawing groups are present on the aromatic ring because these groups make the ring less reactive.

$$-NO_2,\ -\overset{+}{N}Me_3,\ -COOH,\ -COR,\ -CF_3,\ -SO_3H$$

Further the yields are also poor when the ring bears $-NH_2$, –NHR, or $-NR_2$ groups. This is partly due to the fact that the strongly basic nitrogen fixes up the Lewis acid required for ionisation of alkyl halide and partly because of the presence of positive charge on nitrogen due to which the group becomes electron-withdrawing and hence deactivates the benzene nucleus towards electrophilic substitution.

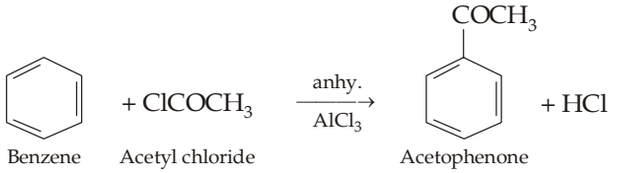


(ii) Alkyl carbocations are susceptible to carbocation rearrangements.

(iii) Aryl and vinyl halides cannot be used as the halide component because they do not form carbocation readily.

5. Friedel-Craft's acylation

This is quite similar to alkylation.



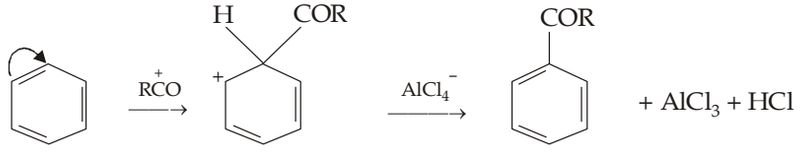
Benzene Acetyl chloride Acetophenone

Mechanism

Here the electrophile is *acylium ion (acyl cation)*.

$$RCOCl + AlCl_3 \longrightarrow R\overset{+}{C}O + AlCl_4^-$$

Formation of carbocation and then the final product.



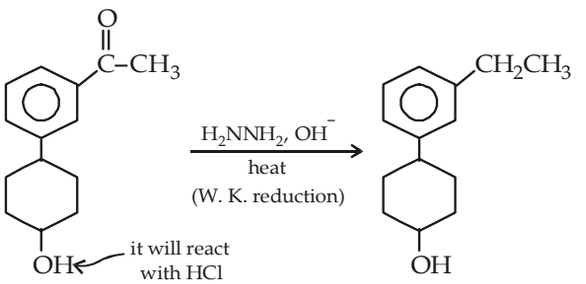
It is important to note that monosubstituted alkylbenzenes (*e.g.* $C_6H_5CH_2CH_3$) are generally prepared through acylation process rather than the direct alkylation. One of the reasons is that in direct alkylation as soon as one alkyl group is introduced, the benzene nucleus becomes more active than benzene itself, because of electron-releasing character of the alkyl group, and hence further substitution takes place leading to the formation of polyalkylated product. On the other hand, in acylation as one acyl (*e.g.*, CH_3CO—) group is introduced, the ring is deactivated and hence the introduction of the second acyl group becomes difficult. The monoacylated benzene is then easily reduced to monoalkylated benzene by Clemmensen reduction (Zn + Hg/HCl) or Wolf-Kishner reduction ($NH_2.NH_2 + OH^-$).

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Acetyl chloride}}{CH_3COCl} \xrightarrow{AlCl_3} \underset{\text{Acetophenone}}{C_6H_5COCH_3} \xrightarrow[\text{or } NH_2\text{–}NH_2 + OH^-]{\text{Zn-Hg/HCl}} \underset{\text{Ethylbenzene}}{C_6H_5CH_2CH_3}$$

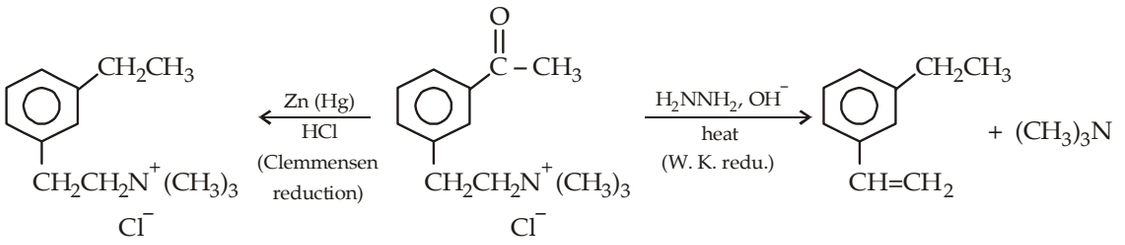
$$[c.f.\ C_6H_6 + CH_3CH_2Cl \xrightarrow{AlCl_3} C_6H_5CH_2CH_3 \longrightarrow C_6H_4(CH_2CH_3)_2].$$

However, reduction of $-\overset{O}{\overset{\|}{C}}-CH_3$ to $-CH_2-CH_3$ must be done carefully.

Since Clemmensen reduction involves acidic conditions, it must be used when the compound does not have any acid sensitive group; similarly, Wolf-Kishner reduction (using basic conditions) must not be used with ketones having base-sensitive functional groups.



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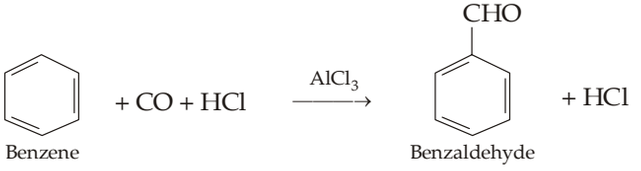


Later on, Friedel-Craft reaction was extended for preparing other compounds by replacing alkyl and acyl halides by other reagents. For example,

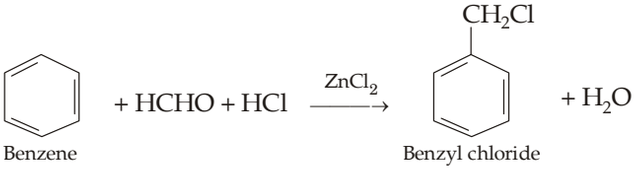
(*a*) $\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Carbonyl chloride}}{Cl.CO.Cl} \xrightarrow{AlCl_3} \underset{\text{Benzoyl chloride}}{C_6H_5COCl} + HCl$

(*b*) $C_6H_6 + \underset{\text{Chloroformamide}}{ClCONH_2} \xrightarrow{AlCl_3} \underset{\text{Benzamide}}{C_6H_5CONH_2} + HCl$

6. Gattermann Koch aldehyde synthesis.



7. Chloromethylation (Blace reaction).



TEST YOUR UNDERSTANDING - 7.1

1. Sometimes nitration of aromatic compounds is done simply by heating with conc. HNO_3 alone instead of a mixture of conc. HNO_3 and conc. H_2SO_4. Name the electrophile and its formation in the reaction from nitric acid alone.

2. Sometimes, HSO_3^+ is found to act as an electrophile in sulphonation, write an equation for its formation from H_2SO_4.

3. Suggest a likely electrophile formed in each of the following electrophilic substitution reaction

(*a*) $C_6H_6 + RCH = CH_2 \xrightarrow{H_3PO_4} C_6H_5—CH(R)CH_3$ (*b*) $ArH + HONO \xrightarrow{H^+} Ar—NO + H_2O$

(*c*) $ArH + Ar'N_2^+Cl^- \longrightarrow Ar—N = N—Ar'$ (*d*) $ArH + Tl(OCOCF_3)_3 \xrightarrow{CF_3COOH} ArTl(OCOCF_3)_2$

4. Suggest mechanism of deuteration of C_6H_6 with DCl.

5. Reaction of benzene with mercuric acetate, $Hg(OCOCH_3)_2$ in presence of H^+ (from $HClO_4$) gives acetoxymercurobenzene. The reaction has a significant isotope effect, suggest the mechanism for mercuration of benzene.

6. How will you prepare *n*-propylbenzene from benzene by Friedel—Craft alkylation in quantitative yield ?

7. Identify A to E in the following :

(*i*)  $\xrightarrow[\text{heat}]{D_2SO_4/D_2O}$ A

(*ii*)  + $CH_3—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}—CH_2Br \xrightarrow{AlCl_3}$ B

(*iii*)  + $CH_2Cl_2 \xrightarrow{AlCl_3}$ C

(*iv*)  + $(CH_3)_2CHCH_2OH \xrightarrow{AlCl_3}$ D

(*v*)  + $CH_3CH_2CH = CH_2 \xrightarrow{AlCl_3}$ E

7.4 Structure of Benzene

1. Kekule's structure of benzene. From analytical data, the empirical formula of benzene is found to be CH and its molecular weight 78. Hence its molecular formula is C_6H_6. Since it has lesser number of hydrogen atoms than the saturated compound having 6 carbon atoms, it seems to be unsaturated. In practice, one molecule of benzene is found to add 3 moles of chlorine (in presence of sunlight), 3 moles of hydrogen at 200°C and 3 moles of ozone indicating that benzene has three double bonds. However, benzene undergoes all the above addition reactions under abnormal conditions, moreover it does not discharge Baeyer's reagent colour ; does not react with halogen acids, these facts indicate that benzene is somewhat less reactive than the unsaturated aliphatic compounds towards addition reactions. Furthermore, benzene gives special substitution reactions like *nitration, chlorination, sulphonation, acylation etc.* very easily (these reactions are not shown by unsaturated compounds.) These observations lead to the conclusion that although benzene contains three double bonds, these double bonds are different from that present in aliphatic compounds. Benzene, when heated with hydrogen in presence of nickel as catalyst, forms cyclohexane, a six-membered cyclic compound.

$$C_6H_6 + 3H_2 \xrightarrow[200°C]{Ni—H_2}$$  or C_6H_{12}

Cyclohexane

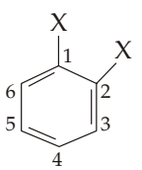
Hence benzene must be cyclohexane having three double bonds. **Kekule** in 1865 proposed given structure for benzene which he saw in dream.



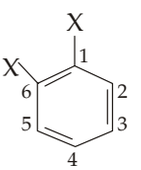
Benzene

2. Objections to Kekule's formula. However, the Kekule's structure could not explain the following characteristic properties of benzene.

(*i*) *Isomer number.* According to Kekule structure, two ortho disubstituted products are possible, *viz.* **1, 2—**(having a single bond between carbon–1 and carbon–2) and **1, 6–** (having a double bond between carbon – 1 and carbon – 6).



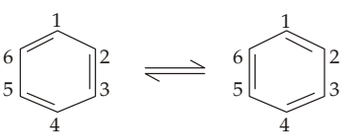
(Substituents on carbons linked via single bond)



(Substituents on carbons linked via double bond)

But in practice only one ortho disubstituted product is known.

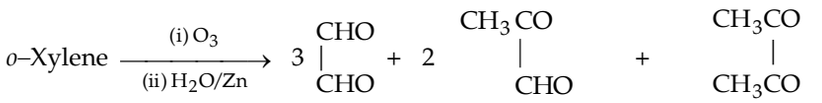
However, Kekule overcame this objection by suggesting that the double bonds in benzene are not *static* but in a state of rapid oscillation between the two forms I and II with the result each C—C pair has a single bond half of the time and a double bond the other half.



I II

Hence there is no difference between any two pairs of adjacent positions *viz.* 1, 2- and 1, 6-positions with the result there will be only one ortho disubstituted benzene.

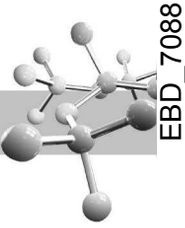
The Kekule's dynamic formula for benzene was supported from the work of Levine and Cole (1932) who subjected *o*-xylene (1, 2-dimethylbenzene) to ozonolysis and obtained a mixture of glyoxal, monomethylglyoxal and dimethylglyoxal in the ratio of 3 : 2 : 1.



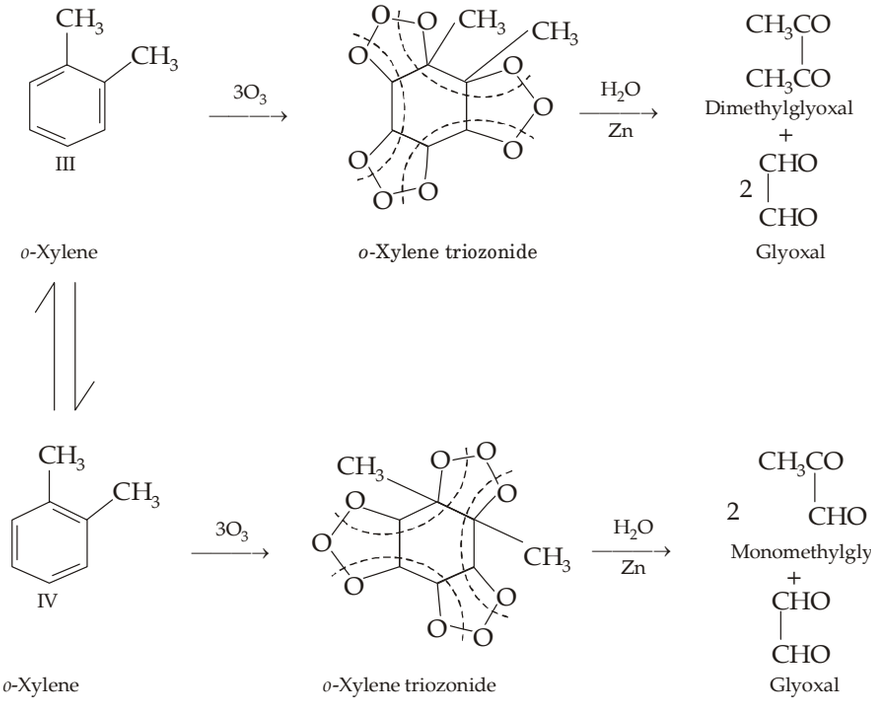
o–Xylene $\xrightarrow[(ii)\ H_2O/Zn]{(i)\ O_3}$ 3 CHO | CHO + 2 CH_3CO | CHO + CH_3CO | CH_3CO

Glyoxal Monomethylglyoxal Dimethylglyoxal

The formation of the above three products in this ratio is possible only if *o*-oxylene exists as a mixture of structure III and IV in dynamic equilibrium.



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(*ii*) *Unusual stability of benzene.* Although benzene contains three double bonds, it is quite stable and does not normally undergo addition reactions. In place of addition reactions, benzene readily undergoes substitution reactions.

(*iii*) *Heat of hydrogenation*[1] *of benzene.* On the basis of the fact that the heat of hydrogenation for a C = C of an alkene is about 28—30 (average 28.6) kcal per mole, heat of hydrogenation for cyclohexatriene (benzene) having three C = C linkages should be about (3 × 28.6) 85.8 kcal/mole, however its actual value is only 49.8 kcal/mole.



Cyclohexene
$\Delta H_{(Obs.\ and\ cal.)}$ = 28.6 kcal.

Cyclohexa-1, 3-diene
$\Delta H_{(cal.)}$ = 28.6 × 2 = 57.2 kcal.
$\Delta H_{(obs.)}$ = 55.4 kcal.

Cyclohexatriene (Benzene)
$\Delta H_{(cal.)}$ = 28.6 × 3 = 85.8 kcal.
$\Delta H_{(obs.)}$ = 49.8 kcal.

This indicates that benzene evolves (85.8 — 49.8) 36 kcal less energy than predicted which means that benzene contains 36 kcal less energy than the cyclohaxatriene (Kekule structure for benzene). In other words, benzene molecule is more stable than cyclohexatriene by 36 kcal.

(*iv*) *Carbon-carbon bond length in benzene.* Kekule's structure for benzene should also have two types of carbon-carbon bonds, *viz.* C—C (bond length 1.54 Å) and C = C (bond length 1.34 Å). However, X-ray diffraction studies have shown that all the six carbon-carbon bonds in benzene are equal with a bond length of 1.39 Å which is intermediate between C—C single bond length and C—C double bond length.

(*v*) *Heat of combustion of benzene.* The calculated heat of combustion[2] for cyclohexatriene (Kekule's structure of benzene) is 824.1 kcal, while the actual value for benzene is only 789.1 kcal. This suggests that the actual benzene molecule is more stable than the cyclohexatriene type by (824.1 – 789.1) 35 kcal.

3. Present day position regarding structure of benzene. The peculiar behaviour (*i.e.* limitations of Kekule's structure) of benzene is explained on the basis of valence bond theory and the molecular orbital theory.

(A) Valence bond theory (Resonance theory). According to the valence bond or resonance theory, benzene can't be represented by any one structural formula but as a hybrid of structures I and II.



I II

1. It is the quantity of heat evolved when one mole of an unsaturated compound is fully hydrogenated. It is abbreviated as ΔH.
2. There is a characteristic contribution from each type of bond, *e.g.* for C—H bond the value is 54 kcal, for C—C it is 49.3 kcal and for C = C it is 117.4 kcal. Thus the calculated value of the heat of combustion for cyclohexatriene (having 6C—H, 3C—C and 3C = C bonds) will be 6 × 54 + 3 × 49.3 + 3 × 117.4 = 824.1 kcal.

In other words the true structure of benzene is represented neither by I nor by II, it lies somewhere in between the two. This imaginary intermediate stage is known as **resonance hybrid.** It has 36 kcal/mole of energy less than either of the contributing structures ; this represents the resonance energy of the mole-cule. As the contributing structures (I and II) are exactly equivalent and have same stability, they make equal contribution to the overall resonance hybrid. Further since the contributing structures are identical, stabilisation of benzene due to resonance is expected to be large. The resonance hybrid structure of benzene explains all the properties of benzene.

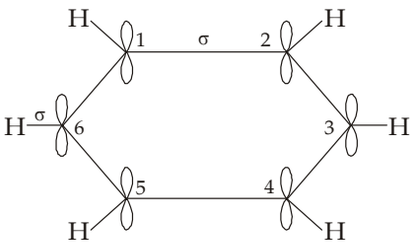
(*i*) *Isomer number.* Since all the carbon-carbon bonds in benzene are equivalent, there can be no distinction between any two ortho disubstituted products. Hence in all, only three disubstituted products (one *o*-, one *m*- and one *p*-) are possible.

(*ii*) *Bond lengths.* According to resonance hybrid structure, benzene contains no true carbon-carbon double and single bonds. In other words, all the carbon-carbon bonds in benzene are equivalent and are intermediate between single and double bonds which agrees with the observed carbon-carbon bond length (1.39 Å) in benzene.

(*iii*) *Unusual stability.* The unusual stability and peculiar behaviour of benzene is due to high resonance energy (36 kcal/mole) of benzene. In general, a *resonance hybrid is always more stable than any of the contributing structures.*

Substitution reactions in benzene rather than addition are due to the fact that in the former reactions resonance-stabilised benzene ring system is retained while the addition reactions lead to the destruction of benzene system. For example, addition of one molecule of hydrogen on benzene would destroy benzene ring and forms cyclohexadiene which is less stable than benzene.

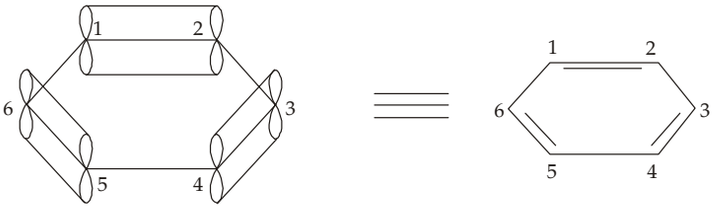
(B) Molecular orbital theory. The molecular orbital theory provides the fullest description of the benzene ring. It is based on spectroscopic and X-ray analysis according to which benzene is a flat regular hexagon molecule with all the six carbon atoms lying in the same plane and each C—C—H angle of 120°, the C—C bond length as 1.39Å and C—H bond length as 1.09Å. Therefore, each carbon atom of benzene must be in a state of sp^2 hybridisation (trigonal hybridisation) *i.e.* it possesses three sp^2 hybrid orbitals inclined at an angle of 120° and a fourth p_z orbital disposed perpendicularly to the plane of sp^2 orbitals. Two of the three sp^2 hybrid orbitals of each carbon atom overlap with the two sp^2 hybrid orbitals of the two adjacent carbon atoms forming two C—C σ bonds, and the third sp^2 hybrid orbital of each carbon atom overlaps with the *s* orbital of hydrogen atom to form a C—H σ bond. Thus after overlapping of the sp^2 orbitals, each carbon atom has two C—C σ bonds, one C—H σ bond, and one unused p_z orbital disposed at right angle to the plane of ring.



Each sp^2 hybridised carbon of benzene forming two C–C σ and one C–H σ bond and containing a *p*-orbital with one electron.

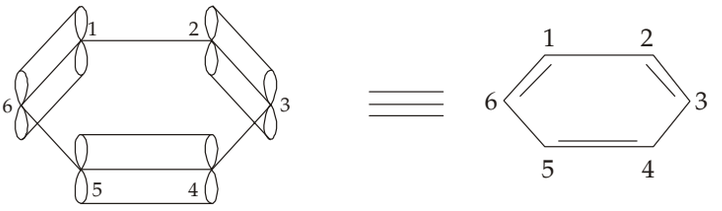
Now as in the formation of ethylene and other olefins, sideways overlapping of the remaining six p_z orbitals may generate three π-bonds in benzene. But in benzene molecule, the p_z orbital on each carbon atom can overlap in two manners. In one way, the p_z orbitals of C_1 and C_2, C_3 and C_4, and C_5 and C_6 can overlap to form three π-bonds between the respective atoms [Fig. (*i*)]. In other way, the p_z orbitals of C_2 and C_3, C_4 and C_5, and C_6 and C_1 can overlap to form three π-bonds between the respective atoms [Fig. (*ii*)].

(*i*)



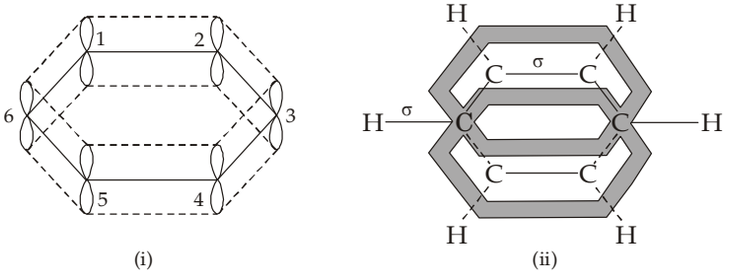
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(*ii*)



Overlapping of p_z orbitals in two possible ways.

Note that the above formulae (*i*) and (*ii*) correspond to the two Kekule structures. However, the p_z orbital of any one carbon can overlap with either of the two adjacent p_z orbitals since they are at an equal distance. Further since the system is cyclic and planar, all the six p_z orbitals overlap equally and continuously to form a π molecular orbital [Fig. (*i*)] comprising of two continuous ring-like electron clouds, one lying above and the other below the plane of carbon atoms [Fig. (*ii*)].



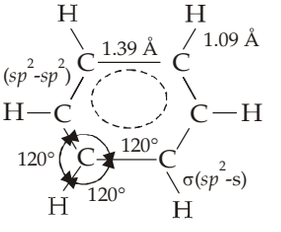
(i) (ii)

Orbital picture of benzene showing the ring-like electron clouds.

Thus we see that the six electrons of the *p* orbitals cover all the six carbon atoms, and are said to be **delocalised.** *This delocalisation of π electrons results in stronger bonds and more stable molecule.* Note that the above **structure** (*ii*) **corresponds to the resonance hybrid of the Kekule structures.** The delocalisation of π electrons of the benzene molecule explains its unusual stability. The delocalisation (resonance) energy of benzene is 36 kcal.

Evidence in favour of orbital structure. The molecular orbital structure (*ii*) of benzene explains all the known characteristics of benzene.

(*i*) *Flat ring structure.* Since each carbon atom of benzene ring is in sp^2 hybridised state, each C—C—H bond angle is of 120° and hence the resulting molecule will be flat. It is this flatness that permits the overlap of the *p* orbitals in both directions, resulting delocalization of electrons and thus stability of the molecule.



Bond angles and bond lengths in benzene.

(*ii*) *Bond length.* In benzene molecule, each C—C bond length = 1.39 Å, each C—H bond length = 1.09 Å.

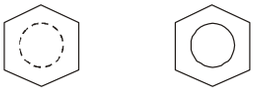
(*iii*) *Isomer number.* According to molecular orbital theory, since all the six carbon atoms of benzene are completely equivalent, hydrogen atom attached to these will also be equivalent. Hence benzene should form only one monosubstituted and three disubstituted products.

(*iv*) *Unusual stability.* This is due to delocalisation of electrons. Due to delocalisation of electrons, the term resonance energy is sometimes replaced by delocalisation energy.

(*v*) *Electrophilic substitution.* Since benzene ring is surrounded by the loosely held π-electrons cloud above and below the plane of atoms, it is readily attacked by electron-seeking reagents (electrophiles). Remember that despite of delocalisation, π electrons are more loosely held than the σ electrons and are thus readily available to an electrophile. Further, since substitution reactions lead to resonance stabilised substituted benzene derivatives, electrophilic substitutions are the main reactions of benzene.

4. Representation of benzene. For convenience, benzene ring is generally represented as a regular hexagon containing a dotted line circle [Fig. (*i*)] or a solid line circle [Fig. (*ii*)]; actually the circle denotes the cloud π electrons.

It is understood that a carbon is present at each corner of the hexagon, and each carbon carries a hydrogen atom, unless another atom or group is indicated specifically.



(i) (ii)

Representation of benzene ring.

7.5 Concept of Aromatic Character (Aromaticity)

Benzene and other organic compounds which resemble benzene in certain characteristic properties are called **aromatic compounds.** These characteristic properties constitute what is commonly known as **aromatic character** or **aromaticity.** Such important properties are summarised here.

(*i*) **Unusual stability.** Aromatic compounds are highly stable as shown by their low heats of hydrogenation and low heats of combustion. For example, heat of hydrogenation of benzene is only 49.8 kcl/mole as compared to that of the hypothetical cyclohexatriene (85.8 kcal/mole). Similarly, heat of combustion of benzene (789.1 kcal) is low as compared with that for cyclohexatriene (about 824.1 kcal).

(*ii*) **Substitution rather that addition reactions.** Aromatic compounds although possess double bonds, they do not undergo addition reactions. On the other hand, *they undergo electrophilic substitution reactions like nitration, halogenation, sulphonation and Friedel Craft's reactions.*

(*iii*) **Resistant to oxidation.** Aromatic compounds are resistant to oxidation by aq. $KMnO_4$, HNO_3 and other mild oxidising agents.

(*iv*) **Cyclic flat molecules.** Aromatic compounds generally contain five-, six- or seven-membered rings and are found to have flat (or nearly flat) structures.

7.5.1 Theoretical Criteria for Aromaticity

On the basis of molecular orbital treatment of various aromatic compounds, it has been observed that an aromatic compound must fulfill the following theoretical requirements.

(a) It must have an uninterrupted cyclic cloud of π electrons above and below the plane of the molecule (often called a π cloud). Let us look what has this means?

(i) For the π cloud to be cylic, the molecule must be cyclic.

(ii) For the π cloud to be uninterrupted, every atom in the ring must have a *p* orbital.

(iii) For the π cloud to be formed, each *p* orbital must be able to overlap with the *p* orbitals on either side of it. Therefore, the molecule must be planar.

(b) The π cloud must contain an odd number of pairs of π electrons. **(4*n* + 2)** π electrons, where *n* is an integer *i.e.* its value may be 0, 1, 2, 3, 4 ... This rule is known as **4n + 2π rule** or **Huckel rule.** Thus according to Huckel rule, the number of π electrons in an aromatic compound may be 2 ($n = 0$), 6* ($n = 1$), 10 ($n = 2$), 14 ($n = 3$), 18 ($n = 4$), etc. ; in benzene it is 6 ($n = 1$). Huckel's rule is strongly supported by several examples.

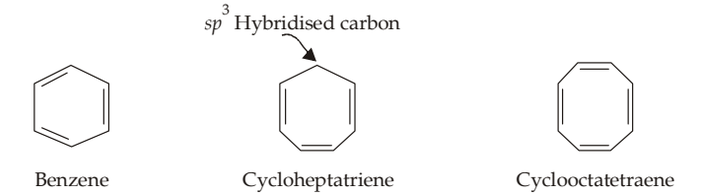
Let us observe the beauty of validity of the above two points in deciding aromaticity of benzene, cycloheptatriene and cyclooctatetraene.

1. **Benzene.** It is a cyclic and planar compound having three alternate double bonds. Thus each carbon of the ring has a *p* orbital (electron) and hence a continuous (cyclic) cloud of 6 π electrons is present. Thus according to Huckel rule :

$$4n + 2 = 6 \; ; \qquad \therefore \quad 4n = 4 \quad \text{or} \quad n = 1$$

Now since here $n = 1$ which is an integer, the compound (benzene) obeys Huckel rule and hence must be aromatic.

2. **Cycloheptatriene.** It is a cyclic and planar. It has three double bonds and six π electrons. But not that here one of the carbon is saturated (sp^3 hybridised) and hence does not possess a *p* orbital with the result a continuous (cyclic) bond of π electrons is not possible. Therefore, this compound although obeys Huckel rule (because here *n* comes out to be 1 as in benzene), it is not aromatic because of absence of cyclic cloud of π electrons.



Benzene
Aromatic, $n = 1$

Cycloheptatriene
Non-aromatic, $n = 1$

Cyclooctatetraene
Non-aromatic, $n = 1.5$

Absence of cyclic cloud of π electrons

* The Huckel number 6 is the most common in aromatic system and hence the term aromatic is commonly used for the 6 π electrons.

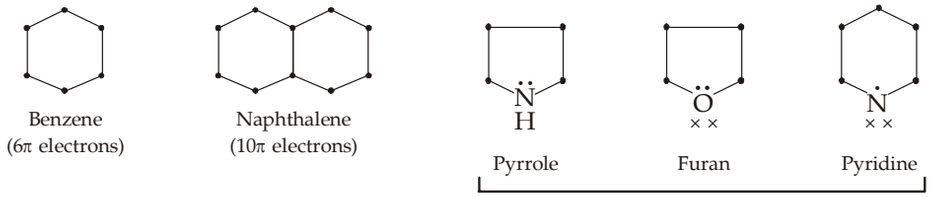
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3. **Cyclooctatetraene.** It is a cyclic compound having four alternate double bonds. Thus here the number of π electrons is 8 which does not fit in Huckel rule (because n comes out to be 1.5 which is not an integer).

$$4n + 2 = 8 \; ; \qquad \therefore \quad 4n = 6 \quad \text{or} \quad n = 1.5$$

Hence cyclooctatetraene is non-aromatic. Moreover, it is found to be tub-shaped (not planar).

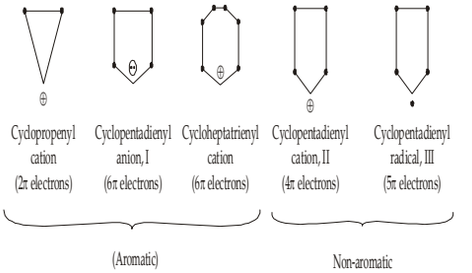
4. **Non-benzenoid compounds.** On the basis of the above considerations, it is apparent that an aromatic compound need not necessarily contain a benzene ring, and actually several compounds not having benzene ring are found to be aromatic in nature. Thus in other words, we can say that an aromatic compound may be **benzenoid** (having benzene ring) or **non-benzenoid**[1] (without benzene ring). In fact **all that is required for aromaticity is the presence of a flat ring** (whether benzenoid or not) **with (4*n* + 2) π electrons in the form of continuous electron clouds above and below the plane of the ring.** The following cyclic systems fulfil the above two conditions of aromaticity and thus are found to be aromatic in nature.



NOTE

Dot (or a pair of dots) represents the electron(s) present in a *p* orbital lying parallel to each other and hence are capable of overlapping and ultimately producing electron clouds. On the other hand, a pair of '×' represents unused electrons in an sp^2 orbital lying perpendicular to the ring and hence do not take part in the formation of electron clouds.

5. **Cyclic ions.** In addition to the above neutral molecules, there are number of cyclic ions which are aromatic according to Huckel's rule. For example, cyclopropenyl cation, cyclopentadienyl anion and cycloheptatrienyl cation.



dfdfd

Further, the Huckel rule is supported by the fact that unlike cyclopentadienyl anion I (having 6π electrons), the corresponding cation II (having 4π electrons), and the free radical III (having 5π electrons) do not exhibit aromaticity.

It may be noted that the Huckel number 6 is the most common in aromatic system and hence the term **aromatic sextet** is commonly used for these 6π electrons. Lastly, it must be noted that **benzene is a perfect aromatic compound as it has 6π electrons over a flat hexagonal ring.** Since the regular hexagonal angle (*i.e.* 120°) is exactly the same as that of sp^2 hybridised orbitals, there is no angle strain at all in the molecule. However, in case of other flat rings of smaller or bigger size than benzene, there is always some angle strain which adversely affects the aromatic stability.

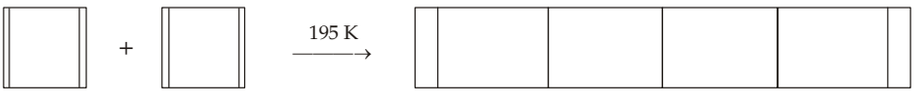
Earlier it was thought that other cyclic hydrocarbons with conjugated systems of alternating single and double bonds would show similar stability. These cyclic hydrocarbons with alternating single and double bonds are called **annulenes**. For example, benzene is the six-membered annulene, so it can be named [6] annulene, cyclobutadiene as [4] annulene, cyclooctatetraene [8] annulene, and so on. However, cyclobutadiene and cyclooctatetraene are not aromatic, but these are antiaromatic, as explained below.

7.5.2 Aromaticity

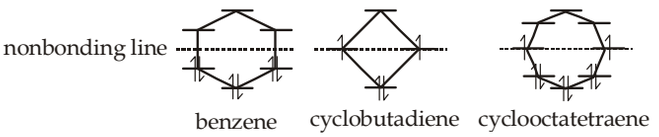
Planar cyclic conjugated species, less stable than the corresponding acyclic unsaturated species, are called **antiaromatic.** Molecular orbital calculations have shown that such compounds have $4n\pi$ electrons. In fact, such cyclic compounds which have $4n\,\pi$ electrons are called **anti-aromatic compounds,** and this characteristic is called **anti-aromaticity.** Thus antiaromatic compounds fulfill the first criterion for aromaticity but it does not fulfill the second criterion, $(4n + 2)\pi$ electrons.

1. Certain compounds (*e.g.* pyrrole, furan, etc.), although do not contain benzene ring, behave like benzene and hence grouped under aromatic compounds ; such compounds are called **non-benzenoid aromatic compounds.**

It is important to note that 1, 3-cyclobutadiene, is less stable than the acyclic 1, 3-butadiene which is confirmed by the higher π electron energy of cyclobutadiene than that of 1,3-butadiene. Cyclobutadiene is such an unstable molecule that even at 195 K, it undergoes Diel's-Alder cycloaddition to form a dimer. The reactivity is probably due to **anti-aromaticity.**



Thus cyclic conjugation, although necessary for aromaticity, is not the only criterion for aromaticity. Actually all π electrons should be present in bonding orbitals in pairs. Cyclobutadiene and cyclooctatetraene are not aromatic because in each case the two π electrons are present not in bonding orbitals but one in each, non-bonding orbitals.



Distribution of π electrons in benzene, cyclobutadiene and cyclooctatetraene

Cyclobutadiene is rectangular (not square) in shape while cyclooctatetraene is nonplanar (tub-shaped) molecule. None of the two compounds show resonance.

In terms of Huckel rule, antiaromatic compounds have cyclic, non-planar structures with $4n$ π electrons. They are destabilised by resonance. Some more examples of antiaromatic species are



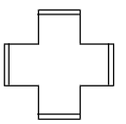
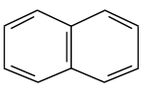
Cyclopropenyl anion (4π electrons) | Cyclopentadienyl cation (4π electrons) | Cycloheptatrienyl anion (8π electrons) | Cyclooctatetraene (8π electrons)

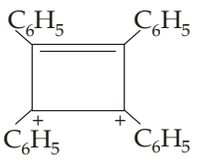
Relative stability order : Aromatic > Non-aromatic > Anti-aromatic

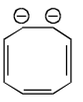
TEST YOUR UNDERSTANDING - 7.2

1. Using the Huckel rule, indicate whether the following species are aromatic or antiaromatic

(*i*) 
(*ii*) 
(*iii*) 
(*iv*) 
(*v*) 

(*vi*) 
(*vii*) 
(*viii*) 
(*xi*) 
(*x*) 

(*xi*) 

(*xii*) 

2. Cyclopentadiene and cycloheptatriene are not aromatic in nature, but azulene (having these two rings fused through two adjacent carbon atoms) is aromatic in nature. Explain.

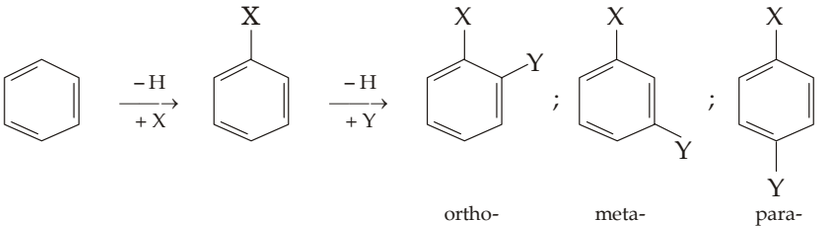
3. A red coloured compound is formed by the reaction of 2 moles of $AgBF_4$ with 1 mole of 1, 2, 3, 4-tetraphenyl-3, 4-dibromocyclobut-1-ene. Comment on the solubility, coloured nature and aromatic character of the compound.

4. Can you correlate the basic character of pyridine and pyrrole on the basis of delocalisation of π electrons of the cyclic cloud ?

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7.6 Substitution in the Monosubstitutedbenzenes

As discussed earlier, all the six hydrogen atoms of benzene nucleus are identical ; hence when one group (say X) is introduced into the benzene nucleus only one product is obtained. On the other hand, when a second substituent (say Y) is introduced in a monosubstituted derivative, three isomeric disubstituted products are possible.

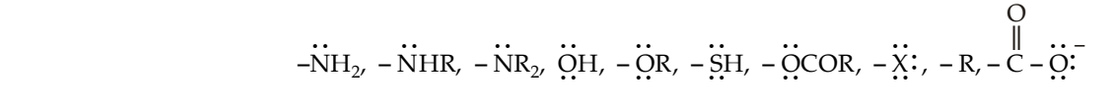


Disubstituted derivatives

However, experiments have shown that all the three products are never formed in quantitative yield and actually the main product is either a mixture of *ortho*- and *para*-isomers (*m*-isomer being negligible in amount) or only the *meta*-isomer (*o*- and *p*-isomers being negligible in amount). Further experiments have shown that it is the nature of the group already present (X in the above case) on the benzene nucleus that directs the new incoming group (Y in the above case) either to *ortho* and *para* positions (both) or only to *meta* position. *This effect of the group already present on the nucleus is known as* **directing influence of the group** or **orientation effect.** On the basis of this effect all the known groups in organic chemistry have been classified into two types.

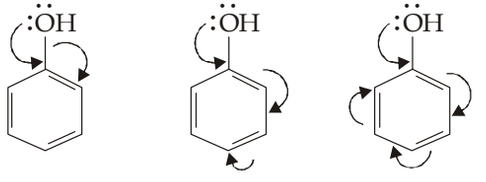
7.6.1 *o-, p-*Directing Groups

These groups direct the incoming group predominantly to the o- and p-positions (the *m*-product, being negligible). Some of the important groups of this type are

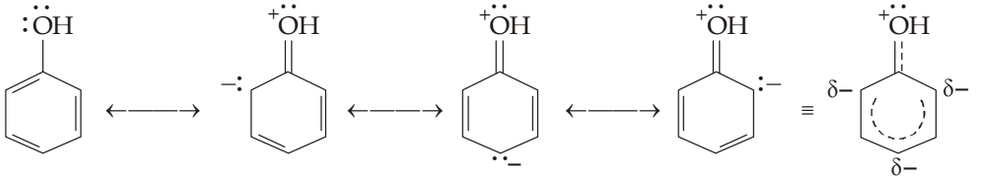


(– COO^- is – COOH group in presence of alkali)

Note that all the *o*-, *p*-directing groups except alkyl and —COO^- have unshared pair of electrons on the atom attached to the benzene nucleus (**key atom).** Such groups, *except halogens*[1], are **electron releasing groups** due to + E and + M effects and hence increase the electron density on the benzene nucleus in the *o*- and *p*-positions (*activation of the ring*) and thus they direct the new entrant to the *o*- and *p*-positions.



Electromeric effect (+ E) in *o*-, *p*-directing groups



Mesomeric effect (+ M) in *o*-, *p*-directing groups

Further since such groups increase electrons density in the nucleus, they facilitate further, electrophilic substitution and hence known as **activating groups.**

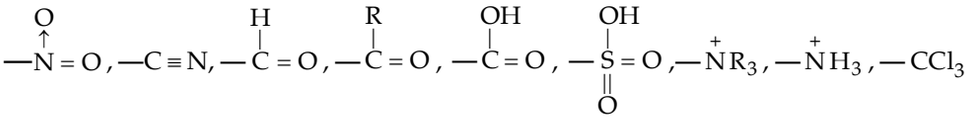
1. Halogens are strongly electron-attracting due to their high electronegativity.

Chlorine (halogen) *is although o-, p-directing due to + E and + M effects, it deactivates the ring due to strong – I effect.* But since + T^* > – I, substitution will be taking place in *o*- and *p*- positions, but with difficulty (it is difficult to carry out the substitution in chlorobenzene than in benzene).

Thus benzene having any of the activating groups undergoes electrophilic substitution very easily as compared to benzene itself. Thus toluene ($C_6H_5CH_3$), phenol (C_6H_6OH), aniline ($C_6H_5NH_2$), etc. undergoes bromination very readily than benzene.

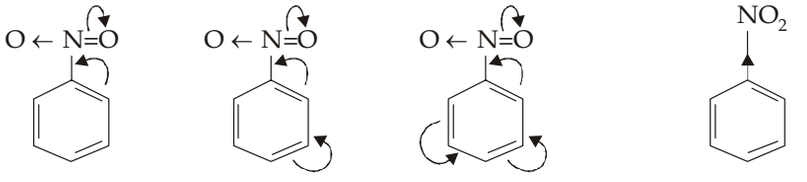
7.6.2 *m*-Directing Groups

These groups direct the incoming group predominantly to the *m*-position (the *o*- and *p*-isomers, being negligible in amount). Some of the important *m*-directing groups are

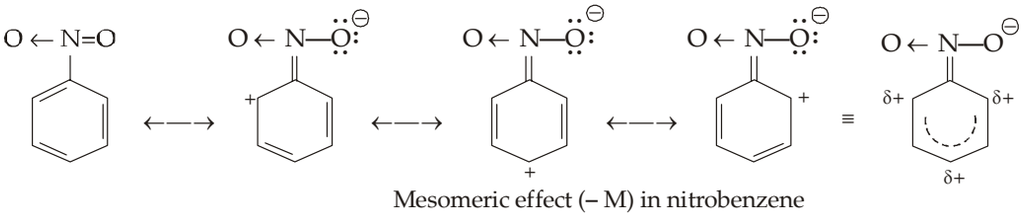


(—N^+H_3 is —NH_2 group, *e.g.* aniline, in presence of acid)

Note that all the *m*-directing groups, *except* — CCl_3 , either possess a positive charge or the key atom of the substituent has an electronegative atom linked by a multiple bond. The benzene nucleus containing these groups will undergo all the three** effects (—E, —M and —I) in such a manner that the displacement of the electrons takes place away from the nucleus and towards the group, *i.e.* they withdraw electrons from the *o*- and *p*-positions, and thus direct the new entering electrophile to the *m*-position which is having relatively high electrons density (since *m*-positions are not affected by the existing group). Moreover, since *m*-positions are almost unaffected and the *o*- and *p*-positions have less electron density, these groups are said to *deactivate the benzene nucleus, i.e.* they hinder the further substitution and hence known as **deactivating groups.**



Electromeric effect (– E) in nitrobenzene Inductive effect (– I) in nitrobenzene



Mesomeric effect (– M) in nitrobenzene

Thus benzene ring having any of the deactivating group undergoes electrophilic substitution with a great difficulty as compared to benzene itself. Thus nitrobenzene ($C_6H_5NO_2$), benzoic acid (C_6H_5COOH) etc. are very difficult to nitrate while benzene can be nitrated easily.

Summary of effect of groups on electrophilic aromatic substitution

(*i*) **Activating : *o*, *p*-directors**

(*a*) Strongly activating : —NH_2,—NHR, —NR_2, —OH, — $\ddot{O}:^-$

(*b*) Moderately activating : —$NHCOCH_3$, —OCOR, —OR

(*c*) Weakly activating : —C_6H_5, —R, –CH = CH_2

(*ii*) **Deactivating : *m*-directors** —NO_2, —NMe_3^+, —CCl_3, —CN, —COOH, —COOR, —SO_3H, —CHO, —COR

(*iii*) **Deactivating : *o*, *p*-directors** : —F, —Cl, —Br, —I

---

* The sum of E and M effects is known as tautomeric effect (T) or conjugative effect.

** The —CCl_3 , —$\overset{+}{N}H_3$ and —$\overset{+}{N}R_3$ groups undergo only —I effect.

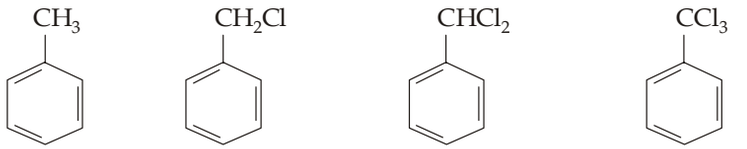
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7.7 Role of Inductive and Hyperconjugative Effects in Aromatic Substitution of the Substitutedbenzenes

7.7.1 Effect of Alkyl Group

Since the alkyl group does not have any lone pair of electrons, it will neither undergo electromeric effect nor mesomeric effect (except Kekule's structures for benzene). However, the alkyl group, *e.g.*, methyl undergoes strong + I effect which increases electron density in the *op*-positions and hence directs the entering group in these positions.

The importance of inductive effect in directing further substitution in toluene can be illuminated by the following observation : as the hydrogen atoms of the methyl group are replaced by halogens, which exert —I effect, % of *m*-product increases at the expense of the *o*, *p*-products.

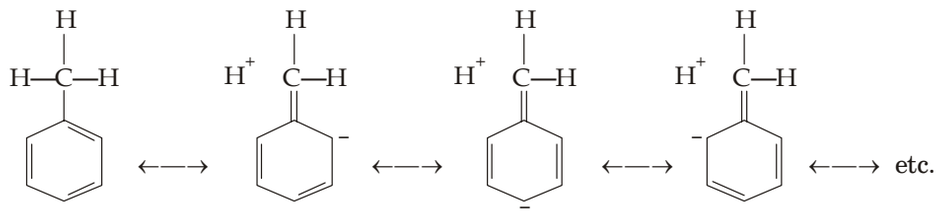


% of meta :	4	14	34	64
Activating influence :	Activating	Weakly deactivating	Moderately deactivating	Strongly deactivating

The orienting influence of the alkyl group should, therefore, be entirely due to inductive effect (but it is not so, see later) which is in the following order :

$$CH_3 < CH_2CH_3 < CH(CH_3)_2 < C(CH_3)_3$$

It means that the activating effect (orienting effect) of an alkyl group should also be in the same order, but in a number of cases the order is found to be reverse. It is explained on the basis of *hyperconjugation* effect which is greatest in the methyl group and lowest in *tert*-butyl group.

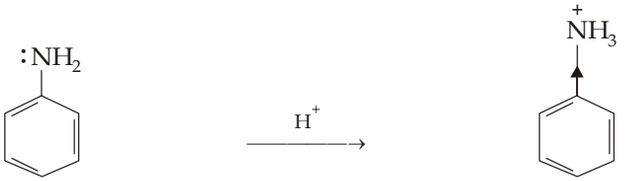


Hyperconjugation in toluene

Thus the *o*, *p*-directing influence of methyl group is due to inductive as well as hyperconjugation effect. Formation of a lesser amount of *ortho*-product in case of *tert*-butyl group may partly be explained on the basis of steric hindrance.

7.7.2 Effect of Anilinium Ion ($\overset{+}{N}H_3$)

It is very important to note that aniline is *o*, *p*-directing in aqueous solution but in presence of strong acids it mainly gives the *m*-substitution product. The formation of the latter product is explained by the fact that in presence of strong acids it forms anilinium ion which exerts a strong —I effect, due to the presence of positive charge, and thus mainly yield the *m*-substituted product.

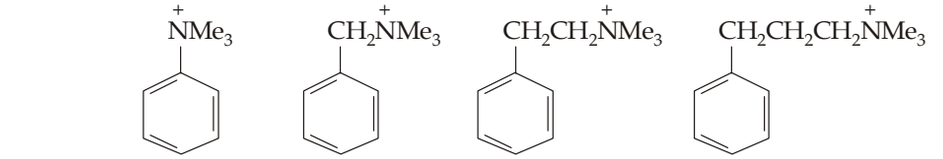


Aniline (*o*, *p*-directing due + T effect) Anilinium ion (*m*-directing due to – I effect)

However, the formation of a small amount of *o*- and *p*-substituted anilines in presence of strong acid is due to the small residual concentration of free aniline, a very weak base. Due to the activated nucleus, the free aniline undergoes *o*- and *p*-substitution very fast.

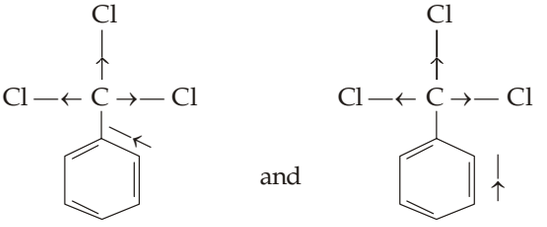
7.7.3 Effect of $\overset{+}{N}R_3$ Group

Due to the presence of positive charge, the group will exert a strong —I effect and withdraws electrons from the *o*- and *p*-positions and thus leaves the *m*-positions, the point of relatively high electrons density where the substitution will take place. That the positive charge on the nitrogen atom (or —I effect) is responsible for the *m*-substitution can be proved by the fact that as the distance of the positive center from the benzene nucleus is increased by the introduction of CH_2 the percentage of *m*-product decreases, *e.g.*



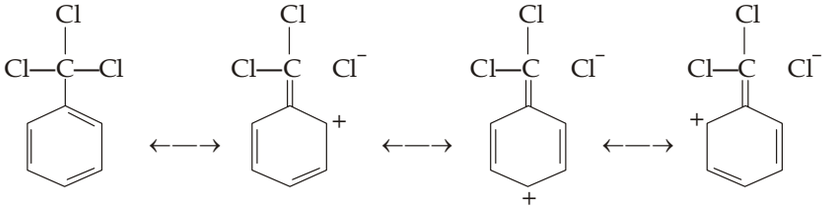
7.7.4 Effect of —CCl_3 Group

The *m*-directing influence of the —CCl_3 group is again mainly due to —I effect which can be represented as below in case of benzorichloride.



Inductive effect (– I) in benzotrichloride

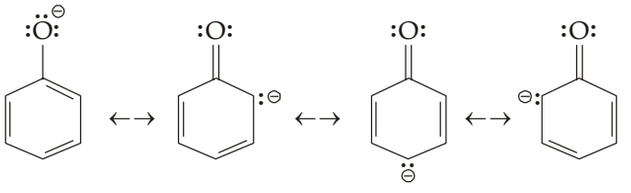
The *m*-directing influence of the —CCl_3 group may also be explained by hyperconjugation.



7.8 Orientation of Some Special Groups

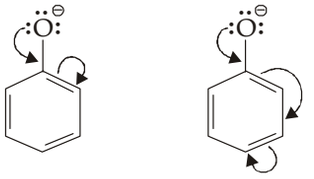
7.8.1 Effect of Phenoxide

(*Phenol in presence of alkali*)**.** In presence of strong alkali, phenol forms sodium phenate which easily ionises into phenoxide ion. The phenoxide ion is *o*-, *p*-directing due to all the three effects *viz.* + M, + E and + I effects.

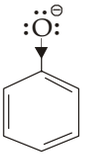


Mesomeric effect (+ M effect) in phenoxide ion

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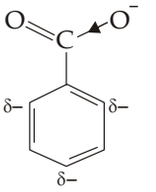
Electromeric effect (+ E) in phenoxide ion



Inductive effect (+ I) in phenoxide ion due to the presence of negative charge

Since in the phenoxide ion, all the three effects reinforce each other, substitution is very easy.

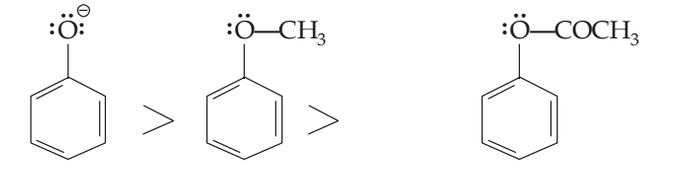
7.8.2 Effect of Carboxylate Ion



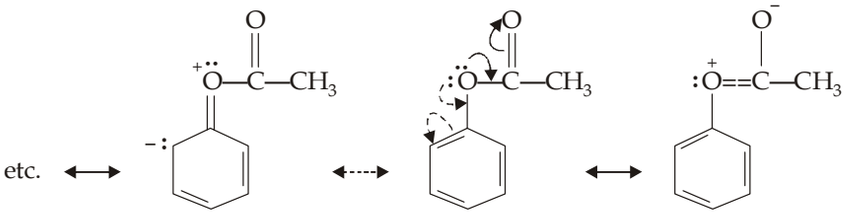
(*Carboxylic acid in the presence of alkali*)**.** Like the phenoxide ion, ions of acids in presence of base undergo *o*-, *p*-substitution (whereas the acids undergo *m*-substitution). It is again explained on the basis of inductive effect; the presence of negative charge on the oxygen atom pushes the electrons into the *o*- and *p*-positions of the nucleus which become the point of attack for the electrophilic attack.

7.8.3 Effects Produced by the Protection of Hydroxy and Amino Groups

It is very important to note that the *o*-, *p*-substitution of the following three derivatives of phenol follows the order given below.



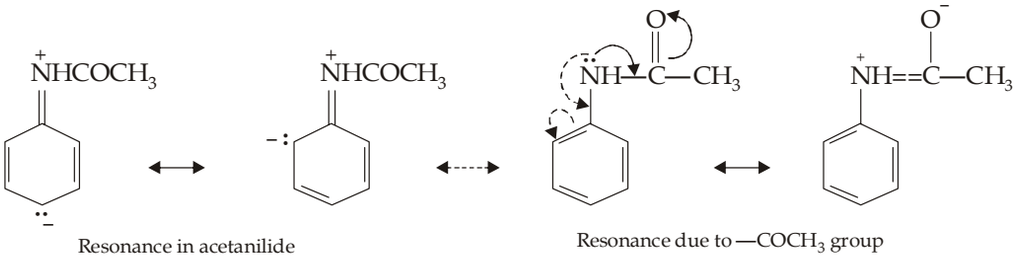
Phenoxide ion > Anisole > Acetyl phenyl ether (Phenyl acetate)



Acetyl pheyl ether showing the resonance of acetyl group.

The maximum ease for *o*, *p*-substitution of phenoxide ion is due to the fact that the negatively charged oxygen with its three unshared electron pairs can supply electrons very effectively due to + I, + E and + M effects. On the other hand, the methoxy and acetoxy groups have only two unshared electron pairs instead of three, so they are less susceptible to electrophilic attack than the phenoxide ion. Moreover, in the acetoxy group the electron availability to the benzene nucleus is further diminished by resonance in acetoxy group. Thus, **although the acetoxy group is an activating** *o*, *p*-**directing group, its activating effect is less than the methoxy group and much lesser than that of the phenoxide ion.**

Similarly, deactivation effect of the amino group is produced by its acetylation.



Resonance in acetanilide

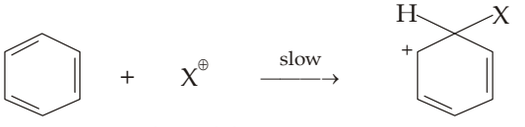
Resonance due to —$COCH_3$ group

Summary of Directive Influence of Groups

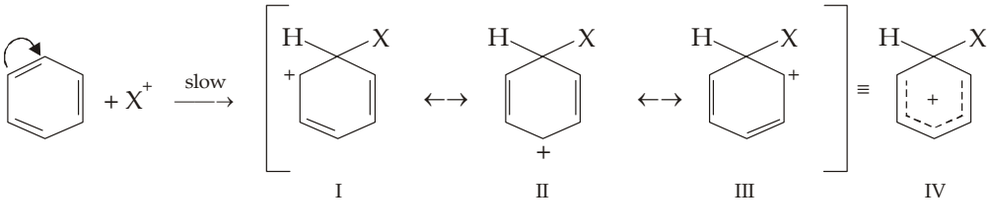
Group	*Electronic effects and their net result*	*Rate controlling effect*	*Oreinting effect*
—$\ddot{O}:^-$ (Phenoxide ion)	+ E, + M, + I (Electron release)	Strongly activating	*o, p*
—$\ddot{N}R_2$, —$\ddot{N}HR$,	+ E, + M, – I (Electron release)	Strongly activating	*o, p*
—$\ddot{N}H_2$, —$\ddot{O}H$, —$\ddot{O}R$			
—$\ddot{N}HCOR$, —$\ddot{O}COR$	+ E, + M, – I (Electron release)	Moderately activating	*o, p*
—C_6H_5	+ M, – I (Electron release)	Weakly activating	*o, p*
—R	+ I, hyperconjugation	Weakly activating	*o, p*
—CH = CH_2	+M (Electron release)		*o, p*
—$\ddot{Cl}:$, —$\ddot{Br}:$, $\ddot{I}:$	+ E, + M, – I (Electron release)	Weakly deactivating	*o, p*
—NO_2, —CN, —SO_3H, —COOH, —COOR, —CHO, —COR	– E, – M, – I (Electron withdrawl)	Strongly deactivating	*m*
—$\overset{+}{N}H_3$, —$\overset{+}{N}R_3$	– I (Electron withdrawl)	Strongly deactivating	*m*
—CCl_3	—I, hyperconjugation (Electron withdrawl)	Strongly deactivating	*m*

7.9 Theory of Reactivity Based on Carbocation (σ-Complex) Stability

We know that in every electrophilic aromatic substitution reaction, first step (slow and thus rate determining) is the attack of an electrophile on benzene ring to form a carbocation.



Further we know that the carbocation is a resonance hybrid (represented as IV) of structures I, II and III, *i.e.* its positive charge is not localised on one carbon atom but dispersed over the entire ring, of course it is strongest at positions ortho and para to the carbon atom being attacked.

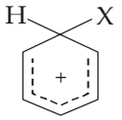


Now since dispersal of the positive charge stabilizes the carbocation, more the chances for the dispersal of positive charge more is the stability of the carbocation and hence greater is the reactivity of the compound toward electrophilic

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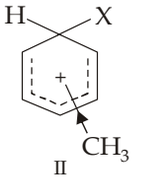
substitution. Thus *any substituent (e.g. electron-releasing groups) which stabilises the intermediate carbocation by dispersing the positive charge will increase the overall rate of reaction, while a substituent (e.g. electron-atitracing groups) which destabilises the intermediate carbocation by intensifying (concentrating) the positive charge will decrease the rate of reaction.*

Let us compare the rates of substitution in benzene, toluene and nitrobenzene. The intermediate carbocations of the three compounds with the electrophile X^+ have the following structures.



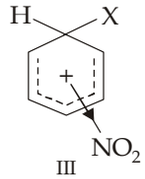
I

Carbocation has no substituent hence less stable than II but more than the III



II

Carbocation stabilised by dispersal of positive charge by electron-releasing —CH_3 group



III

Carbocation destabilised by intensification of positive charge by electron-withdrawing —NO_2 group

Note that in II, the —CH_3 group, being electron-releasing, releases electrons and thus tends to neutralise positive charge of the ring and itself becomes somewhat positive. This dispersal of positive charge of the ring stabilises the carbocation and hence facilitates its formation which ultimately results an increased rate of reaction. Now since such factor (substituent) is not present in benzene, its carbocation I is relatively less stable than II. Hence toluene undergoes electrophilic substitution at a faster rate than benzene. This is also true when benzene has —NH_2, —OH, —OCH_3, —$NHCOCH_3$,or —C_6H_5 group in place of —CH_3 group. However, remember that electron release by —NH_2, —OH and their derivatives (—$NHCOCH_3$, —OCH_3, —$OCOCH_3$) is not due to the inductive effect but due to resonance.

On the other hand, in carbocation III the —NO_2 group (an electron-withdrawing group) intensifies positive charge on the ring and thus destabilises the carbocation III and hence its formation becomes difficult which ultimately results a slower reaction. Now since such substituent is not present in benzene, its carbocation I is relatively more stable than the III. Hence nitrobenzene undergoes electrophilic substitution at a slower rate than benzene. This is also true when benzene has —N^+Me_3, —CN, —SO_3H, —COOH, —CHO, —COR or — X group in place of —NO_2 group.

Summary

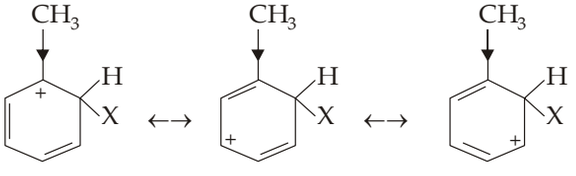
We can say that an electron-releasing group stabilises the carbocation by dispersing its positive charge and thus activates the ring while an electron-withdrawing group destabilises the carbocation by intensifying its positive charge and thus deactivates the ring. Further, an activating group activates although all positions of the benzene ring, its activating effect is much more on ortho and para positions than on meta position with the result substitution occurs mainly on the ortho and para position. Similarly, a deactivating group deactivates although all positions in the ring, its deactivating effect is much more on ortho and para positions than on meta position with the result further reaction occurs mainly on the meta position. In short, the activating or deactivating effect of a group is strongest at the ortho and para-positions.

7.10 Theory of Orientation and Carbocation Stability

The *ortho-, para- or meta-* directing nature of the groups can also be explained on the relative stabilities of the intermediate carbocations. For convenience, the effects of different substituents are considered under four sub-heads.

7.10.1 Ortho-, para- Directing Groups with + I Effect

The simplest example of such group is a methyl group. So let us draw and compare the intermediate carbocations formed by electrophilic attack at the ortho, para and meta positions of toluene. Each of these carbocations is a resonance hybrid of three structures as shown below.



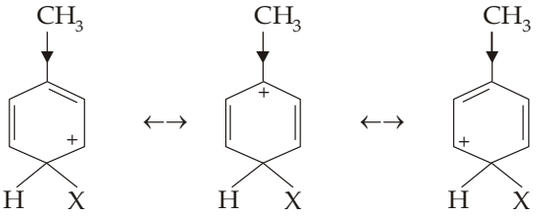
Ortho substitution

Ia

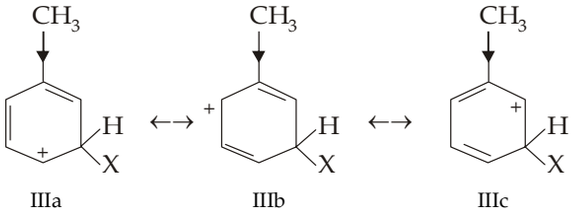
Especially stable (because positive charge is present on C carrying + I group and hence easily neutralised)

Ib

Ic



Para substitution



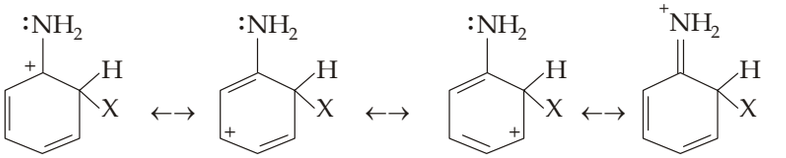
Meta substitution

It is to be noted that in the contributing structures Ia of the ortho substitution and IIb of the para substitution, the positive charge is located on the carbon atom carrying the methyl (an electron-releasing) group. These structures have special significance because the electron-releasing methyl group although releases electrons to all positions of the ring, it does so most strongly to the carbon atom nearest to it with the result the positive charge on such a carbon is highly dispersed and hence the concerned structures (Ia and IIb) are particularly stable. On account of contribution from structures Ia and IIb, the hybrid carbocations formed during attack at ortho and para positions are more stable than the hybrid carbocation (having no structure like Ia and IIb) formed during the attack at meta position. As a result, *o, p*-substitution is faster than *meta* substitution in toluene. The situation is practically the same in case of all other alkyl groups.

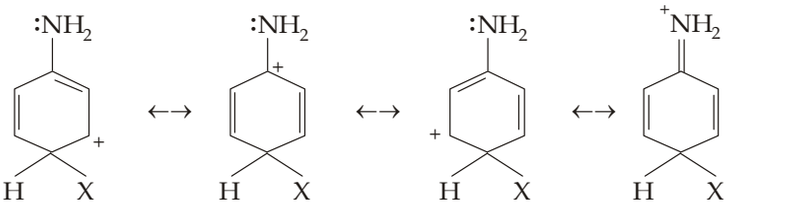
7.10.2 Ortho–, para– Directing Groups having Weaker –I and Stronger + M Effects

From our previous study we know that all *o, p*-directing groups, *except alkyl groups*[1], exert – I and + M effects and further that in all such groups, *except halogens*[2], + M effect is much stronger and hence more important than the —I effect with the result all *o, p*-directing groups, except halogens, activate the benzene ring for further substitution. Since activating effect is stronger in *o, p*-positions than in the *m*-position, further substitution occurs in *o, p*-positions. Now let us explain the *o, p*-directing effect of such groups (*e.g.* —NH_2 group) on the basis of stabilities of the intermediate carbocations.

The carbocations formed by electrophilic attack at the *o*-, *p*- and *m*-positions of aniline are resonance hybrids of the corresponding structures shown below.

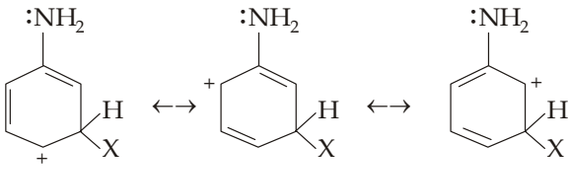


Ortho substitution



Para substitution

1. Alkyl groups undergo + I effect and no mesomeric effect.
2. In halogens, two opposite effects (– I and + M) are operating. Here, although further substitution takes place in *o, p*-positions due to + M effect, the ring is weakly deactivated due to —I effect, *i.e.* further substitution is not easy.



VIa VIb VIc

Meta substitution

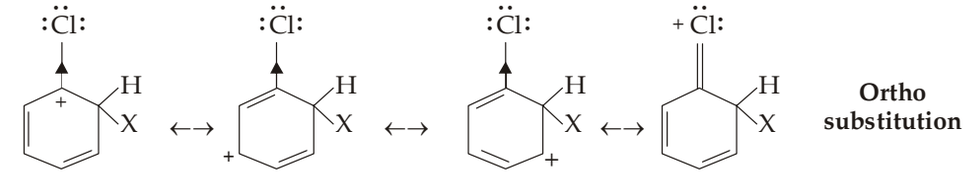
Note that the carbocations of *ortho* and *para* substitutions are hybrids of four contributing structures, while that of *meta* substitution is a hybrid of only three structures. Further, it must also be noted that the contributing structures IVd (of the ortho substitution) and Vd (of the para substitution) are particularly stable since in these, every atom has a complete octet of electrons except hydrogen which has a duplet. Consequently the hybrid carbocations formed during *ortho* and *para* substitutions are much more stable than the hybrid carbocation formed during *meta* substitution, which has no structure comparable to IVd and Vd, or during the attack on benzene itself. Hence substitution in aniline occurs faster than in benzene and mainly in the *ortho*- and *para*-positions.

A similar explanation is applicable to other groups like —$\ddot{N}$HR, —$\ddot{N}R_2$, —$\ddot{O}$H, $\ddot{O}$R, etc.

7.10.3 *o, p*-Directing Groups having Stronger —I and Weaker + M Effects (Effect of halogens)

The effect of halogens is partly similar to that of the type of —NH_2 group discussed just above (both exert + M effect) with the significant difference that the halogens exert strong – I effect while the —NH_2 type of groups exert weak —I effect. The strong —I effect of halogens bears an important implication on the stability of the carbocations formed by the attack of an electrophile on the ortho and para positions.

The various contributing structures of the carbocations formed by the attack of an electrophile (X^+) on the *o*-, *p*- and *m*-positions of a halogenobenzene (*e.g.* chlorobenzene) are drawn below.



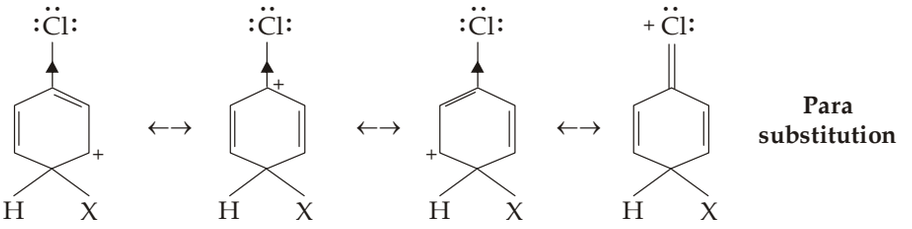
VIIa
Especially unstable (positive charge is present on C carrying strong – I group)

VIIb

VIIc

VIId
Comparatively stable (Every atom has complete octet)

Ortho substitution



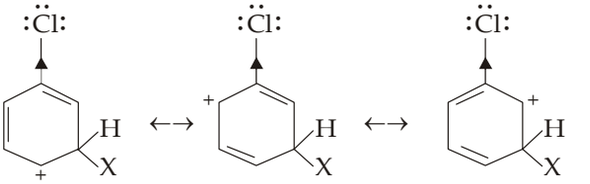
VIIIa

VIIIb
Especially unstable (positive charge intensified on C carrying —Cl group)

VIIIc

VIIId
Extra resonance form comparatively stable (Every atom has octet of electrons)

Para substitution



IXa IXb IXc

Meta substitution

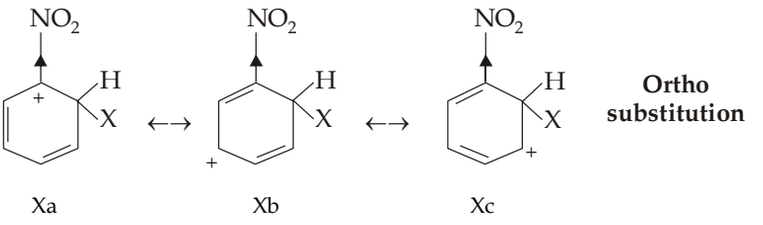
Evidently, structures VIId (in ortho substitution) and VIIId (in para substitution) are comparatively stable since in these structures every atom (except hydrogen) has a complete octet of electrons, while structures VIIa (in ortho substitution) and VIIIb (in para substitution) are particularly unstable since in these structures the positive charge is intensified to the maximum extent because electron-withdrawing substituent (—Cl) is present nearest to the carbon bearing positive charge. However, the stabilisation by structures VIId and VIIId is more than the destablisation by structures VIIa and VIIIb. The net result is that the carbocations formed by ortho and para substitutions are more stable than that of meta. Hence the substitution will predominantly take place in *o*, *p*-positions.

The inductive effect (—I) of —Cl deactivates the ring particularly at ortho and para positions. However, the —I effect is opposed by electron releasing mesomeric effect (+ M effect) which is effective only for attack at ortho and para positions. The net result is that the ortho and para positions are deactivated to a lesser extent than the meta position. Consequently, further substitution can take place primarily at ortho and para positions (due to + M effect) although the rate of reaction is slower (due to —I effect) than in case of benzene.

Thus we see that **in halogenobenzenes, reactivity is controlled by the stronger inductive effect while orientation is controlled by the resonance effect.**

7.10.4 Effect of *m*-Directing Groups

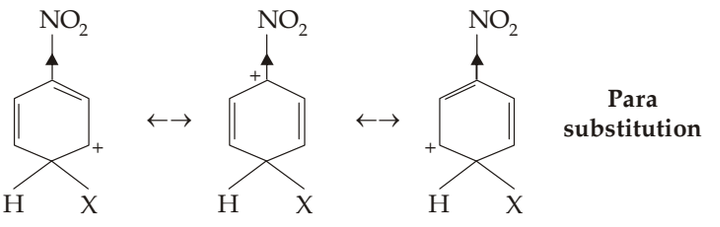
From our previous study we know that all *m*-directing groups are deactivating and, except $—\overset{+}{N}H_3$ and $—\overset{+}{N}R_3$, exhibit —I and —M effects, while the two exceptional groups show only —I effect. Let us explain the deactivation and meta orientation effect on the basis of carbocation stability. The carbocations formed by attack at the ortho, para and meta positions of nitrobenzene are hybrids of the contributing structures given below in each case.



Ortho substitution

Xa Xb Xc

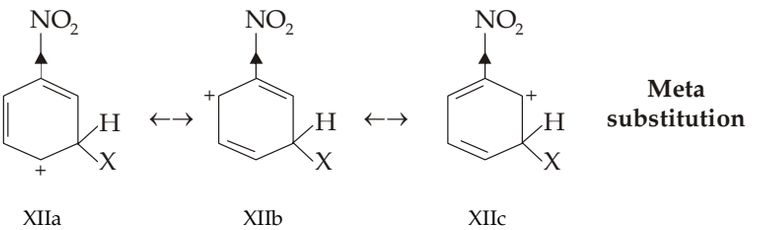
Especially unstable
(Positive charge on C,
carrying –I group, intensified)



Para substitution

XIa XIb XIc

Especially unstable
(Positive charge on C,
carrying – I group, intensified)



Meta substitution

XIIa XIIb XIIc

Evidently, structures Xa (in ortho substitution) and XIb (in para substitution) are particularly unstable because in these structures positive charge is located on the carbon atom carrying the electron-attracting ($—NO_2$) substituent and hence is not dispersed but intensified. Thus these structures (Xa and XIb) are particularly unstable and contribute little to stabilise the carbocations. Thus virtually the ortho and para substituted carbocations are resonance hybrids of only two structures while the meta substituted carbocation is a resonance hybrid of three structures and hence more stable than the carbocations obtained from ortho and para attacks. Therefore, substituion mainly takes place at meta position.

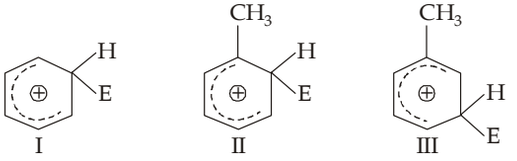
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TEST YOUR UNDERSTANDING - 7.3

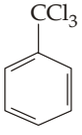
1. Arrange the following groups in order of activating a benzene ring toward electrophilic substitution.

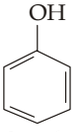
(*i*) $-NH_2$, $-CONH_2$ and $-NHCOCH_3$ (*ii*) $-OH$, $-OCOCH_3$ and $-COCH_3$

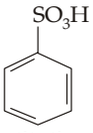
2. Arrange the following carbocations in decreasing stability (increasing potential energy)



3. Identify the products A to C.

(*i*)  $\xrightarrow{NO_2^+ BF_4^-}$ A,

(*ii*)  $\xrightarrow[\text{heat}]{D_2SO_4/D_2O}$ B,

(*iii*)  $\xrightarrow[\text{heat}]{D_2SO_4/D_2O}$ C

4. Arrange the following compounds of each set in order of reactivity towards electrophilic substitution

(*i*) $C_6H_5CH_3$ (I) $C_6H_5CH_2COOCH_3$ (II) $C_6H_5C(COOCH_3)_3$ (III)

(*ii*) $C_6H_5N^+Me_3$ (I) $C_6H_5CH_2N^+Me_3$ (II) $C_6H_5CH_2CH_2N^+Me_3$ (III)

(*iii*) $-\ddot{O}H$ (I) $-\ddot{O}:^{\ominus}$ (II) $-\ddot{O}-\overset{O}{\overset{\|}{C}}-CH_3$ (III)

5. Give the resonance hybrid structure for the three possible benzenonium ions formed during electrophilic substitution of monosubstituted benzene with the electrophile E^+.

6. Arrange the following compounds in order of decreasing reactivity to ring monobromination :

(*i*) $C_6H_5NH_2$, $C_6H_5NH_3^+Cl^-$, $C_6H_5NHCOCH_3$, C_6H_5Cl, $C_6H_5COCH_3$

(*ii*) $C_6H_5CH_3$, C_6H_5COOH, C_6H_6, C_6H_6Br, $C_6H_5NO_2$

(*iii*) *p*-xylene, *m*-xylene, toluene, *p*-toluic acid, terphthalic acid.

HOMOLOGUES OF BENZENE (ARENES)

Benzene and its alkyl derivatives have C_nH_{2n-6} as general formula, where *n* is the number of carbon atoms.

In case hydrogen atom of benzene is replaced by *alkenyl* or *alkynyl groups*, compounds are known as alkenylbenzenes or alkynylbenzenes respectively.

$$\underset{\text{Phenylacetylene}}{C_6H_5C\equiv CH} \longleftarrow C_6H_6 \longrightarrow \underset{\substack{\text{Phenylethylene (Styrene)}\\\text{(Vinylbenzene)}}}{C_6H_5CH=CH_2}$$

Alkyl-, alkenyl- and alkynylbenzenes are collectively known as **arenes**. Thus *arenes may be defined as those hydrocarbons which contain a benzene nucleus in their structures.*

7.11 Methods of Preparation of Alkylbenzenes

1. By Friedel-Craft reaction (alkylation and acylation). For details, consult reactions of benzene.

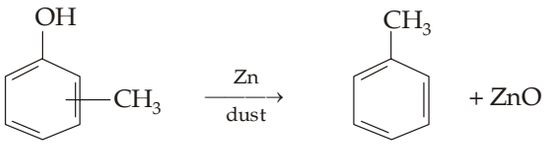
2. By Wurtz-Fittig reaction

(*a*) $C_6H_5Cl + 2Na + ClCH_3 \xrightarrow[\text{ether}]{Na} C_6H_5CH_3 + 2NaCl$

(*b*) $2C_6H_5Cl + 2Na \xrightarrow[\text{Fittig reaction}]{\text{Na, ether}} \underset{\text{Biphenyl}}{C_6H_5C_6H_5} + 2NaCl$

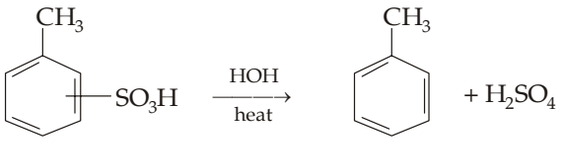
Such reactions may proceed via free radical or ionic mechanism. However, ionic mechanism involving formation of organometallic compounds is found to be more reasonable.

3. From phenols



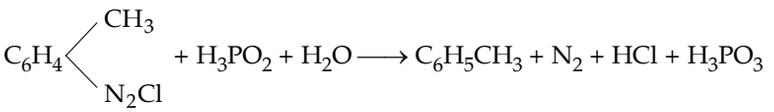
o-, *m*-, *p*-Cresols Toluene

4. From aromatic sulphonic acids



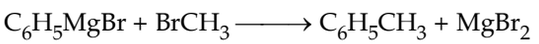
o-, *m*-, *p*-Toluene– sulphonic acids

5. By the reduction of arenediazonium salts with hypophosphorous acid



o-, *m*-, *p*-Toluenediazonium chlorides

6. From Grignard reagents



TEST YOUR UNDERSTANDING - 7.4

1. Predict the product when excess of benzene is treated in presence of $AlCl_3$ with (*a*) 1, 2-dichloroethane, (*b*) chloroform and (*c*) tetrachloromethane.

2. Of the three isomeric xylenes, which has maximum melting point and lowest solubility in water.

3. How will you carry out the following conversions ?

(*i*) Benzene to *p*-nitrochlorobenzene (*ii*) Benzene to *m*-nitrochlorobenzene

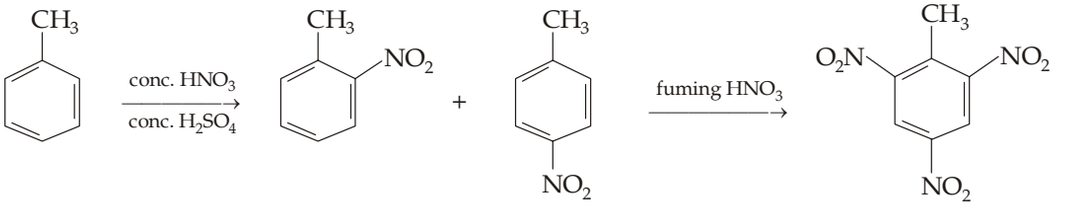
(*iii*) Toluene to *p*-nitrobenzoic acid and *m*-nitrobenzoic acid.

7.12 Reactions of Alkylbenzenes

1. Substitution in the ring (electrophilic aromatic substitution). Since the alkyl groups are activating, alkylbenzenes undergo electrophilic substitutions more readily than benzene.

Further, substitution will occur mainly in the *o*- and *p*-positions because the corresponding intermediate benzenonium is more stable than that of *m*-. Important examples are given below.

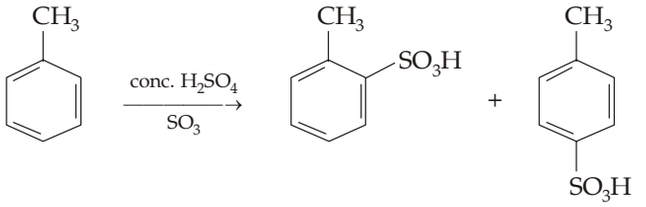
(*i*) **Nitration**



2, 4, 6-Trinitrotoluene
(TNT)

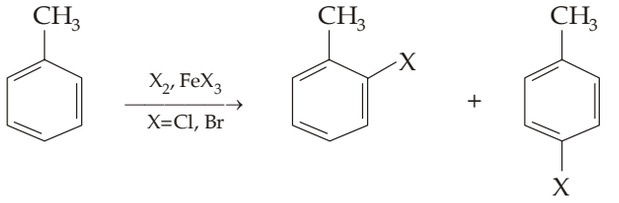
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(*ii*) **Sulphonation**



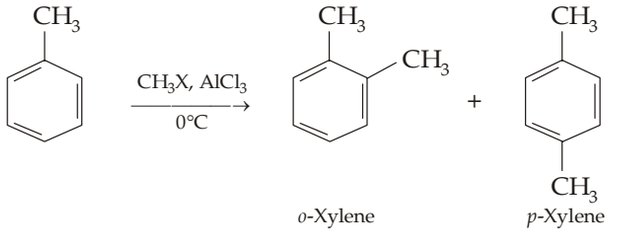
o- and *p*-Tulenesulphonic acids

(*iii*) **Halogenation**



(*iv*) **Friedel Craft alkylation**

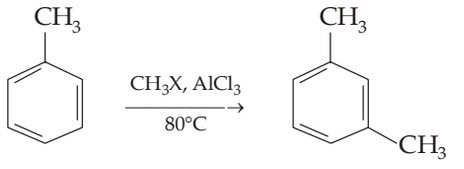
(*a*)



o-Xylene *p*-Xylene

At 0°C, rate controlled products (*o*- and *p*-xylenes) are formed.

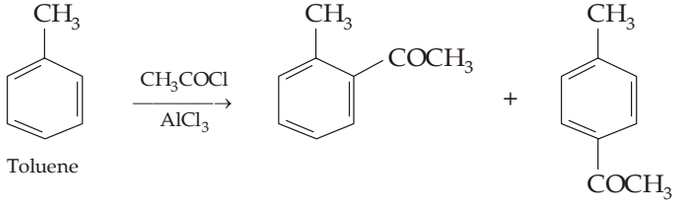
(*b*)



m-Xylene

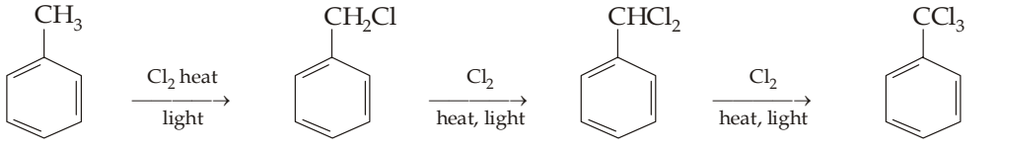
At 80°C, equilibrium controlled product (*m*-xylene) is formed.

(*v*) **Friedel Craft acylation**



Toluene

2. Substitution in the side chain (Free-radical halogenation). Alkylbenzenes when treated with Cl_2 or Br_2 at high temperature, in the presence of sunlight and absence of halogen carrier undergo **halogenation in the side chain.** Thus



Toluene Benzyl chloride Benzyl chloride Benzo trichloride

Mechanism

This is similar to that of halogenation of alkanes (*free radical mechanism*). The essential steps are summarised below.

(*i*) *Formation of free radical :* $Cl—Cl \xrightarrow[\text{or light}]{\text{heat}} Cl\cdot$

(*ii*) *Chain initiating step :* $C_6H_5CH_3 + Cl^{\bullet} \longrightarrow \underset{\substack{\text{Benzyl free radical}\\ \text{(More stable than toluene)}}}{C_6H_5\dot{C}H_2} + HCl$

(*iii*) *Chain propagating step* $C_6H_5\dot{C}H_2 + Cl_2 \longrightarrow \underset{\text{Benzyl chloride}}{CH_6CH_2Cl} + Cl\cdot$

Steps (*ii*) and (*iii*) are repeated to form more and more benzyl chloride. Simultaneously benzyl radical can form a new radical which can lead to formation of benzal chloride.

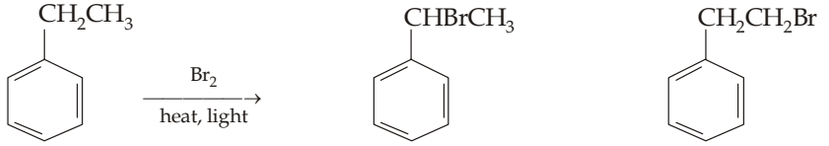
$$C_6H_5CH_2Cl + Cl^{\bullet} \longrightarrow C_6H_5\dot{C}HCl + HCl$$

$$C_6H_5\dot{C}HCl + Cl_2 \longrightarrow \underset{\text{Benzal chloride}}{C_6H_5CHCl_2} + Cl\cdot, \text{ and so on.}$$

Similarly, $C_6H_5CHCl_2 + Cl\cdot \longrightarrow C_6H_5\dot{C}Cl_2 + HCl$

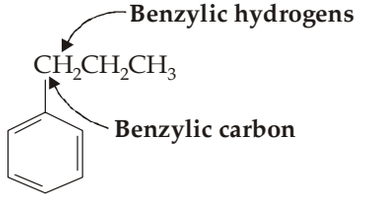
$$C_6H_5\dot{C}Cl_2 + Cl_2 \longrightarrow \underset{\text{Benzotrichloride}}{C_6H_5CCl_3} + Cl^{\bullet}, \text{ and so on.}$$

Side chain halogenation* of alkylbenzenes having a side chain more complex than methyl. For example,

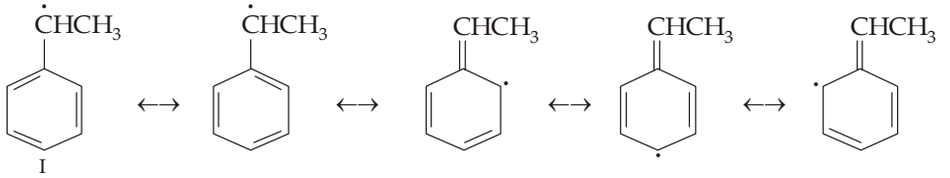


1-Bromo-1-phenylethane (sole product) — 2-Bromo-1-phenyl ethane (not formed)

In general, it has been observed that the hydrogen atom(s) attached to carbon directly linked to the benzene ring is(are) preferentially replaced. Such hydrogens are know as **benzylic hydrogens.**

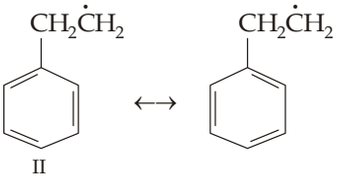


The greater reactivity of benzylic hydrogens (*i.e.* predominance of α-substituted product) is due to greater stability of benzylic free radical[1] than the other. For example, the benzylic radical ($C_6H_5\dot{C}HCH_3$) I obtained from ethylbenzene is a hyrbid of the following contributing structures.



I

On the other hand, the second radical ($C_6H_5CH_2\dot{C}H_2$) II, obtained from ethylbenzene is a resonance hybrid of only two Kekule structures shown below.



II

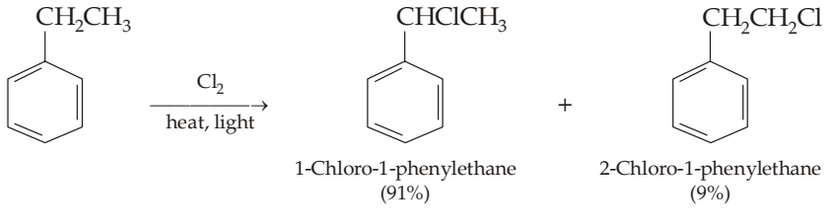
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The greater relative stability of benzylic radical and therefore, its greater ease of formation are responsible for the relatively greater ease of substitution of benzylic hydrogens.

It may be interesting to note that the energy content of benzyl radical (85 kcal) is almost similar to that of allyl radical (88 kcal) ; hence the stability of the two radicals is nearly similar. The relative order of stability of the various radicals is as given below.

Benzyl ≃ allyl > tertiary > secondary > primary > methyl > vinyl

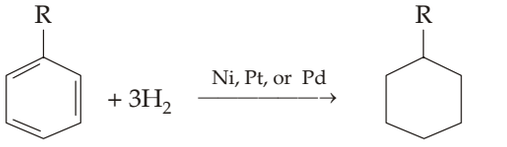
It is important to note that as in alkanes, orientation of side chain chlorination of ethylbenzene shows that although chlorine atoms (chlorine free radicals) also preferentially attack benzylic hydrogen, here the preference is less than that in bromination.



1-Chloro-1-phenylethane (91%) + 2-Chloro-1-phenylethane (9%)

This is due to the fact that the more reactive chlorine is less selective (selectivity reactivity principle). Under conditions where 3°, 2° and 1° hydrogens show relative reactivities of 5.0 : 3.8 : 1.0, the relative rate per benzylic hydrogen atom of toluene is found to be only 1.3.

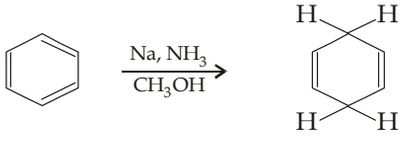
3. Hydrogenation.



Alkylcyclohexane

4. Birch reduction.

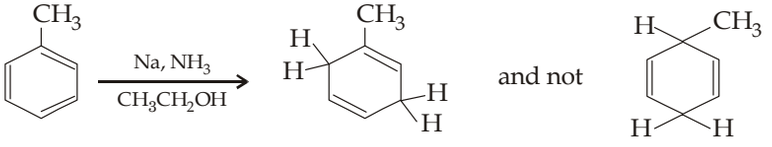
Alkali metal and liquid ammonia is a powerful reducing system. In presence of alcohol, this combination of reagent reduces arenes to 1,4-*cyclohexadienes (nonconjugated dienes)*. This metal-ammonia-alcohol reductions of aromatic rings are known as **Birch reductions**.

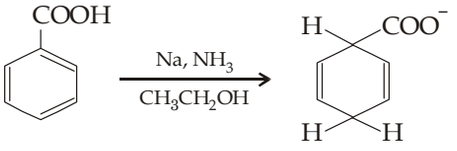


Benzene 1,4-Cyclohexadiene

Mechanism of Birch reduction is analogous to the mechanism for the metal-ammonia reduction of alkynes to alkenes.

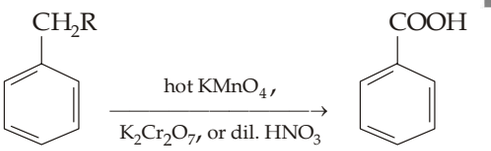
The reaction involves the formation of anionic intermediates, thus electron-withdrawing substituents stabilize the carbanions. Therefore, reduction takes place on carbon atoms bearing electron-withdrawing substituents and not on carbon atoms bearing electron releasing substituents like alkyl and alkoxy groups. Thus alkyl substituted arenes give 1,4-cyclohexadienes in which the alkyl group is a substituent on the double bond.



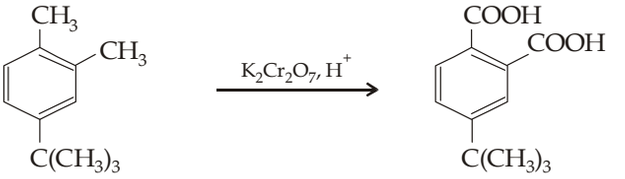


5. Oxidation.

Although benzene and alkanes are quite unreactive toward the usual oxidizing agents ($KMnO_4$, $K_2Cr_2O_7$ etc.), alkylbenzenes can be oxidised to benzoic acid. It is important to note that the alkyl side chain, irrespective of its size or nature, is completely oxidised to carboxylic group.



An exception to this is a *tert*-alkyl substituent. Thus



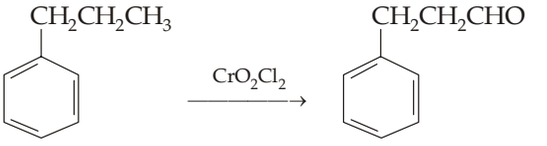
4-*tert*-Butyl-1,2-dimethylbenzene

Actually, any alkyl group having benzylic hydrogen is susceptible to oxidation; since *tert*-butyl group has no benzylic hydrogen atom, it will not be oxidised.

However, remember that oxidation of a side chain is more difficult than that of an alkene, and requires prolonged treatment with hot $KMnO_4$.

6. Partial oxidation.

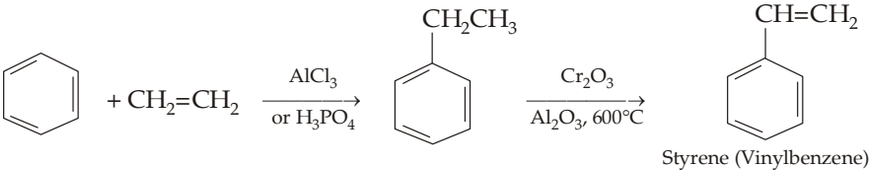
Milder oxidising agents like chromyl chloride (CrO_2Cl_2) or chromium oxide in presence of acetic anyhydride oxidise the end methyl group of the side chain to aldehydic group **(Etard reaction).**



7.13 Alkenylbenzenes

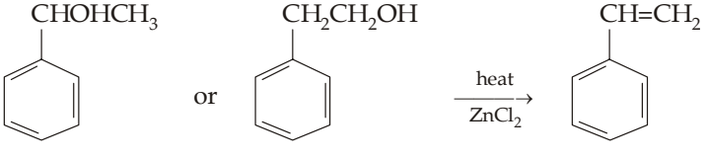
7.13.1 Preparation

1. By dehydrogenation of the side chain.

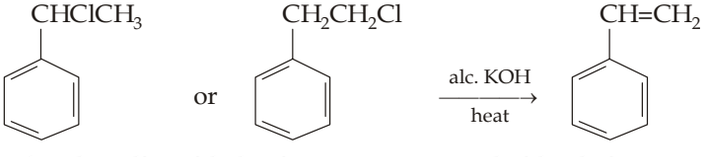


Styrene (Vinylbenzene)

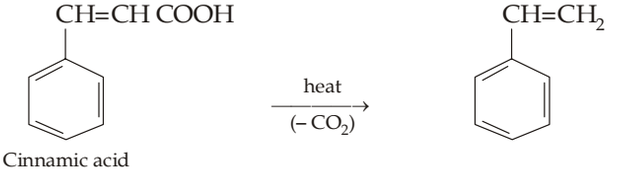
2. By dehydration of hydroxyalkylbenzenes.



3. By dehydrohalogenation of haloalkylbenzenes.



4. By decarboxylation of carboxylic acids having an unsaturated side chain.



Cinnamic acid

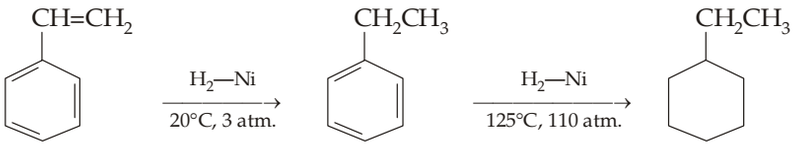
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7.13.2 Chemical Reactions

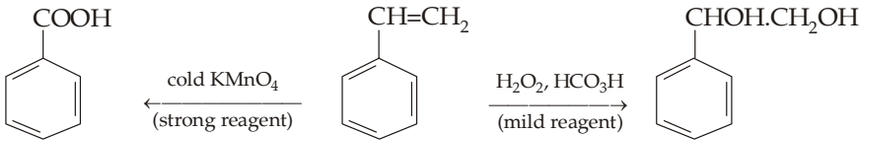
Alkenylbenzenes undergo electrophilic substitution (in benzene ring) and electrophilic addition (in unsaturated side chain and also in benzene ring) reactions.

Some important reactions are given below.

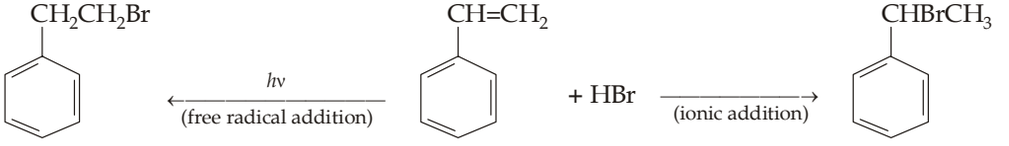
1. Hydrogenation



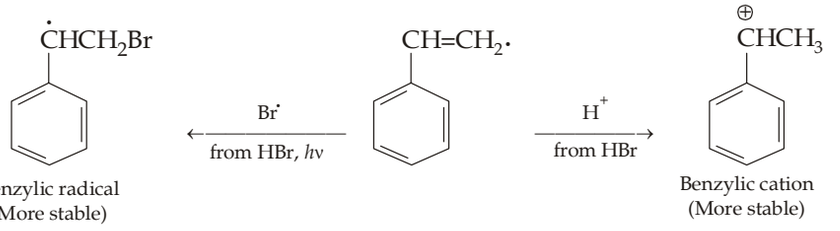
2. Oxidation



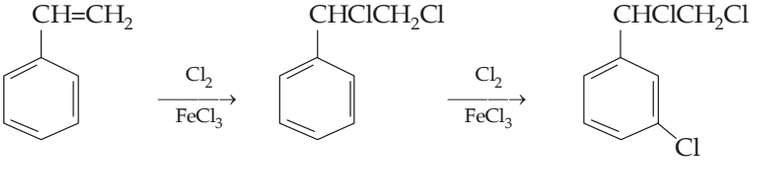
3. Addition of halogen acids



In above two reactions, opposite products is explained on the basis of the fact that in ionic reaction the electrophile H^+, while in free radical addition reaction the bromine atom (Br.), adds to the double bond in the first step of the addition producing benzylic cation and benzylic radical respectively.



4. Addition of halogens. In dark and in presence of a suitable catalyst, halogens react with the double bond (electrophilic addition) as well as benzene ring (electrophilic substitution) of alkenylbenzenes. This is because of the fact that the first step (attack of X^+ ion on the π electron cloud) in both reactions is common. However, experimental results show that addition of halogens to the side chain is first completed before the electrophilic substitution takes place. This is due to the fact the side chain double bond is more susceptible to electrophilic attack than the resonance stabilised benzene ring.



TEST YOUR UNDERSTANDING - 7.5

1. (*a*) Although styrene $C_6H_5CH = CH_2$ has extended conjugation, yet it reacts faster than the simple alkenes. Explain.

(*b*) Tetraphenylethylene does not react with bromine in carbon tetrachloride. Comment.

2. How will you prepare *p*-chlorostyrene in quantitative yield from styrene ?

3. How will you prove that 1-phenylpropene ($C_6H_5CH = CHCH_3$) is more stable than the isomeric 3-phenylpropene ($C_6H_5CH_2CH = CH_2$)?

4. Give all steps in the conversion of

(*a*) ethylbenzene into phenylacetylene (*b*) *trans*-1-phenylpropene to *cis*-phenylpropene.

7.14 Tests of Arenes

Following reactions of aromatic hydrocarbons with saturated side chains are used as their chemical tests to distinguish from other hydrocarbons.

1. They are easily sulphonated by (and thus dissolve in) **cold fuming sulphuric acid** (difference from alkanes). However, they do not dissolve immediately in cold conc. H_2SO_4 (difference from alcohols).
2. They give orange to red colours upon treatment with chloroform and aluminium chloride. These colours are due to the formation of triarylmethyl cations, Ar_3C^+ which are formed by a Friedel-Craft reaction followed by a transfer of hydride ion.

$$ArH \xrightarrow[AlCl_3]{CHCl_3} ArCHCl_2 \xrightarrow[AlCl_3]{ArH} Ar_2CHCl \xrightarrow[AlCl_3]{ArH} Ar_3CH$$

$$Ar_2CHCl \xrightarrow{AlCl_3} Ar_2\overset{+}{C}HAlCl_4^- \xrightarrow{Ar_3CH} Ar_2CH_2 + \underset{\substack{\text{Triarylmethyl cation}\\ \text{(orange to red colour)}}}{Ar_3C^+AlCl_4^-}$$

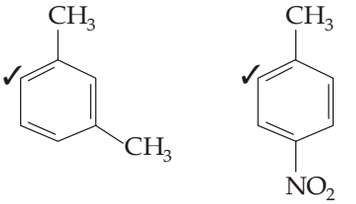
This test is given by all benzenoid compounds which can undergo Friedel-crafts reaction. The colour produced depends upon the nature of the aromatic system.

Benzene system gives orange to red colour — Naphthalene system gives blue colour

Phenanthrene system gives purple colour — Anthracene system gives green colour.

7.15 Predicting Orientation in Disubstitutedbenzenes

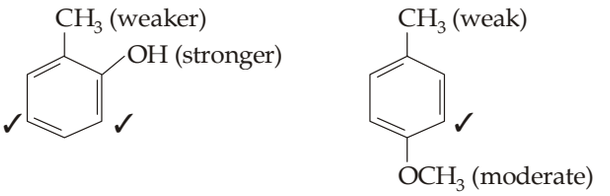
1. If the two groups reinforce each other, there is no competition between two positions and hence only one product is formed, *e.g.*



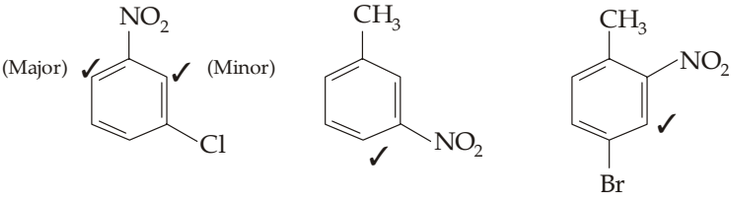
2. If there is a competition between two *op*-directing groups, the one with stronger tendency to release electrons will control the orientation. The various activating groups can be arranged in the following order of decreasing activation of the ring

$$O^-, NR_2, NH_2, OH > OR > OCOR > NHCOCH_3 > C_6H_5 > CH_3 > X$$

Thus, further substitution will take place at the site marked 3.



3. If the competition is between *op*-directing and *m*-directing groups, the *op*-director controls the orientation. However, if the *m*-director is situated *meta* to an *op*-director, the third group enters *o* to the *m*-directing group,

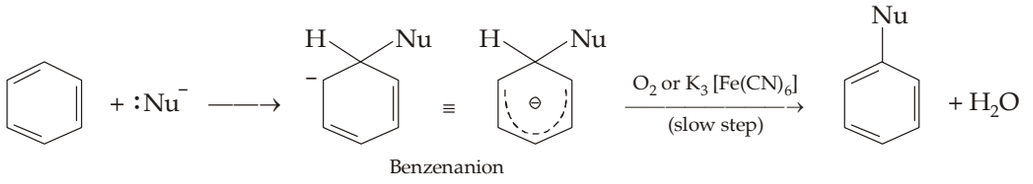


Although no suitable explanation is available for this observation, it may be presumed that the *meta*-directing group possibly gives intramolecular assistance.

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7.16 Nucleophilic and Free-Radical Substitutions

Nucleophilic aromatic substitutions of H are rare. The intermediate benzenanion in aromatic nucleophilic substitution is analogous to the intermediate benzenonium ion in aromatic electrophilic substitution.



Benzenanion

Oxidants such as O_2 and K_3 $Fe(CN)_6$ facilitate the second step, which may be rate-controlling, by oxidising the ejected hydride ion (a powerful base and a very poor leaving group), to H_2O.

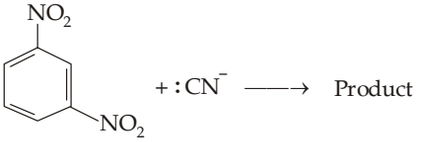
Free radical substitutions also proceed by an intermediate, similar to benzenonium ion and benzenanion, having free-radical character distributed to the *op*-positions. Note the following two special features of the aromatic radical substitutions.

(*i*) Substituents have **much less effect** than in electrophilic or nucleophilic substitutions, *i.e.* the new group may enter at *o*, *p* or *m*-position.

(*ii*) Both electron-withdrawing as well as electron donating groups increase reactivity at *o*- and *p*-positions, except in case of steric hindrance.

TEST YOUR UNDERSTANDING - 7.6

1. Predict the product in the following reaction :



2. Predict the products in the following reaction :

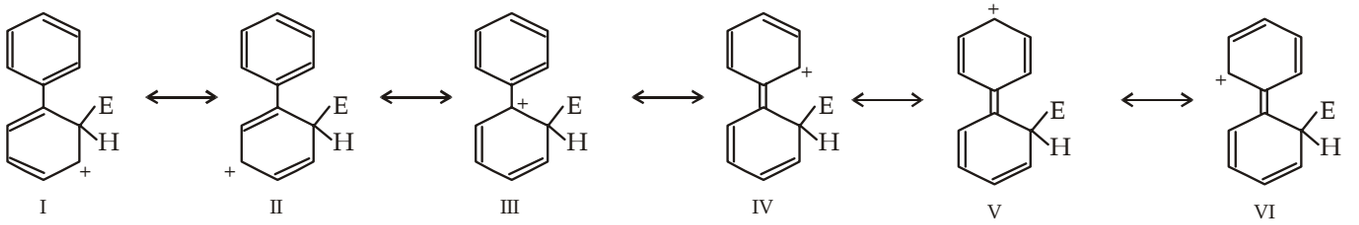
$$C_6H_5N = NOCOCH_3 + C_6H_6 \xrightarrow{\text{heat}} P$$

Example 1 :

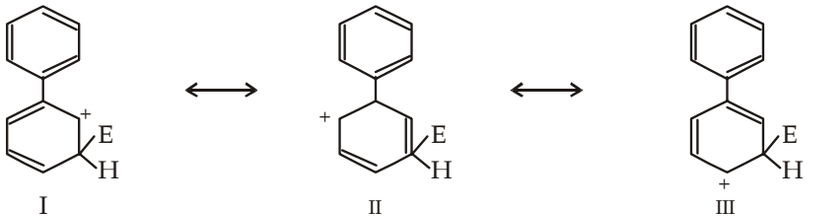
Taking biphenyl as an example, draw resonance forms of a sigma complex to show that a phenyl group is o,p-directing.

Solution :

Let us draw resonance forms of the σ complex of ortho attack.



Similar structures are possible for the σ complex of para attack; however, meta attack does not permit delocalisation of the positive charge on the phenyl substituent, i.e. resonance structures corresponding to IV to VI are not possible because here none of the resonating structure has a positive charge on the carbon atom adjacent to the phenyl group (*cf* structure III).



I II III

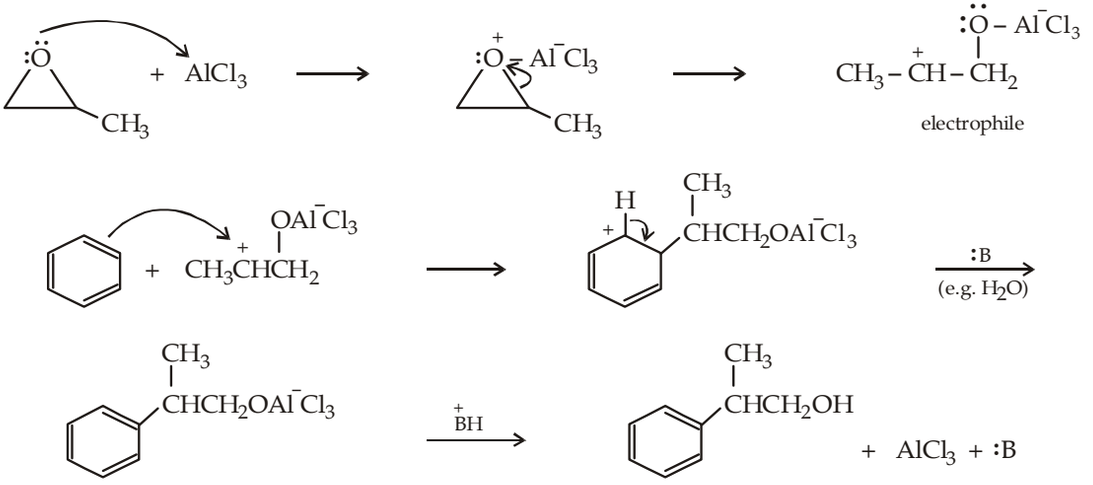
Thus the σ complex corresponding to ortho and para attack are much more stable than that from *m* attack.

Example 2 :

Write down the structure of the product formed when benzene is treated with propylene oxide in presence of aluminium chloride. Propose a mechanism for the reaction.

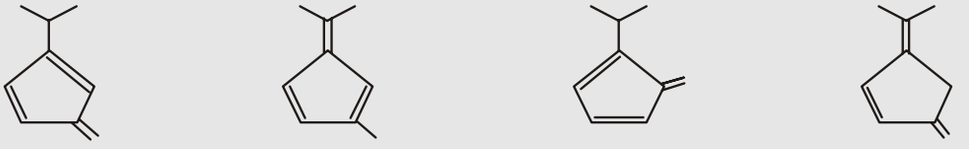
Solution :

We know that epoxides are quite reactive compounds and undergo ring opening under acidic conditions. This leads to formation of an electrophile which reacts with benzene to form substituted product.



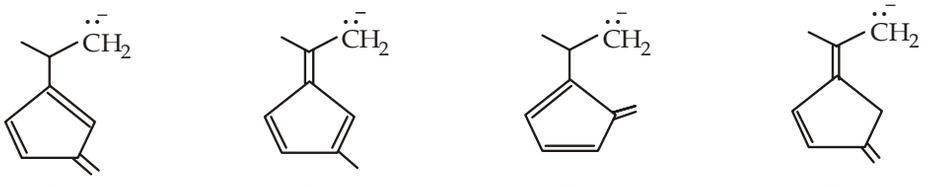
Example 3 :

Which of the following compound is much more acidic than the others. Pick it up and explain.



Solution :

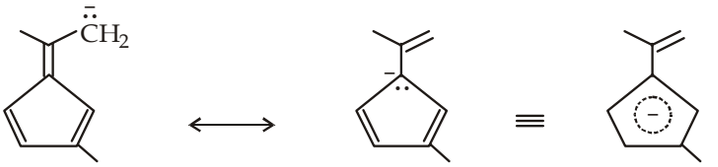
More the stability of the corresponding carbanion, more will be the acidic character of the present hydrocarbon. Thus the corresponding carbanion formed by the four compounds will be



I II III IV

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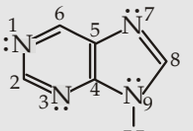
Although all the four structures are resonance stabilized, structure II is especially stable as its one of the resonating structures (IIa) has an aromatic sextet. Thus among the four structures, structure II is most likely to be formed, thus its conjugate acid is the most acidic.



II IIa Aromatic

Example 4 :

Purine has four nitrogen atoms, which one of them is expected to be basic? Explain.



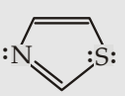
Purine

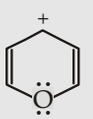
Solution :

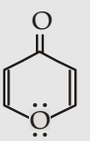
Purine has two types of nitrogens. Lone pair of electrons on N on N_1, N_3 and N_7 is in an sp^2 orbital which is planar with the ring. These electrons are available for bonding, and thus these three nitrogens are basic. The other type of nitrogen is N_9 whose nonbonding electron pair has in a *p* orbital which is perpendicular to the ring system, hence involved in delocalisation, i.e. it forms a part of the aromatic π system. With this pair of electrons, the π system is aromatic and has *10 electrons, a Huckel number*. So this electron pair is not available for bonding and N_9 is not basic.

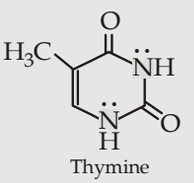
Example 5 :

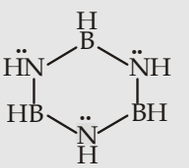
Explain why each compound is aromatic, antiaromatic, or nonaromatic.

(a)  1,3-Thiazole

(b)  Pyrylium ion

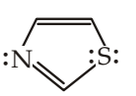
(c)  γ-Pyrone

(d)  Thymine

(e)  Borazole

Solution :

(a) **Aromatic :** 4π electrons form two double bonds plus one pair of electrons (lying in *p* orbital) from sulphur. The other pair of electrons on S and the pair of electrons of N lie in sp^2 orbitals.

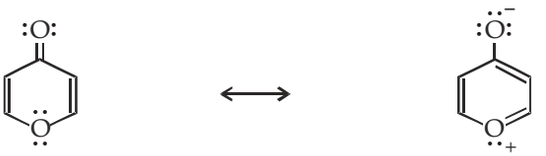


1,3-Thiazole

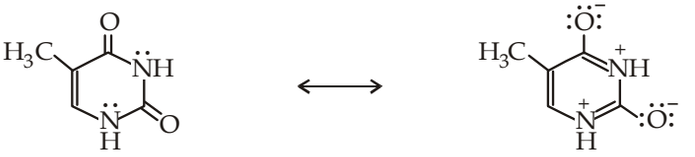
Both N and S are sp^2 hybridised; only one *lp* of electrons is in *p* orbital, hence form part of aromatic system.

(b) **Aromatic :** 4π electrons form two double bonds plus a pair of electrons from O making total of 6π electron system.

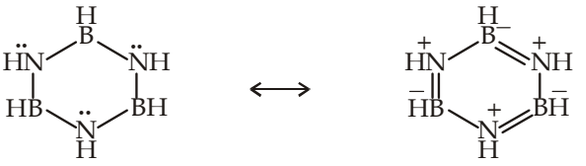
(c) Resonance form of γ-pyrone has 6π electron aromatic system; hence **aromatic**.



(d) Resonance of thymine shows the presence of a cyclic π system with 6π electrons, hence **aromatic**.



(e) In borazole, each B as well as N is sp^2 hybridised. Further each N has a pair of electrons in its *p* orbital which gives rise to a cyclic system of six π electrons. Hence it is **aromatic**.



Borazole

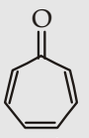
Example 6 :

Explain the following :

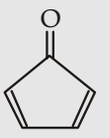
(a) Cyclopropenone (I) and even cycloheptatrienone (II) is more stable than cyclopentadienone (III).



Cyclopropenone, I

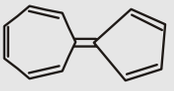


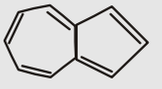
Cycloheptatrienone, II



Cyclopentadienone, III

(b) The following hydrocarbons have unusually large dipole moments.

(i) 

(ii) 

Solution :

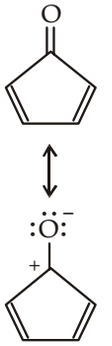
(a) This is due to stability of the structure obtained due to polarization of the ketonic group.



2π electrons, **aromatic,** hence stable

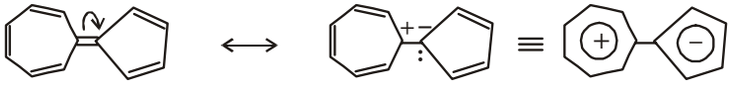


6π electrons, **aromatic,** hence stable



4π electrons, **antiaromatic,** hence unstable

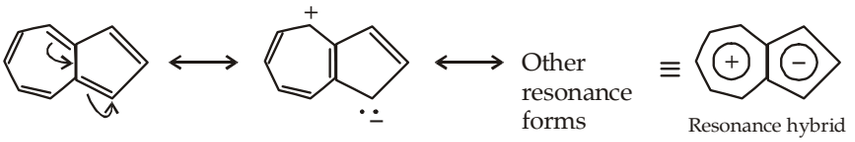
(b) (i) Exceptionally large dipole moment is due to the presence of a highly stable charged resonating structure in which one ring has positive charge and the other ring has negative charge. Further, both of the charged rings are highly stable due to presence of aromatic system in each.



6π electrons in each ring, hence both are aromatic and quite stable

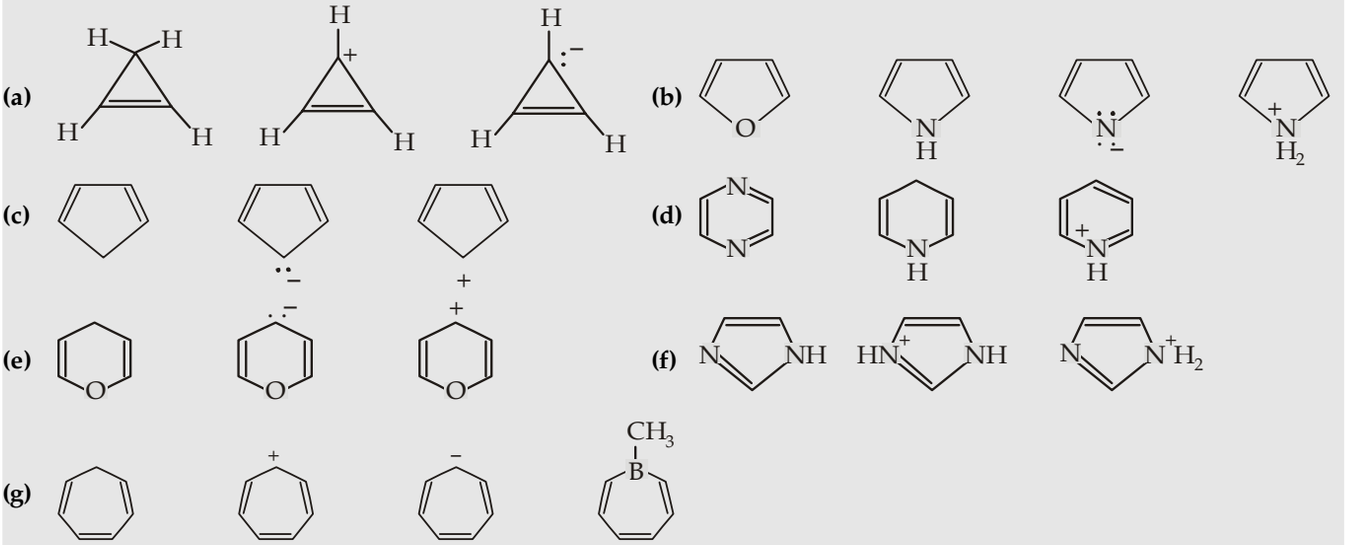
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(ii) In azulene too, major contributors to the hybrid have separated charges.



Example 7 :

Classify each member of the group as aromatic, nonaromatic, or antiaromatic. For the aromatic and antiaromatic species, give the number of π electrons in the ring.

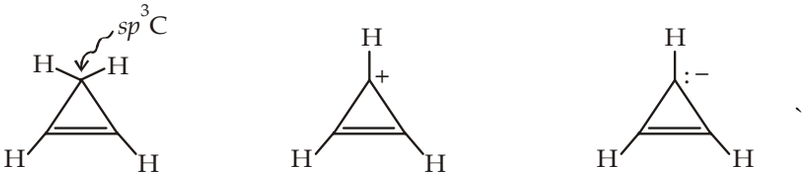


Solution :

(i) Observe sp^3 character of any cyclic atom, if it is present, the compound will be **nonaromatic**, for aromatic species all cyclic atoms should have a *p* orbital.

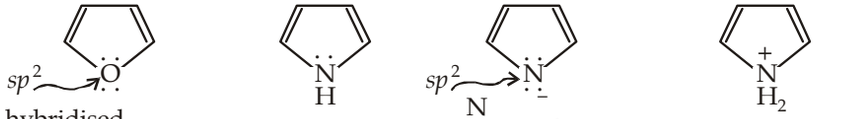
(ii) Count the number of π electrons or *p* electrons, if it corresponds to $(4n + 2)$ number, i.e. 2, 6, 10, 14, etc. it is **aromatic**, if it corresponds to $(4n)$ number, i.e. 4, 8, 12, 16, etc. the species is **antiaromatic**.

(a)



nonaromatic **aromatic,** 2π electrons **antiaromatic,** 4π electrons

(b)



hybridised

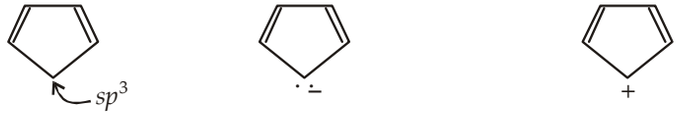
aromatic, 6 π electrons (2 electrons are present in sp^2 orbital, 2 in p-orbital)

aromatic, 6 π electrons

aromatic, 6 π electrons (2 electrons are present in sp^2 orbital)

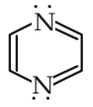
nonaromatic (N is sp^3 hybridised)

(c)

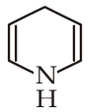


nonaromatic 6π electrons, **aromatic** 4π electrons, **antiaromatic**

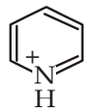
(d)



aromatic, 6π electrons, each N is sp^2, lone pair of electrons belong to sp^2N, hence does not form a part of sextet



nonaromatic

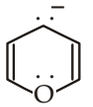


aromatic 6π electrons

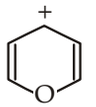
(e)



nonaromatic

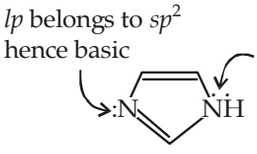


(i) if O is sp^2, 8π electrons, hence **antiaromatic**
(ii) if O is sp^2, nonaromatic

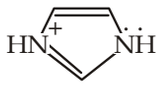


aromatic 6π electrons, O is sp^2

(f)



aromatic, 6π electrons

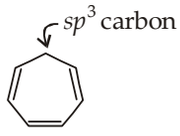


aromatic, 6π electrons

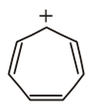


nonaromatic

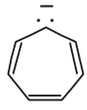
(g)



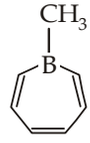
nonaromatic



aromatic 6π electrons



antiaromatic 8π electrons



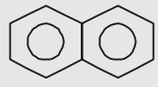
aromatic, 6π electrons (although B is sp^2, it has no free electron)

Example 8 :

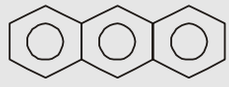
Arrange the following hydrocarbons in order of decreasing stability with proper explanation.



Benzene



Naphthalene

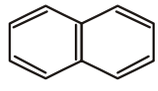


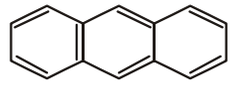
Anthracene

Solution :

The stability order can be explained on the basis of resonance energy.







Total RE per mol.	36 kcal	60 kcal	84 kcal
RE per aromatic ring	36 kcal	30 kcal	28 kcal

So the stability order is, Benzene > Naphthalene > Anthracene

The difference in resonance energy is due to difference in the number of π electrons per molecule which is 6 in benzene, 10 in naphthalene (i.e. 2 short of isolated benzene rings) and 14 in anthracene, i.e. 4 short of the three isolated benzene rings.

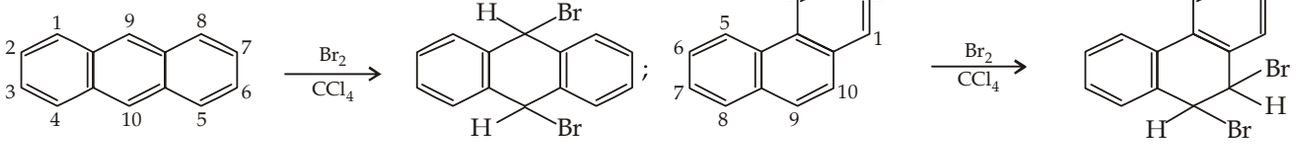
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Example 9 :

Although anthracene and phenanthrene are aromatic, they undergo addition reactions easily with Br_2 in CCl_4 and that too at different positions in the two isomers.

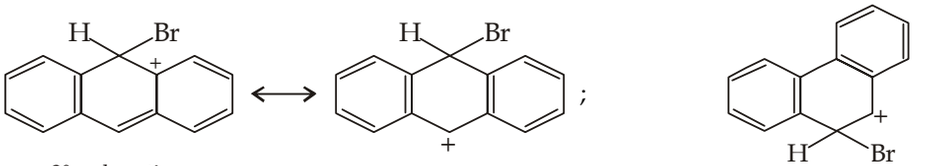
Solution :

Anthracene and phenanthrene have less resonance energy per aromatic ring of benzene, hence these are not as strongly stabilized as benzene. Hence they can undergo addition reactions, anthracene undergoes 1,4-addition (at the 9- and 10- positions), while phenanthrene undergoes 1,2-addition (at the 9- and 10- positions) to give products with fully aromatic rings.



Anthracene *cis-* and *trans-* Phenanthrene *cis-* and *trans-*

1,4- and 1,2- additions in the two cases is due to the formation of following more stable carbocations.



3° carbocation

2° carbocation with with two aromatic rings

Example 10 :

Give steps involved in the following conversions.

(i) Benzene to phenylacetylene

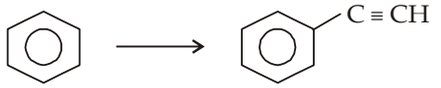
(ii) Toluene to 1-bromo-2-trichloromethylbenzene and 1-bromo-3-trichloromethylbenzene (separately)

(iii) Methoxybenzene to 2-cyclohexenone **(iv) Aniline to o-nitroaniline**

(v) Benzene to 2-phenylcyclopentanol **(vi) Phenol to 2,4-dichlorophenol**

Solution :

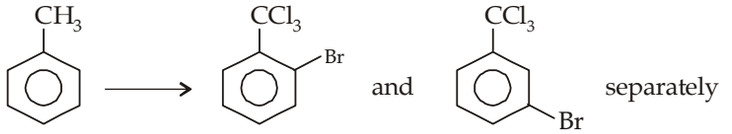
First write down the structure of the two concerned compounds and then work backward, retrosynthetic analysis. Conversions involving aniline and phenol are here given only for making clear the concept of their directive influence.

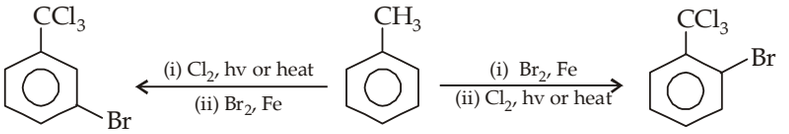
(i) 

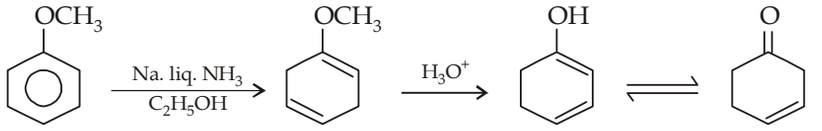
$$C_6H_6 \xrightarrow[AlCl_3]{CH_3COCl} C_6H_5COCH_3 \xrightarrow[H_2O]{Zn,\ Hg} \mathbf{C_6H_5CH_2CH_3} \xrightarrow[light]{NBS} C_6H_5CHBrCH_3$$

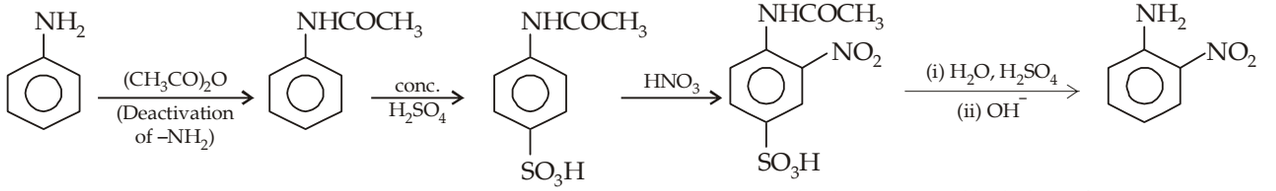
$$\xrightarrow[heat]{KOH} C_6H_5CH=CH_2 \xrightarrow{Br_2,\ CCl_4} C_6H_5CHBrCH_2Br \xrightarrow[(ii)\ H_3O^+]{(i)\ NaNH_2} C_6H_5-C\equiv CH$$

or $$C_6H_5CH_2CH_3 \xrightarrow[light]{NBS} C_6H_5CBr_2CH_3 \xrightarrow[(ii)\ H_3O^+]{(i)\ NaNH_2,\ heat} C_6H_5C\equiv CH$$

(ii) 

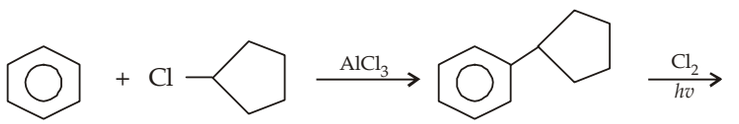


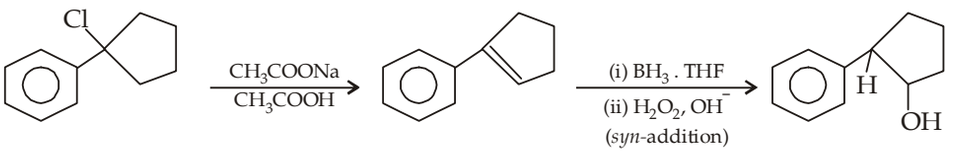
(iii) 

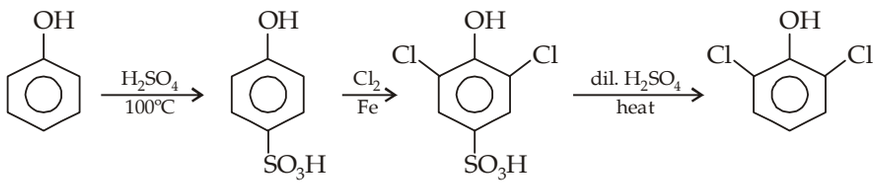
(iv) 

(100%)
(Blocking of para position)

(desulphonation and hydrolysis of $-NHCOCH_3$)

(v) 



(vi) 

(blocking of para position)

Example 11 :

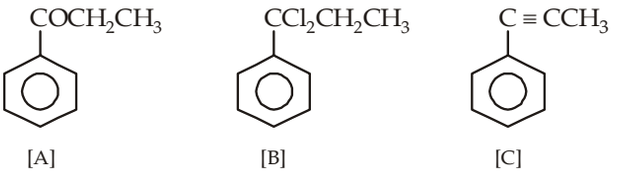
Give structures for the bracketed compound in the following series of reactions.

$$C_6H_6 + CH_3CH_2COCl \xrightarrow{AlCl_3} [A] \xrightarrow{PCl_5} [B] \xrightarrow[\text{heat}]{2NaNH_2} [C]$$

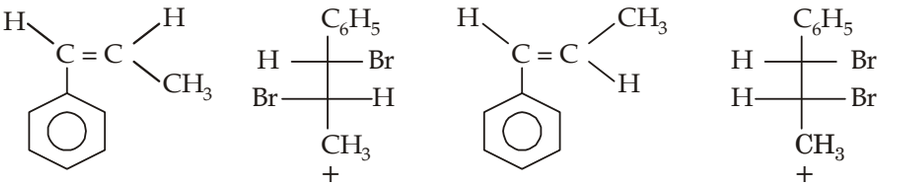
$$[G] \xleftarrow[CCl_4]{Br_2} [F] \xleftarrow[\text{liq.}NH_3]{Na} \mathbf{[C]} \xrightarrow{H_2,\ Ni_2B\ (P-2)} [D] \xrightarrow[CCl_4]{Br_2} [E]\ \text{(Two isomers)}$$

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Solution :



[A] [B] [C]



cis [D] | Enantiomer [E] | *trans* [F] | Enantiomer [G]

Example 12 :

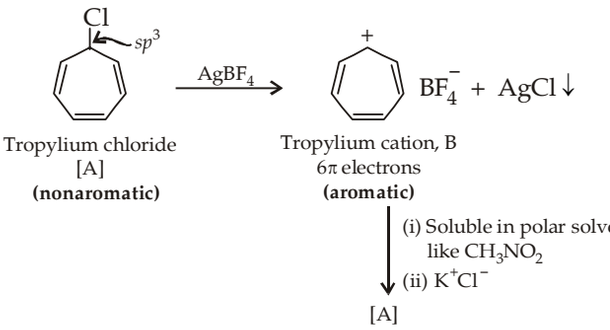
An organic compound, A of the molecular formula C_7H_7Cl, when treated with silver borofluoride gives white precipitate of AgCl alongwith other organic crystalline material B. The compound A takes up three equivalent of H_2 in presence of catalyst, while B does not respond such reaction. The compound B is soluble in nitromethane and this solution when treated with KCl regenerates compound A. Assign structures to A and B and explain the reactions.

Solution :

$$C_7H_{13}Cl \xleftarrow[Ni]{3H_2} \underset{[A]}{C_7H_7Cl} \xrightarrow{AgBF_4} AgCl\downarrow + \underset{(Crystalline)}{B}$$

$$\text{No reaction} \xleftarrow{H_2} \textbf{[B]} \xrightarrow[(ii)\ KCl]{(i)\ CH_3NO_2} \underset{[A]}{C_7H_7Cl}$$

Given facts suggest that [A] has reactive Cl (Cl attached to sp^3 carbon) and it is nonaromatic compound having three double bonds (indicated by hydrogenation), while B is an aromatic comound. All the given facts suggest following structures to A and B.



Tropylium chloride [A] **(nonaromatic)**

Tropylium cation, B 6π electrons **(aromatic)**

EXERCISE 7.1 (MCQ - ONE option correct)

1. Which one of the following is true ?
(*a*) Coal consists of only free carbon atoms.
(*b*) Coal is a mixture of free carbon, hydrogen and carbon compounds.
(*c*) Coal is a mixture of free carbon and several organic compounds.
(*d*) Coal is a mixture of organic compounds with no free carbon.

2. Which one of the following is a direct source of aromatic compounds ?
(*a*) Coal (*b*) Petroleum
(*c*) Both (*d*) None.

3. Reduction of benzene with sodium in liquid ammonia in presence of ethanol gives

(*a*)  (*b*) 

(*c*)  (*d*) 

4. Observe the following two reactions of benzene

(*i*) $C_6H_6 + \text{conc. } H_2SO_4 \xrightarrow{K_1} C_6H_5SO_3H + H_2O$

(*ii*) $C_6H_5D + \text{conc. } H_2SO_4 \xrightarrow{K_2} C_6H_5SO_3H + HOD$

The relation between rate constants of the two reactions will be
(*a*) $K_1 > K_2$ (*b*) $K_2 > K_1$
(*c*) $K_1 = K_2$ (*d*) Not definite.

5. During nitration of benzene with nitrating mixture, HNO_3 acts as
(*a*) an acid (*b*) a base
(*c*) catalyst (*d*) reducing agent.

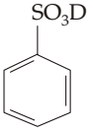
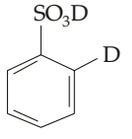
6. Which of the following fact is not observed during nitration of benzene ?
(*a*) Formation of benzenonium ion
(*b*) Restoration of benzenoid nucleus
(*c*) An acid-base equilibrium
(*d*) All above facts are observed.

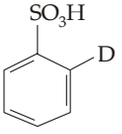
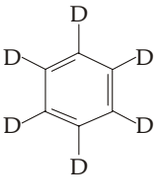
7. The C—H homolytic bond dissociation energy for benzene is found to be 110 kcal, what should be the C—H homolytic bond dissociation energy of cyclohexane ?
(*a*) > 110 kcal (*b*) < 110 kcal
(*c*) 110 kcal (*d*) Nothing certain.

8. Borazole ($B_3N_3H_6$), like benzene, has 6π electrons which come from
(*a*) 3 from one B and 3 from one N
(*b*) 2 from each B
(*c*) 2 from each N
(*d*) In one structure 2 from each B and in other 2 from N.

9. Give the possible structure of X in the following reaction :

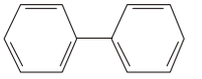
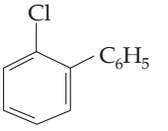
$$C_6H_6 + D_2SO_4 \xrightarrow{D_2O} X$$

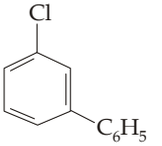
(*a*)  (*b*) 

(*c*)  (*d*) 

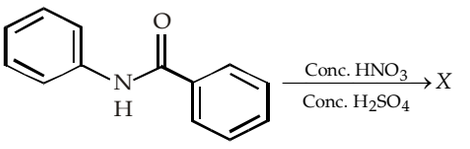
10. During monoalkylation of benzene with CH_3Cl in presence of anhydrous $AlCl_3$, an excess of C_6H_6 must be used because this will
(*a*) increase the chance for collision between CH_3^+ and C_6H_6
(*b*) decrease collision between CH_3^+ and $C_6H_5CH_3$
(*c*) Both (*a*) and (*b*)
(*d*) decrease the chance for collision between CH_3^+ and C_6H_6.

11. $C_6H_6 + C_6H_5Cl \xrightarrow{AlCl_3} P$
In the above reaction, P is

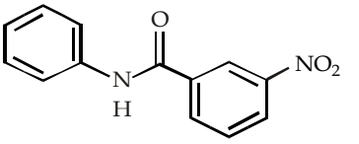
(*a*)  (*b*) 

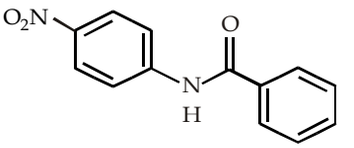
(*c*)  (*d*) No reaction.

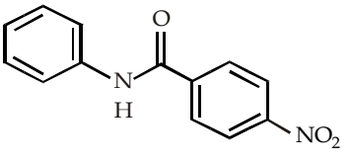
12. In the following reaction,

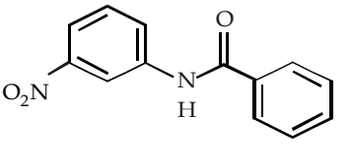


the structure of the major product 'X' is

(a) 

(b) 

(c) 

(d) 

13. What happens when one mole of 1, 3, 5, 7-cyclooctatetraene is treated with two moles of potassium ?
(*a*) The corresponding dianion is formed with the liberation of hydrogen gas
(*b*) The corresponding dianion is formed with no liberation of hydrogen gas

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(*c*) The corresponding dication is formed with the liberation of hydrogen gas

(*d*) No reaction takes place.

14. Which of the following statement is true ?

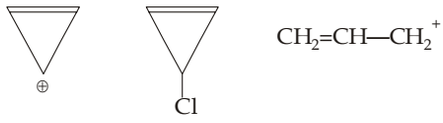
(*a*) 7-Bromo cycloheptatriene (tropylium bromide) completely dissociates in water to form Br^- ion and thus gives precipitate with $AgNO_3$ solution

(*b*) Cyclooctatetraene is non-aromatic, white its corresponding dianion is aromatic

(*c*) Both are true

(*d*) Neither is true.

15. The order of stability of the following three compounds is

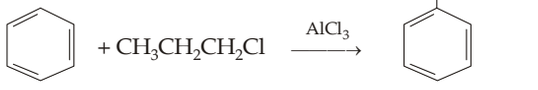


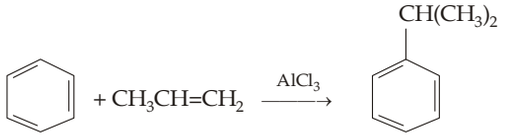
I II III

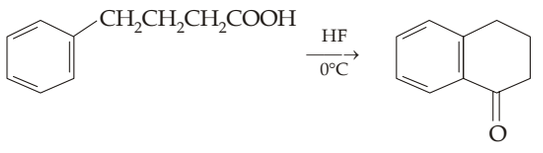
(*a*) III > I > II (*b*) III > II > I

(*c*) I > III > II (*d*) I > II > III.

16. Which of the following is not an example of Friedal Craft reaction?

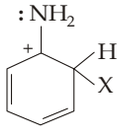
(*a*) 

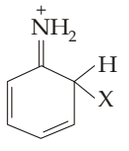
(*b*) 

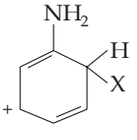
(*c*) 

(*d*) None of these.

17. Which of the following is more stable ?

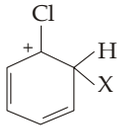
(*a*) 

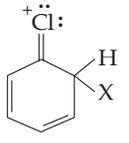
(*b*) 

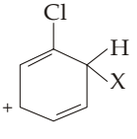
(*c*) 

(*d*) All are equally stable.

18. Which of the following structure is least stable ?

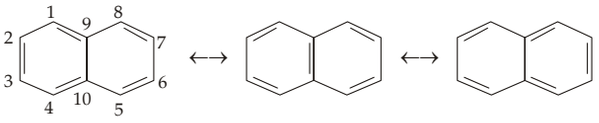
(*a*) 

(*b*) 

(*c*) 

(*d*) All are equally stable.

19. Naphthalene is regarded as a resonance hybrid of the following three structures.

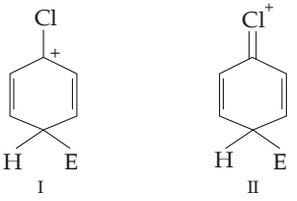


What is true about their bond lengths of the two adjacent carbon atoms ?

(*a*) $C_1—C_2 > C_2—C_3$ (*b*) $C_1—C_2 < C_2 — C_3$

(*c*) $C_1 — C_2 = C_2 — C_3$ (*d*) All bond lengths are equal.

20. Which of the following is comparatively stable ?



(*a*) I (*b*) II

(*c*) Both are equally stable (*d*) None is stable.

21. *n*-Propylbenzene can be obtained in quantitative yield by following method :

(*i*) By treating benzene with *n*-propyl chloride in presence of $AlCl_3$

(*ii*) By treating excess of benzene with *n*-propyl chloride in presence of $AlCl_3$

(*iii*) By treating benzene with allyl chloride in presence of $AlCl_3$ followed by reduction

(*iv*) By treating benzene with propinoyl chloride in presence of $AlCl_3$ followed by Clemmensen reduction.

(*a*) By (*ii*), (*iii*) and (*iv*) (*b*) By (*i*), (*iii*) and (*iv*) (*c*) By (*iii*) and (*iv*) (*d*) By (*ii*) only.

22. Ethylbenzene can be prepared from benzene by Friedal-Craft reaction in the following manner

(*i*) By treating with ethyl chloride in presence of $AlCl_3$

(*ii*) By treating excess of benzene with ethyl chloride in presence of $AlCl_3$

(*iii*) By treating benzene with vinyl chloride in presence of $AlCl_3$ followed by reduction

(*iv*) By acetylation of benzene followed by Clemmensen reduction.

(*a*) By all methods (*b*) By (*ii*), (*iii*) and (*iv*) (*c*) By (*ii*) and (*iv*) (*d*) By (*iii*) and (*iv*).

23. The ortho to para ratio of the product formed by nitration of toluene was found to be 1.5. The *o*- to *p*-ratio of the product formed by nitration of *tert*-butylbenzene should be

(*a*) 1.5 (*b*) > 1.5

(*c*) < 1.5 (*d*) either of the three.

24. Chlorination of *tert*-butylbenzene gives substantial amount of *o*-substituted product, while its bromination gives nearly negligible amount of the product. This is due to which factor.

(*a*) The benzenonium ion formed in the first case is more stable than in the second case

(*b*) It is difficult to produce Br^+ ion than Cl^+ ion

(*c*) Difference in size of the electrophile

(*d*) Chlorine is more reactive than bromine.

25. Acetanilide on nitration at room temperature gives *o*- and *p*-nitroacetanilides in significant amounts. What is true about the same reaction at 0°C.

(*a*) Proportion of the *o*-product will be more than that of the *p*-product

(*b*) Proportion of *p*-isomer will be somewhat more than that of the *o*-isomer

(*c*) *p*-Isomer will almost be the exclusive product

(*d*) Proportion of both isomeric products will be equal.

26. Which of the following is not characteristic of a carbocation ?

(*i*) It can rearrange to a more stable carbocation

(*ii*) It can eliminate a hydride ion to form an alkene

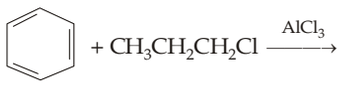
(*iii*) It can add to an alkene to form a new carbocation

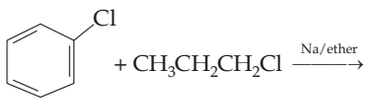
(*iv*) It can abstract a hydride ion from an alkane.

(*a*) (*ii*) (*b*) (*iii*)

(*c*) (*iv*) (*d*) (*ii*) and (*iv*).

27. Which method is preferred for the preparation of *n*-propyl chloride from benzene ?

(*a*) 

(*b*) 

(*c*) Both are undesirable

(*d*) Both give similar result.

28. Melting point of toluene ($C_6H_5CH_3$) is very low (–95°C) as compared to benzene (5°C). This is because

(*a*) benzene molecules have strong van der Waal's forces than that of toluene

(*b*) methyl group in toluene does not allow toluene molecules to associate due to electropositive nature

(*c*) of unsymmetrical structure of toluene

(*d*) of none of the above.

29. Which of the following reagents can not give *tert*-pentylbenzene as the major product ?

(*a*) Benzene + 3-Methyl-2-butanol $\xrightarrow{BF_3}$

(*b*) Benzene +Neopentyl alcohol $\xrightarrow{BF_3}$

(*c*) Benzene + 3-Methyl-1-butanol $\xrightarrow{BF_3}$

(*d*) None of the above.

30. What happens when aniline is treated with methyl chloride in presence of $AlCl_3$?

(*a*) It undergoes Friedel Craft reaction to form a mixture of *p*-methyl and *o*-methylaniline

(*b*) It does not undergo Friedel Craft reaction because $AlCl_3$ reacts with aniline instead of reacting with alkyl halide

(*c*) Aniline gets positive charge and deactivated for electrophilic substitution

(*d*) Both (*b*) and (*c*).

31. When carbon tetrachloride is treated with excess of benzene in presence of $AlCl_3$, the product formed is

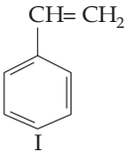
(*a*) only $(C_6H_5)_3CCl$

(*b*) only $(C_6H_5)_4C$

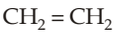
(*c*) a mixture of (*a*) and (*b*)

(*d*) None of the two.

32. Which of the following is more reactive towards electrophilic addition reactions ?



I



II

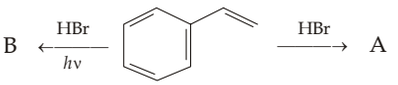
(*a*) I > II

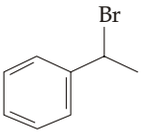
(*b*) II > I

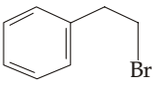
(*c*) Both are equal reactive

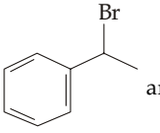
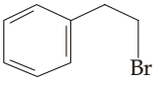
(*d*) Depends upon the nature of reagent.

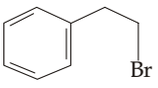
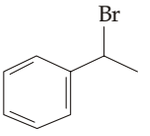
33. Observe the following reactions and predict the nature of A and B



(*a*) A and B both are 

(*b*) A and B both are 

(*c*) A is  and B is  (*d*)

A is  and B is 

34. Which of the following statement is true ? Among three iosmeric xylenes :

(*a*) *o*-Xylene is sulphonated most easily

(*b*) *p*-Xylene is sulphonated most easily

(*c*) *m*-Xylene is sulphonated most easily

(*d*) All the three xylenes are sulphonated at same rate.

35. Which of the following statement is true ?

(*a*) Allyl cation is more stable than the cyclopropenyl cation due to resonance

(*b*) Cyclopropenyl cation is more stable than the allyl cation due to resonance

(*c*) Cyclopropenyl cation is more stable than the allyl cation due to aromatic character of the former

(*d*) Both are equally stable because both shows resonance.

36. How many isomeric diaminobenzoic acids can be converted into *m*-phenylenediamine on decarboxylation ?

(*a*) 1 (*b*) 2

(*c*) 3 (*d*) 4.

37. Which of the monocylic polyenes is/are expected to be aromatic?

C_9H_{10} (I), $C_9H_9^+$ (II), $C_9H_9^-$ (III)

(*a*) II (*b*) III

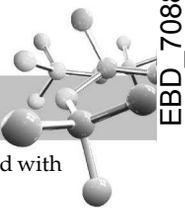
(*c*) II and III (*d*) None.

38. The stability order of the three carbocations follows the order

$\overset{+}{C}HCl$ (I), $\overset{+}{C}H_2CH_2Cl$ (II), $CH_3CH_2^+$ (III)

(*a*) I > II > III (*b*) III > I > II

(*c*) III > II > I (*d*) II > I > III.



39. Which effect controls the reactivity and orientation of electrophilic addition on vinyl chloride ?

$$CH_2 = CHCl \xrightarrow{HCl} CH_3CHCl_2$$

(*a*) Inductive
(*b*) Resonance
(*c*) Reactivity is controlled by the stronger inductive effect, and orientation by weaker but more selective resonance effect
(*d*) Reactivity is controlled by resonance effect, while orientation is controlled by inductive effect.

40. In nitration which of the following reaction is involved in the formation of NO_2^+ ?
(*a*) $HONO_2 \longrightarrow OH^- + NO_2^+$
(*b*) $H_2O^+NO_2 \longrightarrow H_2O + NO_2^+$
(*c*) Both (*a*) and (*b*)
(*d*) None of the two.

41. A 50 : 50 mixture of C_6H_6 and C_6D_6 are allowed to react with a limited amount of an electrophile Y. The product will consist of
(*a*) equal amounts of C_6H_5 Y and C_6D_5Y
(*b*) $C_6H_5Y > C_6H_5D$
(*c*) $C_6H_5Y < C_6H_5D$
(*d*) No reaction will take place.

42. 1, 3, 5-Trideuteriobenzene is allowed to react with the electrophile X to form monosubstituted product. Predict the relation between D : H ratio of the reactant and product.
(*a*) $[D : H]_{Product} = [D : H]_{Reactant}$
(*b*) $[D : H]_{Product} > [D : H]_{Reactant}$
(*c*) $[D : H]_{Product} < [D : H]_{Reactant}$
(*d*) All the above three possibilities exist.

43. An aromatic molecule will
(*i*) have $4n$ π-electrons (*ii*) have $(4n + 2)$ π electrons
(*iii*) be planar (*iv*) be cyclic.
Which of the above statement(s) is/are correct ?
(*a*) All the four (*b*) (*i*), (*iii*) and (*iv*)
(*c*) (*ii*), (*iii*) and (*iv*) (*d*) (*ii*) and (*iv*).

44. When nitrobenzene is treated with Br_2 in presence of $FeBr_3$, the major product formed is *m*-bromo-nitrobenzene. Statement which is related to obtain the *m*-isomer is
(*a*) the electron density on *meta* carbon is increased than that on *ortho* and *para* positions
(*b*) the intermediate carbonium ion formed after initial attack of Br^+ at the *meta* position is least destabilised
(*c*) loss of aromaticity when Br^+ attacks at the *ortho* and *para* positions and not at *meta* position
(*d*) easier loss of H^+ to regain aromaticity from the *meta* position than from *ortho* and *para* positions.

45. Toluene reacts with chlorine in the presence of light to give
(*a*) benzyl chloride (*b*) benzal chloride
(*c*) *p*-chlorotoluene (*d*) *o*-chlorotoluene.

46. The reaction of $H_3CCH = CH$—C$_6$H$_4$—OH with HBr gives

(*a*) $CH_3CHBrCH_2$—C$_6$H$_4$—OH

(*b*) CH_3CH_2CHBr—C$_6$H$_4$—OH

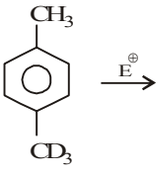
(*c*) $CH_3CHBrCH_2$—C$_6$H$_4$—Br

(*d*) CH_3CH_2CHBr—C$_6$H$_4$—Br.

47. What will be the final product when ethylbenzene is treated with the reagent listed, below :
(I) NBS, peroxide, heat (II) alcoholic KOH, Δ
(III) B_2H_6 (IV) H_2O_2, $HO^{\ominus}$

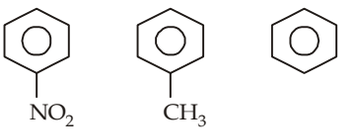
(*a*) $Ph-CH_2-CH_2-OH$ (*b*) $Ph-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_2-OH$

(*c*) $Ph-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$ (*d*) $Ph-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2Br$

48. 

(*a*) $E^{\oplus}$ attacks preferably at *o*-position to CH_3
(*b*) $E^{\oplus}$ attacks preferably at *o*-position to CD_3
(*c*) $E^{\oplus}$ can attack equally at any of the four positions
(*d*) Not predictable here

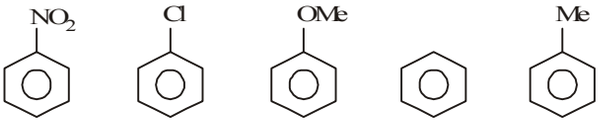
49. Ease of oxidation in following will be



(I) (II) (III)

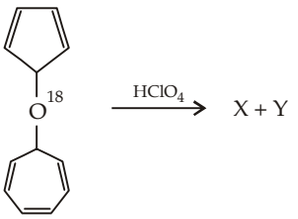
(*a*) I > II > III (*b*) III > II > I
(*c*) I > III > II (*d*) II > III > I

50. Arrange the following in the order of reactivity towards an electrophilic attack

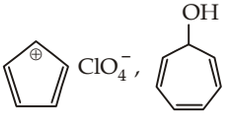


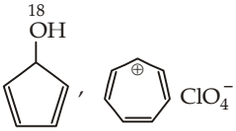
(I) (II) (III) (IV) (V)

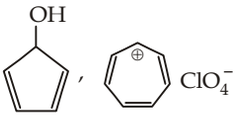
(*a*) V > IV > III > II > I (*b*) III > V > IV > II > I
(*c*) III > IV > V > II > I (*d*) V > IV > III > I > II

51. 

The products X and Y are :

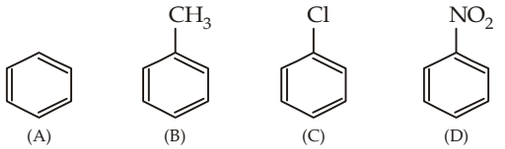
(*a*) 

(*b*) 

(*c*) 

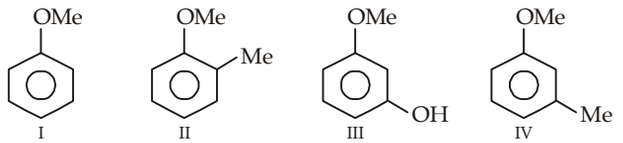
(*d*) 

52. Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds



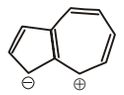
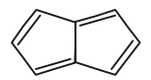
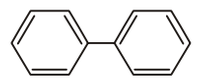
(*a*) A > B > C > D (*b*) D > C > B > A
(*c*) B > A > C > D (*d*) B > C > A > D

53. Arrange the compounds in decreasing order of reactivity towards bromine :



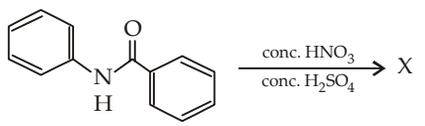
(*a*) III > II > IV > I (*b*) II > IV > I > III
(*c*) III > IV > II > I (*d*) IV > II > I > III

54. Which species are aromatic :

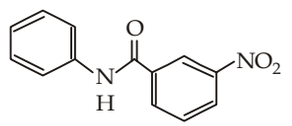
(I) 
(II) 
(III) 
(IV) 

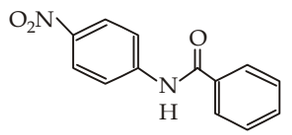
(*a*) I, II & III (*b*) I, III & IV
(*c*) I & III (*d*) II & III

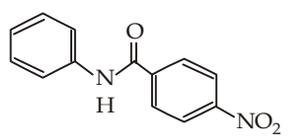
55. In the following reaction,

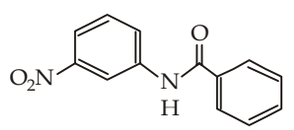


the structure of the major product 'X' is

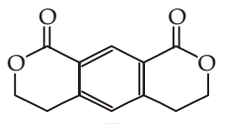
(*a*) 

(*b*) 

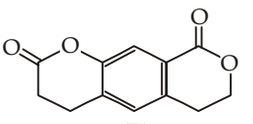
(*c*) 

(*d*) 

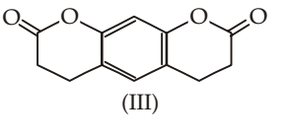
56. Increasing order of rate of reaction with HNO_3/H_2SO_4 is



(I)



(II)



(III)

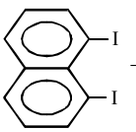
(*a*) III < II < I (*b*) II < III < I
(*c*) I < III < II (*d*) I < II < III

57. $A \xrightarrow[R-OH]{Na/liq.NH_3} B \xrightarrow[\Delta]{(i)O_3/H_2O} 2CO_2 + 2CH_3COOH$

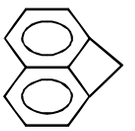
Compound 'A' is

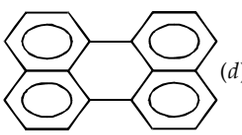
(*a*) Benzene (*b*) $CH_3-\overset{O}{\overset{\|}{C}}-C\equiv C-\overset{O}{\overset{\|}{C}}-CH_3$

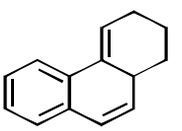
(*c*) Toluene (*d*) 

58. 

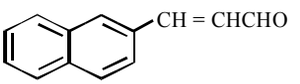
Product is

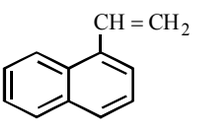
(*a*)  (*b*) 

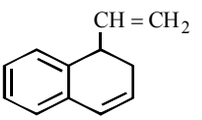
(*c*)  (*d*) Reaction not possible

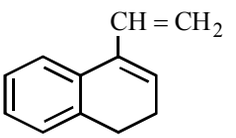
59. $[A] + CH_2 = CH_2 \longrightarrow$ 

Compound [A] is

(*a*) 

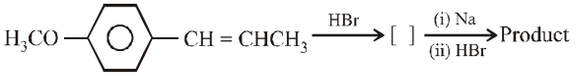
(*b*) 

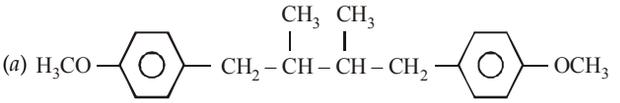
(*c*) 

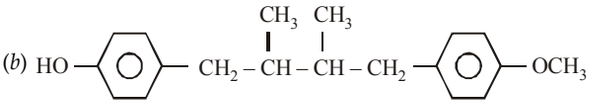
(*d*) 

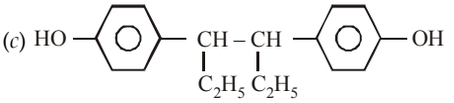
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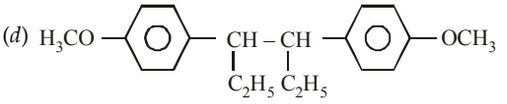
60. The final product in the following series of reactions should be



(*a*) 

(*b*) 

(*c*) 

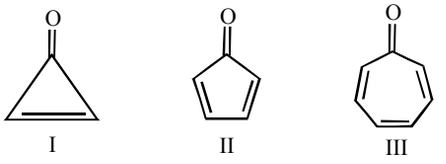
(*d*) 

61. $C_6H_6 + D_2SO_4 \longrightarrow$ Product is

(*a*) $C_6H_5SO_3H$ (*b*) $C_6H_5SO_3D$

(*c*) C_6D_6 (*d*) No reaction

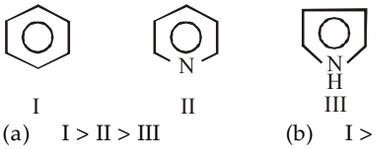
62. Which of the following is least stable ?



(*a*) I (*b*) II

(*c*) III (*d*) All are equally stable

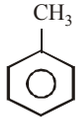
63. Arrange the following compounds in decreasing order of reactivity towards electrophilic substitution?

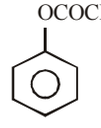


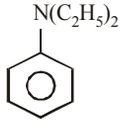
(a) I > II > III (b) I > II = III

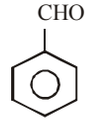
(c) III > II > I (d) III > I > II

64. Which of the compound undergoes electrophilic substitution most easily ?

(*a*) 

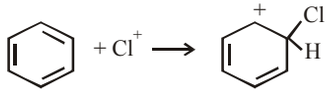
(*b*) 

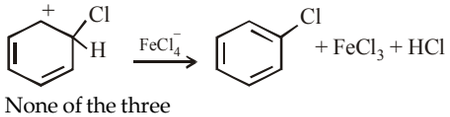
(*c*) 

(*d*) 

65. Which one is the slow step in the chlorination of benzene?

(*a*) $Cl_2 + FeCl_3 \rightarrow FeCl_4^- + Cl^+$

(*b*) 

(*c*) 

(*d*) None of the three

66. During nitration of benzene using a mixture of conc. HNO_3 and conc. H_2SO_4, function of conc. H_2SO_4 is to increase the rate of reaction by increasing the concentration of NO_2^+ according to following reaction.

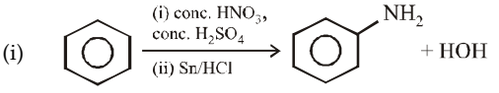
$$HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$$

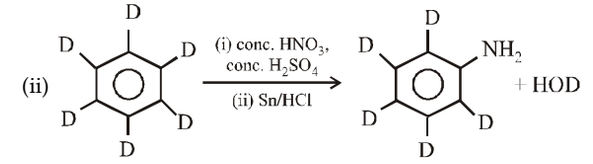
Here nitric acid acts as

(*a*) a stronger acid (*b*) a weaker acid

(*c*) a base (*d*) none of the three

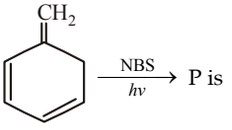
67. Which of the two reactions proceed faster ?

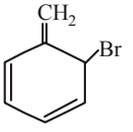
(i) 

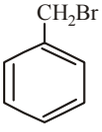
(ii) 

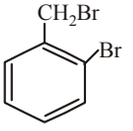
(*a*) (i) (*b*) (ii)

(*c*) (i) = (ii) (*d*) Not definite

68. 

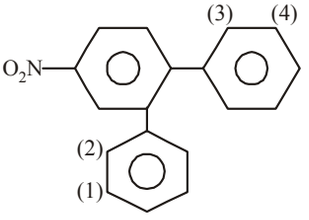
(*a*) 

(*b*) 

(*c*) 

(*d*) All the three

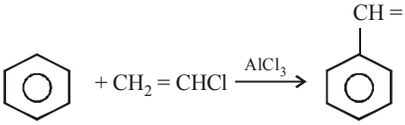
69. Which of the position in the following compound is liable to be attacked by an electrophile ?

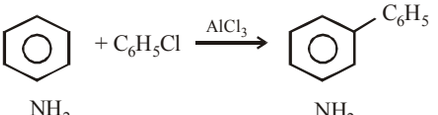


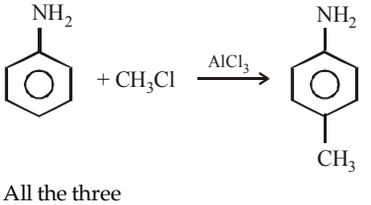
(*a*) 1 (*b*) 2

(*c*) 3 (*d*) 4

70. Which of the reaction is not possible ?

(*a*) 

(*b*) 

(*c*) 

(*d*) All the three

EXERCISE 7.2 (MCQ >1 option correct, Passage based, Matching, A/R)

DIRECTIONS for Q. 1 to Q. 21 : Multiple choice questions with one or more than one correct option(s).

1. The product obtained in the reaction

$$C_6H_5CH_2-CH_3 \xrightarrow[273K]{Cl_2,\ h\nu}$$ is

(a) $C_6H_5CHCl-CH_3$ (b) $C_6H_5CH_2CH_2Cl$

(c) $C_6H_5CCl_2-CH_3$ (d) $C_6H_5CHClCH_2Cl$

2. Which of the following are true?

(a) Benzene tends to undergo substitution rather than addition reactions

(b) All hydrogen atoms of benzene are equivalent

(c) The carbon-carbon bonds of benzene are alternatively short and long around the ring

(d) There can be two o-disubstituted derivatives

3. Which of the following characteristics does an aromatic compound exhibit?

(a) it should have (4n + 2) π-electrons

(b) it should be planar and conjugated

(c) it should have 4n π-electrons

(d) it should possess high resonance energy

4. Which of the following are obtained by the fractionation of coal tar?

(a) light oil (b) middle oil

(c) heavy oil (d) vegetable oil

5. Which of the following statements are true for benzene?

(a) it is a flat, regular, hexagonal molecule

(b) each C–C–C angle is 109°28'

(c) the C–C bond length is 1.39Å

(d) All carbon atoms are sp^3-hybridized

6. Which of the following meet the requirements of the Huckel rule?

(a) Naphthalene

(b) Anthracene

(c) 1,3,5,6-Cyclo-octateraene

(d) 1,3-Cyclobutadiene

7. Benzene can be obtained by

(a) $C_6H_5COOH + NaOH \xrightarrow[\Delta]{CaO}$

(b) $C_6H_5OH + Zn \xrightarrow{\Delta}$

(c) $C_6H_5N{=}NCl + H_2O \longrightarrow$

(d) All of these

8. Benzene can undergo

(a) substitution (b) addition

(c) elimination (d) oxidation

9. Which of the following acid can be used as catalyst in Friedel-Craft reaction?

(a) $AlCl_3$ (b) BF_3

(c) HCl (d) HNO_3

10. Toluene, when treated with Br_2/Fe, gives *p*-bromotoluene as the major product because CH_3 group

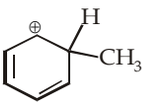
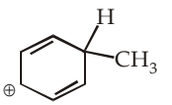
(a) is *para* directing

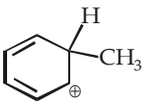
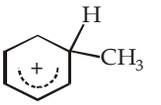
(b) is *meta* directing

(c) activates the ring by hyperconjugation

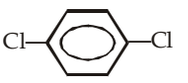
(d) deactivates the ring

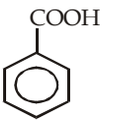
11. In the alkylation of benzene, stable σ complex

(a)  (b) 

(c)  (d) 

12. Moth repellent is /are :

(a)  (b) perchlorethane

(c)  (d) 

13. Toluene when treated with Br_2 / Fe gives *p*-bromotoluene as the major product because the $-CH_3$ group.

(*a*) is *para*-directing

(*b*) is *meta*-directing

(*c*) activates the ring by hyperconjugation

(*d*) deactivates the ring

14. An aromatic molecule will

(*a*) have $4n\,\pi$ electrons (*b*) have $(4n + 2)\pi$ electrons

(*c*) be planar (*d*) be cyclic

15. Benzene is obtained from benzene diazonium chloride by

(*a*) reduction with alkaline stannous chloride

(*b*) reduction with acidic stannous chloride

(*c*) action of hypophosphorus acid

(*d*) action of ethyl alcohol

16. Which of the following are *meta*-directing?

(*a*) SO_2Cl (*b*) $COCH_3$

(*c*) CN (*d*) NHR

17. The type of substitution reactions of benzene hydrocarbons are

(*a*) elimination (*b*) electrophilic

(*c*) nucleophilic (*d*) free radical

18. Benzene molecule has

(*a*) 9 sigma and 3 pi-bonds

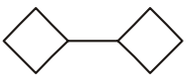
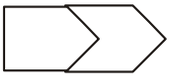
(*b*) 30 electrons

(*c*) 12 sigma and 3 pi-bonds

(*d*) 21 electrons

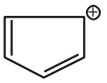
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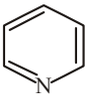
19. Which of the following hydrocarbons contains 12 secondary and 2 tertiary hydrogen atoms ?

(*a*)  (*b*) 

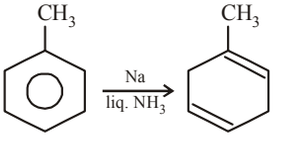
(*c*)  (*d*) 

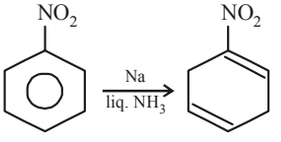
20. Which of the following are antiaromatic ?

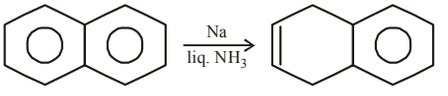
(a)  (b) 

(c)  (d) 

21. Which of the following are examples of Birch reduction ?

(a) 

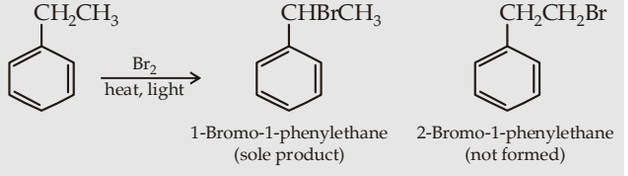
(b) 

(c) 

(d) $CH_3C \equiv CCH_3 \xrightarrow[\text{liq. } NH_3]{Na} CH_3CH = CHCH_3$

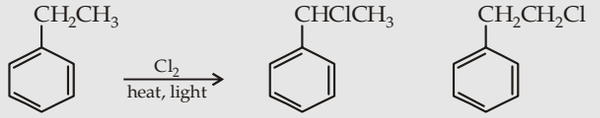
INSTRUCTION for Q. 22 to 36 : Read the passages given below and answer the questions that follow.

PASSAGE 1

I. 

1-Bromo-1-phenylethane (sole product) 2-Bromo-1-phenylethane (not formed)

{It is important to note that as in alkanes, orientation of side chain chlorination of ethylbenzene shows that although chlorine atoms (chlorine free radicals) also preferentially attack benzylic hydrogen, here the preference is less than that in bromination.}

II. 

1-Chloro-1-phenylethane (91%) 2-Chloro-1-phenylethane (9%)

22. The intermediates formed in both of the above products differ in their stability remarkably; which of the following statement is true?

(a) Leaving Kekule's structure, the intermediate formed in I has 3 resonating structures while that formed in II has 2 resonating structures

(b) the intermediate formed in I is a resonance hybrid of 3 structures, while that formed in II has no possibility of resonance

(c) the intermediate formed in I is a resonance hybrid of two structures, while that formed in II has three such structures.

(d) None of the statement is correct.

23. Which of the above two reactions is regiospecific and which one is regioselective?

	Chlorination	*Bromination*
(a)	regiospecific	regioselective
(b)	regioselective	regiospecific
(c)	regiospecific	regiospecific
(d)	regioselective	regioselective

24. From the above set of reactions, it can be concluded that

(a) bromine is more reactive and less selective than chlorine

(b) bromine is less reactive and more selective than chlorine

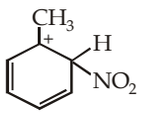
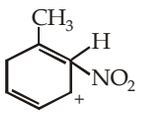
(c) chlorine is more reactive and more selective than bromine

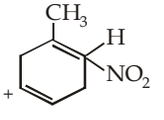
(d) bromine is more reactive and more selective than chlorine

PASSAGE 2

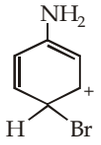
We can say that electron-realeasing group stablises the carbocation by dispersing its positive charge and thus activates the ring, while an electron-withdrawing group destabilises the carbocation by intensifying its positiive charge and thus deactivates the ring. Further, an activating group activates although all positions of the benzene ring, its activating effect is much more on *ortho* and *para* positions than on meta position with the result substitution occurs mainly on the ortho and para positions. Similarly, a deactivating group deactivates although all positions in the ring, its deactivating effect is much more on ortho and para positions than on meta position with the result further reaction occurs mainly on the meta position. In short, the activating or deactivating effect of a group is strongest at the ortho and para-positions.

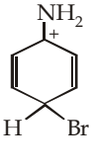
25. Toluene when treated with a nitrating mixture forms o-nitrotoluene as one of the products. Which of the inntermediate best explains this ortho substitution?

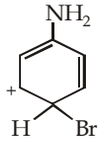
(a)  (b) 

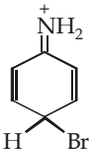
(c)  (d) All equally

26. On bromination, aniline undergoes substitution in ortho and para positions. Substitution in para position involves a resonance-stabilized intermediate, which resonating structure contributes most to the concerned hybrid

(a) 

(b) 

(c) 

(d) 

27. The correct order for the monobromination of the following compounds is

$\underset{I}{C_6H_5NH_2}$ $\underset{II}{C_6H_5\overset{+}{N}H_3Cl^-}$ $\underset{III}{C_6H_5NHCOCH_3}$

$\underset{IV}{C_6H_5Cl}$ $\underset{V}{C_6H_5COCH_3}$

(a) I > II > III > IV > V (b) II > I > III > IV > V

(c) I > III > IV > V > II (d) I > III > II > V > IV

PASSAGE 3

On the basis of the molecular orbital treatment of various aromatic compounds, it has been observed that an aromatic compound must fulfill the following theoretical requirements.

(a) It must have an uninterrupted cyclic cloud of π electrons above and below the plane of the molecule (often called as π cloud). Let us look what does this mean ?

(i) For the π cloud to be cyclic, the molecule must be cyclic.

(ii) For the π cloud to be uninterrupted, every atom in the ring must have a p orbital

(iii) For the π cloud to be formed, each *p* orbital must be able to overlap with the *p* orbitals on either side of it. Therefore, the molecule must be planar.

(b) The π cloud must contain an odd number of pair of electrons, (4n +2)π electrons, where *n* is an integer.

28.  is

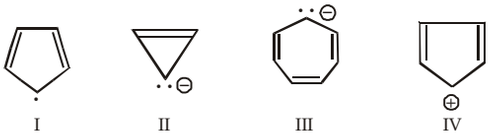
(a) aromatic

(b) non-aromatic due to (a) (ii)

(c) non-aromatic due to (a)(iii)

(d) non-aromatic due to (b)

29. Which of the following structure is not aromatic ?

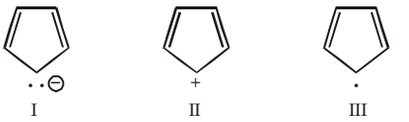


I II III IV

(a) I and II (b) II and IV

(c) IV (d) All the four

30. The stability order of the three compounds is



I II III

(a) I>II>III (b) I>III>II

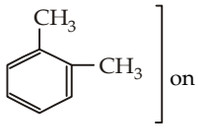
(c) I>II=III (d) I=III>II

PASSAGE 4

In the electrophilic substitution of benzene ring, the second substituent is directed by the group already present. Electron releasing groups (+*I* and +*M*) are *ortho-para*-directing and activating, whereas the electron withdrawing groups (–*I* and –*M*) are *meta*-directing and deactivating.

Halogens are placed under the category of +T (Tautomeric) groups because they have –Inductive and +Mesomeric effect. These groups are deactivating but *ortho-para*-directing.

In the introduction of third group to the benzene ring, the product of minimum steric hindrance is formed.

31. *Ortho*-xylene  on mononitration gives :

(*a*) two products (*b*) three products

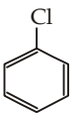
(*c*) one product (*d*) four products

32. Which of the following is not an *ortho, para*-directing group?

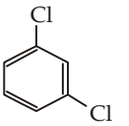
(*a*) –F (*b*) –NC

(*c*) $-OCOCH_3$ (*d*) $-CCl_3$

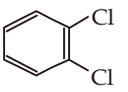
33. Which of the following substituted benzene derivatives would furnish three isomers when one more substituent is introduced?



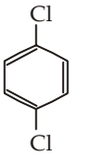
I



II



III



IV

(*a*) Only I (*b*) I and II

(*c*) I, II and III (*d*) IV only

PASSAGE 5

Benzene undergoes Friedel-Craft alkylation as well as acylation. With long *n*-alkyl chains, rearranged products are obtained, thus for preparing benzene derivatives with *n*-alkyl chains, Friedel-Craft acylation or some other suitable method is used.

EBD_7088

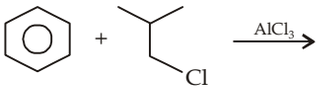
34. Using anhydrous $AlCl_3$ as catalyst, which of the following reactions produces ethylbenzene?

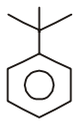
(*a*) $CH_3CH = CH_2 + C_6H_6$

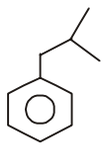
(*b*) $CH_2 = CH_2 + C_6H_6$

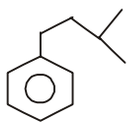
(*c*) $CH_3CH_2OH + C_6H_6$

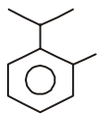
(*d*) $CH_3CH_3 + C_6H_6$

35.  P; Here P is

(*a*) 

(*b*) 

(*c*) 

(*d*) 

36. Wurtz Fittig reaction between bromobenzene and *n*-propyl bromide in presence of metallic sodium in dry ether mainly gives

(*a*) *n*-hexane (*b*) biphenyl

(*c*) *n*-propylbenzene (*d*) isopropylbenzene

Instructions for Q. 37 to 43 : Following questions are Multiple Matching type Questions :

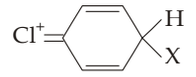
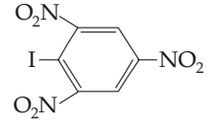
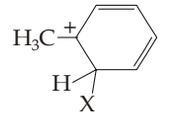
37.

	Column I **(Group present on benzene)**		***Column II*** **(Electronic effect responsible for directive influence)**
(A)	—CH = CH_2	(a)	+ M
(B)	—$COOCH_3$	(b)	– I
(C)	—$OCOCH_3$	(c)	– M
(D)	—O^-	(d)	– E

38.

	Column I		***Column II***
(A)		(a)	Aromatic with 6π electrons
(B)		(b)	Aromatic with 2π electrons
(C)		(c)	Nonaromatic
(D)		(d)	Antiaromatic

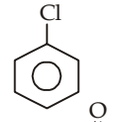
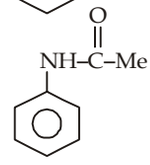
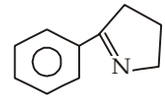
39.

	Column I		***Column II***
(A)		(a)	Especially unstable
(B)		(b)	Especially stable
(C)		(c)	Deactivating but *o*, *p*-directing
(D)		(d)	Steric inhibition

40.

	Column I		***Column II***
(A)	Directing influence of $-CCl_3$	(a)	Inductive effect
(B)	Electrophilic substitution in phenoxide ion	(b)	Mesomeric effect
(C)	Electrophilic substitution in $C_6H_5NH_2$ in presence of HCl	(c)	Hyperconjugation
(D)	Directing influence of $C_6H_5^-$	(d)	Electromeric effect

41.

	Column I		***Column II***
(A)		(a)	Group attached to benzene ring is a +M group here.
(B)		(b)	Group attached to benzene ring is a –M group here.
(C)		(c)	Electrophile would attack on ortho or para position
		(d)	Rate of electrophilic substitution is less than that of benzene.

42.

	Column I **Reactants**		***Column II*** **No. of chlorinated products**
(A)	Benzene $\xrightarrow{Cl_2, light}$	(a)	Three compounds
(B)	Toluene $\xrightarrow{Cl_2, light}$	(b)	Four compounds
(C)	Methane $\xrightarrow{Cl_2, light}$	(c)	Single monochloro derivative
(D)	Benzene $\xrightarrow{Cl_2, AlCl_3}$	(d)	Six isomeric compounds

43.

	Column I		***Column II***
(A)	$-COOCH_3$	(a)	Activating
(B)	–N = O	(b)	*o*, *p*-Directing
(C)	$-NH_2$	(c)	Deactivating
(D)	–Cl	(d)	*m*-Directing

Instructions for Q. 44 to 53 : Following questions are Assertion and Reasoning Type Questions :

Note : Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 5 choices (a), (b), (c), (d) and (e) out of which ONLY ONE is correct.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement -1 is True, Statement-2 is False.
(d) Statement -1 is False, Statement-2 is True.
(e) Statement -1 is False, Statement-2 is False.

44. **Statement - 1 :** Alkyl benzene is not prepared by Friedel-Craft alkylation of benzene.
Statement - 2 : Alkyl halides are less reactive than acyl halides.

45. **Statement - 1 :** Rates of nitration of benzene and hexadeuterobenzene are different.
Statement - 2 : C–H bond is stronger than C–D bond.

46. **Statement - 1 :** Cyclopentadienyl anion is much more stable than allyl anion.
Statement - 2 : Cyclopentadienyl anion is aromatic in character.

47. **Statement 1 :** Benzene undergo nucleophilic substitution reactions easily and electrophilic substitutions with difficulty.
Statement 2 : Due to the presence of 6π electrons, benzene behaves as rich source of electrons

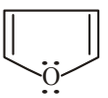
48. **Statement - 1 :** Bromobenzene upon reaction with Br_2/Fe gives 1,4-dibromobenzene as the major product.
Statement - 2 : In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile.

49. **Statement 1 :** Rates of nitration of benzene and hexadeuterobenzene are different.
Statement 2 : C–H bond is stronger than C–D bond.

50. **Statement-1 :** Nitration of benzene and hexadeuterobenzene occur exactly at the same rate.
Statement-2 : The cleavage of C–H bond is not the rate-determining step of the reaction.

51. **Statement-1 :** Alkylbenzene is not prepared by Friedel-Craft's alkylation of benzene.
Statement-2 : Alkyl halides are less reactive than acyl halides.

52. **Statement-1 :** Furan has an aromatic sextet.

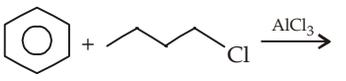


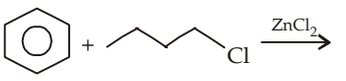
Statement-2 : The two lone pairs of electrons on oxygen and a π electron pair form an aromatic sextet.

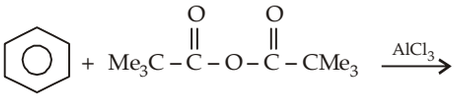
53. **Statement-1 :** Aniline becomes more reactive towards electrophilic aromatic substitution in presence of strongly acidic solution.
Statement-2 : The amino group is completely protonated in strongly acidic medium. Thus the lone pair of electrons on the nitrogen is no longer available for resonance.

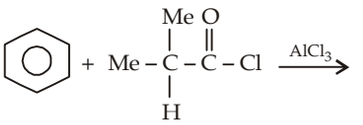
Instructions for Q. 54 to 58 : Following questions are Integer Type Questions :

54. Write total number of hydrogen atoms on all the carbon atoms which are connected directly by a single bond to benzylic carbon (carbon connected to benzene ring) in the product

(*a*) 

(*b*) 

(*c*) 

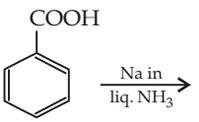
(*d*) 

55.  $\longrightarrow CH_4$

Arrange the steps involved in the above conversion and give answer in four digits, viz. if the steps are 2, 3, 4 and 5, the answer would be 2345.

1. Br_2/hv	2. aq. KOH
3. conc. NaOH/Δ	4. O_3/Zn/H_2O
5. Red P/HI (excess)	6. H_2/Pd (excess)
7. NaOH / CaO / Δ	8. $H^{\oplus}$/ $KMnO_4$ / Δ

56. Give sum of the number of carbon atoms, where hydrogen is added during following reaction



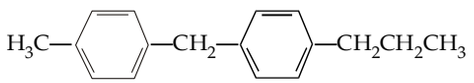
57. Give sum of locants in iso-octane.

58. How many π electrons are present in



EXERCISE 7.3 (Subjective Problems)

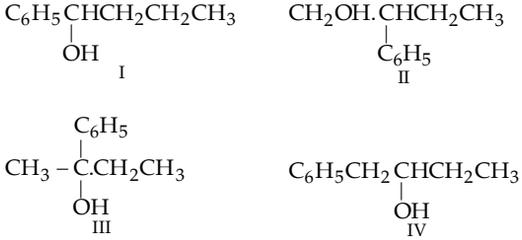
1. Arrange the various hydrogen atoms of the chain in the following compounds in order of their decreasing ease of abstraction by bromine atoms.

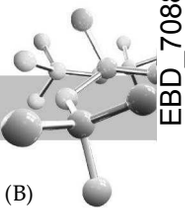
(*i*) 

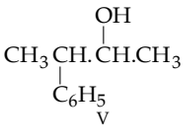
(*ii*) 1, 2, 4-Trimethylbenzene.

2. Label the different hydrogen atoms in order of decreasing reactivity (1 for the most reactive, 2 for the next etc.) of abstraction by bromine atoms in 1-phenyl-2-hexene. Also write down the possible monobromo product (*s*) formed on abstraction of the most reactive, second most reactive and the least reactive hydrogen atoms.

3. Arrange the alcohols in each case in order of ease of dehydration.

(*i*) 





(*ii*) $C_6H_5CH_2CH_2OH$, $C_6H_5CHOHCH_3$, $(C_6H_5)_2C(OH)CH_3$
(*iii*) α-Phenylethyl alcohol, α-(*p*-bromophenyl) ethyl alcohol, α-(*p*-tolyl) ethyl alcohol.

4. Arrange the following compounds in order of reactivity towards addition of HCl :
Styrene, *p*-chlorostyrene, *p*-methylstyrene.

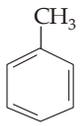
5. When a mixture of toluene and $BrCCl_3$ was irradiated with UV light, benzyl bromide and $CHCl_3$ are formed as the main products along with HBr and C_2Cl_6. Explain with mechanism.

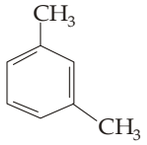
6. How can you distinguish between 1-phenylpropene, 2-phenylpropene and 3-phenylpropene ?

7. Write down the main product in each case

(*i*) $C_6H_5CH_2CH(CH_3)_2 + Br_2 \xrightarrow{UV}$

(*ii*) $C_6H_6 + (CH_3)_2CHCH_2Cl \xrightarrow{AlCl_3}$

(*iii*)  $+ (CH_3)_3CCH_2OH \xrightarrow{BF_3}$

(*iv*)  $+ (CH_3)_3CCl \xrightarrow[100°C]{AlCl_3}$

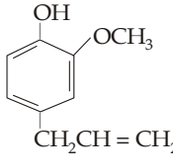
(*v*) $C_6H_6 + (CH_3)_2CHCH_2OH \xrightarrow{H_2SO_4}$

(*vi*) $C_6H_5CH_2CH_3 \xrightarrow[(ii)\ NaCN]{(i)\ Br_2,\ heat,\ light}$

8. Give all possible products in the following reactions and mention the major product, if any

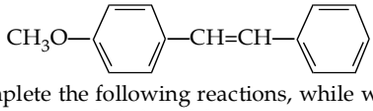
(*a*) $C_6H_5CH_2CHOHCH(CH_3)_2 \xrightarrow{H_2SO_4}$
(*b*) $C_6H_5CH = CHCH_3 + HBr \longrightarrow$
(*c*) $C_6H_5CH = CHCH_3 + HBr \xrightarrow{peroxide}$
(*d*) $C_6H_5CH = CHCH{=}CH_2 + Br_2$ (equal amounts) $\longrightarrow$
(*e*) $Me_3N^+CH = CH_2 + HI \longrightarrow$
(*f*) $CH_2 = CHCF_3 + HBr \xrightarrow{AlBr_3}$.

9. Predict the product in each of the following reaction :

(*i*)  $\xrightarrow[heat]{KOH}$

(*ii*) $C_6H_5CH = CH - CH = CH_2 + H_2 \xrightarrow[30°C]{Ni}$

(*iii*) $C_6H_5C \equiv CCH_2C_6H_5 + H_2 \xrightarrow{Pd}$

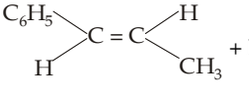
(*iv*)  $+ HBr \longrightarrow$

10. Complete the following reactions, while writing structures of the compounds (A) to (M)

(*a*) $C_6H_5CH_2CH_2CH_3 + Br_2 \xrightarrow{UV}$ (A) $\xrightarrow[KOH]{Alc}$ (B)
$\xrightarrow[KMnO_4]{Cold\ dil}$ (C) $\xrightarrow{hot\ KMnO_4}$ (D) + (E)

(*b*) $C_6H_5Br + Mg \xrightarrow{ether}$ (F) $\xrightarrow{H_2C = CHCH_2Br}$ (G)
$\xrightarrow[heat]{KOH}$ (H) $\xrightarrow[300°C]{Br_2}$ (I)

(*c*) $p\text{-}CH_3 . C_6H_4 . C \equiv C . C_6H_5 \xrightarrow{H_2/Pt}$ (J) $\xrightarrow{HBr}$ (K)

(*d*)  $+ Br_2$ (Fe) $\longrightarrow$ (L)
$\xrightarrow[peroxide]{HBr}$ (M).

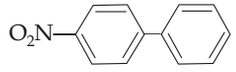
11. Give structures and names of the principal products of *trans*-1-phenyl-1-propene with

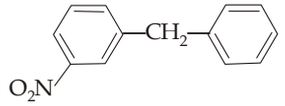
(*i*) H_2, Ni, 200°C, 100 atm
(*ii*) Excess Br_2, Fe
(*iii*) cold dil. $KMnO_4$
(*iv*) hot $KMnO_4$
(*v*) performic acid
(*vi*) $CHBr_3$, *ter*-BuOK.

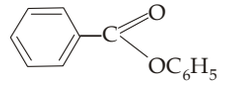
12. Three isomeric dibromobenzenes are converted into dibromonitrobenzenes, predict the total number of the possible isomeric dibromonitrobenzenes.

13. How many isomers are theoretically possible for the ring mononitration of *o*-, *m*- and *p*-bromochlorobenzenes.

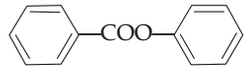
14. (*i*) Indicate the ring which is liable to be attacked in nitration, and give structures of the principal products

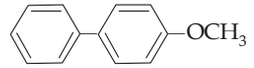
(*a*) 

(*b*) 

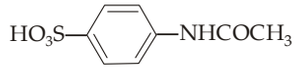
(*c*) 

(*ii*) Write the structures of possible major monosubstituted products formed when Br^+ attacks the following molecules. Justify your answer

(*a*) 

(*b*) 

(*c*) 

(*d*) 

15. Arrange the following compounds in order of acidity.
Toluene, *n*-pentane, diphenylmethane and triphenylmethane.

16. Arrange the following alcohols of each set in order of reactivity towards aqueous HBr :

(*i*) 1-Phenyl-1-propanol, 1-phenyl-2-propanol, 3-phenyl-1-propanol
(*ii*) Benzyl alcohol, *p*-hydroxybenzyl alcohol, *p*-cyanobenzyl alcohol.

17. Predict the order of reactivity for the following chlorides for (*a*) S_{N^1} and (*b*) S_{N^2}
$C_6H_5CH_2Cl$, $C_6H_5CH(Cl)CH_3$, $C_6H_5C(Cl)(CH_3)_2$.

18. Which of the annulenes upto 20 carbon atoms are expected to show aromaticity theoretically. Further, predict in which of these structures aromaticity is permitted by geometry of the molecule?

19. Explain the following observations :
(*a*) When trityl chloride is treated with $AlCl_3$ or trityl alcohol is treated with conc. H_2SO_4, a yellow colour is obtained which is converted to white solid on dilution with water.
(*b*) When triphenylmethane is added to a solution of $NaNH_2$ in liq. NH_3, a deep-red solution is obtained which disappears on dilution with water.
(*c*) When trityl chloride reacts with zinc in benzene, a red colour is obtained which decolorises on reaction with oxygen.
(*d*) Reaction of carbon tetrachloride with excess of benzene in presence of $AlCl_3$ gives $(C_6H_5)_3CCl$ and not $(C_6H_5)_4C$.

20. Explain the following :
(*i*) The C—H homolytic bond dissociation energy for benzene is considerably larger than for cyclohexane.
(*ii*) The relative acidic character of the following three hydrocarbons is
Acetylene > Benzene > *n*-Pentane.
(*iii*) Cyclooctatetraene rapidly decolorizes cold aq. $KMnO_4$, white benzene does not do so.
(*iv*) Benzene reacts with neopentyl bromide in presence of $AlCl_3$ to form *tert*-pentylbenzene.
(*v*) Bromination of benzene in presence of thallium acetate gives only the *p*-isomer.
(*vi*) *m*-Xylene is more reactive towards ring nitration than the *p*-xylene.
(*vii*) Bromination of *tert*-butylbenzene with bromine in presence of $AlBr_3$ gives isobutene as one of the products.
(*viii*) Polysubstitution is a complicating factor in Friedel-Crafts alkylation but not in aromatic nitration, sulphonation or halogenation.
(*ix*) One mole of triphenylmethanol lowers the freezing point of 1000 g of 100% H_2SO_4 twice as much as one mole of methanol.
(*x*) Phenyl group is known to exert negative inductive effect. But each phenyl ring in biphenyl (C_6H_5—C_6H_5) is more reactive than benzene towards electrophilic substitution.
(*xi*) Alkylation of phenol and aniline with alkyl halide in presence of $AlCl_3$ give poor yields.
(*xii*) Toluene reacts with bromine in presence of light to give benzyl bromide while in presence of $FeBr_3$ it gives *p*-bromotoluene.
(*xiii*) Normally, benzene gives electrophilic substitution rather than electrophilic addition although it has double bond.
(*xiv*) *tert*-Butylbenzene does not give benzoic acid on treatment with acidic $KMnO_4$.

21. Account for the high reactivity of pyrrole toward electrophilic substitution than benzene and also the orientation of substitution.

22. Predict the response of allylbenzene to the following reagents :
(*a*) cold conc. H_2SO_4
(*b*) Br_2 in CCl_4
(*c*) cold dilute neutral permanganate
(*d*) $CHCl_3$ and $AlCl_3$
(*e*) CrO_3 and H_2SO_4.

23. Give necessary steps to accomplish the following conversions.
(*i*) Benzene to styrene
(*ii*) Benzene to *p*-chlorostyrene
(*iii*) Benzene to allylbenzene (3-phenylpropene)
(*iv*) Benzene to *n*-propylbenzene.
(*v*) Benzene to 2-phenylpropene
(*vi*) Ethylbenzene to E-1-phenylpropene
(*vii*) Ethylbenzene to *p*-nitrostyrene
(*viii*) Tolune to *p*-bromobenzylbromide
(*ix*) Toluene to *p*-bromobenzoic acid
(*x*) Tolune to *m*-bromobenzoic acid
(*xi*) Toluene to *p*-nitrodiphenylmethane.

24. Give necessary steps involved in the following conversions.
(*i*) Toluene to 1, 2, 3-trimethylbenzene
(*ii*) Benzene to 3, 4-dibromonitrobenzene
(*iii*) Toluene to *p*-benzylnitrobenzene
(*iv*) Benzene to 1, 1-diphenylethane
(*v*) Benzene to *o*-dibromobenzene
(*vi*) Toluene to 2-bromo-4-nitrobenzoic acid
(*vii*) *m*-Xylene to 5-nitroisophthalic acid.

25. Explain the following :
(*i*) Nitrobenzene, but not benzene, is used as solvent for the alkylation of bromobenzene.
(*ii*) In monoalkylation of benzene with an alkyl halide in presence of $AlCl_3$, an excess of benzene is used.
(*iii*) Diphenyl can't be prepared by the following reaction

$$C_6H_6 + C_6H_5Cl \xrightarrow{AlCl_3} C_6H_5C_6H_5 + HCl$$

(*iv*) Sulphonation of toluene at 0°C gives 53% *o*- and 53% *p*- ; while at 100°C it gives 13% *o*- and 79% *p*–.
(*v*) *p*-Chloronitrobenzene has less dipole moment (2.4D) than *p*-nitrotoluene (4.4D).
(*vi*) Nitration of toluene ($C_6H_5CH_3$) gives 50% *o*-nitroderivative, while $(C_6H_5)_3CMe_3$ gives only 16%.
(*vii*) Of all the aryl halides, C_6H_5F gives the least amount of ortho product on nitration.
(*viii*) The percentage of *m*-substitution of toluene varies with the reagent.

Reagent	Br_2 in CH_3COOH	HNO_3 in CH_3COOH	CH_3CH_2Br in $GaBr_3$
% of *m*	0.5	3.5	21

(*ix*) The —OCH_3 group strongly activates the *o, p*-positions but weakly deactivates the *m*-position ; while —CH_3 activates all positions, but mainly *o, p*-.
(*x*) The rate of nitration by conc. HNO_3 falls sharply on addition of salts of nitric acid and increases on addition of conc. H_2SO_4.

26. At low temperature, 1, 3, 5-trimethylbenzene reacts with HF and BF_3 to form a bright-yellow coloured solid having three reactants in the ratio of 1 : 1 : 1. The compound is poorly soluble in organic solvents and when molten conducts an electric current. On heating, the compound evolves BF_3 and regenerates mesitylene. Deduce the structure of the compound.

27. A benzenoid hydrocarbon of the molecular formula C_9H_{12} forms four isomeric mononitro derivatives. Can you write down the structure of the hydrocarbon ?

28. A monosubstituted alkylbenzene of the formula $C_{10}H_{14}$ resists vigorous oxidation to an aryl carboxylic acid. Name the compound and write down its various monosubstituted isomers.

29. An arene of the molecular formula $C_{10}H_{14}$ on vigorous oxidation gives an acidic compound, $C_8H_6O_4$ which forms only one monobrome derivative. Deduce the structure of the arene and draw the structures of its five isomeric monochloro derivatives.

30. An aromatic hydrocarbon A of the molecular formula $C_{16}H_{16}$ decolourises bromine in CCl_4 and adds an equimolar amount of hydrogen. Oxidation of A with hot $KMnO_4$ gives a dicarboxylic acid B of the formula $C_8H_6O_4$. Compound B on chlorination gives only one monochloro derivative. Deduce the structure of the compound A. Also name the two possible isomers of this compound.

EBD_7088

SOLUTIONS

EXERCISE 7.1

1	(c)	**6**	(d)	**11**	(d)	**16**	(d)	**21**	(c)	**26**	(c)	**31**	(a)	**36**	(c)	**41**	(b)	**46**	(b)	**51**	(b)	**56**	(d)	**61**	(c)	**66**	(c)
2	(a)	**7**	(b)	**12**	(b)	**17**	(b)	**22**	(c)	**27**	(b)	**32**	(a)	**37**	(b)	**42**	(b)	**47**	(a)	**52**	(c)	**57**	(b)	**62**	(b)	**67**	(c)
3	(b)	**8**	(c)	**13**	(b)	**18**	(a)	**23**	(c)	**28**	(c)	**33**	(c)	**38**	(b)	**43**	(c)	**48**	(a)	**53**	(c)	**58**	(c)	**63**	(f)	**68**	(b)
4	(c)	**9**	(d)	**14**	(c)	**19**	(b)	**24**	(c)	**29**	(d)	**34**	(c)	**39**	(c)	**44**	(b)	**49**	(d)	**54**	(b)	**59**	(b)	**64**	(c)	**69**	(d)
5	(b)	**10**	(c)	**15**	(c)	**20**	(b)	**25**	(c)	**30**	(d)	**35**	(c)	**40**	(b)	**45**	(a)	**50**	(b)	**55**	(b)	**60**	(c)	**65**	(b)	**70**	(d)

1. Coal is a complex mixture of several organic compounds with varying amounts of free carbon.

2. Aromatic hydrocarbons are directly obtained from coal ; as far as petroleum is concerned this is a direct source of aliphatic compounds which can of course be converted to aromatic compounds.

3. Reduction of conjugated compounds with sodium in liquid ammonia in presence of ethanol (a proton donor) is an example of Birch reduction in which two hydrogen atoms are added in 1 : 4 positions. Remember that, an isolated double bond is not usually affected by the Birch reduction except in the case of end methylene (= CH_2) or in strained alkenes such as cyclopropene and cyclobutene.

4. Electrophilic substitution reactions involve two steps, cleavage of the C—H or C—D step (*i.e.* proton elimination) takes place in the second (fast) step, which being fast does not affect the rate of reaction. The first (slow) step is the formation of carbocation in which C—H or C—D bond is not affected. Thus absence of isotopic effect establishes the two-steps mechanism for electrophilic aromatic substitution in which formation of carbocation (first step) is rate determining step.

5. HNO_3 accepts a proton from H_2SO_4.

6. All facts are observed.

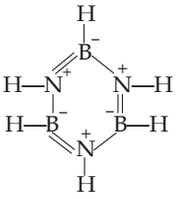
$$\underset{\text{Base}}{HONO_2} + 2\underset{\text{Acid}}{H_2SO_4} \rightleftharpoons \underset{\text{Acid}}{NO_2^+} + 2\underset{\text{Base}}{HSO_4^-} + H_3O^+$$

Note acid-base equilibrium is established

$$C_6H_6 + NO_2^+ \longrightarrow \underset{\text{Benzenonium ion}}{C_6H_5(H)(NO_2)^+} \xrightarrow{HSO_4^-} \underset{\substack{\text{Nitrobenzene}\\ \text{(Benzene nucleus is restored)}}}{C_6H_5NO_2} + H_2SO_4$$

7. The C—H bonds in benzene are sp^2-s, while that in cyclohexane are sp^3-s. Since sp^3-s bond is longer than the sp^2-s bond, the former will be weaker and hence the value will be < 110 kcal.

8. Boron has only 3 electrons in the outermost shell, one forms B—H σ bond, other forms B—N single σ bond and the third forms second σ bond of the double bond. While each N has 5 electrons in the valency shell, one forms N—H σ bond, second forms N—B single σ bond, third forms N—B σ bond of the π bond and the remaining two form one π bond.



9. D_2SO_4 transfers D^+, an electrophile, to form hexadeuterobenzene.

10. Since CH_3 group is an activating group, the mono methylated product ($C_6H_5CH_3$) is more reactive than benzene itself leading to formation of $C_6H_4(CH_3)_2$ and $C_6H_3(CH_3)_3$. To prevent polymethylation an excess of C_6H_6 is used to increase the chance for collision between C_6H_6 and CH_3^+ and to minimise collison between CH_3^+ and $C_6H_5CH_3$.

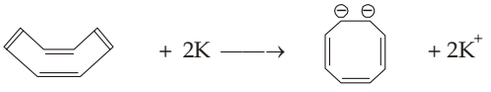
11. This is an example of Friedal Craft reaction, but here benzenonium ion is unstable, so it will not be formed, hence there will be no reaction.

$$C_6H_5Cl + AlCl_3 \longrightarrow \text{(+ charge on ring)} + AlCl_4^-$$

(No resonance, hence not formed)

12. The ring to which –NH group is attached is activated due to the lone pairs on N; while the ring to which –C = O is attached is deactivated. Hence, the electrophile would go to the *para*-position of the activated ring.

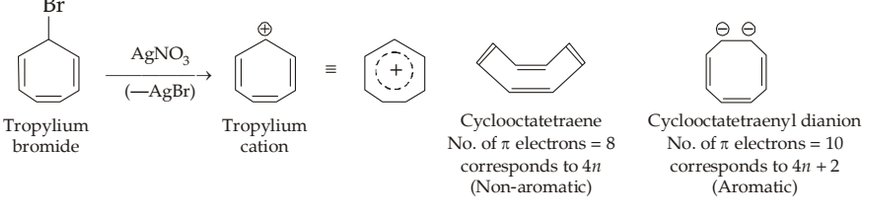
13.



1, 3, 5, 7-Cyclooctatetraene — Cyclooctatetraenyl dianion (No. of π electrons = 10 aromatic, here n = 2)

Cyclooctatetraenyl dianion is stable due to resonance.

14. Tropylium bromide dissociates easily to form tropylium cation, which once formed gets stabilised due to resonance.

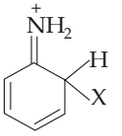


Tropylium bromide — Tropylium cation — Cyclooctatetraene No. of π electrons = 8 corresponds to $4n$ (Non-aromatic) — Cyclooctatetraenyl dianion No. of π electrons = 10 corresponds to $4n + 2$ (Aromatic)

15. 3-Chlorocyclopropene is the least stable because of absence of resonance, while cyclopropenyl cation is the most stable not just due to resonance but due to its aromaticity (it contains π-electrons which fits the Huckel rule $4n + 2$ rule for $n = 0$). Allyl cation is stable only due to resonance.

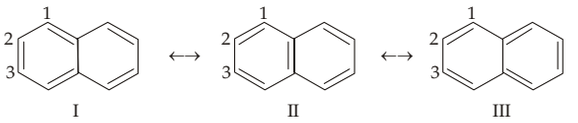
16. (*a*) and (*b*) are examples of Friedal Craft alkylation, while (*c*) is an example of intramolecular Friedal Craft reaction.

17. Resonating structure (*b*) is more stable because here every atom has an octet of electrons.



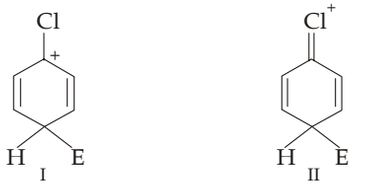
18. Structure (*a*) is unstable because here positive charge is present on C carrying —I group which will further intensify (localise) the charge making the species unstable.

19.



Examination of structures shows that C_1—C_2 bond is double in two structures (II and III) and single in only one (I). On the other hand, the C_2—C_3 bond is single in two structures (II and III) and double in only one (I). Thus the C_1—C_2 bond is expected to have more double bond character (and hence shorter) and the C_2—C_3 bond to have more single bond character (hence longer).

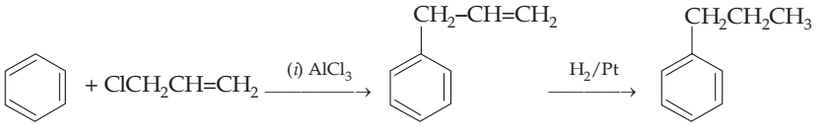
20.



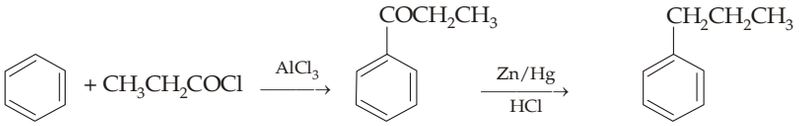
Especially unstable (positive charge is present on C bearing —Cl, a powerful electronegative group)

Comparatively stable (because every atom has octet)

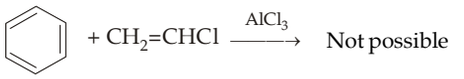
21. (*i*) and (*ii*) methods will form isopropylbenzene because *n*-propyl carbocation, being less stable, rearranges to the more stable (2°) isopropyl carbocation. Moreover, method (*i*) will lead to polyalkylation. Methods (*iii*) and (*iv*) can be used for preparing *n*-propylbenzene.



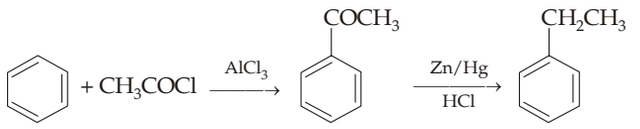
n-Propylbenzene



22. (*i*) and (ii) Direct ethylation using equal amount of both reagents will lead to polyalkylation. Hence method (*i*) is not used. However, polyethylation can be prevented by using excess of benzene which will increase the chance for collision between $CH_3CH_2^+$ and benzene and decrease the chance for collision between $CH_3CH_2^+$ and $C_6H_5CH_2CH_3$. Hence method (*ii*) can be used.

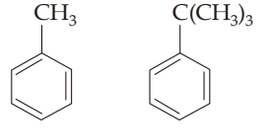
(*iii*) 

Because the carbocation, $CH_2 = \overset{+}{C}H$ formed as an intermediate is unstable.

(*iv*) 

Here polyalkylation is avoided because —$COCH_3$ group introduced in benzene is deactivating and hence further —$COCH_3$ group will not be introduced easily.

23. The bulky size of the *tert*-butyl group will hinder the approach of the electrophile in the *ortho* positions with the result the proportion of the product will be less than that in toluene.



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24. In case of bromination, both the electrophile as well as the group already present are bulky with the result, the steric interaction will be too much to form *o*-product. However, in case of chlorination Cl^+ ion being smaller than Br^+ ion will produce comparatively lesser steric interaction.

25. At 0°C the energy of the benzenonium ions having —NO_2 group at *p*-position is less than that which is having —NO_2 group at the *o*-position, hence the former will be more stable than the latter. Remember that the amount of the *o*-isomer increases with rise in reaction temperature.

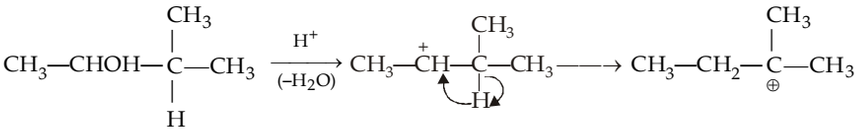
26. A carbocation can lose a proton (not hydride ion) to form alkene.

27. Wurtz-Fittig method is preferred since in this case, no rearranged product is formed. As far as other products, *viz. n*-hexane and biphenyl is concerned, these can be easily removed from *n*-propylbenzene by distillation since their boiling points differ very much from each other.

28. Benzene, being a symmetrical molecule, melts at about 100°C higher than toluene.

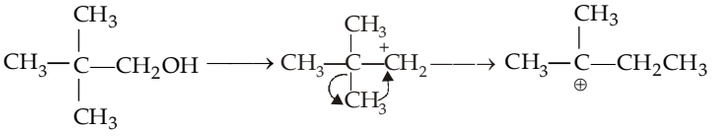
29. Formation of *tert*-pentylbenzene involves the attack of *tert*-pentyl cation on benzene, so any combination which can form *tert*-pentyl cation will form *tert*-pentylbenzene.

(*a*)



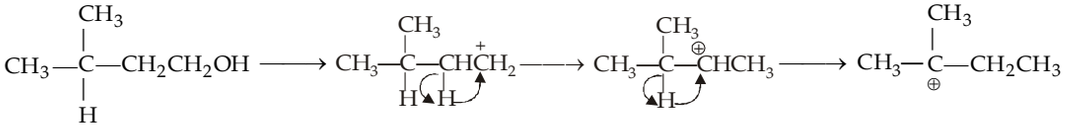
3-Methyl-2-butanol 2°cation 3° cation (*tert*-pentyl cation)

(*b*)



Neopentyl alcohol 1° cation 3° cation (*tert*-pentyl cation)

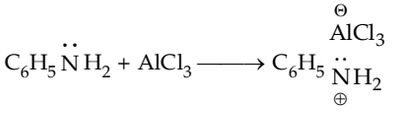
(*c*)



3-Methyl-1-butanol 1° cation 2° cation 3° cation

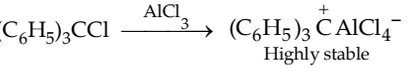
Thus all of the three combinations will form *tert*-pentylbenzene.

30. The lone pair of electrons on N makes aniline (a lewis base) to react with $AlCl_3$, (a Lewis acid); hence $AlCl_3$ is not available to CH_3Cl for forming CH_3^+.



Further, the positive charge on nitrogen makes the substituent strongly deactivating, comparable to $-\overset{+}{N}R_3$.

31. Fourth chlorine atom of the CCl_4 cannot be replaced by phenyl group because the carbocation required for the introduction of the fourth phenyl group is too stable to react with benzene.

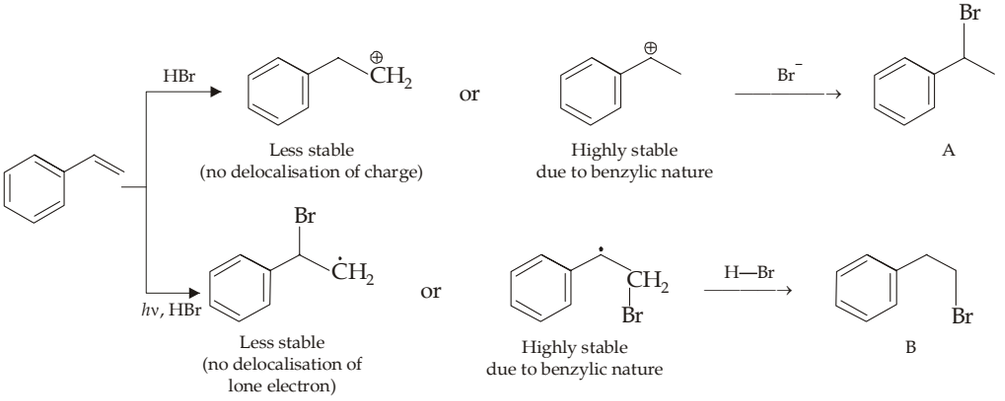


Highly stable

The triphenylmethyl cation is highly stable and moreover further introduction of the C_6H_5— group is improbable due to steric hindrance.

32. $C_6H_5CH = CH_2$ (alkenylbenzenes, in general) undergoes electrophilic addition reactions at a much faster rate than $CH_2 = CH_2$ (simple alkenes). This is due to the fact that the transition state leading to a carbocation (or a free radical, in free radical additions) in the first step of the reaction is resonance stabilised to a greater extent than the substrate itself.

33. Formation of product A involves ionic mechanism while that of B involves radical mechanism. So the intermediate (carbocation or free radical) formed in two cases will be



Less stable (no delocalisation of charge) Highly stable due to benzylic nature A

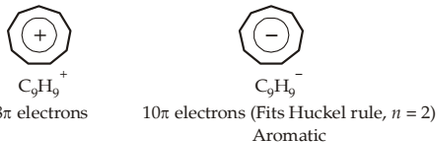
Less stable (no delocalisation of lone electron) Highly stable due to benzylic nature B

34. *m*-Xylene is most reactive and sulphonates at C—4 because the two CH_3 groups reinforce each other.

35. Cyclopropenyl cation is more stable than the allyl cation because the structure fits the Huckel $4n + 2$ rule for $n = 0$.

36. Proceed backwards for solving this type of questions. Remember that *o*-, *m*- and *p*-phenylenediamine on monosubstitution can theoretically give 2, 3 and 1 isomer respectively.

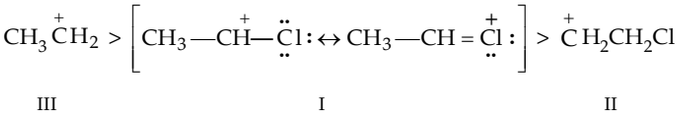
37. Among cyclonoane (C_9H_{10}), its cation ($C_9H_9^+$) and anion ($C_9H_9^-$), only the anion fits in Huckel rule (10π electrons) for $n = 2$.



$C_9H_9^+$ — 8π electrons

$C_9H_9^-$ — 10π electrons (Fits Huckel rule, $n = 2$) Aromatic

38. Carbocations I and II have chlorine which due to inductive effect tends to intensify the positive charge and thus destabilize the carbocations. Out of I and II carbocations, I is stable through its resonance effect.



III > I > II

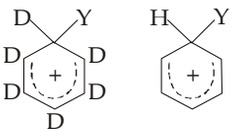
39. $CH_2 = CHCl \xrightarrow{H^+} CH_3\overset{+}{C}HCl$ (I) or $\overset{+}{C}H_2CH_2Cl$ (II)

More stable due to resonance

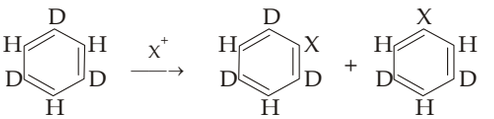
Note that presence of chlorine (a strong electron-withdrawing group), decreases electron density on the two doubly bonded carbon atoms and hence vinyl chloride is less reactive than ethylene towards electrophilic additions. Orientation, *i.e.* whether CH_3CHCl_2 or CH_2ClCH_2Cl is formed, depends upon stability of the carbocation. Since carbocation I is more stable (due to resonance) than the carbocation II, product corresponding to the carbocation I will be formed. Note that the **same statement is applicable to aromatic electrophilic substitution on chlorobenzene.**

40. Protonated nitric acid ($H_2\overset{+}{O}NO_2$) forms NO_2^+ through loss of the good leaving group H_2O. Unprotonated nitric acid ($HONO_2$) would have to lose the more strongly basic OH^- ion ; a weak leaving group.

41. Due to isotopic effect, fewer C—D bonds will be broken than the C—H bonds, hence the amount of C_6D_5Y will be less than that of C_6H_5Y.



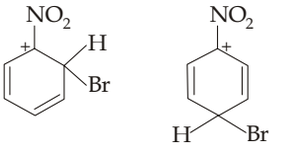
42. Again due to isotopic effect, fewer C—D bonds will be broken than the C—H bonds, hence the amount of $C_6H_2D_3X$ will exceed than that of $C_6H_3D_2X$, hence the $[D : H]_{product}$ ratio will be higher than that of reactant.



$C_6H_3D_3$ → $C_6H_2D_3X$ (More) + $C_6H_3D_2X$

43. According to Huckel rule, aromatic compounds contain $4n + 2\pi$ electrons, further the aromatic species should be cyclic and planar.

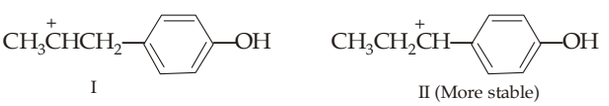
44. Electron withdrawing groups decrease, electron density in the *o*- and *p*-positions without effecting *m*-positions, thus in such cases. *meta* positions will although has relatively higher electron density than the *ortho* and *para* positions it is not increased due to —NO_2 group. The intermediate carbocation formed by the attack of an electrophile on nitrobenzene will have relatively unstable resonating structure in case of *ortho* and *para* position.



Note that the above two structures are relatively unstable as + ive charge is present on C bearing electronegative group, while no such structure exists in case of *meta* substituion.

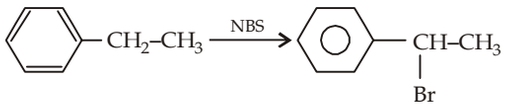
45. Chlorination of toluene in presence of light is a free radical reaction, hence it will take place in the side chain.

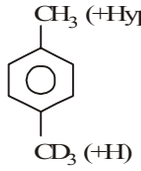
46. Two intermediates are possible by the attack of electrophile (H^+) ; of which II is more stable because positive charge is in conjugation with the benzene ring.



I — II (More stable)

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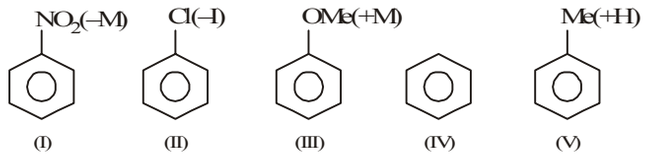
47.(*a*) 

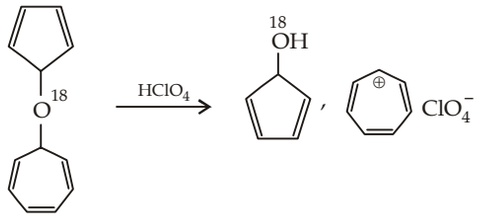
48. (*a*) 

+H of CH_3 is more as compared to CD_3. So attack of $E^{\oplus}$ will take place at ortho position of CH_3.

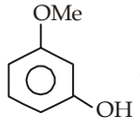
49. (*d*) Ease of oxidation $\propto$ electron density.

50. (*b*)

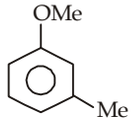


51. (*b*) 

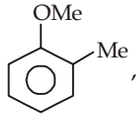
52. (*c*) More stronger the activating group, more will be electrophilic substitution reaction.
$-NO_2$ groups is electron attractive group, so it deactivates the benzene ring largely –Cl atom also deactivates the benzene ring but this deactivation is lower to $-NO_2$ group; while $-CH_3$ group activates.

53. (*c*) 

–OH is most reactive among them.

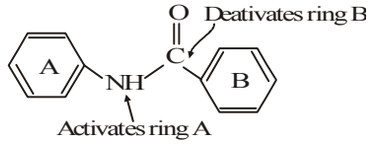


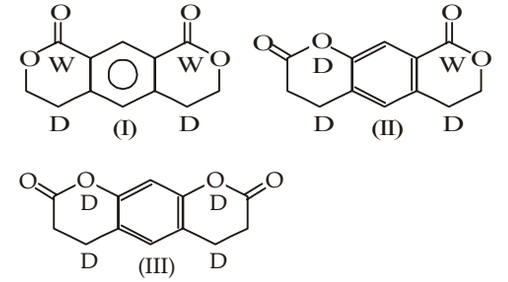
–OMe and –Me both exert same effect on particular site.



, in this case $-CH_3$ exerts only +1 effect.

54. (*b*)

55. (*b*) 

56. (*d*) 

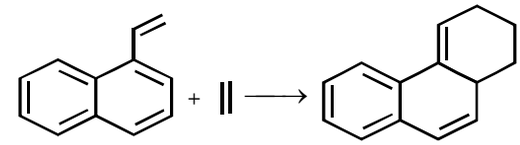
W - withdrawing group
D - donating group

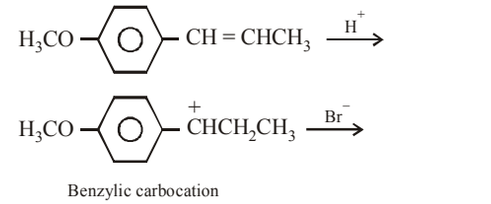
III II I
↓ ↓ ↓
4D 3D 2D

57. (*b*) $CH_3-\overset{O}{\overset{\|}{C}}-C\equiv C-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow 2CH_3COOH + 2CO_2$

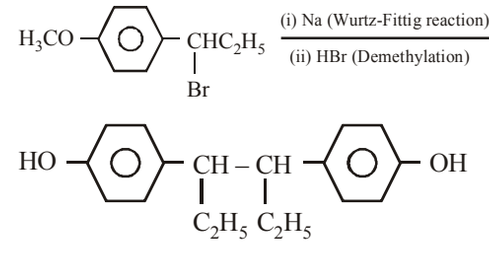
58. (*c*) This is an example of **Ullmann reaction.**

59. (*b*) This is an example of Diels – Alder reaction, here ethylene acts as dienophile.



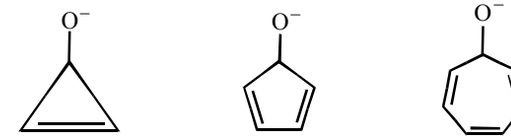
60. (*c*) 

Benzylic carbocation



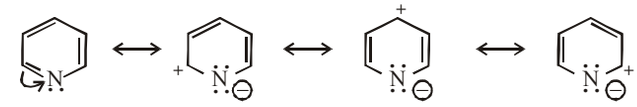
61. (*c*) Here D^+ from D_2SO_4 acts as an electrophile.

62. (*b*) Draw the resonating structure due to C = O group only and observe the stability

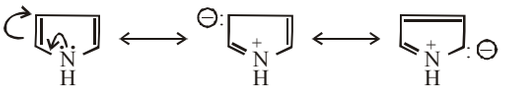


2π electrons (aromatic) | 4π electrons (antiaromatic) (least stable) | 6π electrons (aromatic)

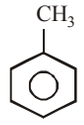
63. (*d*) Pyridine contains a doubly bonded N, so here N attracts electrons from the ring making the ring electron deficient.



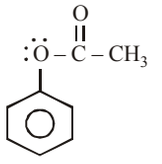
On the other hand, in pyrrole N supplies electron to the ring rather than attracting electrons from the ring.



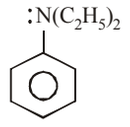
64. (*c*)



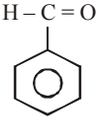
Activating due to +I and hyperconjugation (weak effects)



Electron pair on O delocalised to C = O hence moderate activating group



Electron pair on N causes +M effect (a powerful effect) **(Most activating)**

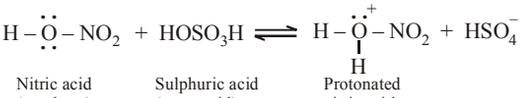


Deactivating group

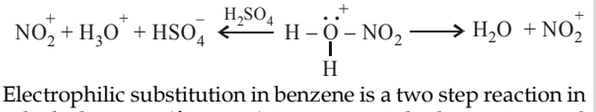
(*d*) None of the three

65. (*b*) Attack of electrophile on benzene ring (step 2) is the slow step.

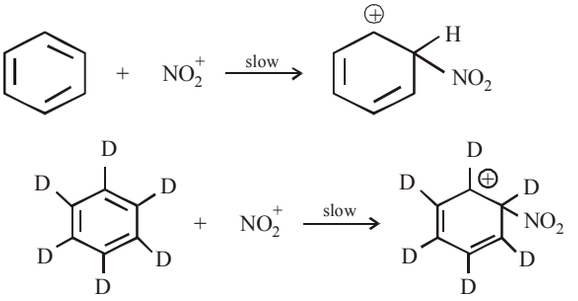
66. (*c*)



Nitric acid (as a base) | Sulphuric acid (as an acid) | Protonated nitric acid

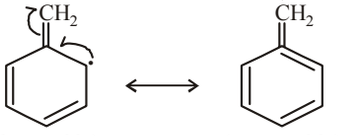


67. (*c*) Electrophilic substitution in benzene is a two step reaction in which slow step (first step) is common in both reactions and it does not involve the breaking of C – H or C – D bond.



Had the rate determining step (slow step) involved the cleavage of C – H or C – D bond, nitration of benzene would have been faster than that of hexadeuterated benzene.

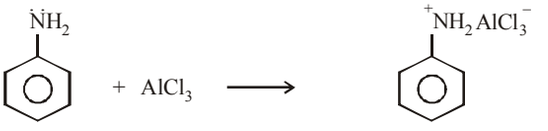
68. (*b*)



(less stable) (more stable)

69. (*d*)

70. (*d*) Vinyl and aryl halides can't be used as the halide component because they do not form carbocations readily ; $-NH_2$, –NHR and $-NR_2$ groups react with Lewis acids used in Friedel-Craft reaction to form electron-withdrawing groups, which deactivate the benzene nucleus for electrophilic substitution.



$-\overset{+}{N}H_2AlCl_3^-$ is electron-withdrawing

On the same reason, presence of electron-withdrawing group like $-NO_2$, $-\overset{+}{N}H_3$, $-CF_3$, – COOH, –COR, $-SO_3H$ etc. make the benzene ring less prone to Friedel-Craft reaction.

EXERCISE 7.2

>1 CORRECT OPTION	**1**	(a, c)	**2**	(a, b)	**3**	(a, b, d)	**4**	(a, b, c)	**5**	(a, c)
	6	(a, b)	**7**	(a, b)	**8**	(a, b, d)	**9**	(a, b)	**10**	(a, c)
	11	(a, b, c, d)	**12**	(a, b, c, d)	**13**	(a, c)	**14**	(b, c, d)	**15**	(a, c, d)
	16	(a, b, c)	**17**	(b, c, d)	**18**	(b, c)	**19**	(a, b, d)	**20**	(a, c)
	21	(a, c)								
PASSAGE 1	**22**	(b)	**23**	(b)	**24**	(b)				
PASSAGE 2	**25**	(a)	**26**	(d)	**27**	(c)				
PASSAGE 3	**28**	(a)	**29**	(d)	**30**	(b)				
PASSAGE 4	**31**	(a)	**32**	(d)	**33**	(b)				
PASSAGE 5	**34**	(c)	**35**	(a)	**36**	(c)				
MATCH THE FOLLOWING	**37**	(A)-a ; (B)-b, c, d ; (C)-a, b; (D) - a								
	38	(A) – b; (B) – d; (C) – a; (D) – c								
	39	(A) – b,c; (B) – a,c; (C) – d; (D) – b								
	40	(A) - a, c; (B) - a, b, d; (C) - a; (D) - a, b								
	41	(A) - a, d; (B) - a, c; (C) - b, d								
	42	(A) - d; (B) - a, c; (C) - b, c; (D) - c								
	43	(A) - c, d; (B) - b, c; (C) - a, b; (D) - b, c								
A/R	**44**	(b)	**45**	(e)	**46**	(a)	**47**	(d)	**48**	(c)
	49	(e)	**50**	(a)	**51**	(c)	**52**	(c)	**53**	(d)
INTEGER	**54**	**1**	**55**	**4375 or 4357**	**56**	**5**	**57**	**8**	**58**	**2**

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41. A-(a, d); B-(a, c); C-(b, d)

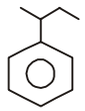
42. (A)-d; (B)-a, c; (C)-b, c; (D)-c

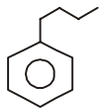
43. (A)-c,d; (B)-b,c; (C)-a,b; (D)-b,c

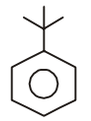
51. (*c*) Alkyl halides give polyalkylation products.

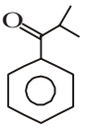
53. (*d*) Assertion is false, explanation is although true but it is not correct explanation of assertion.

54. **1**

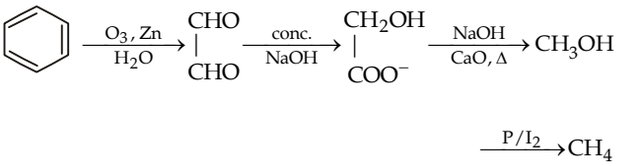
(*a*)  5H

(*b*)  2H

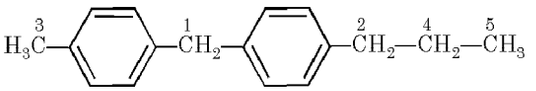
(*c*)  9H

(*d*)  1H

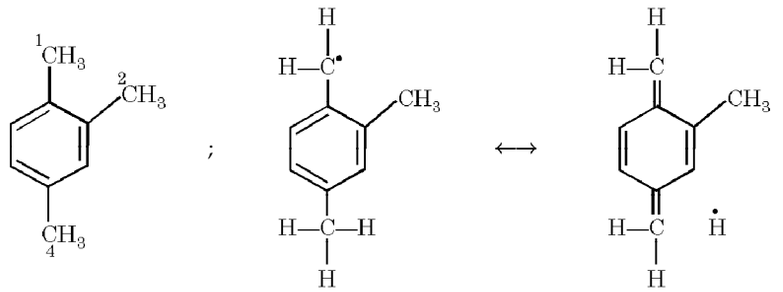
55. **4375** or **4357**



EXERCISE 7.3

1. (*i*) 

Hydrogen atom attached on C_1 is most reactive as it is 2° dibenzylic ; followed by C_2 because of 2° benzylic, then C_3 (1° benzylic), C_4 (2°) and C_5 (1°).

(*ii*) 

Removal of hydrogen from C-1 gives a benzylic free radical stabilized by hyperconjugation (drawn above).

Such structures are not possible for *m*-methyl groups, *i.e.* for hydrogen atoms attached on C-2 and C-4. Thus the ease of removal of hydrogen atom will be 1 —CH_3 > 4 —CH_3, 2 —CH_3.

Alternatively. The C_1-methyl group is *o, p* to other two methyl groups, C_4-methyl is *m, p* to other two methyl groups but less sterically hindered than the C_2-methyl group which is also *m, p* to other methyl groups but more sterically hindered. Thus ease of abstraction of hydrogen will thus be

C_1-methyl > C_4-methyl > C_2-methyl

2. $C_6H_5-\overset{1}{C}H_2-\overset{5}{C}H=\overset{5}{C}H-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{4}{C}H_3$

1-Phenyl-2-hexene

The order of reactivity is

C_1 (allylic, benzylic) > C_2 (allylic) > C_3 (2°) > C_4 (1°) > C_5 (vinylic)

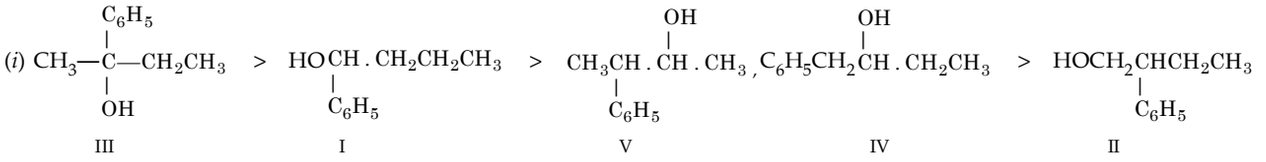
Monobromo products obtained on abstracting three different types of hydrogen atoms will be as follows. Note that abstraction of allylic hydrogen will form two products, as in the first two cases ; via a delocalized allylic radical.

1. $C_6H_5\underset{\underset{Br}{|}}{C}HCH=CHCH_2CH_2CH_3$ and $C_6H_5CH=CH\underset{\underset{Br}{|}}{C}HCH_2CH_2CH_3$

2. $C_6H_5CH_2CH=CH\underset{\underset{Br}{|}}{C}HCH_2CH_3$ and $C_6H_5CH_2\underset{\underset{Br}{|}}{C}HCH=CHCH_2CH_3$

3. $C_6H_5CH_2\underset{\underset{Br}{|}}{C}=CHCH_2CH_2CH_3$ and $C_6H_5CH_2CH=\underset{\underset{Br}{|}}{C}CH_2CH_2CH_3$

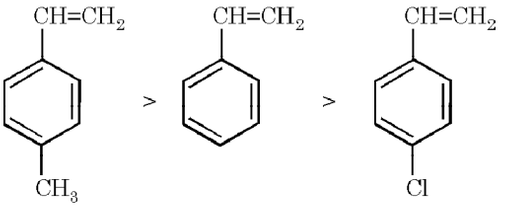
3. Remember that the alcohol that forms the most stable carbocation will be dehydrated faster.



(*ii*) $(C_6H_5)_2C(OH)CH_3$ > $C_6H_5CHOHCH_3$ > $C_6H_5CH_2CH_2OH$

(*iii*) *p*-$CH_3C_6H_4CHOHCH_3$ > $C_6H_5CHOHCH_3$ > *p*-Br-$C_6H_4CHOHCH_3$

4. Reactivity is determined chiefly by the stability of the carbocation being formed. This is affected by the nature of the substituent on the ring, electron-releasing substituent increases stability of the carbocation, while electron withdrawing substituent decreases stability. The correct order of reactivity is shown aside:



5. (*i*) $BrCCl_3 \xrightarrow{\text{light}} Br. + .CCl_3$ (*ii*) $C_6H_5CH_3 + .CCl_3 \longrightarrow C_6H_5CH_2. + \mathbf{CHCl_3}$

(*iii*) $C_6H_5CH_2. + BrCCl_3 \longrightarrow \mathbf{C_6H_5CH_2Br} + .CCl_3$

Above reactions (*ii*) and (*iii*) are repeated again and again.

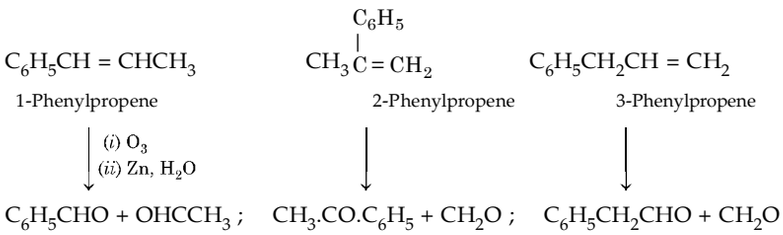
(*iv*) $C_6H_5CH_3 + Br. \longrightarrow C_6H_5CH_2. + \mathbf{HBr}$

Benzyl radical formed here also further undergoes reactions (*iii*), (*ii*), (*iii*), (*ii*) etc. and thus forming $C_6H_5CH_2Br$ and $CHCl_3$ as the main products.

(*v*) Chain terminating reaction leads to C_2Cl_6.

$$.CCl_3 + .CCl_3 \longrightarrow \mathbf{Cl_3C—CCl_3 \text{ or } C_2Cl_6}$$

6. 1-Phenylpropene, 2-phenylpropene and 3-phenylpropene can be distinguished on the basis of ozonolysis.

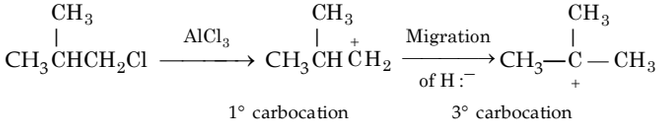


7. (*i*) $C_6H_5CH_2CH(CH_3)_2 + Br_2 \xrightarrow{UV} \underset{\text{(Major) I}}{C_6H_5CHBrCH(CH_3)_2} + \underset{\text{(Minor) II}}{C_6H_5CH_2CBr(CH_3)_2}$

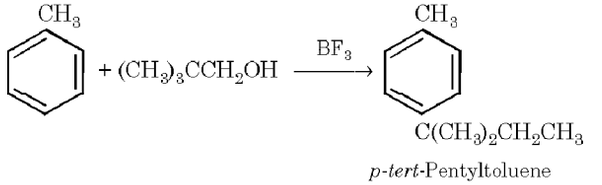
Note that formation of I (major product) involves the more stable benzyl free radical while that of II (minor product) involves the lesser stable 3° free radical.

(*ii*) $C_6H_6 + (CH_3)_2CHCH_2Cl \xrightarrow{AlCl_3} \underset{\textit{tert}\text{-Butylbenzene}}{C_6H_5C(CH_3)_3}$

Formation of the above (unexpected) product can be explained on the basis of the fact that 1° carbocation rearranges to the more stable 3° carbocation.



(*iii*)



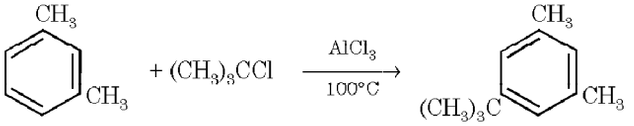
p-tert-Pentyltoluene

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Again formation of the above product can be explained on the basis of rearrangement of the lesser stable 1° carbocation to the more stable 3° carbocation.

$$(CH_3)_3CCH_2OH \xrightarrow{BF_3} \underset{\text{1° carbocation}}{(CH_3)_3\overset{+}{C}CH_2} \xrightarrow[\text{of : } CH_3^{\ominus}]{\text{Migration}} \underset{\text{3-cabocation}}{(CH_3)_2\overset{+}{C}CH_2CH_3}$$

(*iv*)



Note that at high temperature, thermodynamic controlled product will be formed which should have less steric strain. Kinetic controlled product *i.e.* isomer having a bulky *tert*-butyl group ortho to —CH_3 group will be formed at low temperatures.

(*v*) $C_6H_6 + (CH_3)_2CHCH_2OH \xrightarrow{H_2SO_4} C_6H_5C(CH_3)_3$. Here the 1° carbocation undergoes rearrangement to form the more stable 3° carbocation which attacks benzene forming *tert*-butylbenzene.

$$(CH_3)_2CHCH_2OH \xrightarrow{H^+} \underset{\text{1° (less stable)}}{(CH_3)_2CH\overset{+}{C}H_2} \longrightarrow \underset{\text{3° (more stable)}}{(CH_3)_3\overset{+}{C}}$$

(*vi*) $C_6H_5CH_2CH_3 \xrightarrow[\text{light}]{Br_2, \text{heat}} C_6H_5\underset{\underset{Br}{|}}{C}HCH_3 \xrightarrow{NaCN} C_6H_5\underset{\underset{CN}{|}}{C}HCH_3$

8. (*a*) $C_6H_5CH_2CHOHCH(CH_3)_2 \xrightarrow{H_2SO_4} \underset{\text{(Major) I}}{C_6H_5CH = CHCH(CH_3)_2} + \underset{\text{(Minor) II}}{C_6H_5CH_2\,CH = C(CH_3)_2}$

Note that the product I is although a disubstituted alkene, it is more stable due to conjugation with benzene ring than the trisubstituted alkene, II which, being non-conjugated is formed in minor amount.

(*b*) $C_6H_5CH_2CHBrCH_3 \xleftarrow{Br^-} \underset{\text{Less stable, 2°}}{C_6H_5CH_2\overset{+}{C}HCH_3} \xleftarrow{\text{H+ from HBr}} C_6H_5CH = CHCH_3 \xrightarrow[HBr]{H^+ \text{ from}} \underset{\text{(More stable, benzylic)}}{C_6H_5\overset{+}{C}HCH_2CH_3} \xrightarrow{Br^-} \underset{\textbf{(Major)}}{C_6H_5CHBrCH_2CH_3}$

(Minor)

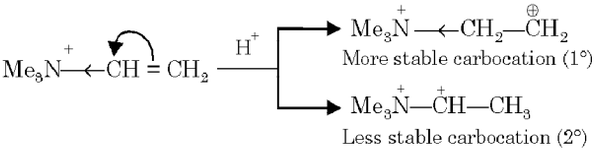
(*c*) $C_6H_5CHBrCH_2CH_3 \xleftarrow{H^{\bullet}} \underset{\text{Less stable, 2°}}{C_6H_5CHBr\dot{C}HCH_3} \xleftarrow{\text{Br. from HBr}} C_6H_5CH{=}CHCH_3 \xrightarrow[HBr]{Br^{\bullet} \text{ from}} \underset{\text{(More stable, benzylic)}}{C_6H_5\dot{C}HCHBrCH_3} \xrightarrow{H^{\bullet}} \underset{\textbf{(Major)}}{C_6H_5CH_2CHBrCH_3}$

(Minor)

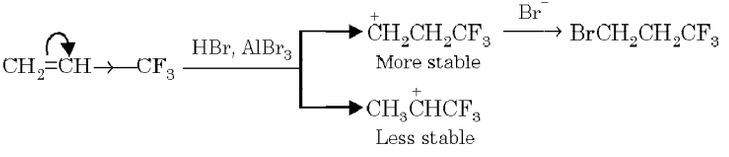
(*d*) $C_6H_5CH = CHCH = CH_2 + Br_2 \longrightarrow \underset{\text{Eqimolar amounts}}{C_6H_5CHBrCHBr\,CH = CH_2} + \underset{\text{(\textbf{Major,} due to conjugated system)}}{C_6H_5CH = CHCHBr\,CH_2Br} + C_6H_5CHBrCH = CHCH_2Br$

(*e*) $Me_3\overset{+}{N}CH = CH_2 + HI \longrightarrow Me_3NCH_2CH_2I$

The substituent —$\overset{+}{N}Me_3$ is a strong electron withdrawing group and thus favours the formation of a carbocation with the charge on the more remote carbon atom.

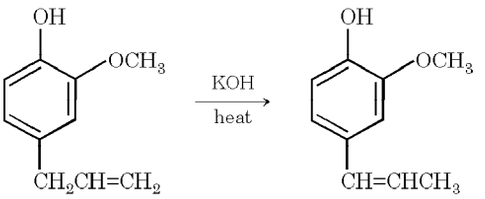


(*f*)



$AlBr_3$ is used to provide the stronger acid $HAlBr_4$ that is needed for attack on the highly deactivated alkene.

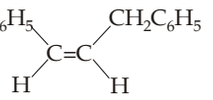
9. (*i*)



Eugenol Isoeugenol

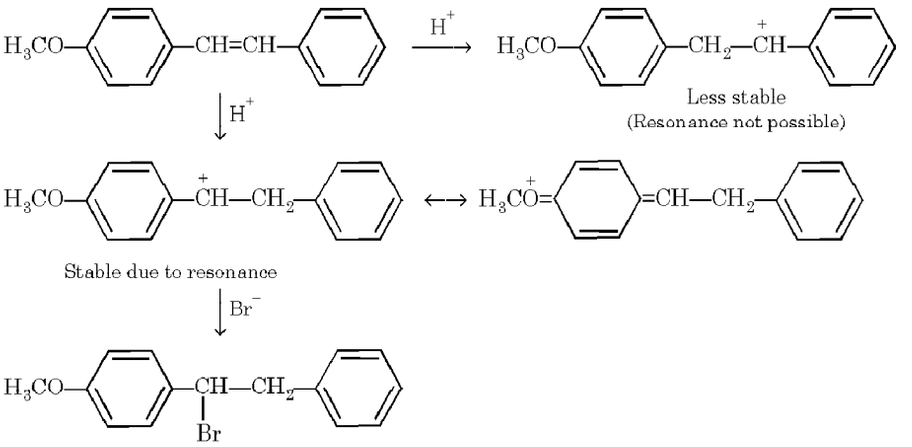
Alkenes when heated with KOH undergo isomerisation to the more stable, conjugated ones.

(*ii*) $C_6H_5CH = CH—CH = CH_2 + H_2 \xrightarrow[30°C]{Ni} \underset{\text{(conjugated alkene)}}{C_6H_5CH = CH—CH_2—CH_3}$

(*iii*) $C_6H_5C \equiv CCH_2C_6H_5 \xrightarrow{H_2—Pd}$ 

Catalytic hydrogenation gives *cis* (Z) – product.

(*iv*)



10. (*a*) $C_6H_5CH_2CH_2CH_3 \xrightarrow[h\nu]{Br_2} \underset{\text{(A)}}{C_6H_5CHBrCH_2CH_3} \xrightarrow[KOH]{alc.}$

$C_6H_5CH = CHCH_3 \xrightarrow[KMnO_4]{\text{Cold dil.}} \underset{\text{(B)}}{} C_6H_5CHOHCHOHCH_3 \xrightarrow[KMnO_4]{hot} \underset{\text{(C)}}{} C_6H_5COOH + HOOCCH_3$

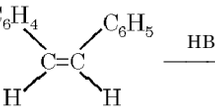
(D) and (E)

(*b*) $C_6H_5Br + Mg \xrightarrow{ether} C_6H_5MgBr \xrightarrow{BrH_2C.CH = CH_2}$

(F)

$C_6H_5CH_2CH = CH_2 \xrightarrow[heat]{KOH} \underset{\text{(G)}}{} C_6H_5CH = CHCH_3 \xrightarrow[300°C]{Br_2} \underset{\text{(H)}}{} C_6H_5CH = CHCH_2Br$

(I)

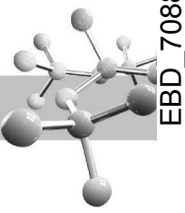
(*c*) $p\text{-}CH_3.C_6H_4.C \equiv C.C_6H_5 + H_2 \xrightarrow{Pt}$ 

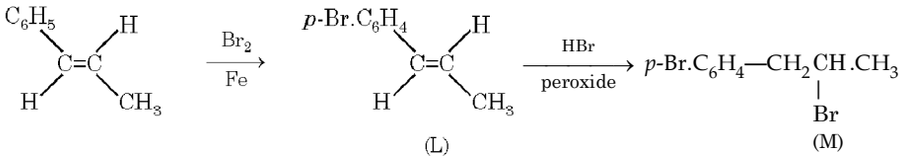
cis (J)

$\xrightarrow{HBr} p\text{-}CH_3.C_6H_4.\underset{\underset{Br}{|}}{CH}CH_2C_6H_5$

(K)

In K, H^+ adds to give more stable R^+ which is $p\text{-}CH_3.C_6H_4\overset{+}{C}HCH_2C_6H_5$ rather than $p\text{-}CH_3.C_6H_4.CH_2\overset{+}{C}HC_6H_5$ because of electron release of $p\text{-}CH_3$.



(*d*) 

(L) (M)

In M, $Br^{\cdot}$ adds to give more stable $R^{\cdot}$, $p\text{-}BrC_6H_4\dot{C}HCHBrCH_3$ which is benzylic.

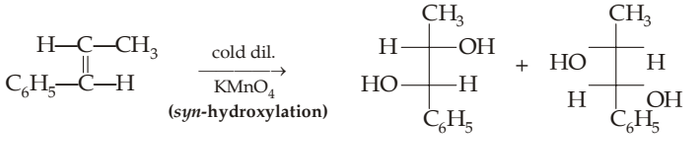
11. (*i*) *trans*-$C_6H_5CH = CHCH_3 \xrightarrow[200°,\ 100\ atm]{H_2,\ Ni} C_6H_{11}CH_2CH_2CH_3$

trans-1-Phenyl-1-propene → *n*-Propylcyclohexane

Remember that hydrogenation conditions are drastic and hence benzene ring will also be reduced to cylcohexane ring.

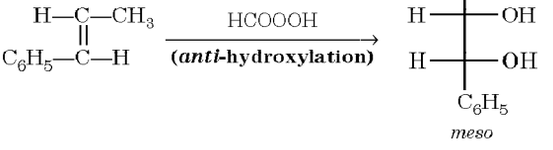
(*ii*) *trans*-$C_6H_5CH = CHCH_3 + Br_2$ (excess) $\xrightarrow{Fe}$ *p*-$Br.C_6H_4.CHBr.CHBrCH_3$

Note that Br_2 in presence Fe acts as an electrophile, hence electrophilic addition on C = C as well as electrophilic substitution in benzene nucleus take place.

(*iii*) 

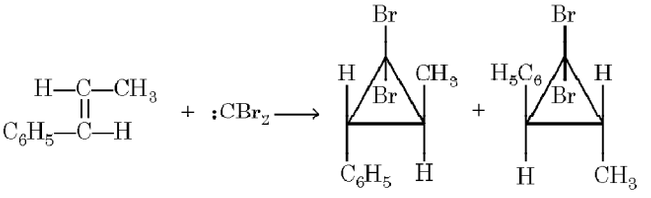
trans-1-Phenyl-1-propene → racemic-mixture

(*iv*) *trans*-$C_6H_5CH = CHCH_3 \xrightarrow[KMnO_4]{hot} C_6H_5COOH + HOOC.CH_3$

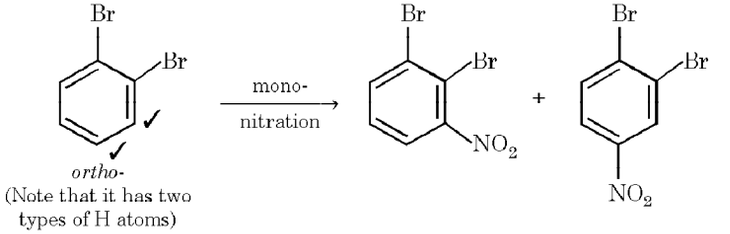
(*v*) 

meso

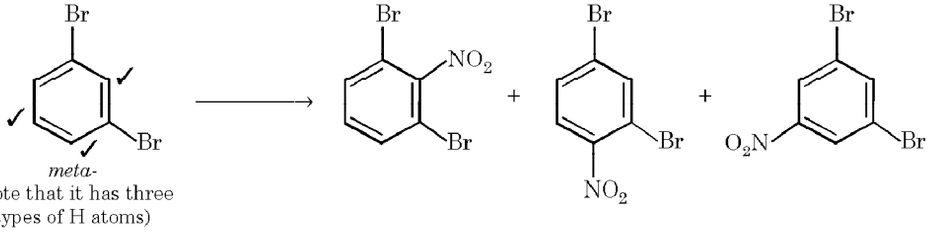
(*vi*) $CHBr_3 \xrightarrow{tert\text{-}BuOK} :CBr_2 + HBr$



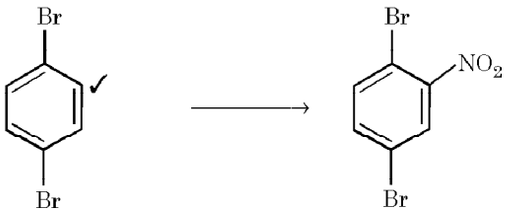
12. Three isomeric dibromobenzenes are *ortho*-, *meta*- and *para*. *ortho*-Isomer on mono-substitution gives two isomers, *meta*-gives three isomers and *para* gives one isomer.



ortho-
(Note that it has two types of H atoms)



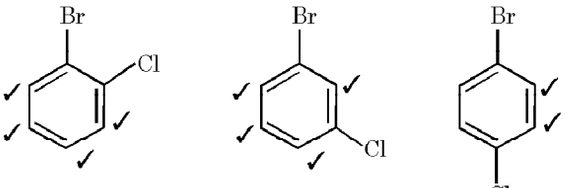
meta-
(Note that it has three types of H atoms)



para-
(It has only one type of H atoms)

Thus, in total six isomeric dibromonitrobenzenes are possible.

13. *o*-Bromochlorobenzene has four different types of hydrogen atoms, thus on nitration it may form four isomeric nitrobromochlorobenzenes; *m*-isomer also has four types of hydrogen atoms ; while *para*-isomer has only two types of hydrogen atoms hence it will form two isomeric nitrobromochlorobenzenes.

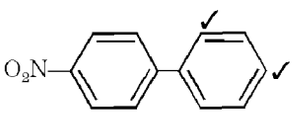


o-Bromochlorobenzene *m*- *p*-

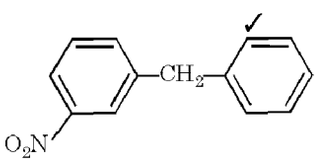
14. In all cases, apply the following points :

1. Substitution is faster in the ring having an activated group or substitution is faster in the ring which is not deactivated.
2. Orientation will be governed by the group present on the ring that is to be substituted.

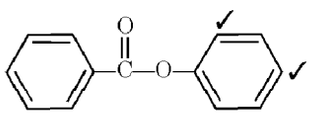
(*i*) (*A*)Substitution is faster in the ring that is not deactivated by —NO_2. Further, Ar—group is a weakly activating group, so substitution will be taking place in *o, p* position to the other ring.

(*a*) 

Deactivated ring

(*b*) 

Deactivated ring

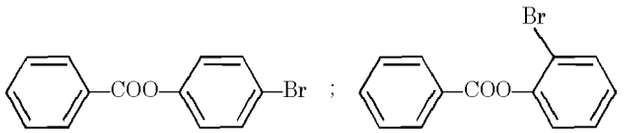
(*c*) 

Deactivated ring Activated ring

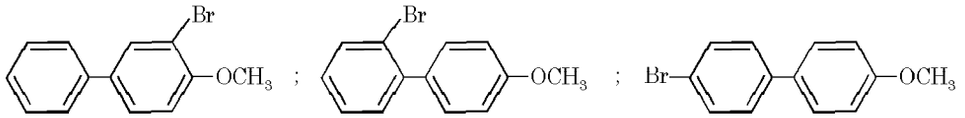
(*B*) Similar explanation as in (*A*), Further group —CH_2Ar is *o,p*-directing.

(*C*) Substitution is faster in the ring that is activated by phenolic oxygen (similar to —OR). The other ring is actually deactivated by —COOAr.

(*ii*) (*a*) This compound is a derivative of phenol, so substitution will be taking place in *o*- and *p*-positions to the —$OCOC_6H_5$ group forming two products.

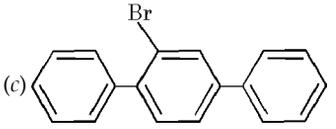


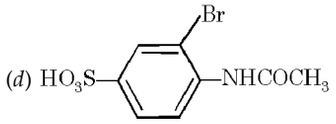
(*b*) —OCH_3 group is activating so substitution will be taking place in the *o*-position to the —OCH_3 group. Further, if we consider *p*-$C_6H_4.OCH_3$ as a group substitution will be taking place in the *o*- and *p*-position to the unsubstituted ring. Thus, in all three monobromo products are possible.



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(*c*) The middle benzene ring is having phenyl rings in the *p*-positions ; so only one product is possible.

(*c*) 

(*d*) 

(*d*) Here both the groups reinforce each other at one positions which is *o*- to —$NHCOCH_3$ and *m*- to —SO_3H ; thus here also one product is possible.

15. Acidity of these hydrocarbons can be explained in terms of resonance stabilization of the anion, with dispersal of negative charge which corresponds to the following order.

$$Ph_3C^- > Ph_2CH^- > PhCH_2^- > n\text{-}C_5H_{11}^-$$

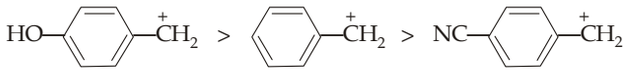
Thus acidic character of the corresponding hydrocarbons follows the order.

$$Ph_3CH > Ph_2CH_2 > PhCH_3 > n\text{-}C_5H_{12}$$

16. For these alcohols, reactivity is largely determined by the stability of the carbocation being formed. This is affected by electron release or electron withdrawl by substituents on the alcohol bearing carbon atom or on the aromatic ring.

(*i*) $C_6H_5\overset{+}{C}H—CH_2CH_3 > C_6H_5CH_2\overset{+}{C}HCH_3 > C_6H_5CH_2CH_2\overset{+}{C}H_2$

Benzylic carbocation; 2° Carbocation; 1° Carbocation

(*ii*) 

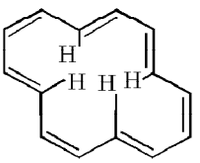
HO is electron releasing; CN is electron withdrawing

17. Reactivity by S_N1 is controlled by the stability of the carbocation formed, and reactivity by S_N2 is controlled mainly by hindrance.

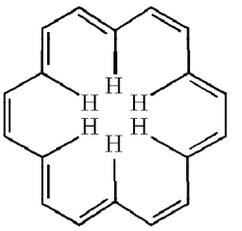
Reactivity by S_N1 $C_6H_5CCl(CH_3)_2 > C_6H_5CHClCH_3 > C_6H_5CH_2Cl$

Reactivity by S_N2 $C_6H_5CH_2Cl > C_6H_5CHClCH_3 > C_6H_5CCl(CH_3)_2$

18. To be aromatic, annulenes [monocyclic compounds of the general formula -[-CH = CH-]-$_n$] should follow the Huckel $4n + 2$ rule for the π electrons (6 for $n = 1$, 10 for $n = 2$, 14 for $n = 3$, 18 for $n = 4$). Thus annulenes (with the number of π electrons indicated within the brackets in each name) that are expected to be aromatic are [6]-annulene (benzene), [10]-annulene, [14]-annulene and [18]-annulene. Actually for [10]-and [14]-annulenes, the geometry is unfavourable, crowding of hydrogens inside the ring causes strain and thus prevents planarity and hence interferes with π overlap, thus ultimately diminishes aromaticity.



[14]-Annulene (Not permitted by geometry)



[18]-Annulene

19. (*a*) The yellow colour is attributed to the stable Ph_3C^+, whose positive charge is delocalised to the *op*-positions of the three benzene rings.

$$Ph_3CCl + AlCl_3 \longrightarrow \underset{\text{(Yellow colour)}}{Ph_3C^+} + AlCl_4^-$$

or $$Ph_3COH + H_2SO_4 \longrightarrow \underset{\text{(Yellow colour)}}{Ph_3C^+} + H_2O + HSO_4^-$$

Appearance of white solid on dilution is due to the formation of Ph_3COH.

$$\underset{\text{Lewis acid}}{Ph_3C^+} + \underset{\text{Lewis base}}{2H_2O} \longrightarrow \underset{\text{(White solid)}}{Ph_3COH\downarrow} + H_3O^+$$

(*b*) The strong base $:\ddot{N}H_2^-$ removes proton from Ph_3CH to form the stable, deep red-purple carbocation $Ph_3C:^-$ whose negative charge is delocalized to the *op*-positions of the three benzene rings.

$$\underset{\text{Acid}_1}{Ph_3CH} + \underset{\text{Base}_2}{:NH_2^-} \longrightarrow \underset{\text{Base}_1}{Ph_3C:^-} + \underset{\text{Acid}_2}{HNH_2}$$

(deep red)

The deep red colour disappears on adding water, a feeble acid, due to protonation to form Ph_3CH.

$$\underset{\text{Base}_1}{Ph_3C:^-} + \underset{\text{Acid}_2}{H_2O} \longrightarrow \underset{\text{Acid}_1}{Ph_3CH} + \underset{\text{Base}_2}{OH^-}$$

(colourless)

(*c*) Zinc removes Cl· from Ph_3CCl to form the red coloured radical Ph_3C·

$$2Ph_3CCl + Zn \longrightarrow \underset{\text{(red colour)}}{2Ph_3C^{\cdot}} + ZnCl_2$$

The red colour disappears on passing oxygen due to formation of peroxide.

$$2Ph_3C. + .\ddot{O}—\ddot{O}. \longrightarrow Ph_3C—\ddot{O}—\ddot{O}—CPh_3$$

Peroxide (colourless)

(*d*) Carbon tetrachloride reacts with excess of benzene forming first $C_6H_5CH_2Cl$, then $(C_6H_5)_2CHCl$ and finally $(C_6H_5)_3CCl$.

$$3C_6H_6 + CCl_4 \xrightarrow{AlCl_3} (C_6H_5)_3CCl + 3HCl$$

However, as soon as $(C_6H_5)_3CCl$ is formed, it reacts with $AlCl_3$ to form $(C_6H_5)_3\overset{+}{C}AlCl_4^-$, whose carbonium ion in too stable to react with benzene. Moreover, $(C_6H_5)_3\overset{+}{C}$ is too sterically hindered to react further.

20. (*i*) **In benzene, C—H bond is of** sp^2-*s* character which is shorter and hence stronger than the sp^3-*s* C—H bond in cyclohexane.

(*ii*) Hydrogen atoms in acetylene are attached on *sp* hybridised carbon atoms, in benzene on sp^2 hybridised carbon atoms while in *n*-pentane on sp^3 hybridised carbon atoms. Now we know that greater the *s* character of a carbon atom more will be the displacement of electrons towards nucleus thus weaker will be the C—H bond. Hence the strength of the C—H bond follows the following order

$$\underset{\text{Most acidic}}{sp\ C—H} > sp_2\ C—H > \underset{\text{Least acidic}}{sp_3\ C—H}$$

$\therefore$ $HC \equiv CH > C_6H_6 > n\text{-}C_5H_{12}$

Alternatively, consider the corresponding three anions, *viz.* $HC \equiv C^-$, $C_6H_5^-$ and $C_5H_{11}^-$. In acetylide anion, the unshared electron pair occupies an *sp* orbital which has maximum *s* character, while the sp^3 orbital of the pentyl anion $C_5H_{11}^-$ has minimum *s* character and sp^2 orbital of the phenyl anion has intermediate *s* character. So electrons in the *sp* orbital are held most tightly, while those in the sp^3 orbital are held least tightly. Therefore, the basicity order of the three anions follows :

$$\underset{\text{Pentyl anion}}{C_5H_{11}^-} > \underset{\text{Phenyl anion}}{C_6H_5^-} > \underset{\text{Acetylide anion}}{HC \equiv C^-}$$

Hence the corresponding acids will have the following acidic order.

$$\underset{\text{Acetylene}}{HC \equiv CH} > \underset{\text{Benzene}}{C_6H_6} > \underset{\text{Pentane}}{C_5H_{12}}$$

(*iii*) The number of π bonds in cyclo-octatetraene is **eight** which is not a Huckel number and hence the compound is not aromatic and thus behaves as an alkene. On the other hand, in benzene the number of π bonds is 6 which is a Huckel number and thus benzene hehaves as an aromatic compound.

(*iv*) Neopentyl cation, being 1° cation, rearranges to the more stable *tert*-pentyl cation (3°) which then reacts with benzene forming *tert*-pentylbenzene.

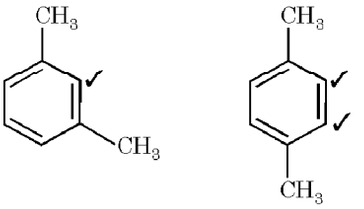
$$\underset{\text{Neopentyl bromide}}{(CH_3)_3CCH_2Br} \xrightarrow{AlCl_3} \underset{\text{Neopentyl cation}}{(CH_3)_3CCH_2^+} \xrightarrow{\text{rearranges}} \underset{\textit{tert}\text{-Pentyl cation (3°)}}{(CH_3)_2\overset{+}{C}CH_2CH_3} \xrightarrow{C_6H_6} \underset{\textit{tert}\text{-Pentylbenzene}}{C_6H_5C(CH_2CH_3)(CH_3)_2}$$

(*v*) An acid-base complex I is formed which transfers bromine without its electrons directly to the ring.

$$(CH_3COO)_3Tl + Br_2 \rightleftharpoons \underset{\text{I}}{(CH_3COO)_3\ Tl^{\ominus}—Br^{\oplus}—Br}$$

Due to bulky size of the complex, it attacks a substituted aromatic ring most readily at the least hindered position, *i.e. para* to the substituent already present.

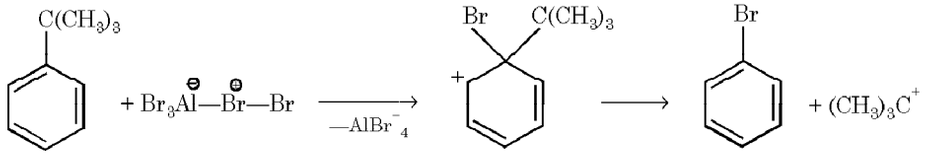
(*vi*) In *m*-xylene the two —CH_3 groups activate (doubly) the same position, while in *p*-xylene the two —CH_3 groups activate different positions.



(*vii*) $$C_6H_5C(CH_3)_3 + Br_2(AlBr_3) \longrightarrow C_6H_5Br + HBr + (CH_3)_2C = CH_2$$

This is an example of *bromodealkylation*.

$$Br_2 + AlBr_3 \rightleftharpoons Br_3Al^{\ominus}—Br^{\oplus}—Br$$



$$(CH_3)_3\overset{+}{C} + AlBr_4^- \longrightarrow (CH_3)_2C = CH_2 + HBr + AlBr_3$$

(*viii*) The newly introduced alkyl group activates the aromatic ring towards further substitution forming polyalkylated product as unwanted products. In other reactions, the newly introduced group, being deactivating, deactivates the ring towards further substitution.

(*ix*) Ionization of Ph_3COH in H_2SO_4 produces twice as many ions per mole as does CH_3OH, hence twice the lowering of the freezing point.

(*a*)
$$Ph_3COH + H_2SO_4 \longrightarrow Ph_3COH_2^+ + HSO_4^-$$
$$Ph_3COH_2^+ \longrightarrow \underset{\text{(Stable)}}{Ph_3C^+} + H_2O$$
$$H_2O + H_2SO_4 \longrightarrow H_3O^+ + HSO_4^-$$

On adding,
$$Ph_3COH + 2H_2SO_4 \longrightarrow \underbrace{Ph_3C^+ + H_3O^+ + 2HSO_4^-}_{\text{Four ions}}$$

(*b*)
$$CH_3OH + H_2SO_4 \longrightarrow \underbrace{CH_3OH_2^+ + HSO_4^-}_{\text{Two ions}}$$

Since CH_3^+ in quite unstable, hence $CH_3OH_2^+$ does not dissociate to form CH_3^+ and H_2O.

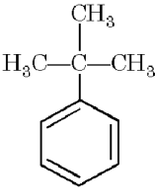
(*x*) In biphenyl, one of the phenyl groups acts as donor and the other as electrons acceptor. This makes the phenyl ring more reactive than benzene towards electrophilic substitution.

(*xi*) In presence of Lewis acid (*e.g.* $AlCl_3$), —NH_2 or —OH group becomes electron withdrawing.

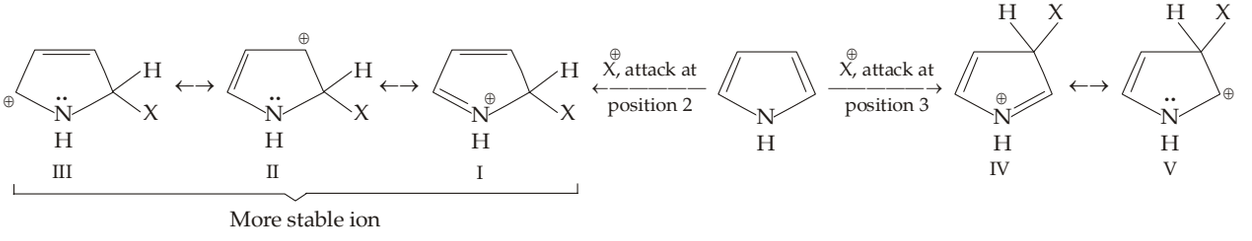
(*xii*) In presence of light, toluene undergoes free radical substitution in the side chain, while in presence of $FeBr_3$ it undergoes electrophilic substitution in the benzene nucleus.

(*xiii*) Benzene ring remains intact in substitution while addition reaction destroys benzenoid structure.

(*xiv*) *tert*-Butylbenzene does not have benzylic hydrogen atom, necessary for oxidation. Hence it can't be oxidised by $KMnO_4$ to C_6H_5COOH.



21. Pyrrole can undergo electrophilic substitution at position 2 or 3. However, the carbocation formed by attack at position 2 is a hybrid of three structures (I, II and III), while the corresponding carbocation formed by attack at position 3 is a hybrid of two structures (IV and V). Hence the carbocation formed by attack at position 2 is more stable, leading to 2-substituted pyrroles.



Pyrrole is highly reactive, compared with benzene, because of contribution from the relatively stable structure I, in which *every atom has an octet of electrons.*

22. (*a*) Allylbenzene, $C_6H_5CH_2CH = CH_2$ dissolves or polymerises in cold conc. H_2SO_4.

(*b*)
$$\underset{\text{Red}}{C_6H_5CH_2CH = CH_2} + Br_2 \text{ (in } CCl_4) \longrightarrow \underset{\text{Colourless}}{C_6H_5CH_2CHBrCH_2Br}$$

(*c*)
$$\underset{\text{Purple}}{C_6H_5CH_2CH = CH_2} + MnO_4^- \longrightarrow C_6H_5CH_2\underset{OH}{CH}—\underset{OH}{CH_2} + MnO_2$$

Colourless Brown ppt.

(*d*) Orange-red colour is developed due to formation of Ar_3C^+ cation.

$$ArH \xrightarrow[\text{Friedel-Craft reaction}]{CHCl_3, AlCl_3} ArCHCl_2 \xrightarrow[\text{Friedel–Craft reaction}]{ArH, AlCl_3} Ar_2CHCl \xrightarrow{ArH, AlCl_3} Ar_3CH$$

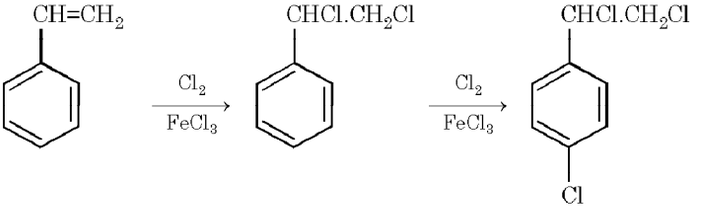
$$Ar_2CHCl \xrightarrow{AlCl_3} Ar_2CH^+AlCl_4^- \xrightarrow[\text{Transfer of hydride ion}]{Ar_3CH} \underset{\text{Orange-red colour}}{Ar_2CH_2} + Ar_3\overset{+}{C}AlCl_4^-$$

(*e*) Allylbenzene does not react with chromic anhydride (CrO_3) in aq. sulphuric acid, *i.e.* orange colour of $HCrO_4^-$ does not disappear.

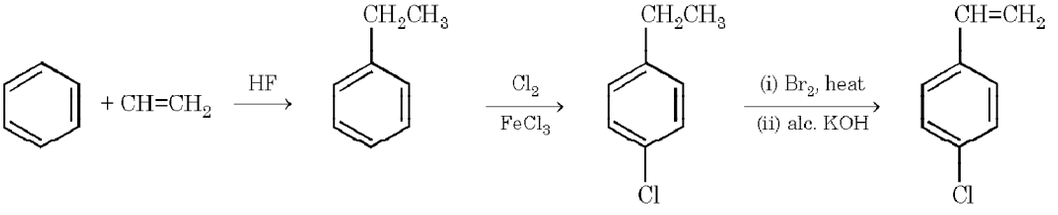
23. (*i*) **Benzene to styrene.** Styrene can't be prepared by Friedel-Craft reaction because $CH_2 = \overset{+}{C}H$ is unstable.

$$\underset{\text{Benzene}}{C_6H_6} + CH_2 = CH_2 \xrightarrow{HF} C_6H_5CH_2CH_3 \xrightarrow[\text{heat}]{Br_2} C_6H_5.CHBr.CH_3 \xrightarrow[\text{(alc.)}]{KOH} \underset{\text{Styrene}}{C_6H_5CH = CH_2}$$

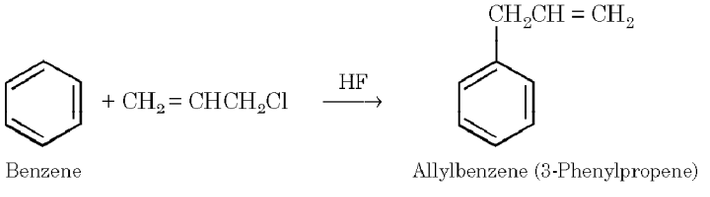
(*ii*) **Benzene to *p*-chlorostyrene.** Remember that chlorine group should be introduced earlier than the introduction of the double bond, otherwise addition of halogen as well as substitution will take place because the first step in both these reactions is common, *i.e.* the attack of positively charged halonium ion on the π electron cloud. Moreover, it has been observed that addition of halogen to the side chain double bond is completed first before the electrophilic substitution.



Conversion of benzene to *p*-chlorostyrene.



(*iii*) **Benzene to allylbenzene.**

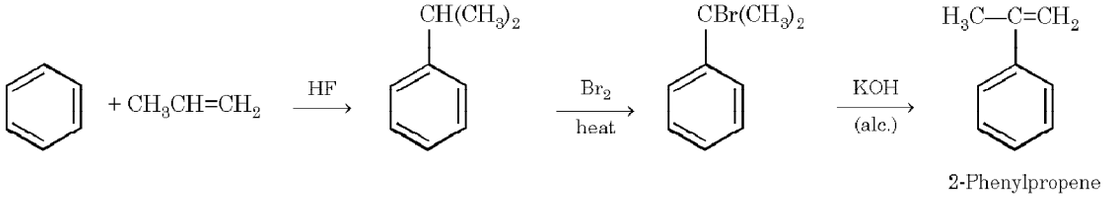


(*iv*) **Benzene to *n*-propylbenzene.**

Direct propylation with *n*-$CH_3CH_2CH_2Cl$ will give isopropylbenzene due to more stability of the 2° carbocation $(CH_3)_2CH^+$, hence *n*-propylbenzene should be prepared in the following way.

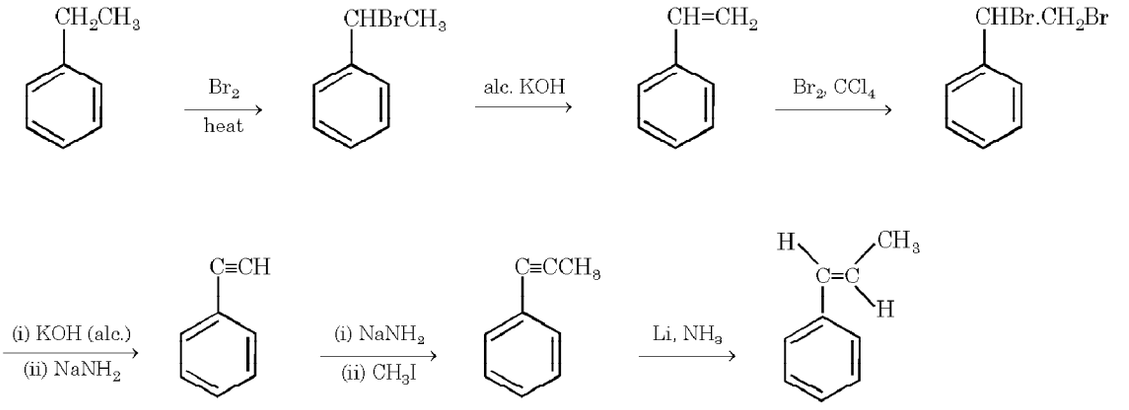
$$C_6H_6 + ClCH_2CH = CH_2 \xrightarrow{AlCl_3} C_6H_5CH_2CH = CH_2 \xrightarrow{H_2/Pt} C_6H_5CH_2CH_2CH_3$$

(*v*) **Benzene to 2-phenylpropene.**

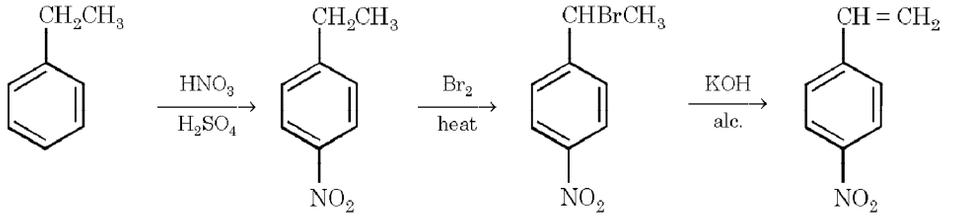


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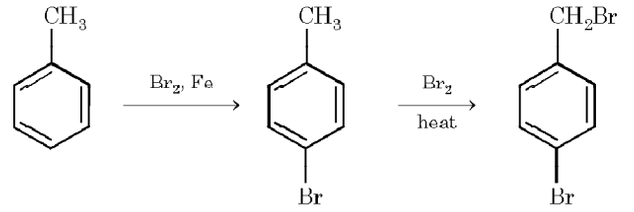
(*vi*) **Ethylbenzene to E-1-penylpropene.**



(*vii*) **Ethylbenzene to *p*-nitrostyrene.**

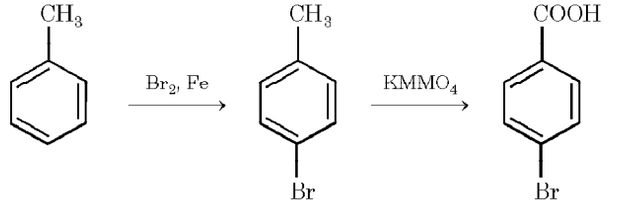


(*viii*) **Toluene to *p*-bromobenzyl bromide.**

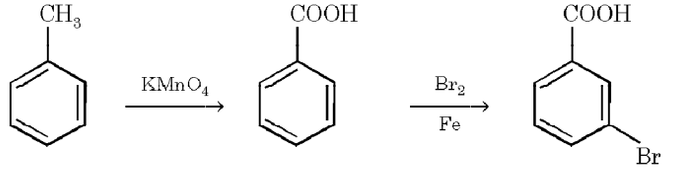


Remember that nuclear substitution is done earlier so as to get better yield. Otherwise —CH_2Br will decrease the yield of *p*-bromo isomer.

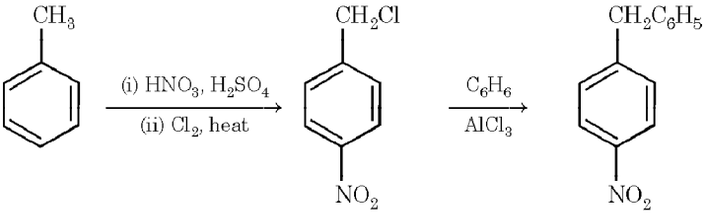
(*ix*) **Toluene to *p*-bromobenzoic acid.**



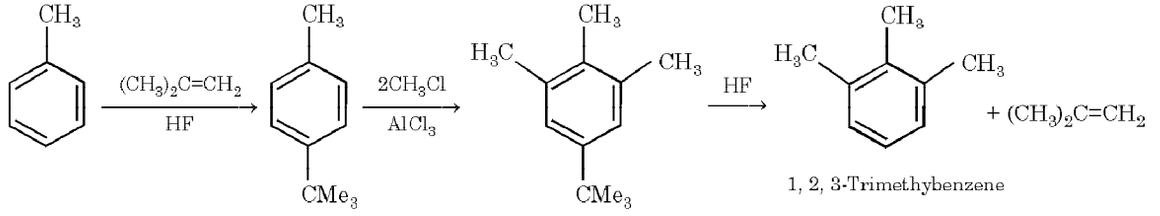
(*x*) **Toluene to *m*-bromobenzoic acid.**



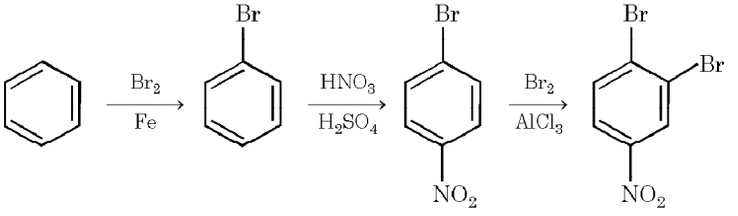
(*xi*) **Toluene to *p*-nitrodiphenylmethane.**



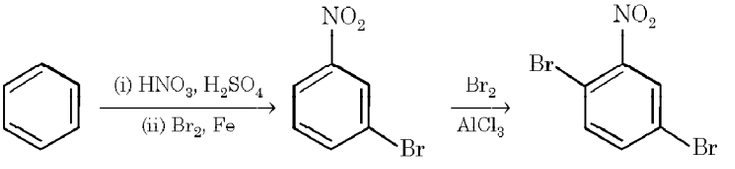
24. (*i*) **Toluene to 1, 2, 3-trimethylbenzene.** Methylation of toluene will give *p*-xylene, therefore it is necessary to block the *para* position with a group that can later be easily removed. Such group is —CMe_3.



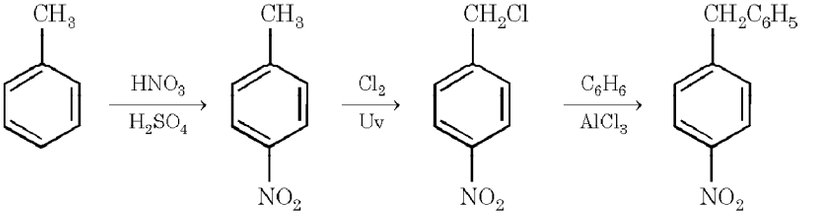
(*ii*) **Benzene to 3, 4-dibromonitrobenzene.**



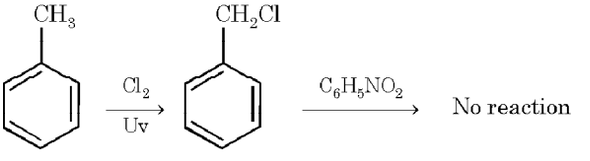
Remember that nitration should not be done earlier than bromination because such sequence will give 2, 5-dibromonitrobenzene according to the rule ''in case *op*-director and *m*-director are not reinforcing, the *op*-director controls the orientation and the incoming group goes mainly *ortho* to the *m*-director''.



(*iii*) **Toluene to *p*-benzylnitrobenzene**



Remember that chlorination should not be done prior to nitration because deactivated nitrobenzene can't be alkylated with $C_6H_5CH_2Cl$.



Furthermore, nitration of benzyl chloride will give lower yield of the *o*- and *p*-isomers.

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(*iv*) **Benzene to 1, 1-diphenylethane**

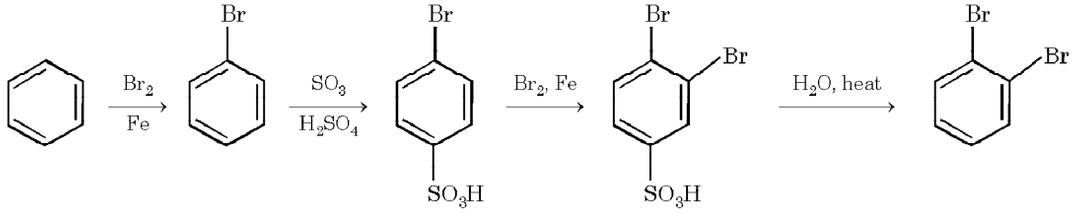
$$C_6H_6 \xrightarrow[AlCl_3]{C_2H_5Cl} C_6H_5CH_2CH_3 \xrightarrow[light]{Br_2} C_6H_5CHBrCH_3 \xrightarrow[KOH]{alc}$$

$$C_6H_5CH = CH_2 \xrightarrow{C_6H_6,\ HF} (C_6H_5)_2CHCH_3$$

Note that last step is an example of Friedel-Craft reaction.

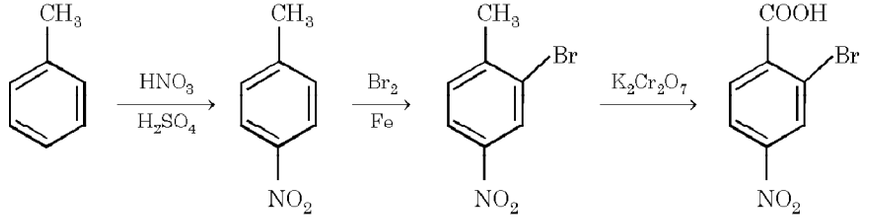
$$C_6H_5CH = CH_2 \xrightarrow{HF} \underset{\text{2° carbocation}}{C_6H_5\overset{+}{C}HCH_3} \xrightarrow{C_6H_6} (C_6H_5)_2CHCH_3$$

(*v*) **Benzene to *o*-dibromobenzene**



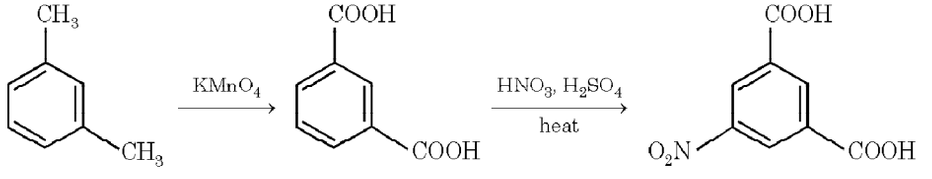
Direct bromination of bromobenzene is not advisable as it would mainly give *p*-dibromobenzene.

(*vi*) **Toluene to 2-bromo-4-nitrobenzoic acid**



Remember that —CH_3 should not be oxidised prior to bromination because in such case bromination of a ring deactivated by —COOH and —NO_2 groups would be very difficult and bromination will occur in the *meta* position to both of the groups —COOH and —NO_2.

(*vii*) ***m*-Xylene to 5-nitroisophthalic acid.**



Here since both of the deactivating groups reinforce each other, appreciable amount of the *m*-isomer can be obtained of course, under drastic conditions.

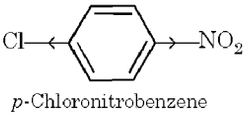
25. (*i*) Benzene is more reactive than bromobenzene and hence would preferentially undergo alkylation. On the other hand, —NO_2 strongly deactivates the nitrobenzene nucleus with the result the latter does not undergo Friedel-Craft alkylation or acylation.

(*ii*) To avoid polyalkylation.

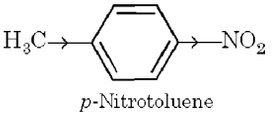
(*iii*) Since $C_6H_5^+$ has a high enthalpy, it is not formed. $C_6H_5Cl + AlCl_3 \longrightarrow \underset{\text{(Not formed)}}{C_6H_5^+} + AlCl_4^-$

(*iv*) Sulphonation is one of the few reversible electrophilic substitutions and therefore gives the kinetic controlled product at 0°C and the thermodynamic controlled product at 100°C.

(*v*)



p-Chloronitrobenzene
(Individual moments are in opposite directions and hence partially cancel)



p-Nitrotoluene
(Both moments are in same direction and hence additive)

(*vi*) Formation of lesser amount of ortho product in $C_6H_5C(CH_3)_3$ is due to steric hindrance ; the bulky —$C(CH_3)_3$ group inhibits formation of the ortho isomer and thus increases the yield of the para isomer.

(*vii*) In aryl halides, inductive effect operates which is strongest at the closer *ortho* position. Now since F has the greatest inductive effect among halogens, its ortho positions are deactivated more than that of other aryl halides hence ortho isomer will be minimum.

(*viii*) This is explained on the basis of selectivity-reactivity principle, *i.e.* the most reactive electrophile is the least selective and gives the maximum amount of meta isomer. The order of reactivity is :

$$CH_3CH_2^+ > NO_2^+ > Br^+$$

(*ix*) —OCH_3 group is electron-releasing and activating by extended π bonding only when it is attached to the positively charged (*o, p*-) positions of the benzenonium ion. It is also electron-withdrawing by induction and this factor prevails in the *m*-position, which is deactivated. On the other hand, —CH_3 group is electron releasing by inductive and hyperconjugative effects, and since hyperconjugation is effective only in the *o-p*-positions, these positions are more activated than the *m*-position.

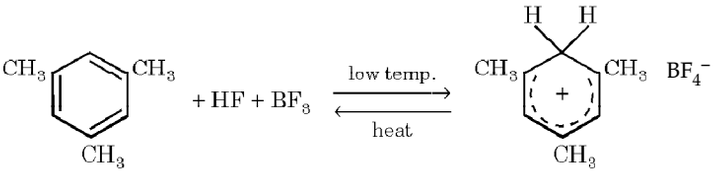
(*x*) Nitronium ion, NO_2^+, the real nitrating agent is produced according to the following scheme.

$$2HNO_3 \rightleftharpoons NO_3^- + H\text{—}\overset{+}{O}(H)\text{—}NO_2 \rightleftharpoons \underset{\text{Nitronium ion}}{NO_2^+} + NO_3^- + H_2O$$

When a salt of nitric acid is added, it shifts the equilibrium to the left causing the formation of undissociated acid molecules. Hence the concentration of the nitronium ion decreases in the reaction mixture with the result rate of nitration also decreases. On the other hand, addition of conc. sulphuric acid helps in producing the nitronium ions and hence increases the rate of nitration.

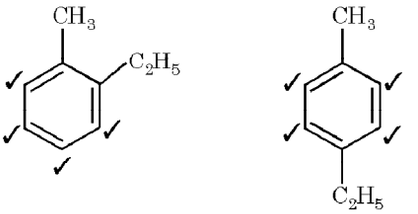
$$\underset{\text{Nitric acid}}{HONO_2} + 2H_2SO_4 \rightleftharpoons \underset{\text{Nitronium ion}}{NO_2^+} + 2HSO_4^- + H_3O^+$$

26.

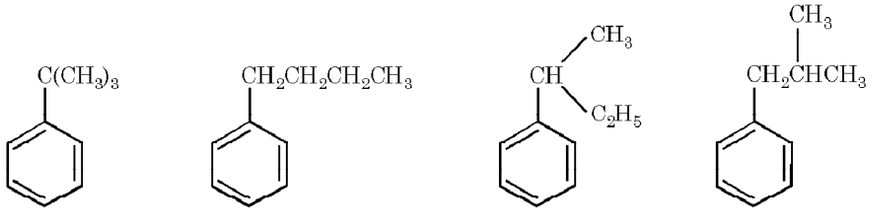


(Bright yellow solid)

27. Four isomers are produced by arenes having two different alkyl groups in *ortho* or *para* positions. Thus C_9H_{12} can be either of the following structures.



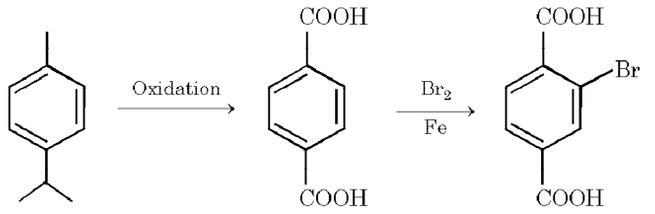
28. An alkyl group, on benzene nucleus, undergoes oxidation if it has at least one benzylic hydrogen atom. Thus to resist oxidation, the benzylic carbon atom should not have any hydrogen atom, *i.e.* it should be *tertiary*. Hence the compound in question is *tert*-butylbenzene whose other isomers are sketched below.



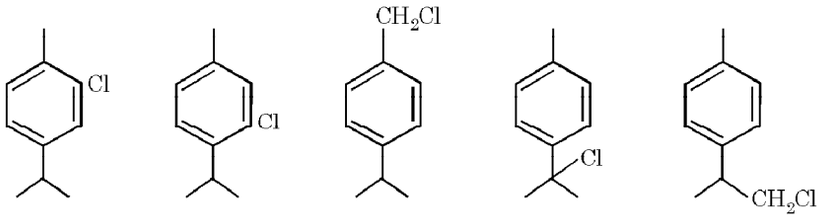
tert-Butylbenzene *n*-Butylbenzene *sec*-Butylbenzene 2-Methylpropylbenzene

29. (*i*) The acidic compound $C_8H_6O_4$ must be a dicarboxylic acid, $C_6H_4(COOH)_2$ and since this gives only one monobromo derivative, the two —COOH groups should be present in *para* position to each other. Hence the arene should be a *p*-dialkylbenzene.

(*ii*) Since the arene forms five isomeric monochloro derivative, it should be *p*-isopropylbenzene only which can give rise to five isomeric monochloro derivatives.



Arene, $C_{10}H_{14}$



Five isomeric monochloro derivatives.

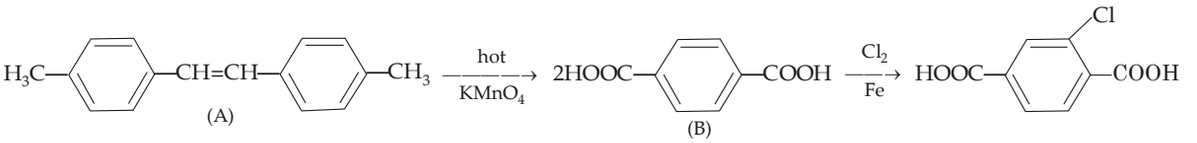
30. (*i*) Molecular formula ($C_{16}H_{16}$) of the compound A indicates 9 degree of unsaturation (saturated hydrocarbon will be $C_{16}H_{34}$).

(*ii*) Since compound A takes up one H_2 molecule, it indicates that it has one C = C linkage, thus the other 8 degree of unsaturation must be present in the form of 2 benzene rings (one benzene ring has 4 degree of unsaturation).

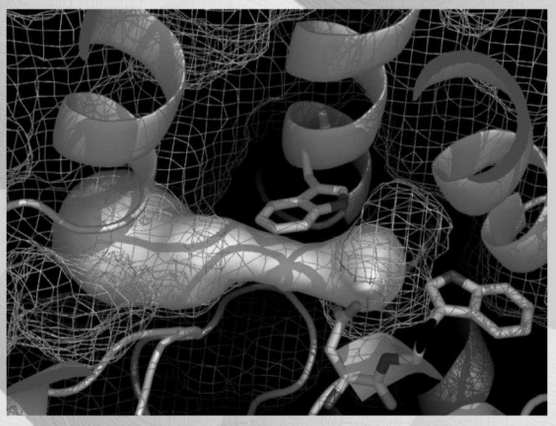
(*iii*) Oxidation of A with hot $KMnO_4$ gives a dicarboxlic acid B of the formula $C_8H_6O_4$ or $C_6H_4(COOH)_2$ indicating that each benzene ring must be disubstituted.

(*iv*) Since the dicarboxylic acid B forms only one monobromo derivative, the two —COOH groups must be *para* to each other.

Thus compound A should have following structure which explains all reactions.



Two isomers of (A) are *cis*- and *trans*.



8

Aliphatic Halogen Derivatives

CHAPTER HIGHLIGHTS

8.1 Preparation of Alkyl Halides
8.2 Physical Properties
8.3 Chemical Properties
ILLUSTRATIVE EXAMPLES
8.4 Halogen Derivatives of Unsaturated Hydrocarbons
8.5 Polyhalogen Compounds
EXERCISES
SOLUTIONS

Compounds obtained by the replacement of one or more hydrogen atom(s) from hydrocarbons are known as **halogen derivatives.** The halogen derivatives of alkanes, alkenes, alkynes and arenes are known a **alkyl halides** (haloalkanes), **alkenyl halides** (haloalkenes), **alkynyl halides** (haloalkynes) and **aryl halides** (halobenzenes), respectively.

Halogen derivatives may be classified in several ways depending upon the type of the halogen atom, number of halogen atom(s) and position of the halogen atom. The last type of classification deserves special attention, *e.g.*, alkyl halides may be classified into *primary (1°)*, *secondary (2°)* and *tertiary (3°)* according to the nature of the carbon atom bearing halogen.

Alkyl halides may show chain, position and optical isomerism, while alkenyl halides may show geometrical isomerism; aryl halides show position isomerism.

TEST YOUR UNDERSTANDING - 8.1

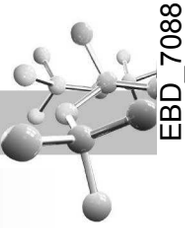
1. Write structural formulas and IUPAC names of all isomers of

(*a*) $C_5H_{11}Cl$. Classify the isomers as 1°, 2° and 3° chlorides.

(*b*) $C_4H_8Cl_2$. Classify the isomers as *vic*-dihalides and *gem*-dihalides.

2. Give the simplest examples (compound having minimum possible carbon) of monohalogen compounds which can show

(*a*) Geometrical isomerism (*b*) Optical isomerism.



8.1 Preparation of Alkyl Halides

8.1.1 From Alcohols

Alcohols are considered the best starting materials for preparing alkyl halides. The most common method is to treat the alcohol with HX. The order of reactivity of the hydrogen halides parallels their acidity : HI > HBr > HCl >> HF.

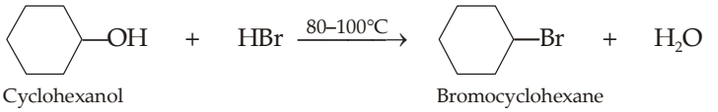
$$R-OH \xrightarrow{HX,\ PX_3 \text{ or } SOCl_2} R-X \qquad (\text{where , X = I, Br, Cl})$$

Among the various classes of alcohols, the order of reactivity with hydrogen halides is

tertiary > secondary > primary > CH_3OH

Tertiary alcohols are so reactive that these are converted to alkyl chlorides in high yield within minutes on reaction with HCl at room temperature, while secondary and primary alcohols give very low yield under these conditions. Therefore, the more reactive HBr is used and that too at elevated temperatures to get quantitative yield of secondary and primary bromides.

$$\underset{\textit{tert}\text{ - Butyl alcohol}}{(CH_3)_2C-OH} + HCl \xrightarrow{25^\circ C} \underset{\textit{tert}\text{ - Butyl chloride}}{(CH_3)_3C-Cl} + H_2O$$



Cyclohexanol Bromocyclohexane

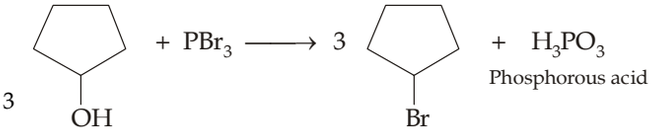
$$CH_3(CH_2)_5CH_2OH + HBr \xrightarrow{120^\circ C} CH_3(CH_2)_5CH_2Br + H_2O$$

$$CH_3CH_2CH_2CH_2OH \xrightarrow[\text{heat}]{NaBr,\ H_2SO_4} CH_3CH_2CH_2CH_2Br$$

Tertiary alcohols react with HX by S_N1 pathway, while primary alcohols react via S_N2, secondary may follow either or both of the paths (discussed in detail in Ch. 4).

Primary and secondary alcohols can best be converted to the corresponding chlorides, bromides and iodides by the use of thionyl chloride, phosphorus bromide and phosphorus + iodine (PI_3) respectively.

$$CH_3CH_2CH_2OH + SOCl_2 \xrightarrow{\text{pyridine}} CH_3CH_2CH_2Cl + SO_2\uparrow + HCl\uparrow$$



Cyclopentanol Cyclopentyl bromide

$$CH_3CH_2OH \xrightarrow{P + I_2} CH_3CH_2I$$

IMPORTANT POINTS

1. Mixture of conc. HCl and anhydrous $ZnCl_2$ is called **Lucas reagent.**
2. $SOBr_2$ is less stable and SOI_2 does not exist.
3. PBr_5 and PI_5 are highly unstable compounds, hence can't be used for preparing bromides and iodides.

TEST YOUR UNDERSTANDING - 8.2

1. Give steps involved in the conversion of an alcohol into alkyl halide in presence of conc. HCl and anhydrous $ZnCl_2$.

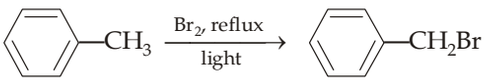
8.1.2 Halogenation of Certain Hydrocabons

Alkyl halides are almost never prepared by direct halogenation of alkanes because the reaction generally gives a mixture of several compounds. Details have already been discussed in Ch. 5.

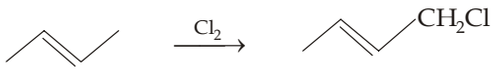
$$CH_4 \xrightarrow[\text{heat or light}]{Cl_2} CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 \xrightarrow{Cl_2} CCl_4$$

$$CH_3CH_2CH_3 \xrightarrow[\text{heat or light}]{Cl_2} CH_3CH_2CH_2Cl + CH_3CHClCH_3 \xrightarrow{Cl_2} \text{.....}$$

However, certain compounds can form monohalogen product in good yield, *e.g.* CH_4, CH_3CH_3, $(CH_3)_4C$, $C_6H_5CH_3$, $CH_3CH = CH_2$, etc.because in all of them hydrogen atom to be replaced by halogen are equivalent (remember that allylic hydrogen atoms are much more reactive than the inert vinylic hydrogens).

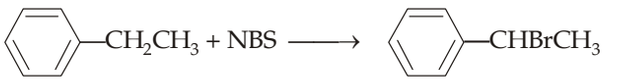


Toluene Benzyl bromide



But-2-ene 1-Chlorobut-2-ene

Bromination at allylic and benzylic positions may best be carried out by another brominating reagent, N-bromosuccinimide (for details, consult Ch. 6).



Ethylbenzene 1-Bromo-1-phenylethane

Halogenation of alkanes takes place through free-radical mechanism.

8.1.3 Addition of Hydrogen Halides to Alkenes

Alkenes add hydrogen halides to form alkyl halides. In case of unsymmetrical alkenes, hydrogen halides add according to **Markownikov's rule** (For details, refer Ch. 6).

$$CH_3—CH = CH_2 + HX \longrightarrow CH_3CHX—CH_3$$

Addition of hydrogen halides to alkenes is an example of electrophilic addition involving carbocations as intermediates.

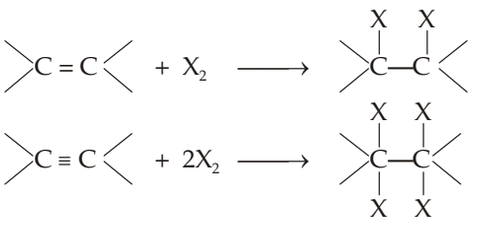
However, addition of H—Br (not HCl, HI and HF) on alkenes in presence of peroxides takes place in **anti-Markownikov's way**, *the peroxide effect.* (For details, refer Ch. 6).

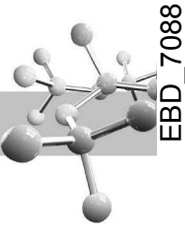
$$CH_3—CH = CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3CH_2CH_2X$$

Here the addition takes place via **free-radical mechanism.**

8.1.4 Addition of Halogens to Alkenes and Alkynes

[For details consult Ch. 6).





8.1.5 Halide Exchange Method

Alkyl fluorides and alkyl iodides are best prepared by this method. In the preparation of alkyl fluorides, an alkyl chloride, bromide, or iodide is heated with potassium fluoride in a high-boiling alcohol solvent such as ethylene glycol.

$$RCH_2Br + KF \xrightarrow[120°]{\text{ethylene glycol}} RCH_2F + KBr$$

Alkyl fluorides have the lowest boiling points of all the alkyl halides and are removed from the reaction mixture by distillation and thus favouring the reaction to right side (Le Chatelier principle). However, the alkyl fluoride will predominate at equilibrium even when it is not removed by distillation because the reaction favours formation of the stronger C—F bond in place of weaker C—I, C—Br, or C—Cl bond.

Alkyl iodides may be prepared from alkyl chlorides and bromides by treatment with sodium iodide in acetone as the solvent.

$$\underset{\text{2–Bromopropane}}{CH_3CHBrCH_3} + NaI \xrightarrow{\text{acetone}} \underset{\text{2–Iodopropane}}{CH_3CHICH_3} + NaBr\downarrow$$

Since NaCl and NaBr are insoluble in acetone, while NaI is soluble, former are removed from the reaction mixture by filtration causing the reaction to shift towards alkyl iodides (Le Chatelier principle).

8.1.6 Hunsdiecker Method

$$CH_3COOAg + Br_2 \longrightarrow CH_3Br + CO_2 + AgBr$$

Mechanism

$$R-\overset{\overset{O}{\|}}{C}-OAg + X_2 \longrightarrow R-\overset{\overset{O}{\|}}{C}-O-X + AgX$$

$$R-\overset{\overset{O}{\|}}{C}-O-X \longrightarrow R-\overset{\overset{O}{\|}}{C}-O^{\bullet} + X^{\bullet}$$

$$R-\overset{\overset{O}{\|}}{C}-O^{\bullet} \longrightarrow R^{\bullet} + CO_2$$

$$R^{\bullet} + R-\overset{\overset{O}{\|}}{C}-O-X \longrightarrow R-X + R-\overset{\overset{O}{\|}}{C}-O^{\bullet}$$

(*i*) Reaction is used to reduce the length of carbon chain by one carbon atom.

(*ii*) The yield of alkyl bromide follows the order : 1° > 2° > 3°.

(*iii*) Yield in case of chloride is very low, while iodine under such conditions give esters **(Birnbarun reaction).**

$$2RCOOAg + I_2 \longrightarrow RCOOR + CO_2 + 2AgI$$

TEST YOUR UNDERSTANDING - 8.3

1. Give two methods for the preparation of 3-bromo-3-phenylpropane from 3-phenylpropene.

2. How will you prepare following compounds from an alkene only in one step (give chemical reactions).

(*i*) *trans*-1, 2-Dibromocyclopentane

(*ii*) 1-Iodo-2-bromo-2-methylpentane

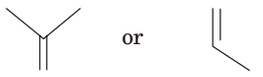
(*iii*) 2-2-Dibromobutane

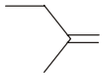
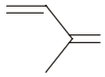
(*iv*) 1, 3-dibromopropane

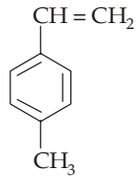
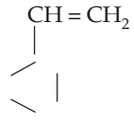
(*v*) 3-Methyl-1-bromobutane

(*vi*) 1, 1-Dichloro-*cis*-2, 3-dimethylcyclopropane

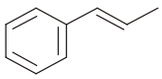
3. (*a*) Predict which compound adds HBr faster.

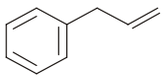
(*i*)  or

(*ii*)  or 

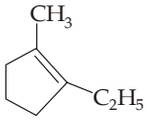
(*iii*)  or 

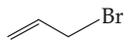
(*b*) Give structure of the product obtained by the addition of HBr on the following alkenes.

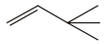
(*i*) 

(*ii*) 

(*iii*) 

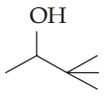
(*iv*) 

(*v*) 

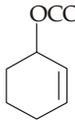
(*vi*) 

Hint. Carbocation stability is the factor.

4. Identify (A) to (E) in the following reactions.

(*i*)  + HCl ⟶ A

(*ii*)  + NBS ⟶ B (Major) + C (Minor)

(*iii*)  + NBS ⟶ D + E

5. Explain the following :

(*i*) Free radical halogenation can be applied for the preparation of Me_3CBr in quantitative yield, while not for Me_3CCl.

(*ii*) Free radical monobromination of ethylbenzene gives only one product while hexene-3 gives two isomers.

8.2 Physical Properties

1. Alkyl halides are although polar in nature, *these are insoluble in water* but soluble in organic solvents. Their insolubility in water is due to their inability to form hydrogen bonds with water molecules or to break the hydrogen bonds already existing in water molecules.

2. Their densities decrease in the following order :

iodide > bromide > chloride > fluoride.

Alkyl bromides and iodides are generally heavier than water, whereas chlorides and fluorides are lighter. *Methyl iodide is the densest alkyl halide* as in this compound contribution of iodine density is maximum relative to the contribution of hydrocarbon part.

3. Boiling points of alkyl halides follow the following order :

Iodide > Bromide > Chloride > Fluoride.

Among isomeric halides, the boiling point decreases as 1° > 2° > 3°

Boiling points of chlorinated derivatives of an alkane increase with number of Cl atoms because of an increase in the induced dipole-induced dipole attractive forces.

4. Stability order of alkyl halides is RF > RCl > RBr > RI

Alkyl iodides, on standing become violet or brown because of their decomposition in presence of light to give iodine.

$$2R - I \xrightarrow{\text{Light}} R — R + I_2$$

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TEST YOUR UNDERSTANDING - 8.4

1. Arrange the four CH_3—X (X = – I, – Br, –F, –Cl) in decreasing order of their

(*a*) C—X bond lengths (*b*) dipole moments

(*c*) polarizability (*d*) C—X bond strength

2. Arrange the following

(*a*) in decreasing order of boiling points

(*i*) CH_3F, CH_3Br, CH_3Cl, CH_3I and CH_4 (*ii*) CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4

(*b*) in decreasing order of densities

(*i*) H_2O, CH_4 and CH_3X's (*ii*) H_2O, CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4.

8.3 Chemical Properties

Alkyl halides mainly undergo three types of reactions : (*a*) nucleophilic substitution, (*b*) elimination, and (*c*) reduction.

8.3.1 Nucleophilic Substitution

Because of high electronegativity of the halogen atom, the carbon halogen (C – X) bond is highly polarised* colvalent bond.

$$\overset{+\delta}{-C} : \overset{-\delta}{X} \quad \text{or} \quad \overset{+\delta}{-C} : \overset{-\delta}{X}$$

Thus the carbon atom of the C – X bond becomes a good site for attack by electron rich species **(nucleophiles or nucleophilic reagents).** In fact **nucleophilic substitution** (replacement of the halide ion by a nucleophile) **reactions are the most common reactions of alkyl halides.** Mechanism of nucleophilic substitutions have already been discussed at length in Ch. 4, so readers are referred to consult Ch.4. In short, remember that 1° alkyl halides mainly undergo S_N2 reaction, 3° halides undergo S_N1 while 2° halides may undergo S_N2 and or S_N1 reaction. Important nucleophilic substitution reactions are summarised in the following table.

Nucleophilic Substitution Reactions of RX

R—X + : Z (nucleophile) ⟶ R : Z + : X^-

Source of : Z	*Product, R—Z*	*Name of product*
Na^+OH^-	R—OH	Alcohols
H_2O (water)	R—OH	Alcohols
$Na^+ {}^-OR'$	R—OR′	Ethers (*Williamson synthesis*)
I^-	R—I	Alkyl iodides
$R'COO^-$	R—OOCR′	Esters
K^+CN^-	R—CN	Nitriles
AgCN (covalent)	R—CN + R—NC	Nitriles and Isonitriles
$K^+NO_2^-$	R—O—N = O	Alkyl nitrites
$AgNO_2$	R—O—N = O + R —N(=O)O	Nitrites and Nitroalkanes

* Polarity in C—halogen bonds produces dipole moment. The dipole moment of alkyl halides is in the order of 2 – 2.2D. Vinyl chloride and chlorobenzene showing resonance have lower dipole moments.

$K^+ SH^-$	R—SH	Thiols (Mercaptans)
$K^+ SR^-$	R—SR′	Thioethers (Sulphides)
N_3^-	$R—N=\overset{+}{N}=\overset{-}{N}$	Azides
NH_3	$R—NH_2$	Primary amines
$R'NH_2$	R—NHR′	Secondary amines
$R_2'NH$	$R—NR'_2$	Tertiary amines
R_3N	R_4NX	Quaternary ammonium salts
$P(C_6H_5)_3$	$[R—P(C_6H_5)_3]^+X^-$	Phosphonium salts
$Na^+ C \equiv CR^-$	R—C ≡ C—R′	Alkynes
Ar—H	Ar—R [Friedel-Craft reaction]	Alkylbenzenes
$Na^+CH(COOC_2H_5)_2^-$	$R—CH(COOC_2H_5)_2$	Malonic esters
$Na^+[CH_3COCHCOOC_2H_5]^-$	$CH_3COCH(R)COOC_2H_5$	Acetoacetic esters
$\overset{\delta-}{R'}—\overset{\delta+}{M}$, *e.g.* $\overset{\delta-}{CH_3}—\overset{\delta+}{Li}$	R—R	Alkanes (Coupling)
H^- : (from $LiAlH_4$)	R—H	Alkanes (Reduction)

TEST YOUR UNDERSTANDING - 8.5

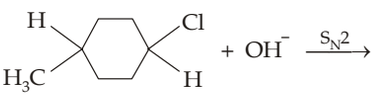
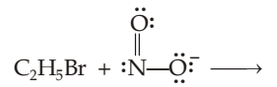
1. Give the structure of the *immediate product* obtained from the reaction of CH_3Br with

(*i*) C_2H_5OH (*ii*) $(CH_3)_2NH$ and (*iii*) $(Ar)_3P$.

2. Supply formulas for the products for the following reactions

(*i*) $CH_3CH_2CH_2Br + (CH_3)_2CHONa \longrightarrow$ (*ii*) Bromocyclopentane + NaI $\longrightarrow$

(*iii*) $CH_3CH_2CH_2Cl + (CH_3)_2S \longrightarrow$ (*iv*) $ClCH_2CH_2I$ (one mole) + CN^- (one mole) $\longrightarrow$

(*v*)  (*vi*) 

(*vii*) n–C_3H_7Br + $[:\ddot{S}—C \equiv N:]^-$ $\longrightarrow$ (*viii*) C_2H_5I + $[:\ddot{S}SO_3]^{2-}$ $\longrightarrow$

3. Account for the fact that the reaction of an alkyl halide with H_2O, or an alcohol always gives the neutral final products, while reaction with NH_3 or $R'NH_2$ gives the cations.

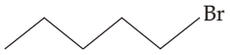
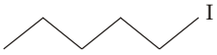
4. Explain that reaction between RF and NaCl is not feasible while reaction between RCl and NaF is feasible.

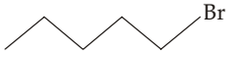
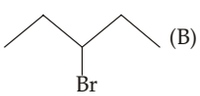
5. A typical nucleophilic substitution reaction of an alkyl halide takes place as

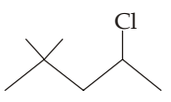
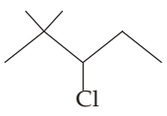
$$H_3\overset{\delta+}{C}—\overset{\delta-}{Cl} + :Nu \longrightarrow H_3C—Nu + Cl^-$$

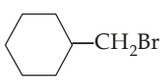
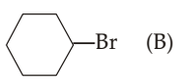
Does the rate of the reaction depend on the amount of δ^+ on the attacked C of alkyl halide ?

6. (*a*) Among the following pairs of compounds, which of the compounds would undergo S_{N^2} reaction faster?

(*i*)  (A) and  (B)

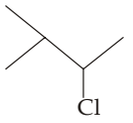
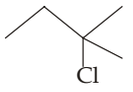
(*ii*)  (A) and  (B)

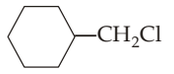
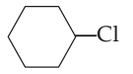
(*iii*)  (A) and  (B)

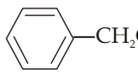
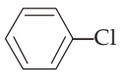
(*iv*)  (A) and  (B)

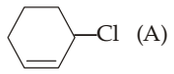
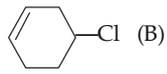
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(*b*) Among the following pairs, which would undergo $S_{N}1$ reaction faster ?

(*i*)  (A) and  (B)

(*ii*)  (A) and  (B)

(*iii*)  (A) and  (B)

(*iv*)  (A) and  (B)

7. Each of the following two ethers can be prepared by nucleophilic substitution of alkyl halides in two different manners.

(*a*) 2-Ethoxypropane (*b*) 2-methoxy-2-methylpropane

Write down the chemical reactions for these two possible sets for each ether and explain which set gives quantitative yield in each case.

8.3.2 Elimination Reaction (Dehydrohalogenation)

In an elimination reaction, a halogen and a hydrogen atom are removed from adjacent carbon atoms to form a double bond. This is sometimes called β-elimination and carried out by a strong base, *viz.* KOH in ethanol. For example,

$$CH_3CH_2CHBrCH_3 \xrightarrow{\text{alc. KOH}} CH_3CH = CHCH_3$$

The order of reactivity of alkyl groups towards elimination is : 3° > 2° > 1°. *In case, an alkyl halide can form two alkenes, more substituted alkene (also known as Saytzeff product) is the major product and less substituted alkene (also known as Hofmann product) is the minor product.*

$$CH_3CH_2CH_2CHClCH_3 \xrightarrow{\text{alc. KOH}} \underset{\substack{\textbf{(Major)}\\ \text{Saytzeff product}}}{CH_3CH_2CH = CHCH_3} + \underset{\substack{\text{(Minor)}\\ \text{Hofmann product}}}{CH_3CH_2CH_2CH = CH_2}$$

However, remember that elimination reactions compete with substitution reactions. Elimination reactions dominate over substitution when strong Bronsted base (*e.g.* NH_2^-, Me_3CO^-, $^-OC_2H_5$ etc.) is used and alkyl halide is 3° or 2°.

Summary of substitution *vs* elimination

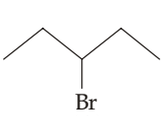
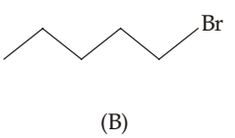
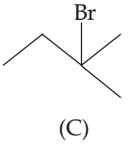
1. When the substrate is a 1° halide, S_N2 predominates except when a hindered strong base like Me_3CO^- is used.
2. When the substrate is a 2° halide S_N2 occurs with weak bases like I^-, CN^-, $RCOO^-$ etc., and E2 occurs with strong bases like RO^-.
3. When the substrate is a 3° halide, S_N1 is favoured at low temperature and in solvolysis (when no strong base/ nucleophile is present and the solvent acts as a nucleophile/base) ; when a strong base (*e.g.* RO^-) is used E2 predominates.

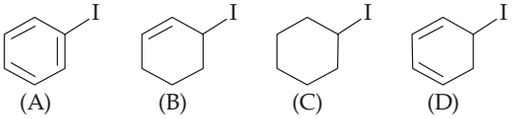
TEST YOUR UNDERSTANDING - 8.6

1. Arrange the following bases in decreasing order of reactivity for β-elimination NH_2^-, OH^-, OR^-, $RCOO^-$, CN^-, NO_3^-, $(CH_3)_3CO^-$

.

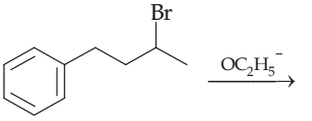
2. Arrange the following compounds in decreasing order of ease of dehydrohalogenation.

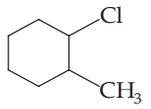
(*a*)  (A)  (B)  (C)

(*b*)  (A) (B) (C) (D)

3. Complete the following :

(*a*) $ClCH_2CHCl_2 \xrightarrow[\text{(ethanol)}]{OH^-}$

(*b*) 

(*c*)  $\xrightarrow{^-OC_2H_5}$ A (Major) + B (Minor)

(*d*) $CH_3CH_2CH_2Br + LiAlD_4 \longrightarrow$

(*e*) $Me_3CBr + HCOOH \longrightarrow$

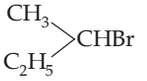
(*f*) $Me_3CBr + HCOOH + HCOONa$ (trace) $\longrightarrow$

(*g*) $Me_2C = CHCl + NaNH_2 \longrightarrow$

4. Give the expected product(s) in each of the following reactions. Mention the mechanism ($S_{N}1$, $S_{N}2$, E1, or E2) followed by each product.

(*a*) $CH_3(CH_2)_{15}CH_2Br + CH_3O^- \xrightarrow{CH_3OH}$

(*b*) $CH_3CH_2CH_2\ Br + (CH_3)_3CO^- \xrightarrow{(CH_3)_3COH}$

(*c*)  $\xrightarrow{CH_3OH}$

(*d*) $(CH_3CH_2)_3CBr + OH^- \xrightarrow{50°C,\ CH_3OH}$

(*e*) $(CH_3CH_2)_3CBr \xrightarrow{25°C,\ CH_3OH}$

(*f*) $CH_3CHBrCH_3 + OCH_3^- \xrightarrow{CH_3OH}$

(*g*) $CH_3CH = CHCl + NH_2^- \longrightarrow$

5. Account for the fact that the reaction of 1-chloro-2-butene with CN^- gives a mixture of two products.

$$CH_3CH = CHCH_2Cl \xrightarrow{CN^-} CH_3CH = CHCH_2CN + CH_3CH(CN)\ CH = CH_2.$$

8.3.3 Reaction with Metals

(*a*) Alkyl halides (1°, 2°, or 3°) react with metals generally in presence of diethyl ether (solvent) to form compounds having C-metal bond (**organometallic compounds**). For example,

$$R—X + 2Li \xrightarrow{\text{diethyl ether}} \underset{\text{Alkyllithium}}{R-LI} + LiX$$

$$R—X + Mg \xrightarrow{\text{diethyl ether}} \underset{\text{Alkylmagnesium halide}}{R-MgX}$$

Alkylmagnesium halides are commonly called **Grignard reagents.**

(*i*) Among alkyl halides, the order of reactivity is : I > Br > Cl > F ; since bromides are readily available and quite reactive, these are most oftenly used

(*ii*) The reactivity of a metal with an alkyl halide depends on its reduction potential ; the more easily a metal is reduced, the more reactive it is *e.g.* Mg > Zn.

(*iii*) The solvent used must be anhydrous because even a trace of water or alcohols react with metals to form insoluble hydroxide or alkoxide salts that coat the surface of the metal and thus prevent it from reacting with the alkyl halide. Moreover, organo-metallic compounds are strong bases and react rapidly with even weak proton sources to form hydrocarbons.

(*b*) Organosodium compounds, formed in the same manner as above, are so reactive that as soon as these are formed, they couple with their parent alkyl halides to form alkane as the final product **(Wurtz reaction).**

$$\underset{\text{Methyl chloride}}{CH_3Cl} + 2Na \xrightarrow[(-NaCl)]{\text{ether}} \underset{\text{Methylsodium}}{[CH_3Na]} \xrightarrow{CH_3Cl} \underset{\text{Ethane}}{CH_3CH_3} + NaCl$$

$$\text{or} \quad CH_3Cl + 2Na + ClCH_3 \xrightarrow{\text{ether}} CH_3CH_3 + 2NaCl$$

Reaction between alkyl halide, aryl halide and sodium in presence of dry ether is known as **Wurtz-Fittig reaction.**

$$C_6H_5Cl + 2Na + ClCH_3 \xrightarrow{Na} C_6H_5CH_3 + 2NaCl$$

(*c*) Ethyl chloride when heated with a sodium-lead alloy under pressure gives **tetraethyl lead, TEL** (an important *anti-knocking compound*).

$$4C_2H_5Cl + 4Na/Pb \longrightarrow (C_2H_5)_4\ Pb + 4NaCl + 3Pb$$

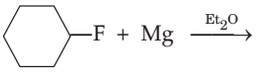
(*d*) Alkyl halides react with lithium to form alkyllithiums which react with copper halide to form higher alkane as the find product **(Corey-House synthesis**, discussed in detail in chapter on Alkanes).

$$\underset{(1°,\ 2°\ \text{or}\ 3°)}{RX} \xrightarrow{Li/Et_2O} RLi \xrightarrow{CuI} R_2CuLi \xrightarrow[(1°\ \text{halide})]{R'X} R-R'$$

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TEST YOUR UNDERSTANDING - 8.7

1. Give the products for the viable reactions.

(*i*) $CH_3Br + Li \xrightarrow{Et_2O}$ (*ii*) $n\text{-}C_3H_7Cl + Mg \xrightarrow{THF}$ (*iii*)  $+ Mg \xrightarrow{Et_2O}$

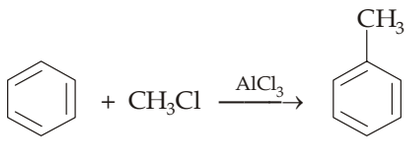
(*iv*) $n\text{-}C_3H_7I + Zn \longrightarrow$ (*v*) $n\text{-}C_3H_7Cl + Zn \longrightarrow$

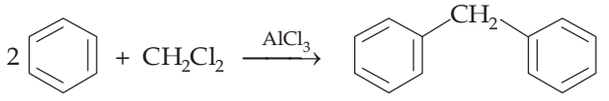
2. Give the products when Mg/Et_2O is treated with

(*i*) $BrCH_2CH_2Br$ (*ii*) $BrCH_2CH_2CH_2Br$ (*iii*) $BrCH_2CH_2CH_2CH_2Br$.

8.3.4 Reaction of Alkyl Halides with Aromatic Hydrocarbons (*Electrophilic Substitution in Benzene)*

Benzene and other aromatic hydrocarbons react with alkyl halides, alkylene halides, and other halogen derivatives in presence of anhydrous $AlCl_3$ to form higher aromatic hydrocarbons.

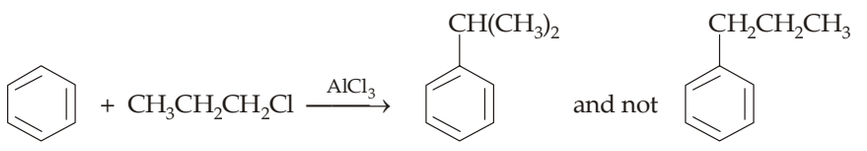
(*a*) 

(*b*) 

Diphenylmethane

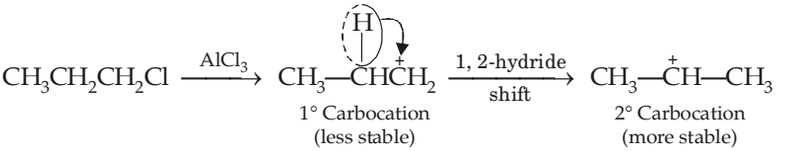
(*c*) $3C_6H_6 + CCl_4 \xrightarrow{AlCl_3} (C_6H_5)_3CCl$

Trityl chloride

(*d*) 

Isopropylbenzene (Cumene)

Formation of cumene is due to more stability of the 2° carbocation as compared to 1°.



1° Carbocation (less stable) — 2° Carbocation (more stable)

Above reaction between alkyl halide and arenes can also be extended between alkyl halide and alkenes, *e.g.*

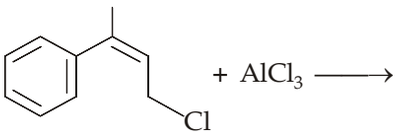
$$CH_2 = CH_2 + Me_3CCl \xrightarrow{AlCl_3,\ -10°C} Me_3CCH_2CH_2Cl$$

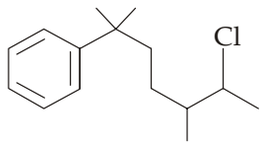
Mechanism

$$Me_3CCl \xrightarrow[(-AlCl_4^-)]{AlCl_3} Me_3C^+ \xrightarrow{CH_2 = CH_2} Me_3CCH_2C^+H_2 \xrightarrow{AlCl_4^-} Me_3CCH_2CH_2Cl + AlCl_3$$

TEST YOUR UNDERSTANDING - 8.8

1. Give mechanism involved in the following reactions.

(*a*)  + $AlCl_3$ ⟶

(*b*)  + $AlCl_3$ ⟶

8.3.5 Reduction

Most alkyl halides may be reduced either *via* the Grignard reagent or directly with metal (usually zinc) and acid or with $LiAlH_4$ to produce an alkane.

(*a*) $R—X + Mg \longrightarrow R—MgX \xrightarrow{H_2O\,(D_2O)} RH\ (or\ RD)$

(*b*) $R—X + Zn + HX \longrightarrow R—H + ZnX_2$

In these reactions, zinc atoms transfer electrons to the carbon atom of the alkyl halide. Zinc is a good reducing agent because it has two electrons in an orbital far from the nucleus, which are readily donated to an electron acceptor.

(*c*) $R—X \xrightarrow{LiAlH_4} R—H$

Example 1 :

Arrange the following nucleophiles in order of decreasing nuclephilicity in aqueous solution.

$$OH^-,\ C_6H_5O^-,\ CH_3OH,\ CH_3S^-,\ CH_3COO^-$$

Solution :

Let us divide the nucleophiles into groups.

(i) Nucleophiles with a negatively charged atom, viz. S and O.

(ii) Neutral nucleophiles.

We know that in the polar aqueous solvent, the nucleophile with the negatively charged sulphur is the most nucleophilic because of larger size of sulphur than oxygen. Further, the nucleophile with the neutral (oxygen) atom is the poorest nucleophile. The three nucleophiles lying between them can be arranged on the basis of their conjugate acids.

$$H_2O,\ C_6H_5OH,\ CH_3COOH$$

The three conjugate acids according to their acidic character is

$CH_3COOH > C_6H_5OH > H_2O$ decreasing acidity

$CH_3COO^- < C_6H_5O^- < OH^-$ increasing basicity

Thus the relative nucleophilicity is

$$CH_3S^- > OH^- > C_6H_5O^- > CH_3COO^- > H_2O$$

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Example 2 :

(*S*)-$CH_3CHBrF + CH_3ONa \longrightarrow$ Product

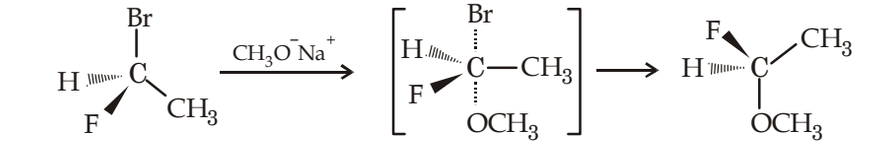
Answer the following, regarding above reaction.

(a) Write down the structure of the product.

(b) Whether the product shows retention or inversion of configuration. Also mention the *R* or *S* designation of the product.

Solution :

(a)



(*S*)-1-Bromo-1-fluoroethane

S

Priority order : Br, F, C and H

F, O, C, H

Here Br^- ion is replaced because it is too weak base to be considered as basic ion, hence it is an excellent leaving group. On the other hand, F^- is the most basic of the halide ions, thus it is a terrible leaving group.

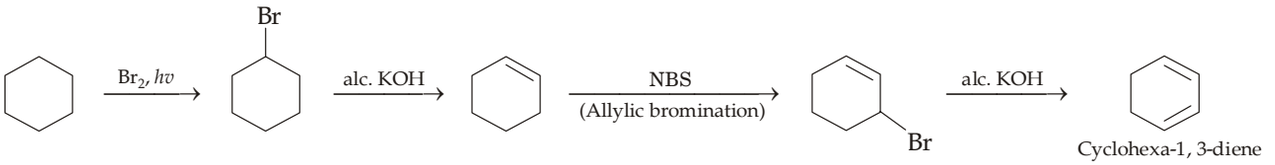
(b) Since the reactant is a 1° alkyl halide, it undergoes S_N2 reaction involving inversion in configuration.

According to *R*, *S*-designation the product is *S*. It is due to change in priority orders of the groups attached on C. Thus there is a change in priority order of F and also there is inversion in configuration with the result the product belongs to *S* series. In case, there were no inversion in configuration, the product would have been *R* instead of *S*.

Example 3 :

Give steps involved in the conversion of cyclohexane to cyclohexa-1, 3-diene.

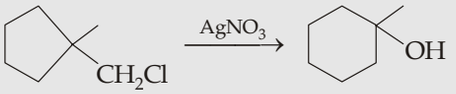
Solution :



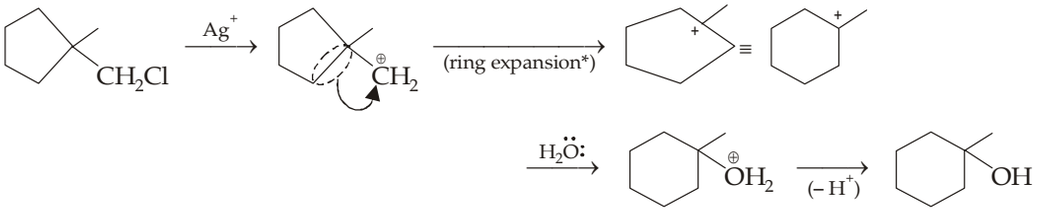
Cyclohexa-1, 3-diene

Example 4 :

Suggest the mechanism for the reaction.



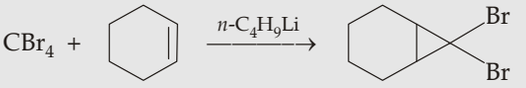
Solution :



* Change in ring size is favourable when a relief in ring strain occurs.

Example 5 :

Give steps involved in the following reaction and give IUPAC name of the product.



Solution :

$$CBr_4 + n\text{-}C_4H_9Li \xrightarrow{\text{halogen-metal exchange}} n\text{-}C_4H_9Br + LiCBr_3$$

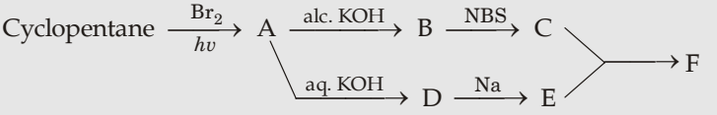
$$LiCBr_3 \longrightarrow LiBr + \underset{\text{Dibromocarbene}}{:CBr_2}$$



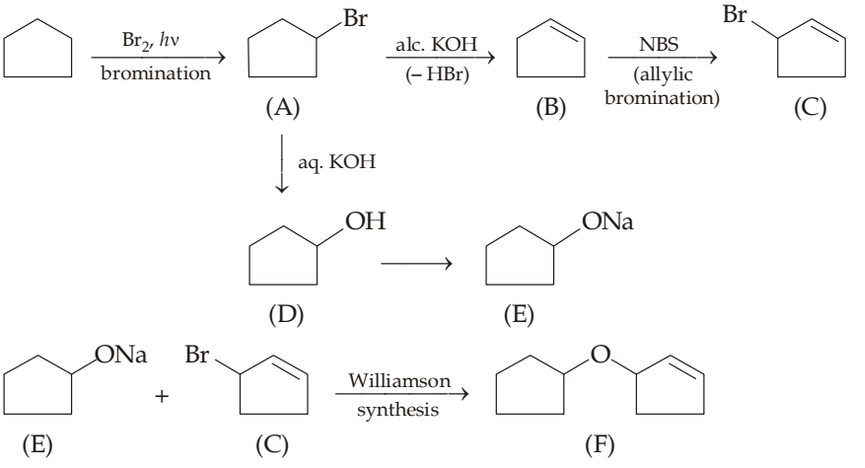
7, 7-Dibromo
[4.1.0]–bicycloheptane

Example 6 :

Identify (A) to (F) in the following series of reactions.



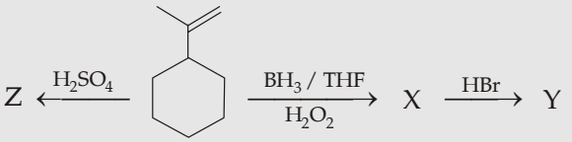
Solution :



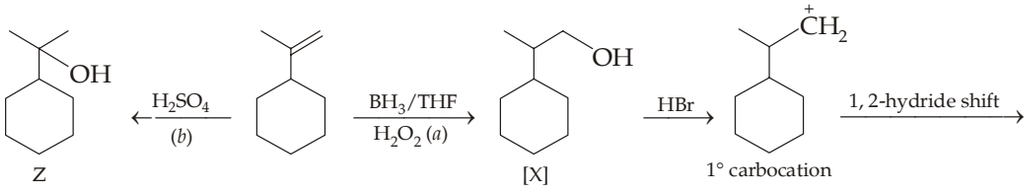
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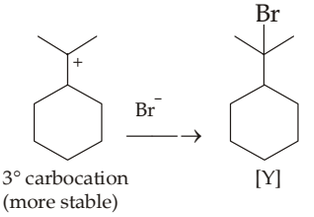
Example 7 :

Identify X to Z in the following series of reactions.



Solution :





Explanation

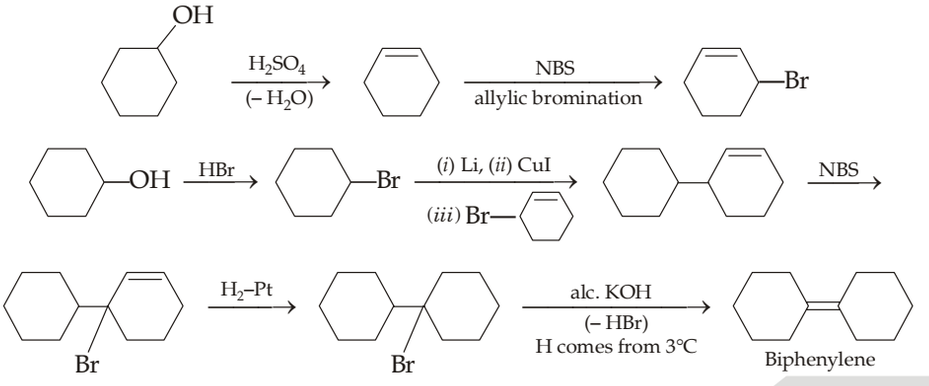
(*a*) It is an example of hydroboration (recall that hydroboration takes place in *anti*-Markovnikov's rule).

(*b*) It is an example of hydration (Markovnikov's addition).

Example 8 :

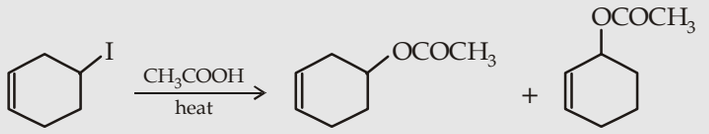
Convert cyclohexanol to biphenylene.

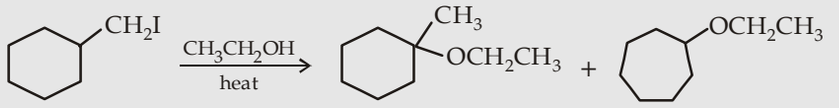
Solution :



Example 9 :

Explain the formation of all products in the following solvolysis reactions.

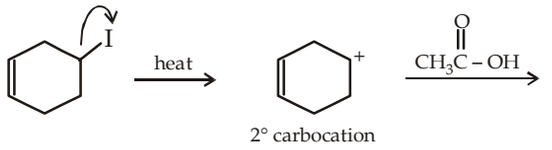
(a) 

(b) 

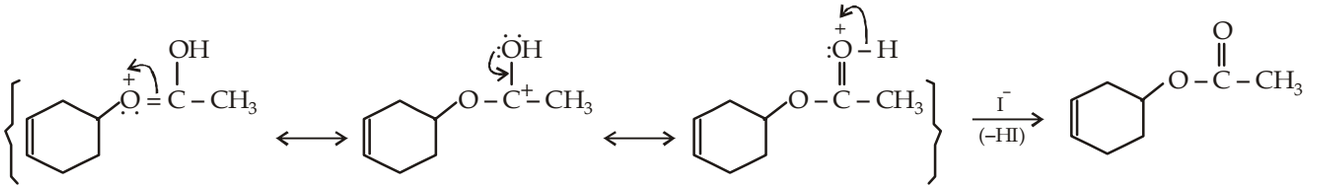
Solution :

Alkyl halides in presence of polar solvents lose halide ions forming carbocations which then react with the nucleophile in its original (provided it is quite stable) form as well as in the rearranged form.

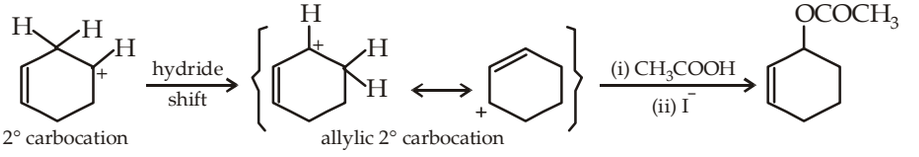
(a) Nucleophilic attack on unrearranged carbocation :



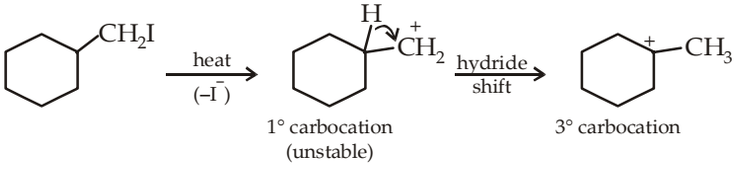
Note : The doubly-bonded oxygen of acetic acid is more nucleophilic because the product so formed is resonance-stabilized.

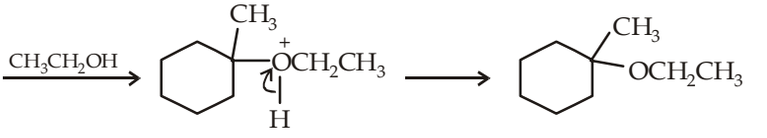


Nucleophilic attack on rearranged carbocation :

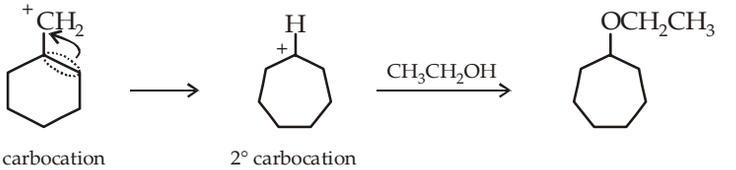


(b) Nucleophilic attack on rearranged 3° carbocation :





Nucleophilic attack on carbocation obtained by ring expansion :



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Example 10 :

A solution of pure (*R*)-2-iodobutane, [α] = –15.9° in acetone is treated with radioactive iodide, until 1.0% of the iodobutane contains radioactive iodine. The specific rotation of the recovered iodobutane is found to be –15.58°.

(a) Determine the percentage of (*S*)- and (*R*)-2-iodobutane in the product mixture.

(b) What inference you get about the mechanism of the reaction?

Solution :

(a) Optical purity = $\frac{-15.58}{-15.90} \times 100\% = 98\%$

Thus the product contains 98% of the (*R*)-enantiomer and 2% of racemic mixture, or 99% *R* and 1% *S*.

(b) The 1% of radioactive has produced exactly 1% of the *S* enantiomer. Each substitution must occur with inversion indicating S_N2 mechanism.

Example 11 :

Explain the following observations :

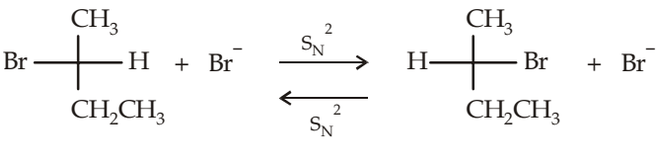
(a) $(R)\text{-}2\text{-Bromobutane} \xrightarrow{KBr(aq.)} (R,S)\text{-}2\text{-Bromobutane}$

(b) $(R)-2-\text{Butanol} \xrightarrow{KOH(aq.)} \text{No reaction}$

(c) $(R)\text{-}2\text{-Butanol} \xrightarrow{\text{dil. acid}} (R,S)\text{-}2\text{-Butanol}$

Solution :

(a)



(*R*)-2-Bromobutane (*S*)-2-Bromobutane

(b) OH^- being a poor leaving group can't be replaced by other nucleophile, e.g. OH^- in the present case.

(c) This is an S_N1 reaction (weaks nucleophile H_2O, ionizing solvent) and involves the formation of carbocation which leads to racemization.

Example 12 :

Observe the following two reactions and explain the difference in the rate of reaction mentioned.

(a) $CH_3\overset{\overset{Br}{|}}{C}HCH_3 \xrightarrow[\text{alcohol}]{KOH} CH_2=CHCH_3$ **much faster than** $D_3C-\overset{\overset{Br}{|}}{C}H-CD_3 \xrightarrow[\text{alcohol}]{KOH} D_2C=CH-CD_3$

(b) $CH_3\overset{\overset{Br}{|}}{C}HCH_3 \xrightarrow[\text{heat}]{H_2O/\text{acetone}} CH_2=CHCH_3$ **equal to** $D_3C\overset{\overset{Br}{|}}{C}HCD_3 \xrightarrow[\text{heat}]{H_2O/\text{acetone}} D_2C=CHCD_3$

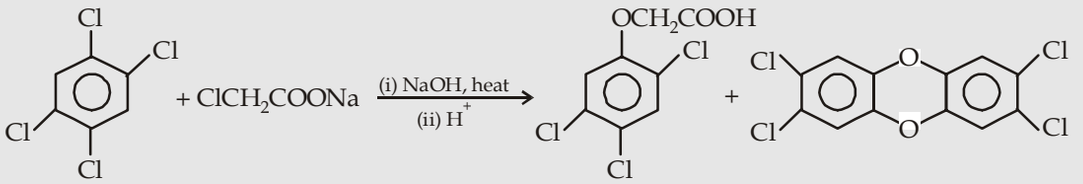
Solution :

(a) Here the elimination follows E2 mechanism (OH^- is a strong base) which is one step (which is also rate determining) i.e. the attack of base (OH^-) and the elimination of H or D take place simultaneously. Now since the C – D bond is slightly stronger than the C – H bond, reaction involving removal of H will be faster than that which involves removal of D.

(b) Here the elimination follows E1 mechanism (strong base is absent, heat removes Br) which involves two steps, the rate-determining step is the removal of Br as Br^-. Elimination of H or D occurs in the second (fast) step, hence it is quite immaterial whether H or D is eliminated. Hence the reaction rate will be same in both reactions.

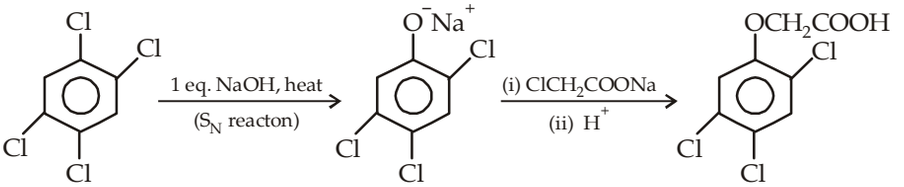
Example 13 :

Give steps involved in the following conversion :

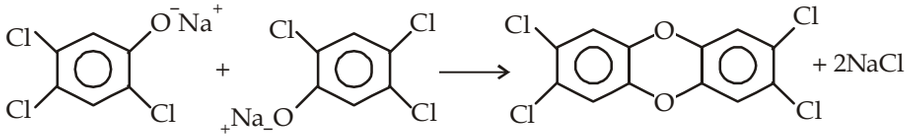


Solution :

Formation of A :



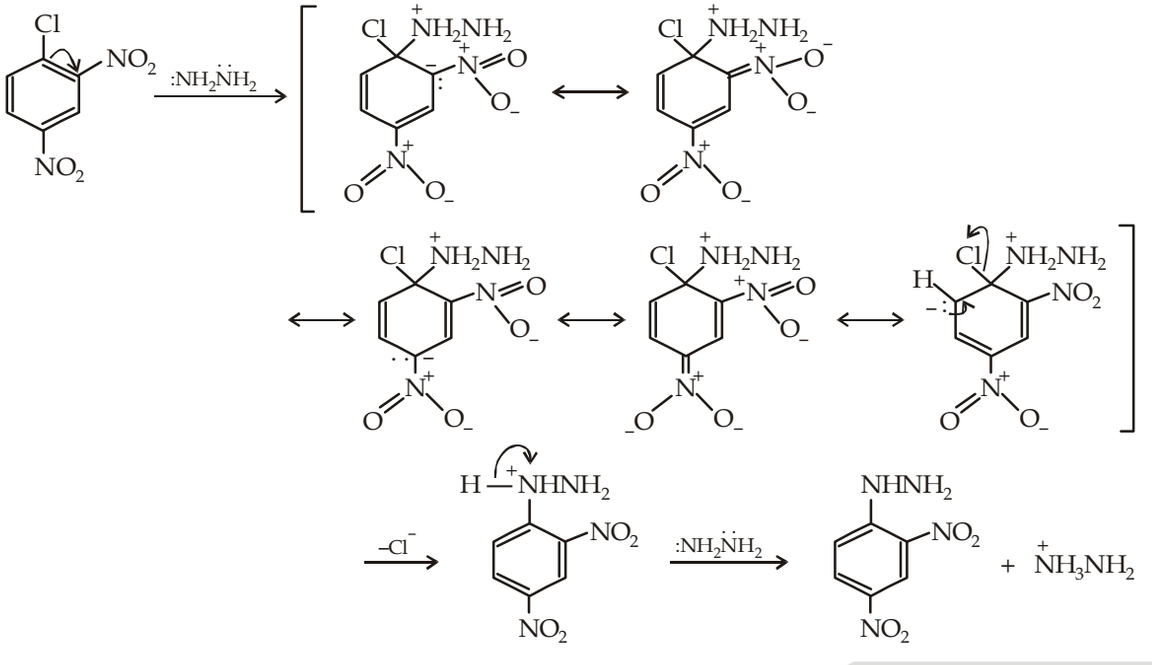
Formation of B :

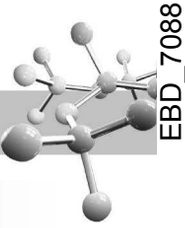


Example 14 :

Propose mechanism and give the product formed when 2,4-dinitrochlorobenzene is treated with excess of hydrazine. Draw all possible reasonating structures of the intermediate carbanion.

Solution :





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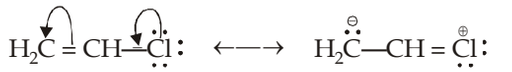
8.4 Halogen Derivatives of Unsaturated Hydrocarbons

These are mainly of two types.

(*i*) Those unsaturated compounds in which halogen is attached to the sp^2 hybridised carbon atom, *e.g.*

$H_2C = CHCl$ (Vinyl chloride) $\qquad CH_3C(Br) = CH_2$ (2-Bromopropene)

In this type of compounds, halogen atom is present on the doubly bonded carbon atom. Since such compounds can show resonance which impart C—Cl bond a partial double bond character due to which it becomes short and hence strong.



Thus such compounds do not undergo nucleophilic substitution and hence do not give precipitate on treatment with alcoholic silver nitrate (similarity with halogenobenzenes ArX).

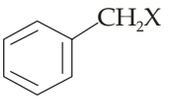
(*ii*) Those unsaturated compounds in which halogen atom is present on the sp^3 hybridised carbon atom, *e.g.*

$H_2C = CH—CH_2—Cl$ (Allyl chloride, 3–Chloropropene) $\qquad CH_3CH = CHCH_2—I$ (Crotyl iodide, 1–Iodobutene–2)

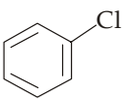
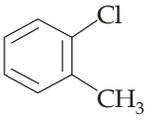
In this type of compounds, halogen atom and double bond are separated by $—CH_2—$grouping discarding the possibility of resonance. Hence such compounds behave like alkyl halides, *i.e.* they undergo nucleophilic substitution and hence give precipitate with alcoholic silver nitrate solution.

Thus halogen compounds are of two types.

(*a*) Those which give precipitate with alcoholic $AgNO_3$ solution.

$CH_3—CH_2—X$ $\qquad CH_2 = CH_2—CH_2—X$ 

(*b*) Those which do not give precipitate with alcoholic $AgNO_3$ solution.

$CH_2 = CH—X$  

8.4.1 Vinyl Halides

Among vinyl halides, vinyl chloride is the most important. It can be prepared by the following methods.

(*i*) $HC \equiv CH + HCl \longrightarrow CH_2 = CHCl$

(*ii*) $CH_2ClCH_2Cl \xrightarrow{OH^-/C_2H_5OH} CH_2 = CHCl \xleftarrow{OH^-/C_2H_5OH} CH_3CHCl_2$

As mentioned above, halogen atom of vinyl chloride is inert to nucleophilic substitution.

However, like alkyl halides, vinyl chloride undergoes elimination reaction and also form Grignard reagent.

$$CH_2 = CHCl \xrightarrow{\text{alc. KOH}} \underset{\text{Acetylene}}{CH \equiv CH}$$

$$CH_2 = CHCl + Mg \xrightarrow[\text{instead of ether}]{\text{THF as solvent}} \underset{\text{Vinylmagnesium chloride}}{CH_2 = CHMgCl}$$

Further, like alkenes it undergoes the usual addition reactions such as addition of hydrogen, halogens acids, etc. and polymerisation.

$CH_2 = CHCl + HBr \longrightarrow CH_3CHBrCl$ **(Markownikoff's product)**

$$CH_2 = CHCl + HBr \xrightarrow{\text{peroxide}} \underset{\text{1-Bromo-2-Chloroethane}}{CH_2Br—CH_2Cl} \quad \textbf{(}\textit{anti}\textbf{-Markownikoff product)}$$

$$n CH_2 = CHCl \xrightarrow[\text{(polymerisation)}]{\text{benzoyl peroxide}} —(—CH_2—\underset{|}{\overset{Cl}{CH}}—CH_2—\underset{|}{\overset{Cl}{CH}}—)_n—$$

Polyvinyl chloride (PVC)

Polyvinyl chloride is a plastic of great importance.

8.4.2 Allyl Halides

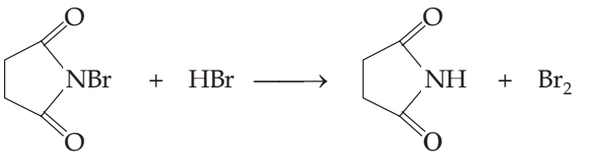
Allyl chloride can best be prepared by allylic chlorination of propene with chlorine at about 400°C.

$$Cl—Cl \xrightarrow{400°C} \dot{Cl}$$

$$\dot{Cl} + H—CH_2—CH = CH_2 \xrightarrow[(-HCl)]{} [\dot{C}H_2—CH = CH_2 \longleftrightarrow CH_2 = CH—\dot{C}H_2] \xrightarrow{Cl_2} \underset{\text{Allyl chloride}}{CH_2 = CH—CH_2Cl} + \dot{Cl}$$

Allyl free radical

Allyl bromide is best prepared by allylic bromination using N-bromosuccinimide (NBS) in presence of sunlight. NBS functions as a bromine reservoir maintaining a low concentration of molecular bromine by reacting with HBr formed initially as a side product.



NBS Succinimide

$$Br_2 \xrightarrow{h\nu} 2\dot{Br}$$

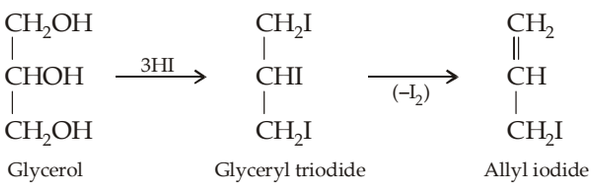
Further steps are similar as described above.

Allyl iodide can be prepared by following methods.

(*i*) By heating allyl chloride with sodium iodide in acetone.

$$CH_2 = CHCH_2Cl + NaI \xrightarrow[\text{(Finkelstein reaction)}]{\text{acetone}} CH_2 = CHCH_2I + NaCl$$

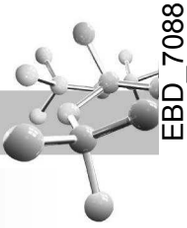
(*ii*) By heating glycerol with hydrioidc acid or white phosphorus and iodine.



Glycerol Glyceryl triodide Allyl iodide

Allyl halides give the addition reactions of the double bond and also nucleophilic substitution reactions of alkyl halides. Remember that allyl halides undergo nucleophilic substitutions much faster than the alkyl halides because of resonance stabilisation of the allyl cation.

$$CH_2 = CH—\overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2—CH = CH_2$$

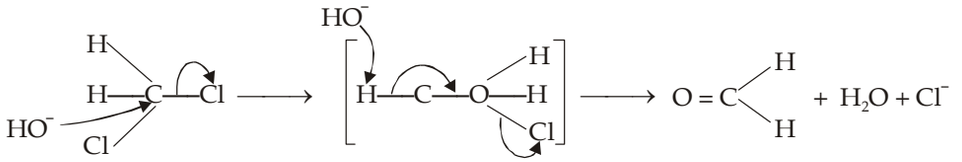


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8.5 Polyhalogen Compounds

The three polyhalogen compounds of methane are methylene chloride, chloroform and carbon tetrachloride.

Methylene chloride (CH_2Cl_2) is formed by controlled free-radical chlorination of methane. It is a colourless non-polar liquid and undergoes typical S_N2 displacement when treated with sodium hydroxide.



Methylene chloride Chloromethanol Formaldehyde

Remember that the hydrolysis of methylene chloride is slower than that of methyl chloride. Low reactivity of methylene chloride is believed to be due to the presence of two chlorine atoms having unshared pairs of electrons which tend to repel the negatively charged nucleophile.

Higher alkanes can form two or more isomeric dihalogen derivatives, differing in relative positions of the two halogen atoms, of which three are more important.

$CH_3CH_2CH_2CHCl_2$ and $CH_3CH_2C(Cl_2)CH_3$

1, 1-Dichlorobutane 2, 2-Dichlorobutane

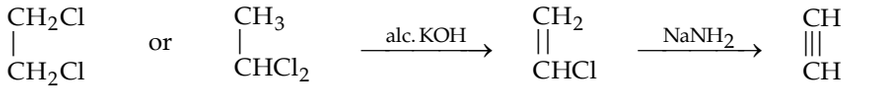
(*gem*-Dihalides *or* Alkylidene halides)

$CH_3CH_2CH(Cl)\,CH_2Cl$ and $CH_3CH(Cl)\,CH(Cl)CH_3$ $ClCH_2CH_2CH_2CH_2Cl$

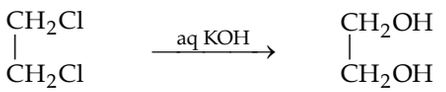
1, 2-Dichlorobutane 2, 3-Dichlorobutane 1, 4-Dichlorobutane

(*vic*-Dihalides *or* Alkylene halides) (α, ω*-Dihalides or Polymethylene dihalides)

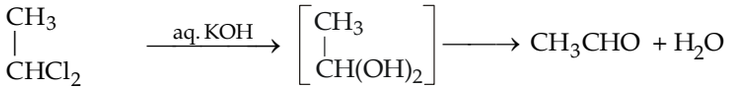
Vicinal and ***gem*-dihalides** resemble in their reaction with alcoholic KOH, but differ in reaction towards *aq*. KOH and reaction with KCN followed by hydrolysis.

(*i*) 

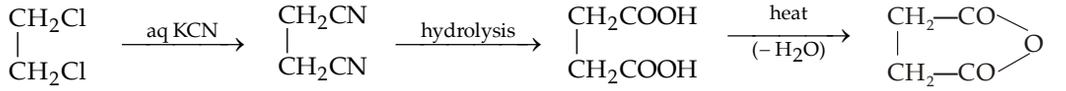
Ethylene chloride Ehtylidene chloride Vinyl chloride Acetylene

(*ii*) 

Ethylene chloride Ethylene glycol



Ethylidene chloride Ethanal

(*iii*) 

Ethylene chloride Succinic acid Succinic anhydride

* Symbol *ω* represents the end carbon atom.

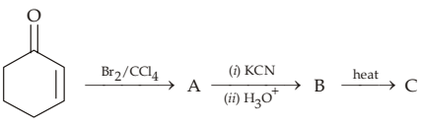
$$\underset{\text{Ethylidene chloride}}{\overset{CH_3}{\underset{CHCl_2}{|}}} \xrightarrow{\text{aq. KCN}} \overset{CH_3}{\underset{CH(CN)_2}{|}} \xrightarrow{\text{hydrolysis}} \overset{CH_3}{\underset{CH(CN)_2}{|}} \xrightarrow[(-CO_2)]{\text{heat}} \underset{\text{Propanoic acid}}{\overset{CH_3}{\underset{CH_2COOH}{|}}}$$

Methylmalonic acid

Remember that on heating, dicarboxylic acids having two —COOH groups on the same carbon atom give monocarboxylic acids, while dicarboxylic acids having —COOH groups on C_1 and C_2 or on C_1 and C_3 give anhydrides on similar treatment **(Blanc rule).**

TEST YOUR UNDERSTANDING - 8.9

1. Draw the structures of the various isomers of dibromoderivatives, and give their reaction with zinc dust and methanol.
2. Identify A to C with proper explanation, where necessary.



3. Identify X, Y and Z in the following series of reactions

$$\underset{(C_4H_8Cl_2)}{X} \xrightarrow{NaOH} Y \xrightarrow[Cl_2]{NaOH} CHCl_3 + Z$$

Write down structures of all structural isomers of X.

8.5. 1. Chloroform or Trichloromethane, $CHCl_3$

It is the most important trihalogen derivative of alkanes and can be prepared by the following methods.

1. $CH_4 + 3Cl_2 \xrightarrow[\text{(controlled chlorination)}]{\text{Sunlight}} CHCl_3 + HCl$

2. In laboratory and commercial scale, it is prepared by the distillation of ethanol or acetone with a paste of bleaching powder in water. This reaction is an example of haloform reaction; bleaching powder supplies the necessary chlorine and slaked lime (alkali) for the reaction.

$$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

Other steps involved in the reaction can be summarised below.

(a) $\underset{\text{Ethanol}}{CH_3CH_2OH} + Cl_2 \xrightarrow{\text{oxidation}} \underset{\text{Ethanal}}{CH_3CHO} + 2HCl$

$$\underset{\text{Ethanal}}{CH_3CHO} + 3Cl_2 \longrightarrow \underset{\text{Chloral}}{CCl_3CHO} + 3HCl$$

$$2CCl_3CHO + Ca(OH)_2 \longrightarrow \underset{\text{Chloroform}}{2CHCl_3} + \underset{\text{Cal. formate}}{(HCOO)_2Ca}$$

(b) $\underset{\text{Acetone}}{CH_3COCH_3} + 3Cl_2 \longrightarrow \underset{\text{Trichloroacetone}}{CCl_3COCH_3} + 3HCl$

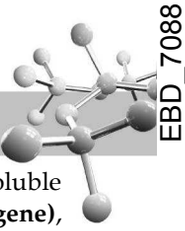
$$2CCl_3CO.CH_3 + Ca(OH)_2 \longrightarrow 2CHCl_3 + (CH_3COO)_2Ca$$

3. In industry, chloroform is also prepared by the reduction of carbon tetrachloride.

$$CCl_4 + 2[H] \xrightarrow{Fe/steam} CHCl_3 + HCl$$

4. Pure chloroform is prepared by treating pure chloral hydrate (or chloral) with sodium hydroxide.

$$CCl_3.CH(OH)_2 + 2NaOH \longrightarrow CHCl_3 + HCOONa + H_2O$$



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Properties : Chloroform is a colourless, heavy, sweet-smelling liquid (hence collected with water as lower layer), insoluble in water but soluble in alcohol and ether. When exposed to air and sunlight, it oxidises to **carbonyl chloride (phosgene)**, a highly poisonous substance, used in warfare.

$$2CHCl_3 + O_2 \longrightarrow 2COCl_2 + 2HCl$$

To avoid its oxidation, chloroform is always stored in amber coloured bottles to cut off light. Moreover, bottles are filled to the neck and well stoppered to exclude air.

Caution

Thus when chloroform is used as anaesthetic it must be tested for the presence of poisonous phosgene, for which it is treated with aqueous $AgNO_3$ solution—appearance of white precipitate of AgCl ($HCl + AgNO_3 \longrightarrow AgCl$) indicates that some chloroform has decomposed to $COCl_2$ and HCl and hence it is contaminated with the poisonous phosgene.

Further, a small amount of alcohol (~ 1%) is added to chloroform bottle which converts the toxic phosgene, if formed, to harmless diethyl carbonate.

$$2C_2H_5OH + \underset{\text{Phosgene}}{Cl_2C=O} \longrightarrow \underset{\text{Diethyl carbonate}}{(C_2H_5O)_2C=O} + 2HCl$$

Other important reactions of chloroform can be summed up as below.

(*i*) **Reduction.** Different products are formed by different reducing agents, *e.g.* reduction with Zn and HCl, Zn and alcoholic KOH and Zn and water gives methylene chloride, methyl chloride and methane respectively.

(*ii*) **Chlorination.** $CHCl_3 + Cl_2\,(gas) \xrightarrow[\text{sunlight}]{\text{diffused}} CCl_4 + HCl$

(*iii*) **Nitration.** Chloroform can be nitrated with concentrated nitric acid to form *nitro-chloroform*, commonly known as **chloropicrin** which is a useful insecticide and lachrymatry substance.

$$HCCl_3 + HONO_2 \longrightarrow \underset{\text{Chloropicrin}}{O_2NCCl_3} + H_2O$$

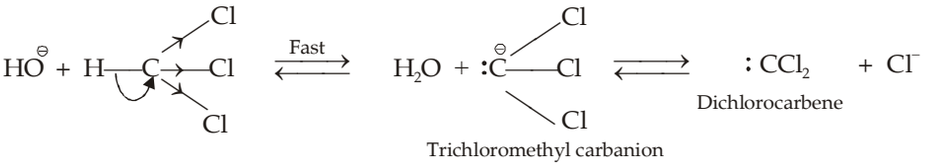
(*iv*) **Dehalogenation.** Chloroform, when heated with silver powder, gives acetylene.

$$HCCl_3 + 6Ag + Cl_3CH \xrightarrow{\text{heat}} HC \equiv CH + 6AgCl$$

(*v*) **Hydrolysis.** On warming with aqueous sodium hydroxide solution, it is hydrolysed to carbon monoxide and sodium formate.

$$CHCl_3 + 4OH^- \longrightarrow 3Cl^- + HCOO^- + 2H_2O$$
$$CHCl_3 + 3OH^- \longrightarrow 3Cl^- + CO + 2H_2O$$

Mechanism of alkaline hydrolyses of chlorform is different from that of other alkyl halides particularly methylene chloride. Due to the presence of three strong electron-withdrawing chlorine atoms, hydrogen atom of chloroform is highly acidic and hence the base (OH^-) easily abstracts proton from chloroform rather than displacing its one of the chlorine atoms by S_N2 mechanism.



Existence of above steps in the mechanism of alkaline hydrolysis of chloroform gets support from the following observations.

(*a*) Since removal of proton from $CHCl_3$ (having three —Cl atoms) is easier than that from CH_2Cl_2 (having two —Cl atoms), while CCl_4 has no proton for elimination, **$CHCl_3$ undergoes alkaline hydrolysis much more rapidly than CH_2Cl_2 and CCl_4.**

(*b*) When chloroform is hydrolysed in presence of D_2O and the reaction is stopped before completion, the unreacted chloroform is found to contain deuterium. This indicates that the removal of proton takes place in a fast and reversible step.

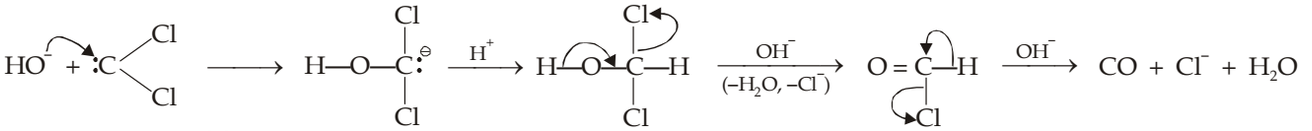
$$HO^- + H—CCl_3 \rightleftharpoons :\overset{\ominus}{C}Cl_3 \rightleftharpoons CDCl_3 + {}^-OD$$

(*c*) The rate of reaction is slowed down by the addition of chloride ions. This indicates that step 2 and hence step 1 is reversed by excess of Cl^- and thus confirms that step 2 is a reversible step.

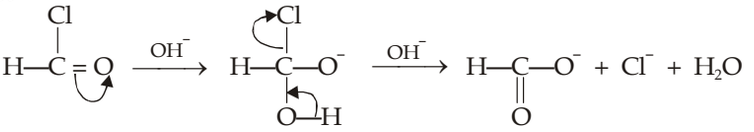
(*d*) When the alkaline hydrolysis of $CHCl_3$ in presence of I^- is interrupted, $CHCl_2I$ is also recovered along with $CHCl_3$ confirming the formation of : CCl_2 and : CCl_3^- as intermediates and reversibility of both the steps. Remember that $CHCl_3$ does not react with I^- ion in the absence of base.

Dichlorocarbene, formed above, undergoes hydrolysis to form carbon monoxide or sodium formate in the following way.

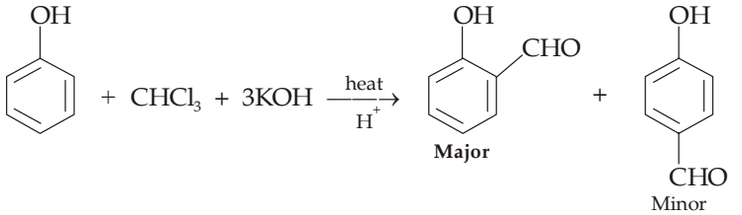
Formation of carbon monoxide



Formation of formate

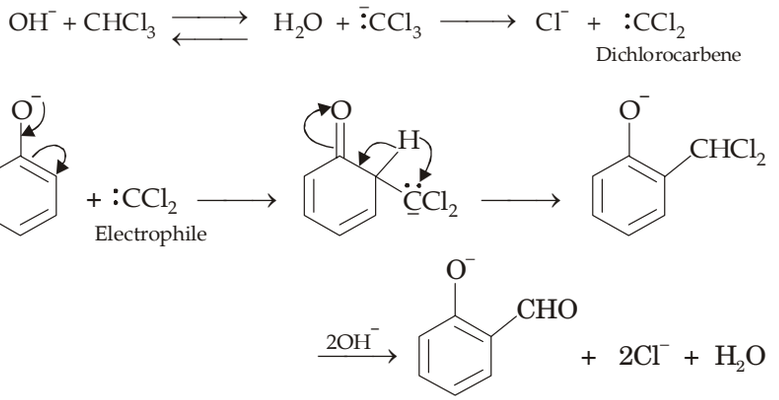


(*vi*) **Reimer-Tiemann reaction.** When alkaline solution of phenol is refluxed with chloroform at 60°C a mixture of *o*-hydroxybenzaldehyde (salicylaldehyde) and *p*-hydroxybenzaldehyde is formed.

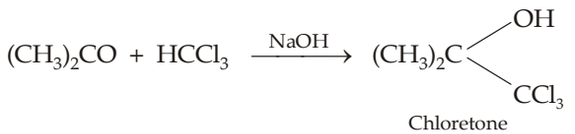


Since the *o*-isomer is only sparingly soluble in water and has low boiling point than the *p*-isomer, the two can be separated by steam distillation very easily.

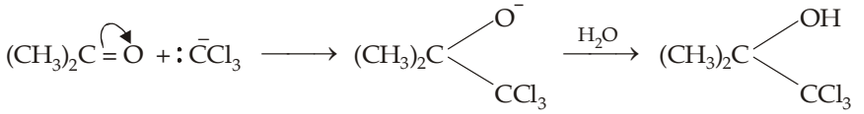
Mechanism of Reimer-Tiemann reaction



(*vii*) **Condensation with ketones.** Chloroform reacts with acetone in alkaline solution to form **chloretone**, used as a *hypnotic (substance used to produce artificial sleep).*



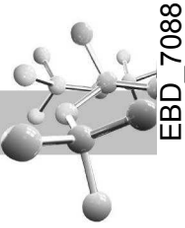
Mechanism



(*viii*) **Action of alcoholic potash and primary amines** (*Carbylamine reaction*) with chloroform forms **isocyanides,** also known as *carbylamines* which are easily detected due to their foul smell.

$RNH_2 + CHCl_3 + 3KOH \longrightarrow RNC + 3KCl + 3H_2O$

This reaction is used for the identification of primary amines.



EBD_7088

Relative reactivity of haloforms

$$CHI_3 > CHBr_3 > CHCl_3 >> CHF_3.$$

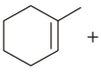
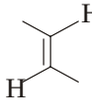
Thus iodoform is very much reactive as compared to chloroform which is evident from the following facts.

(*i*) Iodoform decomposes easily to free iodine, when it comes in contact with organic matter. This explains the antiseptic use of iodoform.

(*ii*) Iodoform gives yellow precipitate of AgI on heating with silver nitrate, while chloroform does not give any precipitate with $AgNO_3$ solution.

TEST YOUR UNDERSTANDING - 8.10

1. Complete the following reactions :

(*i*)  + $CHCl_3$ + $(CH_3)_3COK$ ⟶ (*ii*)  + $CBrCl_3$ ⟶ (*iii*)  + $CHCl_3$ + NaOH ⟶

2. Explain the following :

(*a*) Chloroform undergoes alkaline hydrolysis much more rapidly than CH_2Cl_2 as well as CCl_4.

(*b*) Alkaline hydrolysis of chloroform slows down in presence of sodium chloride.

8.5.2 Carbon Tetrachloride *or* Tetrachloromethane, CCl_4

It is the most common per- halogenated aliphatic compound ; corresponding ethane derivative, C_2Cl_6 is a solid compound known as *artificial camphor*. Carbon tetrachloride can be prepared by the following methods.

1. By the chlorination of chloroform or methane.
2. By chlorinolysis (cleavage by chlorine) of hydrocarbons.

$$CH_3CH_2CH_3 + 9Cl_2 \xrightarrow[74\text{-}100\ atm.]{400°C} CCl_4 + C_2Cl_6 + 8HCl\uparrow$$

3. By the action of chlorine on carbon tetrachloride.

$$CS_2 + 3Cl_2 \xrightarrow[as\ catalyst]{AlCl_3,\ Fe\ or\ SbCl_5} CCl_4 + \underset{\text{Sulphur monochloride}}{S_2Cl_2}$$

Sulphur monochloride is separated by fractional distillation and treated with fresh carbon disulphide to form carbon tetrachloride.

$$CS_2 + 2S_2Cl_2 \longrightarrow CCl_4 + 6S$$

Properties : Carbon tetrachloride is a colourless, non-flammable, poisonous liquid, soluble in ethanol and ether. On heating with steam at about 500°C, it undergoes oxidation to form carbonyl chloride (*phosgene*).

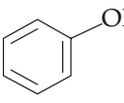
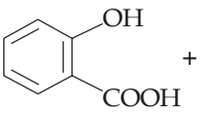
$$CCl_4 + H_2O\ (steam) \xrightarrow{500°C} COCl_2 + 2HCl$$

It reacts with hydrogen fluoride in presence of $SbCl_5$ forming *dichlorodifluoromethane*, commonly known as **freon-12**, a widely used refrigerant and propellant in aerosol sprays.

$$CCl_4 + 2HF \xrightarrow{SbCl_5} CCl_2F_2 + 2HCl$$

$$\text{or} \quad 3CCl_4 + 2SbF_3 \longrightarrow 3CCl_2F_2 + 2SbCl_3$$

Like chloroform, it undergoes **Reimer-Tiemann reaction** to form *o*-hydroxybenzoic acid (*salicylic acid*).

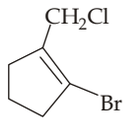
 + CCl_4 + 4NaOH ⟶  + 4NaCl + $2H_2O$

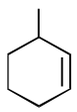
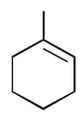
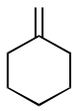
Carbon tetrachloride as a fire extinguisher : Carbon tetrachloride is used as an important fire extinguisher under the name of *pyrene*. It gives dense, incombustible vapours which cover the burning substance and hence does not allow oxygen from reaching the burning substance. However, after the use of pyrene the room should be well ventilated to remove phosgene vapours (a toxic substance), formed by the oxidation of carbon tetrachloride. Other uses of CCl_4 are as anthelmentic, fumigant, solvents, laboratory reagent and in dry cleaning.

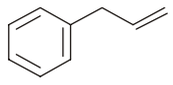
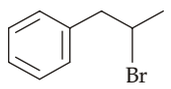
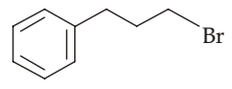
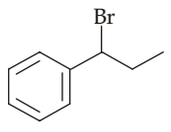
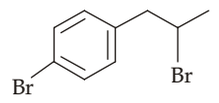
Freons cause destruction to ozone layer in the atmosphere, hence they are being replaced by other referigerants.

EXERCISE 8.1 (MCQ - ONE option correct)

1. Which statement is correct regarding isomers of C_4H_9Cl ?
(*a*) It has three isomers : one 1°, one 2° and one 3° alkyl chloride
(*b*) It has four isomers : two 1°, one 2°, and one 3° alkyl chloride
(*c*) It has four isomers : one 1°, two 2° and one 3° alkyl chloride
(*d*) It has four isomers : two 1° and two 2°.

2.  can be classified as
(*a*) an alkyl halide (*b*) vinyl halide
(*c*) an allyl halide (*d*) all the three.

3. 1-Bromo-1-methylcyclohexane can be obtained by the addition of HBr on
(*a*)  (*b*) 
(*c*)  (*d*) both from (*b*) and (*c*).

4.  + HBr ⟶ X
In the above reaction, X is
(*a*)  (*b*) 
(*c*)  (*d*) 

5. Which alkyl halide can't be prepared by free radical halogenation of alkanes ?
(*a*) CH_3Cl and CH_3F (*b*) $CHCl_3$ and CH_3I
(*c*) CCl_4 and $CHBr_3$ (*d*) CH_3F and CH_3I.

6. Which of the following statement is correct ?
(*a*) The weaker the Bronsted basicity of X^-, the better the leaving group is X^- and the more reactive is RX.
(*b*) The stronger the Bronsted basicity of X^-, the better the leaving group is X^- and the more reactive is RX.
(*c*) The weaker the Bronsted basicity of X^-, the weaker the leaving group is X^-, and the more reactive is RX.
(*d*) The weaker the Bronsted basicity, the weaker the leaving group and the less reactive is RX.

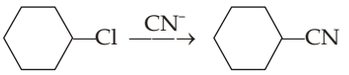
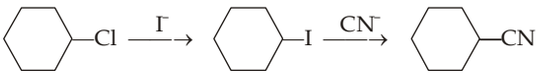
7. The increasing order of basicities of X^- is
(*a*) $I^- < Br^- < Cl^- < F^-$ (*b*) $I^- < Br^- < Cl^- << F^-$
(*c*) $F^- < Cl^- < Br^- < I^-$ (*d*) $F^- < Cl^- < Br^- << I^-$.

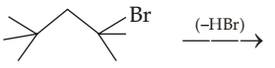
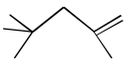
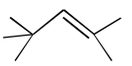
8. Which of the following statement is true ?
(*a*) Increased temperature favours elimination reactions over substitutions
(*b*) Increased temperature favours substitution reactions over eliminations
(*c*) Increased temperature favours both substitution reactions as well as eliminations reactions to the same extent
(*d*) Increased temperature has no effect on the rate of substitution/elimination reactions.

9. Pick up the correct statement regarding following reaction

$$(CH_3)_3CCl \xrightarrow[20\%\ H_2O]{80\%\ C_2H_5OH} X$$

(*a*) Product X is $(CH_3)_3COC_2H_5$ and formed by S_{N^2} reaction
(*b*) Product X is $(CH_3)_3\ COC_2H_5$ and formed by S_{N^1} pathway involving attack of the nucleophile (C_2H_5OH)
(*c*) Product X is $(CH_3)_3COC_2H_5$ and formed by S_{N^1} pathway involving attack of the base (C_2H_5OH)
(*d*) Product X is $(CH_3)_2C = CH_2$ formed by E_2 pathway.

10. Which one of the following method gives good yield for preparing cyclohexanenitrile ?
(*a*) 
(*b*) 
(*c*) Both methods give equally good yield
(*d*) Neither of the two methods can be applied because each has its own drawback.

11. Pick up the major product in the following elimination reaction :

(*a*) 
(*b*) 
(*c*) Both will be formed in equal amounts
(*d*) Third product having rearranged skeleton will be formed.

12. Reaction between phenol and alkaline chloroform to form *o*-hydroxybenzaldehyde is said to be an example of electrophilic substitution. Pick up the electrophile involved in this reaction.
(*a*) HCHO (*b*) $\ddot{:}CCl_3$
(*c*) $:CCl_2^{2-}$ (*d*) $:CCl_2$.

13. Which of the following compounds undergo alkaline hydrolysis most rapidly ?
(*a*) CH_2Cl_2 (*b*) $CHCl_3$
(*c*) CCl_4 (*d*) All at the same rate.

14. Alkaline hydrolysis of chloroform involves the formation of
(*a*) $:CCl_2$ (*b*) HCOCl
(*c*) Both (*a*) and (*b*) (*d*) None of the two.

15. Butanonitrile may be prepared by heating
(*a*) propyl alcohol with KCN
(*b*) butyl alcohol with KCN
(*c*) butyl chloride with KCN
(*d*) propyl chloride with KCN.

16. Identify the main product in the reaction

$$SnCl_4 + C_2H_5Cl + Na \longrightarrow$$

(*a*) $C_2H_5C_2H_5$ (*b*) C_2H_5Na
(*c*) $(C_2H_5)_2Sn$ (*d*) $(C_2H_5)_4Sn$.

17. Vinyl chloride on treatment with dimethyl copper gives

(*a*) $CH_2 = CHCH_3$ (*b*) $CH_2 = CHCu$
(*c*) $CH_2 = CHCH = CH_2$ (*d*) $(CH_2 = CH)_2\,Cu$.

18. Which of the following will react with water ?

(*a*) $CHCl_3$ (*b*) CCl_3CHO
(*c*) CCl_4 (*d*) $ClCH_2CH_2Cl$.

19. Ethylene chloride and ethylidene chloride are isomeric compounds. Identify the statement which is not common to both of them

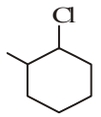
(a) Both of them are derivatives of ethane
(b) Both of them react with aqueous potash and give the same product
(c) Both of them react with alcoholic potash and give the same product
(d) Both of them respond Beilstein's test

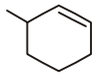
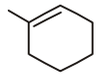
20. CH_3CHCl_2 and $CH_2Cl.CH_2Cl$ show which type of isomerism

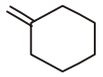
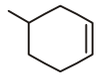
(a) Functional (b) Chain
(c) Position (d) Metamerism

21. Which of the following give white precipitate of silver chloride when boiled with alcoholic silver nitrate?

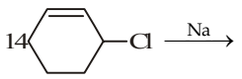
(a) Methyl chloride (b) Carbon tetrachloride
(c) Benzyl chloride (d) Vinyl chloride

22  $\xrightarrow[\text{(ii) AgOH, }\Delta]{\text{(i) } Me_3N}$ major product is

(a)  (b) 

(c)  (d) 

23. How many products having 12 carbon are obtained in following reaction ?



(a) 3 (b) 4
(c) 10 (d) 12

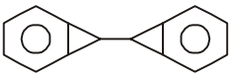
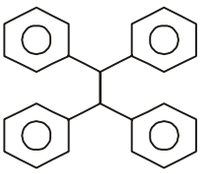
24. A compound 'A' of formula $C_3H_6Cl_2$ on reaction with alkali can give 'B' of formula C_3H_6O or 'C' of formula C_3H_4. 'B' on oxidation a compound of the foumula $C_3H_6O_2$. 'C' with dilute H_2SO_4 containing Hg^{2+} ion gave 'D' of formula C_3H_6O, which with bromine and alkali gave the sodium salt of $C_2H_4O_2$. Then 'A' is

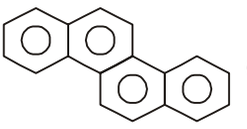
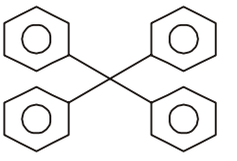
(a) $CH_3CH_2CHCl_2$ (b) $CH_3CCl_2CH_3$
(c) $CH_3ClCH_2CH_2Cl_2$ (d) $CH_3CHClCH_2Cl$

25. Identify the product (Y) in the following reaction.

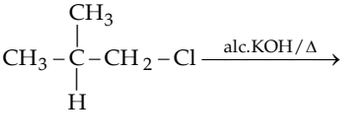
(i) $H-C\equiv C-H \xrightarrow{2Br_2/CCl_4} (X)$

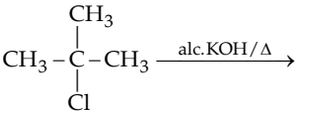
(ii)  $+ (X) \xrightarrow{AlBr_3} (Y) + 4HBr$

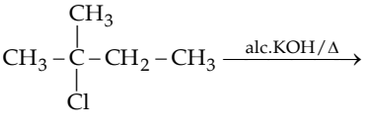
(a)  (b) 

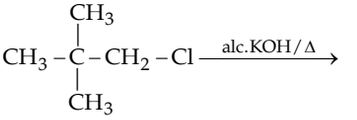
(c)  (d) 

26. In which of the following reaction, regioselectivity can be observed.

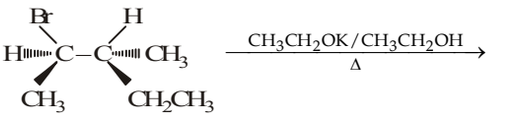
(a) 

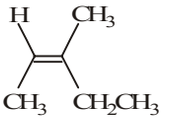
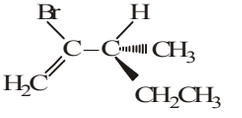
(b) 

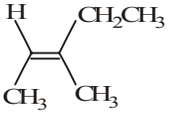
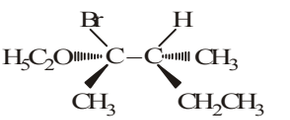
(c) 

(d) 

27. Select the formula representing the major product of the following reaction.



(a)  (b) 

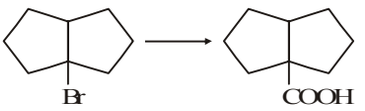
(c)  (d) 

28. Compare the two methods shown for the preparation of carboxylic acids :

Method -1 : $R-Br \xrightarrow[Et_2O]{Mg} R-MgBr \xrightarrow[(ii)\ H_3O^+]{(i)\ CO_2} RCO_2H$

Method - 2 : $R-Br \xrightarrow{NaCN} R-CN \xrightarrow[\Delta]{(i)\ H^+/H_2O} RCO_2H$

Which of the following statement correctly describes this conversion



(a) Both method 1 and method 2 are appropriate, for carrying out this conversion.
(b) Neither method 1 nor method 2 are appropriate for carrying out this conversion.
(c) Method 1 will work well, but method 2 is not appropriate.
(d) Method 2 will work well, but method 1 is not appropriate.

29. Isobutyl magnesium bromide with dry ether and ethyl alcohol gives :

(a) $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2OH$ & CH_3CH_2MgBr

(b) $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$ & $MgBr(OC_2H_5)$

(c) $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}H=CH_2$ & $Mg(OH)Br$

(d) $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$ & CH_3CH_2OMgBr

30. During debromination of *meso*-2,3-dibromobutane, the major compound formed is

(a) *n*-butane (b) 1-butene
(c) *cis*-2-butene (d) *trans*-2-butene

31. $(CH_3)_3CMgCl$ on reaction with D_2O produces :

(a) $(CH_3)_3$ CD (b) $(CH_3)_3COD$
(c) $(CD_3)_3CD$ (d) $(CD_3)_3COD$

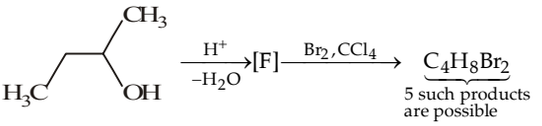
32. A solution of (+) –2–chloro–2–phenylethane in toluene racemises slowly in the presence of small amount of $SbCl_5$, due to the formation of

(a) carbanion (b) carbene
(c) free-radical (d) carbocation

33. Identify the set of reagent / reaction conditions 'X' and 'Y' in the following set of transformations

$$CH_3-CH_2-CH_2Br \xrightarrow{X} Product \xrightarrow{Y} CH_3-\underset{\displaystyle Br}{\underset{|}{C}}H-CH_3$$

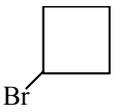
(a) X = dilute aqueous NaOH, 20°C;
Y = HBr/acetic acid, 20°C
(b) X = concentrated alcoholic NaOH, 80°C;
Y = HBr/acetic acid, 20°C
(c) X = dilute aqueous NaOH, 20°C ; Y = $Br_2/CHCl_3$, 0°C
(d) X = concentrated alcoholic NaOH, 80°C;
Y = $Br_2/CHCl_3$, 0°C

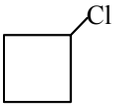
34. 

. How many structures for F are possible?

(a) 2 (b) 5
(c) 6 (d) 3

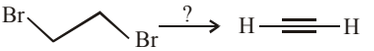
35. What would be the product formed when 1-bromo-3-chlorocyclobutane reacts with two equivalents of metallic sodium in ether?

(a) 

(b) 

(c) 
(d) 

36. The reagent(s) for the following conversion,



is/are

(a) alcoholic KOH
(b) alcoholic KOH followed by $NaNH_2$
(c) aqueous KOH followed by $NaNH_2$
(d) Zn/CH_3OH

37. In $CH_3CH_2CH_2I$, the C–I bond is formed by the overlapping of

(a) $2sp^3 - 2p_z$ orbitals (b) $2sp^3 - 3p_z$ orbitals
(c) $2sp^3 - 4p_z$ orbitals (d) $2sp^3 - 5p_z$ orbitals

38. Although hexafluoroethane (C_2F_6, b.p. –79°C) and ethane (C_2H_6, b.p. – 89°C) differ very much in their molecular weights, their boiling points differ only by 10°C. This is due to

(a) low polarizability of F
(b) nearly similar size of F and H
(c) both (a) and (b)
(d) Neither of the two

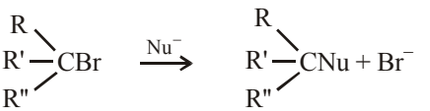
39. Which of the following is not possible ?

(a) $ICH_2COOH + NaCl \xrightarrow{acetone} ClCH_2COOH + NaI$

(b) $ClCH_2COOH + NaI \xrightarrow{acetone} ICH_2COOH + NaCl$

(c) Both
(d) None

40. Which of the statement(s) is/are true, regarding following reaction?



(i) The reaction involves the formation of transition state.
(ii) Higher the nucleophilic character of the nucleophile, faster will be the reaction.
(iii) The product is always optically inactive.

(a) (ii) (b) (ii) and (iii)
(c) All the three (d) None of the three

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41. Predict the major products, P_1 and P_2 in the following two reactions

(i) $Me_2CHBr \xrightarrow{CH_3COO^-} P_1$

(ii) $CH_3(CH_2)_{15}CH_2CH_2Br \xrightarrow{(CH_3)_3CO^-} P_2$

(a) P_1 is $Me_2CHOCOCH_3$, P_2 is $CH_3(CH_2)_{15}CH_2CH_2OCMe_3$
(b) P_1 is $Me_2CHOCOCH_3$, P_2 is $CH_3(CH_2)_{15}CH = CH_2$
(c) P_1 is $CH_3\,CH = CH_2$, P_2 is $CH_3(CH_2)_{15}CH_2CH_2OCMe_3$
(d) P_1 is $CH_3\,CH = CH_2$, P_2 is $CH_3(CH_2)_{15}CH = CH_2$

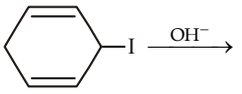
42. Nucleophilic substitution and elimination reactions of alkyl halides oftenly compete each other, elimination reactions are favoured under which conditon.
(a) By carrying out the reaction at high temperature
(b) By using sterically hindered nucleophile
(c) By using strong but slightly polarizable base
(d) All the above three

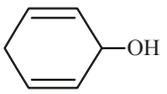
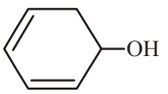
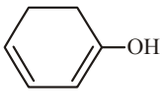
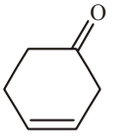
43. Which of the following alkyl halide undergoes E2 mechanism most easily ?

(a) $Me_2CH\,CH(Br)CH_3$ (b) $Me_3C\,CH_2Br$

(c) $Me_3C\,CH_2CH_2Br$ (d) $Me_3C\,\underset{|}{\overset{CMe_3}{C}}HCH_2Br$

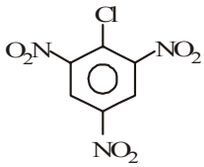
44. Which of the following is major product in the following reaction ?



(a) 
(b) 
(c) 
(d) 

45. Which of the following gives white precipitate when treated with silver nitrate solution ?

(a) $CHCl_3$ (b) $CH_2 = CHCH_2Cl$

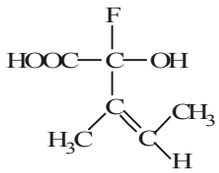
(c) $C_6H_5CH_2Cl$ (d) 

46. The number of stereoisomers obtained by bromination of *trans*-2-butene is
(a) 1 (b) 2
(c) 3 (d) 4

47. How many stereoisomers does this molecule have $CH_3CH = CHCH_2CHBrCH_3$?
(a) 6 (b) 12
(c) 16 (d) 4

48. How many numbers of possible stereoisomers are there for 2, 3, 4-trichloropentonic acid ?
(a) 8 (b) 12
(c) 16 (d) 4

49. The configuration of the chiral centre and the geometry of the double bond in the following molecule can be described by

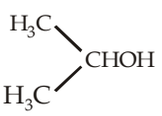


(a) R and E (b) S and E
(c) R and Z (d) S and Z

EXERCISE 8.2 (MCQ 1 or >1 option correct, Passage based, Matching, A/R)

DIRECTIONS for Q. 1 to Q. 20 : Multiple choice questions with one or more than one correct option(s).

1. Which of the following reagents can be used to prepare an alkyl halide from an alcohol?
(a) NaCl (b) $HCl + ZnCl_2$
(c) $SOCl_2$ (d) PCl_5

2. Which of the following compounds, on being warmed with iodine solution and NaOH, will give iodoform?
(a) CH_3CH_2OH (b) CH_3COCH_3
(c)  (d) CH_3OH

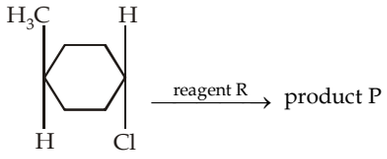
3. Which of the following occurs during the formation of $CHCl_3$ from C_2H_5OH and bleaching powder?
(a) oxidation (b) reduction
(c) hydrolysis (d) chlorination

4. Which of the following statements are true about chloroform?
(a) it is used as anaesthetic
(b) it is used as a solvent
(c) it has sp^2 hybridized carbon
(d) it has a distorted tetrahedral shape

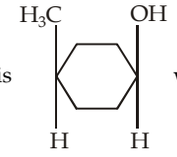
5. Which of the following methods can be used for the preparation of acetylene?
(a) $CH_3CHCl_2 + \text{alc. KOH} \longrightarrow$
(b) $ClCH_2CH_2Cl + \text{alc. KOH} \longrightarrow$
(c) $ClCH_2CH_2Cl + NaNH_2 \xrightarrow[\Delta]{\text{liq. } NH_3}$
(d) none of these

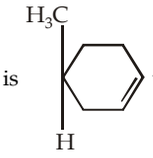
6. The haloform test is given by
(a) formaldehyde (b) acetaldehyde
(c) acetone (d) α-phenylethyl alcohol

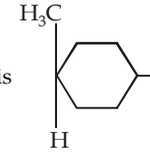
7. Which of the following can be used for the preparation of chloroform?
(a) $CH_3CH_2.CO.CH_2CH_3$
(b) $CH_3.CO.C_2H_5$
(c) $CH_3CH_2.CO.C_3H_7$
(d) CH_3CHO

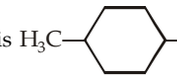
8.  product P

Which are true statements about reagent R and product P :

(a) P is  when R is aq. KOH in S_{N^2} reaction

(b) P is  when R is t-BuOK

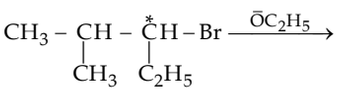
(c) P is  when R is NH_3

(d) P is  when R is $KMnO_4$

9. CH_3CH_2OH can be converted into CH_3CH_2Cl by
(a) thionyl chloride
(b) sulphuryl chloride
(c) phosphorus pentachloride
(d) phosphorus oxychloride

10. Product obtained from the reaction of chloroform with nitric acid is used as :
(a) insecticide (b) war gas
(c) anaesthetic (d) dye

11. Possible products of the following reaction can be :



(a) $CH_3-\underset{CH_3}{\underset{|}{CH}}-\overset{*}{\underset{C_2H_5}{\underset{|}{CH}}}-OC_2H_5$ by S_{N^2} reaction (reaction takes place with inversion)

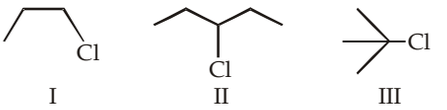
(b) $CH_3-\underset{CH_3}{\underset{|}{CH}}-\overset{*}{\underset{C_2H_5}{\underset{|}{CH}}}-OC_2H_5$ by S_{N^2} reaction (reaction mixture)

(c) $CH_3-\overset{CH_3}{\underset{OC_2H_5}{\underset{|}{\overset{|}{C}}}}-\overset{*}{C}H_2-C_2H_5$ by S_{N^1} reaction

(d) none is correct

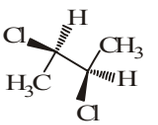
12. $C_3H_6Cl_2 \xrightarrow[KOH]{\text{alcoholic}} A \xrightarrow[H_2SO_4]{HgSO_4} B$

B gives iodoform test. Hence A is :
(a) 1, 1 dichloropropane (b) 1, 2 dichloropropane
(c) 2, 2 dichloropropane (d) 1, 3 dichloropropane

13. 
I II III

Which are correct statements :
(a) reactivity for S_{N^1} reaction is I < II < III
(b) reactivity for S_{N^2} reaction is I < II < III
(c) reactivity for S_{N^1} reaction is I > II > III
(d) reactivity for S_{N^2} reaction is I > II > III

14. The correct statement(s) about the compound



given below is/are
(a) The compound is optically active
(b) The compound possesses centre of symmetry
(c) The compound possesses plane of symmetry
(d) The compound possesses axis of symmetry

15. In the reaction,

$$CHCl_3 + 4OH^- \longrightarrow HCOO^- + 3Cl^- + 2H_2O$$

the intermediate species formed are
(a) CCl_3^- (b) $:CCl_2$
(c) $CH(OH)_3$ (d) $COCl_2$

16. Which of the following compounds will give haloform test ?
(a) CH_3COCH_2I (b) $CH_3-CHCl-CH_3$
(c) $C_6H_5COCH_3$ (d) $CH_3COOC_2H_5$

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17. Benzyl chloride ($C_6H_5CH_2Cl$) can be prepared from toluene by chlorination with

(a) SO_2Cl_2/peroxide (b) $SOCl_2$

(c) Cl_2/hv (d) NaOCl

18. The correct statement(s) about the compound

$H_3C(OH)CH - CH = CH - CH(OH)CH_3(X)$

is/are

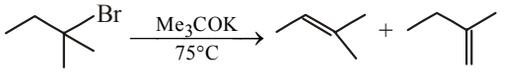
(a) The total number of stereoisomers possible for X is 6

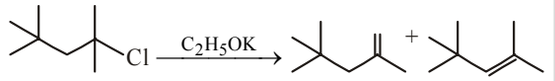
(b) The total number of diastereomers possible for X is 3

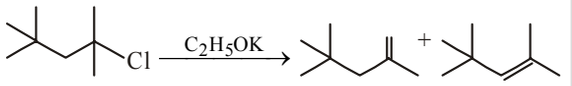
(c) If the stereochemistry about the double bond in X is *trans*, the number of enantiomers possible for X is 4

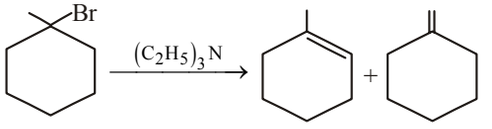
(d) If the stereochemistry about the double bond in X is *cis*, the number of enantiomers possible for X is 2

19. Pick up the reaction in which Hofmann elimination is the major product.

(a) 

(b) 

(c) 

(d) 

20. Which of the organic compounds will give white precipitate with $AgNO_3$ solution ?

(a) C_6H_5Cl

(b) NaCl

(c) $C_6H_5\overset{+}{N}H_3Cl^-$

(d) 2, 4, 6 - trinitrochlorobenzene

DIRECTIONS for Q. 21 to Q. 35 : Read the following passages and answer the questions that follows :

PASSAGE 1

A characteristic of alkyl halides is their ability to undergo nucleophilic substitution reactions with nucleophiles and elimination reactions with bases, although reactants are often both nucleophiles and bases. Depending on factors such as the relative strength of nucleophile versus base, steric effects, temperature, and carbocation stability, the reaction mechanism and most abundant products of certain reactions involving alkyl halides can be predicted

21. What is the major product of the reaction below, and what is the mechanism by which it is produced?

$CH_3CH_2Br + CH_3O^- \rightarrow$

temperature: 50°C; solvent: CH_3OH

(a) ethene; E_1

(b) ethene; E_2

(c) ethyl methyl ether; S_N2

(d) ethyl methyl ether; S_N1

22. What is the major product of the reaction below, and what is the mechanism by which it is produced?

$(CH_3CH_2)_3CBr + OH^- \rightarrow$

temperature: 500°C; solvent: CH_3OH

(a) $(CH_3CH_2)_3COH$; S_N1

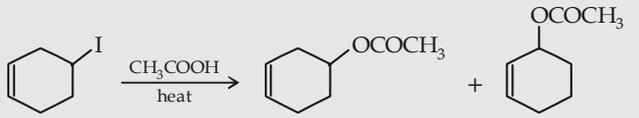
(b) $(CH_3CH_2)_3COH$; S_N2

(c) $CH_3CH{=}C(CH_2CH_3)_2$; E_2

(d) $CH_3CH{=}C(CH_2CH_3)_2$; E_1

PASSAGE 2

Alkyl halides in presence of polar solvents lose halide ions forming carbocations which then react with the nucleophile.



23. The carbocation formed by the loss of halide ion is

(a) 1° (b) 2°

(c) 3° (d) allylic

24. Formation of two products is because

(a) $CH_3-\overset{\overset{O}{\|}}{C}-OH$ has two nucleophilic sites

(b) the carbocation formed initially rearranges to the more stable carbocation

(c) Both of the two

(d) None of the end

25. The product II is formed through a

(a) 2° carbocation (b) 3° carbocation

(c) allylic 2° carbocation (d) vinylic 2° carbocation

PASSAGE 3

Observe the following two reactions :

(a) $CH_3\overset{\overset{Br}{|}}{C}HCH_3 \xrightarrow[\text{alcohol}]{KOH} CH_2=CHCH_3$ is **much faster than**

$D_3C-\overset{\overset{Br}{|}}{C}H-CD_3 \xrightarrow[\text{alcohol}]{KOH} D_2C=CH-CD_3$

(b) $CH_3\overset{\overset{Br}{|}}{C}HCH_3 \xrightarrow[\text{heat}]{H_2O/\text{acetone}} CH_2=CHCH_3$ is equal to

$D_3C\overset{\overset{Br}{|}}{C}HCD_3 \xrightarrow[\text{heat}]{H_2O/\text{acetone}} D_2C=CHCD_3$

26. The reaction (a) follows
(a) E1 (b) E2
(c) either of the two (d) E1CB

27. The difference in the two reactions of the set (a) is due to the fact that
(a) these reactions follow E2 path
(b) the C–D bond is slightly stronger than the C–H bond
(c) both of the above statements
(d) these reactions follow E1 mechanism

28. The two reactions in the set (b) follow equal rate because
(a) the reaction occurs in two steps
(b) the rate determining step involves removal of Br as Br^-
(c) both (a) and (b)
(d) in presence of acetone C–H and C–D bonds are cleaved at the same rate

29. Which of the reactions of the set (b) follows E1 mechanisms?
(a) $CH_3\overset{\overset{Br}{|}}{C}HCH_3$ (b) $D_3\overset{\overset{Br}{|}}{C}CHCD_3$
(c) Both (d) None

PASSAGE 4

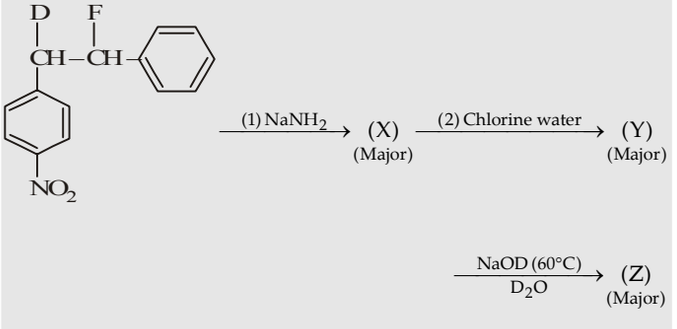
Although both nucleophilicity and basicity depend upon the availability of electrons, they do not always parallel each other. In going from left to right in a period, both basicity and nucleophilicity decrease. However, down a group nucleophilicity increases while basicity decreases. In case, the nucleophilic centre is the same, two things happen : (i) nucleophilicity parallels basicity and (ii) nucleophilicity decreases and the basicity increases as the size of nucleophile increases.

30. Which of the following has the highest nucleophilicity ?
(a) F^- (b) OH^-
(c) CH_3^- (d) NH_2^-

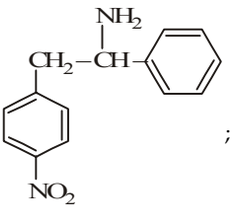
31. The weakest base among the following is
(a) $(CH_3)_3CO^-$ (b) $CH_3CH_2O^-$
(c) $(CH_3)_2CHO^-$ (d) $C_6H_5O^-$

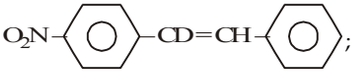
32. The most reactive nucleophile among the following is
(a) CH_3O^- (b) $C_6H_5O^-$
(c) $(CH_3)_2CHO^-$ (d) $(CH_3)_3CO^-$

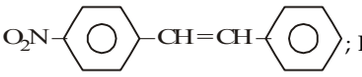
PASSAGE 5

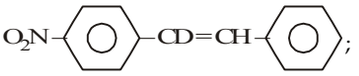


33. The product (X) and the related most probable mechanism of its formation are respectively

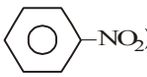
(a)  ; S_N2

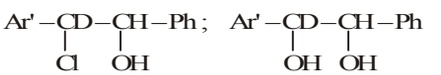
(b)  ; E1

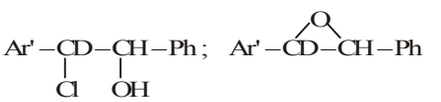
(c)  ; E2

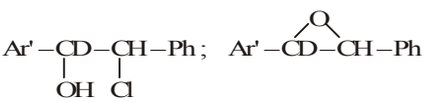
(d)  ; E1cB

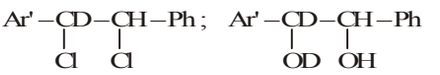
34. The correct information about formation of Y are
(a) Regioselective, nonstereospecific, nucleophilic addition
(b) Nonregioselective, nonstereospecific, electrophilic addition
(c) Regioselective, stereospecific, electrophilic substitution
(d) Regioselective, stereospecific, electrophilic addition

35. The product Y and Z are where (Ar′ is ) and (Ph is $-C_6H_5$)

(a) 

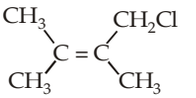
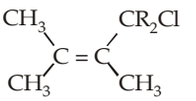
(b) 

(c) 

(d) 

DIRECTIONS for Q. 36 to Q. 40 : The following questions are matching type questions. Match Column I with Column II

36.

Column I		*Column II*	
(A)		(a)	S_{N^1}
(B)		(b)	S_{N^2}
(C)	$(CH_3)_3CCl$	(c)	E_1
(D)	CH_3CH_2Cl	(d)	E_2

37.

	Column I		*Column II*
(A)	Carbon tetrachloride	(a)	Laboratory reagent
(B)	Chloroform	(b)	Easiest hydrolysis
(C)	Methylene chloride	(c)	Reimer-Tiemann reaction
(D)	Phenol	(d)	Methanal

38. Match the column-1 with column-II :

	Column-I (Reaction)		**Column-II (Products)**
A.	Chloroform reacts with HNO_3 to form an insecticide	(a)	Gammaxene
B.	Silver acetate gets converted into methyl bromide on reaction with Br_2 in CCl_4	(b)	Dichlorodiphenyl trichloroethane
C.	Chrobenzene in the presence of conc. H_2SO_4, reacts with trichloroacetaldehyde	(c)	Chloropicrin
D.	Benzene reacts with Cl_2 in presence of sun light	(d)	Compound containing oxygen.
		(e)	Borodiene Hunsdiecker reaction

39.

	Column-I		**Column-II**
A.	$(CH_3)_3CCl$	(a)	Hofmann product
B.	$CH_3CH_2CH_2CH_2Cl$	(b)	Saytzeff product
C.	$CH_3CHClCH_2CH_3$	(c)	E1
D.	$CH_3CHFCH_2CH_3$	(d)	E2

40.

	Column-I		**Column-II**
A.	S_N1	(a)	Inversion
B.	S_N2	(b)	Carbocation
C.	E2	(c)	Transition state
D.	E1	(d)	Retention

Instructions for Q. 41 to 49 : Following questions are Assertion and Reasoning Type Questions :

Note : Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 5 choices (a), (b), (c), (d) and (e) out of which ONLY ONE is correct.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.

(c) Statement -1 is True, Statement-2 is False.

(d) Statement -1 is False, Statement-2 is True.

(e) Statement -1 is False, Statement-2 is False.

41. **Statement 1 :** 3-bromocyclohexene is less reactive than 4-bromocyclohexene in hydrolysis with aqueous NaOH.

Statement 2 : Reactions of the given halides with aqueous NaOH is expected to proceed via S_N1 mechanism.

42. **Statement 1 :** Alkyl halides, though polar, are immiscible with water.

Statement 2 : Alkyl halides (haloalkanes) are polar due to the presence of polar C – X bond.

43. **Statement 1 :** neo-pentyl bromide undergoes nucleophilic substitution reactions very fast.

Statement 2 : The reactivity of neopentyl bromide in S_N1 mechanism is very fast.

44. **Statement 1 :** Vinyl chloride is unreactive in nucleophilic substitution reactions.

Statement 2 : Due to delocalization of electrons by resonance.

45. **Statement 1 :** n-Butyl chloride reacts with aqueous sodium hydroxide by S_N2 mechanism while tert-butyl chloride S_N1 mechanism.

Statement 2 : The carbocation formed is a tertiary carbocation, in case of tert-butylchloride whereas in the case of n-butyl chloride, the carbocation formed is a primary carbocation.

46. **Statement-1 :** S_{N^2} reaction of an optically active aryl halide with an aqueous solution of KOH always gives an alcohol with opposite sign of rotation.

Statement-2 : S_{N^2} reactions always proceed with inversion of configuration.

47. **Statement-1 :** Grignard reagents are prepared in ether but not in benzene.

Statement-2 : Grignard reagents are soluble in benzene.

48. **Statement-1 :** Treatment of 1, 3-dichloropropane on reaction with alc. KOH gives allene.

Statement-2 : It is nucleophilic elimination reaction.

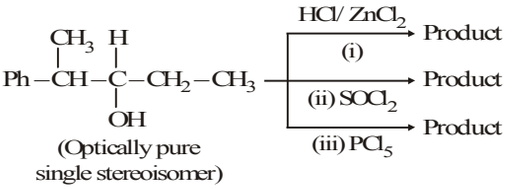
49. **Statement-1 :** Alkyl halides give elimination reaction with alcoholic KOH, but nucleophilic substitution with aqueous KOH.

Statement-2 : In alcoholic KOH, attacking ion is ^-OR which is stronger base than OH^-.

Instructions for Q. 50 to 52 : Following questions are Integer Type Questions :

50. The number of structural and configurational isomers of a bromo compound, C_5H_9Br, formed by the addition of HBr to 2-pentyne respectively are

51.



Find the sum of total number of isomeric chlorides obtained in these reactions (consider only the major products)

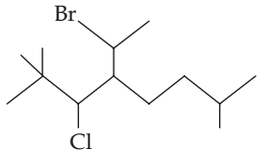
52. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is

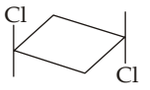
EXERCISE 8.3 (Subjective Problems)

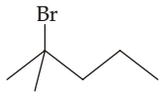
1. Write IUPAC names for :

(*i*) allyl iodide (*ii*) *tert*-amyl bromide

(*iii*) neopentyl chloride

(*iv*) 

(*v*) 

2. (*a*) 

can be prepared from two alkenes. Name them

(*b*) Prepare *n*-butyl iodide from butene-1.

3. How will you prepare (*a*) allyl iodide, and (*b*) allyl fluoride from propene ?

4. (*a*) Assign structure to the hydrocarbon (molecular weight = 72) which gives a single monochloride and two isomeric dichlorides on photochlorination.

(*b*) Assign structure to the hydrocarbon (M.W. = 70) which gives a single monochloride and three isomeric dichlorides on photochlorination.

5. Arrange the following species in increasing order of their fugicity (leaveability).

H_2O, OH^-, CH_3OH, $\bar{O}CH_3$, $\bar{O}COCH_3$, H^-, CN^-, R^-, $ArSO_2O^-$.

6. Arrange the following alkoxide ions in order of decreasing order of S_{N^2} reactivity :

Me_3CO^-, MeO^-, $MeCH_2O^-$, Me_2CHO^-, and 

.

7. Explain the following :

(*a*) Although CH_3—O—CH_2Cl is a primary alkyl halide, it undergoes S_{N^1} reaction.

(*b*) $AgNO_3$ increases the rate of solvolysis in S_{N^1} reactions.

(*c*) Ethyl alcohol is added to water during solvolysis of alkyl halides by water.

(*d*) Account for the trend observed in relative rates for the formation of alcohols in the following alkyl halides with H_2O/C_2H_5OH at 25°C.

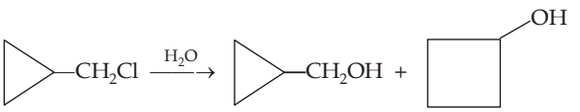
MeBr (2140) : $MeCH_2Br$ (172) ; Me_2CHBr (4.99) ; Me_3CBr (1010)

(*e*) PHO^- is a weaker nucleophile than RO^-.

(*f*) An S_{N^2} solvolysis (where solvent is the nucleophile) appears to follow a first order rate law, rather than a second order one.

(*g*) 4-Bromo-2-pentene forms a racemic product on treatment with sodium iodide.

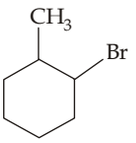
8. Suggest a suitable mechanism for the following transformation.

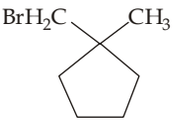


+ $CH_2 = CH—CH_2—CH_2OH$

9. Give the possible products when the following alkyl halides are treated with sodium ethoxide.

(*a*) $(CH_3)_2CHCHClCH_3$

(*b*) 

(*c*) 

10. Name the chief product obtained by the reaction of *n*-C_4H_4Br with

(*a*) Zn, H^+ (*b*) Li, then CuI, C_2H_5Br

(*c*) NaI in presence of $(CH_3)_2CO$

(*d*) Mg, ether, and then D_2O (*e*) CH_3COOAg

(*f*) Li, CuI.

11. Arrange the following alkyl bromide in decreasing order toward S_{N^2} reactivity.

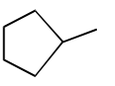
(*a*) 1-Bromo-3-methylbutane, 2-bromo-2-methylbutane, 3-bromo-2-methylbutane

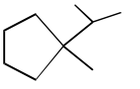
(*b*) 1-Bromobutane, 1-bromo-2, 2--dimethylpropane, 1-bromo-2-methylbutane, 1-bromo-3-methylbutane

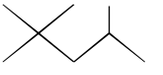
12. Arrange the following alkyl bromides in decreasing order toward S_{N^1} reactivity.

2-Bromo-2-methylbutane, 1-bromopentane, 2-bromopentane

13. Give the principal product obtained by the free radical bromination of each of the following :

(*a*) 

(*b*) 

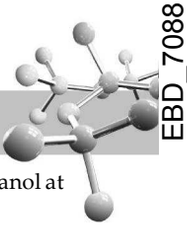
(*c*) 

14. Explain the following :

(*i*) Bromine is less electronegative than chlorine, yet the dipole moments of CH_3Cl and CH_3Br are very similar.

(*ii*) Carbon-carbon bond dissociation energy of ethane and propane are different.

(*iii*) Dry gaseous hydrohalic acids and not their aqueous solutions are used to prepare alkyl halides from alkenes.



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(*iv*) Iodoform gives precipitate with silver nitrate on heating, while chloroform does not.

(*v*) On treatment with base, CH_3CH_2I loses HI easily than CD_3CH_2I loses DI

(*vi*) The carbocation F_3C^+ is stable while $F_3C—CH_2^+$ is not stable.

15. Categorise the following compounds

(*i*) bromobenzene (*ii*) *tert*-butyl bromide

(*iii*) *n*-hexyl chloride (*iv*) *n*-hexyl iodide

(*v*) benzyl bromide (*vi*) carbon tetrachloride

(*vii*) *sec*-butyl chloride.

On the basis of their reactivity with alcoholic silver nitrate in the following three categories.

(*a*) react rapidly at room temperature

(*b*) react rapidly only on heating

(*c*) inert even on heating.

16. Calculate the rate of reaction between CH_3I and CN^-, when they react by the S_{N^2} process in a solution in which the concentration of each is 0.1 mol dm^{-3} (0.1 molar), given that the rate at 0.01 molar concentration is 5.44×10^{-9} mol dm^{-3} s^{-1}.

17. Isopropyl bromide reacts with hydroxide ion, in 80% ethanol at 55°C, according to the following kinetic equation

Rate in moles L^{-1} S^{-1} = 4.7×10^{-5} [RX] [OH^-] + 0.24×10^{-5} [RX]

Determine the percentage of isopropyl bromide reacting by S_{N^2} mechanism when [OH^-] is :

(*a*) 0.001 molar (*b*) 0.1 molar and

(*c*) 1. 0 molar

18. Optically pure (S) – (+)-$CH_3CHBr\ C_2H_5$ has specific rotation of + 36°. A partially racemized sample of this bromide with specific rotation of + 30° is treated with dilute NaOH to form an alcohol (R) – (–) – $CH_3CHOHC_2H_5$ of specific rotation – 5.97° ; whose optically pure form has a specific rotation of – 10.3°.

Write the equation for the reaction using projection formula and calculate

(*i*) the percent optical purity of reactant and product

(*ii*) the percentage of racemization and inversion

(*iii*) the percentage of the front side and backside attack.

Can we increase the percentage of inversion by changing the condition of the reaction ?

SOLUTIONS

EXERCISE 8.1

1	(b)	**6**	(a)	**11**	(a)	**16**	(d)	**21**	(d)	**26**	(c)	**31**	(a)	**36**	(b)	**41**	(b)	**46**	(a)
2	(d)	**7**	(b)	**12**	(d)	**17**	(a)	**22**	(a)	**27**	(c)	**32**	(d)	**37**	(d)	**42**	(d)	**47**	(d)
3	(d)	**8**	(a)	**13**	(b)	**18**	(b).	**23**	(a)	**28**	(c)	**33**	(b).	**38**	(c)	**43**	(a).	**48**	(a).
4	(c)	**9**	(b)	**14**	(c)	**19**	(b)	**24**	(a)	**29**	(d)	**34**	(d)	**39**	(a)	**44**	(b)	**49**	(c)
5	(d)	**10**	(b)	**15**	(d)	**20**	(c)	**25**	(b)	**30**	(b)	**35**	(d)	**40**	(d)	**45**	(d)		

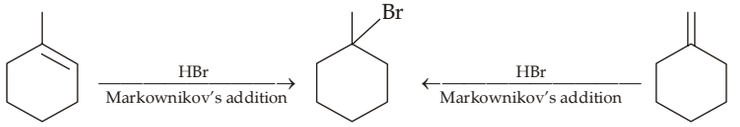
1.



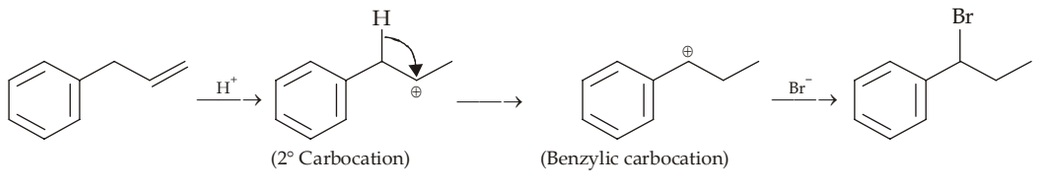
1-Chlorobutane (1°) 1-Chloro-2-methylpropane (1°) 2-Chlorobutane (2°) 2-Chloro-2-methylpropane (3°)

2. Alkyl halide because Cl is attached to sp^3 hybridised C, vinyl halide because Br is attached to sp^2 hybridised carbon, allyl halide because Cl is attached to sp^3 hybridised carbon which in turn is attached to the sp^2 hybridised carbon.

3.



4. It is an electrophilic addition and involves the formation of carbocation. Here 2° carbocation undergoes 1, 2-hydride shift to form the more stable benzylic carbocation.



(2° Carbocation) (Benzylic carbocation)

5. RCl and RBr can be prepared by free radical halogenation of alkanes, but RF and RI can't be prepared because fluorination is so fast that explosion occurs, while iodination is slowest and produces HI a strong reducing agent which causes the reaction to proceed backward.

6. Weaker a Bronsted base, more will be its stability than its conjugate acid, and hence more will be the tendency of the base to be removed and thus more will be reactivity of the RX.

7. Among halides, fluoride ion is the smallest ion, so it provides minimum volume for spreading of electrons and thus electrons are easily available. Further, F has no *d* orbital while Cl has *d* orbital so delocalisation in Cl^- further increases and thus its basicity (availability of electrons for protonation) decreases much more than F^-.

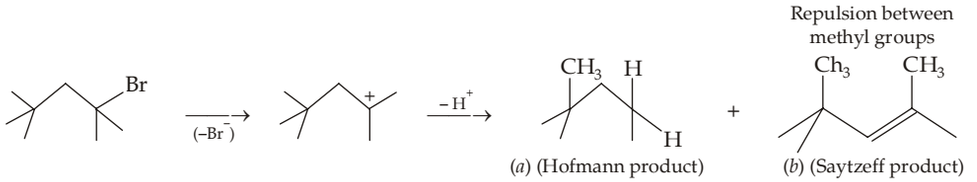
8. Increased temperature increases the rates of both substitutions and eliminations. However, increased temperature favours eliminations over substitutions because elimination reactions have higher free energies of activation than substitutions since the former involve more changes in bonding (*i.e.* more bonds are broken and formed).

9. 3° Halide does not undergo S_{N^2} reaction because of bulky alkyl group present on C bearing the leaving group. Ethyl alcohol is a weak base but good nucleophile, hence $(CH_3)_3C^+$ formed as intermediate is attacked by the nucleophile, C_2H_5OH (remember it is an example of solvolysis). Elimination reaction is not possible because C_2H_5OH is a weak base.

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10. Iodide ion is excellent nucelophile as well as a leaving group, while Cl^- is a poor leaving group as compared to I^-. So in the two step method, both steps are fast and hence the two step route is preferred as compared to first which proceeds at a slower rate (poor yield).

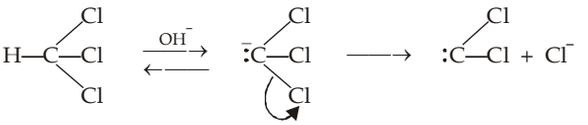
11.



(*a*) (Hofmann product) (*b*) (Saytzeff product)

Thus here, Saytzeff product (having more alkyl groups on the doubly bonded carbon atoms) is not stable due to steric repulsion between bulky methyl groups.

12. Dichlorocarbene is a neutral bivalent electron deficient species having two non-bonding electrons on the carbon atom. It is formed by the loss of Cl^- from trichloromethyl carbanion.



13. Hydrogen of $CHCl_3$ is acidic than that of CH_2Cl_2 because the former has three —Cl (electronegative groups) while CH_2Cl_2 has two, hence it is easily eliminated by alkali ; CCl_4 has no hydrogen atom, so it will not react with alkali.

14. See mechanism of alkaline hydrolysis of chloroform.

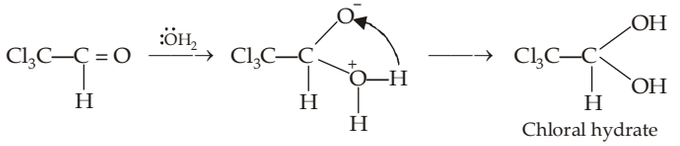
15. During reaction of an alkyl halide with KCN, one carbon atom is introduced by KCN in the form of —CN, hence alkyl halide should be propyl chloride.

$$CH_3CH_2CH_2Cl + KCN \longrightarrow CH_3CH_2CH_2CN + KCl$$

16. $4C_2H_5Cl + SnCl_4 + 8Na \longrightarrow (C_2H_5)_4\,Sn + 8NaCl$

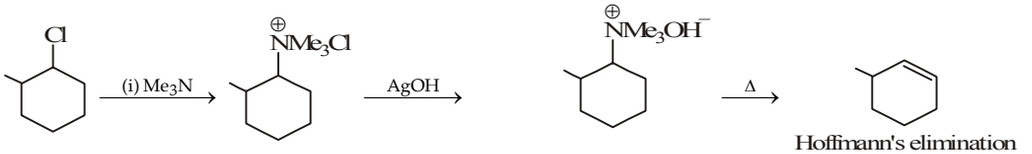
17. $CH_2 = CHCl + \underset{\text{Lithium dimethylcuprate}}{(CH_3)_2\,\overset{-}{Cu}\,\overset{+}{Li}} \xrightarrow[\text{ether}]{\text{diethyl}} CH_2 = CHCH_3$

18.



Chloral hydrate

22. (a)



Hoffmann's elimination

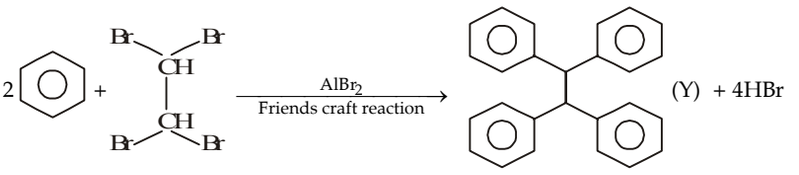
24. (a) $\underset{\text{(A)}}{CH_3 - CH_2 - CHCl_2} \xrightarrow{OH^-} \underset{\text{(B)}}{CH_3CH_2CHO}$ or $\underset{\text{(C)}}{CH_3C \equiv CH}$

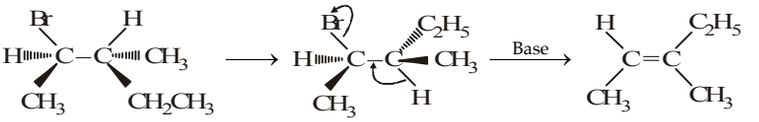
$$\underset{\text{(B)}}{CH_3 - CH_2 - CH = O} \xrightarrow{[O]} CH_3 - CH_2 - COOH$$

$$\underset{\text{(C)}}{CH_3 - C \equiv C - H} \xrightarrow{\text{Dil.}H_2SO_4} \underset{\text{(D)}}{CH_3 - \overset{\overset{O}{\|}}{C} - CH_3} \xrightarrow{Br_2 / NaOH} CH_3COONa$$

25. (b)

(i) $H-C\equiv C-H+2Br_2 \longrightarrow CHBr_2CHBr_2(X)$

(ii) 

27. (c) 

28. (c) Since alkyl halide is 3°, so in presence of NaCN it will follow E2 path rather S_N2, so method 2 is not appropriate.

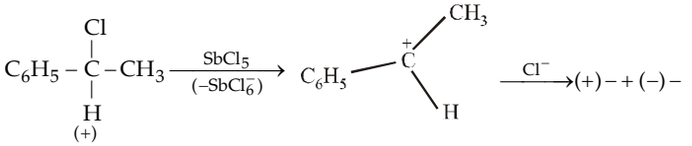
29. (b) $(CH_3)_2CHCH_2MgBr \xrightarrow{C_2H_5OH} (CH_3)_2CHCH_3 + MgBr(OC_2H_5)$

30. (d) Debromination is a *trans*-elimination reaction.

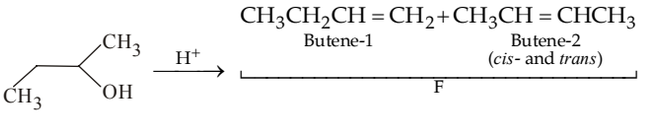
meso- 2, 3-Dibromobutane on debromination gives *trans*-2-butene.

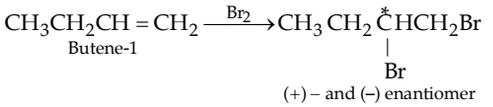
31. (a) $(CH_3)_3C-MgCl+D_2O \longrightarrow (CH_3)_3C-D+Mg(OD)Cl$

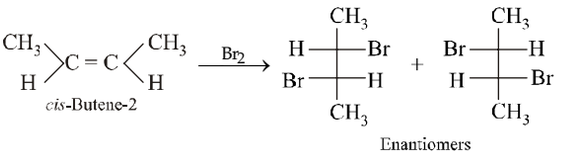
32. (d) Occurrence of racemization points towards the formation of carbocation as intermediate, which being planar can be attacked from either side.

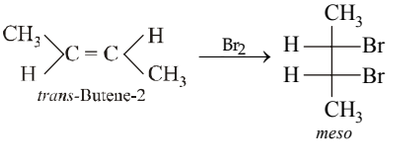


33. (b) Dehydrobromination by strong base (alc. NaOH) followed by Markownikoff addition of HBr.

34. (d) 

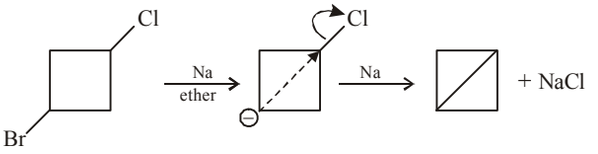






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35. (d) It is an example of intramolecular Wurtz reaction.



Br^- is a better leaving group than chloride. In this reaction alkali metal (Na) is electron donor.

36. (b) $BrCH_2 - CH_2Br \xrightarrow{Alc.KOH} CH_2 = CHBr \xrightarrow{NaH_2} CH \equiv CH$

Elimination of HBr from CH_2 = CHBr requires a stronger base because here, Br acquires partial double bond character due to resonance.

37. (d) Carbon belongs to 2nd period, while iodine belongs to 5th period, hence the C-I bond in $CH_3CH_2CH_2I$ must be formed by the overlapping of $2sp^3$ orbital of C with the $5p_z$ orbital of iodine.

38. (c) Small difference in boiling points of C_2F_6 and C_2H_6 is due to the fact that (i) the F atom is only slightly larger than H, and (ii) F has low polarizability

39. (a) Sodium chloride is far less soluble in acetone than NaI, hence reaction (b) is possible, but not (a)

40. (d) *tert*-Alkyl halides undergo S_{N^1} reactions, hence they involve the formation of quite stable carbocations, and not the transition state.

In S_{N^1} reactions, the nucleophile is not involved in rate determining (first) step, hence its stronger or weaker nature does not influence the reaction rate. In S_{N^1}, the product has more percentage of the inverted configuration than the retained configuration, i.e. only partial racemization takes place, hence the product will be having some optical activity.

41. (b) (i) Weak bases like CH_3COO^-, Cl^- etc. favours substitution rather elimination.

(ii) Sterically hindered base favours elimination reaction, no matter the alkyl halide is primary.

42. (d) (a) Elimination reactions have higher free energies of activation than substitution reactions because they involve a greater change in bonding, i.e., more number of bonds are broken and formed than in substitution reactions. Now the increase in temperature although increases the number of molecules crossing the barrier in both reactions, the proportion of such molecules is significantly higher in elimination reaction leading to increased rate of elimination reaction.

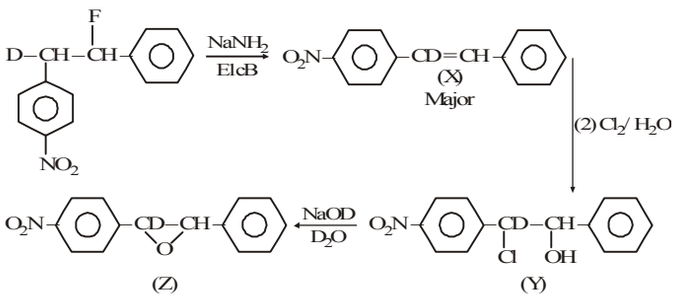
(b) The sterically hindered nucleophile will inhibit the formation of transition state leading to substitution reaction, hence the alkyl halide will mainly undergo elimination reaction .

(c) Use of strong and slightly polarizable base, e.g. NH_2^- ion favours elimination reaction.

EXERCISE 8.2

>1 CORRECT OPTION	1	(b, c, d)	2	(a, b, c)	3	(a, c, d)	4	(a, b, d)	5	(a, b, c)
	6	(b, c, d)	7	(b, d)	8	(a, b)	9	(a, c)	10	(a, b)
	11	(a, c)	12	(a, b, c)	13	(a, d)	14	(a, d)	15	(a, b)
	16	(a, b, c, d)	17	(a, c)	18	(a, d)	19	(a, c, d)	20	(c, b)
PASSAGE 1	21	(c)	22	(a)						
PASSAGE 2	23	(b)	24	(b)	25	(c)				
PASSAGE 3	26	(b)	27	(c)	28	(c)	29	(c)		
PASSAGE 4	30	(c)	31	(d)	32	(a)				
PASSAGE 5	33	(d)	34	(d)	35	(b)				
MATCH THE FOLLOWING	36	(A)-a, b ; (B) a, c ; (C) a, c ; (D) b, d								
	37	(A) - a, c, (B) - a, b, c, (C) - d, (D) - a, c								
	38	(A)-c, d ; (B) d ; (C) b ; (D) a								
	39	(A)- c ; (B) d ; (C) b, d ; (D) a, d								
	40	(A)-a, b, d ; (B) a, c ; (C) c ; (D) b								
A/R	41	(d)	42	(b)	43	(c)	44	(a)	45	(a)
	46	(d)	47	(c)	48	(a)	49	(a)		
INTEGER	50	2 & 4	51	4	52	5				

Sol. (33-35)



33. (d) **34.** (d) **35.** (b)

46. (d) **A** is false, because aryl halides do not undergo nucleophilic substitution under ordinary conditions. This is due to resonance, because of which the carbon–chlorine bond acquires partial double bond character, hence it becomes shorter and stronger and thus cannot be replaced by nucleophiles. However (**R**) is true.

47. (c) The correct reason is : Grignard reagents are soluble in ether but not in benzene

50. **2 & 4**

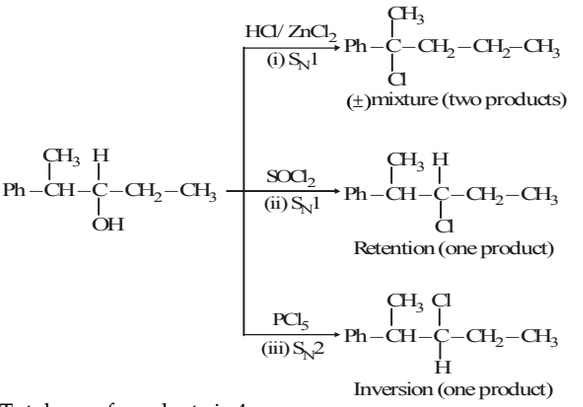
Addition of HBr to 2-pentyne gives two structural isomers (I) and (II)

$$CH_3-C\equiv C-CH_2CH_3 \xrightarrow{HBr}$$

$$\underset{(I)}{CH_3C(Br)=CHCH_2CH_3} + \underset{(II)}{CH_3CH=C(Br)CH_2CH_3}$$

Each one of these will exist as a pair of geometrical isomers. Thus, there are two structural and four configurational isomers.

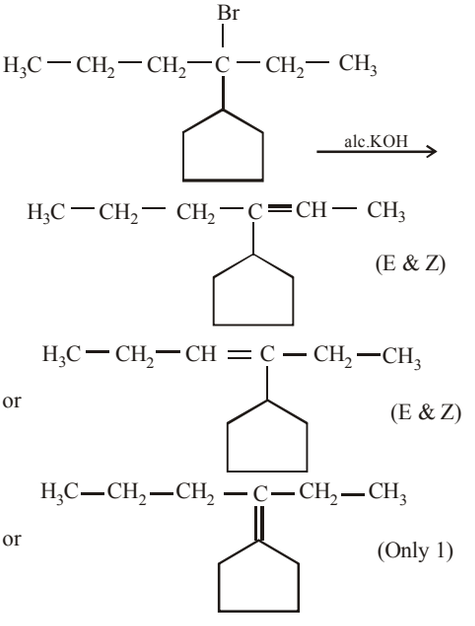
51. **4**

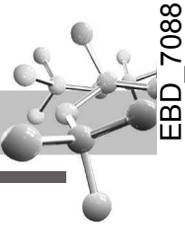


Total no. of products is 4.

52. **5**

Total no. of alkenes will be = 5

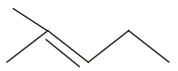




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EXERCISE 8.3

1. (*i*) $CH_2 = CH\,CH_2I$ is 3-iodo-1-propene (*ii*) $(CH_3)_2C(Br)CH_2CH_3$ is 2-bromo-2-methylbutane
(*iii*) $(CH_3)_3\,CCH_2Cl$ is 1-chloro-2, 2-dimethylpropane (*iv*) 4-(1-bromoethyl)-3-chloro-2, 2, 7-trimethyloctane
(*v*) *trans*-1, 3-Dichlorocyclobutane.

2. (*a*)  and 
2-Methylpentene-2 2-Methylpentene-1

(*b*) $CH_3CH_2CH = CH_2 \xrightarrow{\overset{CH_3}{|}\;CHCH_2CH_2Br\;(1°)} CH_3CH_2CH_2CH_2Br \xrightarrow[\text{acetone}]{NaI} CH_3CH_2CH_2CH_2I$

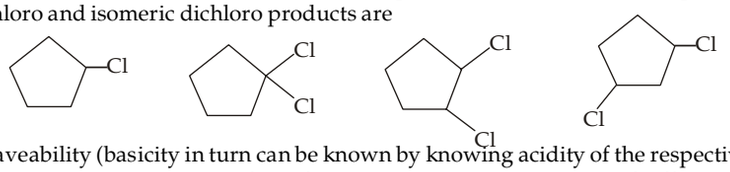
3. (*a*) $CH_3CH = CH_2 \xrightarrow{Cl_2,\,h\nu} ClCH_2CH = CH_2 \xrightarrow[\text{acetone}]{NaI} ICH_2CH = CH_2 + NaCl\downarrow$

(*b*) $CH_3CH = CH_2 \xrightarrow{Cl_2,\,h\nu} ClCH_2CH = CH_2 \xrightarrow{AgF} FCH_2CH = CH_2 + AgCl\downarrow$

4. (*a*) Hydrocarbon (MW = 72) should contain 5 C atoms, hence its molecular formula is C_5H_{12}. Since it forms only one monochloro derivative, its all 12 hydrogen atoms should be equivalent which is possible only in $(CH_3)_4C$. Thus its monochloro and two isomeric dichloro derivatives are

$(CH_3)_3CCH_2Cl$; $(CH_3)_3CCHCl_2$ and $(CH_3)_2C(CH_2Cl)_2$

(*b*) Hydrocarbon of MW 70 should again have 5 carbon atoms, thus it should have molecular formula of C_5H_{10}. Which indicates the presence of 1° of unsaturation. No alkene with five C's has all equivalent H's, hence the compound should be cycloalkane, *i.e.* cyclopentane. Its monochloro and isomeric dichloro products are



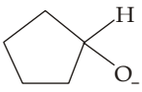
5. Weaker a base, better is its leaveability (basicity in turn can be known by knowing acidity of the respective conjugate acid, remember that weaker a base stronger is its conjugate acid). Thus first of all write down conjugate acids of different bases and then arrange them in decreasing acidity.

Conjugate acid. H_3O^+, H_2O, $CH_3\overset{+}{O}H_2$, CH_3COOH, H_2, HCN, RH, $ArSO_2OH$

Decreasing acidity. $\underset{\text{very strong acids}}{H_3\overset{+}{O},\ CH_3\overset{+}{O}H_2} > \underset{\text{Strong acid}}{ArSO_2OH} > \underset{\text{Weak acids}}{HCN,\ CH_3COOH} > \underset{\text{feeble acids}}{H_2O, CH_3OH} > \underset{\text{Weakest acids}}{H_2,\ RH}$

Remember that only conjugate bases of very strong acids are weak enough to be good leaving groups. Thus
H^-, $R^- < CH_3O^-$, $OH^- < CN^-$, $CH_3COO^- < ArSO_2O^- < H_2O$, CH_3OH
(Increasing fugicity or decreasing basicity of the parent species)

6. Remember that the S_N2 reactivity is susceptible to steric hindrance by the nucleophile as well as R's around the site of displacement. Hence as the number of R's accumulate on the C bonded to O^-, the nucleophile becomes bulkier and its backside approach to the reaction site is retarded, causing a decline in the rate of S_N2 reaction. Thus the order will be

$MeO^- > MeCH_2O^- >$  $> Me_2CHO^- > Me_3CO^-$

Note that both A and B belong to R_2CHO^- type, but the R's of A form the sides of the ring and are ''tied back'' away from the —O. This arrangement permits a more facile approach than by Me_2CHO^-.

7. (*a*) The carbonium ion from chloromethyl methyl ether is resonance stabilized. Remember that stability of R^+ is determining factor between S_N1 and S_N2 reactions.

$$ClCH_2—\ddot{O}—CH_3 \longleftrightarrow \overset{+}{C}H_2—\ddot{O}—CH_3 \longleftrightarrow CH_2=\overset{+}{\ddot{O}}—CH_3$$

(*b*) Ag^+ has a stronger affinity for X^- than a solvent molecule ; the precipitation of AgCl accelerates the dissociation of X^-. This is an example of *electrophilic catalysis*. Remember that Lewis and Bronsted acids (Ag^+, $AlCl_3$ and strong HA) or weak Lewis base (*e.g.* H_2O) catalyses S_N1 reaction.

(*c*) Water is a poor solvent for alkyl halides and ethyl alcohol is added to aid the reaction in their solution.

(*d*) The first three halides react mainly by the S_{N^2} pathway and their rate decline as Me's replace H's on the attacked C, because of steric hindrance. A change to the S_{N^1} pathway accounts for the sharp rise in the reactivity of Me_3CBr.

(*e*) In PhO^-, the pair of electrons on oxygen is involved in resonance and thus nucleophilic character of PhO^- decreases. No such resonance is possible in case of alkoxide ion.

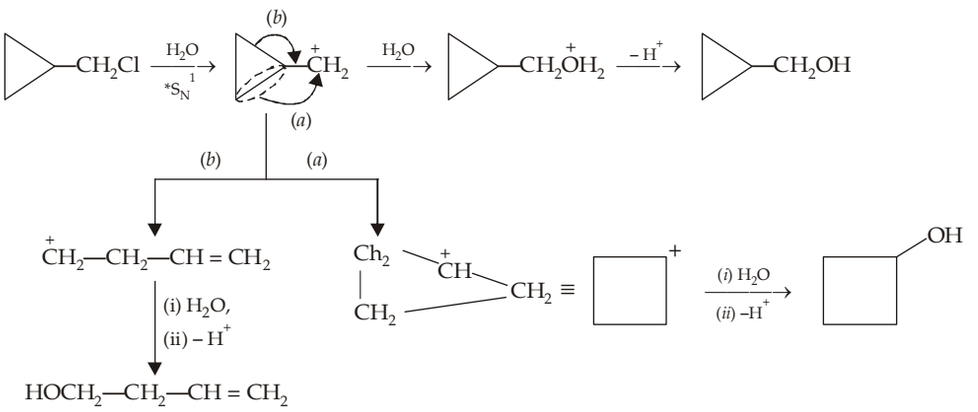
(*f*) In S_{N^2} solvolysis, the concentration of solvent (one of the components) is very large, hence reaction follows the pseudo first order rate law.

(*g*) It is a 2° halide, hence follows S_{N^1} pathway which gives racemic mixture.

$$CH_3—CH=CH—CH(Br)—CH_3 \longrightarrow CH_3—CH=CH—\overset{+}{C}HCH_3 \xrightarrow{I^-} CH_3CH=CH\underset{|}{\overset{I}{C}}HCH_3$$

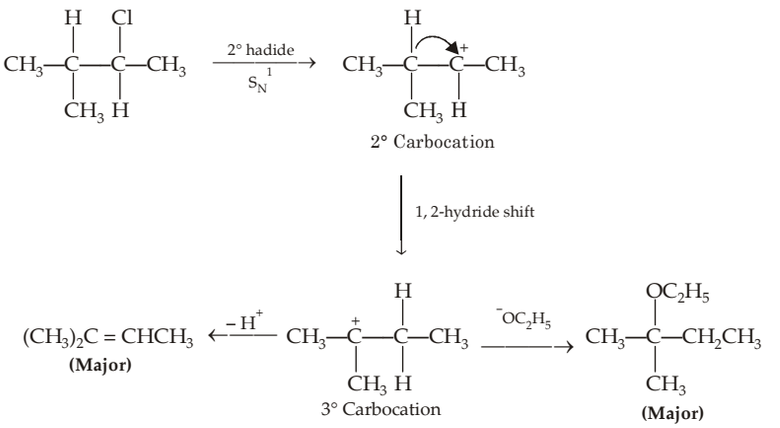
(+) or (–) (±)

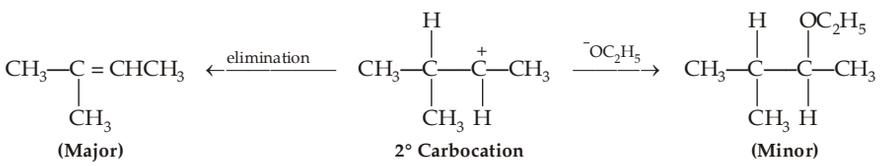
8.



*Sterically hindered C bearing —Cl and weak base favours S_{N^1} reaction.

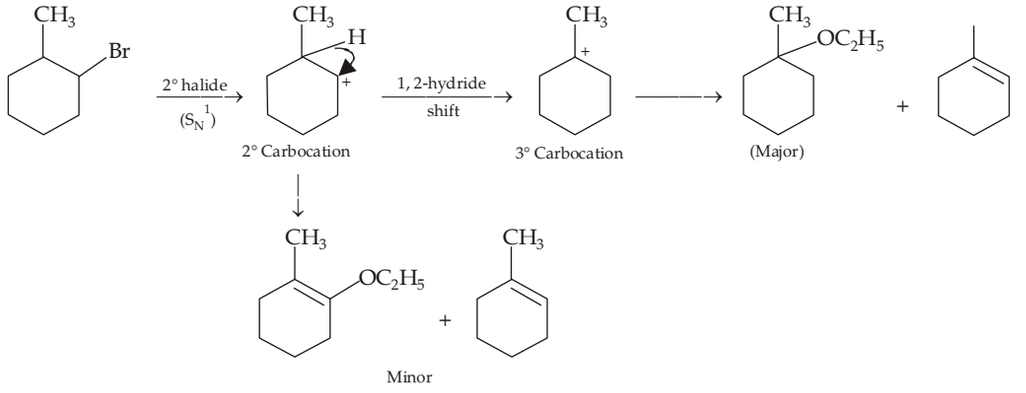
9. (*a*)



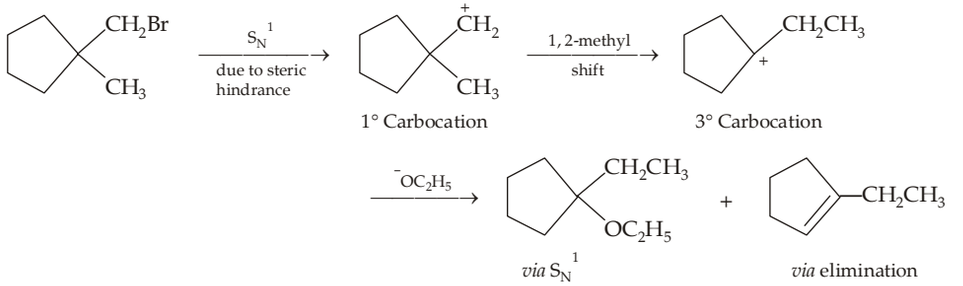


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(*b*)



(*c*)



10. (*a*) $CH_3CH_2CH_2CH_3$ n-Butane (*b*) $CH_3CH_2CH_2CH_2CH_2CH_3$ n-Hexane (*c*) $CH_3CH_2CH_2CH_2I$ n-Butyl iodide

(*d*) $CH_3CH_2CH_2CH_2D$ 1-Deuteratedbutane (*e*) $n\text{–}C_4H_9OC(=O)CH_3$ Methyl pentanoate (*f*) $(n\text{-}C_4H_9)_2CuLi$ Lithium di-n-butylcopper

11. Steric factors are controlling. The usual S_{N^2} order is 1° > 2° > 3°. In case all halides are 1°, rate decreases with increase in branching on the carbon attached to — CH_2Br.

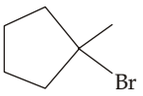
(*a*) $\underset{1°}{CH_3CHCH_2CH_2Br} > \underset{2°}{CH_3CHCHBrCH_3} > \underset{3°}{CH_3C(CH_3)(Br)CH_2CH_3}$

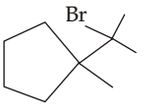
(*b*) $\underset{1°}{CH_3CH_2CH_2CH_2Br} > \underset{1°}{CH_3CH(CH_3)CH_2Br} > \underset{1°}{CH_3CH_2CH(CH_3)CH_2Br} > \underset{1°}{CH_3C(CH_3)_2CH_2Br}$

12. Polar factors are controlling, the more stable the cation being formed in the initial ionization, the faster the reaction. The usual order is 3° > 2° > 1°

$\underset{3°}{CH_3CH_2C(CH_3)(Br)CH_3} > \underset{2°}{CH_3CH_2CH_2CH(Br)CH_3} > \underset{1°}{CH_3CH_2CH_2CH_2CH_2Br}$

13. We know that the order of reactivity of hydrogen atoms is 3° > 2° > 1°.

(*a*) 

(*b*) 

(*c*) 

14. (*i*) The C—Br bond is longer than the C—Cl bond, therefore while the change in *e* in the dipole moment expression ($\mu = e \times d$) is smaller for the bromine than for the chlorine compound, the distance *d* is greater.

(*ii*) Write down the products obtained on homolytic C—C bond cleavage in the two cases.

$$\underset{\text{Ethane}}{H_3C{-}CH_3} \longrightarrow \underset{\text{Two methyl radicals}}{H_3\dot{C} + \dot{C}H_3} \quad ; \quad \underset{\text{Propane}}{H_3CCH_2CH_3} \longrightarrow \underset{\text{Ethyl radical}}{CH_3\dot{C}H_2} + \underset{\text{Methyl radical}}{\dot{C}H_3}$$

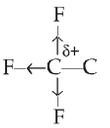
Now observe the relative stability of the products in the two cases : more the stability of the product, easier will be its formation and thus lesser will be the energy required to break that C—C bond. In present case, ethyl radical (formed in propane) is more stable than methyl radicals (formed in ethane), hence less energy will be required to break C—C bond in propane than in ethane.

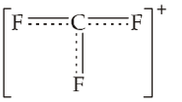
(*iii*) Dry hydrogen halides are stronger acids and better electrophiles than the H_3O^+, formed in aqueous solution of hydrogen halides. Furthermore, H_2O is a nucleophile that can react with R^+ to give ROH.

(*iv*) Carbon-iodine bond is weak (bond energy 45.5 Kcal mol^{-1}) than the carbon-chlorine bond (bond energy 66.5 Kcal mol^{-1}), hence C—I breaks up easily to give I^- ions than the C—Cl bond.

(*v*) This reaction is an E2 reaction ; and involves the cleavage of the C—H (or C—D) bond in the rate determining step. Now the C—H bond, being weaker, breaks rapidly than the stronger C—D bond, hence CH_3CH_2I loses HI faster than the CD_3CH_2I loses DI.

(*vi*) In $F_3C{-}\overset{+}{C}H_2$, carbon bearing three electronegative atoms develops partial positive charge. Such species having similar charge on the adjacent carbon atoms will be unstable.





On the other hand, in $F_3\overset{+}{C}$, the unshared electron pair in the *p*-orbital of each of the fluorine can delocalize to electron deficient carbon (*p-p* overlapping) with the result the carbocation $F_3\overset{+}{C}$ is stabilised.

15. The more stable the carbocation, more reactive will be the corresponding alkyl halide. Further the C—I bond is weak, it will be quite reactive in case when iodine is present on sp^3-hybridised carbon, than the C—Cl or C—Br.

(*a*) *tert*-Butyl bromide and benzyl bromide will be most reactive because their corresponding carbocations ($Me_3\overset{+}{C}$ and $C_6H_5\overset{+}{C}H_2$) are quite stable. *n*-Hexyl iodide is also very reactive because of weak C—I bond and the carbocation is not destabilised.

(*b*) *n*-Hexyl chloride and *sec*-butyl chloride.

(*c*) *Inert even on heating.* Bromobenzene ($C_6H_5^+$ is very unstable) and CCl_4 ($\overset{+}{C}Cl_3$ is unstable because of —I effect of chlorine atoms).

16. We know that rates are proportional to the products of the concentrations of the reactants, thus

$$\frac{\text{Rate}}{5.44 \times 10^{-9}\ \text{mol dm}^{-3}\text{s}^{-1}} = \frac{(0.1\ \text{mol dm}^{-3})\,(0.1\ \text{mol dm}^{-3})}{(0.01\ \text{mol dm}^{-3})(0.01\ \text{mol dm}^{-3})}$$

$\therefore$ Rate = **5.44×10^{-7} mol dm^{-3} s^{-1}.**

17. The given rate expression indicates that the rate is made up of two parts

$$\text{Rate} = \underbrace{4.7 \times 10^{-5}[\text{RX}][\text{OH}^-]}_{S_{N^2}} + \underbrace{0.24 \times 10^{-5}[\text{RX}]}_{S_{N^1}}$$

Hence, Percentage due to $S_{N^2} = \dfrac{S_{N^2}}{S_{N^2} + S_{N^1}} \times 100$

$$= \frac{4.7 \times 10^{-5}[\text{RX}][\text{OH}^-]}{4.7 \times 10^{-5}[\text{RX}][\text{OH}^-] + 0.24 \times 10^{-5}[\text{RX}]} \times 100 = \frac{4.7\,[\text{OH}^-]}{4.7\,[\text{OH}^-] + 0.24} \times 100$$

Thus, percentage due to S_{N^2} at various OH^- concentrations can be calculated as below.

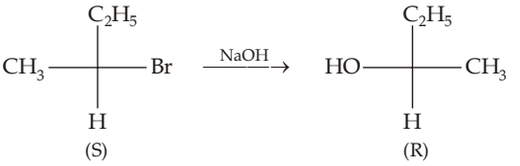
(*a*) When $[OH^-] = 0.001$, $\quad \%\ S_{N^2} = \dfrac{4.7 \times 0.001}{4.7 \times 0.001 + 0.24} \times 100 = 1.9\%$

(*b*) When $[OH^-] = 0.1$, $\quad \%\ S_{N^2} = \dfrac{4.7 \times 0.1}{4.7 \times 0.1 + 0.24} \times 100 = 66.2\%$

(*c*) When $[OH^-] = 1.0$, $\quad \%\ S_{N^2} = \dfrac{4.7 \times 1.0}{4.7 \times 1.0 + 0.24} \times 100 = 95.1\%$.

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18. According to given statement



$[\alpha]_{Actual}$	+ 30°	– 5.97°
$[\alpha]_{\text{for optically pure}}$	+ 36°	– 10.3°

(*i*) % of optical purity of the bromide $= \frac{+30°}{+36°} \times 100 = 83\%$

% of optical purity of the alcohol $= \frac{-5.97°}{-10.3°} \times 100 = 58\%$

(*ii*) Percentage of inversion is calculated by dividing the percentage of optically active alcohol of opposite configuration by that of reacting bromide, *i.e.*

$$\% \text{ inversion} = \frac{58}{83} \times 100 = 70\%$$

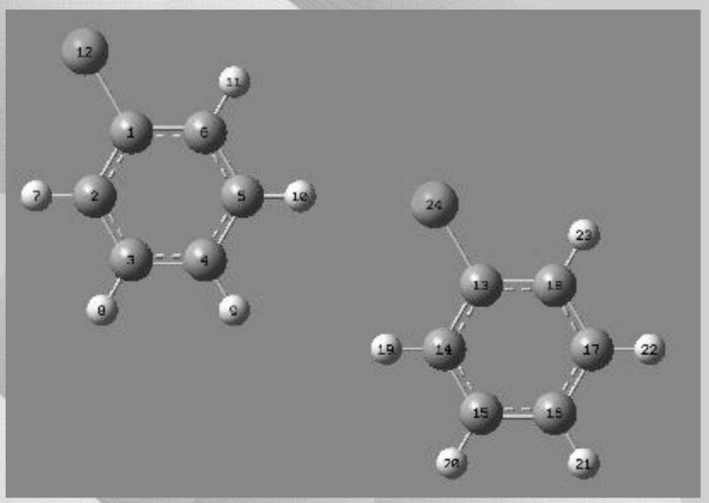
$\therefore$ % racemisation = 100%—70% = 30%

(*iii*) We know that inversion involves only backside attack, while racemization results from equal backside and frontside attack. The percentage of backside reaction is the sum of inversion and one-half of the racemization ; while percentage of frontside attack is the remaining half of the percentage of racemization. Thus

$$\% \text{ Backside reaction} = 70\% + \frac{1}{2}(30\%) = \mathbf{85\%}$$

$$\% \text{ Frontside reaction} = \frac{1}{2}(30\%) = \mathbf{15\%}$$

The inversion takes place in S_{N^2} reaction, thus more the rate of S_{N^2} reaction higher will be inversion. The S_{N^2} rate can be increased by increasing the concentration of the nucleophile, *i.e.* OH^-.



9

Aryl Halides

CHAPTER HIGHLIGHTS

9.1 Methods of Preparation

9.2 Physical Properties

9.3 Chemical Properties

9.4 Nucleophilic Aromatic Substitution

9.5 Arylalkyl Halides

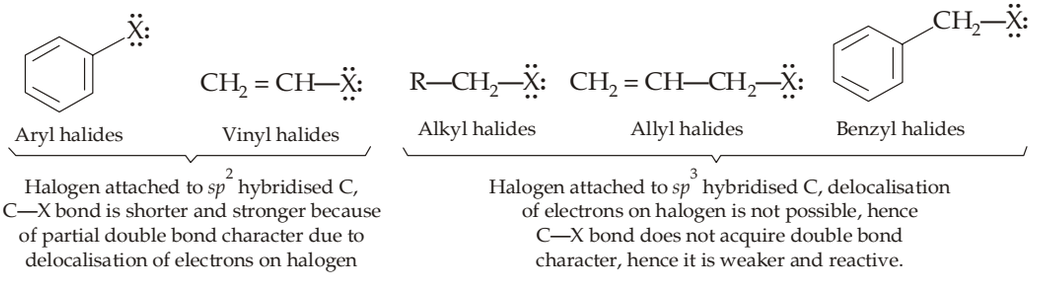
EXERCISES

SOLUTIONS

Aryl halides are the compounds having halogen atom directly attached to the aromatic ring. They are represented by the general formula AR—X where Ar may be phenyl, substituted phenyl or other aromatic system *e.g.* naphthyl.

All compounds containing aromatic ring and a halogen atom should not be considered as aryl halides *e.g.* benzyl chloride ($C_6H_5CH_2Cl$) is not an aryl halide because chlorine is not directly attached to the ring ; rather benzyl chloride and other related compounds resemble alkyl halides in structure and properties too.

The carbon-halogen bonds of aryl halides are both shorter and stronger than the carbon-halogen bonds of RX, and in this respect as well as in their chemical behaviour, they resemble vinyl halides ($H_2C = CH—X$) more than alkyl halides.



The strength of the C—X bonds causes aryl halides to react very slowly in reactions in which cleavage of C—X bond is rate-determining, *i.e.* nucleophilic substitution. However, we will study certain examples of such reactions that do take place at reasonable rates either at high temperatures or by mechanisms, distinctly different from the classical S_N1 and S_N2 pathways.

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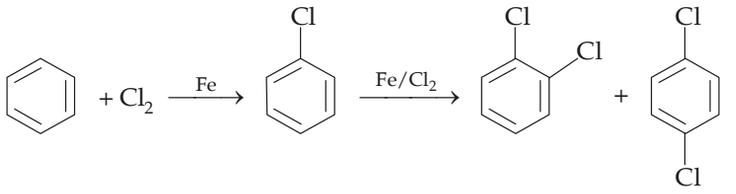
TEST YOUR UNDERSTANDING - 9.1

1. Write down all isomers of an aromatic compound of the formula C_7H_7Cl. Comment on the C—Cl bond strength of the various isomers.

9.1 Methods of Preparation

Methods used for the preparation of alkyl halides are not applicable for the synthesis of aryl halides, *e.g.* alkyl halides are most readily prepared from the corresponding alcohols ; while **aryl halides are not prepared from the phenols.** The reason being *the stronger Ar—OH bond in phenols because of partial double bond character of the C—O bond and/ or sp^2 hybridization of the carbon bearing —OH group. Important methods are given below.*

1. **By direct halogenation of arenes.** Aryl chlorides and bromides are conveniently prepared by treating the corresponding arene with chlorine (or bromine) at low temperature and in the presence of halogen carrier (Fe, $FeCl_3$, AlX_3 etc.). The reaction is an example of **electrophilic aromatic** substitution and has already been discussed.



NOTE THAT

(*i*) fluorination is difficult to control.

(*ii*) iodination is too slow to be useful.

2. **By the decomposition of diazonium salts.** Arene diazonium salts are obtained by treating aromatic amines with nitrous acid at 0—5°C. The diazonium salts decompose easily on heating with cuprous chloride or cuprous bromide in presence of haloge acids to form the corresponding chloride or bromide (**Sandmeyer reaction).**

$$Ar—NH_2 \xrightarrow[0°C]{HONO} Ar—N_2^+ \xrightarrow[\text{or CuBr}]{CuCl} Ar—Cl \quad \text{or} \quad Ar—Br$$

Aryl fluorides are obtained by treating the diazonium salt with fluoroboric acid (HBF_4) or its salt by to form sparingly soluble arenediazonium fluoroborate. The solid so obtained is carefully heated after drying to form aryl flouride (**Balz-Schiemann reaction).**

$$Ar—N_2^+X^- + HBF_4 \longrightarrow Ar—N_2^+BF_4^- \xrightarrow{heat} Ar—F + N_2 + BF_3$$

Aryl iodides are obtained by treating the diazonium salt with aqueous potassium iodie.

$$Ar—N_2^+X^- + KI \longrightarrow Ar—I + N_2 + KX$$

NOTE

Preparation of aryl halides from diazonium salts is more important than direct halogenation of arenes due to following reasons.

(*i*) Fluorides and iodides can be easily prepared.

(*ii*) Halogenation gives a mixture of *ortho* and *para* isomers which are difficult to separate, while it is not so in method involving diazonium salt.

3. **Hunsdiecker method.** Silver salts of aromatic acids are heated with chlorine or bromine.

$$C_6H_5COOAg + Cl_2 \longrightarrow C_6H_5Cl + CO_2 + AgCl$$

4. **Industrial method for chlorobenzene.** $2C_6H_6 + 2HCl\ (g) + O_2\ (air) \xrightarrow[heat]{CuCl_2} 2C_6H_5Cl + 2H_2O$

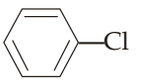
TEST YOUR UNDERSTANDING - 9.2

1. Give steps invovled in the preparation of *o*-nitrochlorobenzene and *p*-nitrochlorobenzene from benzene.

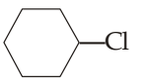
9.2 Physical Properties

(*i*) Aryl halides resemble alkyl halides in many of their physical properties like insolubility in water and denser than water. Insolubility in water is due to their incapability of forming hydrogen bonds.

(*ii*) Aryl halides are less polar than alkyl halides because in aryl halides, halogen is present on sp^2 hybridised carbon which is more electronegative than the sp^3 hybridised carbon of alkyl halides or halocyclohexane. Consequently, the electronegativity difference between C and Cl is low in aryl halides than in alkyl halides.



Chlorobenzene
(C—Cl bond is less polar and shorter in length)
μ = 1.7 D



Chlorocyclohexane
(C—Cl bond is more polar and longer in length)
μ = 2.2 D

Further due to possibility of resonance in chlorobenzene, the C—Cl bond becomes shorter and hence dipole moment of chlorobenzene is less than that of chlorcyclohexane.

(*iii*) The isomeric dihalobenzenes have nearly the same boiling points, yet the melting points of the isomers show a considerable difference, the *para* **isomer has 70—100°C higher melting poing than the** *ortho* **and** *meta* isomers. This is due to the fact that the *para* isomers, being symmetrical, are better packed in the crystal lattice. This explains why **only the** *para isomer* **crystallises on cooling** a solution containing *ortho* and *para* isomers. Further, due to strong intracrystalline forces, the higher-metling **para isomer is less soluble in a given solvent than the ortho isomer.**

9.3 Chemical Properties

1. **Formation of organometallic compounds.** Aryl halides react with magnesium in presence of dry ether to form the corresponding arylmagnesium halides (**Grignard reagents**).

$$ArX + Mg \xrightarrow{\text{ether}} Ar\,MgX$$

Aryl iodides are the most reactive, while aryl fluorides the least.

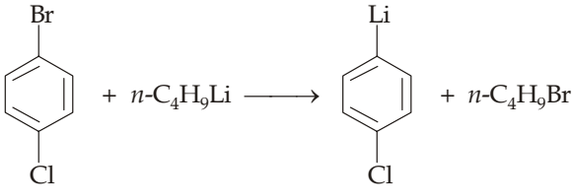
Remember that (*a*) ArX is less reactive than RX in forming Grignard reagents, and (*b*) tetrahydrofuran is used as a solvent for ArCl.

Aryllithiums are obtained by treating an ethereal solution of aryl halides with lithium metal.

$$\underset{(X = Cl, Br)}{C_6H_5X} + 2Li \xrightarrow{\text{ether}} C_6H_5Li + LiX$$

$$C_6H_5X + 2Li \xrightarrow{\text{ether}} LiX + \underset{\text{Phenyllithium}}{C_6H_5 : Li} \longleftrightarrow C_6H_5^- : Li^+$$

Aryllithium compounds may also be obtained by the halogen-metal exchange when aryl halides are treated with *n*-butyllithium.



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2. Wurtz-Fittig and Fittig reactions.

(*a*) $C_6H_5X + 2Na + XC_2H_5 \xrightarrow{\text{ether}} C_6H_5C_2H_5 + 2NaX$

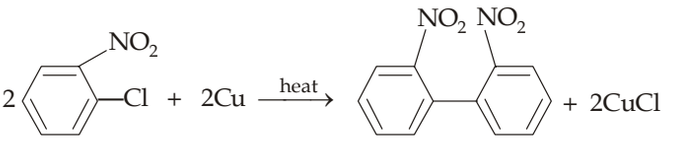
$C_6H_5Cl + 2Na + ClCH_2C_6H_5 \xrightarrow{\text{ether}} \underset{\text{Diphenylmethane}}{C_6H_5CH_2C_6H_5} + 2NaCl$

(*b*) $C_6H_5Cl + 2Na + ClC_6H_5 \xrightarrow[\text{Fittig reaction}]{\text{ether}} \underset{\text{Diphenyl}}{C_6H_5C_6H_5} + 2NaCl$

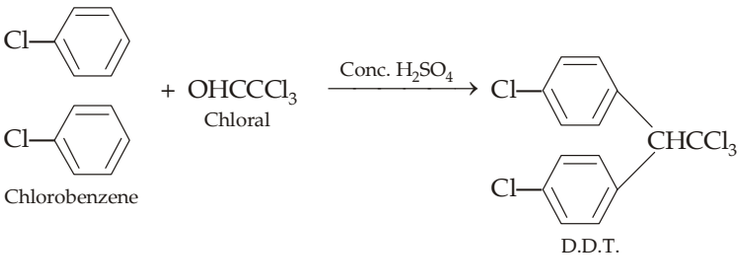
3. Ullmann reaction.

$$2C_6H_5I + 2Cu \xrightarrow[\text{sealed tube}]{\text{heat in a}} C_6H_5C_6H_5 + 2CuI$$

Aryl chlorides and bromides respond Ullmann reaction only when an electron-withdrawing group is present in *ortho* or *para* position.



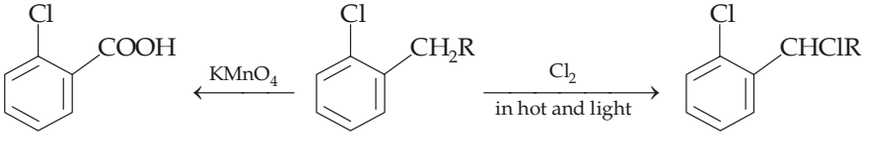
4. Reaction with chloral. When chlorobenzene is heated with chloral in presence of conc. H_2SO_4, a powerful insecticide DDT (*p, p'*-dichlorodiphenyl trichloromethane).



IUPAC name of DDT is 2, 2'-*bis* (*p*-chlorophenyl)1, 1, 1-trichloroethane.

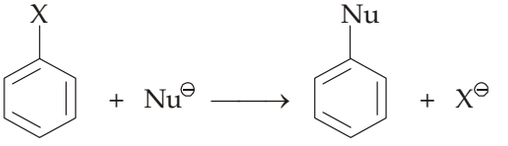
5. Electrophilic aromatic substitution. Aryl halides undergo the typical electrophilic substitution reactions in the *ortho* and *para*-positions, though less readily than benzene because halogens deactivate the benzene nucleus due to its high electro-negativity. However, inspite of deactivating nature, halogens are *o, p*-directing due to + M and + E effects (*difference from other o, p-directing groups which are activating*). Its mechanism has already been discussed.

6. Reactions of the side chain of aryl halides. Side chain, if present, may undergo (*i*) halogenation in presence of light (free radical substitution), and (*ii*) oxidation.

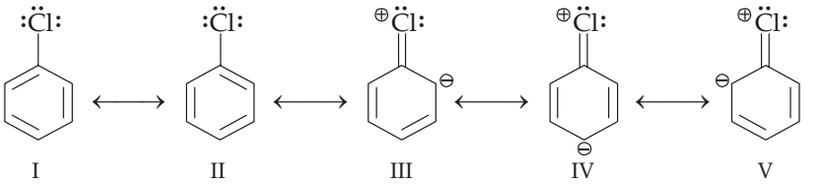


9.4. Nucleophilic Aromatic Substitution

Aromatic nucleophilic substitution are those reactions in which a leaving group is displaced along with its bonding electrons from a ring carbon atom by a nucleophile.

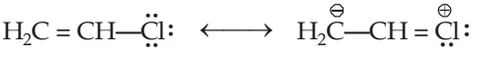


However, aryl halides (like vinyl halides) do not undergo nucleophilic substitutions under ordinary conditions (difference from alkyl halides which undergo these reactions very easily). For example, aryl halides (*e.g.* chlorobenzene) do not react with nucleophiles like OH^-, OR^-, NH_3, CN^- etc. Under ordinary conditions, low reactivity or inert nature of aryl halides towards nucleophilic substitution is due to the fact that the non-bonding pair of electrons on the halogen are in conjugation with the ring causing resonance stabilisation of the compound by delocalisation of electrons.



I II III IV V

Resonance stabilization of chlorobenzene



VI VII

Resonance stabilisation of vinyl chloride

TEST YOUR UNDERSTANDING - 9.3

1. Which halogen best delocalizes electron density to the benzene ring ?

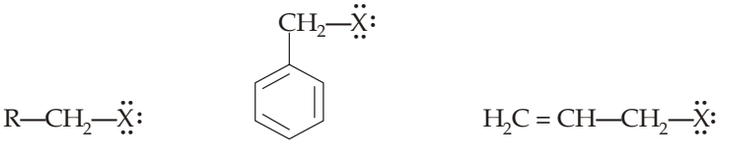
Possibility of resonance in aryl halides and vinyl halides produces following important results.

(*a*) Stabilisation of the molecule by delocalisation of electrons.

(*b*) The carbon-halogen bond acquires double bond character (structures III, IV, V and VII) and thus becomes shorter and stronger than a single bond present between carbon-halogen in alkyl halides. Both these factors reduce reactivity of the halogen.

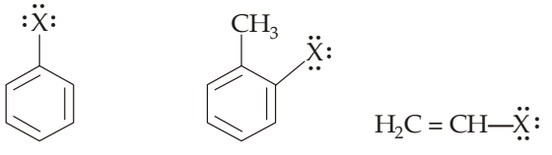
Low reactivity of aryl halides and vinyl halides than alkyl halides can **alternatively be interpreted in terms of hybridisation** of the carbon atom bearing halogen. In alkyl halides, the carbon hearing halogen is sp^3-hybridised. In aryl and vinyl halides, carbon is sp^2-hybridised ; and thus the carbon-halogen bond is shorter (due to more electronegative nature of sp^2 carbon than that of sp^3) and stronger. Thus halogen derivatives can be categorised in two main groups on the basis of reactivity of the halogen atom.

(*i*) Those in which halogen is present on sp^3-hybridised carbon atom, such halogens are highly reactive. For example,



Alkyl halides Aryl substituted alkyl halides Allyl halides

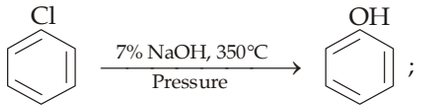
(*ii*) Those in which halogen is present on sp^2-hybridised carbon atom, such halogens are relatively inert. For example,



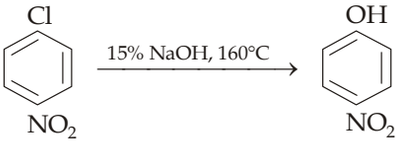
Aryl halides Vinyl halides

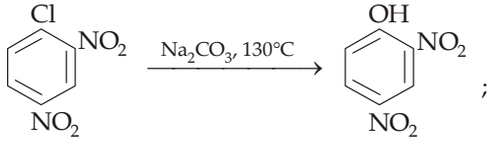
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However, aryl halides having electron-attracting substituents* (like —NO_2, —CN, —$\overset{+}{N}Me_3$, —SO_3H, —COOH, —CHO, —COR), in *ortho* and *para* positions undergo nucleophilic substitution very easily. Further, greater the number of such groups in *o*-and *p*-positions, more rapid is the reaction and less vigorous conditions are needed. For example,

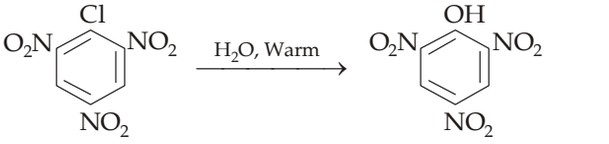


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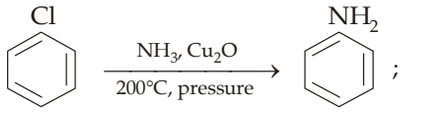


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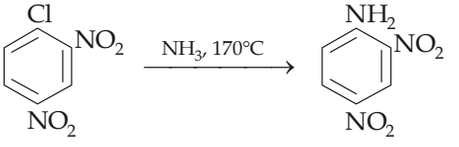


2, 4, 6-Trinitrochlorobenzene 2, 4, 6-Trinitrophenol (Picric acid)

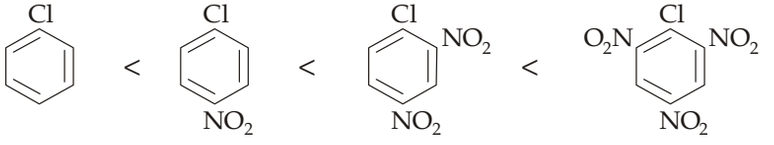
Similar effects are observed when other nucleophilic reagents *e.g.* NH_3, CH_3ONa are used.



;



Thus the relative rate of nucleophilic substitution for the various chlorobenzenes is



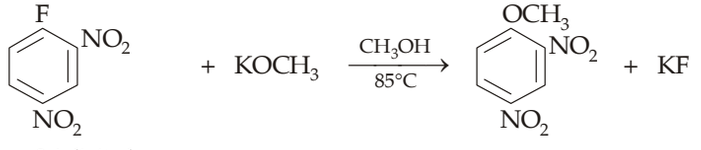
Since electron-withdrawing groups activate toward nucleophilic substitution, electron-releasing groups deactivate, the various groups can be categorised in three groups for nucleophilic substitution.

(*i*) Strongly electron-releasing groups, —NH_2 and —OH deactivate strongly.

(*ii*) Moderately electron-releasing groups, *e.g.* —OR deactivate moderately.

(*iii*) Weakly electron-releasing groups (like —R group) deactivate moderately.

Relative reactivity of halogens toward nucleophilic substitution. In contrast to nucleophilic substitution in alkyl halides, where alkyl fluorides are exceedingly unreactive, aryl fluorides undergo nucleophilic substitution readily when the ring bears an *o*- or *p*-nitro group.



1-Fluoro-2,4-dinitrobenzene
(Sanger's reagent)

Indeed, the order of leaving-group reactivity in nucleophilic substitution is opposite to that observed in aliphatic substitution; in aromatic nucleophilic substitution fluoride is the most reactive and iodide the least.

Ar—F > Ar—Cl > Ar—Br > Ar—I **(Relative reactivity of halogens in S_N2Ar).**

The unusually high reactivity of aryl fluorides (although having a strong C—F bond) is due to very high electronegativity of fluorine due to which it can disperse the negative charge of the intermediate carbanion most easily leading to increased rate of formation of the intermediate carbanion (see mechanism discussed just after this).

Mechanism. Nucleophilic aromatic substitution takes place by two mechanisms (*i*) Bimolecular mechanism is applicable to reaction of aryl halides, having electron withdrawing group, with the usual nucleophiles like NaOH, CH_3ONa etc. (*ii*) Benzyne mechanism is applicable when aryl halides are treated with strong base like NH_2^- or with usual nucleophiles like NaOH, NH_3, CH_3ONa etc. under drastic conditions.

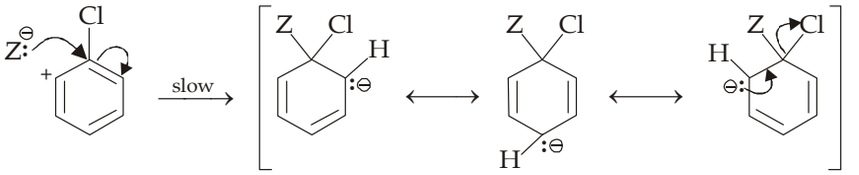
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* Note that all these groups are deactivating and *meta*-directing towards electrophilic substitution.

9.4.1 Bimolecular Displacement Mechanism (Addition-Elimination Mechanism)

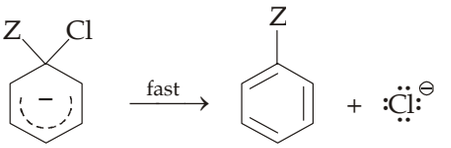
It has two steps.

(*i*) *Addition of nucleophile* **(slow step).** Resonating structures III, IV and V of chlorobenzene indicate that C_1, C_3 and C_5 are relatively electron-deficient. Further among these three, C_1 is most electron-deficient because it has strongly electron-withdrawing group. Hence the nucleophile will undoubtedly attack on C_1 to form carbanion.

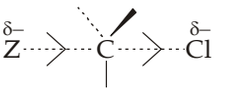


A resonance stabilised cyclohexadienyl carbanion

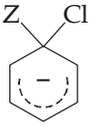
(*ii*) *Expulsion of halide ion from the carbanion* **(fast step)** to form the product, having a stable benzenoid nucleus.



Comparison of intermediate in biomolecular nucleophilic aliphatic substitution (S_N2) and bimolecular nucleophilic aromatic substitution (S_N2Ar). Recall that in aliphatic S_N2 reactions, there is no intermediate, actually a transition state is formed in which a carbon bonded to five atoms is present which is unstable. On the other hand, in nucleophilic aromatic substitution, the intermediate is an actual compound which is quite stable because of delocalization of the negative charge.



Transition state in aliphatic S_N2
(Note the pentavalent carbon)



Intermediate in aromatic nucleophilic substitution
(Note the tetrahedral carbon)

TEST YOUR UNDERSTANDING - 9.4

1. Compare bimolecular aromatic nucleophilic and electrophilic substitution reactions with aliphatic S_N2 reactions in terms of (*a*) number of steps and transition states, (*b*) character of intermediates.

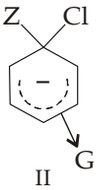
Effect of substituents on nucleophilic aromatic substitution (Relative reactivity in nucleophilic aromatic substitution).

We have seen that in S_NAr (aromatic nucleophilic substitution) reactions, a carbanion is formed as an intermediate, so any substituent that increases the stability of the intermediate carbanion and hence the transition state leading to its formation will enhance the S_NAr reaction.

To compare the rates of substitution in chlorobenzene, chlorobenzene having electron-withdrawing group, and chlorobenzene having electron-releasing group, we compare the structures carbanion I (from chlorobenzene), II (from chlorobenzene containing electron-withdrawing group) and III (from chlorobenzene containing electron-releasing group).



I



II

G withdraws electrons, neutralises (disperses) –ve charge of the ring, stabilises carbanion, facilitates S_N reaction (**activation effect**)



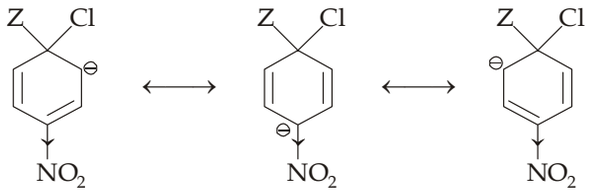
III

G releases electrons, intensifies –ve charge, destabilizes carbanion, retards S_N reaction (**deactivation**)

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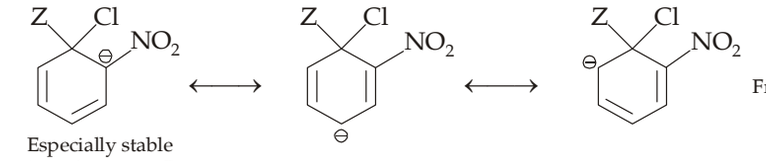
Common groups that activate S_N Ar reactions are —NMe_3^+, —NO_2, —CN, —SO_3H, —COOH, —CHO, —COR and —X ; while the corresponding deactivating groups are —NH_2, —OH, —OR and —R. Note that S_N Ar activating groups are deactivating groups for electrophilic aromatic substitution, while the S_N Ar deactivating groups act as activating groups for electrophilic aromatic substitution.

Ortho- **and** *para-***Nitrochlorobenzenes are more reactive than the** *m-***isomer.** This is again due to more stability of the intermediate carbanion from *o-* and *p-* than that from *meta*.



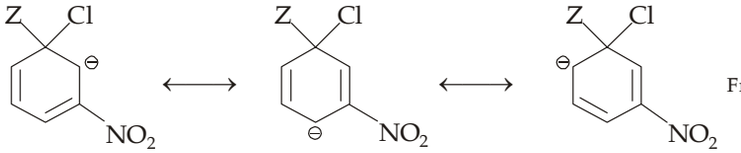
Especially stable (because –ve charge on C bearing —NO_2 is neutralised most)

Resonating structures of the intermediate carbanion from the *p*-isomer



Especially stable (–ve charge on C bearing —NO_2 group)

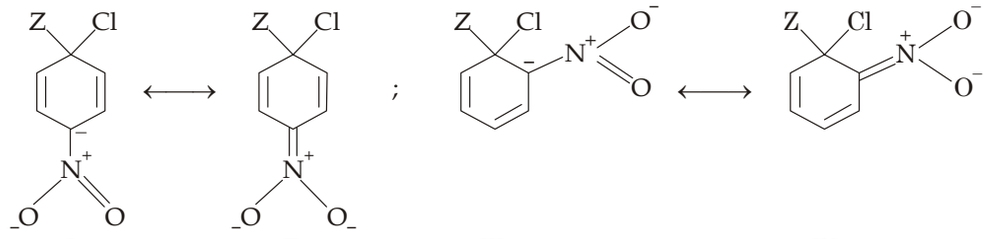
From the *o*-isomer



From the *m*-isomer

Similarly, we can see that deactivation by an electron-releasing group is strongest when it is *ortho* or *para* to the halogen.

The activating effect of a number of electron-withdrawing groups (like —NO_2, —CN, —COOH, —COR, —NO etc.) toward nucleophilic substitution can also be accounted by resonance, this is in addition to explanation by inductive effect. For example, the intermediate carbanions from *p*-and *o*-isomer are especially stable due to structures II and IV respectively than that from the *m*-chloronitrobenzene or chlorobenzene itself.



I II III IV

Especially stable (oxygen readily accommodates negative charge)

Especially stable

TEST YOUR UNDERSTANDING - 9.5

1. Write resonance structures to account for activation in S_N2Ar from delocalization of the charge of the intermediate carbanion by —CN and —NO groups present in *para*-position.

2. Nitrosogroup, —NO activates *ortho* and *para* positions toward nucleophilic as well as electrophilic aromatic substitution. Explain.

Comparision of S_N1, S_N2 (observed in R—X) **and S_N2** (observed in Ar—X).

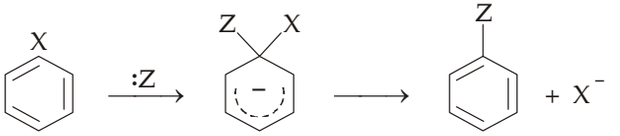
(*i*) In S_N1, the leaving group departs the molecule before the entering group, thus a full positive charge is developed on carbon. Hence such reactions are favoured by electron release.

(*ii*) In alkyl S_N2, the leaving group and entering group departs and enters respectively simultaneously and thus no charge develops on carbon. Hence these reactions are insensitive to electronic factors.

(*iii*) In Ar S_N2, the leaving group departs the molecule in the last and thus a negative charge is developed on the molecule. Hence such reactions are favoured by electron withdrawal

$$R{-}X \xrightarrow[(-X^-)]{} R^+ \xrightarrow{:Z} R{-}Z \qquad \mathbf{S_N1}$$

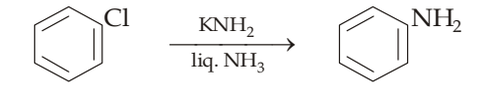
$$R{-}X \xrightarrow{:Z} [^{\delta-}Z\text{------}R\text{------}X^{\delta-}] \longrightarrow R{-}Z + X^- \qquad \mathbf{S_N2}$$



$\mathbf{S_N2Ar}$

9.4.2 Benzyne Mechanism (Elimination-Addition Mechanism)

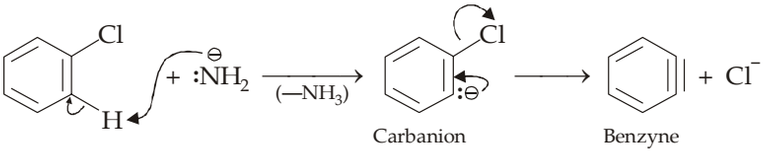
Unactivated aryl halides (aryl halides not having electron-withdrawing group) when treated with strongly basic nucleophiles, such as amide ion or with usual nucleophiles under drastic conditions undergo substitution by an elimination-addition (**benzyne**) mechanism.



Chlorobenzene Aniline

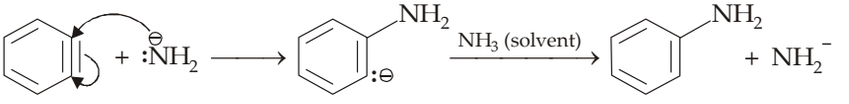
The most important requirement for this mechanism is the presence of an ortho hydrogen atom. The reaction is initiated by a two-step elimination of HX generating a highly reactive intermediate called **benzyne (dehydrobenzene)** which then readily reacts with nucleophile to regenerate aromatic system.

Elimination step.



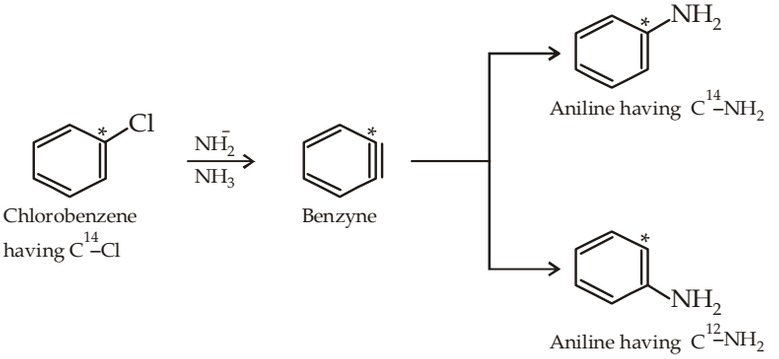
Carbanion Benzyne

Addition step.



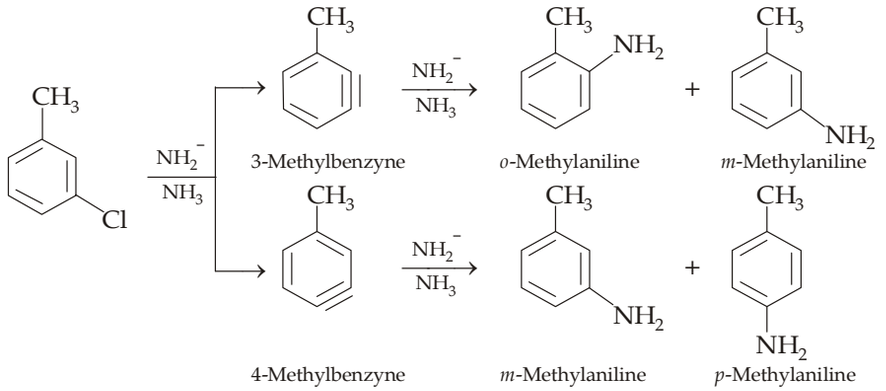
Carbanion

The above mechanism involving benzyne intermediate is proved by isotopic method. Labelled chlorobenzene (a chlorobenzene molecule in which carbon bearing chlorine is labelled *i.e.* it is C^{14} carbon), when treated with amide ion, two different anilines are formed nearly in equal amounts : (*i*) aniline having —NH_2 group on the usual carbon (C^{12}) and (*ii*) aniline having —NH_2 group on the labelled carbon (C^{14}).

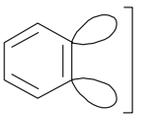


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Formation of benzyne as an intermediate also explains why *m*-chlorotoluene gives all the three isomers (*o*-, *m*- and *p*-) of methylanilines.



Structure of benzyne. Aromatic compounds related to benzyne are known as **arynes.** The triple bond in benzyne is somewhat different from the usual triple bond of an alkyne. In benzyne, one of the π components of the triple bond is similar to that of other π bonds of benzene, *i.e.* it is formed by the *p*-*p*-overlap of the two concerned carbon atoms and hence it is a part of the delocalized π system of the aromatic ring. However, the second π bond of the triple bond of benzyne is formed from overlapping of two sp^2 hybridized orbitals. This π bond lies in the plane of the ring, and does not interact with the aromatic π system. Since the contributing sp^2-orbitals are not oriented properly for effective overlap, this π bond is relatively weak.



Degree of overlap of the two sp^2 orbitals is very poor because they lie in the plane of the ring.

Absence of linearity of the C—C ≡ C—C unit due to benzene ring and weak nature of one of the π bonds of the triple bond make **benzyne a strained and highly reactive species.**

TEST YOUR UNDERSTANDING - 9.6

1. Explain the following :

(*i*) When a mixture containing equal amount of bromobenzene and *o*-deutereobromobenzene is treated with sodamide, the unreacted mixture contains more amount of *o*-deutereobromobenzene.

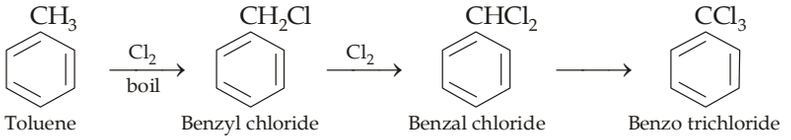
(*ii*) *m*-Bromoanisole when treated with sodamide gives mainly *m*-anisidine.

9.5 Arylalkyl Halides

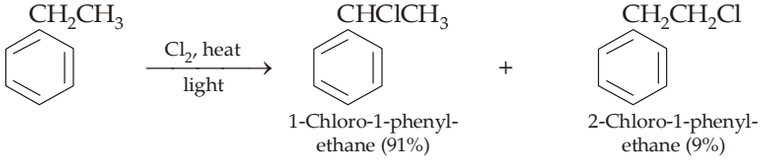
Arylalkyl halides resemble alkyl halides, in their preparation as well as reactions, rather than aryl halides.

Preparation

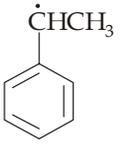
1. By direct halogenation with chlorine or bromine in presence of light and in absence of halogen carrier.



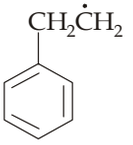
Recall that side chain halogenation of ethylbenzene and other higher alkylbenzenes gives mainly one isomer.



This is due to more stability of the corresponding (benzyl) radical

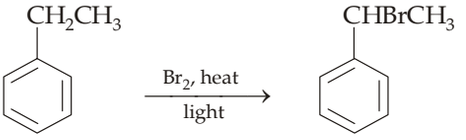


Benzyl radical **(More stable)**
(due to delocalisation of odd electron)



β-Phenylethyl radical (1°)

Note that although chlorination of ethylbenzene gives 1-chloro- (major) as well as 2-chloro-(minor) products, bromination of ethylbenzene gives exclusively 1-bromo-1-phenylethane.



1-Bromo-1-phenylethane
(only product)

This can be explained on the basis of *selectivity reactivity principle.* Chlorine, being more reactive, is less selective and hence gives another product although in less quantity; while bromine, being less reactive, is more selective, hence will replace more selectively α-hydrogen atom giving exclusively 1-bromo-1-phenylethane.

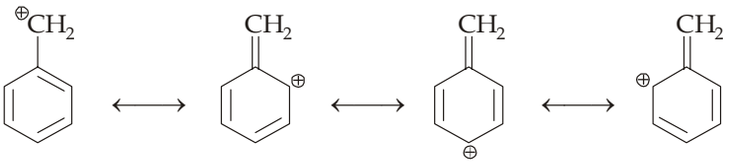
2. Like alkyl halides (but not aryl halides), arylalkyl halides can be prepared by the action of PCl_5 or $SOCl_2$ on benzyl alcohol.

$$C_6H_5CH_2OH + PCl_5 \text{ (}or\text{ } SOCl_2) \longrightarrow C_6H_5CH_2Cl + HCl + POCl_3 \text{ (}or\text{ } SO_2)$$

Benzal chloride can directly be prepared by the action of PCl_5 on benzaldehyde.

$$C_6H_5CHO + PCl_5 \longrightarrow C_6H_5CHCl_2 + POCl_3$$

Properties. As already mentioned and explained in the beginning, arylalkyl halides, *e.g.* benzyl chloride, resemble alkyl halides closely in their chemical properties and thus differ from aryl halides, *e.g.* chlorobenzene and vinyl halides. Actually benzyl halides are more reactive than alkyl halides which is due to resonance stabilisation of the benzyl cation.



Resonating structures of benzyl cation.

Important reactions of benzyl chloride are summarised below.

1. Nucleophilic substitution reactions.

$$C_6H_5CH_2Cl + :\overset{\ominus}{N}u \longrightarrow C_6H_5CH_2Nu + Cl^-$$

(Where $:\overset{\ominus}{N}u = OH^-, NH_2^-, CN^-, OC_2H_5^-$ etc.)

Benzal chloride and benzotrichloride undergo alkaline hydrolysis to form benzaldehyde and benzoic acid respectively (*industrial methods*).

$$\underset{\text{Benzal chloride}}{C_6H_5CHCl_2} \xrightarrow{Ca(OH)_2} \underset{\text{Unstable}}{C_6H_5CH(OH)_2} \xrightarrow{-H_2O} \underset{\text{Benzaldehyde}}{C_6H_5CHO}$$

$$\underset{\text{Benzo trichloride}}{C_6H_5CCl_3} \xrightarrow{Ca(OH)_2} \underset{\text{Unstable}}{C_6H_5C(OH)_3} \xrightarrow{-H_2O} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

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2. Reaction with certain metals

(*i*) $C_6H_5CH_2Cl + 2Na + ClH_2CC_6H_5 \xrightarrow[\text{ether}]{\text{dry}} \underset{\text{Dibenzyl}}{C_6H_5CH_2CH_2C_6H_5}$ **(Wurtz reaction)**

(*ii*) $C_6H_5CH_2Cl + 2Na + ClC_6H_5 \xrightarrow[\text{ether}]{\text{dry}} \underset{\text{Dipenylmethane}}{C_6H_5CH_2C_6H_5}$ **(Wurtz-Fittig reaction)**

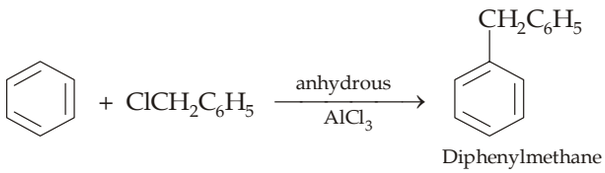
(*iii*) $C_6H_5CH_2Cl + 2Cu + ClCH_2C_6H_5 \xrightarrow[(-Cu_2Cl_2)]{} C_6H_5CH_2CH_2C_6H_5$ **(Ullmann reaction)**

(*iv*) $C_6H_5CH_2Cl + Mg \xrightarrow{THF} C_6H_5CH_2MgCl \xrightarrow{ClCH_2C_6H_5} \underset{\text{Dibenzyl}}{C_6H_5CH_2CH_2C_6H_5}$

(*v*) $C_6H_5CH_2Cl + 2[H] \xrightarrow[\text{(Reduction)}]{Zn/Cu} \underset{\text{Toluene}}{C_6H_5CH_3} + HCl$ **(Reduction)**

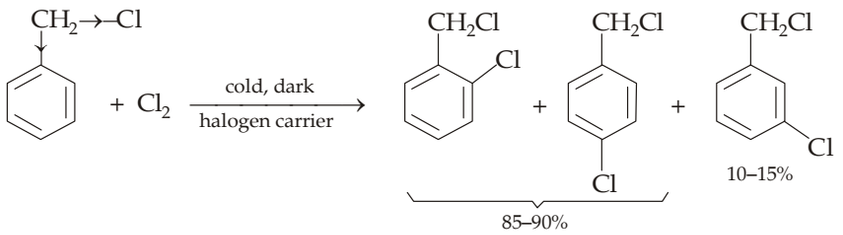
3. Friedel-Craft reaction.

Like alkyl halides, it reacts with benzene to form alkyl-benzenes (difference from chlorobenzene which does not undergo Friedel-Craft reaction because of unstability of the $C_6H_5^+$ cation)

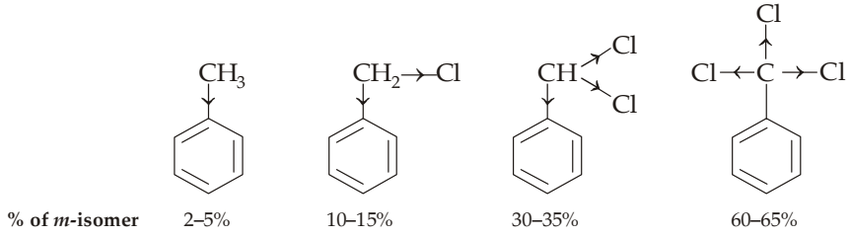


4. Aromatic electrophilic substitution reactions.

Due to presence of benzene nucleus, benzyl chloride undergoes electrophilic substitution mainly in the *o*- and *p*-positions, but with significant (10—15%) amount of the *m*-isomer. Formation of *m*-isomer is due to the presence of Cl in —CH_2Cl which decreases the electron-releasing power of the parent —CH_3 group.

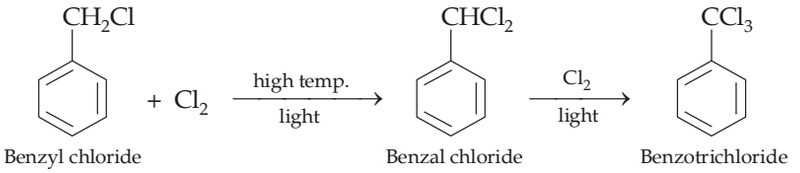


Thus we can explain the increased percentage of the *m*-isomer during electrophilic substitution, with the increase in number of Cl atoms in the —CH_3 group.



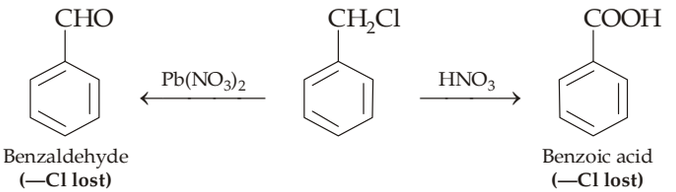
5. Halogenation in the side chain.

Halogenation, when carried out in presence of sunlight or UV rays, takes place in the side chain **(free-radical halogenation).**

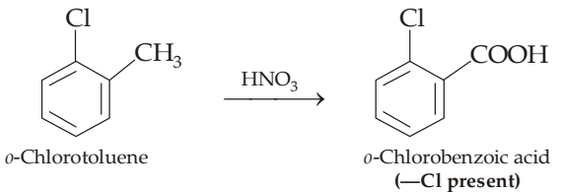


6. Oxidation of the side chain.

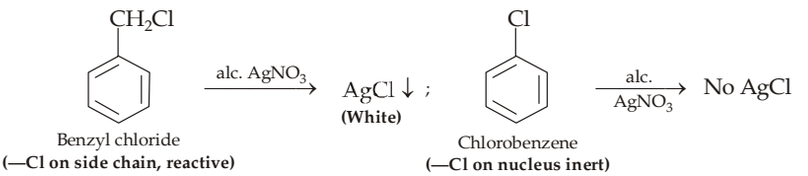
On oxidation, the side chain along with the halogen atom is oxidised to either —CHO or —COOH group depending upon the nature of the oxidising agent.



Recall that —Cl present on the benzene nucleus is inert to oxidation and hence it will be present in the oxidised product.



Thus oxidation along with reaction with alcoholic silver nitrate can be used for differentiating between —Cl present on nucleus and on the side chain.

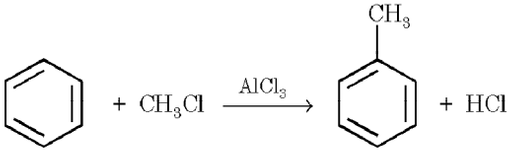


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EXERCISE 9.1 (MCQ - ONE option correct)

1. IUPAC name of DDT is
(*a*) *p, p'*-dichlorodiphenyl trichloroethane
(*b*) 4, 4'-dichlorodiphenyl trichloroethane
(*c*) 2, 2-*bis* (*p*-chlorophenyl)-1,1,1-trichloroethane
(*d*) 2, 2'-*bis* (*p*-chlorophenyl)-1,1,1-trichloroethane.

2. Which of the following statement is true regarding the following reaction



(*a*) It is an example of aromatic electrophilic aromatic substitution.
(*b*) It is an example of aliphatic nucleophilic substitution
(*c*) Both (*a*) as well as (*b*) are true
(*d*) None of the two is correct.

3. Which of the reaction is not possible ?

(*i*) $C_6H_6 + C_2H_5Cl \xrightarrow{AlCl_3} C_6H_5C_2H_5 + HCl$

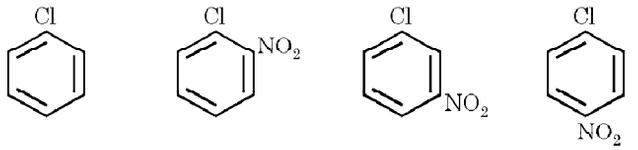
(*ii*) $C_6H_6 + C_6H_5Cl \xrightarrow{AlCl_3} C_6H_5C_6H_5 + HCl$

(*iii*) $C_6H_6 + CH_2 = CHCH_2Cl \xrightarrow{AlCl_3} C_6H_5CH_2CH = CH_2 + HCl$

(*a*) (*ii*) and (*iii*)
(*b*) (*ii*)
(*c*) (*iii*)
(*d*) All the three reactions are possible.

4. Aromatic nucleophilic substitutions are activated by
(*a*) electron-withdrawal (*b*) electron-release
(*c*) by both (*a*) and (*b*) (*d*) no definite relation.

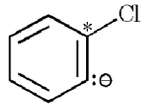
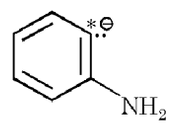
5. Arrange the following compounds in decreasing order of their reactivity with sodium methoxide in methanol at 50°C.

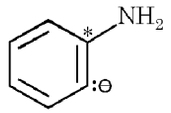


I II III IV

(*a*) II > III > IV > I (*b*) II ≈ IV > III > I
(*c*) II ≈ III > I > IV (*d*) II ≈ IV ≈ III > I.

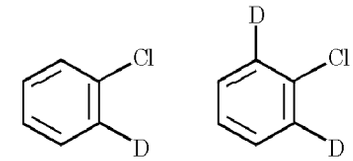
6. Reaction of chlorobenzene with sodamide in presence of liquid ammonia involves the formation of

(*a*)  (*b*) 

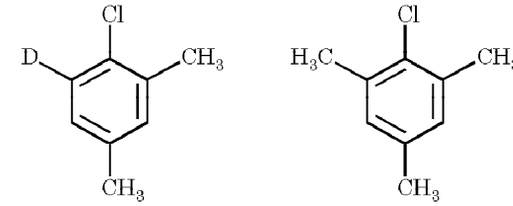
(*c*)  (*d*) All the three.

7. Benzyne has four π bonds, how many of them are identical ?
(*a*) 2 (*b*) 3
(*c*) 4 (*d*) None of the four.

8. Which of the following will not undergo nucleophilic substitution ?



I II

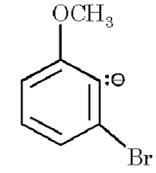
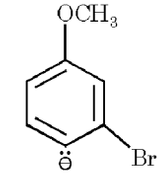


III IV

(*a*) II, III and IV (*b*) II and IV
(*c*) III and IV (*d*) only IV

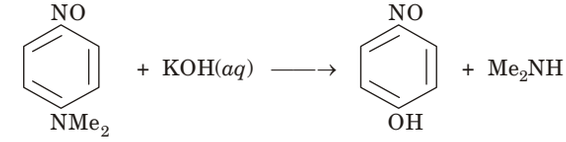
9. Which chlorine is more reactive, in the compound drawn on side, toward nucleophilic substitution ?
(*a*) Cl^a (*b*) Cl^b
(*c*) Cl^c (*d*) all are equal reactive.

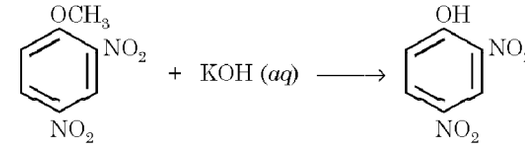
10. Which of the following carbanion is more stable ?

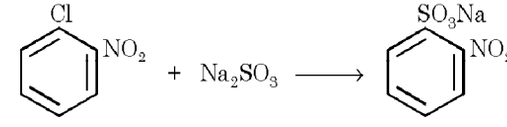
(*a*)  (*b*) 

(*c*) Both are equally stable
(*d*) Neither of the two is possible.

11. Which of the following is an example of nucleophilic aromatic substitution ?

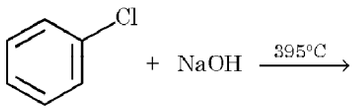
(*a*) 

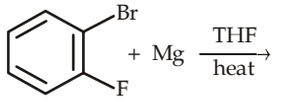
(*b*) 

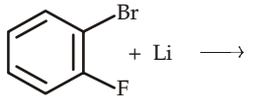
(*c*) 

(*d*) All the three.

12. Which of the reactions can form benzyne ?

I. 

II. 

III. 

(*a*) I (*b*) II and III

(*c*) All the three (*d*) None of the above.

13. In the reaction of *p*-chlorotoluene with KNH_2 in liquid NH_3, the major product is

(*a*) *o*-toluidine (*b*) *m*-toluidine

(*c*) *p*-toluidine (*d*) *p*-chloroaniline.

14. Which of the following statement is true regarding the reaction of 2, 6-dimethylchlorobenzene with aqueous NaOH ?

(*a*) It reacts only at high temperature

(*b*) It does not react even at high temperature because it has two electron-withdrawing groups.

(*c*) It does not react even at high temperature because it has no *ortho* hydrogen.

(*d*) None of the above is correct.

15. Which of the following method should be used for preparing ethylphenyl ether ?

I. $C_6H_5Cl + CH_3CH_2ONa \longrightarrow C_6H_5OCH_2CH_3$

II. $C_6H_5ONa + CH_3CH_2Br \longrightarrow C_6H_5OCH_2CH_3$

(*a*) Method I (*b*) Method II

(*c*) Both (*d*) None.

16. *o*-Chlorotoluidine can undergo

(*i*) electrophilic aromatic substitution

(*ii*) nucleophilic aromatic substitution

(*iii*) nucleophilic aliphatic substitution

(*iv*) free radical substitution

(*a*) only (*i*) (*b*) (*i*) and (*iv*)

(*c*) (*i*), (*ii*) and (*iv*) (*d*) all the four.

17. Chlorobenzene can be prepared by reacting aniline with

(a) hydrochloric acid

(b) cuprous chloride

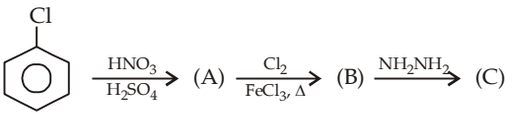
(c) chlorine in presence of anhydrous aluminium chloride

(d) nitrous acid followed by heating with cuprous chloride

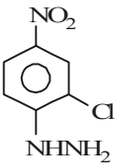
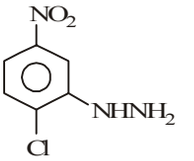
18. Benzyl chloride ($C_6H_5CH_2Cl$) can be prepared from toluene by chlorination with

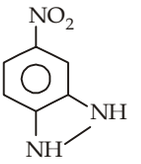
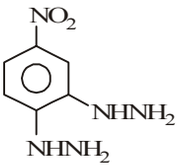
(a) SO_2Cl_2 (b) $SOCl_2$

(c) Cl_2 (d) NaOCl

19. 

(C) is :

(*a*)  (*b*) 

(*c*)  (*d*) 

20. When *p*-chlorotoluene is treated with amide ion in liquid NH_3, the major product is

(*a*) *p*-toluidine (*b*) *m*-toluidine

(*c*) *o*-toluidine (*d*) N-methylaniline

21. An aromatic compound has molecular formula C_7H_7Br. Give the possible isomers and the appropriate method to distinguish them.

(*a*) 3 isomers; by heating with $AgNO_3$ solution

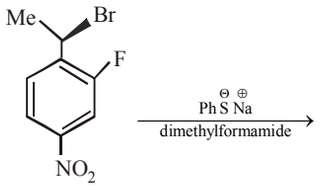
(*b*) 4 isomers; by treating with $AgNO_3$ solution

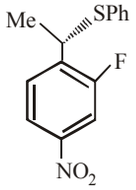
(*c*) 4 isomers; by oxidation

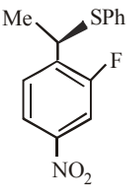
(*d*) 5 isomers; by oxidation

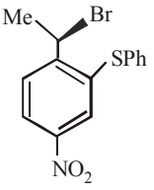
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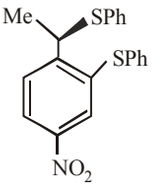
22. The major product of the following reaction is

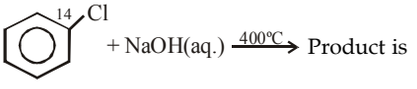


(a) 

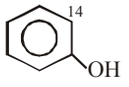
(b) 

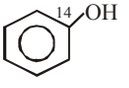
(c) 

(d) 

23. 

Product is

(a) 

(b) 

(c) Both

(d) No reaction

24. When *m*-chloronitrobenzene is treated with sodamide in presene of liquid ammonia, main product is

(a) *o*-Nitroaniline (b) *p*-Nitroaniline

(c) *m* - Nitroaniline (d) All the above

25. Which of the following statement is true regarding benzyne ?

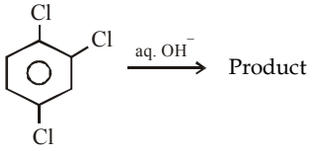
(a) It has one type of π bonds

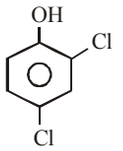
(b) It has two types of π bonds ; one is formed by the overlap of *p* - *p* orbitals and other by sp^2 - *p*

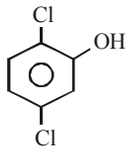
(c) It has two types of π bonds ; one is formed by the overlap of *p* - *p* orbitals and other by sp^2 - sp^2

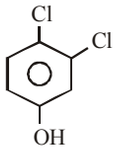
(d) It does not have benzene ring

26. Predict the product, if any, for the following reaction



(a) 

(b) 

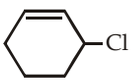
(c) 

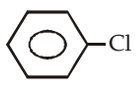
(d) No reaction

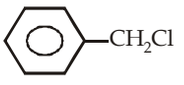
EXERCISE 9.2 (MCQ 1 or >1 option correct, Passage based, Matching, A/R)

DIRECTIONS for Q. 1 to Q. 9 : Multiple choice questions with one or more than one correct option(s).

1. Organic compound A $\xrightarrow{HNO_3 / AgNO_3}$ white ppt. A can be :

(a) NH_4Cl (b) 

(c) 

(d) 

2. Which of the following give (gives) white precipitate when boiled with alcoholic silver nitrate?

(a) Chlorobenzene

(b) Benzyl chloride

(c) Alkyl chloride

(d) Vinyl chloride

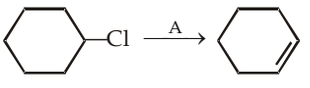
3. Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides due to :

(a) The formation of less stable carbonium ion

(b) Resonance stabilization

(c) Longer carbon-halogen bond

(d) sp^2 hybridized carbon attached to the halogen.

4. 

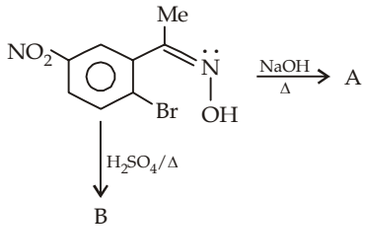
A can be :

(a) NH_3

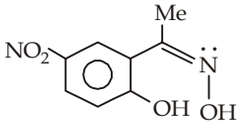
(b) alcoholic KOH

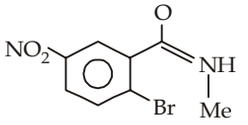
(c) Et_3N

(d) KNH_2

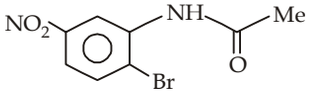
5. 

Which of the following is/are correct?

(*a*) Product A is 

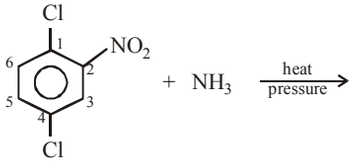
(*b*) Product B is 

(*c*) Product A is formed by aromatic nucleophilic substitution reaction

(*d*) Product B is 

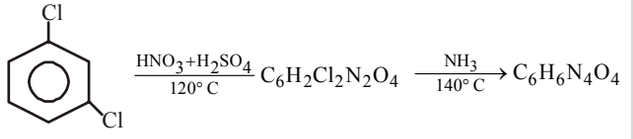
6. Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides due to :
(a) The formation of less stable carbonium ion
(b) Resonance stabilization
(c) Longer carbon-halogen bond
(d) The inductive effect
(e) sp^2 hybridized carbon attached to the halogen.

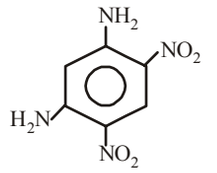
7. Which of the following statement is false regarding following reaction ?

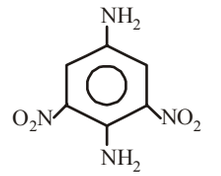


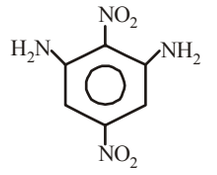
(a) No reaction is possible because —Cl is present on benzene ring.
(b) A nucleophilic substitution will take place in which both —Cl will be replaced by two —NH_2 groups.
(c) A nucleophilic substitution will take place in which only —Cl attached on C_1 will be replaced by —NH_2.
(d) A nucleophilic substitution will take place in which only —Cl attached on C_4 will be replaced by —NH_2.

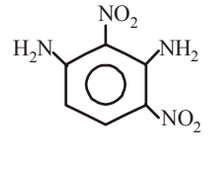
8. Identify the final possible product(s) in the following series of reactions.



(a) 

(b) 

(c) 

(d) 

9. *p*-Chlorotoluene when treated with strong NaOH at 340°C gives
(a) *o*-cresol (b) *m*-cresol
(c) *p*-cresol (d) All of these

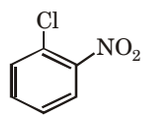
INSTRUCTION for Q. 10 to 15 : Read the passages given below and answer the questions that follow.

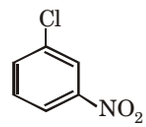
PASSAGE 1

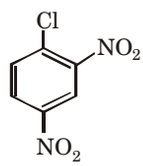
There are two (A and B) chlorine containing organic compounds; one of which (A) does not react with aqueous NaOH, while the second (B) easily reacts with sodium hydroxide. Compound (B) can be easily obtained by treating compound (A) with a mixture of conc. HNO_3 and H_2SO_4. compound (B) is a useful intermediate in the synthesis of picric acid (2,4,6- trinitrophenol).

10. Compound A can be
(a) C_6H_5Cl (b) $C_6H_5CH_2Cl$
(c) $CH_2 = CHCH_2CH_2Cl$ (d) *o*-$CH_3C_6H_4Cl$

11. Compound B can most likely to be

(a) 

(b) 

(c) 

(d) Any of the three

12. Reaction of 2,4- dinitrochlorobenzene with aquous NaOH to from 2, 4-dinitrophenol is an example of
(a) S_N1 (b) S_N2
(c) Ar S_N2 (d) benzyne

PASSAGE 2

Although chlorobenzene is inert to nucleophilic substitution, it gives quantitative yield of phenol when heated with aq. NaOH at high temperature and under high pressure. Phenol, so formed, is a weaker acid than the carboxylic acid; hence it dissolves only in strong bases like NaOH, but not weak like $NaHCO_3$. It reacts with acid chlorides and acid anhydrides in the absence of $AlCl_3$ to form esters. As far as electrophilic substitution in phenol is concerned, the –OH is an activating group, hence its presence enhances the electrophilic substitution in the *o*- and *p*-positions.
Condensation with formaldehyde is one of the important property of phenol. The condensation may take place in presence of acids or alkalis and leads to the formation of bakelite, an important industrial polymer.

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13. Phenol undergoes electrophilic substitution more readily than benzene because

(a) the intermediate carbocation is a resonance hybrid of more resonanting structures than that from benzene

(b) the intermediate is more stable as it has positive charge on oxygen, which can be better accommodated than on carbon

(c) in one of the canonical structures, every atom (except hydrogen) has complete octet

(d) the –OH group is o, p–directing which like all other o,p-directing groups is activating

14. Phenol undergoes electrophilic substitution more readily in presence of alkali than the phenol itself because

(a) of the formation of a more stable carbocation as an intermediate

(b) of the formation of a more stable carbanion as an intermediate

(c) of the formation of a more stable neutral intermediate

(d) in presence of alkali, a stronger electrophile is produced

15. Condensation of phenol with formaldehyde is an electrophilic substitution, in which

(a) $CH_2 = O$ as such is the electrophile in both acidic as well as basic medium

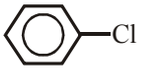
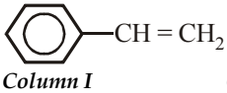
(b) $CH_2 = O$ is the real electrophile in acidic medium while in basic medium $\overset{+}{C}H_2 - O^-$ is the real electrophile

(c) $CH_2 = \overset{+}{O}H$ and $CH_2 = O$ are the electrophiles in acidic and basic medium respectively.

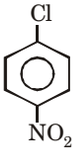
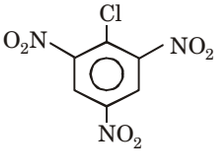
(d) $CH_2 = O$ and $\overset{+}{C}H_2 - O^-$ are the electrophiles in acidic and basic medium respectively.

Instructions for Q. 16 to 17 : Following questions are Multiple Matching type Questions :

16.

	Column I	*Column II*
(A)	$CH_2 = CH\,CN$	(a) Electophilic addition
(B)	$CH_2 = CHCH_2Cl$	(b) Nucleophilic substitution
(C)		(c) Electrophilic substitution
(D)		(d) Nucleophilic addition

17.

	Column I	*Column II*
(A)	$C_6H_5Cl + NaNH_2$	(a) Addition-elimination mechanism
(B)	 + NaOH	(b) Elimination-addition mechanism
(C)	$C_6H_5CHCl_2$ can be prepared	(c) $C_6H_5CH_3$
(D)		(d) C_6H_5CHO

Instructions for Q. 18 to 23 : Following questions are Assertion and Reasoning Type Questions :

Note : Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 5 choices (a), (b), (c), (d) and (e) out of which ONLY ONE is correct.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.

(c) Statement -1 is True, Statement-2 is False.

(d) Statement -1 is False, Statement-2 is True.

(e) Statement -1 is False, Statement-2 is False.

18. **Statement 1 :** The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.
Statement 2 : Benzene molecule (or ring) is flat (planar) with all carbon and hydrogen atoms lying in the same plane while in cyclohexyl chloride the ring of cyclo hexane is not planar.

19. **Statement 1 :** Benzyl bromide when kept in acetone it produces benzyl alcohol.
Statement 2 : The reaction follows S_{N^2} mechanism.

20. **Statement 1 :** The presence of nitro group facilitates nucleophilic substitution reactions in aryl halides.
Statement 2 : The intermediate carbanion is stabilized due to the presence of nitro group.

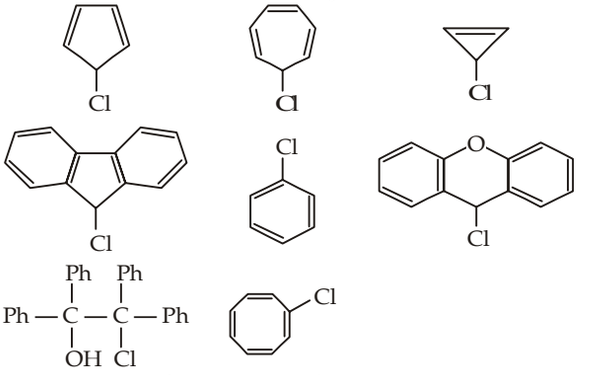
21. **Statement-1 :** Bromobenzene upon reaction with Br_2/Fe gives 1,4-dibromobenzene as the major product.
Statement-2 : In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile.

22. **Statement-1 :** Aryl halides undergo nucleophilic substitution with ease.
Statement-2 : Carbon-halogen bond in aryl halides has partial double bond character.

23. **Statement-1 :** 4-Nitrochlorobenzene undergoes nucleophilic substitution more readily than chlorobenzene.
Statement-2 : Chlorobenzene undergoes nucleophilic substitution by elimination-addition mechanism while 4-nitrochlorobenzene undergoes nucleophilic substitution by addition-elimination mechanism.

Instructions for Q. 24 to 26 : Following questions are Integer Type Questions :

24. How many of the following compounds will give white precipitate with aqueous $AgNO_3$.



25. IUPAC name of DDT is 2,2-*bis* (*p*-chlorophenyl)-1,1,1-trichloroethane. How many reactive chlorine atoms are there in the compound?

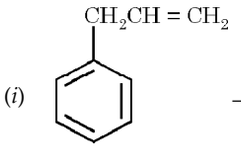
26. How many methylanilines are formed when 3 methylchlorobenzene is treated with sodamide in liquid ammonia.

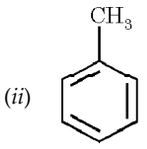
EXERCISE 9.3 (Subjective Problems)

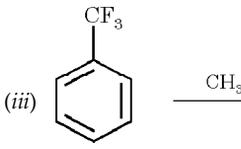
1. Give structures and names of products of the reaction (if any) when bromobenzene is treated with

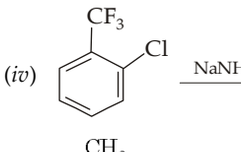
(*i*) hot 50% aqueous NaOH (*ii*) Cl_2 and Fe
(*iii*) boiling alcoholic KOH (*iv*) sodium ethoxide
(*v*) fuming sulphuric acid (*vi*) boiling aq. NaCN
(*vii*) I_2 and Fe (*viii*) C_6H_6 and $AlCl_3$
(*ix*) CH_3CH_2Cl and $AlCl_3$ (*x*) NH_3, copper powder
(*xi*) Cu at 200°C (*xii*) sodium acetylide.

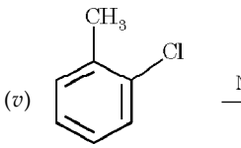
2. (*a*) Identify (A) to (J) in the following reactions.

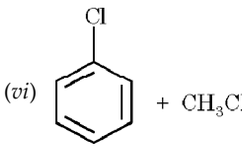


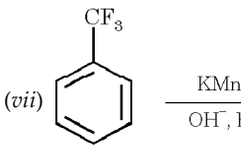


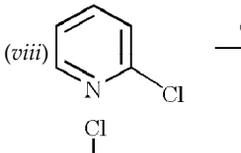


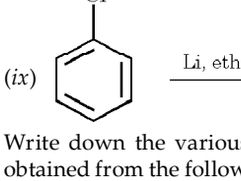




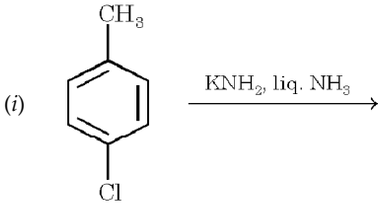


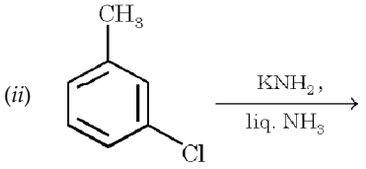






(*b*) Write down the various possible products that can be obtained from the following reactions.





3. Give the main product(s) obtained in each of the following reactions.

(*i*) 2, 3-Dibromopropene with aq NaOH
(*ii*) *p*-Bromobenzyl bromide with aq. ammonia
(*iii*) 3, 4, 5-Trichloronitrobenzene with one mol of sod. methoxide
(*iv*) *p*-Bromochlorobenzene with magnesium in presence of ether
(*v*) α-[*o*-chlorophenyl) ethyl bromide with alcoholic KOH
(*vi*) *p*-Bromotoluene with one mol of chlorine on heating
(*vii*) *o*-Bromobenzotrifluoride with sodamide in liq. NH_3
(*viii*) 2, 3, 4, 5, 6-Pentadeutereobromobenzene with sodamide in liq. ammonia.

4. Give necessary steps involved in each of the following conversions.

(*i*) Toluene to *m*-bromobenzoic acid
(*ii*) Toluene to *p*-bromobenzoic acid
(*iii*) Benzene to 3, 4-dibromonitrobenzene
(*iv*) Benzene to 2, 4-dinitroaniline
(*v*) Benzene to *p*-bromostyrene.

5. Categorise the following organic halides

Bromobenzene, *tert*-butyl bromide, *n*-hexyl chloride, *n*-hexyl iodide, benzyl bromide, *sec*-butyl chloride and carbon tetrachloride

towards their reaction with alcoholic silver nitrate in either of the three groups.

(*a*) Those which react rapidly at room temperature
(*b*) Those which react readily only when heated
(*c*) Those which are inert even to hot alcoholic silver nitrate.

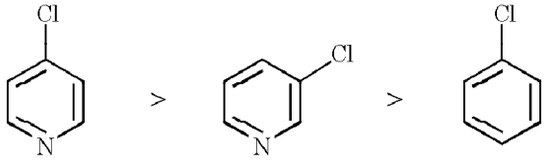
6. Arrange the compound in each set in order of reactivity toward the indicated reagent.

(*i*) Chlorobenzene, 3-chloronitrobenzene, 2-nitrochlorobenzene, 2, 4-dinitrochlorobenzene, and 2, 4, 6-trinitrochlorobenzene **toward NaOH**
(*ii*) Benzyl chloride, chlorobenzene and ethyl chloride **toward KCN**
(*iii*) 2, 4-Dinitrochlorobenzene, *p*-nitrochlorobenzene, *m*-nitrochlorobenzene and chlorobenzene **toward sodium ethoxide**
(*iv*) Bromobenzene, *p*-bromotoluene, *p*-dibromobenzene, toluene **toward fuming sulphuric acid**
(*v*) 1-Bromobenzene, 3-bromo-1-butene and 4-bromo-1-butene **toward alcoholic silver nitrate**
(*vi*) 2-Bromo-1-phenylethene, α-phenylethyl bromide and β-phenylethyl bromide **toward alcoholic silver nitrate.**

7. Write the most stable resonance structure for the cyclohexadienyl anion formed by reaction of methoxide ion with *o*-fluoronitrobenzene.

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8. Account for the following order of reactivity toward nucleophiles.



9. Explain the following :

(*i*) *p*-Nitrobenzenesulphonic acid can be prepared from the reaction of *p*-nitrochlorobenzene with $NaHSO_3$ or Na_2SO_3 but benzenesulphonic acid can't be formed from chlorobenzene by this reaction.

(*ii*) Crude *m*-dinitrobenzene can be separated from the *o*- and *p*-isomers by washing with aqueous sodium sulphite.

(*iii*) Although amides can be hydrolysed by either aqueous acid or aqueous alkali, hydrolysis of *p*-nitroacetanilide is best carried out in acidic solution.

(*iv*) Reaction between 2, 4, 6-trinitroanisole with sodium ethoxide or between 2, 4, 6-trinitrophenetole with sodium methoxide gives the same product.

(*v*) In the preparation of 2, 4-dinitrochlorobenzene from chlorobenzene, excess of acids is removed by aqueous $NaHCO_3$ but not by aqueous NaOH.

(*vi*) When *p*-iodotoluene is treated with aqueous NaOH at 340°C, a mixture of *p*-cresol and *m*-cresol in nearly equal amounts is obtained. However, at 250°C, the same becomes slow and yields only *p*-cresol.

(*vii*) When *o*-deuteriofluorobenzene is treated with sodamide in liquid ammonia it mainly gives fluorobenzene and only a small amount of aniline. On the other hand, similar reaction with *o*-deuteriobromobenzene mainly gives aniline.

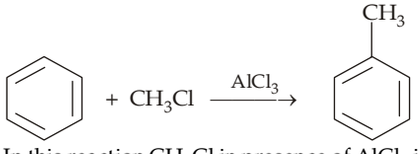
(*viii*) A hydrocarbon, $C_{25}H_{20}$, is formed when one mole each of chlorobenzene and $Ph_3C^{-}\ K^{+}$ are reacted with a small amount of potasamide in liquid ammonia.

SOLUTIONS

EXERCISE 9.1

1	(c)	**6**	(d)	**11**	(d)	**16**	(c)	**21**	(c)	**26**	(a)
2	(c)	**7**	(b)	**12**	(c)	**17**	(d)	**22**	(a)		
3	(b)	**8**	(d)	**13**	(c)	**18**	(c)	**23**	(c)		
4	(a)	**9**	(a)	**14**	(c)	**19**	(a)	**24**	(c)		
5	(b)	**10**	(a)	**15**	(b)	**20**	(a)	**25**	(c)		

1. Observe the structure. It is a derivative of ethane whose *one* carbon atom is having two *p*-chlorophenyl groups.

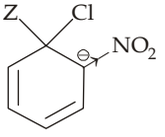
2.  ; $CH_3Cl + C_6H_6 \xrightarrow{AlCl_3} CH_3C_6H_5 + HCl$

In this reaction CH_3Cl in presence of $AlCl_3$ is an electrophile, hence the reaction is an electrophilic aromatic substitution. Simultaneously, benzene is acting as a nucleophile and displaces —Cl along with its bonding electrons from CH_3Cl to form $C_6H_5CH_3$, hence the reaction may also be considered an aliphatic nucleophilic substitution in which —Cl is replaced by $C_6H_5^{-}$.

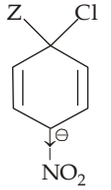
3. Chlorine in C_6H_5Cl can't be displaced easily because of strong C—Cl bond nature due to its double bond character due to resonance.

4. Nucleophiles are electron-rich species, and attack electron deficient sites, thus any factor which reduces electron density of benzene nucleus will activate the ring towards nucleophilic substitution.

5. The reaction is an example of nucleophilic aromatic substitution which involves the formation of carbanion as intermediate. The carbanion from *o*- and *p*-chloronitrobenzenes are more stable than that from the *m*-isomer which in turn is more stable than that from chlorobenzene, devoid of electron-withdrawing —NO_2 group.



Especially stable



Especially stable

No especially stable carbanion is possible in case of *m*-isomer.

6. Consult benzyne mechanism for nucleophilic substitution.

7. One of the π bonds of the triple bond is formed by overlapping of sp^2-sp^2 hybridised orbitals, hence it will be different from the remaining three which are formed by *p*-*p* overlap.

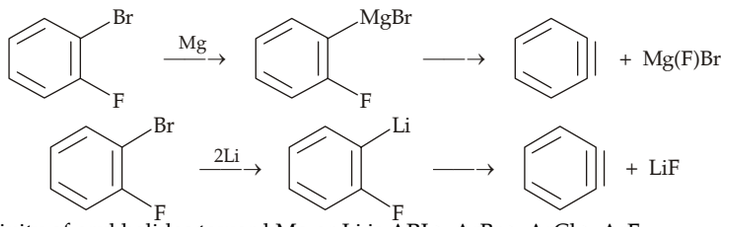
8. In IV, no hydrogen or deuterium is present in the position *ortho* to fluorine.

9. Chlorines present in *o*- and *p*-positions activate the ring toward nucleophilic substitution ; so Cl^a which is *ortho* and *para* to the other two chlorines, Cl^b and Cl^c, will be most reactive.

10. Methoxy group is electronegative so it can help in dispersing the negative charge, the effect is more pronounced on the carbon atom adjacent to it.

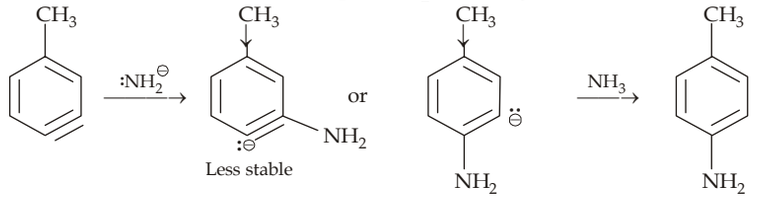
11. In (*a*), (*b*) and (*c*), —NMe_2, —OCH_3 and —Cl respectively are the leaving groups while OH^{-}, OH^{-} and SO_3^{2-} are the corresponding nucleophiles.

12. Chlorobenzene under drastic conditions undergo nucleophilic substitution via benzyne mechanism. *o*-Bromofluorobenzene forms benzyne when treated with Mg or Li.



Recall that order of reactivity of aryl halides toward Mg or Li is ARI > ArBr > ArCl > ArF.

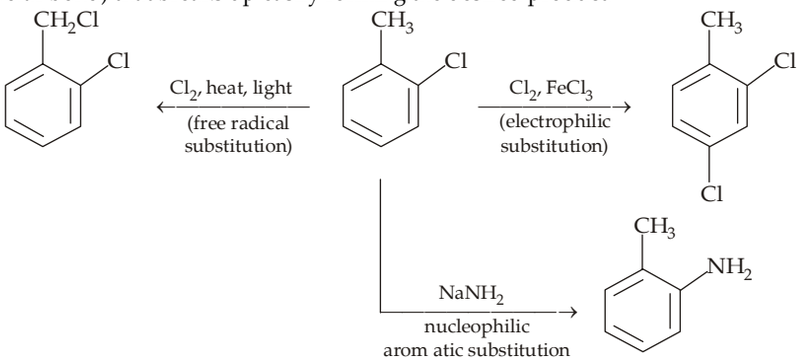
13. Following intermediates will be formed in the addition step of NH_2^- on benzyne.



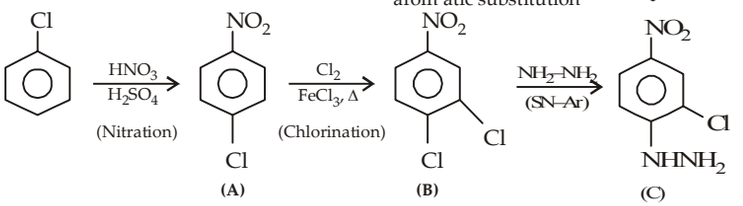
14. With no hydrogen in *ortho* position to Cl, benzyne formation is not possible.

15. C_6H_5Cl does not undergo nucleophilic substitution due to stable C — Cl bond, while in $C_6H_5O^-Na^+$, it is the bond between O and Na (polar bond) that breaks up easily forming the desired product.

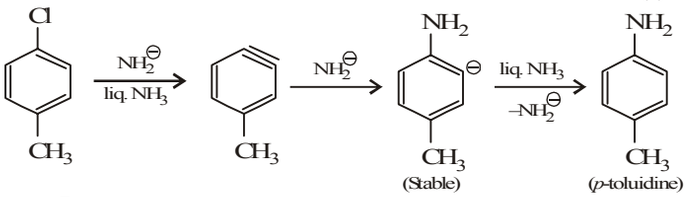
16.



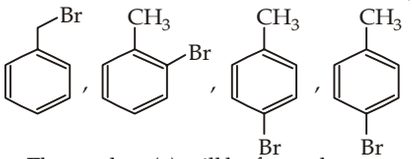
19.(*a*)



20.(*a*)



21.(*c*)

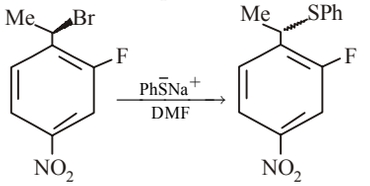


22. (*a*) The product (a) will be formed.

Nucleophilic substitution of an alkyl halide is easier as compared to that of an aryl halide.

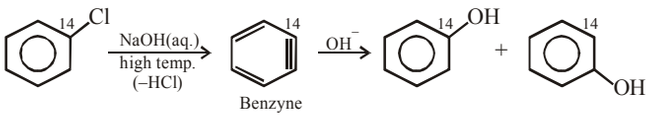
PhS^- is a strong nucleophile and dimethyl formamide $\left(\begin{matrix}O\\ \|\\ HCNMe_2\end{matrix}\right)$ is a highly polar aprotic solvent. These reagents favour S_N2 reactions at 2° benzylic carbon.

In a S_N2 reaction, the major product formed is inversion product.

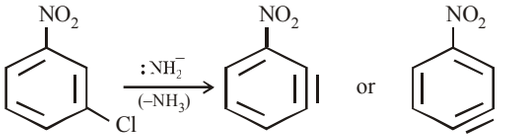


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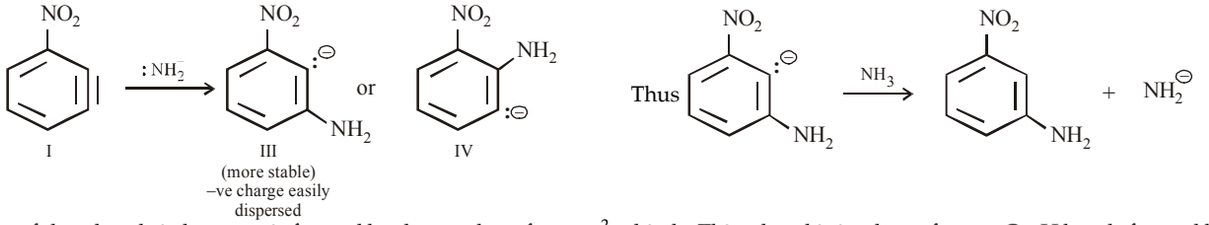
23. (*c*)



24. (*c*)

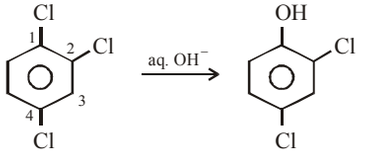


I is more likely to be formed because hydrogen ortho to the $-NO_2$ group is more acidic than that of para, hence removed. Further I can form two nitroanilines as explained below.



25.(c) One of the π bonds in benzyne is formed by the overlap of two sp^2 orbitals. This π bond is in place of two σ C – H bonds formed by the overlap of sp^2 orbital of C with *s* orbital of H. Since this additional π bond of the triple bond lies in the plane of the ring and hence does not interact with the aromatic π system. Thus we can say that benzyne has a benzene nucleus with aromatic sextet and an additional π bond which does not form a part of the sextet.

26.(a) Although ordinarily chlorine present on benzene nucleus is difficult to be replaced, however if it has electron-withdrawing group in the *o*- and *p*-position it is easily replaced. In the present case Cl (electronegative group) present on C_2 and C_4 are ortho and para respectively to Cl present on C_1, hence the latter can be replaced by OH^-. Note that other two chlorines (at C_2 and C_4) are meta to one chlorine, so these are not replaced.

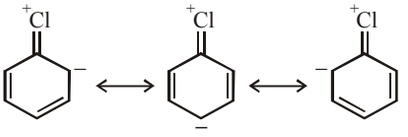


EXERCISE 9.2

>1 CORRECT OPTION	**1**	(b, d)	**2**	(b, c)	**3**	(b, d)	**4**	(a, b, c, d)	**5**	(b, c)
	6	(b, e)	**7**	(a,c, d)	**8**	(a, d)	**9**	(b, c)		
PASSAGE 1	**10**	(a)	**11**	(c)	**12**	(d)				
PASSAGE 2	**13**	(c)	**14**	(c)	**15**	(c)				
MATCH THE FOLLOWING	**16**	(A) - a, d ; (B) - a, b ; (C) - c ; (D) –a, c								
	17	(A) - (b), (B) - (a), (C) - (c, d), (D) - (a)								
A/R	**18**	(a)	**19**	(c)	**20**	(c)				
	21	(c)	**22**	(d)	**23**	(b)				
INTEGER	**24**	**5**	**25**	**3**	**26**	**3**				

6. (*b, e*) Aryl halides are stable due to resonance stabilization.

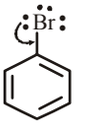
The resonating structures



stabilise the aryl halide. These structures include a double bond between C and Cl which is shorter and thus stronger than the usual C – Cl single bond. The sp^2 hybridised carbon, being electronegative, makes the C – Cl bond shorter and stronger.

7.(*a,c,d***)** Recall that the —Cl group present in the *o*- and *p*- positions to the electron-withdrawing group is activated toward nucleophilic substitution, hence only —Cl present on the *o*- and/or *p*-position to the —NO_2 group will be replaced.

21. (*c*) When halogen is present directly on the benzene nucleus it produces two opposing effects namely + M (activating effect) and –I (deactivating)



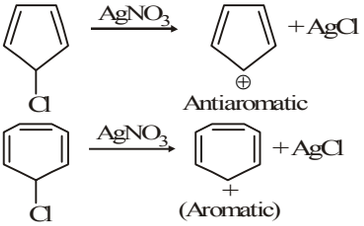
(–I effect, + M effect)

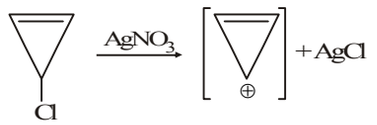
However, + M > –I hence halogens are said to be *o*, *p*- directing (due to + M effect) but deactivating group (due to –I effect) groups giving mainly *p*-substituted product.

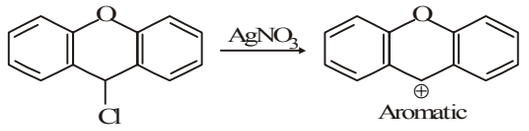
22. (*d*) Aryl halides undergo nucleophilic substitution with difficulty.

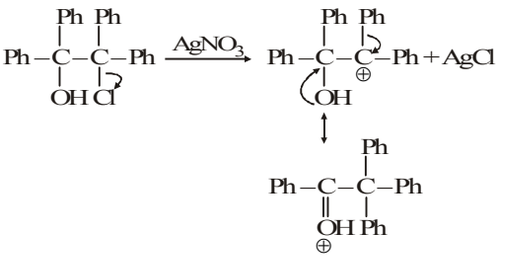
23. (*b*) **Correct explanation :** As compared to chlorobenzene, the intermediate carbanion resulting from 4-nitrochlorobenzene is stabilized by –R-effect of the NO_2 group.

24. 5



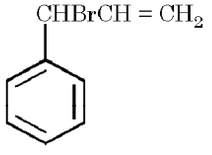




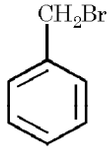


EXERCISE 9.3

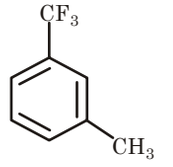
1. No reaction in (*i*), (*iii*), (*iv*), (*vi*), (*vii*), (*viii*), (*x*) and (*xii*)
(*ii*) *o*- and *p*-BrC_6H_4Cl (*v*) *o*- and *p*-$BrC_6H_4SO_3H$
(*ix*) *o*- and *p*-$BrC_6H_4CH_2CH_3$ (*xi*) Biphenyl.

2. *(a)* (*i*) 

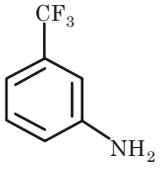
A (Allylic and benzylic substitution)

(*ii*) 

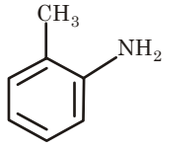
B (Side chain free radical subst.)

(*iii*) 

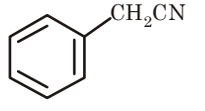
C (Electrophilic arom. substitution)

(*iv*) 

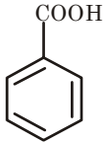
D* (due to –I effect of CF_3)

(*v*) 

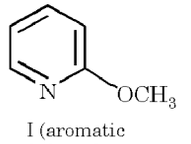
E** (due to + I effect of CH_3)

(*vi*) 

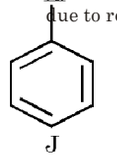
F (CH_2CN^- is better nucleophile than NH_2^-, due to resonance)

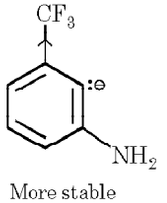
(*vii*) 

G (oxidation of the side chain)

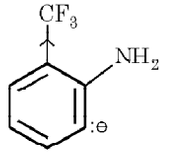
(*viii*) 

I (aromatic nucleophilic substitution)

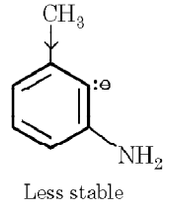
(*ix*) 

Note : * 

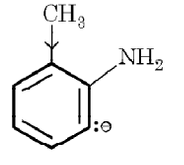
More stable (better dispersal of –ve charge)



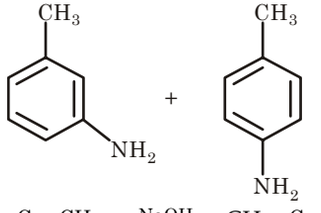
Less stable (less dispersal of –ve charge)

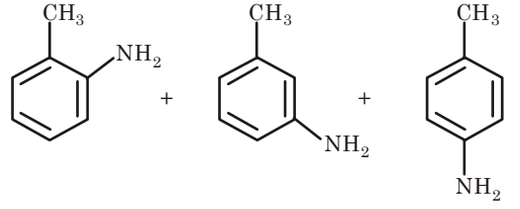
; ** 

Less stable (–ve charge more intensified)

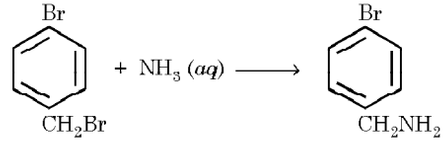


More stable (–ve charge less intensified)

(b) (*i*) 

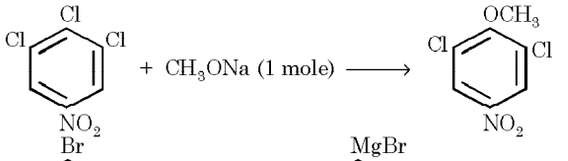
(*ii*) 

3. (*i*) $CH_2=C(Br)-CH_2Br \xrightarrow{NaOH} CH_2=C(Br)-CH_2OH$ **Recall that allylic halogen is more reactive than vinylic**

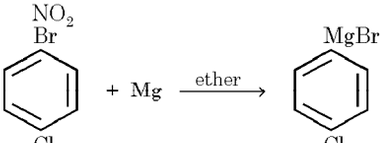
(*ii*) 

Benzylic halogen is more reactive than arylic.

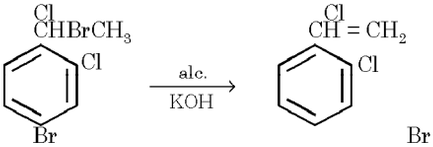
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(*iii*) 

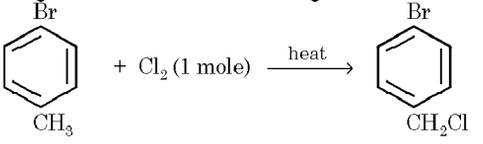
p - Halogen / o - halogen wrt to —NO_2 gp. is more reactive than the m - halogen

(*iv*) 

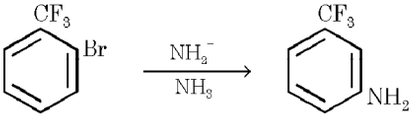
Aryl bromides are more reactive than ArCl

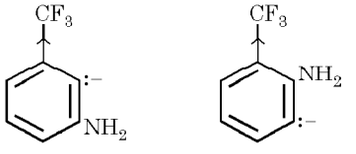
(*v*) 

Benzylic halogen is more reactive than arylic

(*vi*) 

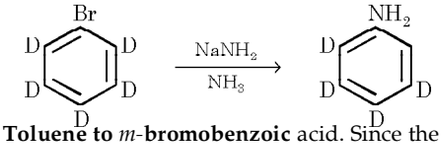
In presence of light, substitution (free radical) occurs in the side chain

(*vii*) 



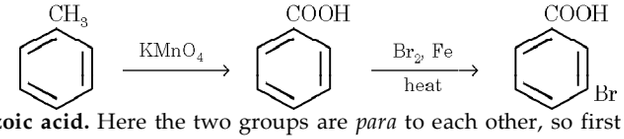
More stable **Less stable**

Carbanions

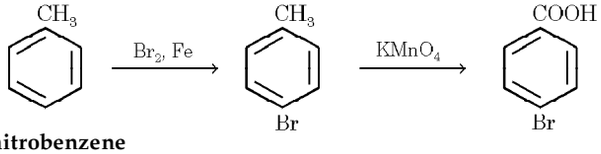
(*viii*) 

N—H bond is weaker than the N—D, H^+ from NH_3 is added and NH_2D is formed as product.

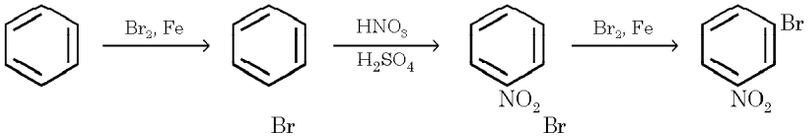
4. (*i*) **Toluene to *m*-bromobenzoic** acid. Since the two groups are *m*- to each other, first we must first introduce *m*-directing group of the two groups, *i.e.*, —COOH.

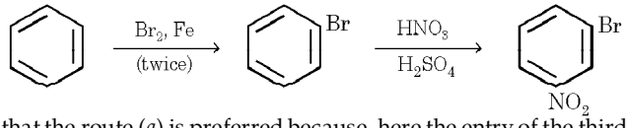


(*ii*) **Toluene to *p*-bromobenzoic acid.** Here the two groups are *para* to each other, so first group must be introduced in the *para* position.



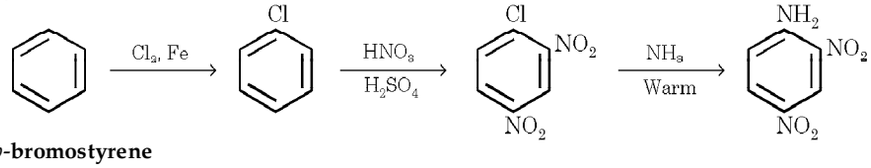
(*iii*) **Benzene to 3, 4-dibromonitrobenzene**

(*a*) 

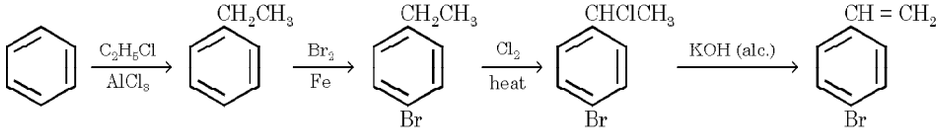
(*b*) 

Note that the route (*a*) is preferred because, here the entry of the third group (Br) is directed by both the existing groups (Br and NO_2) in the parent compound.

(*iv*) **Benzene to 2, 4-dinitroaniline**



(*v*) **Benzene to *p*-bromostyrene**



5. The more stable the R^+, the more reactive is RX (ArX).

(*a*) Following compounds react rapidly with alcoholic $AgNO_3$ at room temperature.

(*i*) *tert*-Butyl bromide-due to a stable (3°) R^+.

(*ii*) Benzyl bromide—due to stable $C_6H_5CH_2^+$.

(*iii*) *n*-Hexyl iodide—due to weak C—I bond and more insolubility of the AgI formed, although *n*-hexyl chloride reacts with alcoholic $AgNO_3$ rapidly only on heating.

(*b*) Following compounds react readily with alcoholic $AgNO_3$ only on heating.

(*i*) *sec*-Butyl chloride—due to 2° R^+ which is less stable than the 3° R^+.

(*ii*) *n*-Hexyl chloride—although 1° R^+, it can go substitution by slower S_N2 pathway.

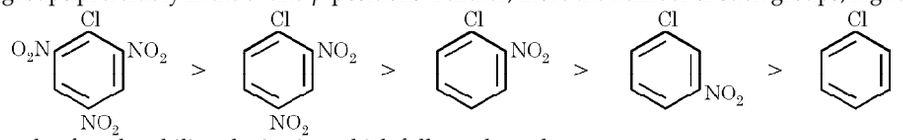
(*c*) Following compounds do not react at all with alc. $AgNO_3$

(*i*) Bromobenzene—an aryl halide, Ar^+ is very unstable.

(*ii*) Carbon tetrachloride —CCl_3^+ is unstable because of electron-withdrawing effect of the three chlorine. Moreover, there is too much steric hindrance towards S_N2 attack.

6. First write down the structure of the various compounds and observe the nature of halogen in each compound.

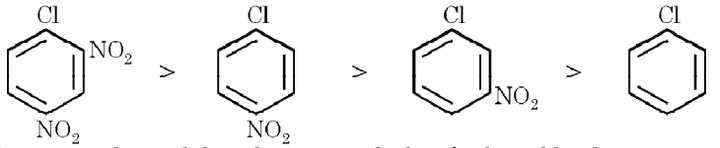
(*i*) This is an example of aromatic nucleophilic substitution of the —Cl group which is facilitated by the presence of electron-withdrawing groups preferably in the *o*- and *p*-positions. Further, more the number of such groups, higher will be the reactivity.



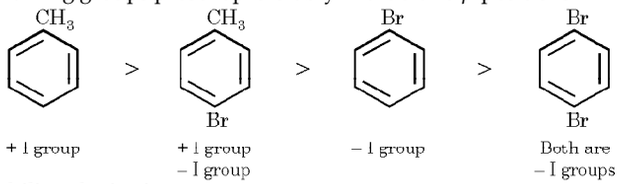
(*ii*) This is an example of nucleophilic substitution which follows the order.

$$\underset{\text{Benzylic chlorine}}{C_6H_5CH_2Cl} > \underset{1° \text{ Chlorine}}{CH_3CH_2Cl} > \underset{\text{Arylic chlorine}}{C_6H_5Cl}$$

(*iii*) Same as above.



(*iv*) This is an example of aromatic electrophilic substitution which is facilitated by the presence of electron-releasing groups and retarded by electron-withdrawing groups present preferably in the *o*-and *p*-positions.



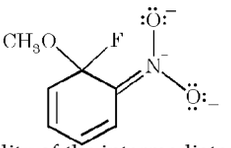
(*v*) It is an example of nucleophilic substitution.

$$\underset{\text{Allylic bromine}}{CH_3CHBrCH=CH_2} > \underset{1° \text{ Bromine}}{BrCH_2CH_2CH=CH_2} > \underset{\text{Aryl bromine}}{C_6H_5Br}$$

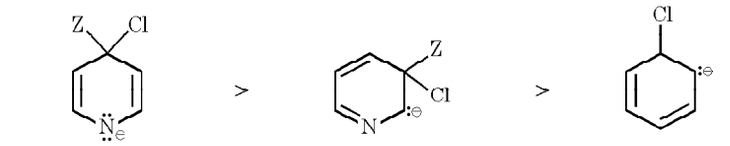
(*vi*) It is an example of nucleophilic substitution

$$\underset{\text{Benzylic bromine}}{C_6H_5CHBrCH_3} > \underset{1° \text{ Bromine}}{C_6H_5CH_2CH_2Br} > \underset{\text{Vinylic bromine}}{C_6H_5CH=CHBr}$$

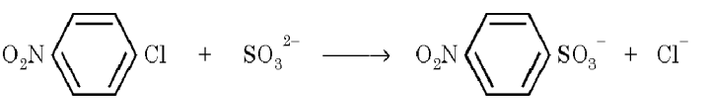
7. This structure is most stable because the negative charge is present on the more electronegative atom and positive charge on the less electronegative atom.



8. Relative reactivity is attributed to the relative stability of the intermediate formed in the addition step of each of reactant.

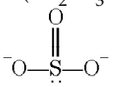


9. (*i*) The reaction is an example of nucleophilic aromatic substitution which is possible when —NO_2 group is present in the *p*-position to the —Cl group, because —NO_2 stabilizes the carbanion. Sodium sulphite produces the nucleophile, SO_3^{2-}.



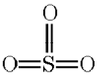
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Note that here the sulphonating reagent (Na_2SO_3 or SO_3^{2-}) is completely different from the reagent used in ordinary sulphonation, *i.e.* SO_3.



SO_3^{2-} (from Na_2SO_3)

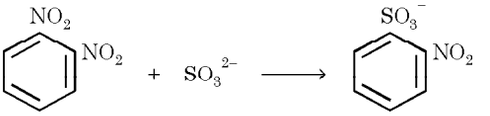
(Note that S has an unshared pair of electrons, hence acts as nucleophile)



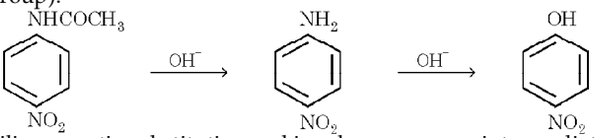
SO_3

(Note that S is electron-deficient, hence acts as an electrophile)

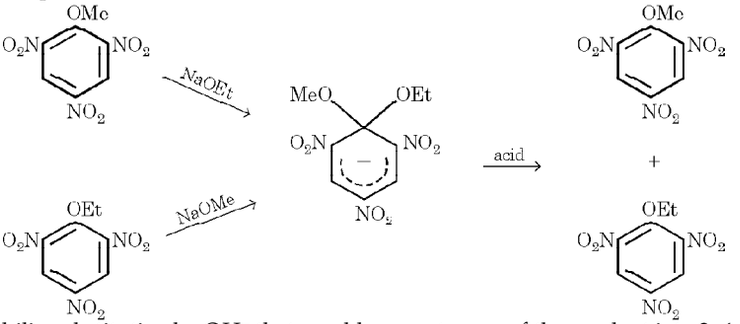
(*ii*) In *o*- and *p*-dinitrobenzenes, since one $—NO_2$ activates the other, they undergo nucleophilic aromatic substitution to form water soluble benzenesulphonates ($—NO_2$ group is a leaving group). The *m*-isomer does not react and thus remains insoluble.



(*iii*) In presence of alkali, *p*-nitroaniline formed after hydrolysis may undergo nucleophilic aromatic substitution to form *p*-nitrophenol (here $—NH_2$ is the leaving group).

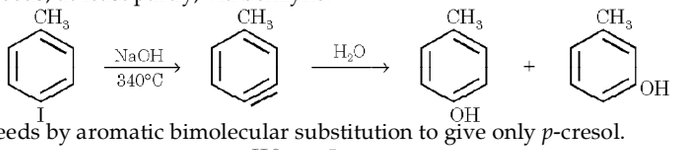


(*iv*) Both reactions are nucleophilic aromatic substitution and involve a common intermediate carbanion.

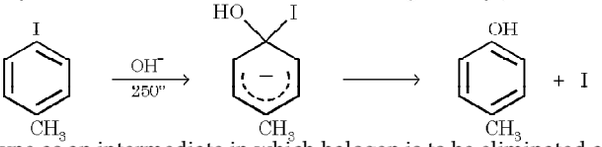


(*v*) To minimize nucleophilic substitution by OH^- that would convert some of the product into 2, 4-dinitrophenol.

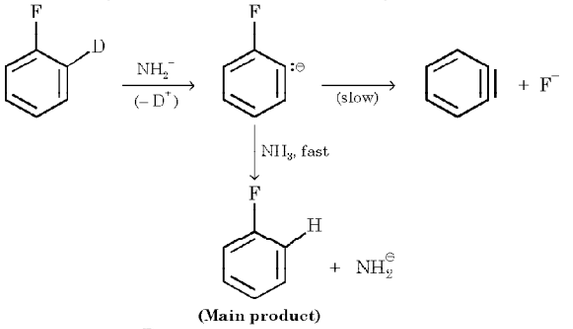
(*vi*) At 340°C, reaction proceeds, at least partly, via benzyne.



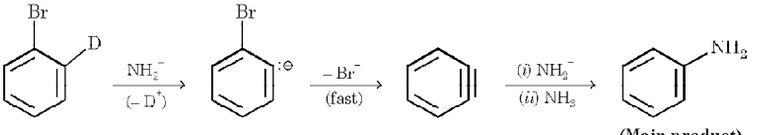
At 250°C, reaction proceeds by aromatic bimolecular substitution to give only *p*-cresol.



(*vii*) This reaction involves benzyne as an intermediate in which halogen is to be eliminated as an anion. F^- is a much poorer leaving group than Br^-, hence formation of benzyne intermediate will be very slow in fluoro compound than in bromo compound.

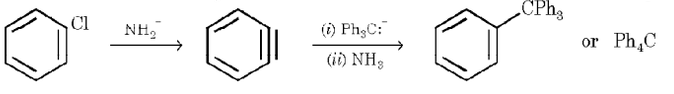


(Main product)

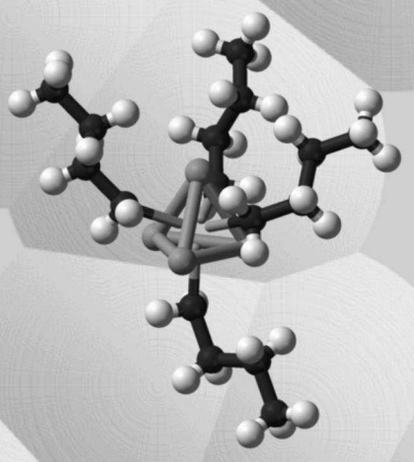


(Main product)

(*viii*) Benzyne formed from chlorobenzene adds $Ph_3C:^-$ and then H^+ from ammonia to form Ph_4C.



or Ph_4C



n-butyllithium

10

Organometallic Compounds

CHAPTER HIGHLIGHTS

10.1 Definition and Nomenclature

10.2 Preparation of Organolithium and Organomagnesium Compounds

10.3 Reactions of Organolithium and Organomagnesium Compounds

10.4 Grignard Reagents as Synthetic Agent

10.5 Limitations in the Use of Grignard Reagents

10.6 Organozinc Reagents for Cyclopropane Synthesis

10.7 Organocadmium Compounds

10.8 Organocuprates (Gilman reagents)

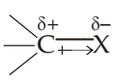
EXERCISES

SOLUTIONS

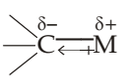
10.1 Definition and Nomenclature

Organometallic compounds are compounds that contain a carbon-metal bond. The nature of the carbon-metal bond may be ionic, partly ionic or primarily covalent depending upon the nature of the metal.

Carbon, a group 14 element is neither strongly electropositive nor strongly electronegative. Its electronegativity on the Pauling scale is 2.5 which is slightly more than hydrogen (2.1) and hence C—H bond is not very polar. When carbon is bonded to an atom which is more electronegative than carbon, *viz* O or Cl, the electron distribution in the bond makes carbon slightly positive and the more electronegative atom slightly negative. Conversely, when carbon is bonded to a more electropositive atom, such as a metal, the electrons in the bond are more strongly attracted towards carbon with the result carbon becomes slightly negative.



X is more electronegative than carbon



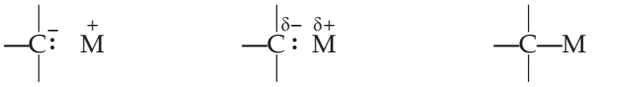
X is less electronegative than carbon

A species having negatively charged carbon is referred to as a **carbanion**. In general, the percentage of ionic character of the C—M bond depends largely upon the electronegativity of the metal, *i.e.* lesser the electronegativity (or greater the electropositivity) of the metal more will be the ionic character of the C—M bond. Thus the ionic character of the C—M bond follows the order :

	C—K	>	C—Na	>	C—Li	>	C—Mg	>	C—Al	>	C—Zn	>	C—Cd	>	C—Hg
Electronegativity of the metal	0.8		0.9		1.0		1.2		1.5		1.6		1.8		1.9

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Thus carbon-sodium and carbon-potassium bonds are largely ionic ; carbon-lead, carbon-zinc, carbon-cadmium and C-mercury are essentially covalent ; and carbon-lithium and carbon-magnesium lie between these two extremes.



Primarily ionic (M = Na or K) | (M = Mg or Li) | Primarily covalent (Mg = Zn, Cd or Hg)

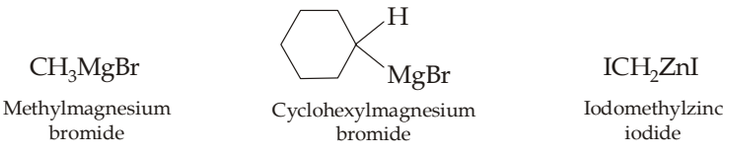
The reactivity of organometallic compounds increases with the increase in ionic character of the C—M bond. Thus alkylsodium and alkylpotassium compounds are highly reactive and are among the most powerful bases. They react explosively with water and burst into flame when exposed to air. Organomercury and organolead compounds are less reactive, they are often volatile and are stable in air.

Organometallic compounds of lithium and magnesium are neither too reactive nor inert, hence these are of great importance in organic synthesis. Since C—Li and C—Mg bonds are polar, organolithium and organomagnesium compounds have significant carbanionic character and *it is the carbanionic character of such bonds that is responsible for their importance as synthetic reagents.*

Nomenclature. (*i*) Organometallic compounds are named as substituted derivatives of metals.

CH_3Li	$CH_2 = CHNa$	$(CH_3CH_2)_2Mg$	$(CH_3)_3CLi$
Methyllithium	Vinylsodium	Diethylmagnesium	*tert*-Butyllithium or 1, 1-Dimethylethyllithium

(*ii*) When the metal has a substituent other than alkyl group, the substituent is treated as if it were an anion and hence named separately.



CH_3MgBr		ICH_2ZnI
Methylmagnesium bromide	Cyclohexylmagnesium bromide	Iodomethylzinc iodide

10.2 Preparation of Organolithium and Organomagnesium Compounds

1. Organolithium compounds are prepared by the reaction of organic halides with lithium metal in presence of solvents like diethyl ether, tetrahydrofuran (a cyclic ether) or hydrocarbons like pentane and hexane.

$$R—X,\ CH_2 = CH—X \text{ or } Ar—X + 2Li \xrightarrow{(C_2H_5)_2O} R—Li,\ CH_2 = CHLi \text{ or } ArLi + LiX$$

(*i*) The order of reactivity of halides is RI > RBr > RCl > RF (fluorides are seldom used). Bromides are readily available and quite reactive, these are used most often.

(*ii*) Solvent used should be anhydrous because even a trace of water or alcohol reacts with lithium to form insoluble hydroxide or alkoxide that coats the surface of the metal and prevents it from reacting with the alkyl halide. Moreover, organolithium compounds are strong bases, as soon as these are formed they react rapidly with even weak proton sources like H_2O or ROH to form hydrocarbons.

(*iii*) Most organolithium compounds slowly attack ethers by bringing about an elimination reaction.

$$\overset{\delta-}{R}:\overset{\delta+}{Li} + \underset{\text{Ether (solvent)}}{HCH_2CH_2OCH_2CH_3} \longrightarrow RH + CH_2 = CH_2 + LiOCH_2CH_3$$

Due to this reason, organolithium compounds are not usually stored but are used immediately after their preparation.

TEST YOUR UNDERSTANDING - 10.1

1. Give equations showing the formation of

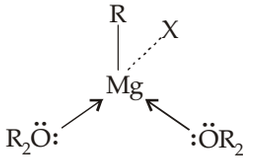
(*a*) *sec*-Butyllithium (*b*) Isopropenyllithium (*c*) Benzylsodium.

2. Organomagnesium halides (discovered by the French chemist, Victor Grignard, Nobel prize winner in chemistry in 1912), commonly called **Grignard reagent**s are the most important organometallic reagents. These are prepared by the reaction of an organic halide and magnesium metal (turnings) in an ether solvent.

$$RX + Mg \xrightarrow[35°C]{\text{ether}} RMgX$$

(R may be methyl, 1°, 2°, or 3° alkyl, a cycloalkyl, alkenyl, or aryl group)

(*i*) The solvent (usually diethyl ether or tetrahydrofuran) plays a crucial role in the formation of a Grignard reagent. The magnesium atom of a Grignard reagent is surrounded by only four electrons, it needs two more pairs of electrons to form an octet. Solvent molecules provide these electrons by coordinating to the metal. Coordination allows the Grignard reagent to dissolve in the solvent and thus prevents the Grignard reagent from coating the magnesium shavings, which would make them unreactive.



Tetrahedral arrangement around Mg

(*ii*) The order of halides reactivity is RI > RBr > RCl > RF. However, alkyl bromides are most widely used because they react more readily than alkyl chlorides and are less expensive than alkyl iodides.

(*iii*) Alkyl halides are more reactive than aryl and vinyl halides. Indeed, aryl and vinyl chlorides do not form Grignard reagents in diethyl ether, a solvent of low b.p. 35°C. These are, however, prepared by using tetrahydrofuran, a solvent of higher b.p., 65°C.

$$CH_2 = CHCl + Mg \xrightarrow[60°C]{\text{THF}} CH_2 = CHMgCl$$

(*iv*) Allyl and benzyl halides are so reactive that they readily couple with their Grignard reagents (as soon as they are formed) to form diallyl or dibenzyl. Hence, it is difficult to prepare Grignard reagents of allyl halides and benzyl halides.

TEST YOUR UNDERSTANDING - 10.2

1. Write down the reaction and the structure of the Grignard reagent formed by the following organic halides.

(*a*) Allyl chloride (*b*) 1-Bromocyclohexene (*c*) *p*-Bromofluorobenzene.

10.3 Reactions of Organolithium and Organomagnesium Compounds

1. Organolithium and organomagnesium compounds as Bronsted bases. (Reactions with compounds containing acidic hydrogen atom). Due to their carbanionic character, organolithium compounds and Grignard reagents are very strong bases. Thus they can abstract proton from any species more acidic than the hydrogen atoms of an alkane or alkene ; *viz.* terminal alkynes and any compound that has a hydrogen attached to an electronegative atom such as O, N, or S. In these reactions, a proton is transferred to the negatively polarized carbon of the reagent to form a hydrocarbon. This is the reason, that Grignard reagents are not prepared in presence of compounds containing —OH, —SH or —NH groupings.

$$\underset{\text{Stronger base}}{CH_3CH_2CH_2CH_2Li} + \underset{\text{Stronger acid}}{HOH} \longrightarrow \underset{\text{Weaker acid}}{CH_3CH_2CH_2CH_3} + \underset{\text{Weaker base}}{LiOH}$$

$$\underset{\substack{\text{Phenylmagnesium}\\ \text{bromide}}}{C_6H_5MgBr} + \underset{\text{Methanol}}{HOCH_3} \longrightarrow C_6H_6 + \underset{\substack{\text{Methoxymagnesium}\\ \text{bromide}}}{CH_3OMgBr}$$

$$CH_3CH_2MgBr + H_3N \longrightarrow CH_3CH_3 + MgBr(NH_2)$$

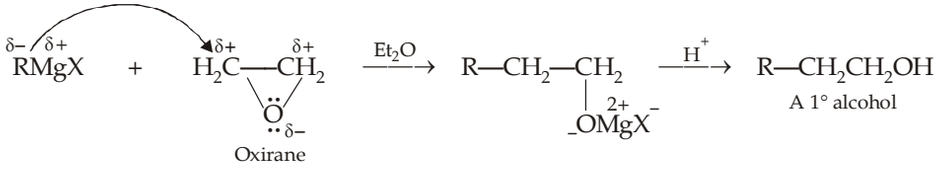
$$\underset{\substack{\text{Ethylmagnesium}\\ \text{bromide}\\ \text{(Stronger base)}}}{CH_3CH_2MgBr} + \underset{\substack{\text{Propyne}\\ \text{(Stronger acid)}}}{HC \equiv CCH_3} \longrightarrow \underset{\text{(Weaker acid)}}{CH_3CH_3} + \underset{\substack{\text{Propynylmagneisum}\\ \text{bromide}\\ \text{(Weaker base)}}}{BrMgC \equiv CCH_3}$$

From above reactions, it is clear that for every active hydrogen atom in the compound one molecule of alkane (22.4 litres at NTP) is produced which can be measured easily. This principle is used in the estimation of groups containing active hydrogen atom such as —OH, —NH_2, —SH etc. (*Zerewitnoff method*).

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2. Organolithium and Grignard reagents as nucleophiles. Grignard reagents are not only strong bases, they are also powerful nucleophiles. In fact, reactions in which Grignard reagents act as nucleophiles are by far the most important. Grignard reagents act as nucleophiles by attacking saturated and unsaturated carbon atoms.

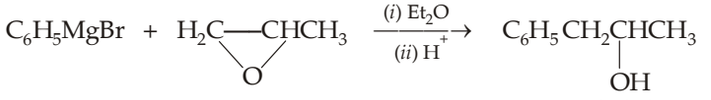
(A) *Grignard reagents as nucleophile for a saturated carbon atom, e.g.* oxiranes (epoxides).



Oxirane

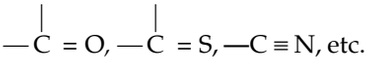
A 1° alcohol

Grignard reagents react primarily at the less-substituted ring carbon atom of substituted oxiranes because compartively it is more electrophilic.

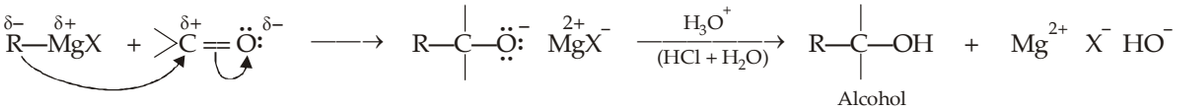


A 2° alcohol

(B) *Grignard reagents as nucleophile for an unsaturated carbon atom, viz.*

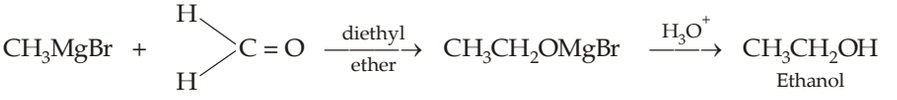


(*i*) Grignard reagents are nucleophilic and add to the electrophilic carbon atom of the carbonyl group, forming a new carbon-carbon bond.

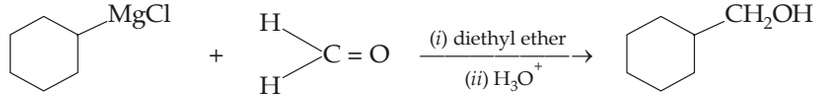


Alcohol

The type of alcohol (1°, 2° or 3°) produced depends on the nature of the carbonyl compound used. Note that the two substituents present on the carbonyl carbon stay in the product, an alkyl group from the Grignard reagent attaches on the carbonyl carbon and carbonyl oxygen is converted to hydroxy group. **Thus formaldehyde (HCHO) gives 1° alcohols.**

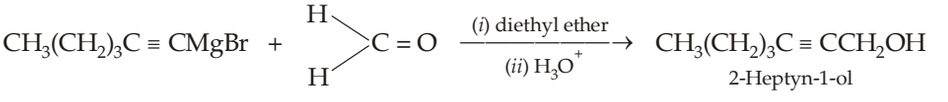


Ethanol



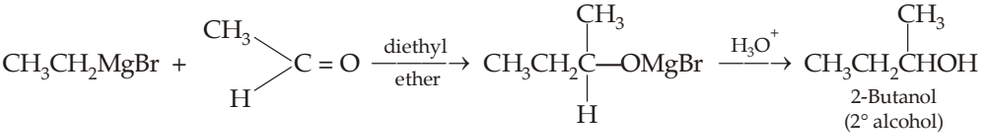
Cyclohexyl-magnesium chloride

Cyclohexylmethanol



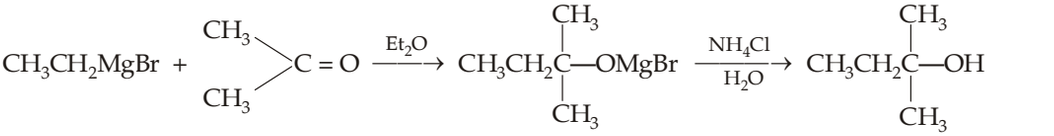
2-Heptyn-1-ol

Aldehydes other than formaldehyde give secondary alcohols.

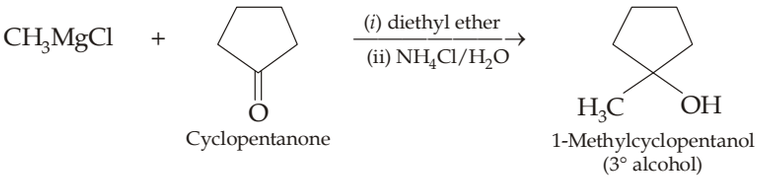


2-Butanol (2° alcohol)

Ketones give tertiary alcohols.



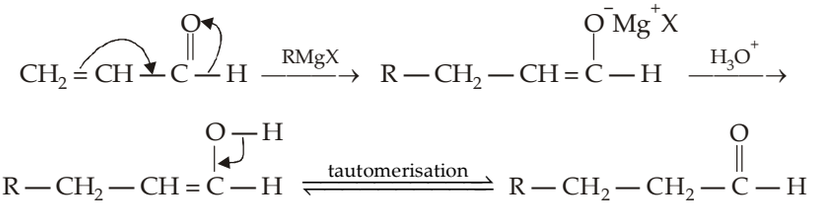
2-Methyl-2-butanol (3° alcohol)



Since 3° alcohols are susceptible to acid-catalysed dehydration, a solution of NH_4Cl in water is often used for hydrolysing the intermediate because it is acidic enough to convert ROMgX (a strong base) formed in the product to ROH, thus avoiding dehydration of the *tert*-alcohol.

Addition of Grignard reagent on α, β-unsaturated carbonyl group

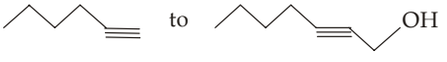
If carbonyl group is conjugated with a double bond, Grignard reagent gives nucleophilic addition on the double bond.



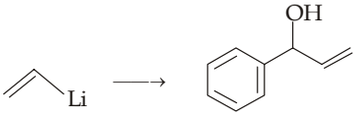
(*ii*) Organolithium reagents react with carbonyl groups in the same way as Grignard reagents, however they are somewhat more reactive than Grignard reagents.

TEST YOUR UNDERSTANDING - 10.3

1. Give necessary steps involved in the following conversions.

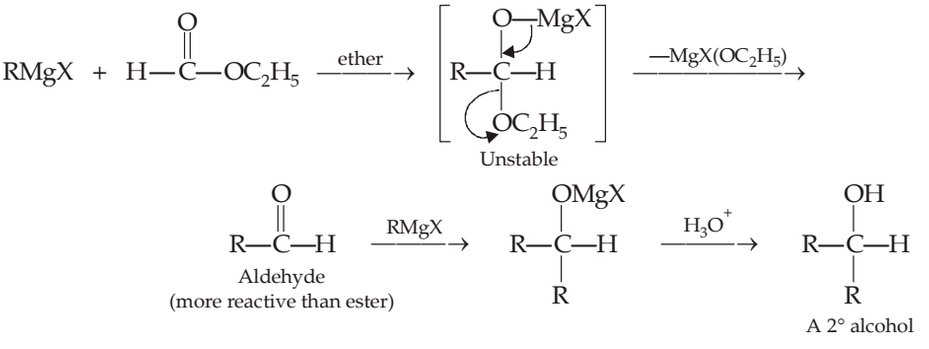
(*i*) 

(*ii*) Sodium acetylide to 1-ethynylcyclohexanol.

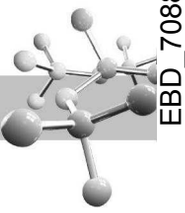
(*iii*) 

(*iii*) Grignard reagents react with other functional groups having >CO as part in their structures in the same manner to form different products. For example,

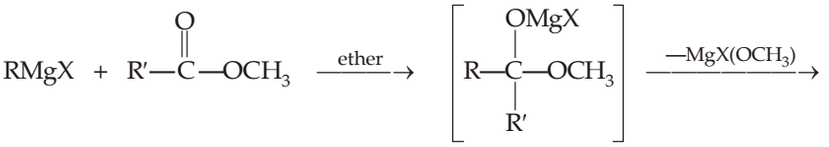
(*a*) One mole of alkyl formates *i.e.* methyl or ethyl esters of formic acid react with two moles of the Grignard reagents to form secondary alcohols as the final product.

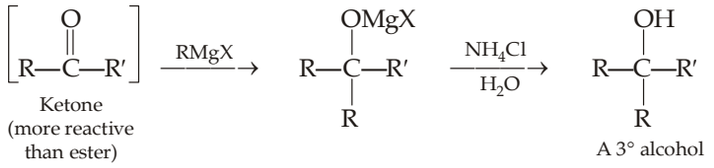


(*b*) One mole of methyl or ethyl esters of acids other than formic acid, *viz*. methyl acetate reacts with two moles of the reagent to form 3° alcohol as the final product. Ketones formed initially are not isolated but reacts with the second mole of the Grignard reagent to form 3° alcohol as the final product.

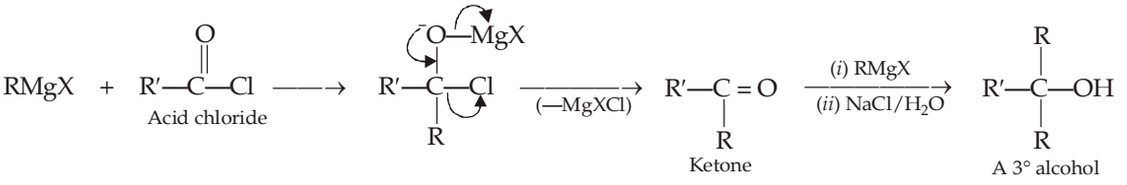


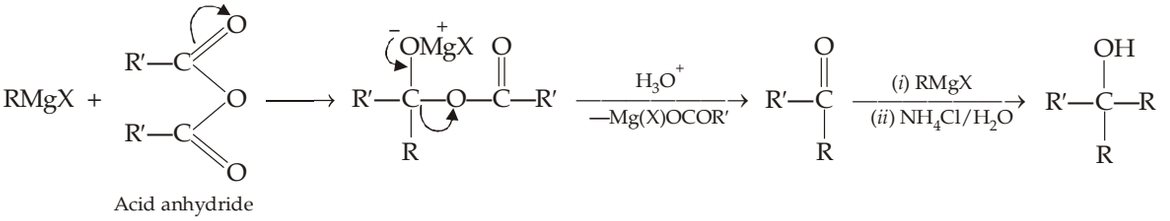
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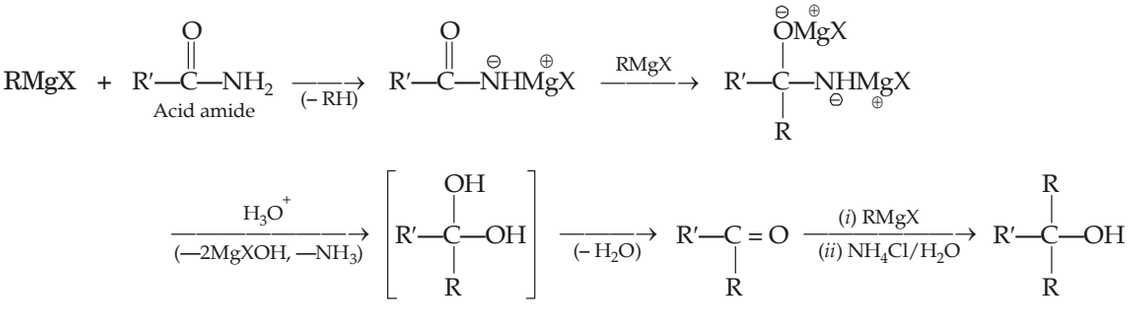




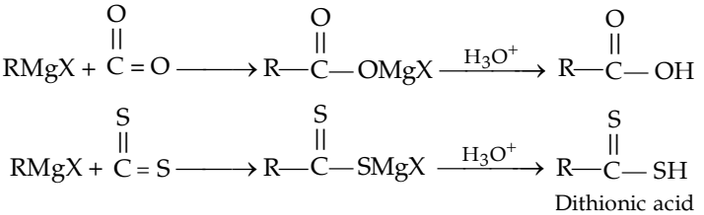
(*c*) Reaction with acid chlorides, acid anhydrides and acid amides give first ketones and finally *tert*-alcohols.







(*d*) Grignard reagents react with CO_2 and CS_2 exactly in the same way forming carboxylic acids and dithionic acids respectively.



TEST YOUR UNDERSTANDING - 10.4

1. Give as many combinations as possible for the synthesis of 2-phenyl-2-butanol using Grignard reagent as one of the reactants.

(*iv*) *Grignard reagents as nucleophile for the carbon atom of the nitrile group*, C ≡ N. These reactions are used for the preparation of aldehydes (from HCN) and ketones (from RCN).

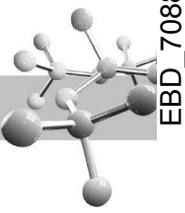
(*a*) $CH_3MgX + H{-}C{\equiv}N \longrightarrow H{-}\overset{CH_3}{\overset{|}{C}}{=}NMgX \xrightarrow{H_3O^+} H{-}\underset{\text{Aldimine}}{\overset{CH_3}{\overset{|}{C}}{=}NH} \xrightarrow{H_2O} H{-}\underset{\text{Ethanal}}{\overset{CH_3}{\overset{|}{C}}{=}O} + NH_3$

(*b*) $CH_3MgX + CH_3{-}C{\equiv}N \longrightarrow CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}NMgX \xrightarrow{H_3O^+} CH_3{-}\underset{\text{Ketimine}}{\overset{CH_3}{\overset{|}{C}}{=}NH} \xrightarrow{H_2O} CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}O + NH_3$

10.4 Grignard Reagents as Synthetic Agent

The ease of its preparation and reactivity of Grignard reagent make it very important synthetic reagent. Nearly every type of organic compound starting from alkane upto other organometallic compounds can be prepared.

	Class of organic compound	*Starting materials*
1.	Alkanes	$RMgX + HOH(ROH, NH_3 \text{ etc.}) \longrightarrow RH$
2.	Higher alkanes	$RMgX + XR' \longrightarrow R{-}R' + MgX_2$ **(S_N reaction)**
3.	Higher alkynes	$RMgX + IMgC{\equiv}CCH_3 \longrightarrow RC{\equiv}CCH_3$
4.	Primary alcohols	(*i*) $RMgX + CH_2O \longrightarrow RCH_2OH$ Methanol can't be prepared by this method
		(*ii*) $RMgX + \underset{\diagdown O \diagup}{CH_2{-}CH_2} \longrightarrow RCH_2CH_2OH$
		(*iii*) $RMgX + \frac{1}{2}O_2 \xrightarrow{Ag} ROMgX \xrightarrow{H_3O^+} ROH$
5.	Secondary alcohols	(*i*) $RMgX + R'CHO \longrightarrow \underset{R'}{\overset{R}{\diagdown\!\diagup}}CHOH$
		(*ii*) $\underset{\text{(2 moles)}}{2RMgX} + HCOOR' \longrightarrow \underset{R}{\overset{R}{\diagdown\!\diagup}}CHOH$
6.	Tertiary alcohols	(*i*) $RMgX + R_2'CO \longrightarrow \underset{R'}{\overset{R}{\diagdown\!\diagup}}{-}COH$
		(*ii*) $\underset{\text{(2 moles)}}{2RMgX} + R'COOCH_3 \longrightarrow R{-}\underset{R'}{\overset{R}{\diagdown\!\diagup}}C{-}OH$
7.	Aldehydes	$RMgX + HC{\equiv}N \longrightarrow RCHO$
8.	Ketones	$RMgX + R'C{\equiv}N \longrightarrow \underset{R'}{\overset{R}{\diagdown\!\diagup}}CO$
9.	Carboxylic acids	$RMgX + \underset{\text{Dry ice}}{CO_2} \longrightarrow RCOOH$
10.	Thioalcohols	$RMgX + S \longrightarrow RSMgX \longrightarrow RSH$
11.	Nitriles	(*i*) $RMg + \underset{\text{Cyanogen chloride}}{ClCN} \longrightarrow RCN + MgXCl$
		(*ii*) $RMgX + \underset{\text{Cyanogen}}{(CN)_2} \longrightarrow RCN + MgXCN$



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12.	Amines	$RMgX + \underset{\text{Chloramine}}{ClNH_2} \longrightarrow RNH_2$	
13.	Other organometallic compounds	(*i*) $2RMgX + ZnCl_2 \longrightarrow R_2Zn + 2MgXCl$	
		(*ii*) $4RMgX + 2PbCl_2 \longrightarrow R_4Pb + Pb + 4MgXCl$	

TEST YOUR UNDERSTANDING - 10.5

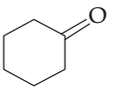
1. Write the structure of the product formed by the reaction of propylmagnesium iodide with each of the following compounds :

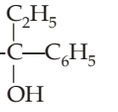
(*i*) Methanal (*ii*) 2-Butanone (*iii*) Cyclopentanone

(*iv*) Benzaldehyde (*v*) Dry ice (*vi*) Butanenitrile

(*vii*) Pentyne-1, followed by reaction with cyclohexanone (*viii*) Benzoyl chloride.

2. Identify A to C in the following reactions :

(*i*) CH_3CH_2MgBr +  $\xrightarrow{H^+}$ [A]

(*ii*) $C_6H_5Br \xrightarrow[THF]{Mg} C_6H_5MgBr \xrightarrow[(ii)\ H^+]{(i)\ [B]}$ 

(*iii*) $HC \equiv CH \xrightarrow{NaNH_2} HC \equiv CNa \xrightarrow[(ii)\ H^+]{(i)\ \text{Cyclopentanone}}$ [C]

10.5 Limitations in the Use of Grignard Reagents

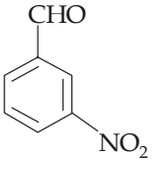
Extraordinary reactivity of Grignard reagent as a nucleophile and a base are also responsible for its certain limitations.

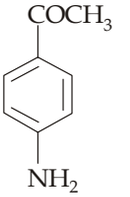
(*i*) Due to powerful basic nature of Grignard reagents, we cannot prepare a Grignard reagent from a compound containing an —OH, —NH—, —SH, —COOH, or $—SO_3H$ group. Even, if a Grignard reagent were to form, it would immediately react with the acidic group.

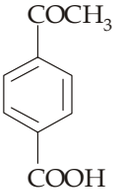
(*ii*) Since Grignard reagents are powerful nucleophiles, we cannot prepare a Grignard reagent from any organic halide containing a carbonyl, epoxy, or cyano group. Any Grignard reagent formed would react with the unreacted starting material.

(*iii*) The nitro ($—NO_2$) group oxidizes a Grignard reagent, so alkyl halides having $—NO_2$ group can't be converted into Grignard reagent.

(*iv*) A compound to be reacted with a Grignard reagent should also not contain either of the above mentioned groups because in such cases Grignard reagent would be decomposed by these groups ($—NO_2$, $—NH_2$, —COOH, etc.) before reacting with the main functional group, the carbonyl group in the following examples.







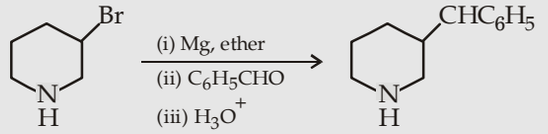
This means that we can prepare Grignard reagents effectively from alkyl halides or analogous organic halides containing C—C double bonds, internal triple bonds, ether linkages, and $—NR_2$ groups.

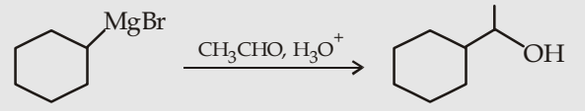
Protecting groups : An alkyl halide containing an alcoholic –OH group can be converted to Grignard reagent by first protecting the –OH group by converting it to a *tert*-butyldimethylsilyl ether which is inert to Grignard reagent. The protecting group is finally liberated by treatment with fluoride ion.

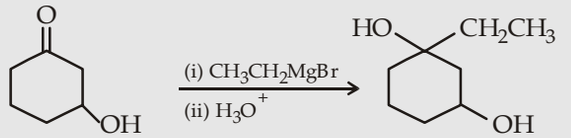
$$R-O-H + \underset{\substack{\text{tert-Butylchlorodimethylsilane}}}{Cl-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-C(CH_3)_3} \longrightarrow R-O-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-C(CH_3)_3 \xrightarrow[THF]{(C_4H_9)_4N^+F^-} R-O-H + F-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-C(CH_3)_3$$

Example 1 :

Which of the following reaction is feasible?

(a) 

(b) 

(c) 

Solution :

(a) As Grignard reagent is formed, it would instantaneously react with the >NH present in other molecules of the same substance.

(b) The reagent used (CH_3CHO and H_3O^+) must be numbered, viz. (i) and (ii), otherwise it indicates that the Grignard reagent is exposed to acidic medium which will decompose it to alkane.

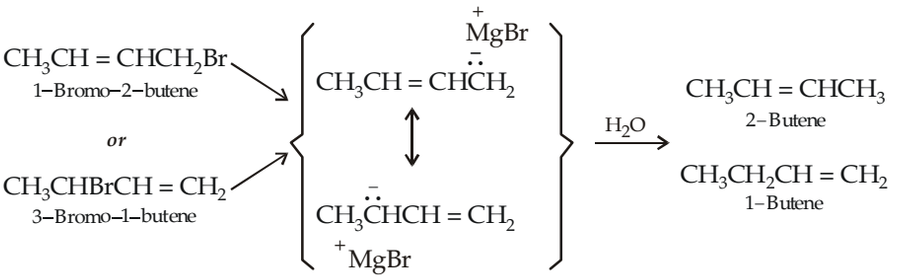
(c) The Grignard reagent will immediately react with the –OH part of the reagent.

So none of the three options is feasible.

Example 2 :

When 1-bromo-2-butene is treated with magnesium metal in dry ether, a Grignard reagent is formed. Addition of water to this Grignard reagent gives a mixture of 1-butene and 2-butene. Further, 3-bromo-1-butene under similar treatment gives the same products. Explain.

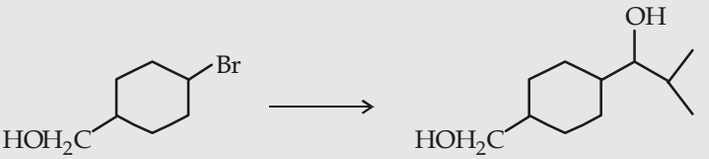
Solution :



Allylic carbanion

Example 3 :

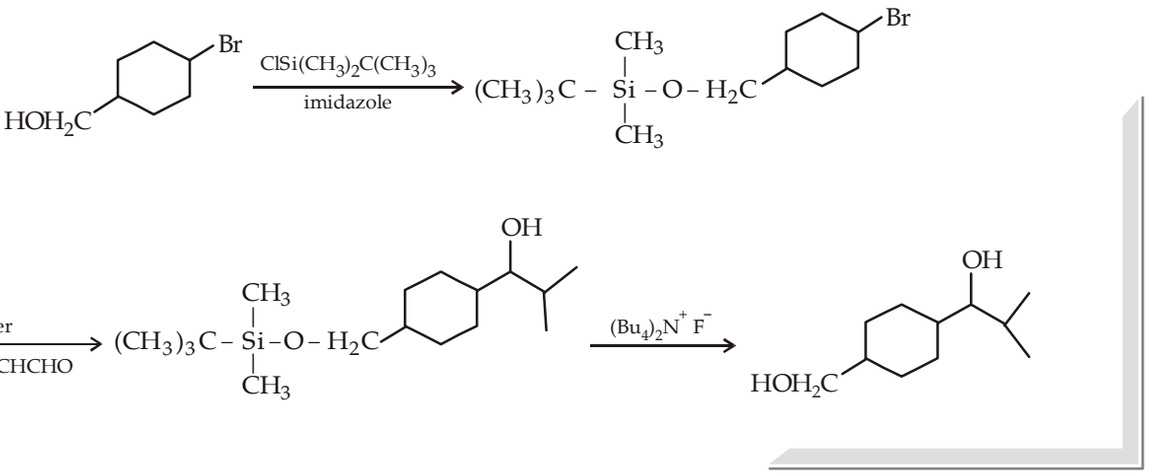
Give steps involved in the following transformation using Grignard Synthesis.



Solution :

Since Grignard reagents decompose the alcoholic –OH group, the latter is first protected by converting it to a *tert*-butyldimethylsilyl ether.

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10.6 Organozinc Reagents for Cyclopropane Synthesis

Zinc reacts with alkyl halides in a manner similar to that of magnesium.

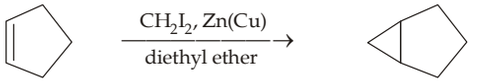
$$RX + Zn \xrightarrow{\text{ether}} RZnX$$

Organozinc reagents are less reactive toward aldehydes and ketones than Grignard reagents and organolithium compounds. An organozinc compound important in organic synthesis, is *iodomethylzinc iodide,* ICH_2ZnI. It is prepared by the reactions of zinc-copper couple with diiodomethane is ether.

$$\underset{\text{Di-iodomethane}}{ICH_2I} + Zn \xrightarrow[Cu]{\text{diethyl ether}} \underset{\text{Iodomethylzinc iodide}}{ICH_2ZnI}$$

Iodomethylzinc iodide is very important in synthesising cyclopropanes. It reacts with alkenes to give cyclopropanes (*Simmons-Smith reaction*). In this reaction methylene is transferred from iodomethylzinc iodide to the double bond converting latter to cyclopropane derivative.

$$R_2C = CR_2 + ICH_2ZnI \xrightarrow[\text{ether}]{\text{diethyl}} \begin{array}{c} R \quad R \\ \diagdown / \\ C \\ / \diagdown \\ R \quad R \end{array} + ZnI_2$$

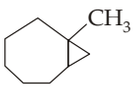


Cyclopentene — Bicyclo [3.1.0] hexane

The reaction is stereospecific, addition of —CH_2 takes place in *syn* manner.

TEST YOUR UNDERSTANDING - 10.6

1. Identify the starting material in each case which can be converted into following cyclopropane derivatives by reaction with iodomethylzinc iodide.

(*i*) 

(*ii*) 

10.7 Organocadmium Compounds

These are quite similar to organozinc compounds and best prepared by the reaction of Grignard reagents with cadmium chloride

$$2CH_3MgBr + CdCl_2 \longrightarrow (CH_3)_2Cd + 2MgBrCl$$

These reagents have linear geometry (metal is *sp* hybridised). Chemically, they are similar to dialkylzincs but are less reactive. When treated with acid chlorides, they form the corresponding ketones.

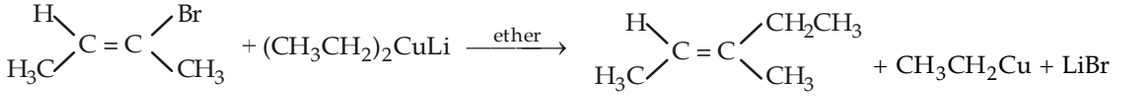
$$(C_2H_5)_2Cd + 2CH_3COCl \longrightarrow 2C_2H_5.CO.CH_3 + CdCl_2$$

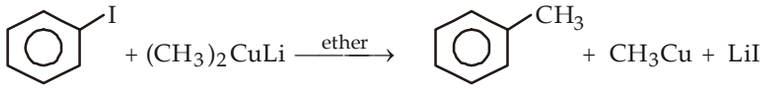
Since cadmiumalkyls are less reactive, they do not react with ketones, hence cadmium alkyls are considered useful for the synthesis of ketones.

10.8 Organocuprates (Gilman reagents)

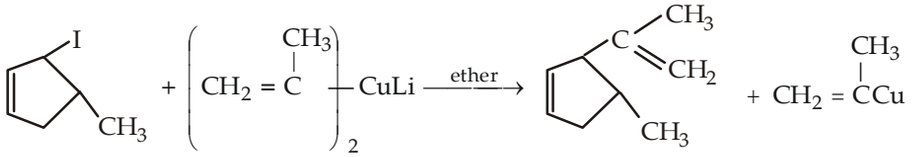
$$2CH_3Li + CuI \xrightarrow{\text{other or THF}} \underset{\text{Gilman reagent}}{(CH_3)_2CuLi} + LiI$$

Gilman reagents are useful in synthetic chemistry. They react with alkyl halides (except alkyl fluorides) and replace the halogen by one of the alkyl groups of the Gilman reagent.

(i) 

(ii) 

(iii) $CH_3\underset{\underset{Br}{|}}{C}HCOCH_3 + (CH_3)_2CuLi \xrightarrow{\text{ether}} CH_3\underset{\underset{CH_3}{|}}{C}HCOCH_3 + CH_3Cu + LiBr$

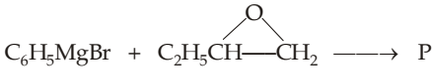
(iv) 

EBD_7088

EXERCISE 10.1 (MCQ - ONE option correct)

1. IUPAC name of HC ≡ CNa is
(*a*) sodium acetylide (*b*) ethynylsodium
(*c*) sodium acetylene (*d*) both (*a*) and (*b*).

2. Predict the nature of P in the following reaction :



(*a*) $C_6H_5CH(C_2H_5)CH_2OH$ (*b*) $C_6H_5CH_2CH(OH)C_2H_5$ (*c*) both (*a*) and (*b*) (*d*) None of the two.

3. Which can be other reactant for synthesising methyl alcohol from Grignard reagent ?
(*a*) Formaldehyde (*b*) An oxirane
(*c*) Oxygen (*d*) Any of the three.

4. 3-Phenyl-3-pentanol can be prepared from a Grignard reagent and other component which can be
(*a*) 3-Pentanone (*b*) Ethyl benzoate
(*c*) Ethyl phenyl ketone (*d*) Any of the three.

5. Identify the nature of main product(s) in the following reaction:

$$CH_3MgBr + CH_3COCH_2CH_2OH \xrightarrow[(ii)\ NH_4Cl/H_2O]{(i)\ \text{diethyl ether}}$$

(*a*) CH_4
(*b*) CH_3CH_3
(*c*) 3-Methylbutane-1, 4-diol
(*d*) Both (*a*) and (*c*).

6. Which of the following is an organometallic compound ?
(*a*) Lithium methoxide
(*b*) Lithium acetate
(*c*) Lithium dimethylamide
(*d*) Methyllithium.

7. The addition of the Grignard reagent, CH_3MgBr to acetaldehyde is a nucleophilic addition to the carbonyl group. The nucleophile in this reaction is
(*a*) CH_3CHO (*b*) $\overset{+}{C}H_3$
(*c*) Br^- (*d*) $:CH_3^-$

8. $(CH_3)_3CMgCl$ on reaction with D_2O produces
(*a*) $(CH_3)_3CD$ (*b*) $(CH_3)_3COD$
(*c*) $(CD_3)_3CD$ (*d*) $(CD_3)_3COD$.

9. Grignard reagent is not prepared in aqueous medium but prepared in ether medium, because
(*a*) the reagent is highly reactive in ether
(*b*) the reagent becomes inactive in water
(*c*) the reagent reacts with water
(*d*) none of three is correct.

10. Reaction of Grignard reagent with formaldehyde followed by acidification gives
(*a*) an aldehyde (*b*) a primary alcohol
(*c*) a carboxylic acid (*d*) a ketone.

11. Reaction of elemental sulphur with Grignard reagent followed by acidification leads to the formation of
(*a*) mercaptan (*b*) sulphoxide
(*c*) thioether (*d*) sulphonic acid.

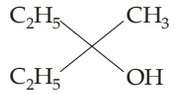
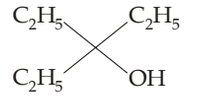
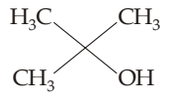
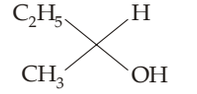
12. 1-Phenylethanol can be prepared by the reaction of benzaldehyde with
(*a*) methyl bromide
(*b*) ethyl iodide and magnesium
(*c*) methyl iodide and Mg
(*d*) methyl bromide and aluminium bromide.

13. Which of the following compounds on reaction with CH_3MgBr will give a tertiary alcohol ?
(*a*) C_6H_5CHO (*b*) $C_2H_5COOCH_3$
(*c*) C_2H_5COOH (*d*) $CH_3CH(O)CHCH_3$.

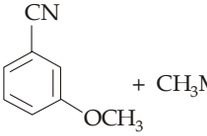
14. Reaction of CH_3MgBr with acetone and hydrolysis of the resulting product gives
(*a*) $CH_3CH_2CH_2OH$ (*b*) $CH_3CH_2CH_2CH_2OH$
(*c*) $(CH_3)_2CHOH$ (*d*) $(CH_3)_3COH$.

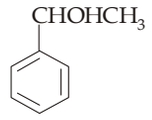
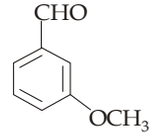
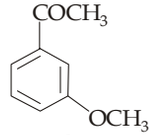
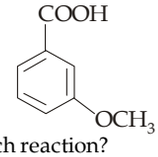
15. To prepare 3-ethylpentan-3-ol, the reagents needed are
(*a*) $CH_3CH_2MgBr + CH_3COCH_2CH_3$
(*b*) $CH_3MgBr + n\text{-}C_3H_7COCH_2CH_3$
(*c*) $C_2H_5MgBr + C_2H_5COC_2H_5$
(*d*) $n\text{-}C_3H_7MgBr + CH_3COC_2H_5$.

16. Ethyl ester $\xrightarrow[\text{excess}]{CH_3MgBr}$ P. The product P will be

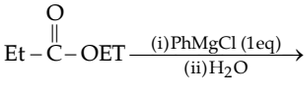
(*a*) 
(*b*) 
(*c*) 
(*d*) 

17. $C_6H_5MgBr \xrightarrow[(ii)\ H_3O^+]{(i)\ CO_2}$ P. Here P is
In the above reaction, P is
(*a*) C_6H_5CHO (*b*) C_6H_5COOH
(*c*) C_6H_5OH (*d*) $C_6H_5COC_6H_5$.

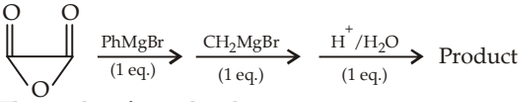
18.  + $CH_3MgBr \longrightarrow A \xrightarrow{H_3O^+} B$. Here B is

(*a*) 
(*b*) 
(*c*) 
(*d*) 

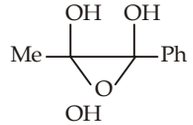
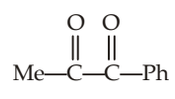
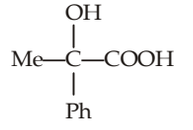
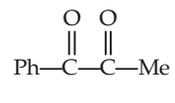
19. Ketones are best prepared by which reaction?
(a) RCOCl + RMgX (b) RCN + RLi
(c) RCOCl + R_2Cd (d) All the three

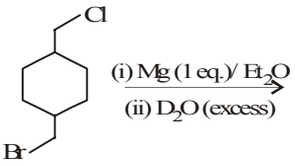
20. 

True about product of above reaction is
(*a*) One of the product will give positive iodoform test
(*b*) Product will give CO_2 on heating
(*c*) Product will give only one oxime with NH_2OH
(*d*) Product will give achiral alcohol with EtMgBr followed by hydrolysis

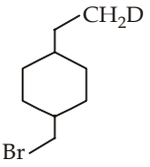
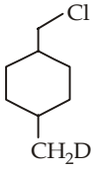
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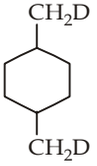
The product formed in the reaction is :

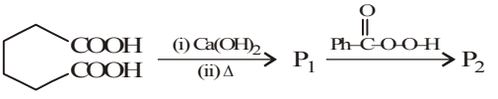
(*a*) 
(*b*) 
(*c*) 
(*d*) 

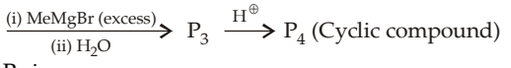
22. 

Major product is

(*a*)  (*b*) 

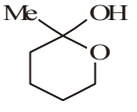
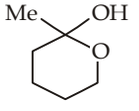
(*c*)  (*d*) None of these

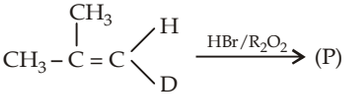
23. 



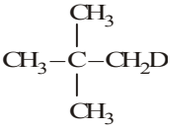
P_4 is :

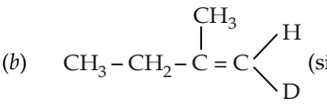
(*a*)  (*b*) 

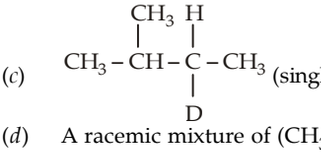
(*c*)  (*d*) 

24. (i) 

(ii) P (dextrorotatory) $\xrightarrow{CH_3MgBr}$ The end product is :

(*a*) 

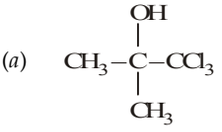
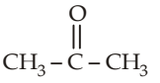
(*b*)  (single stereoisomer)

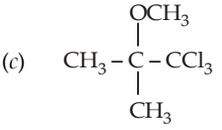
(*c*)  (single stereoisomer)

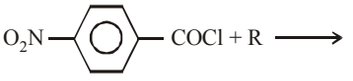
(*d*) A racemic mixture of $(CH_3)_2CH–CHD–CH_3$

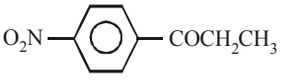
25. 

B is

(*a*)  (*b*) 

(*c*)  (*d*) None of these

26. 



The reagent R may be

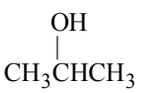
CH_3CH_2MgBr I	CH_3CH_2Li II
$(CH_3CH_2)_2Cd$ III	$(CH_3CH_2)_2CuLi$ IV

(a) I or II (b) I or II or III
(c) III or IV (d) Any of the four

27. Ethyl magnesium bromide when treated with methanal forms an addition product which when hydrolysed with water in presence of acids forms propanol. What would be the major product when the above reaction is carried out in the following sequence ?

$$CH_3CH_2Mg\,Br \xrightarrow[(ii)\ HCHO]{(i)\ H_3O^+}$$

(a) $CH_3CH_2CH_2OH$ (b) CH_3CH_2CHO

(c) CH_3CH_3 (d) 

EXERCISE 10.2 (MCQ >1 option correct, Passage based, Matching)

DIRECTIONS for Q. 1 to Q. 11 : Multiple choice questions with one or more than one correct option(s).

1. Grignard reagents easily react with
(a) carbonyl compounds (b) esters
(c) carbon dioxide (d) hydrogen cyanide

2. Which of the following statement(s) is(are) true?
(a) Sodium forms ionic organometallic compounds
(b) Sodium does not form any organometallic compound
(c) Mercury forms ionic organomercury compounds
(d) Mercury forms covalent organomercury compounds

3. The solvent used in preparing organometallic compounds belongs to which series of organic compounds?
(a) An ether (b) Hydrocarbon
(c) A cyclic ether (d) Dry alcohol

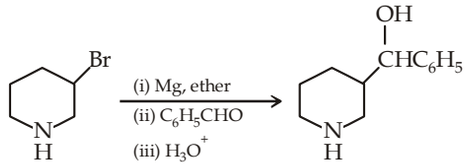
4. Solvent used during preparation of organolithium compounds should be completely dry because
(a) lithium forms insoluble hydroxide
(b) the organolithium compound formed will react with water
(c) the solvent is protonated and thus becomes inactive
(d) solvent is insoluble in water

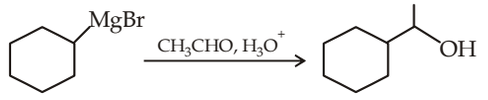
5. Which of the following statement(s) is/are true?
(a) Methylmagnesium iodide is a powerful Bronsted base
(b) Methylmagnesium iodide is a powerful Lewis base
(c) Methylmagnesium bromide is a powerful nucleophile
(d) Methylmagnesium bromide is a weak nucleophile

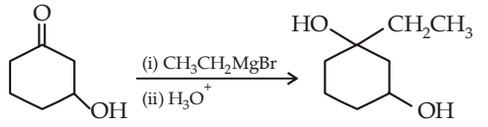
6. An organic halide containing which of the following group does not form easily the corresponding Grignard reagent
(a) C = C (b) $–NO_2$
(c) $–N(CH_3)_2$ (d) –SH

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7. Which of the following reaction(s) is(are) not feasible?

(a) 

(b) 

(c) 

(d) All the three are feasible

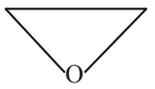
8. Methyl magnesium iodide may react with
(a) 1 mole of ethyl formate
(b) 2 moles of ethyl formate
(c) no reaction with ethyl formate
(d) zinc chloride

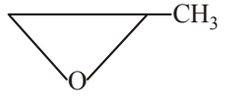
9. Isobutyl magnesium bromide with dry ether and absolute alcohol gives

(a) $CH_3CH(CH_3)CH_2OH$ (b) $CH_3CH(CH_3)CH_2CH_2CH_3$

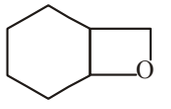
(c) Mg(OH)Br (d) CH_3CH_2OMgBr

10. Primary alcohols can be obtained from Grignard reagent by reacting with

(i) 

(ii) 

(iii) 

(iv) 

(a) (i) (b) (i) and (iii)
(c) (i), (ii) and (iii) (d) All the four

11. 2-Phenylbutanol-2 can be prepared by which of the following combinations ?
(*a*) $C_6H_5COCH_3 + C_2H_5MgBr$
(*b*) $C_2H_5COCH_3 + C_6H_5MgBr$
(*c*) $C_6H_5COC_2H_5 + CH_3MgBr$
(*d*) $C_6H_5COC_6H_5 + C_2H_5MgBr$

INSTRUCTION for Q. 12 to 20 : Read the passages given below and answer the questions that follow.

PASSAGE 1

Observe the following reactions and answer the questions

(i) $CH_3CH=CHCH_2Br \xrightarrow[\text{dry ether}]{Mg} CH_3CH=CHCH_2MgBr \xrightarrow{H_2O}$ Alkene

(ii) $CH_3\underset{Br}{\underset{|}{C}}HCH=CH_2 \xrightarrow[\text{dry ether}]{Mg} CH_3\underset{MgBr}{\underset{|}{C}}HCH=CH_2 \xrightarrow{H_2O}$ Alkene

12. The alkene formed in reaction (i) is
(a) but-2-ene (b) but-1-ene
(c) both (d) none

13. The second step of each of the above reactions is an example of
(a) acid-base reaction
(b) nucleophilic addition
(c) nucleophilic substitution
(d) none of these

14. The Grignard reagent formed in each of the above reactions are stable due to
(a) electronegativity of Br (b) resonance
(c) presence of MgBr (d) unstable

PASSAGE 2

Grignard reagents (organomagnesium halides) were discovered by the French chemist Victor Grignard in 1900. He was awarded the Nobel Prize for his discovery in 1912. Grignard reagents behave as if they were carbanions.They have extensive use in organic synthesis. They are usually prepared by reacting an organic halide with magnesium in an anhydrous ether solvent as follows

$$RX + Mg \rightarrow RMgX$$

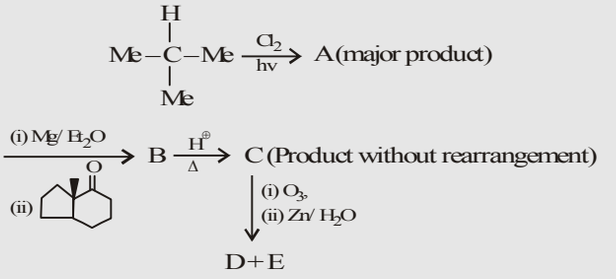
where R is a suitable organic group and X is I, Br, or Cl

15. Grignard reagents are
I. Strong acids II. Strong bases
III. Strong electrophiles IV. Strong nucleophiles
(a) I is correct (b) II is correct
(c) I & III are correct (d) II & IV are correct

16. In the preparation of a Grignard reagent, the reason why the ether solvent must be anhydrous is that
(a) hydrogen ions from any water present would immediately react with any Grignard reagent produced
(b) grignard reagents are insoluble in water
(c) water is necessary for Grignard reagents to ionize
(d) water is the universal solvent

17. Which of the following are suitable organic reactants for synthesizing Grignard reagents?
I. C_3H_7I II. CH_3OCH_2Br
III. $HSCH_2CH_2I$ IV. CH_3COCH_2Br
(a) I and II (b) II and III
(c) III and IV (d) I and IV

PASSAGE 3



18. Select the correct statement
(*a*) D is a bicyclo compound and doesn't give aldol condensation with NaOH
(*b*) D is a bicyclo compound and it givs aldol condensation with NaOH at two different α-positions.
(*c*) E is an open chain compound and doesn't give aldol condensation with NaOH
(*d*) E is an open chain compound and will give aldol condensation with NaOH

19. How many enantiomeric pairs are formed when C is treated with NBS
(*a*) 3 (*b*) 2
(*c*) 1 (*d*) None of these

20. How many deuterium atoms are present in the compound which is formed when compound D is kept with dil. KOD for long time and then heated ?
(*a*) 1 (*b*) 2
(*c*) 3 (*d*) 4

Instructions for Q. 21 to 22 : Following questions are Multiple Matching type Questions :

21.

	Column I	*Column II*
(A)	CH_3MgBr + epoxide	(a) Zerewittnoff estimation
(B)	$C_6H_{11}MgCl + CH_2O$	(b) 2° alcohols
(C)	Solvent in preparing RMgX	(c) Pentane
(D)	n-$C_5H_{11}MgBr + NH_3$	(d) 1° alcohols

22

	Column I	*Column II*
(A)	RMgX + Methyl ester	(a) Ketones
(B)	RMgX + Acid anhydrides	(b) 3° alcohols
(C)	Most reactive organometallic compound	(c) Me_2CuLi
(D)	Gilman reagents	(d) $CH_2=CHCH_2MgBr$

Instructions for Q. 23 to 25 : Following questions are Assertion and Reasoning Type Questions :
Note : Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 5 choices (a), (b), (c), (d) and (e) out of which ONLY ONE is correct.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement -1 is True, Statement-2 is False.
(d) Statement -1 is False, Statement-2 is True.
(e) Statement -1 is False, Statement-2 is False.

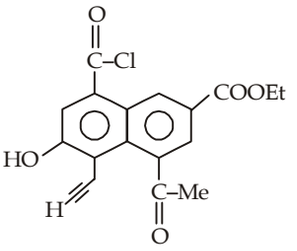
23. **Statement-1 :** Grignard reagents are prepared in ether but not in benzene.
Statement-2 : Grignard reagents are soluble in benzene.

24. **Statement-1 :** Hydroxyketones are not directly used in Grignard reaction.
Statement-2 : Grignard reagents react with hydroxyl group.

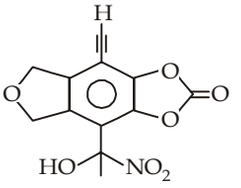
25. **Statement-1 :** All the iron-carbon bond distances in ferrocene are equal.
Statement-2 : The π electrons in the cyclopentadienyl group of ferrocene are delocalised.

Instructions for Q. 26 to 29 : Following questions are Integer Type Questions :

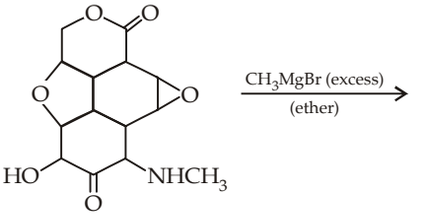
26. How many moles of Grignard reagent can react with one mole of following compound.



27. Calculate number of molecules of Girgnard reagent consumed by 1 molecule of following compound.



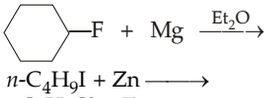
28.



Find the number of CH_3MgBr molecules used by the given reactant, to react completely.

29. How many total possible Grignard reagent can give 3-methylpentane on treatment with $H^{\oplus}$.

EXERCISE 10.3 (Subjective Problems)

1. (*a*) Give the products for the viable reactions.
(*i*) $CH_3CH_2CH_2Cl + Mg \xrightarrow{THF}$
(*ii*)  $\xrightarrow{Et_2O}$
(*iii*) n-$C_4H_9I + Zn \longrightarrow$
(*iv*) n-$C_4H_9Cl + Zn \longrightarrow$.
(*b*) Discuss the role of metal reactivity in the viability of the reaction.

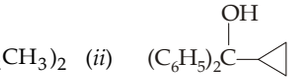
2. Give the product formed from the reaction of Mg/Et_2O with
(*i*) $BrCH_2CH_2Br$ (*ii*) $Br(CH_2)_3Br$
(*iii*) $Br(CH_2)_4Br$.

3. Explain the following.
(*i*) Vinyllithium is recommended rather than vinylmagnesium
(*ii*) $BrCH_2C \equiv CH$ cannot be converted into corresponding Grignard or organolithium reagent.

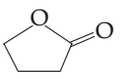
4. Write product (products) formed by the reaction of ethylmagnesium bromide with each of the following.
(*i*) D_2O (*ii*) Acetophenone
(*iii*) Cyclohexanone (*iv*) Cyclopentadiene
(*v*) Butyne-1, followed by CH_3CHO and then H_3O^+.

5. Butyllithium is commercially available, give reactions for converting it into lithium diethylamide and lithium 1-hexanolate.

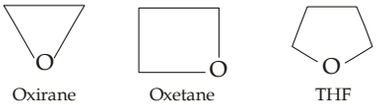
6. Suggest as many as possible ways by which following alcohols can be prepared by using a Grignard reagent.
(*i*) 2-Hexanol (*ii*) 2-Phenyl-2-butanol.

7. What combination of ester and Grignard reagent should be used to prepare following alcohols.
(*i*) $C_6H_5 . \overset{OH}{\overset{|}{C}}(CH_2CH_3)_2$ (*ii*) 

8. Predict how many moles of a Grignard reagent can be consumed by one mole of the compound drawn on side. Give also structure of the final product.



9. Although oxirane (oxacyclopropane) and oxetane (oxacyclobutane) react with Grignard reagents and organolithiums to form alcohols, tetrahydrofuran (oxacyclopentane) is so unreactive that it is used as a solvent in the preparation of these reagents. Explain.



Oxirane Oxetane THF

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SOLUTIONS

EXERCISE 10.1

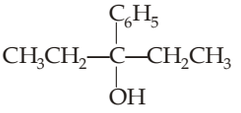
1	(d)	**6**	(d)	**11**	(a)	**16**	(c)	**21**	(c)	**26**	(c)
2	(b)	**7**	(d)	**12**	(c)	**17**	(b)	**22**	(d)	**27**	(c)
3	(c)	**8**	(a)	**13**	(b)	**18**	(c)	**23**	(a)		
4	(d)	**9**	(c)	**14**	(d)	**19**	(c)	**24**	(c)		
5	(a)	**10**	(b)	**15**	(c)	**20**	(d)	**25**	(d)		

2. When Grignard reagent attacks on an oxirane, alkyl or aryl group attacks on the less substituted carbon atom.

3. Formaldehyde will give as alcohol having one carbon atom more than that of the alkyl group of Grignard reagent. Simplest oxirane (ethylene oxide) will increase two carbon atoms ; while reaction of oxygen will form alcohol corresponding to the alkyl group of Grignard reagent.

$$CH_3MgBr + \frac{1}{2}O_2 \longrightarrow CH_3OMgBr \xrightarrow{H_3O^4} CH_3OH.$$

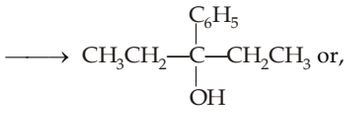
4. 3-Phenyl-3-pentanol (a 3° alcohol) can be prepared from Grignard reagent and a ketone or an ester. Possible combinations will be



3-Phenyl-3-pentanol

(*a*) $CH_3CH_2.CO.CH_2CH_3$ (Pentanone-3) $+ C_6H_5MgBr$, or

(*b*) $C_6H_5COOC_2H_5$ (Ethyl benzoate) $+ 2CH_3CH_2MgBr$



(*c*) $C_6H_5.CO.CH_2CH_3$ (Ethyl phenyl ketone) $+ CH_3CH_2MgBr$

5. Grignard reagent would react as a base with the acidic hydrogen rather than reacting at the carbonyl group as a nucleophile for which excess of Grignard reagent must be used (1 mole for reacting with the —OH group and the second mole for > CO group).

6. Only methyllithium has C—M bond.

7. Electronegativity of C is more than that of Mg hence carbon of methyl will be electron rich, *i.e.* it acts as a nucleophile.

8. $(CH_3)_3CMgCl + D_2O \longrightarrow (CH_3)_3CD + MgCl(OD)$.

9. Grignard reagents are strongly basic in character due to carbanionic nature, hence it will react with water, a weak acid.

10. Formaldehyde reacts with RMgX to form 1° alcohols.

11. $RMgX + S \longrightarrow RSMgX \xrightarrow{H_3O^+} RSH + MgXOH.$

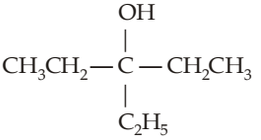
12. 1-Phenylethanol $C_6H_5.\underset{OH}{\underset{|}{C}}H.CH_3$ is a 2° alcohol so it can be prepared from benzaldehyde and Grignard reagent,

CH_3MgX ($CH_3I + Mg$).

13. Tertiary alcohols are formed by treating Grignard reagents either with ketones or excess of an ester other than formate which will give 2° alcohol.

14. Same as above.

15. Write down the formula of the required compound, examine the nature of functional group and then recollect its preparation from Grignard reagents. So here, the component should be diethyl ketone and ethylmagnesium bromide.



16. In the reaction an ester is treated with excess of CH_3MgBr (a Grignard reagent), so the product can be either a 2° alcohol (when ethyl ester is $HCOOC_2H_5$) or a 3° alcohol (when ethyl ester is $RCOOC_2H_5$) having at least *two methyl groups* (from excess of CH_3MgBr). Only option *C* has at least two methyl groups.

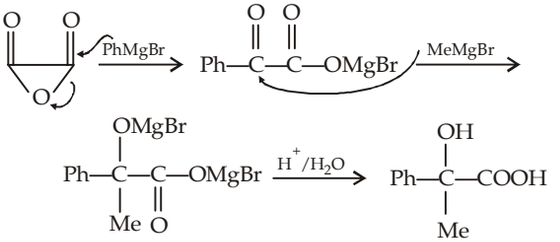
17. Recall that dry ice (solid CO_2) give caboxylic acids, when treated with Grignard reagents.

18. Recall that cyanides when treated with Grignard reagents give ketones.

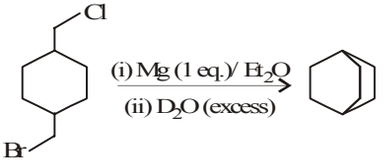
20. $Et-\underset{\underset{O}{\|}}{C}-OEt \xrightarrow[(ii)\ H_2O]{(i)\ PhMgCl} Et-\underset{\underset{Ph}{|}}{\overset{\overset{OH}{|}}{C}}-OH \xrightarrow{(-H_2O)}$

$$Et-\underset{\underset{Ph}{|}}{\overset{\overset{O}{\|}}{C}}-Et \xrightarrow{EtMgBr} Et-\underset{\underset{Ph}{|}}{\overset{\overset{Et}{|}}{C}}-OH$$

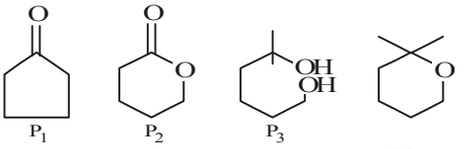
21.



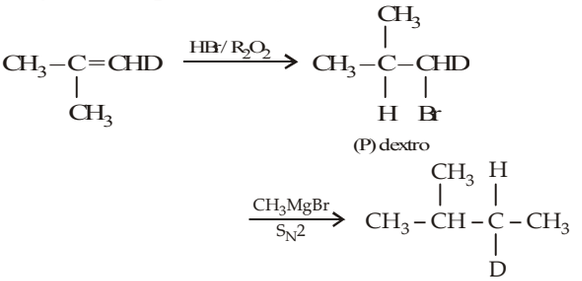
22.



23.



24.



(P) dextro

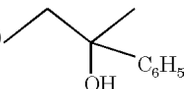
(single stereoisomer)

26. Organomagnesium and organolithium compounds can't be prepared from the alkyl (or aryl) halide having $-NO_2$ group. On the other hand, organocopper and organocadmium compounds, do not react with the $-NO_2$ group.

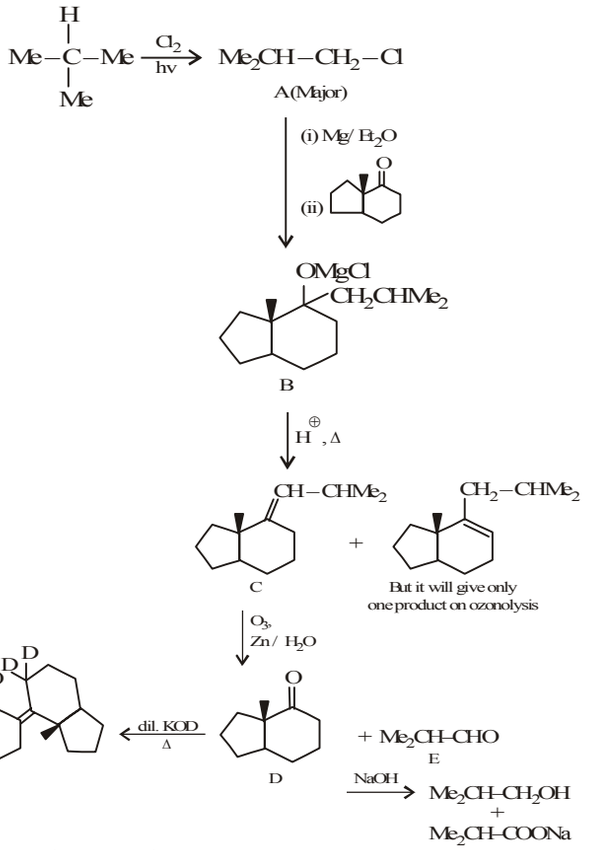
27. $CH_3CH_2MgBr \xrightarrow{H^+} CH_3CH_3$

EXERCISE 10.2

>1 CORRECT OPTION	1	(a, b, c, d)	5	(a, c)	9	(b, c)
	2	(a, d)	6	(b, d)	10	(b)
	3	(a, b, c)	7	(a, b, c)	11	(a, b, c)
	4	(a, b)	8	(a, b, d)		
PASSAGE 1	12	(c)	13	(a)	14	(b)
PASSAGE 2	15	(d)	16	(a)	17	(a)
PASSAGE 3	18	(c)	19	(d)	20	(b)
Match the Following	21	(A) - b, d, (B) - d, (C) - c, (D) - a, c				
	22	(A) - a, b, (B) - a, b, (C) - d, (D) - c				
A/R	23	(c)	24	(a)	25	(a)
INTEGER	26	7	27	6	28	6
	29	4				

11.(*a,b,c*)  is a 3° alcohol ; the first three combinations can be applied for its preparation.

Sol. 18-20 :



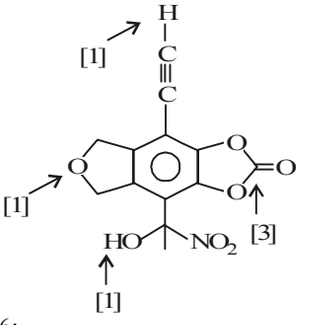
18.(*c*) **19.**(*d*) **20.** (*b*)

23.(*c*) The correct reason is : Grignard reagents are soluble in ether but not in benzene

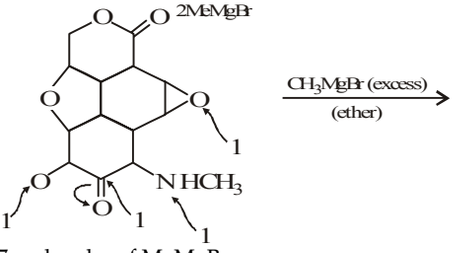
24.(*a*) **R** is the correct explanation of **A**.

26. one mole for $-COCH_3$
two moles for –COOEt
two moles for –COCl
one mole for $-C\equiv CH$
one mole for –OH
Total 7 moles.

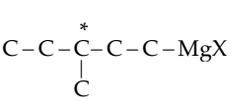
27. **6**



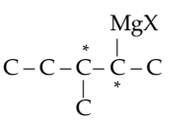
28. 6;



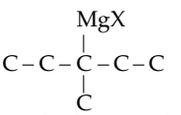
7 molecules of MeMgBr.

29. 

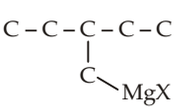
(±)(2)enantiomers



4 Chiral compounds



achiral compound

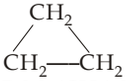


achiral compound

EXERCISE 10.3

1. (*a*) (*i*) $CH_3CH_2CH_2MgCl$ (THF is a better solvent than Et_2O for RCl's)
(*ii*) No reaction
(*iii*) n-C_4H_9ZnI
(*iv*) No reaction.
(*b*) The reactivity of a metal depends on its reduction potential; the more easily a metal is reduced, the less reactive it is, *e.g.* Mg > Zn.

2. (*i*) $H_2C = CH_2$ (elimination of *vic* halogens)

(*ii*) 

(*iii*) $BrMg(CH_2)_4MgBr$. Here intermolecular cyclization does not occur because a 4-membered ring is not formed as readily as a 3-membered ring.

3. (*i*) Vinyl halides, especially chloride, react sluggishly with Mg. Further, *n*-C_4H_9Li is easily available in the market it can used for preparing vinyllithium from vinyl chloride (*metal-halogen exchange method*).

$CH_2 = CHCl + n\text{-}C_4H_9Li \longrightarrow CH_2 = CHLi + n\text{-}C_4H_9Cl$

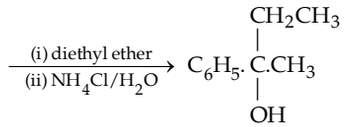
Remember that the compound bearing metal to the more electronegative carbon is more stable, thus in the above reversible reaction, $CH_2 = CHLi$ is more stable than *n*-C_4H_9Li.

(*ii*) Grignard reagent formed will instantaneously react with the terminal acidic hydrogen.

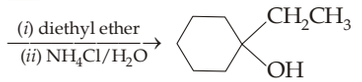
$$BrCH_2C \equiv CH \xrightarrow{Mg} [BrMgCH_2C \equiv CH] \xrightarrow{BrCH_2C \equiv CH} CH_3C \equiv CH + BrCH_2C \equiv CMgBr$$

4. (*i*) $CH_3CH_2MgBr + D_2O \longrightarrow CH_3CH_2D + MgBr(OD)$

(*ii*) $CH_3CH_2MgBr + C_6H_5.CO.CH_3$



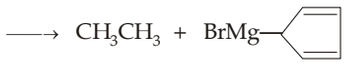
(*iii*) CH_3CH_2MgBr + 



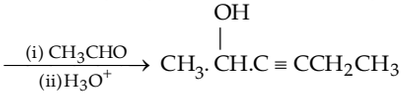
1-Ethylcyclohexanol

(*iv*) CH_3CH_2MgBr + 

Cyclopentadiene



(*v*) $CH_3CH_2MgBr + HC \equiv CCH_2CH_3 \longrightarrow CH_3CH_3 + BrMgC \equiv CCH_2CH_3$



Hex-3-yn-2-ol

5. *n*-Butyllithium is a strong base and hence can abstract proton from compounds having —OH, —NH_2 or —SH.

$(CH_3CH_2)_2NH$ + $CH_3CH_2CH_2CH_2Li$

Diethylamine (Stronger acid); Butyllithium (Stronger base)

$\longrightarrow$ $(CH_3CH_2)_2NLi$ + $CH_3CH_2CH_2CH_3$

Lithium diethyl amide (Weaker base); Butane (Weaker acid)

$CH_3(CH_2)_4CH_2OH$ + $n\text{-}C_4H_9Li$

Hexanol-1

$\longrightarrow$ $CH_3(CH_2)_4CH_2OLi$ + $n\text{-}C_4H_{10}$

Lithium1-hexanolate; Butane

6. First of all draw structure for the compound to be synthesised and examine the functional group in it. Then apply your memory that from which functional group this functional group can be introduced

(*i*) 2-Hexanol, $CH_3.CH(OH).(CH_2)_3CH_3$, is a secondary alcohol, hence the two main reactants are Grignard reagent and an aldehyde other than formaldehyde. The two possible pairs for this are

(*a*) CH_3CHO + $BrMgCH_2(CH_2)_2CH_3$

Ethanal; Butylmagnesium bromide

$\longrightarrow$ $CH_3CH(OH).CH_2(CH_2)_2CH_3$

2-Hexanol

(*b*) $CH_3CH_2CH_2CH_2CHO$ + CH_3MgBr

Pentanal

$\longrightarrow$ $CH_3CH_2CH_2CH_2CH(OH)CH_3$

2-Hexanol

(*ii*) 2-Phenyl-2-propanol, $CH_3.\underset{\displaystyle C_6H_5}{\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}—CH_3$. It is a 3° alcohol, hence it can be prepared by the reaction of Grignard reagent and ketone. Two possible combinations are

(*a*) $C_6H_5MgBr + CH_3.CO.CH_3 \longrightarrow CH_3—\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}—CH_3$ (C_6H_5)

(*b*) $CH_3MgBr + C_6H_5.CO.CH_3 \longrightarrow CH_3—\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}—CH_3$ (C_6H_5)

(*c*) Since the product (a 3° alcohol) has two similar alkyl groups (methyl), it can also be prepared by reacting 1 mole of ester ($C_6H_5COOCH_3$) with two moles of alkyl magnesium halide (CH_3MgI).

$C_6H_5COOCH_3$ + $2CH_3MgI$

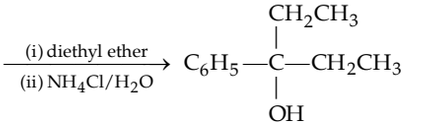
$\longrightarrow$ $C_6H_5—\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}—OH$ (CH_3)

Methyl benzoate; 2-Phenyl-2-propanol

7. (*i*) Note that the 3° alcohol is having two ethyl groups, so these should be introduced *via* Grignard reagents CH_3CH_2MgBr, hence the other component should be an ester of benzoic acid.

$C_6H_5COOCH_3 + 2CH_3CH_2MgBr$

Methyl benzoate

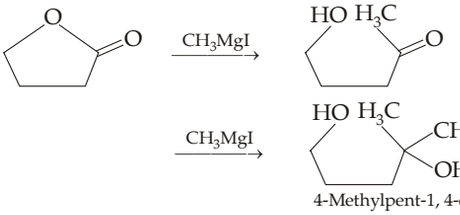


3-Phenyl-3-pentanol

(*ii*) Here the Grignard reagent is C_6H_5MgBr and ester is alkyl cyclopropanecarboxylate.



8. Compound has two functional groups that can react with the Grignard reagent, *viz*. oxirane and ketonic group, each will be taking one mole of the reagent.



4-Methylpent-1, 4-diol

9. The three- and four-membered rings are strained, and hence they open on reaction with RMgX or RLi. THF, on the other hand, has an unstrained five-membered ring hence it is highly resistent to be attacked by RMgX or RLi.

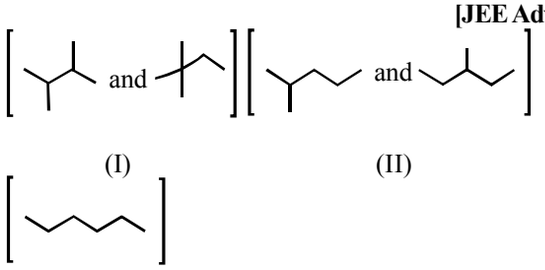
HYDROCARBONS AND HALOGEN DERIVATIVES

PAST YEAR QUESTIONS JEE ADVANCED/IIT-JEE (2013 - 2017)

MCQs with One Correct Answer

1. Isomers of hexane, based on their branching, can be divided into three distinct classes as shown in the figure.

[JEE Adv. 2014]



(I) (II)

(III)

The correct order of their boiling point is

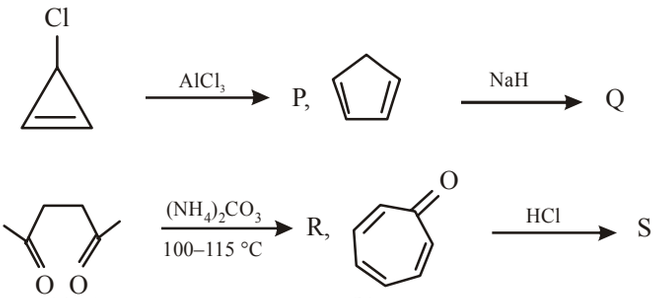
(a) I > II > III (b) III > II > I

(c) II > III > I (d) III > I > II

MCQs with One or More Than One Correct

1. Among P, Q, R and S, the aromatic compound(s) is/are

[JEE Advanced 2013-I]

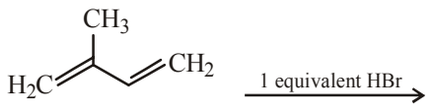


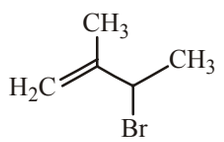
(a) P (b) R

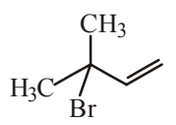
(c) Q (d) S

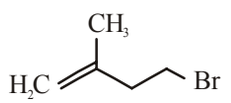
2. In the following reaction, the major product is

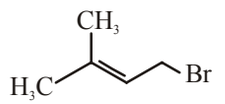
[JEE Adv. 2015]



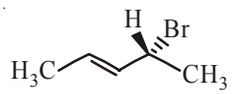
(a) 

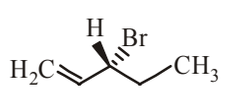
(b) 

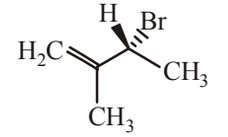
(c) 

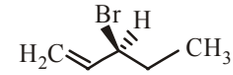
(d) 

3. Compound(s) that on hydrogenation produce(s) optically inactive compound(s) is (are) **[JEE Adv. 2015]**

(a) 

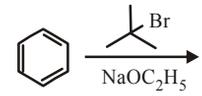
(b) 

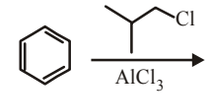
(c) 

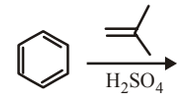
(d) 

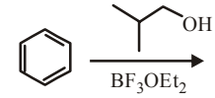
4. Among the following, reaction(s) which gives(give) tert-butyl benzene as the major product is(are)

[JEE Adv. 2016]

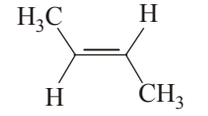
(a) 

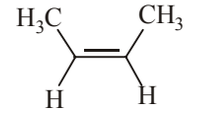
(b) 

(c) 

(d) 

5. The correct statement(s) for the following addition reactions is(are) **[JEE Adv. 2017]**

(i) 

(ii) 

(a) O and P are identical molecules

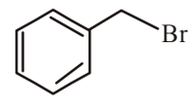
(b) (M and O) and (N and P) are two pairs of diastereomers

(c) (M and O) and (N and P) are two pairs of enantiomers

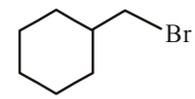
(d) Bromination proceeds through *trans*-addition in both the reactions

6. For the following compounds, the correct statement(s) with respect to nucleophilic substitution reaction is(are)

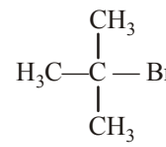
[JEE Adv. 2017]



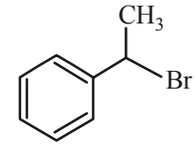
(I)



(II)



(III)



(IV)

(a) I and III follow S_N1 mechanism

(b) I and II follow S_N2 mechanism

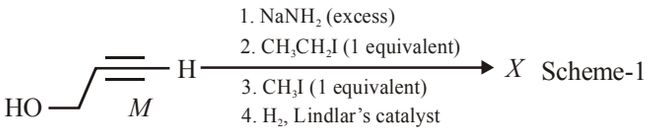
(c) Compound IV undergoes inversion of configuration

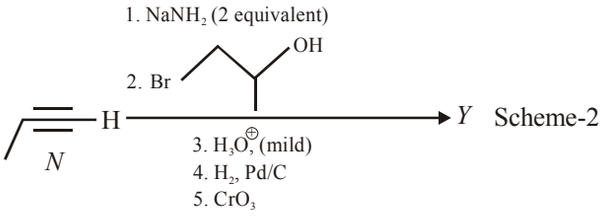
(d) The order of reactivity for I, III and IV is : IV > I > III

Comprehension Based Questions

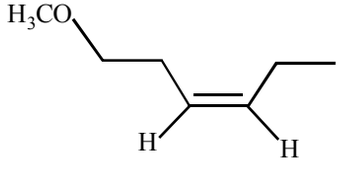
PASSAGE - I

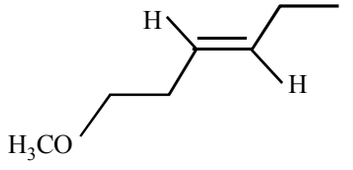
Schemes 1 and 2 describe sequential transformation of alkynes *M* and *N*. Consider only the major products formed in each step for both the schemes.

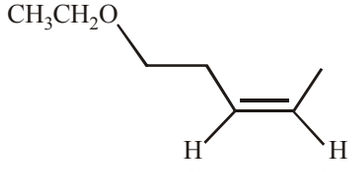


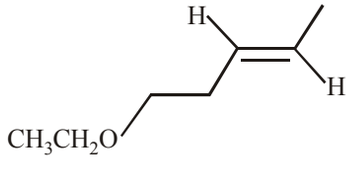


1. The product *X* is **[JEE Adv. 2014]**

(a) 

(b) 

(c) 

(d) 

2. The correct statement with respect to product *Y* is **[JEE Adv. 2014]**

(a) It gives a positive Tollen's test and is a functional isomer of *X*

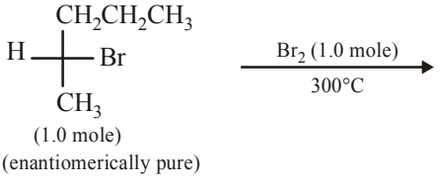
(b) It gives a positive Tollen's test and is a geometrical isomer of *X*

(c) It gives a positive iodoform test and is a functional isomer of *X*

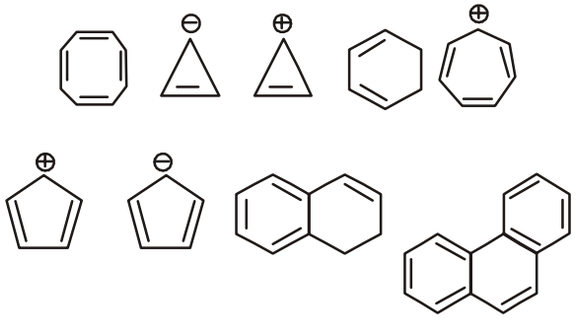
(d) It gives a positive iodoform test and is a geometrical isomer of *X*

Integer Value Correct Type

1. In the following monobromination reaction, the number of possible chiral products is ***(JEE Adv. 2016)***

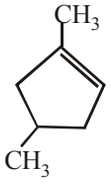


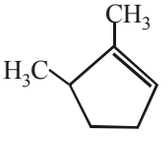
2. Among the following, the number of aromatic compound(s) is **(JEE Adv. 2017)**

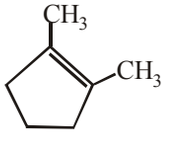


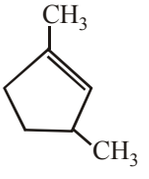
PAST YEAR QUESTIONS JEE MAIN/AIEEE (2013 - 2017)

1. Which compound would give 5 - keto - 2 - methylhexanal upon ozonolysis ? **[JEE M 2015]**

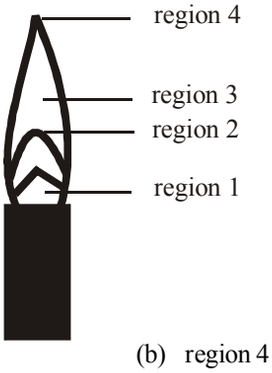
(a) 

(b) 

(c) 

(d) 

2. The hottest region of Bunsen flame shown in the figure below is : **[JEE M 2016]**



(a) region 3 (b) region 4

(c) region 1 (d) region 2

3. At 300 K and 1 atm, 15 mL of a gaseous hydrocarbon requires 375 mL air containing 20% O_2 by volume for complete combustion. After combustion the gases occupy 330 mL. Assuming that the water formed is in liquid form and the volumes were measured at the same temperature and pressure, the formula of the hydrocarbon is: **[JEE M 2016]**

(a) C_4H_8 (b) C_4H_{10}
(c) C_3H_6 (d) C_3H_8

4. The reaction of propene with HOCl ($Cl_2 + H_2O$) proceeds through the intermediate: **[JEE M 2016]**

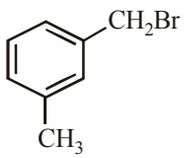
(a) $CH_3-CH(OH)-CH_2^+$

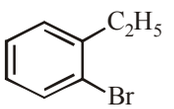
(b) $CH_3-CHCl-CH_2^+$

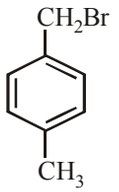
(c) $CH_3-CH^+-CH_2-OH$

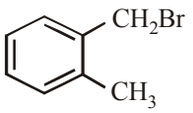
(d) $CH_3-CH^+-CH_2-Cl$

5. Compound (A), C_8H_9Br, gives a white precipitate when warmed with alcoholic $AgNO_3$. Oxidation of (A) gives an acid (B), $C_8H_6O_4$. (B) easily forms anhydride on heating. Identify the compound (A). **[JEE M 2013]**

(a) 

(b) 

(c) 

(d) 

6. In S_N2 reactions, the correct order of reactivity for the following compounds: **[JEE M 2014]**

$CH_3Cl, CH_3CH_2Cl, (CH_3)_2CHCl$ and $(CH_3)_3CCl$ is:

(a) $CH_3Cl > (CH_3)_2CHCl > CH_3CH_2Cl > (CH_3)_3CCl$

(b) $CH_3Cl > CH_3CH_2Cl > (CH_3)_2CHCl > (CH_3)_3CCl$

(c) $CH_3CH_2Cl > CH_3Cl > (CH_3)_2CHCl > (CH_3)_3CCl$

(d) $(CH_3)_2CHCl > CH_3CH_2Cl > CH_3Cl > (CH_3)_3CCl$

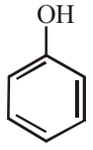
7. The major organic compound formed by the reaction of 1, 1, 1-trichloroethane with silver powder is: **[JEE M 2014]**

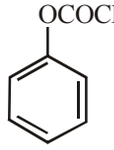
(a) Acetylene (b) Ethene
(c) 2 - Butyne (d) 2 - Butene

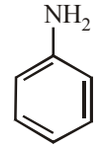
8. The synthesis of alkyl fluorides is best accomplished by : **[JEE M 2015]**

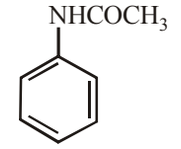
(a) Finkelstein reaction (b) Swarts reaction
(c) Free radical fluorination (d) Sandmeyer's reaction

9. Which of the following compounds will form significant amount of meta product during mono-nitration reaction ? **[JEE M 2016]**

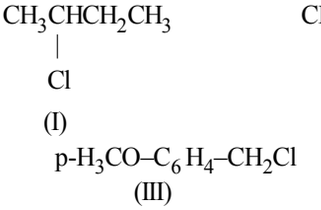
(a) 

(b) 

(c) 

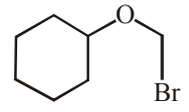
(d) 

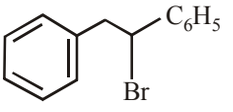
10. The increasing order of the reactivity of the following halides for the S_N1 reaction is **[JEE M 2017]**

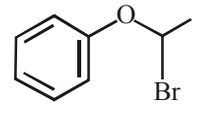


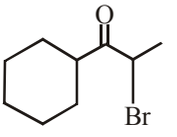
(a) (III) < (II) < (I) (b) (II) < (I) < (III)
(c) (I) < (III) < (II) (d) (II) < (III) < (I)

11. Which of the following , upon treatment with tert-BuONa followed by addition of bromine water, fails to decolourize the colour of bromine? **[JEE M 2017]**

(a) 

(b) 

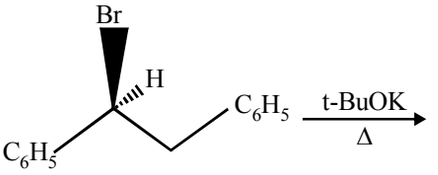
(c) 

(d) 

12. 3-Methyl-pent-2-ene on reaction with HBr in presence of peroxide forms an addition product. The number of possible stereoisomers for the product is : **[JEE M 2017]**

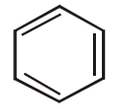
(a) Six (b) Zero
(c) Two (d) Four

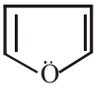
13. The major product obtained in the following reaction is :

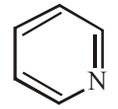


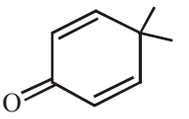
(a) $(\pm)C_6H_5CH(O^tBu)CH_2C_6H_5$ **[JEE M 2017]**
(b) $C_6H_5CH=CHC_6H_5$
(c) $(+)C_6H_5CH(O^tBu)CH_2C_6H_5$
(d) $(-)C_6H_5CH(O^tBu)CH_2C_6H_5$

14. Which of the following molecules is least resonance stabilized? **[JEE M 2017]**

(a) 

(b) 

(c) 

(d) 

SOLUTIONS

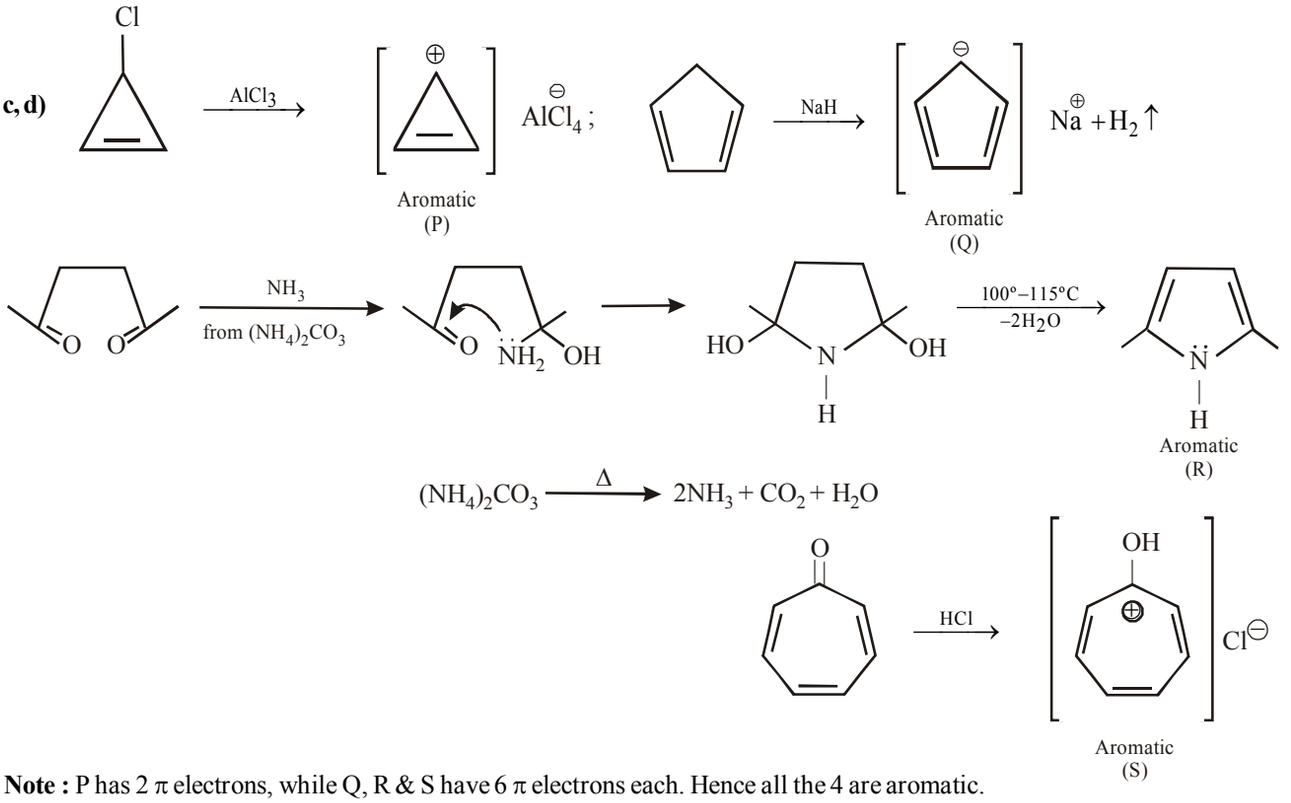
PAST YEAR QUESTIONS JEE ADVANCED/IIT-JEE (2013 - 2017)

MCQs with One Correct Answer

1. (b) Greater the extent of branching, lesser is the boiling point of the hydrocarbon, so order of b.p is III > II > I.

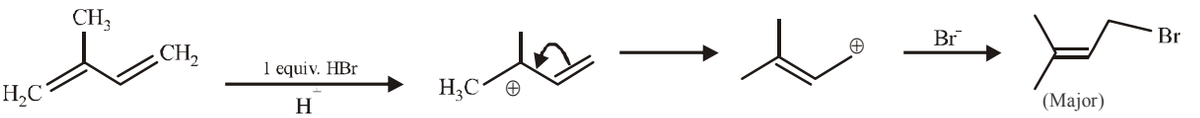
MCQs with One or More Than One Correct

1. (a, b, c, d)

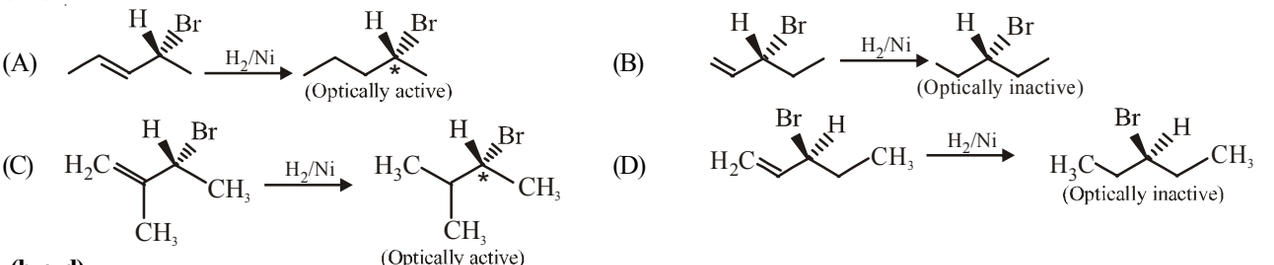


Note : P has 2 π electrons, while Q, R & S have 6 π electrons each. Hence all the 4 are aromatic.

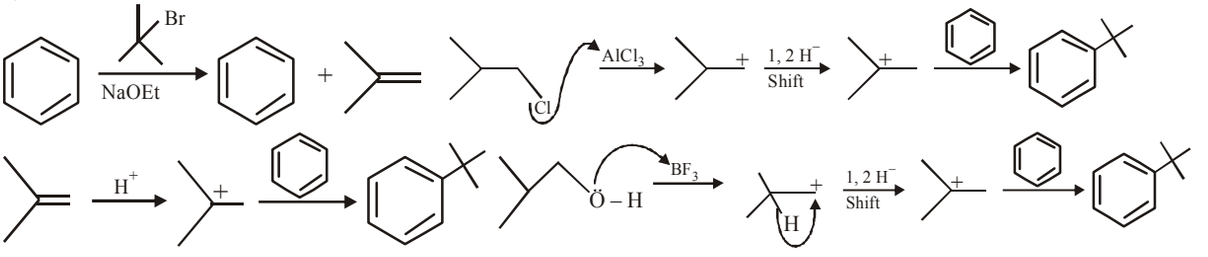
2. (d)



3. (b, d)



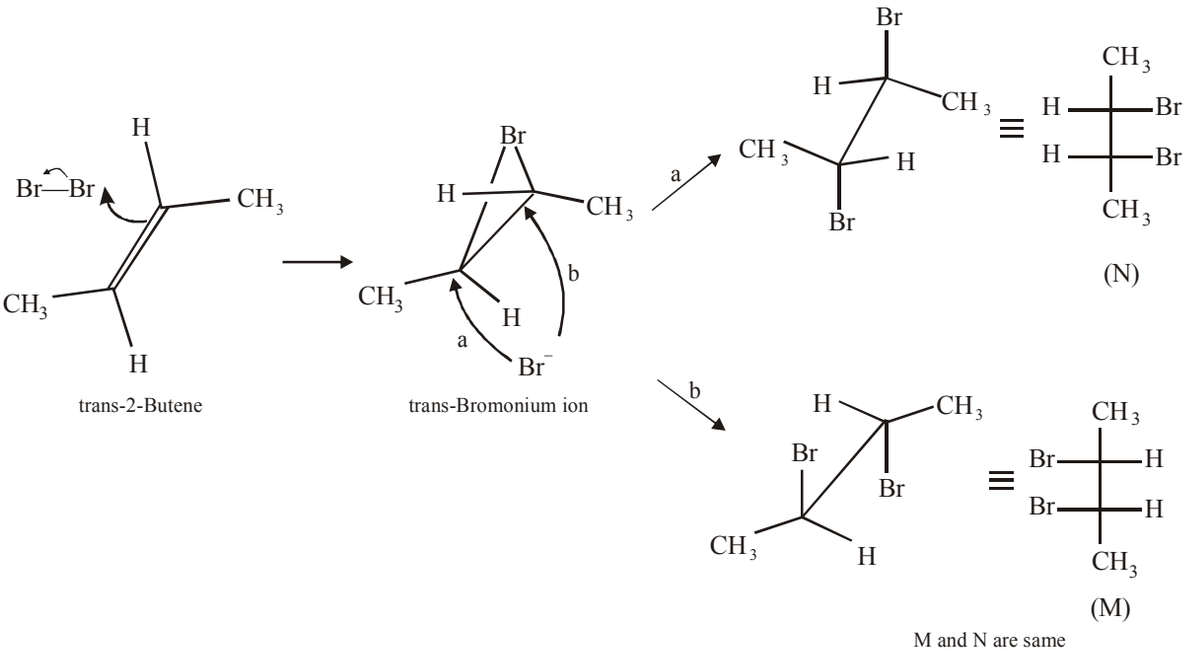
4. (b, c, d)

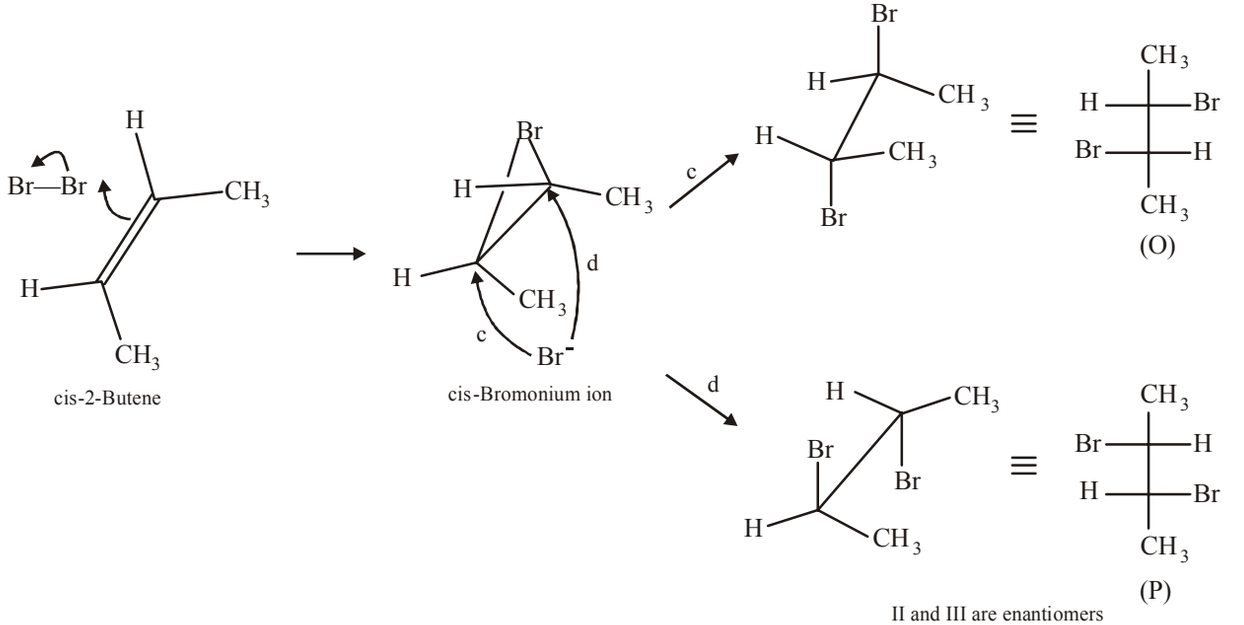


5. (b, d)

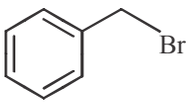
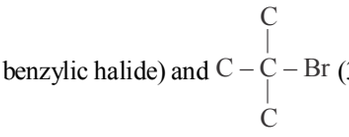
(b) Bromination proceeds through trans-addition in both the reactions.
M and N are identical, hence, M and O and N and P are two set of diastereomers.

(d)





6. (a, b, c)

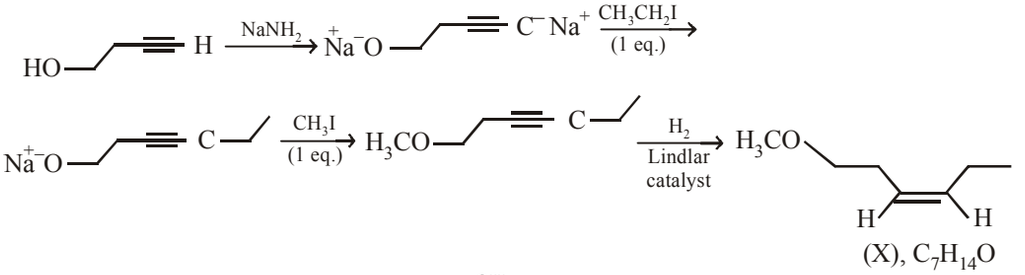
(a) I is  (1° benzylic halide) and  (3° alkylhalide). Follow S_N1.

(b) I and II follow S_N2 also, as both are 1° halide.

(c) Compound (IV) undergoes inversion of configuration due to presence of chiral carbon atom.

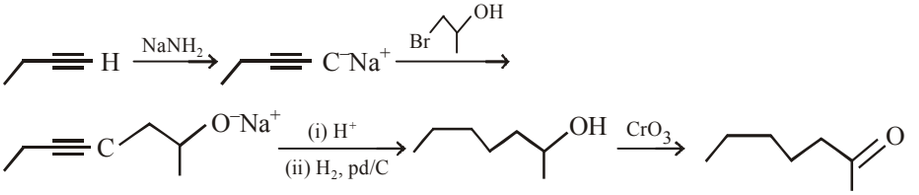
Comprehension Based Questions

1. (a)



(X), $C_7H_{14}O$

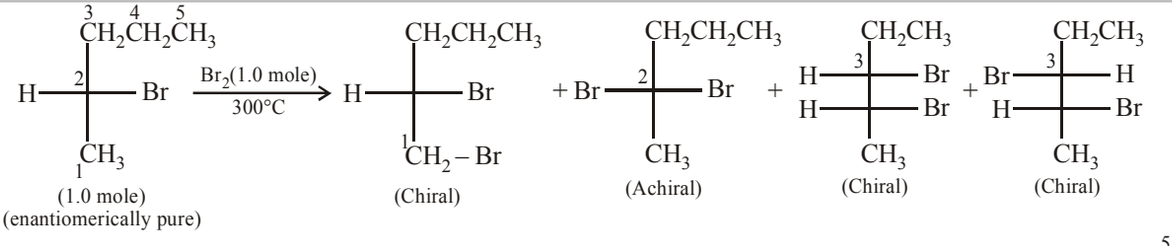
2. (c)



(Y), $C_7H_{17}O$

Integer Value Correct Type

1. **(5)**



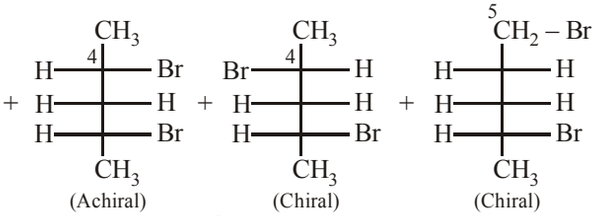
(1.0 mole)
(enantiomerically pure)

(Chiral)

(Achiral)

(Chiral)

(Chiral)

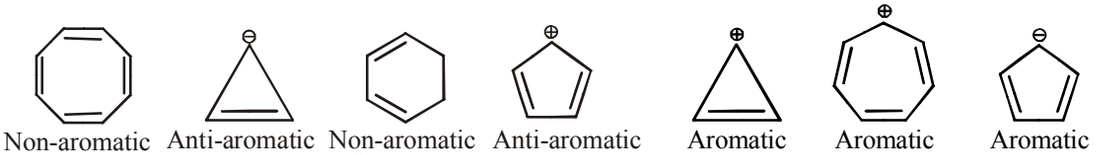


(Achiral)

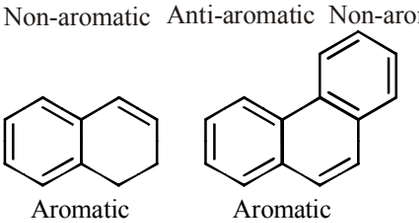
(Chiral)

(Chiral)

2. **(5)**



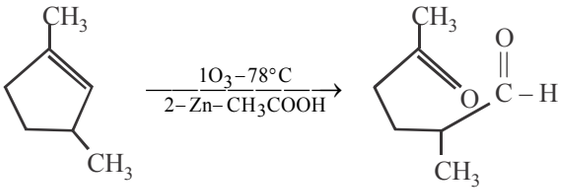
Non-aromatic Anti-aromatic Non-aromatic Anti-aromatic Aromatic Aromatic Aromatic

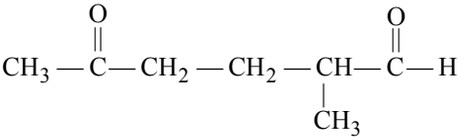


Aromatic Aromatic

PAST YEAR QUESTIONS JEE MAIN/AIEEE (2013 - 2017)

1. **(d)** When 1, 3-dimethylcyclopentene is heated with ozone and then with zinc and acetic acid, oxidative cleavage leads to keto - aldehyde.





5- keto – 2 – methylhexanal

2. **(d)** Region 2 (blue flame) will be the hottest region of Bunsen flame shown in given figure

3. **(d)** $C_xH_{y(g)} + \left(\frac{4x+y}{4}\right) O_{2(g)} \rightarrow xCO_{2(g)} + \frac{y}{2} H_2O(l)$

Volume of O_2 used $= 375 \times \frac{20}{100} = 75$ ml

$\therefore$ From the reaction of combustion

1 ml C_xH_y requires $= \frac{4x+y}{4}$ ml O_2

$15 \text{ ml} = 15\left(\frac{4x+y}{4}\right) = 75$

So, $4x + y = 20$

$x = 3$

$y = 8$

$\boxed{C_3H_8}$

4. (d) $CH_2 = CH - CH_3 + \overset{\oplus}{Cl}$ → $CH_2 - \overset{\oplus}{C}H - CH_3$ (Cl) More stable intermediate; $\overset{\oplus}{C}H_2 - CH - CH_3$ (Cl)

$CH_2(Cl) - \overset{\oplus}{C}H - CH_3 \xrightarrow{OH^-} CH_2(Cl) - CH(OH) - CH_3$

5. (d) CH_2Br, CH_3 $\xrightarrow[AgNO_3]{\text{Alcholic}}$ AgBr ↓ white ppt

Oxidation HNO_3

COOH, COOH $\xrightarrow{\Delta}$ CO, O, CO

6. (b) Steric congestion around the carbon atom undergoing the inversion process will slow down the S_N2 reaction, hence less congestion faster will the reaction. So, the order is

$CH_3Cl > (CH_3)CH_2 - Cl > (CH_3)_2CH - Cl > (CH_3)_3CCl$

7. (c) $2Cl - \underset{Cl}{\overset{Cl}{C}} - CH_3 + 6Ag \longrightarrow CH_3C \equiv CCH_3 + 6AgCl$

1, 1, 1-trichloroethane 2-butyne

8. (b) Alkyl fluorides are more conveniently prepared by heating suitable chloro – or bromo-alkanes with organic fluorides such as AsF_3, SbF_3, CoF_2, AgF, Hg_2F_2 etc. This reaction is called **Swarts reaction**.

$CH_3Br + AgF \longrightarrow CH_3F + AgBr$

$2CH_3CH_2Cl + Hg_2F_2 \longrightarrow 2CH_3CH_2F + Hg_2Cl_2$

9. (c) Nitration takes place in presence of concentrated

HNO_3 + concentrated H_2SO_4.

In strongly acidic nitration medium, the amine is converted into anilinium ion ($-NH_3^+$); substitution is thus controlled not by $-NH_2$ group but by $-NH_3^+$ group which, because of its positive charge, directs the entering group to the meta-position instead of ortho, and para.

$:NH_2$ $\xrightarrow[Conc.\ H_2SO_4]{Conc.\ HNO_3}$ $\overset{\oplus}{N}H_3$

$-NH_2$ gp : *o*, *p*-directing $-NH_3^+$ gp : *m*-directing

10. (b) Since S_N1 reactions involve the formation of carbocation as intermediate in the rate determining step, more is the stability of carbocation higher will be the reactivity of alkyl halides towards S_N1 route.

Since stability of carbocation follows order.

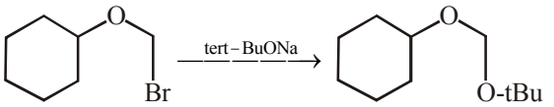
$CH_3 - CH_2 - \overset{\oplus}{C}H_2$

$< CH_3 - \overset{\oplus}{C}H - CH_2 - CH_3$

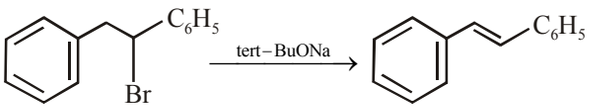
$< p - H_3CO - C_6H_4 - \overset{\oplus}{C}H_2$

Hence correct order is $\boxed{II < I < III}$

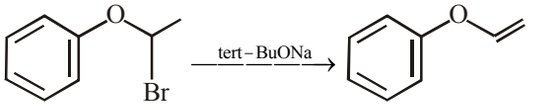
11. (a)

(a) 

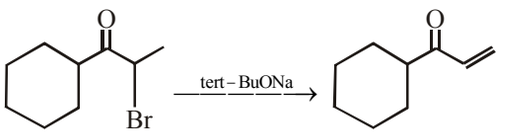
(fails to decolorise the colour of bromine) due to unsaturation

(b) 

(it decolorises bromine solution)

(c) 

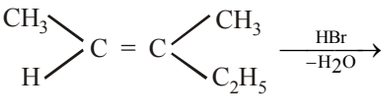
(it decolorises bromine solution)

(d) 

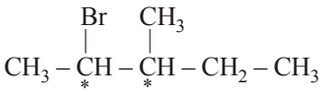
(it decolorises bromine solution)

Products formed in option (b), (c) & (d) decolorises bromine solution due to presence of double bond.

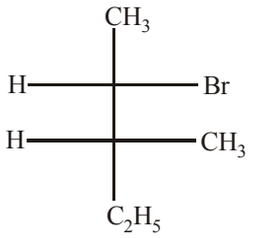
12. (d) If two chirality centres are created as a result of an addition reaction four stereoisomers can be obtained as products.



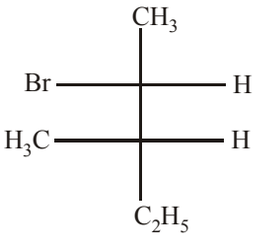
cis-3, methyl pent-2-ene



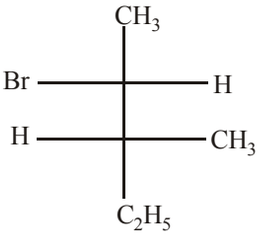
2, Bromo, 3-methyl pentane
(2 chiral centre)



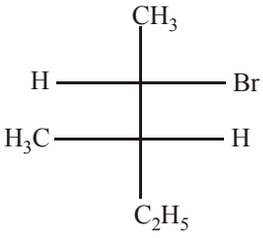
(I)



(II)



(III)



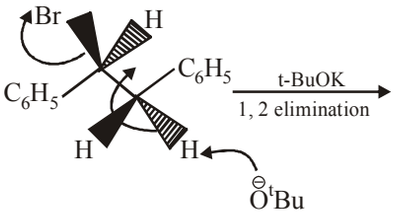
(IV)

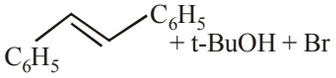
13. (b) Elimination reaction is highly favoured if

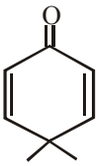
(a) Bulkier base is used

(b) Higher temperature is used

Hence in given reaction biomolecular elimination reaction provides major product.





14. (d) 

is nonaromatic and hence least reasonance stabilized whereas other three are aromatic.

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Alcohols, Phenols & Ethers

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PREFACE

REVISED EDITION

It gives us immense pleasure and satisfaction to bring out the thoroughly revised and updated edition of the book **"Disha's Alcohels, Phenols and Ethers"** The book has been designed to give a better look & feel and to make the text more lucid. The new pattern of JEE Main & Advanced has been kept in mind throughout.

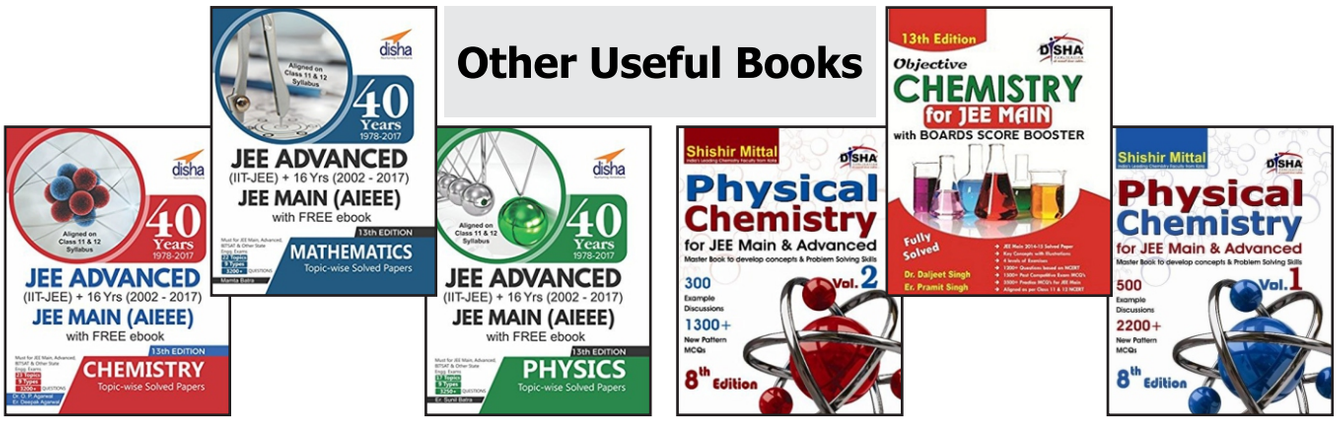
The exercises at the end of each chapter have been designed in the flavour of the new pattern of JEE Main & Advanced. The questions from the previous JEE papers have been incorporated in the different exercises. A separate section having past JEE questions is also provided at the end.

1. **Exercise 1 - MCQ with One correct option :** This exercise contains a collection of question, which has been very carefully selected and it is ensured that there is no repetition. The exercise contains a collection of questions, which has been very carefully selected and it is ensured that there is no repetition. The exercise has been designed so as to cover all the concepts involved in the chapter.
2. **Exercise 2 :** This exercise contains all the four new variety of questions which have been asked in the last 3-4 JEE examinations. These variety of questions are-
   - (i) **MCQ's with one or more than one correct answers :** Around 20-30 well selected problems introduced in each chapter.
   - (ii) **Comprehension based questions :** More than 50 passages which tests the student's comprehension and analytical ability have been added. All these are newly framed problems.
   - (iii) **Matching type question :** Match the following type of question with multiple matching have been introduced in each chapter. These are unique and newly framed problems which will definitely pose a big challenge to the student. I feel that this type of problem is the best way to check a student's concepts.
   - (iv) **Assertion & Reason type questions :** Assertion and Reason type of questions have been incorporated in each and every chapter.
3. **Exercise 3 - Subjective Problems :** This exercise contains a unique collection of subjective problems which will not only give practice to the students but will also help in revising the complete chapter.

In the end, We would like to request all readers to highlight the printing errors and come forward with suggestions for further improvement of the book.

DR. O.P. AGARWAL

Other Useful Books



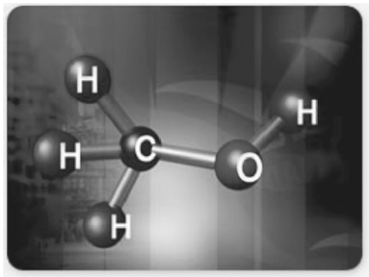
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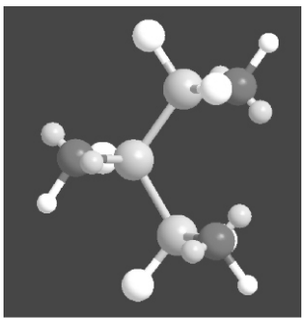
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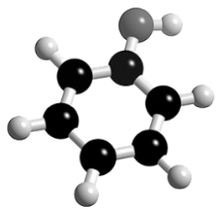
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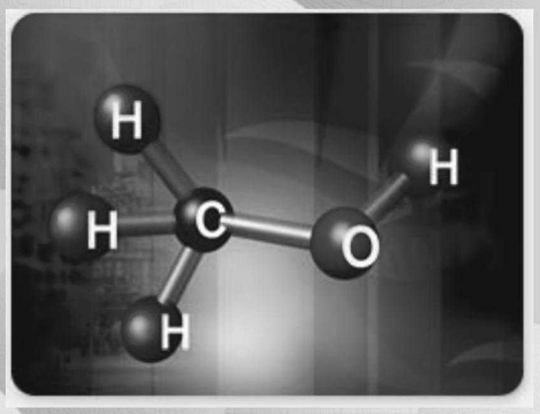
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11

Monohydric Alcohols

CHAPTER HIGHLIGHTS

11.1 Nomenclature

11.2 Preparation

11.3 Industrial Sources of Alcohols

11.4 Physical Properties

11.5 Reactions of Alcohols

11.6 Distinction Between Primary, Secondary and Tertiary Alcohols

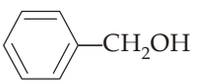
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EXERCISES

SOLUTIONS

11.1 Nomenclature

Alcohols are compounds whose molecules have a hydroxyl group attached to a saturated carbon atom*. The saturated carbon atom may be that of an alkyl group, alkenyl or akynyl or a carbon atom attached to benzene ring.

CH_3CH_2OH, $CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$, $CH_2 = CHCH_2OH$, $HC \equiv CCH_2OH$, 

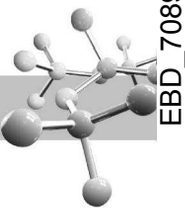
Alcohols may be classified as monohydric, dihydric, trihydric and polyhydric depending upon the number of —OH groups.

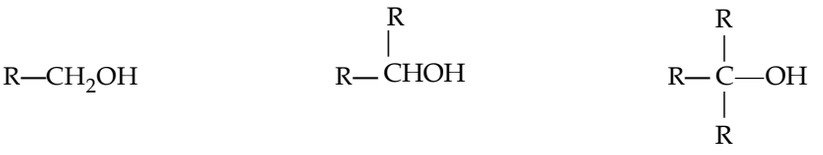
CH_3CH_2OH	$\begin{matrix} CH_2OH \\ \vert \\ CH_2OH \end{matrix}$	$\begin{matrix} CH_2OH \\ \vert \\ CHOH \\ \vert \\ CH_2OH \end{matrix}$	$\begin{matrix} CH_2OH \\ \vert \\ (CHOH)_4 \\ \vert \\ CH_2OH \end{matrix}$
Ethyl alcohol (Monohydric)	Glycol (Dihydric)	Glycerol (Trihydric)	Sorbitol (Polyhydric)

Alternatively, an alcohol can be classified as *primary*, *secondary*, or *tertiary* according to the nature of carbon bearing —OH group.

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* Compounds in which a hydroxyl group is attached to an unsaturated carbon atom of a double bond (*i.e.* C = C—OH) are called **enols.**

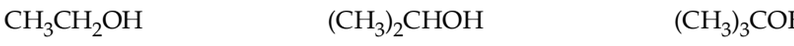




Primary (1°) Secondary (2°) Tertiary (3°)

Alcohols are named by three methods.

(*i*) **Carbinol method.** Alcohols are considered as derivatives of *methyl alcohol*, also known as *carbinol.*



Methylcarbinol Dimethylcarbinol Trimethylcarbinol

(*ii*) **Common names** (*Radicofunctional nomenclature*). This method is most often used for the simpler alcohols. A common name consists simply of the name of the alkyl group followed by the word alcohol, *e.g.*



Ethyl alcohol Isobutyl alcohol *tert*-Butyl alcohol Neopentyl alcohol

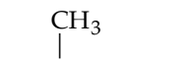
(*iii*) **IUPAC names.** This is is the most versatile system.

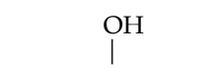


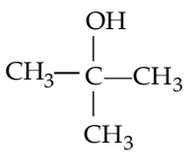
2, 4-Dimethyl-1-pentanol 4-Phenyl-2-pentanol 4-Penten-2-ol

Alcohols are **functional isomers** to ethers, thus $C_4H_{10}O$ can have following seven isomeric structures (four alcohols and three ethers).

(*i*) $CH_3CH_2CH_2CH_2OH$ Butanol-1

(*ii*)  2-Methylpropanol

(*iii*)  Butanol-2

(*iv*)  2-Methylpropanol-2

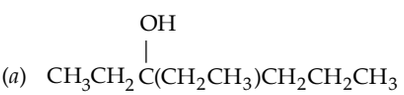
(*v*) $CH_3CH_2OCH_2CH_3$ Ethoxyethane

(*vi*) $CH_3OCH_2CH_2CH_3$ Methoxypropane

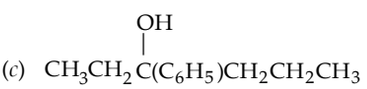
(*vii*) $CH_3O.CH(CH_3)_2$
Methoxy-1-methylethane

TEST YOUR UNDERSTANDING - 11.1

1. (*i*) Name the following alcohols by carbinol and IUPAC methods.

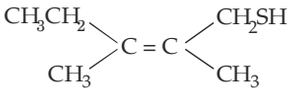
(*a*) 

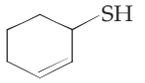
(*b*) Cl_2CHCH_2OH

(*c*) 

(*d*) 

(ii) Give IUPAC names of the following thioalcohols.

(a) 

(b) 

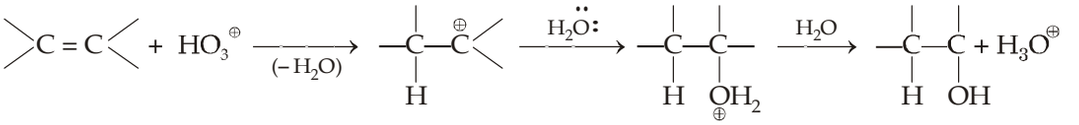
(c) 

(d) $CH_3CH_2S^-Na^+$

11.2 Preparation

1. From alkenes.

(*a*) **Acid-catalyzed hydration of alkenes.** As discussed earlier in the reactions of alkenes, alkenes add water in the presence of an acid catalyst. The addition **follows Markownikov's rule.**



For example,

$$CH_2 = CH_2 + H_2O \xrightarrow{\text{dil.}H_2SO_4} CH_3CH_2OH$$

$$CH_3CH = CH_2 + H_2O \xrightarrow{H^+} CH_3CH(OH)CH_3$$

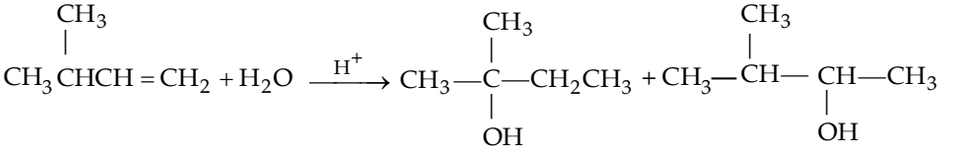
$$(CH_3)_2C = CH_2 + H_2O \xrightarrow{H^+} (CH_3)_3COH$$

(*i*) Hydration takes place in Markovnikov's manner.

(*ii*) Except for the hydration of ethene, the reaction produces 2° and 3° alcohols.

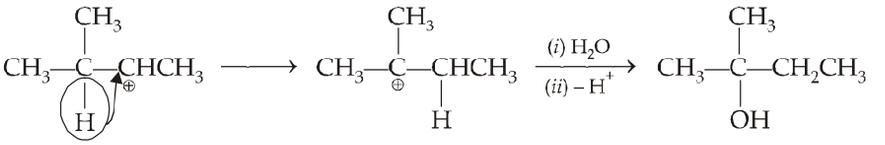
(*iii*) The reaction is reversible and the mechanism of hydration of an alkene is just the reverse of that for dehydration of an alcohol.

(*iv*) Since carbocations are formed as intermediates, rearrangement occurs whenever a less stable carbocation can rearrange by 1, 2-hydride or 1, 2-alkanide shift to the more stable carbocation. Hence this method is not used as a laboratory method for the preparation of alcohols.

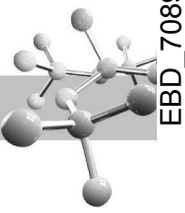


2-Methylbutanol-2 **(Major)** 3-Methylbutanol-2 **(Minor)**

This is due to the fact that the intermediate 2° carbocation rearranges to the more stable 3° carbocation.



2° Carbocation 3° Carbocation 2-Methylbutanol-2

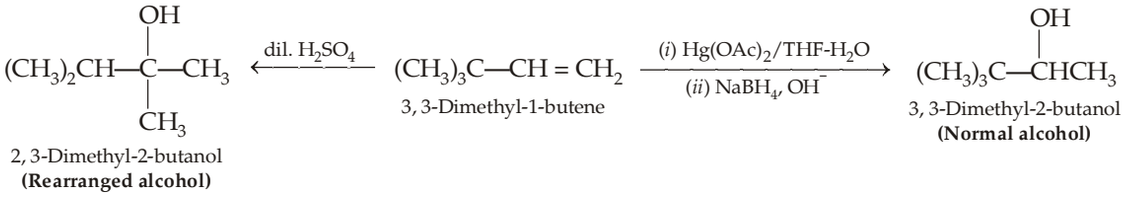


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(*b*) **Oxymercuration-demercuration.** In this method alkene is treated with mercuric acetate in presence of a mixture of water and THF as solvent (*mercuration*). The mercurated product is reduced with sodium borohydride to form alcohol (*demercuration step*).

$$RCH = CH_2 \xrightarrow[H_2O,\ 288\ K]{Hg(OCOCH_3)_2} \underset{\text{Not isolated}}{\left[\begin{array}{l} R\,CH - CH_2 \\ \quad | \quad\ | \\ \quad OH \quad HgOCOCH_3 \end{array}\right]} \xrightarrow[OH^-]{NaBH_4} \underset{OH}{\overset{|}{R\,CH}}—CH_3 + Hg + CH_3COO^-$$

(*i*) The method is fast and convenient. It takes place under mild conditions and gives excellent yield. Like acid-catalysed hydration of alkenes, this reaction is also highly *regioselective* and the elements of water (—H and —OH) add in accordance with **Markovnikov's rule**. Another striking feature of the reaction is that it does not involve any rearrangement.



2, 3-Dimethyl-2-butanol
(Rearranged alcohol)

3, 3-Dimethyl-1-butene

3, 3-Dimethyl-2-butanol
(Normal alcohol)

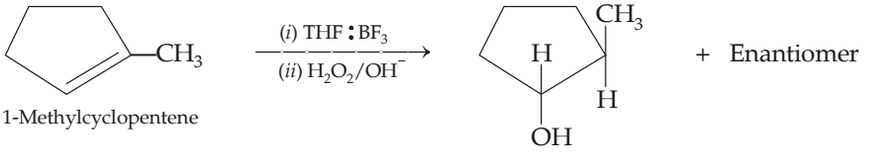
(*ii*) Remember here hydrogen is coming from $NaBH_4$ and hydroxyl group from water present in solvent (THF + H_2O).

(*c*) **Hydroboration-oxidation.** Alkenes react with diborane in presence of ether to form alkylboranes (*hydroboration*). Diborane is used in the form of solution in THF. Alkylboranes are then oxidised and hydrolysed by the addition of hydrogen peroxide in aqueous base.

$$\underset{\text{Propene}}{CH_3CH = CH_2} \xrightarrow{THF:BH_3} \underset{\text{Tripropylborane}}{(CH_3CH_2CH_2)_3B} \xrightarrow{H_2O_2/OH^-} \underset{\text{Propanol}}{3\,CH_3CH_2CH_2OH}$$

Here the net addition of H—OH to alkenes is *anti*-Markovnikov's and free from rearrangement.

(*i*) In hydroboration-oxidation, —H and —OH are added to the same face of the double bond, *i.e.* elements of water adds in *syn*-manner. Hence the reaction is said to be stereoselective.



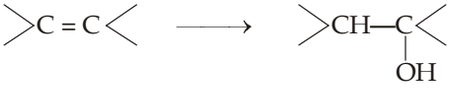
1-Methylcyclopentene

trans-2-Methylcyclopentanol

(*ii*) Here hydrogen that is added to carbon is derived from organoborane, and the hydroxyl group comes from hydrogen peroxide.

(*iii*) Oxymercuration-demercuration and hydroboration-oxidation methods are complement of each other, former adds water molecule in Markovnikov's manner and the latter in *anti*-Markovnikov's manner.

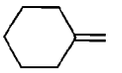
Comparison of the three methods for preparing alcohols from alkenes



		Acid-catalysed hydration method	*Oxymercuration-demercuration method*	*Hydroboration-oxidation method*
1.	Product as per	Markovnikov's rule	Markovnikov's rule	*anti*-Markovnikov's rule
2.	Source of H	H from acid	H from $NaBH_4$	H from BH_3
3.	Source of OH	Water (solvent)	Water (solvent)	H_2O_2
4.	Rearrangement	Occurs, whenever possible	No rearranged product	No rearranged product
5.	Regioselectivity/ Stereoselectivity	Neither regioselective nor stereoselective	Regioselective, but not stereoselective	Regioselective as well as stereoselective.

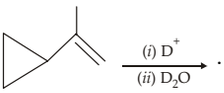
TEST YOUR UNDERSTANDING - 11.2

1. Give the most stable intermediate formed during acid-catalysed hydration of each of the following alkenes.

(*a*) $(CH_3)_2C = CHCH_3$ (*b*) $(CH_3)_2CH.CH = CH_2$ (*c*) $(CH_3)_3C.CH = CH_2$ (*d*) 

2. Give the final product obtained in each of the following reactions.

(*a*) $CH_3CH_2CH = CH_2 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } D^+}$ (*b*) $CH_3CH_2CH = CH_2 \xrightarrow[\text{(ii) } D_2O]{\text{(i) } H^+}$

(*c*) $CH_3CH_2CH = CH_2 \xrightarrow[\text{(ii) } D_2O]{\text{(i) } D^+}$ (*d*)  $\xrightarrow[(ii)\ D_2O]{(i)\ D^+}$.

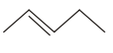
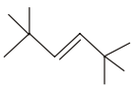
3. Following alcohols can be prepared in quantitative yield by oxymercuration-demercuration of two different alkenes ; write the structures of the two alkenes in each case.

(*a*) 2-Methyl-2-butanol (*b*) 1-Methylcyclopentanol (*c*) 3-Hexanol.

4. Write the structure of the major product obtained by hydroboration-oxidation of each of the following alkenes.

(*a*) *cis*-2-Butene (*b*) Cyclopentene (*c*) 3-Ethyl-2-pentene (*d*) 3-Ethyl-1-pentene.

5. Identify [A] to [D].

(*a*)  $\xrightarrow[(ii)\ NaBH_4,\ OH^-]{(i)\ Hg(OAc)_2,\ THF—H_2O}$ A + B (*b*)  $\xrightarrow[(ii)\ H_2O_2,\ OH^-]{(i)\ B_2H_6,\ \text{ether}}$ [C]

(*c*)  $\xrightarrow[(ii)\ H_2O_2,\ OH^-]{(i)\ B_2H_6,\ \text{ether}}$ [D]

6. Give the structure of the alcohol formed by 3-methylbutene-1 by

(*a*) acid-catalysed hydration method (*b*) oxymercuration-demercuration method

(*c*) hydroboration-oxidation method.

(*d*) **Oxo process** (*Carbonylation or hydroformylation reaction*)

$$2RCH = CH_2 + 2CO + 2H_2 \xrightarrow[\text{heat, under P}]{[Co(CO)_4]_2 \text{ as catalyst}} \underset{\textbf{(Major)}}{RCH_2CH_2CHO} + \underset{\text{(Minor)}}{R\overset{\overset{CH_3}{|}}{C}HCHO}$$

The two aldehydes are separated by fractional distillation and then reduced catalytically to the corresponding alcohols.

(*e*) **Ethanol** can be prepared by passing a mixture of ethylene and steam under pressure over Al_2O_3 or H_3PO_4 on silica at 575 K.

$$CH_2 = CH_2 + H_2O \xrightarrow[575\ K,\ \text{Pressure}]{Al_2O_3} CH_3CH_2OH$$

2. From alkyl halides. Hydrolysis of alkyl halides with aqueous NaOH or KOH or moist Ag_2O yields alcohols (For details, consult chapter on ''Alkyl halides'').

$$R—X + OH^- \longrightarrow R—OH + X^-$$

(*i*) Alkyl halides are converted into alcohols *via* S_N1 and/or S_N2 reactions.

(*ii*) This method although quite general, it is severely limited as a method of synthesizing alcohols because alcohols are usually more available than the corresponding alkyl halides, indeed alcohols are best starting materials for alkyl halides.

(*iii*) *tert*-Alkyl halides undergo a competitive elimination reaction yielding alkenes as major product.

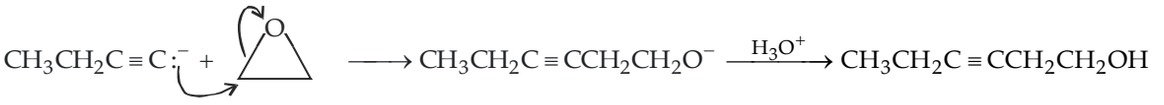
EBD_7089

3. From organometallic compounds. As discussed in the chapter on ''*Organometallic Compounds*'', organolithium and organomagnesium compounds (Grignard reagents) are useful compounds for preparing all the three types (1°, 2° or 3° alcohols).

(*i*) Primary alcohols, except methyl alcohol, can be prepared by treating Grignard reagent (RMgX) with formaldehyde. Methyl alcohol can be prepared by treating the reagent with oxygen followed by hydrolysis.

(*ii*) Primary alcohols, higher than ethanol, can be prepared by treating the reagent with epoxides (oxiranes).

Like Grignard and organolithium reagents, acetylide ions are strong bases and they add to ethylene oxide much like these reagents to form primary alcohol as the final product.



(*iii*) Secondary alcohols are prepared. (*a*) from aldehydes other than formaldehyde, or (*b*) from ester of formic acid (*i.e.* HCOOR) with excess of Grignard reagent. However, in the second method the 2° alcohol will always have identical alkyl groups, *i.e.* R_2CHOH and not RCHOHR′.

(*iv*) Tertiary alcohols are prepared from (*a*) ketones, or (*b*) from esters of monocarboxylic acids other than formic acid (*i.e.* R′COOR) with excess of Grignard reagent. However, in the second method those 3° alcohols can be prepared which have at least two identical alkyl groups, *i.e.* $R_2C(OH)R'$ (R and R′ may be similar or different).

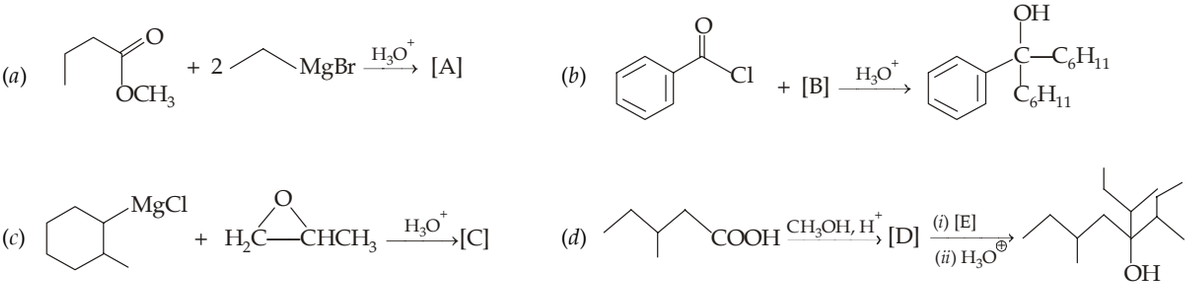
TEST YOUR UNDERSTANDING - 11.3

1. Prepare the following by a Grignard reaction :

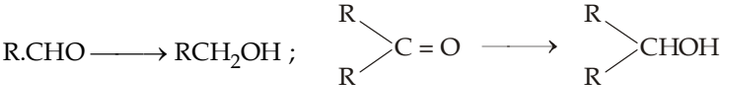
(*a*) 1-Butanol from 1-chloropropane (*b*) *n*-Butanol from ethyl bromide

(*c*) Ethyl *p*-chlorophenylcarbinol.

2. Identify A to E in the following reactions in each of the following reactions.



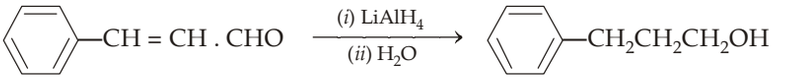
4. By the reduction of aldehydes and ketones. Aldehydes and ketones are readily reduced to primary and secondary alcohols, respectively by (*a*) sodium and alcohol, (*b*) catalytic hydrogenation, (*c*) complex metal hydrides like lithium aluminium hydride, $LiAlH_4$ (LAH) and sodium borohydride, $NaBH_4$(SBH).



Benzaldehyede undergoes coupling reaction with Na/C_2H_5–OH, so it can't be reduced into alcohol by Na/C_2H_5OH

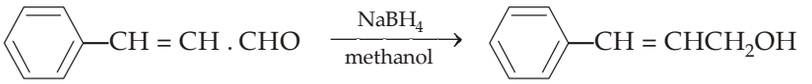
However, reduction by $LiAlH_4$ and $NaBH_4$ are more important. *Lithium aluminium hydride* reacts violently with water and alcohols, so it must be used in solvents such as anhydrous diethyl ether or tetrahydrofuran. Moreover, the reduction requires a separate hydrolysis step to liberate the alcohol product.It does not reduce the α, β-unsaturated linkage which is not conjugated with the benzene ring ; however, it reduces the double bond too when it is having a phenyl group in the β-position.

$$CH_3CH = CH.CHO \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4,\ ether} CH_3CH = CHCH_2OH$$

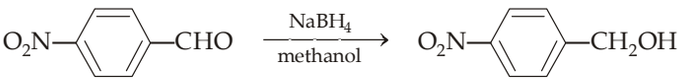


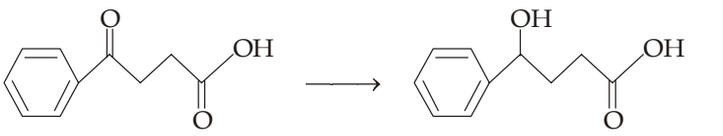
Contrary to $LiAlH_4$ reductions, sodium borohydride reductions are very easy to carry out ; it needs only addition of the reagent to an aqueous or alcoholic solution of an aldehyde or ketone. It is more specific and does not reduce the carbon-carbon double bond, even when conjugated with the benzene ring. It also does not reduce —NO_2, —CN, —COOH, acid anhydrides and esters. However, it reduces —COCl to —CH_2OH.

$$CH_3CH = CHCHO \xrightarrow[methanol]{NaBH_4} CH_3CH = CHCH_2OH$$



$$NCCH_2CH_2CHO \xrightarrow[methanol]{NaBH_4} NCCH_2CH_2CH_2OH$$

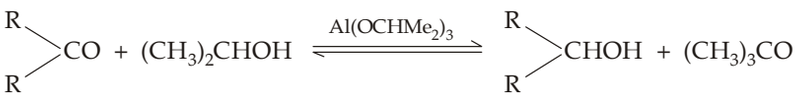




β-Benzoylpropanoic acid γ-Hydroxy-γ-phenylbutanoic acid

Sodium borohydride and lithium aluminium hydride react with carbonyl compounds in much the same way that Grignard reagents do, except that they function as *hydride donors* rather than as carbanion source. Remember that one molecule of the carbonyl compound accepts one hydride ion from the reagent and thus one molecule of the reagent can reduce four molecules of the compound . Second hydrogen is coming as proton from the solvent (H—OH or H—OR) molecule.

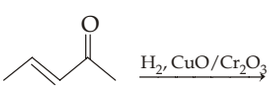
Ketones can also be reduced to secondary alcohols by heating ketones in isopropanol with aluminium isopropoxide. The reaction is more commonly known as **Meerwein-Ponndorf-Verley (MPV) reduction.**

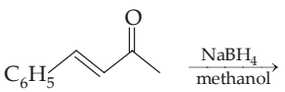


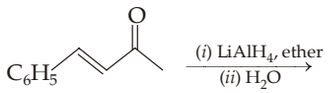
Carbonyl carbon gets hydrogen in the form of hydride from aluminium isopropoxide, while carbonyl oxygen gets hydrogen from the solvent, isopropanol.

TEST YOUR UNDERSTANDING - 11.4

1. Complete the following :

(*a*) 

(*b*) 

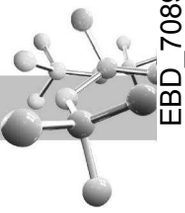
(*c*) 

(*d*) $CH_3CHO \xrightarrow{NaBD_4 \text{ in } H_2O}$

(*e*) $CH_3COCH_3 \xrightarrow[CH_3OD]{NaBD_4 \text{ in}}$

(*f*) $C_6H_5CHO \xrightarrow{NaBD_4 \text{ in } CD_3OH}$

(*g*) $HCHO \xrightarrow[(ii)\ D_2O]{(i)\ LiAlD_4 \text{ in ether}}$



5. By the reduction of carboxylic acids and their derivatives.

(*a*) *Catalytic hydrogenation* follows the order

$$RCOCl > RCHO > R_2CO > RCOOR' > RCOOH$$

However, catalytic hydrogenation is used in industries because extremely high pressures and temperatures are required.

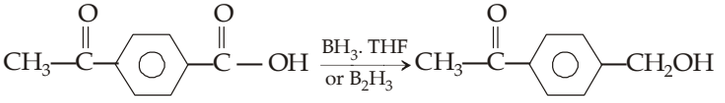
(*b*) *Bouveault-Blanc reduction* (Reduction by sodium metal in alcohol). This is applied only for esters and again used in industry.

$$RCOOC_2H_5 \xrightarrow[\text{alcohol}]{Na} RCH_2OH + C_2H_5OH$$

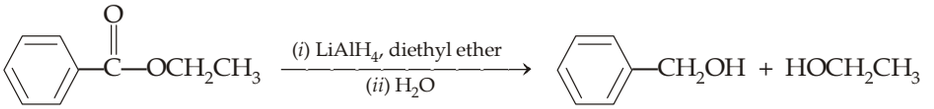
(*c*) *Reduction by lithium aluminium hydride.* Although carboxylic acids are very difficult to reduce, these can be reduced to primary alcohols by $LiAlH_4$ (not by $NaBH_4$).

$$RCOOH \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4,\ \text{diethyl ether}} RCH_2OH$$

Carboxylic acids are readily reduced to primary alcohols by borane. Actually borane, complexed with THF, reacts with the carboxyl group faster than with any other carbonyl function. It reduces selectively the –COOH group without affecting a ketonic group.



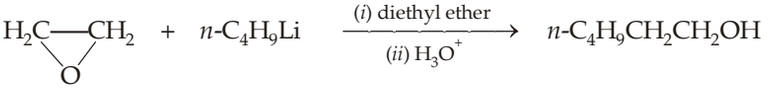
Esters are more easily reduced than carboxylic acids by $LiAlH_4$. Two alcohols are formed from each ester molecule ; one is derived from the acyl part and other from the alcoholic part.

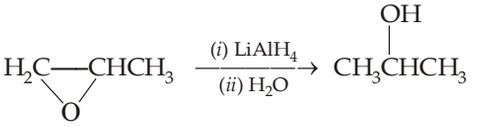


Ethyl benzoate Benzyl alcohol

Although esters can also be reduced by $NaBH_4$, the reaction is too slow to be useful. Anhydrides can be reduced to alcohols by $LiAlH_4$ as well as by $NaBH_4$; however, acid chlorides can be reduced only by $LiAlH_4$.

6. By the reduction of epoxides. Epoxides can be converted into alcohols by reacting with Grignard reagents, organolithium compounds and lithium aluminium hydride.

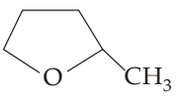


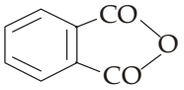


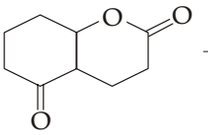
Like Grignard reagents, *hydride ion* (nucleophile) attacks the less substituted carbon atom.

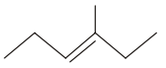
TEST YOUR UNDERSTANDING - 11.5

1. Identify [A] to [H] in the following reactions :

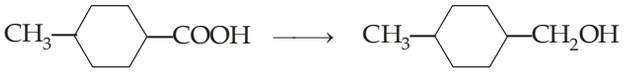
(*a*) $CH_3CH = CH_2 \xrightarrow{C_6H_5CO_3H}$ [A] $\xrightarrow[(ii)\ H^+]{(i)\ LiAlH_4}$ [B] (*b*)  $\xrightarrow[(ii)\ H^+]{(i)\ LiAlH_4}$ [C]

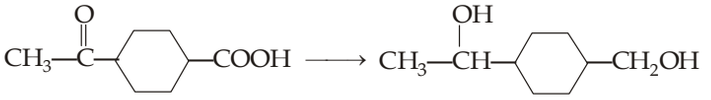
(*c*)  $\xrightarrow[(ii)\ H^+]{(i)\ LiAlH_4}$ [D]

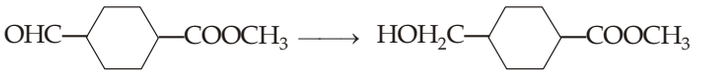
(*d*) [F] $\xleftarrow[\text{methanol}]{NaBH_4}$  $\xrightarrow[(ii)\ H^+]{(i)\ LiAlH_4}$ [E]

(*e*)  $\xrightarrow[(ii)\ LiAlH_4/H^+]{(i)\ O_3/H_2O/Zn}$ [G] + [H]

2. Which reducing agent, $LiAlH_4$ or $NaBH_4$, would you use to carry out the following transformations ?

(*a*) 

(*b*) 

(*c*) 

3. Give the structure of an ester that will yield a mixture containing equimolar amounts of 1-propanol and 2-propanol on reduction with lithium aluminium hydride.

4. Arrange the following in decreasing ease of reduction with LAH and SBH.

RCHO, RCOOH, RCOOR' and RCOR.

---

7. Other methods used for preparing alcohols are hydrolysis of esters and ethers ; and by the action of nitrous acid on primary amines.

$$RCOOR' \xrightarrow{H^+ \text{ or } OH^-} RCOOH + R'OH$$

$$R{-}O{-}R \xrightarrow[\text{pressure}]{\text{dil.}H_2SO_4} 2ROH$$

$$RCH_2NH_2 + HONO \longrightarrow RCH_2OH + N_2 + H_2O$$

11.3 Industrial Sources of Alcohols.

Natural resources constitute important ways for preparing alcohols on large scale.

(*a*) Petroleum is an important source of alkenes which can be converted into alcohols by (*i*) hydration and (*ii*) oxo process.

(*b*) Methanol is manufactured

(*i*) as a by-product by the destructive distillation of wood, hence also known as *wood spirit or wood alcohol or naphtha*, during the manufacture of charcoal. Destructive distillation of wood gives *pyroligenous acid* (10% CH_3COOH + 2.5% CH_3OH + 0.5% acetone) from which methanol is separated by suitable treatment.

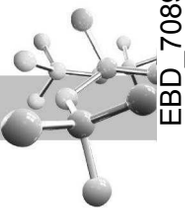
(*ii*) Methanol is also obtained by heating a mixture of water gas (a mixture of CO and H_2 in equimolar ratio) with half of its volume of hydrogen in presence of catalyst.

$$C + H_2O\,(\text{steam}) \longrightarrow \underbrace{CO + H_2}_{\text{water gas}} ; \underbrace{CO + H_2}_{\text{water gas}} + H_2 \xrightarrow[573\ K]{Cr_2O_3,\ ZnO} CH_3OH$$

(*c*) Ethanol is commercially obtained by fermentation of sugars present in the form of cane-sugar (in molasses) and starch (from various grains like, maize, barley, rice etc.). Fermentation (decomposition of complex compounds into simplar by yeast) is still the most widely used method for preparing **ethanol** on large scale.

Chemical reactions involved in preparation of C_2H_5OH from molasses (a dark-brown coloured mother liquor left after the crystallization of sucrose from concentrated sugar-cane juice).

$$\underset{\substack{\text{Surose (present}\\ \text{in molasses)}}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[(\text{yeast})]{\text{invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6} \xrightarrow[(\text{yeast})]{\text{Zymase}} 2C_2H_5OH + 2CO_2\uparrow$$



Ethyl alcohol from starchy grains (hence also known as grain alcohol).

$$\text{Germinated barley seeds} \xrightarrow[(ii)\ \text{Crushed with } H_2O \\ (iii)\ \text{Filter}]{(i)\ 60°C \text{ to prevent further growth}} \underset{\substack{\text{(Malt extract)} \\ \text{(It contains diastase)}}}{\text{Filtrate}} \xrightarrow[\text{(starchy material + steam)} \\ \text{at } 50°C]{\text{heat with mash}}$$

$$\text{Maltose} \xrightarrow[(ii)\ \text{yeast and keep for 2— 3 days}]{(i)\ \text{cool to } 30°C} \underset{(10\%\ C_2H_5OH)}{\text{Wort}} \xrightarrow[(ii)\ \text{rectifi.}]{(i)\ \text{distil.}} \text{Rectified sprit}$$

Chemical reactions involved are as follows

$$\underset{\text{Mash (starch)}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[50—60°C]{\substack{\text{Malt extract} \\ \text{(diastase)}}} \underset{\text{Maltose}}{2C_{12}H_{22}O_{11}}$$

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6} \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2\uparrow.$$

In this process, a smaller amount of **fusel oil** is also obtained in addition to ethanol. Fusel oil is a mixture of primary alcohols mostly isopentyl alcohol with smaller amounts of *n*-propyl, isobutyl and 2-methyl-1-butanol (active amyl alcohol). Isopentyl and active amyl alcohols are formed by enzymatic transformation of the amino acids leucine and isoleucine derived from the hydrolysis of proteins present in starch.

$$\underset{\substack{\text{Leucine } (\textit{chiral molecule})}}{(CH_3)_2CHCH_2\overset{*}{C}H(N^+H_3)COO^-} \xrightarrow{\text{enzymes}} \underset{\text{Isopentyl alcohol } (\textit{achiral})}{(CH_3)_2CHCH_2CH_2OH}$$

$$\underset{\text{Isoleucine } (\textit{chiral})}{CH_3CH_2\overset{*}{C}H(CH_3)\overset{*}{C}H(NH_3^+)COO^-} \xrightarrow{\text{enzymes}} \underset{\text{Active amyl alcohol } (\textit{chiral})}{CH_3CH_2\overset{*}{C}H(CH_3)CH_2OH}$$

Alcoholic beverages. Ethanol is the alcohol of alcoholic beverages. The particular alcoholic beverage obtained depends upon following factors.

(*a*) Nature of fermented substance, *i.e.* where rye, corn, grapes, elderberries, barley etc.

(*b*) Way of fermentation, *i.e.* whether CO_2 is allowed to escape or it is bottled up.

(*c*) Treatment after fermentation, *i.e.* whether it is distilled or not remember that the special flavour of a beverage is not due to ethanol but it is either due to characteristic of the particular source or due to some flavouring substance added from outside.

Absolute alcohol (100% pure ethyl alcohol). Rectified spirit (containing 95.87% C_2H_5OH + 4.13% H_2O) cannot be converted into absolute alcohol simply by distillation because the mixture of ethanol and water in the ratio of 95.87 : 4.13 (a ratio present in rectified spirit) is a constant boiling mixture **(azeotropic mixture)** having b.p. 78.13°C. Following two special methods are used for getting absolute alcohol.

(*i*) *Laboratory method.* Rectified spirit is kept in contact with quick lime (CaO) for 24 hours and then distilled over it. Final traces of water are removed by adding anhydrous $CuSO_4$ (white in colour) till it ceases to turn blue. It is then distilled to get absolute alcohol.

(*ii*) *Industrial method.* By mixing rectified spirit with excess of benzene followed by distillation when first ternary mixture (74.1% benzene + 18.4% ethanol + 7.4% water) is distilled at 64.8°C, then binary mixture (67.6% benzene + 32.4% ethanol) at 68.2°C and finally absolute alcohol at 78.3°C.

In certain reactions, even a slight trace of water found in commercial absolute alcohol must be removed. This can be accomplished by treating the alcohol with metallic magnesium ; water is converted into insoluble $Mg(OH)_2$, from which dry alcohol, called absolute alcohol is collected by distillation.

$$Mg + 2H_2O \longrightarrow Mg(OH)_2\downarrow + H_2$$

Methylated spirit (Denatured alcohol). It is rectified spirit (industrial alcohol) mixed with poisonous substances like CH_3OH, pyridine, acetone, etc. to make it unfit for drinking purposes. The usual composition of denatured alcohol is 85—90% rectified spirit + 10—15% methanol.

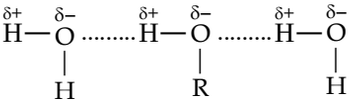
Power alcohol. Alcohol used for the generation of power is called power alcohol. It is a mixture of petrol and alcohol in the ratio of 4 : 1 in presence of benzene or ether.

TEST YOUR UNDERSTANDING - 11.6

1. Describe exactly what will happen when a mixture of 200 g of 95% alcohol and 74 g of benzene is distilled ?

11.4 Physical Properties

1. The lower alcohols are readily soluble in water and the solubility decreases with the increase in molecular weight. The solubility of alcohols in water can be explained due to the formation of hydrogen bond between the highly polarised —OH groups present both in alcohol and water.

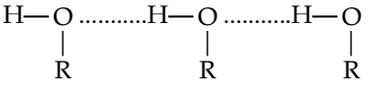


Hydrogen bonding between alcohol and water molecules

However, in higher alcohols the hydrocarbon character (alkyl chain) of the molecule increases and thus alcohols tend to resemble hydrocarbon (which are insoluble in water) and hence the solubility in water decreases. When the ratio of C to OH is more than 4, alcohols have little solubility in water.

Relative solubility of isomeric alcohols in water is 1° > 2° > 3°. Remember that ethers are also able to form hydrogen bonds with water, hence like alcohols, ethers are also soluble in water, *e.g.* diethyl ether and 1-butanol have the same solubility in water (nearly 8 g per 100 mL at room temperature).

2. Boiling points of alcohols are much higher than those of the corresponding alkanes and ethers. It is due to the formation of hydrogen bonding between the hydroxyl groups of the two molecules of an alcohol with the result several molecules are associated to form a large molecule.



Hydrogen bonding in alcohol molecules.

Among the isomeric alcohols, b.p. and m.p. show the following trend.

Primary > Secondary > Tertiary

This is because of the fact that in secondary and tertiary alcohols, the alkyl part (hydrocarbon character) outweighs the —OH group due to branching.

3. Lower alcohols form solid addition compounds with anhydrous metallic salts like $CaCl_2$ and $MgCl_2$, *viz.*, $CaCl_2.4C_2H_5OH$ anD $MgCl_2.6C_2H_5OH$.

By analogy to water of crystallisation, these alcohol molecules are referred to as **alcohol of crystallisation.** *For this reason, alcohols cannot be dried over anhydrous calcium chloride.*

4. Methanol is highly toxic. Ingestion of even small quantities of methanol can cause blindness; large quantities cause death. Methanol poisoning can also occur by inhalation of the vapours or by prolonged exposure to the skin. Ethanol is a **hypnotic** (*sleep producer*). Ethanol is much less toxic than methanol.

TEST YOUR UNDERSTANDING - 11.7

1. Explain why

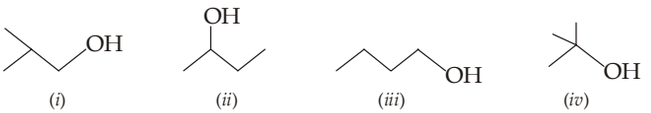
(*a*) Propanol, unlike propane or butane, is soluble in water.

(*b*) *n*-Butanol is soluble in water, while *n*-hexanol is insoluble.

(*c*) Dimethyl ether and ethyl alcohol have the same molecular weight, yet dimethyl ether boils at a very low temperature (– 24°C) than ethanol (78°C).

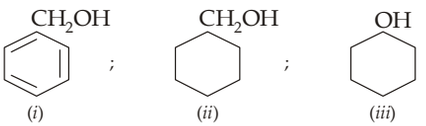
2. Compare the solubility and boiling point of following alcohols.

(*a*)



(*i*) (*ii*) (*iii*) (*iv*)

(*b*)



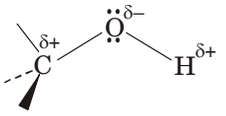
(*i*) (*ii*) (*iii*)



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11.5 Reactions of Alcohols

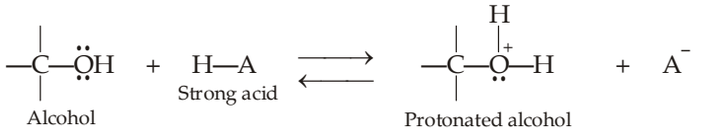
Let us examine the electron distribution in the alcoholic functional group, and study its impact on the reactivity.



(*i*) Oxygen atom of an alcohol polarizes both the C—O bonds and the O—H bond of an alcohol. Polarization of the O—H bond makes the hydrogen partially positive and explains why *alcohols are weak acids.* In such reactions alcohols act as acids and cleavage of the O—H bond takes place. The order of reactivity of different alcohols for such reactions is

$$CH_3OH > 1° > 2° > 3° \text{ alcohols}$$

(*ii*) Polarisation of the C—O bond makes the carbon atom partially positive, and hence it would have been susceptible to nucleophilic attack if OH^- were not a strong base, *i.e.* if OH^- were not a poor leaving group. However, electron pairs on the oxygen atom make alcohols both *basic* and *nucleophilic.*



(Basic character of alcohols)

Protonation of the alcohol converts a poor leaving group (OH^-) into a good leaving one (H_2O). Protonation of the alcohol also makes the carbon atom even more positive (because $-\overset{+}{O}H_2$ is more electron withdrawing than —OH) and hence protonated alcohols become more susceptible to nucleophilic attack. In other words, protonated alcohols easily undergo nucleophilic substitution which may be S_N2 or S_N1 depending upon the class of alcohol. Thus these reactions involve the cleavage of the C—OH bond and replacement of —OH group by other nucleophile (substituent). The order of reactivity of different alcohols for such reactions is

$$3° > 2° > 1° > CH_3OH$$

(*iii*) At a high temperature, and in the absence of a good nucleophile, protonated alcohols are capable of undergoing elimination reactions (*e.g.* dehydration).

(*iv*) Alcohols act as nucleophiles while reacting with protonated alcohol (to form ethers), PBr_3 and $SOCl_2$ (to form alkyl bromides and alkyl chlorides).

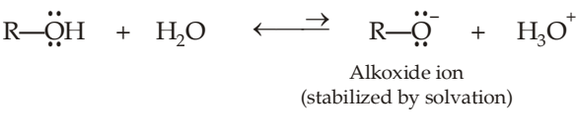
(*v*) Differences in the structure of the group R cause differences in reactivity and in few cases even the course of reaction is changed.

Let us apply above concepts on the various properties of alcohols.

1. Alcohols as acids and bases. The polarity of the O—H bond in alcohols facilitates the departure of a proton. Further, the negative charge developed after the removal of proton can easily be accommodated by electronegative oxygen. Hence alcohols behave as acids. Acidity of alcohols is reflected by their reaction with active metals to liberate hydrogen gas.

$$\underset{\substack{\text{An alcohol}\\\text{(a weak acid)}}}{ROH} + Na \longrightarrow \underset{\substack{\text{Sod. alkoxide}\\\text{(a stronger base)}}}{RONa} + \frac{1}{2}H_2$$

Except methanol, all alcohols are somewhat weaker acids than water. Methanol is a slightly stronger acid than water. Among alcohols, acidity decreases with the increase in size of the alkyl group. With simpler alkyl group, water molecules are able to surround and solvate the negative oxygen of the alkoxide ion formed due to loss of a proton to a strong base. Solvation, thus stabilizes the alkoxide ion and hence increases the acidity of the alchohol.



With the increase in the size of the alkyl group of the alcohol, solvation of the alkoxide ion (ion-dipole interaction) is hindered, and the alkoxide ion is not so effectively stabilized and consequently the alcohol behaves as a weak acid. Relative acidic character of some alcohols and water are given below.

	CH_3OH	>	H_2O	>	CH_3CH_2OH	>	$(CH_3)_3COH$	**(Relative acidic character)**
pK_a	15.5		15.74		15.9		18.0	

All alcohols are much stronger acids than terminal alkynes, and very much stronger than hydrogen, ammonia and alkanes.

$CH_3OH > H_2O > ROH > RC \equiv CH >> H_2 > NH_3 >> RCH = CH_2 > RH$ **(Relative acidity)**

$CH_3O^- < OH^- < RO^- < RC \equiv C^- < H^- < NH_2^- < RCH = CH^- < R^-$ **(Relative basicity)**

The conjugate base of an alcohol is an **alkoxide ion.** Alkoxide ions of the primary or secondary alcohols are prepared by the action of sodium metal, however in case of *tert*-alcohols (least reactive), more reactive metal (potassium) is normally used. Alternatively, sodium alkoxides are sometimes prepared by the reaction of an alcohol with sodium hydride.

$$ROH + NaH \longrightarrow RONa + H_2$$

Since most alcohols are weaker acids than water, most alkoxide ions are stronger bases than the hydroxide ion and hence an alkoxide (except methoxide) is not prepared by the reaction of an alcohol with sodium hydroxide.

$(CH_3)_3CO^- > C_2H_5O^- > OH^- > CH_3O^-$ **(Relative basic character)**

Alkoxides are often used as bases in organic syntheses. Sometimes alkoxide ions are used to carry out a reaction in an alcohol rather than in water (due to difference in solubility).

Like water and ammonia, alcohols are enormously stronger acids than alkanes, and hence they readily displace them from their salts, *viz*. Grignard reagents.

$$\underset{\text{Stronger acid}}{ROH} + R'MgX \longrightarrow \underset{\text{Weaker acid}}{R'H} + Mg(OR)X$$

In general, *a compound is shown to be a stronger acid than another by its ability to displace the second compound from salts* as illustrated below.

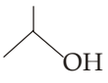
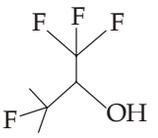
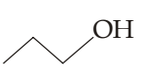
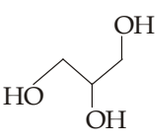
$$\underset{\text{Stronger acid}}{A—H} + B^-M^+ \longrightarrow \underset{\text{Weaker acid}}{B—H} + A^-M^+$$

Due to presence of unshared electron pairs on oxygen, alcohols also act as Lewis bases.

$$\underset{\text{Stronger base}}{ROH} + H_2SO_4 \rightleftharpoons \underset{\text{Protonated alcohol}}{ROH_2^+} + \underset{\text{Weaker base}}{HSO_4^-}$$

TEST YOUR UNDERSTANDING - 11.8

1. Which of the member of following pairs is a stronger acid ?

(*a*) (*i*)  and (*ii*)  (*b*) (*i*)  and (*ii*) 

(*c*) Which of the above member of each pairs is a stronger nucleophile ?

2. Action of acids (Esterification).

(*a*) **Esters of carboxylic acids.** Carboxylic acids react with alcohols in presence of a little amount of conc. H_2SO_4 or dry hydrogen chloride to form esters, and the reaction is known as **Fischer esterification.**

$$R'COOH + H—OR \overset{H^+}{\rightleftharpoons} R'COOR + H_2O$$

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(*i*) Fischer esterification is an acid catalyzed reaction. It proceeds very slowly in the absence of strong acids.

(*ii*) It is a reversible reaction and the position of equilibrium can be made more favourable towards esters by using either the alcohol or the carboxylic acid in excess. The yield of ester can also be increased by removing water from the reaction mixture as soon as it is formed. This can be accomplished by adding benzene as a co-solvent and distilling the azeotropic mixture of benzene and water. (Benzene-water azeotrope contains 9% water and boils at 69°C).

On the other hand, if we want to hydrolyze an ester, we must use a large excess of water, *i.e.* ester is refluxed with dilute aqueous HCl or dil aqueous H_2SO_4.

(*iii*) The presence of bulky groups near the site of reaction, whether in the alcohol or in the acid slows down esterification (as well as its reverse, hydrolysis).

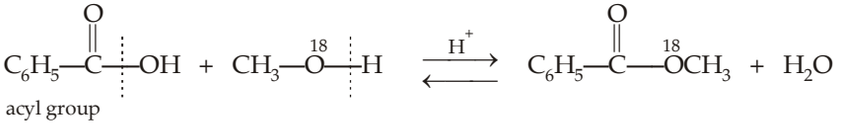
Reactivity in esterification

$CH_3OH > 1° > 2° > 3°$

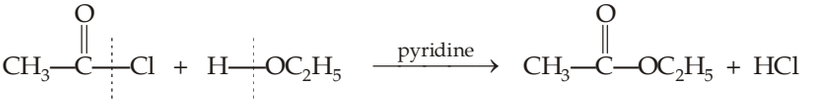
$HCOOH > CH_3COOH > RCH_2COOH > R_2CHCOOH > R_3CCOOH$

Thus *tert*-alcohols react so slowly in acid-catalyzed esterifications that they usually undergo elimination reaction to form alkenes ; or they form *tert*-alkyl chlorides. Hence for the preparation of esters of *tert*-alcohols or esters of acids like 2, 4, 6-trimethyl benzoic acid, the steric hindrance is so marked that special methods are used for their preparation.

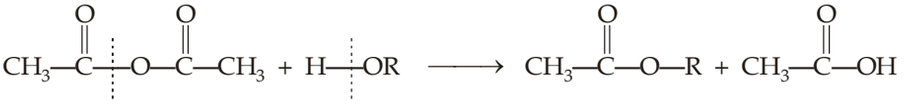
(*iv*) With the help of labelled experiment (by taking O^{18} in alcohols), it has been proved that esterification involves cleavage of the O—H bond of alcohols and not the C—OH bond, *i.e.* H atom is removed from alcohol and OH group from acid.



(*v*) Esters are also formed by the reaction of alcohols with acyl chlorides or acid anhydrides.

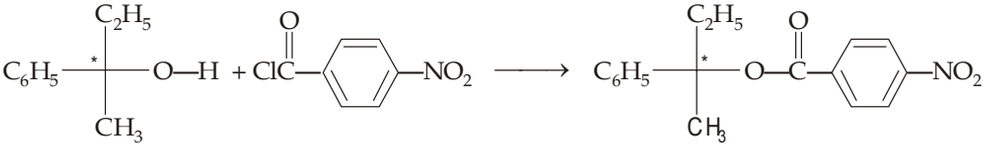


Pyridine is often added to react with the HCl formed.



Unlike the reaction with carboxylic acids, these reactions are irreversible, hence yields of esters *via* this route are always high.

(*vi*) The fact that the acyl group of the carboxylic acid, acyl chloride or acid anhydride is transferred to the oxygen of the alcohol is most clearly evident in the esterification of chiral alcohols.



R-(+)-2-Phenyl-2-butanol

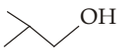
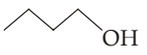
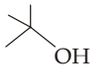
(R)-(–)-1-Methyl-1-phenylpropyl-*p*-nitrobenzoate

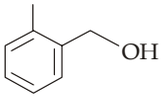
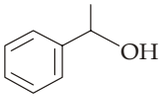
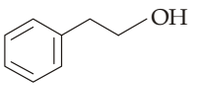
Retention in configuration indicates that none of the bonds to the stereogenic center is broken in the process.

Mechanism of esterification will be discussed in detail in the chapter on ''carboxylic acids''. Further note that since acid-catalysed esterification is a reversible reaction, the mechanism of acidic hydrolysis of esters will be the exact reverse of esterification.

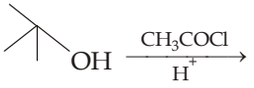
TEST YOUR UNDERSTANDING - 11.9

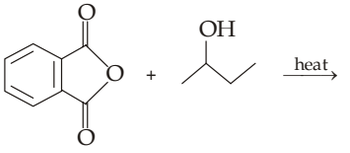
1. Arrange the following alcohols in the decreasing tendency of ester formation with acetic acid in presence of conc. H_2SO_4.

(*a*) (*i*)  (*ii*)  (*iii*)  (*iv*) 

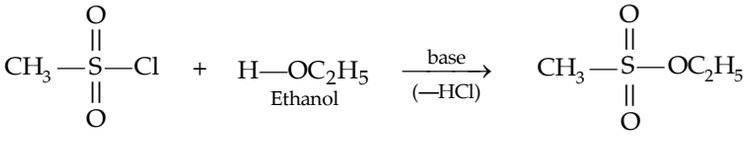
(*b*) (*i*)  (*ii*)  (*iii*) 

2. Complete the following reactions.

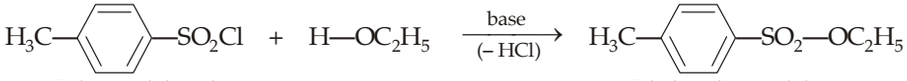
(*a*) 

(*b*) 

(*b*) **Esters of sulphonic acids.** Alcohols react with sulphonyl chlorides (remember that like carboxylic acids, sulphonic acids are less reactive than the corresponding chlorides and anhydrides) to form **sulphonates.**

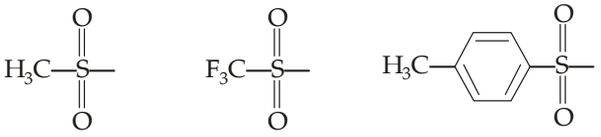


Methanesulphonyl chloride — Ethyl methanesulphonate (Ethyl mesylate)



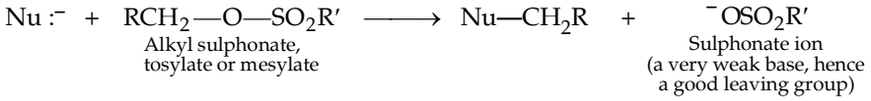
p-Toluenesulphonyl chloride — Ethyl *p*-toluenesulphonate (Ethyl tosylate)

Name of methanesulphonyl, trifluoromethanesulphonyl and *p*-toluenesulphonyl groups are shortened to mesyl (Ms), trifyl (Tf) and tosyl (Ts) respectively.



Mesyl or Ms — Trifyl or Tf — Tosyl or Ts

Since sulphonate ions are excellent leaving groups*, alkyl sulphonates are frequently used as substrates for nucleophilic substitution or elimination reactions.

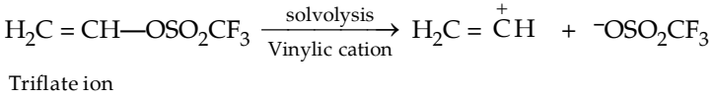


Alkyl sulphonate, tosylate or mesylate — Sulphonate ion (a very weak base, hence a good leaving group)

(where Nu:$^-$ = $^-$OH, $^-$C≡N, Br^-, $^-$OR, :NH_3, $LiAlH_4$)

Trifluoromethanesulphonate ($CF_3SO_2O^-$) is one of the best known leaving groups.

Actually, the triflate ion is such a good leaving group that even vinylic triflates undergo S_N1 reactions.



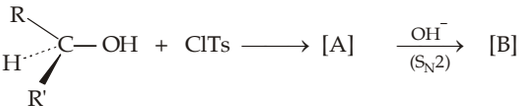
Triflate ion — Vinylic cation

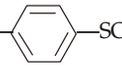
* Although protonation of alcohols also generates a good leaving group (—$\overset{+}{O}H_2$), it limits our choice of reagents to those compatible with an acidic medium. Alkyl sulphonates, on the other hand, can be used with any nucleophile or base.

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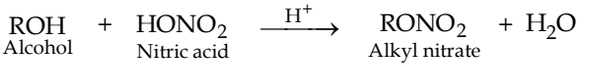
TEST YOUR UNDERSTANDING - 11.10

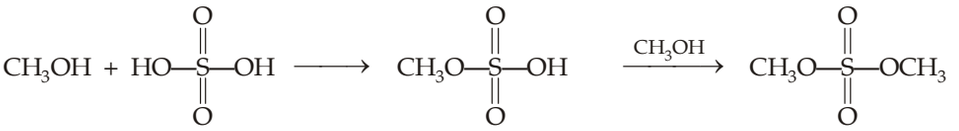
1. Write down the structure of products A and B in the following reaction.



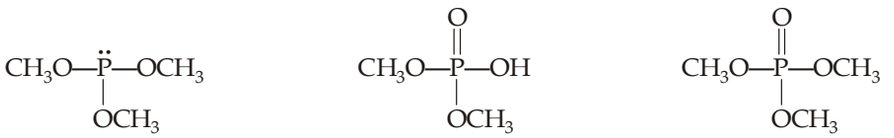
(where Ts is *p*-toluenesulphonyl, H_3C—  —SO_2—).

(*c*) **Esters of inorganic acids.** Alcohols react with inorganic acids, *viz.* nitric acid, sulphuric acid, H_3PO_3 and H_3PO_4 to form esters of inorganic acids. For example,





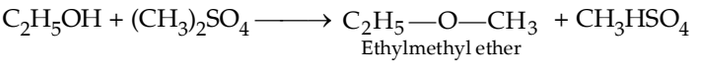
Methyl hydrogen sulphate — Dimethyl sulphate



Trimethyl phosphite (Ester to phosphorous acid, H_3PO_3) — Dimethyl hydrogen phosphate — Trimethyl phosphate

(Esters of phosphoric acid, H_3PO_4)

Dimethyl sulphate is used as methylating agent in synthetic organic chemistry ; *e.g.*



Ethylmethyl ether

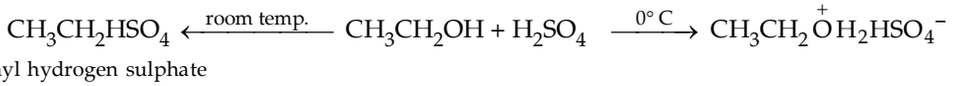
Methylation is used for determining the number of – OH group in alcohols.

$$\text{No. of – OH gps.} = \frac{\text{Mol. mass of methylated product} - \text{Mol. mass of alcohol}}{14}$$

Action of conc. sulphuric acid on alcohols is very interesting as it gives different products under different conditions.

(*i*) Alcohols dissolve in cold conc. H_2SO_4 (*i.e.* at 0°C) forming oxonium salts, $R\overset{+}{O}H_2HSO_4^-$.

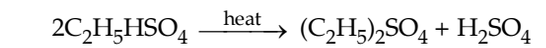
(*ii*) At room temperature, esterification takes place forming alkyl hydrogen sulphate.



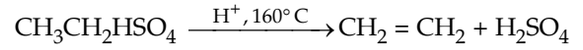
Ethyl hydrogen sulphate

Ethyl hydrogen sulphate is an important intermediate and can be converted into different products under different conditions.

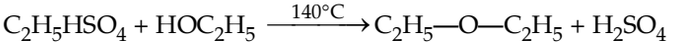
(*a*) When heated alone, it forms diethyl sulphate



(*b*) When heated with excess of H_2SO_4 at 160°C, it forms ethylene.



(*c*) When heated with excess of ethanol, it forms diethyl ether



3. Conversion of alcohols into alkyl halides

(*a*) **Reaction with hydrogen halides.**

$$R—OH + HX \longrightarrow R—X + H_2O$$

The order of reactivity of the hydrogen halides is **HI > HBr > HCl** (HF is generally unreactive), and the order of reactivity of alcohols is **3° > 2° > 1° < CH_3.**

(*i*) The reaction is *acid-catalysed**. Alcohols react with strongly acidic hydrogen halides, but not with non acidic NaCl, NaBr or NaI. Primary and secondary alcohols can be converted to alkyl chlorides and bromides by allowing them to react with a mixture of sodium halide and sulphuric acid.

$$R—OH + NaX \xrightarrow{H_2SO_4} R—X + NaHSO_4 + H_2O \ (X = Cl \text{ or } Br)$$

(*ii*) The least reactive hydrogen halide, *i.e.* HCl **generally requires the presence of $ZnCl_2$*** (a Lewis acid) for reaction with 1° and 2° alcohols ; however, the highly reactive 3° alcohols do not require $ZnCl_2$.

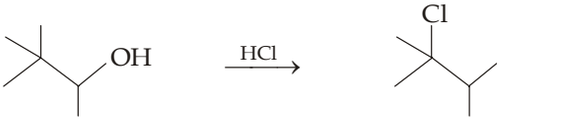
$$CH_3CH_2CH_2CH_2OH \xrightarrow[\text{heat}]{\text{dry HBr or NaBr} + H_2SO_4} CH_3CH_2CH_2CH_2Br$$

$$CH_3CH_2CH_2OH \xrightarrow{HCl + ZnCl_2, \text{ heat}} CH_3CH_2CH_2Cl$$

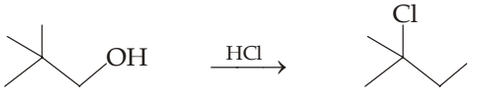
$$\underset{\textit{tert}\text{-Butyl alcohol}}{(CH_3)_3COH} \xrightarrow{\text{conc. HCl, room temperature}} \underset{\textit{tert}\text{-Butyl alcohol}}{(CH_3)_3COH}$$

This relative reactivity of alcohols towards HCl forms the basis of **Lucas test.**

(*iii*) Except with *most primary alcohols*, rearrangement of the alkyl group occurs, *i.e.* rearranged halides are formed.



3, 3-Dimethyl-2-butanol (a 2° alcohol) — 2-Chloro-2, 3-dimethylbutane



Neopentyl alcohol (a 1° alcohol) — *tert*-Pentyl chloride

(*iv*) One of the important aspects of this reaction is that by converting an ROH into RX , we have replaced a very poor leaving group (—OH) into a very good leaving group (—X) instantaneously ; *i.e.* highly reactive compounds are formed from lesser reactive compounds.

Mechanism. Secondary, tertiary, allylic, and benzylic alcohols appear to react by S_N1 mechanism.

Step 1. $(CH_3)_3C—OH + H—Cl \rightleftharpoons (CH_3)_3C—\overset{+}{O}H_2 + Cl^-$

Step 2. $(CH_3)_3C—\overset{+}{O}H_2 \rightleftharpoons (CH_3)_3C^+ + H_2O$

Step 3. $(CH_3)_3C^+ + Cl^- \longrightarrow (CH_3)_3C—Cl$

tert-Butyl chloride

Most of the primary alcohols and methyl alcohol react by S_N2 mechanism.

$$R—\overset{+}{O}H_2 + X^- \longrightarrow \left[\overset{\delta-}{X}\cdots\cdots R\cdots\cdots\overset{\delta+}{O}H_2\right] \longrightarrow X—R + H_2O$$

Why CH_3OH reacts faster than other primary alcohols ? Actually, methyl substrate is least capable of heterolysis and thus reacts by a full-fledged S_N2 reaction. Although most of the primary substrates also react by S_N2 mechanism, but because of greater steric hindrance they react less rapidly than the methyl.

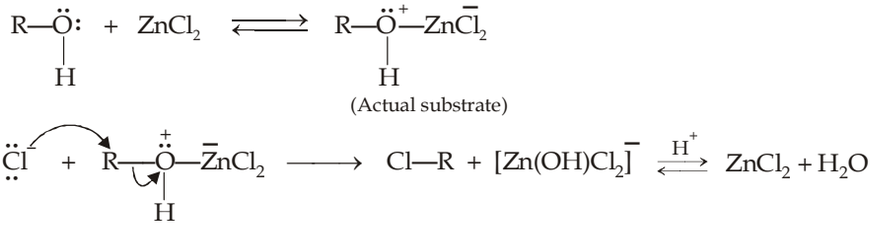
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* Although the aqueous HX are themselves strong acids, presence of H_2SO_4 speeds up the reaction.

** Recall that Cl^- is a weaker nucleophile than Br^- or I^-.

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Function of $ZnCl_2$ in Lucas reagent. Since chloride ion is a weaker nucleophile than bromide or iodide ions, HCl does not react with less reactive 1° and 2° alcohols unless some good Lewis acid like $ZnCl_2$ is added to the reaction mixture. Primary alcohols, being least reactive, requires some heat in addition to $ZnCl_2$. Zinc chloride, a good Lewis acid, forms a complex with the alcohol. This complex provides a better leaving group for the reaction than H_2O.

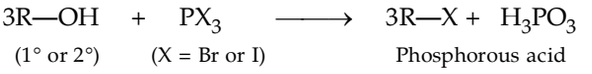


Now we can explain why the reactions of alcohols with hydrogen halides are acid catalyzed.

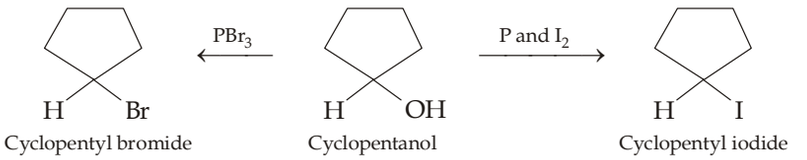
(*i*) In case of 3° and 2° alcohols, the function of acid is to help in the formation of carbocations.

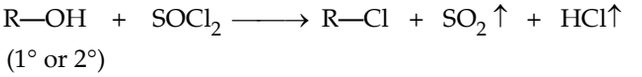
(*ii*) In case of methyl and 1° alcohols, the function of acid is to produce a substrate in which the leaving group is a weakly basic species (H_2O or $Zn(OH)Cl_2^-$) rather than a strongly basic hydroxide ion.

(*b*) **Reaction with phosphorus trihalides or thionyl chloride.**



Phosphorus is a water-soluble and may be removed by washing the alkyl halide with water or with dilute aqueous base.





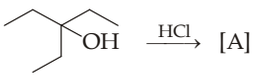
Since SO_2 and HCl, both are gases at room temperature, these are easily removed. Reactions with thionyl chloride are normally carried out in the presence of potassium carbonate or the weak organic base pyridine.

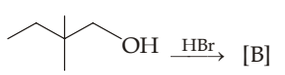
(*i*) Since *tert*-alcohol are readily converted into halides, phosphorous trihalides and thionyl chloride are mainly used for preparing primary and secondary halides.

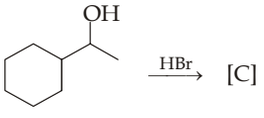
(*ii*) Since carbocations are not formed as intermediates, the reaction with both the reagents occurs *without rearrangement.*

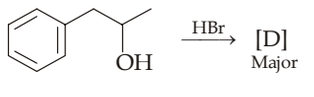
TEST YOUR UNDERSTANDING - 11.11

1. Identify [A] to [D] in the following reactions.

(*a*) 

(*b*) 

(*c*) 

(*d*) 

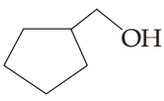
2. Explain the following :

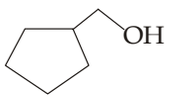
(*a*) Neopentyl alcohol reacts with hydrogen halides slowly.

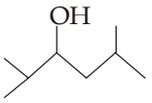
(*b*) 1-Chloro-2-propanol is although a secondary alcohol, it reacts with hydrogen halides slowly than the parent compound, 2-propanol.

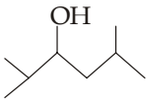
3. Neopentyl chloride can't be prepared from neopentyl alcohol, can you suggest a method for the preparation of neopentyl chloride in quantitative yield ?

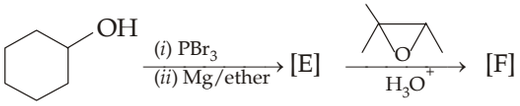
4. Identify the compounds [A] to [F] in the following reactions.

(*a*)  [A]

(*b*)  [B]

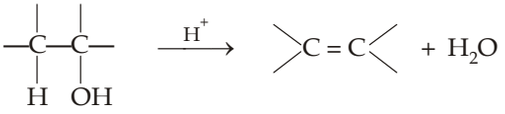
(*c*)  [C]

(*d*)  [D]

(*e*) 

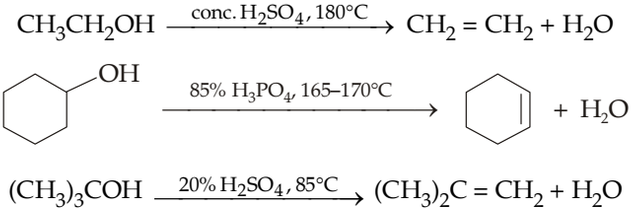
4. Dehydration to alkenes. (Intramolecular dehydration)

Heating of most of alcohols with a strong acid causes loss of a water molecule to form alkenes (for mechanism, consult chapter on ''Alkenes'').



(*i*) The reaction is an elimination and is favoured at high temperatures. Most commonly used acids in the laboratory are H_2SO_4 and H_3PO_4, while alumina is often used in industries.

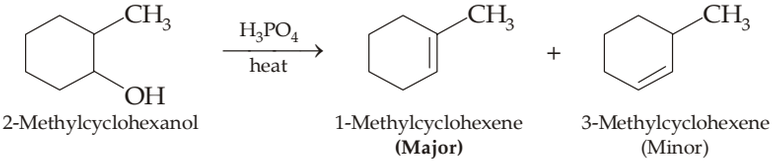
(*ii*) The order of dehydration among three types of alcohols is 3° > 2° > 1°. Thus dehydrating conditions become milder as we proceed from 1° to 3° alcohols.



This behaviour is related to the relative stabilities of carbocations (3° > 2° > 1°).

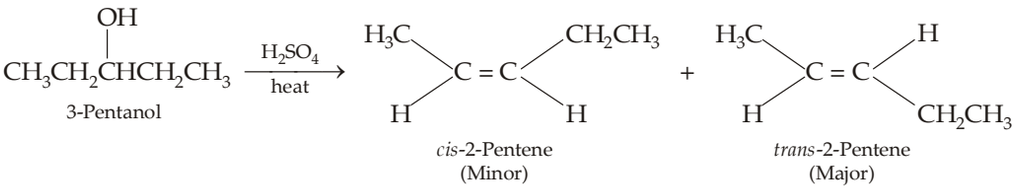
(*iii*) Since carbocations are formed as intermediate, rearranged olefins, where possible, are formed (consult Ch. on alkenes).

(*iv*) Whenever dehydration can produce two different alkenes, major product is formed according to **Saytzeff rule** *''poor becomes poorer'' i.e.* more substituted alkene (alkene having lesser number of hydrogen atoms on the two doubly bonded carbon atoms) is the major product.



Such reactions which can produce two or more structural isomers but one of them in greater amounts than the other are called **regioselective** *;* in case a reaction is 100% regioselective, it is termed as **regiospecific.**

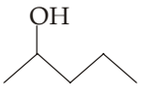
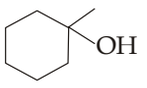
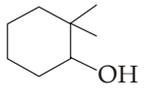
(*v*) In addition to being regioselective, alcohol dehydrations are **stereoselective** (*a reaction in which a single starting material can yield two or more stereoisomeric products, but gives one of them in greater amount than any other).*

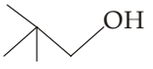
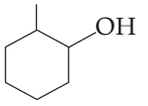


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TEST YOUR UNDERSTANDING - 11.12

1. Write down the structure of the compound(s) by the acid-catalyzed dehydration of the following alcohols. Mention the major product, if any, in each case.

(*a*)  (*b*)  (*c*) 

(*d*)  (*e*)  (*f*)  .

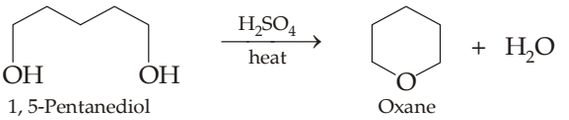
5. Dehydration to ethers (Intermolecular dehydration). Primary alcohols when heated in presence of an acid catalyst (usually H_2SO_4) undergo intermolecular dehydration to form ethers.

$$R—OH + HO—R \xrightarrow{H^+,\ heat} R—O—R$$

(*i*) Dehydration of an alcohol to an ether usually takes place at a lower temperature than dehydration to alkene.

$$CH_2=CH_2 \xleftarrow[180°C]{\text{excess of } H_2SO_4} CH_3CH_2OH \xrightarrow[H_2SO_4,\ 140°C]{\text{excess of ethanol}} CH_3CH_2OCH_2CH_3$$

(*ii*) As mentioned above, the reaction is effective only with primary alcohols ; secondary and tertiary alcohols on such treatment mainly give alkenes. However, diols having primary alcoholic groups can undergo dehydration (intramolecular) to form a 5-membered or 6-membered ring.

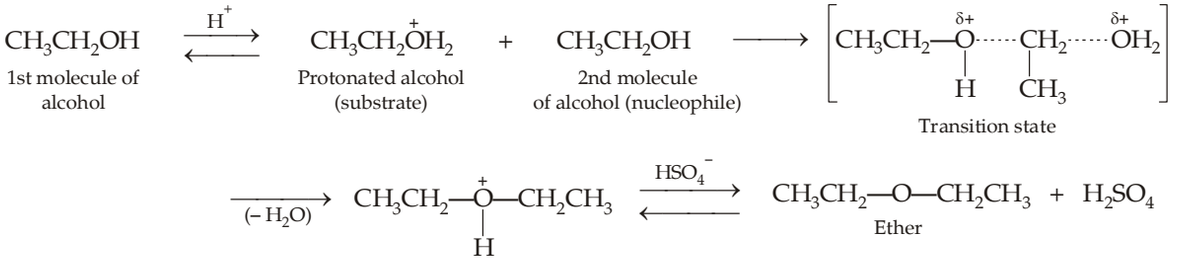


(*iii*) This method is not useful for the preparation of unsymmetrical ethers because the reaction leads to a mixture of products.

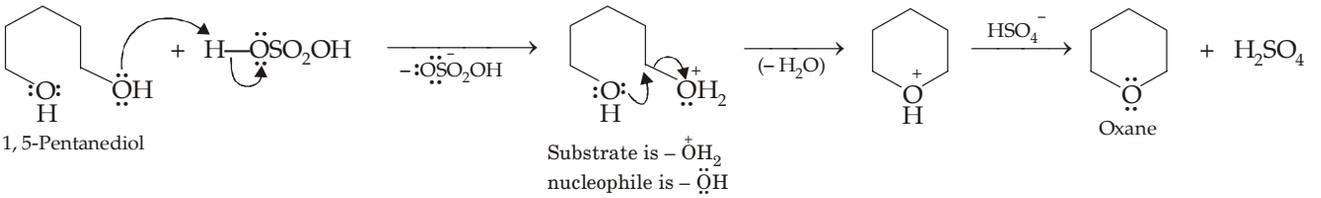
$$R—OH + HO—R' \xrightarrow{H^+} R—O—R' + R—O—R + R'—O—R'$$

The most common method for preparing unsymmetrical ethers is **Williamson synthesis** (discussed in ethers).

Mechanism. Reaction is a nucleophilic substitution in which substrate is a protonated alcohol and nucleophile is the second alcohol molecule.

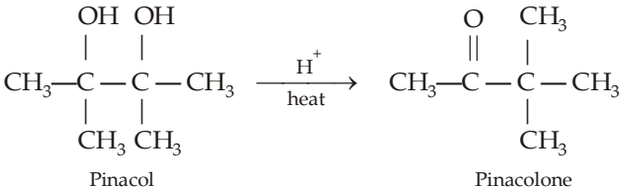


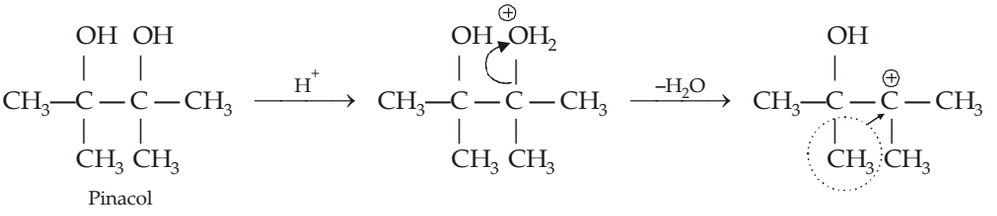
Mechanism for the conversion of 1, 5-pentanediol to oxane.

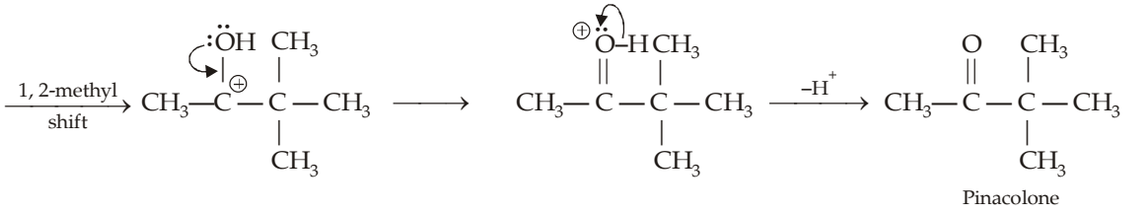


Pinacol–pinacolone rearrangement.

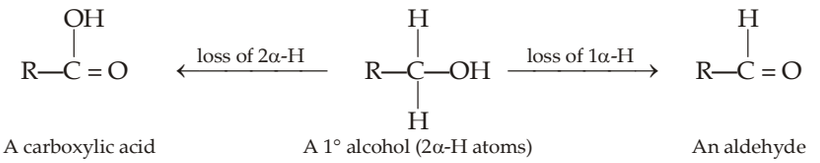
Pinacols, ditertiary 1, 2-diols, on heating with acids lose a molecule of water along with the rearrangement to form ketones, commonly known as pinacolones.

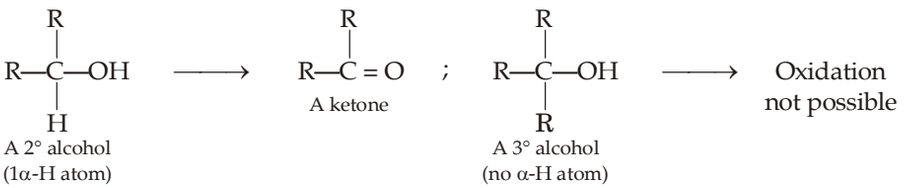






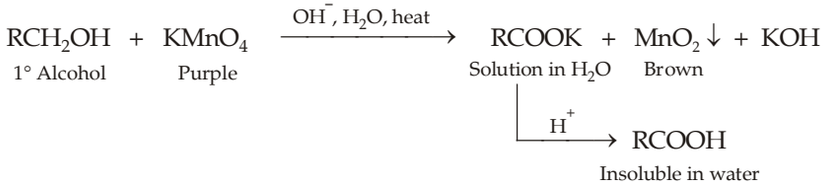
6. Oxidation of alcohols. Oxidation of an alcohol involves the loss of one or more hydrogens (α-hydrogens) from the carbon bearing the —OH group. Hence the nature of product obtained depends upon the number of α-hydrogen atoms present in the alcohol. Thus,





Thus, in short a primary alcohol may be oxidised to an aldehyde or a carboxylic acid, a secondary alcohol to a ketone, and a tertiary alcohol is not oxidisable easily. However, a tertiary alcohol can be dehydrated by an acidic oxidising agent to an alkene which can then be oxidised.

(*a*) **Oxidation of primary alcohols to carboxylic acids.** Primary alcohols can be oxidised to carboxylic acids by acidic or basic aqueous solution of potassium permanganate. As the oxidation takes place Mn (VII) is reduced to Mn (IV) in the form of brown precipitate of MnO_2.



Primary alcohols can be oxidised to carboxylic acids also by $Cr_2O_7^{2-} + H_2SO_4 + H_2O$ and chromic acid, H_2CrO_4, prepared by dissolving CrO_3 or $K_2Cr_2O_7$ in aqueous sulphuric acid.

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(*b*) **Oxidation of primary alcohols to aldehydes.** The oxidation of aldehydes to carboxylic acids **in aqueous solution** usually takes place with less powerful oxidizing agents than those required to oxidize 1° alcohols to aldehydes, thus **it is difficult to stop oxidation at the aldehydic stage in aqueous solution.** Hence special oxidizing agents must be used for oxidizing 1° alcohols to the aldehydic stage. One of the best and most convenient reagents for this purpose is **pyridinium chlorochromate (PCC),** obtained by dissolving chromium oxide (CrO_3) in hydrochloric acid in presence of pyridine.

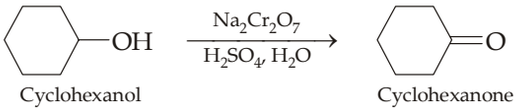
$$CrO_3 + HCl + \text{pyridine} \longrightarrow \text{pyridinium chlorochromate (PCC)}$$

Other such reagent is **pyridinium dichromate (PDC),** $(C_5H_5NH)_2^+\ Cr_2O_7^{2-}$. Both of these reagents are used in presence of dichloromethane, CH_2Cl_2 in which these reagents are soluble.

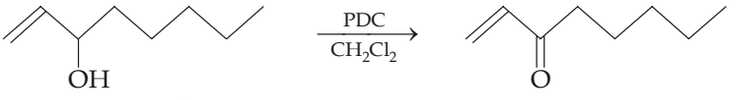
$$CH_2 = CH—CH_2OH \xrightarrow{PCC/CH_2Cl_2} CH_2 = CHCHO$$

Remember that aldehyde hydrates, $RCH(OH)_2$ are more easily oxidisable than aldehydes, hence aqueous medium is avoided whenever aldehyde is to be obtained as final product.

(*c*) **Oxidation of secondary alcohols to ketones.** Secondary alcohols are oxidised to ketones, at which stage reaction usually stops because further oxidation requires breaking of C—C bond. Secondary alcohols can be oxidised to ketone either by (*i*) chromic acid (H_2CrO_4), prepared by adding CrO_3 or $Na_2Cr_2O_7$ to aqueous sulphuric acid, or by a complex of chromium trioxide and pyridine (**Collins reagent)** or by (*iii*) CrO_3 in aqueous acetone **(Jones reagent)** ; or by (*iv*) PDC/PCC in CH_2Cl_2. Although Jones reagent rarely affects double bond, the last reagent is especially useful for oxidising unsaturated alcohols to unsaturated carbonyl compounds.



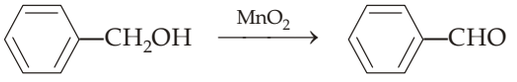
Cyclohexanol — Cyclohexanone

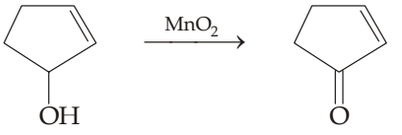


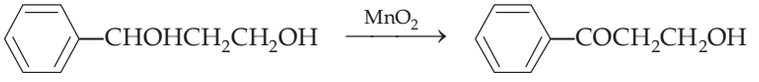
1-Octen-3-ol — 1-Octen-3-one

(*d*) **Oxidation by manganese dioxide.** Manganese dioxide selectively oxidises the alcoholic groups of allylic and benzylic 1° and 2° alcohols to give aldehydes and ketones respectively.

(*i*) $HOCH_2CH_2CH = CHCH_2OH \xrightarrow{MnO_2} HOCH_2CH_2CH = CHCHO$

(*ii*) 

(*iii*) 

(*iv*) 

(*e*) **Swern oxidation** of 1° and 2° alcohols gives aldehydes and ketones respectively. It uses dimethylsulfoxide (DMSO) as as the oxidizing agent; DMSO and oxalyl chloride are added to the alcohol at low temperature, followed by a hindered base such as triethylamine. The by-products of this reaction are all volatile, and are easily separated from the organic products. Thus it provides a useful alternative to PCC that uses chromium reagents.

$$\underset{(R'=H \text{ or alkyl})}{R-CHOH} + \underset{DMSO}{H_3C-S-CH_3} + Cl-C(=O)-C(=O)-Cl \xrightarrow[CH_2Cl_2]{(CH_3CH_2)_3N} R-C(=O)-R' + H_3C-S-CH_3 + CO_2 + CO + 2HCl$$

(*f*) **Chemical test for 1° and 2° alcohols.** Primary and secondary alcohols can be easily distinguished from tertiary alcohols on the basis of the fact that the former are readily oxidised by a solution of CrO_3 in aqueous sulphuric acid which is accompanied by change of clear orange solution containing Cr (VI) ions to greenish opaque solution containing Cr(III) ions.

$$\underbrace{RCH_2OH \text{ or } R_2CHOH + CrO_3/\text{aq. } H_2SO_4}_{\text{Clear orange solution}} \longrightarrow \underbrace{\text{Oxidation products} + Cr^{3+}}_{\text{Greenish opaque solution}}$$

This colour change, associated with the reduction of $Cr_2O_7^{2-}$ to Cr^{3+} forms the basis for **Breathalyzer tubes** used to detect intoxicated auto drivers. In the Breathalyzer, the dichromate salt is coated on granules to silica gel.

(*g*) **Distinction between 1°, 2° and 3° alcohols.** We have learnt that

(*i*) Oxidation of 1° alcohols gives first aldehydes and then acids, both having same number of carbon atoms as the parent alcohol.

$$\underset{2C}{CH_3CH_2OH} \longrightarrow \underset{2C}{CH_3CHO} \longrightarrow \underset{2C}{CH_3COOH}$$

(*ii*) Oxidation of 2° alcohols gives ketones which are difficult to oxidise, however on vigourous oxidation ketones give carboxylic acids having lesser number of carbon atoms than the parent alcohol.

$$\underset{3C}{(CH_3)_2CHOH} \longrightarrow \underset{3C}{(CH_3)_2CO} \longrightarrow \underset{2C}{CH_3COOH} + \underset{1C}{HCOOH}$$

(*iii*) Tertiary alcohols are not oxidised easily, however on treatment with acidic reagents, they first undergo **dehydration** to form alkenes. Alkenes are then oxidized first to ketones and then to acids, both having lesser number of carbon atoms than the parent alcohol.

$$\underset{4C}{CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3} \xrightarrow[\text{oxidizing agent}]{\text{acidic}} \underset{\text{Alkene}}{\left[CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2\right]} \xrightarrow{[O]} \underset{3C}{(CH_3)_2CO} \xrightarrow{[O]} \underset{2C}{CH_3COOH} + \underset{1C}{HCOOH}$$

7. Dehydrogenation (oxidation) of alcohols by copper at 573 K. This reaction is also considered as oxidation. In this reaction primary alcohols give aldehydes and secondary give ketones ; while tertiary alcohols undergo dehydration to form alkenes.

$$\underset{1° \text{ Alcohol}}{CH_3CH_2OH} \longrightarrow \underset{\text{Aldehyde}}{CH_3CHO} \; ; \quad \underset{2° \text{ Alcohol}}{(CH_3)_2CHOH} \longrightarrow \underset{\text{Ketone}}{(CH_3)_2CO} \; ; \; \underset{3° \text{ Alcohol}}{(CH_3)_3COH} \longrightarrow \underset{\text{An alkene}}{(CH_3)_2C=CH_2}$$

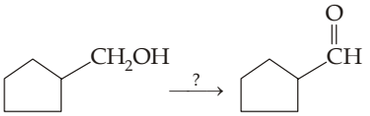
8. Oxidation of alcohols by hypohalites. Ethyl alcohol and secondary alcohols having at least one of the alkyl groups as —CH_3 undergo haloform reaction on treatment with alkaline halogen, (X_2 + NaOH) or hypohalites. For details, consult iodoform in the chapter on "**Alkyl Halides**".

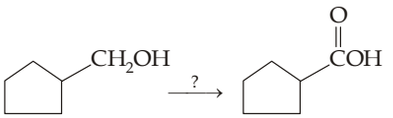
Remember that the reaction takes place in presence of alkaline solution, so CH_3CH_2Cl and CH_3CHClR will also respond haloform test because these halides are converted by aqueous alkali into corresponding alcohols which then undergo haloform reaction.

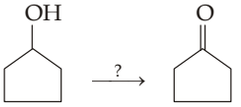
TEST YOUR UNDERSTANDING - 11.13

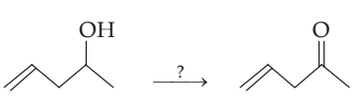
1. Predict the product obtained by the oxidation of benzyl alcohol with (*a*) $KMnO_4/OH^-$, (*b*) $CrO_3/aq.\ H_2SO_4$, (*c*) CrO_3/pyridine HCl.

2. Show how each of the following transformations could be accomplished ?

(*a*) 

(*b*) 

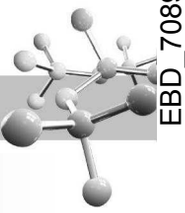
(*c*) 

(*d*) 

3. Which of the following compounds give a positive haloform test ? Also give the structure of the carboxylic acid formed.

(*a*) $C_6H_5CH_2OH$ (*b*) $C_6H_5CHOHCH_3$

(*c*) Cyclopentylmethyl carbinol (*d*) 1-Methylcyclohexanol.

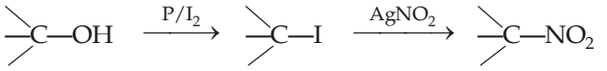


11.6 Distinction Between Primary, Secondary and Tertiary Alcohols

1. **Lucas test.** Lucas reagent (a mixture of conc HCl and zinc chloride) reacts with alcohols to form corresponding alkyl chlorides which are insoluble. Formation of a chloride from an alcohol is indicated by the cloudiness that appars when the chloride separates from the solution. Hence the time required for cloudiness to appear is a measure of reactivity of the alcohol.

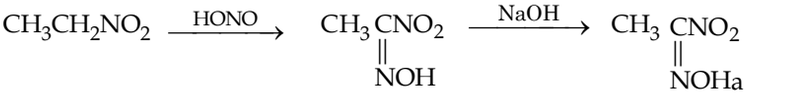
   A tertiary alcohol reacts immediately, a secondary alcohol reacts within five minutes, and a primary alcohol does not react appreciably at room temperature. However, remember that allyl alcohol, $CH_2 = CHCH_2OH$ reacts as rapidly as tertiary alcohols with the Lucas reagent to form *soluble* allyl chloride.

2. **Victor Meyer test.** This test is based upon the fact that the three types (1°, 2° or 3°) of nitroalkanes (formed by alcohols) react differently with nitrous acid followed by sodium hydroxide. The three types of alcohols are first converted to corresponding nitro compounds.

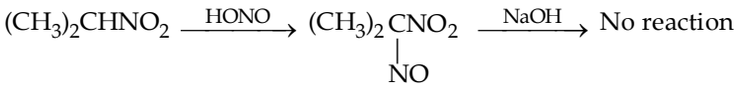


Nitroalkane

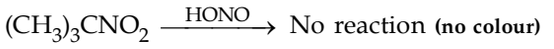
Nitroalkane, so obtained, is treated first with nitrous acid and then with sodium hydroxide to get different colours at the end.



1° Nitroalkane (from 1° alcohol) — Nitrolic acid (blue) — Sod. nitrolate **(red)**



2° Nitroalkane (from 2° alcohol) — Pseudonitrol **(blue)**



3° Nitroalkane

3. **Oxidation method :** With this method, we can distinguish 1° and 2° alcohols from 3° alcohols; primary and secondary alcohols are easily oxidised by chromic anhydride (CrO_3) in aqueous sulphuric acid, indicated by change in colour from clear orange solution to blue-green opaque.



1° or 2° alcohol — Clear orange solution — greenish opaque

tert-Alcohols are not oxidised, hence do not respond this test.

TEST YOUR UNDERSTANDING - 11.14

1. There are five isomeric compounds of the molecular formula $C_5H_{12}O$, only one of which (A) gives white turbidity immediately with conc. $HCl/ZnCl_2$, while the other four do not respond the reagent at room temperature. Identify the five compounds.
2. Identify the alcohol(s) from the given reaction.
   (*a*) An alcohol of the formula C_3H_8O decolorises acidic $KMnO_4$ solution.
   (*b*) An aromatic compound of the formula C_7H_8O turns orange solution of dichromate to green.
   (*c*) A cyclic alcohol of the formula $C_7H_{14}O$ reacts immediately with Lucas reagent.

11.7 Illustrative Examples

Here some problems in the form of reactions or descriptive language are given. Each problem has one or more concept in it.

Example 1 :

Identify A and B in the following reactions.

$$B \xleftarrow[(ii)\,H_2O_2/OH^-]{(i)\,BH_3.THF} CH_3C \equiv CH \xrightarrow{H_2SO_4/Hg^{2+}} A.$$

Solution :

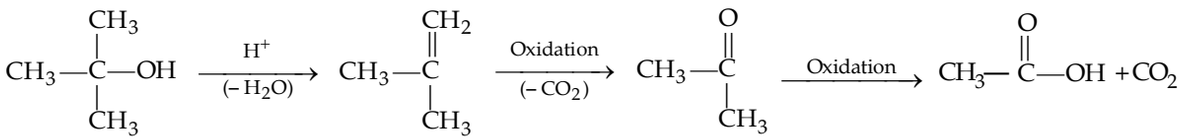
Recall that hydration of alkenes/alkynes by H_2SO_4 takes place in Markovnikov's way, while hydration by hydroboration-oxidation occurs in *anti*-Markovnikov's manner.

$$\underset{(A)}{CH_3COCH_3} \qquad \underset{(B)}{CH_3CH_2CHO}$$

Example 2 :

Write steps in the acidic degradative oxidation of $(CH_3)_3COH$ to CH_3COOH and CO_2.

Solution :



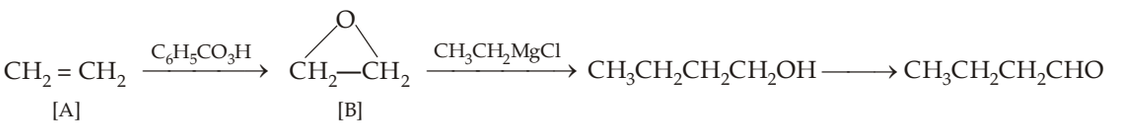
Example 3 :

Supply the missing compounds in the following series of reactions.

$$[A] \xrightarrow{C_6H_5CO_3H} [B] \xrightarrow{CH_3CH_2MgCl} CH_3CH_2CH_2CH_2OH \xrightarrow[CH_2Cl_2]{PCC} [C]$$

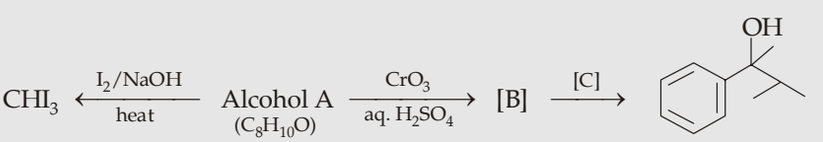
Solution :

Note that the product has two carbon atoms more than the Grignard reagent used, hence the compound B should be ethylene oxide, and hence A as ethylene.



Example 4 :

Identify A to [C] in the following reactions.



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Solution :

Above reactions indicate that alcohol A has benzene nucleus and —$CHOHCH_3$ part, hence it is $C_6H_5CHOH\ CH_3$. Thus



[A]

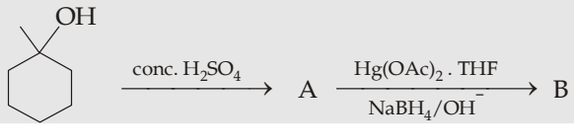
[B]

$(CH_3)_2CHMgCl$ or ClMg 

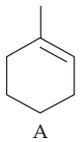
[C]

Example 5 :

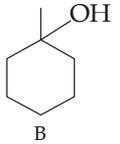
Identify A and B ; what is relation of B with the starting compound ?



Solution :



A ;



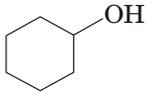
B ; B and starting compounds are same.

Example 6 :

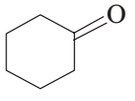
Give the structures of A, B and C

A cyclic alcohol A ($C_6H_{12}O$) $\xrightarrow{\text{conc. } H_2SO_4}$ B $\xrightarrow[\text{heat}]{\text{conc. } HNO_3}$ $C_6H_{10}O_4$ (C)

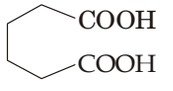
Solution :



(A)



(B)

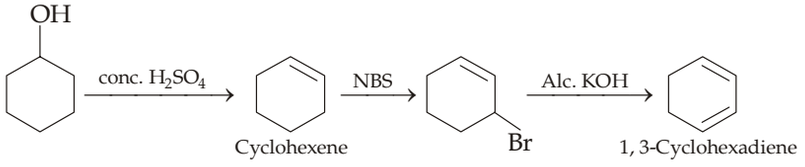


(C) Adipic acid

Example 7 :

Starting from cyclohexanol, prepare cyclohexene, and 1, 3-cyclohexadiene.

Solution :

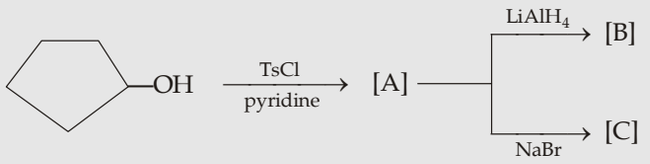


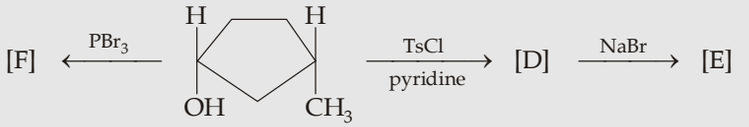
Cyclohexene

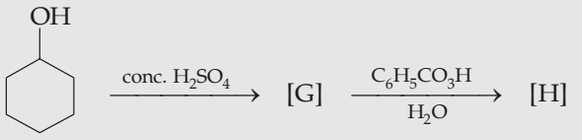
1, 3-Cyclohexadiene

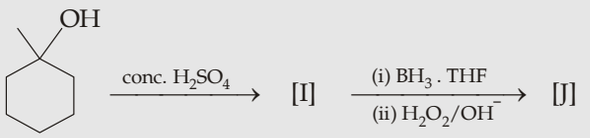
Example 8 :

Complete the following reactions.

(i) 

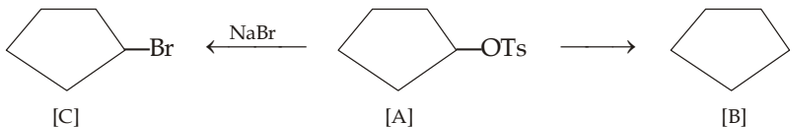
(ii) 

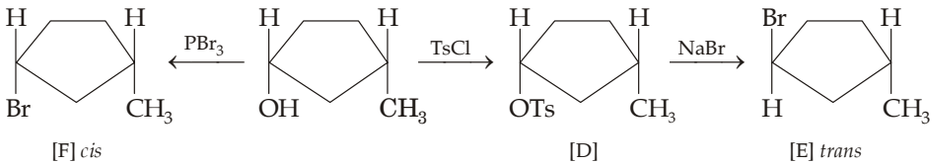
(iii) 

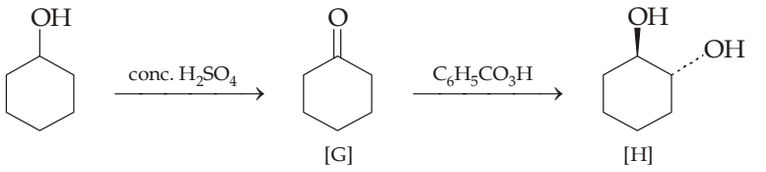
(iv) 

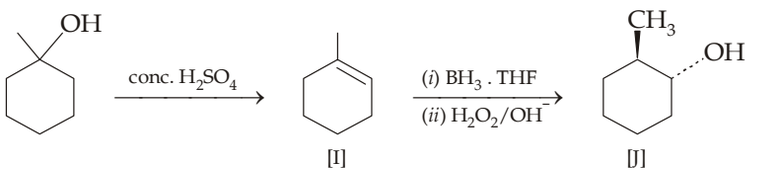
Solution :

Carry out the reactions keeping in mind the stereochemical implication, if any.

(*i*) 

(*ii*) 

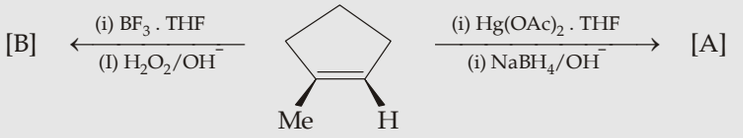
(*iii*) 

(*iv*) 

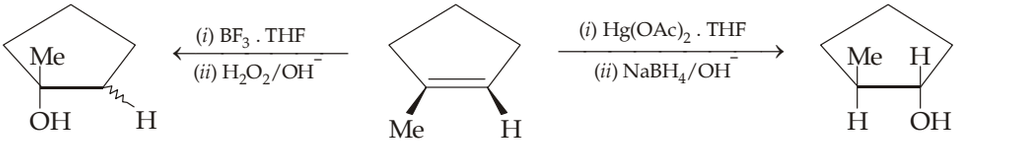
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Example 9 :

Identify the products A and B in the following reaction.



Solution :

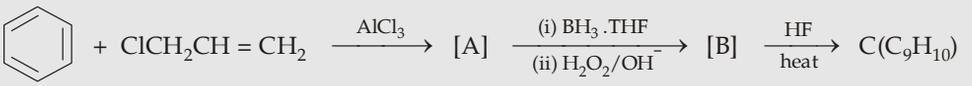


[B] Hydration Markovnikov's way

[A] *syn*-hydration *anti*-Markovnikov's way

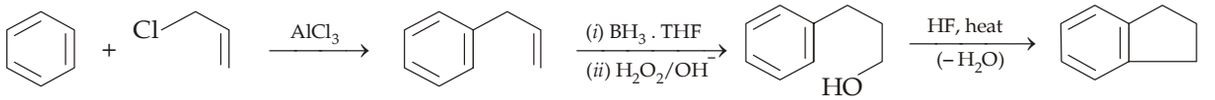
Example 10 :

Supply proper structures to the compounds A to C



Solution :

First step seems to be Friedel-Craft reaction, second *anti*-Markovnikov's hydration and the last step is again an example of Friedel-Craft reaction causing cyclization.

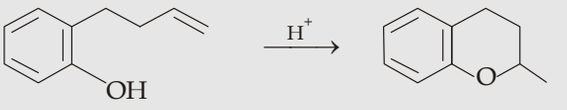


[A] [B] [C] C_9H_{10}

Example 11 :

Write the intermediate steps involved in the following reactions.

(i) $C_6H_5CH(OH)\,C \equiv CH \xrightarrow{H_3O^+} C_6H_5CH = CHCHO$ **(ii)**

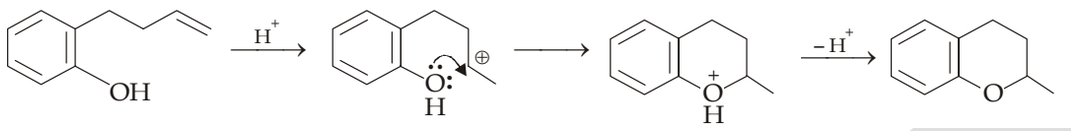


Solution :

(*i*) $C_6H_5CH(OH)\,C \equiv CH \xrightarrow[(ii)\,-H_2O]{(i)\,H^+} C_6H_5\overset{+}{C}H{-}C \equiv CH \longleftrightarrow C_6H_5CH{=}C{=}\overset{+}{C}H \xrightarrow{H_2O}$

$$C_6H_5CH = C = \underset{\oplus OH_2}{\overset{|}{CH}} \xrightarrow{-H^+} C_6H_5CH = C = CHOH \overset{\text{tautomerization}}{\rightleftharpoons} C_6H_5CH = CH{-}CHO$$

(*ii*)



Example 12 :

Prepare *n*-butanol and isobutanol from ethyne.

Solution :

$$HC \equiv CH \xrightarrow{1\ mol\ NaNH_2} HC \equiv CNa \xrightarrow{CH_3CH_2Br} \underset{\text{Butyne-1}}{HC \equiv CCH_2CH_3}$$

$$\underset{\text{Isobutanol}}{CH_3\overset{\overset{OH}{|}}{C}HCH_2CH_3} \xleftarrow[(ii)\ Hg(OAc)_2/NaBH_4]{(i)\ Li/NH_3} \underset{\text{Butyne-1}}{HC \equiv CCH_2CH_3} \xrightarrow[(iii)\ H_2O_2/OH^-]{(i)\ Li/NH_3,\ (ii)\ BH_3.THF} \underset{\text{n-Butanol}}{HOH_2CCH_2CH_2CH_3}$$

Example 13 :

Give chemical reactions involved in the conversion of ethyl chloride to 2-methylbut-3-yn-2-ol.

Solution :

First write down the structure of the required compound, observe the functional group(s) and recall that how these can be introduced. In the present case, the required compound has a 3° alcohol and an acetylenic linkage ; so first introduce acetylenic linkage, convert it to Grignard reagent and then treat it with ketone (acetone) to get 3° alcohol.

$$CH_3CH_2Cl \xrightarrow{alc.\ KOH} CH_2 = CH_2 \xrightarrow{Br_2} BrCH_2{-}CH_2Br \xrightarrow{2NaNH_2} CH \equiv CH$$

$$\xrightarrow{CH_3MgBr} CH \equiv CMgBr \xrightarrow{CH_3COCH_3} CH_3{-}\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}C \equiv CH$$

Example 14 :

You are given acetophenone and methyl iodide as the main organic compounds, how will you convert these into 2-phenyl-2-methylethanol.

Solution :

$$CH_3I \xrightarrow[(ii)\ C_6H_5COCH_3]{(i)\ Mg} C_6H_5\overset{\overset{OH}{|}}{C}(CH_3)_2 \xrightarrow{H_2SO_4} C_6H_5\overset{\overset{CH_3}{|}}{C} = CH_2 \xrightarrow[(ii)\ H_2O_2/OH^-]{(i)\ BH_3/THF} C_6H_5\overset{\overset{CH_3}{|}}{C}H.CH_2OH$$

Example 15 :

Propane can be converted into 1-propanol, 2-propanol and propen-2-ol without using any other organic compound? Illustrate it.

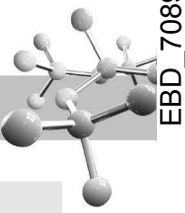
Solution :

$$CH_3CH_2CH_3 \xrightarrow{Cl_2,\ h\nu} CH_3CHClCH_3 \xrightarrow{aq,\ KOH} \underset{\text{2–Propanol}}{CH_3CHOHCH_3}$$

$$CH_3CHClCH_3 \xrightarrow[KOH]{alc.} CH_3CH = CH_2 \xrightarrow[(ii)\ H_2O_2/OH^-]{(i)\ BH_3.THF} \underset{\text{1–Propanol}}{CH_3CH_2CH_2OH}$$

$$\downarrow NBS$$

$$BrCH_2CH = CH_2 \xrightarrow[KOH]{aq.} \underset{\text{Propen-2-ol}}{HOCH_2CH = CH_2}$$



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Example 16 :

How will you prepare 2, 3-dimethyl-2-butanol from isopropanol as the only available organic compound ?

Solution :

Let us draw structure of the required compound, $CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\overset{|}{CH_3}}{CH}-CH_3$

Since it is has six carbon atoms and it is a tertiary alcohol, it can be easily prepared through Grignard reagent route.

$$(CH_3)_2CHOH \xrightarrow{MnO_4^-/H^+} \text{(oxidation)}$$

$$(CH_3)_2CHOH \xrightarrow[(ii)\ Mg]{(i)\ PBr_3} (CH_3)_2CHMgBr \xrightarrow{(CH_3)_2CO} (CH_3)_2\overset{\overset{OH}{|}}{C}-\overset{\overset{CH_3}{|}}{C}HCH_3$$

Example 17 :

You are given methanol and allyl chloride as the main compounds, how these two can be converted into butanol-1 by using inorganic reagents ?

Solution :

$$CH_3OH \xrightarrow{P \text{ and } I_2} CH_3I \xrightarrow[(ii)\ 2CuI]{(i)\ Li} (CH_3)_2CuLi \xrightarrow{ClCH_2CH=CH_2} CH_3CH_2CH=CH_2$$

$$\xrightarrow[(ii)\ H_2O_2/OH^-]{(i)\ BH_3.THF} CH_3CH_2CH_2CH_2OH$$

Example 18 :

Is it possible to carry out the following transformation in quantitative yield ?

$$CH_3CH_2\underset{\overset{|}{CH_3}}{CH}CH_2OH \longrightarrow CH_3CH_2\underset{\overset{|}{CH_3}}{C}=CH_2$$

Solution :

Note that the above dehydration can't be achieved by treating the alcohol with conc. H_2SO_4 since it will lead to the more stable (more substituted) alkene as major product.

$$CH_3CH_2\underset{\overset{|}{CH_3}}{CH}CH_2OH \xrightarrow{H^+} CH_3CH_2\underset{\overset{|}{CH_3}}{\overset{+}{C}}HCH_2 \xrightarrow{\text{1, 2-hydride shift}} CH_3CH_2\underset{\overset{|}{CH_3}}{\overset{\oplus}{C}}CH_3$$

$$\xrightarrow{-H^+} \underset{\text{2-Methyl-2-butene}}{CH_3CH=\overset{\overset{CH_3}{|}}{C}-CH_3} + \underset{\text{2-Methyl-1-butene}}{CH_3CH_2\overset{\overset{CH_3}{|}}{C}=CH_2}$$

(Major) (Minor)

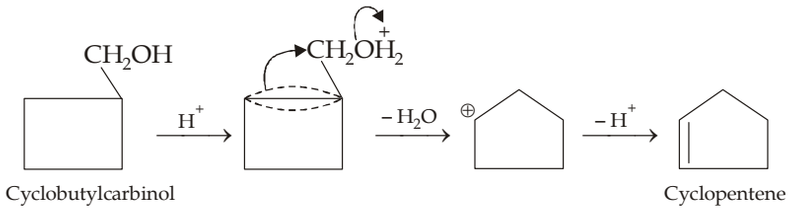
Hence the required alkene is prepared by dehydrohalogenation route.

$$CH_3CH_2\underset{\overset{|}{CH_3}}{CH}CH_2OH \xrightarrow{PBr_3} CH_3CH_2\underset{\overset{|}{CH_3}}{CH}CH_2Br \xrightarrow{\text{alc. KOH}} \underset{\text{2-Methyl-1-butene}}{CH_3CH_2\overset{\overset{CH_3}{|}}{C}=CH_2}$$

Example 19 :

Give the product and write a mechanism for the acid dehydration of cyclobutylcarbinol.

Solution :

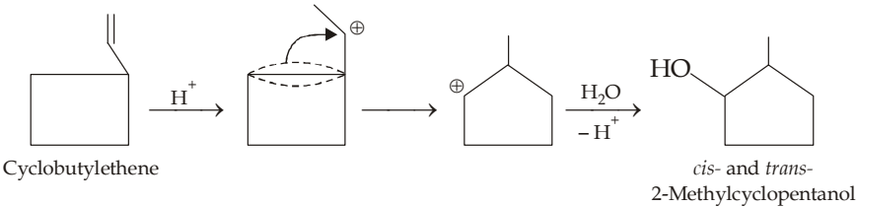


Expansion of four to a five-membered ring relieves ring strain.

Example 20 :

Give the step involved in the hydration of cyclobutylethene in dilute sulphuric acid to 2-methyl cyclopentanol.

Solution :



Example 21 :

An organic compound A ($C_9H_{12}O$) gives a positive iodoform test. On vigorous oxidation, it gives benzoic acid. Identify the compound and give its various isomers which on oxidation gives benzoic acid.

Solution :

Since the compound and its isomers on oxidation gives benzoic acid, these must be monosubstituted benzene. Further, the compound (A) undergoes haloform reaction, it must have —$CHOHCH_3$ or —$COCH_3$ grouping. Thus compound A is $C_6H_5CH_2CHOHCH_3$; $C_6H_5CH_2COCH_3$ is not possible because its molecular formula is $C_9H_{10}O$. Other possible isomers are II, III and IV.

$C_6H_5CH_2CHOHCH_3$	$C_6H_5CHOHCH_2CH_3$	$C_6H_5CH_2CH_2CH_2OH$	$C_6H_5\underset{\displaystyle CH_3}{\underset{\vert}{C}}H.CH_2OH$
A	II	III	IV

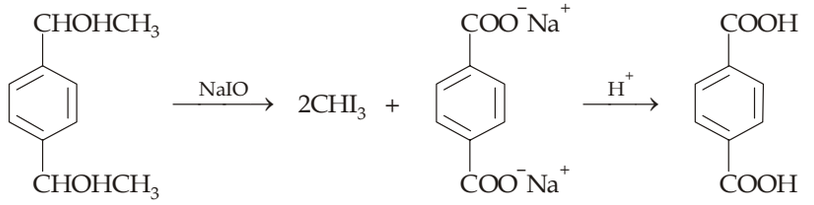
Example 22 :

An aromatic alcohol of the formula $C_{10}H_{14}O_2$ when heated with sodium hypoiodite forms two moles of iodoform per mole of the alcohol, and a dibasic salt which on acidification gives a molecule of terphthalic acid. Identify the compound A.

Solution :

Since the aromatic alcohol undergoes haloform reaction to form two moles of iodoform, it must contain two —$CHOHCH_3$ groupings. Further formation of terphthalic acid indicates that these two groups are present in *p*-position to each other. Hence the alcohol should be *p*-$C_6H_4(CHOHCH_3)_2$.

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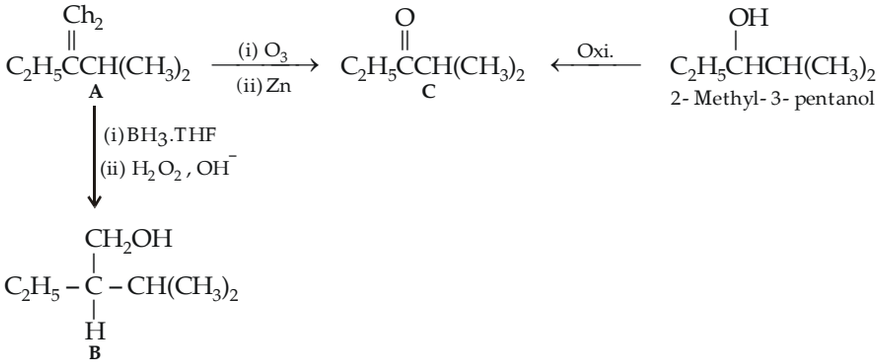


Example 23 :

An alkene A of the formula C_7H_{14} reacts with BH_3.THF followed by H_2O_2/OH^- to give a chiral compound B. Reductive ozonolysis of A gives compound C, which is also obtained by oxidation of 2-methyl-3-pentanol with $KMnO_4$. Identify the alkene A and explain all reactions.

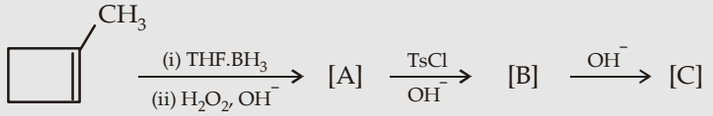
Solution :

Going backward, we can easily solve the problem.

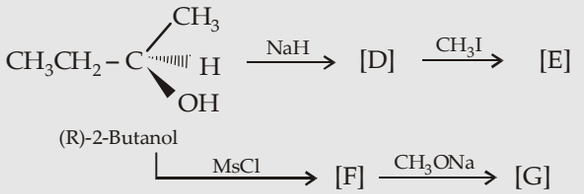


Example 24 :

Give the stereochemical formulas for each of the bracketed compound ,

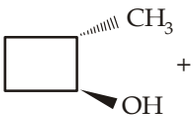
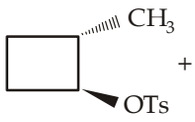
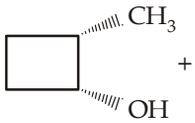
(a) 

What is the stereoisomeric relationship between A and C?

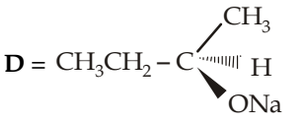
(b) 

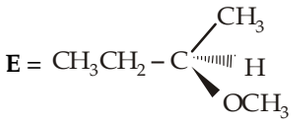
What is the stereoisomeric relationship between [E] and [G] ?

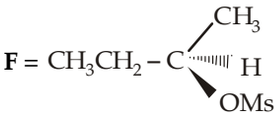
Solution :

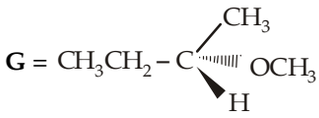
(a) **A** =  + enantiomer **B** =  + enantiomer **C** =  + enantiomer

A and **C** are diastereomers

(b) **D** = 

E = 

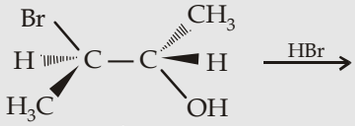
F = 

G = 

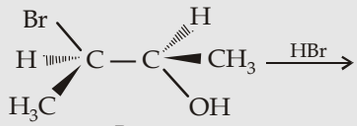
E and **G** are enantiomers.

Example 25 :

Give the product when the two isomeric 3-bromo-2-butanols A and B are treated with HBr. Explain the formation of products by proper mechanism.

(a) 

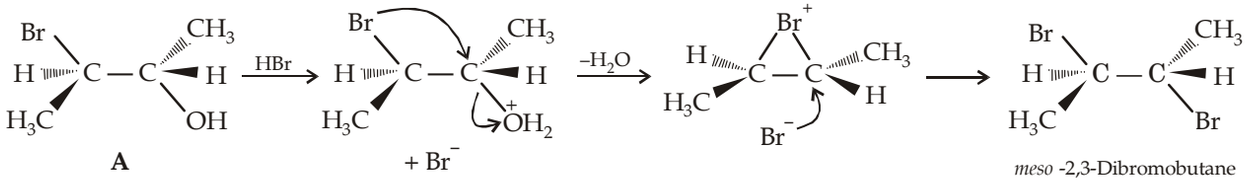
A

(b) 

B

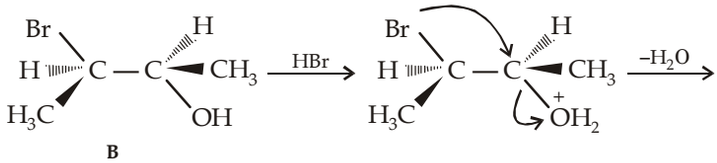
Solution :

The reactions proceed through the formation of bromonium ions identical to those formed in the bromination of *trans*- and *cis*-2-butenes.

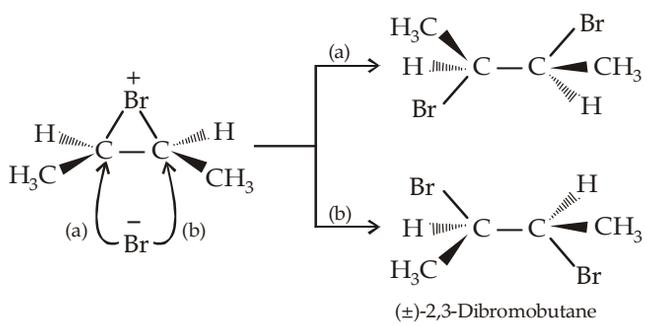
(a) 

A + Br^- *meso* -2,3-Dibromobutane

(Attack at the other carbon atom of the brominium ion gives the same product).

(b) 

B

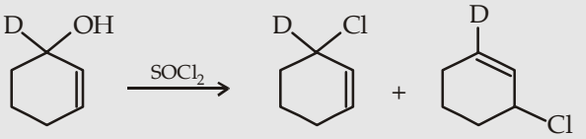


(±)-2,3-Dibromobutane

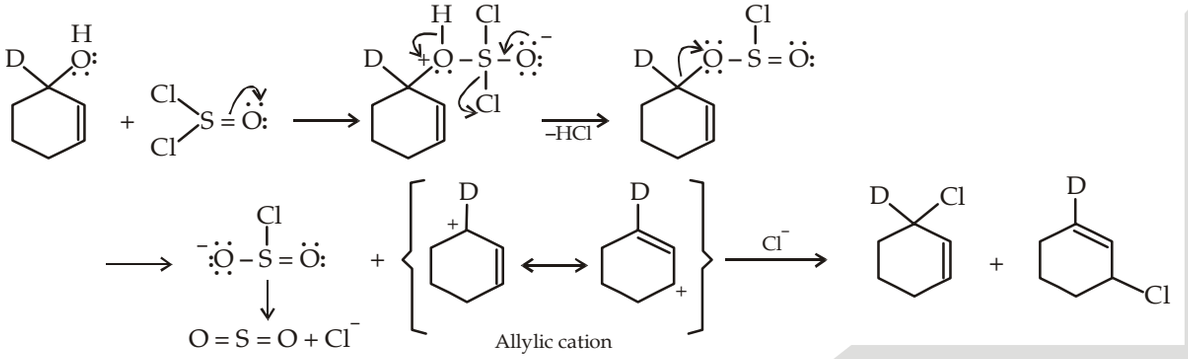
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Example 26 :

Propose a mechanism to explain the formation of two products in the following reaction.

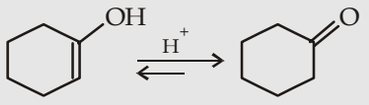


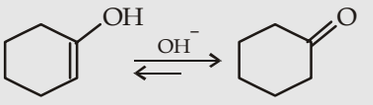
Solution :



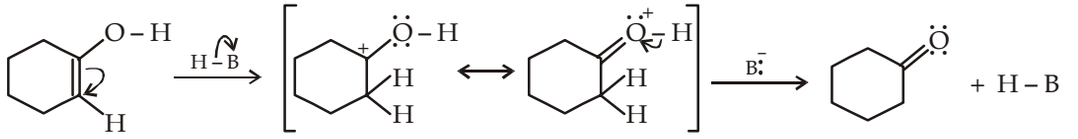
Example 27 :

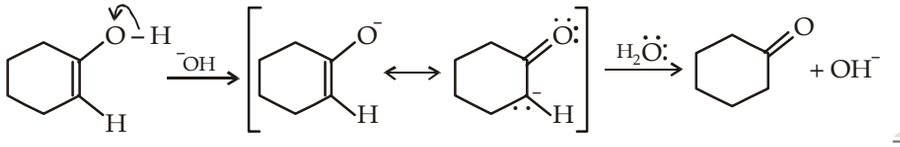
Vinyl alcohols are generally unstable, and quickly isomerize to carbonyl compounds. Propose mechanism for the following isomerizations.

(a) 

(b) 

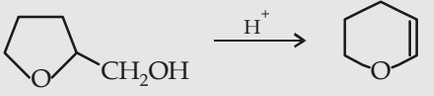
Solution :

(a) 

(b) 

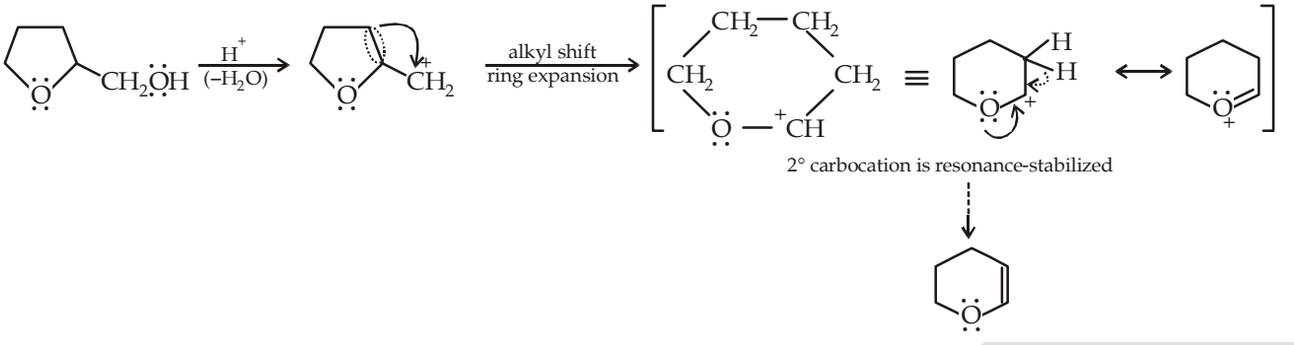
Example 28 :

Propose a mechanism to explain the following unexpected transformation.



Tetrahydrofurfuryl alcohol Dihydropyran

Solution :



Example 29 :

An organic compound A ($C_9H_{12}O$) exhibits following characteristics.

(a) It reacts with metallic sodium to give a colourless odorless gas

(b) It is oxidised by $KMnO_4$ to benzoic acid.

Write all the possible structures for the compound. In addition to the above reactions, the compound A shows following properties.

(c) It can be resolved.

(d) It does not give precipitate with iodine in presence of NaOH.

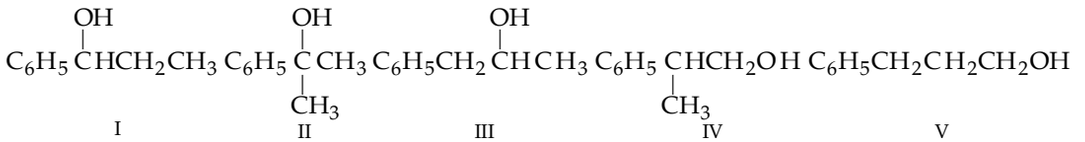
(e) It changes the colour of $Cr_2O_7^{2-}$ from orange to blue, and gives a chiral compound.

Assign structure to compound A.

Solution :

(i) Oxidation to benzoic acid indicates that it is a monosubstituted benzene derivative.

(ii) Its reaction with Na indicates the presence of an alcoholic group. The possible structures for the compound **A** can be

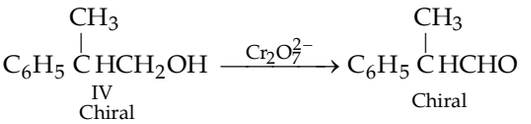


(iii) Since the compound can be resolved, it can't be V.

(iv) The compound does not respond haloform reaction (*d*), it can't be III.

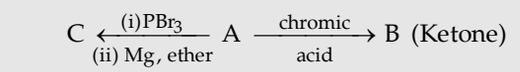
(v) Its oxidation with $Cr_2O_7^{2-}$ indicates that it is either a 1° or a 2° alcohol, hence possibility for the structure II is discarded.

(vi) Its oxidation product with $Cr_2O_7^{2-}$ is found to be a chiral compound, so structure I is discarded and hence the compound **A** has structure IV.



Example 30 :

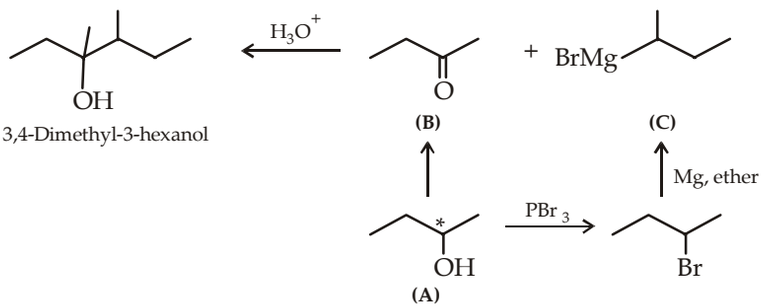
An optically active 2° alcohol A undergoes two different reactions to form compounds B and C.



Compound B is added to the solution of compound C and the resulting solution on acidic hydrolysis gives a compound, identified as 3,4-dimethyl-3-hexanol. Identify compounds A, B and C.

Solution :

Proceed backward, by first writing the structure of the final product.



EBD_7089

EXERCISE 11.1 (MCQ - ONE option correct)

1. According to carbinol system, $C_6H_5CH_2CH_2CH_2OH$ is
(*a*) benzyl carbinol (*b*) β-phenylethylcarbinol
(*c*) benzylmethylcarbinol (*d*) γ-phenylpropylcarbinol.

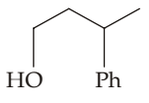
2. Common name for $CH \equiv C.CH_2OH$ is
(*a*) allylcarbinol (*b*) allyl alcohol
(*c*) propargyl alcohol (*d*) none of the three.

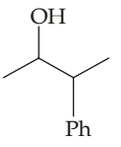
3. Which of the following alcohol is known as rubbing alcohol ?
(*a*) CH_3OH (*b*) C_2H_5OH
(*c*) $CH_3CH_2CH_2OH$ (*d*) $(CH_3)_2CHOH$.

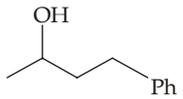
4. When 20 ml of ethanol is mixed with 10 ml of water, the total volume of the solution will be
(*a*) 30 ml (*b*) > 30 ml
(*c*) < 30 ml (*d*) not definite.

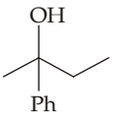
5. The correct order of boiling points of the following alcohols is 1-pentanol (A), 2-methyl-2-butanol (B), 3-methyl-2-butanol(C)
(*a*) A > B > C (*b*) A > C > B
(*c*) C > B > A (*d*) B > C > A.

6. Predict the nature of P in the following hydration reaction of alkenes

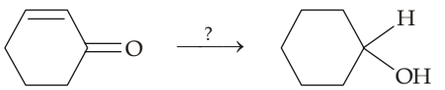
(*a*) 

(*b*) 

(*c*) 

(*d*) 

7. Predict the nature of reducing agent in the following reaction.



(*a*) $LiAlH_4$ (*b*) $NaBH_4$
(*c*) H_2/Pt (*d*) Both (*a*) and (*c*)

8. In the following reaction, alkene A is

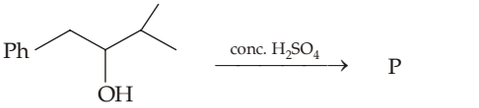
$$A \xrightarrow{\text{cold conc. } H_2SO_4} \text{Intermediate} \xrightarrow{H^+/H_2O} \underset{CH_3CHOHCH_2CH_3}{rac}$$

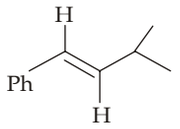
(*a*) *cis*-2-Butene (*b*) *trans*-2-Butene
(*c*) Butene-1 (*d*) All the three.

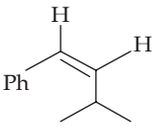
9. Which of the following is the best leaving group toward nucleophilic substitution ?
(*a*) Iodide (*b*) Mesyl
(*c*) Tosyl (*d*) Trifyl.

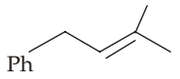
10. Lucas test is useful only for
(*a*) alcohols having at the maximum four carbon atoms
(*b*) alcohols having six or less carbon atoms
(*c*) alcohols having twenty or less carbon atoms
(*d*) all alcohols.

11. Identify the main product P in the following reaction



(*a*) 

(*b*) 

(*c*) 

(*d*) All are formed in equal amounts.

12. Dehydration of 3, 3-dimethylbutanol-2 gives
(*a*) 3, 3-dimethylbutene-1
(*b*) 2, 3-dimethylbutene -1
(*c*) 2, 3-dimethylbutene-2
(*d*) Being 3° alcohol, dehydration is not possible.

13. $CH_3CH = CHCHOHCH_3 \xrightarrow[\text{aq. acetone}]{H_2CrO_4 \text{ in}} X$; here X is
(*a*) $CH_3COOH + COOH.CO.CH_3$
(*b*) $CH_3CHOH.CHOH.CHOH.CH_3$
(*c*) $CH_3CH = CH.COCH_3$
(*d*) $CH_3CHOH.CHOH.CO.CH_3$.

14. Identify the reagent in the following reaction

$$(CH_3)_3CCH_2OH \xrightarrow{\text{reagent}} (CH_3)_3CCH_2Cl$$

(*a*) conc. HCl (*b*) HCl in presence of $ZnCl_2$
(*c*) $SOCl_2$ (*d*) Either of the three.

15. Dehydration of 1-phenyl-2-propanol in acidic medium gives 1-phenyl-1-propene rather than 1-phenyl-2-propene because
(*a*) 1-Phenyl-1-propene is more substituted alkene than 1-phenyl-2-propene
(*b*) In 1-phenyl-1-propene, the double bond is conjugated with the ring
(*c*) Both the above statements are true
(*d*) None of the above statement is true and both alkenes are formed nearly in equal amounts.

16. Identify C in the following series of reactions.

$$CH_3CH = CHCHO \xrightarrow{NaBH_4} [A] \xrightarrow{HCl/ZnCl_2} [B] \xrightarrow{HCN, H^+} [C]$$

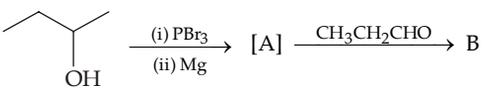
(*a*) $CH_3CH_2CH_2CH_2CN$ (*b*) $CH_3CH_2CH_2CH_2COOH$
(*c*) $CH_3CH = CHCH_2CN$ (*d*) $CH_3CH = CHCH_2COOH$.

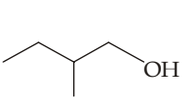
17. Identify [A] and [E] in the following series of reactions.

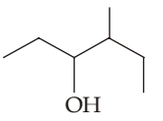
$$[A] \xrightarrow{PBr_5} CH_3CH_2CH_2Br \xrightarrow{\text{alc. KOH}} [B] \xrightarrow{Br_2} [C] \xrightarrow[\text{(ii) } NaNH_2]{\text{(i) alc. KOH}} [D] \xrightarrow{Hg^{2+}, H_2SO_4} [E]$$

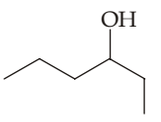
(*a*) $CH_3CH_2CH_2OH$, CH_3CH_2CHO
(*b*) $CH_3CH_2CH_2OH$, $CH_3CH_2CH_2CHO$
(*c*) $CH_3CH_2CH_2OH$, CH_3COCH_3
(*d*) $CH_3CH_2CH_2OH$, $CH_2COCH_2CH_3$.

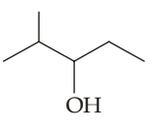
18. The correct structure for the compound B will be



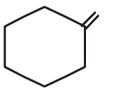
(*a*) 

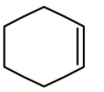
(*b*) 

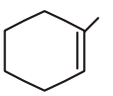
(*c*) 

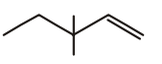
(*d*) 

19. Acid catalysed hydration, hydroboration-oxidation, and oxymercuration-demercuration will give different products in

(a) 

(b) 

(c) 

(d) 

20. During dehydration of t-butanol, which of the following carbocation is more likely to be formed as an intermediate?

(a) $CH_3CH_2CH_2\overset{+}{C}H_2$ (b) $CH_3CH_2\overset{+}{C}HCH_3$

(c) Both (d) None

21. Primary, secondary and tertiary alcohols can be distinguished by the action of

(a) Reduced Cu

(b) Acidic $KMnO_4$

(c) HCl in presence of anhydrous $ZnCl_2$

(d) PCl_5

22. Ethyl alcohol when treated with conc. H_2SO_4 may give

(a) Only diethyl sulphate

(b) Only diethyl ether

(c) Only ethylene

(d) All the three

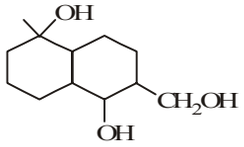
23. 1–Propanol and 2–propanol can be distinguished by

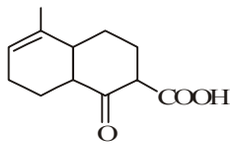
(a) oxidation with alkaline $KMnO_4$ followed by reaction with Fehling solution

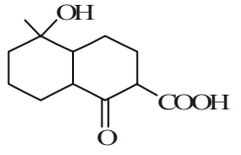
(b) oxidation with acidic dichromate followed by reaction with Fehling solution

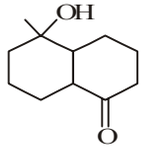
(c) oxidation by heating with copper followed by reaction with Fehling solution

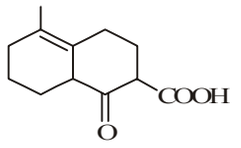
(d) oxidation with concentrated H_2SO_4 followed by reaction with Fehling solution

24.  $\xrightarrow[\Delta]{H^{\oplus}/KMnO_4}$ Product is

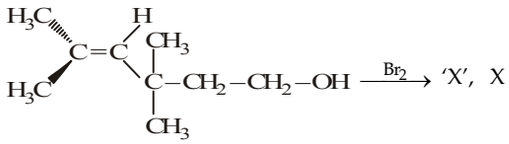
(a) 

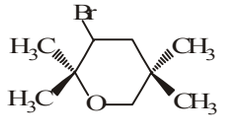
(b) 

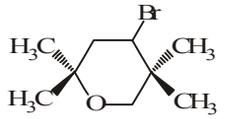
(c) 

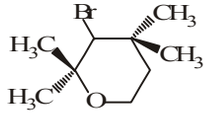
(d) 

25. What will be the product of following reaction ?

 'X', X will be

(a) 

(b) 

(c) 

(d) (a) and (b) both

26. $CH_2=CH-\underset{\displaystyle OH}{\underset{|}{CH}}-CH=CH-CH_3 \xrightarrow{CH_3OH/H^{\oplus}}$

major products is

(a) $CH_3O-CH_2-CH=CH-CH=CH-CH_3$

(b) $CH_2=CH-\underset{\displaystyle OCH_3}{\underset{|}{CH}}-CH=CH-CH_3$

(c) $CH_2=CH-CH=CH-\underset{\displaystyle OCH_3}{\underset{|}{CH}}-CH_3$

(d) $CH_2=CH-CH_2-\underset{\displaystyle OCH_3}{\underset{|}{CH}}-CH=CH_2$

27. $HC\equiv CH \xrightarrow[\text{Fe Tube}]{\text{Red Hot}} P \xrightarrow[(1.\,eq.)]{Br_2/Fe} Q \xrightarrow{Mg/Ether} S$;

$T \xleftarrow[\text{Distill}]{Ca(OH)_2/\Delta} R \xleftarrow{KMnO_4} CH_3CH_2OH$

S and T are mixed and product is hydrolysed and heated in presence of conc. H_2SO_4 and product is ozonolysed then following is obtained.

(a) Acetophenone (b) Benzophenone

(c) Benzaldehyde (d) Acetone

28. $CH_2O \xrightarrow[H_3O^{\oplus}]{CHD_2MgI} X \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} Y$

In the above reaction compound X and Y respectively will be

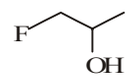
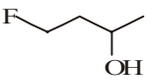
(a) $\underset{\displaystyle OH}{\underset{|}{CHD}}-CH_2-OH,\ CHO-CHO$

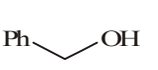
(b) $CHD_2-CH_2-OH, CHO-CHO$

(c) $CHD_2-CH_2-OH, CD_2=CH_2$

(d) $\underset{\displaystyle OH}{\underset{|}{CHD}}-CH_2-OD,\ CD_2=CH_2$

29. The correct order of reactivity of following alcohols towards conc. $HCl/ZnCl_2$ is :

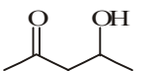
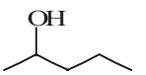
I.  II. 

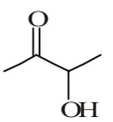
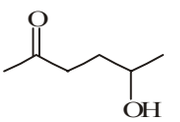
III.  IV. 

(a) I > II > III > IV (b) I > III > II > IV

(c) IV > III > II > I (d) IV > III > I > II

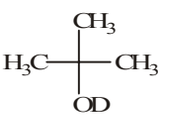
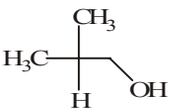
30. Which one of the following will most readily be dehydrated in acidic condition ?

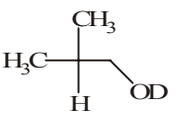
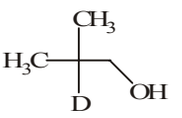
(a)  (b) 

(c)  (d) 

31. The product B in the reaction is

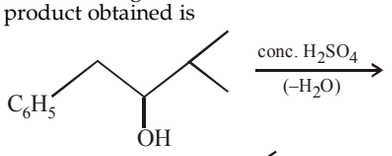
$(CH_3)_3COH \xrightarrow[573K]{Cu} A \xrightarrow[OH^-/D_2O]{B_2H_6} B$

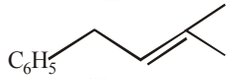
(a)  (b) 

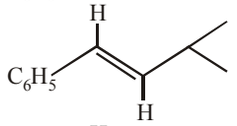
(c)  (d) 

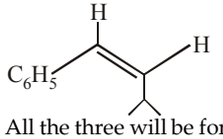
EBD_7089

32. The following alcohol is treated with conc. H_2SO_4, the major product obtained is

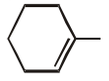


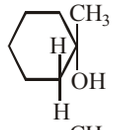
(a) 

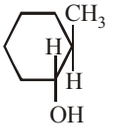
(b) 

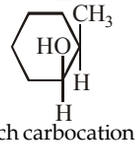
(c) 

(d) All the three will be formed in equal amounts

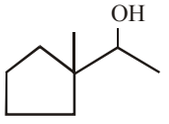
33.  $\xrightarrow[(ii)\ H_2O_2,\ OH^-]{(i)\ B_2H_6}$ X. The compound X is

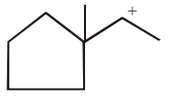
(a) 

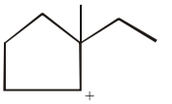
(b) 

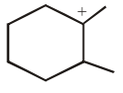
(c) 

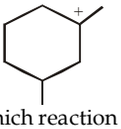
(d) Both (b) and (c)

34. Which carbocation is more likely to be formed in the dehydration of  $\xrightarrow{H^+}$

(a) 

(b) 

(c) 

(d) 

35. Energy of activation is lowest for which reaction ?

(a) $RCH_2\overset{+}{O}H_2 \rightarrow R\overset{+}{C}H_2$ (b) $R_2CH\overset{+}{O}H_2 \rightarrow R_2\overset{+}{C}H$

(c) $R_3C\overset{+}{O}H_2 \rightarrow R_3C^+$ (d) All have same E_{act}

36. Dehydration of an alcohol in presence of sulphuric acid gives alkene

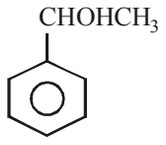
$$CH_3CH_2OH \xrightarrow{H_2SO_4} CH_2 = CH_2 + H_2O$$

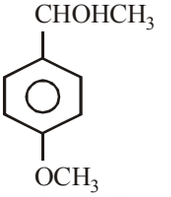
Here sulphuric acid acts as

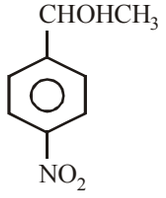
(a) an acid (b) a base

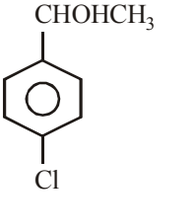
(c) a catalyst (d) all the three

37. Which of the following alcohols is dehydrated most readily with conc. H_2SO_4 ?

(a) 

(b) 

(c) 

(d) 

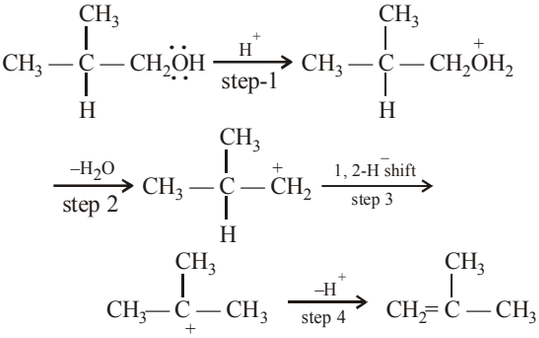
38. $CH_3CH_2OH + HCl \xrightarrow{ZnCl_2} CH_3CH_2Cl + H_2O$

In the above reaction, the leaving group is

(a) OH^- (b) H_2O

(c) $HOZn^-Cl_2$ (d) H_3O^+

39. Dehydration of alcohols by conc. H_2SO_4 takes place according to following steps :



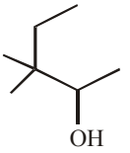
The slowest and fastest steps in the above reaction are

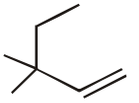
(a) step 1 is slowest, while 3 is fastest

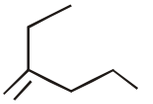
(b) step 2 is slowest, while 3 is fastest

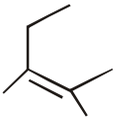
(c) step 2 is slowest, while 4 is fastest

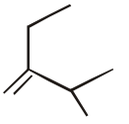
(d) all steps proceed at equal rate

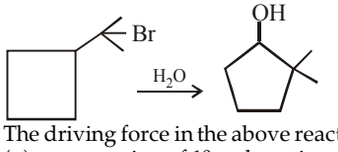
40.  $\xrightarrow{Conc.\ H_2SO_4}$ Major product is

(a) 

(b) 

(c) 

(d) 

41. 

The driving force in the above reaction is

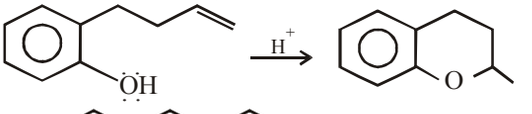
(a) conversion of 1° carbocation to 2° carbocation

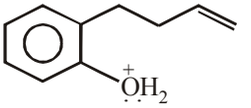
(b) conversion of 1° carbocation to 3° carbocation

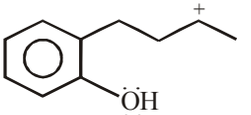
(c) releif in steric strain due to expansion of ring

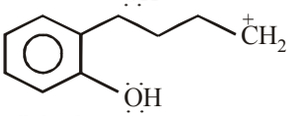
(d) both (a) and (c)

42. Which of the following ion is formed in the following reaction?



(a) 

(b) 

(c) 

(d) All the three

43. Which reacts rapidly with Lucas reagent?

(a) CH_2=$CHCH_2OH$ (b) $(CH_3)_3COH$

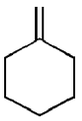
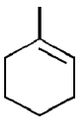
(c) Both (a) and (b) (d) CH_3CH_2OH

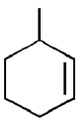
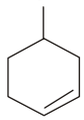
EXERCISE 11.2 (MCQ 1 or >1 option correct, Passage based, Matching, A/R)

DIRECTIONS for Q. 1 to Q. 23 : Multiple choice questions with one or more than one correct option(s).

1. Which of the following statements is false?
(*a*) No aldehyde can be prepared by the oxidation of primary alcohol with acidic $KMnO_4$.
(*b*) Aldehyde having a boiling point less than 100°C can be prepared by the oxidation of primary alcohol with acidic dichromate.
(*c*) Secondary alcohols on oxidation with PCC in dichloromethane give carboxylic acids having lesser number of carbon atoms
(*d*) None of the statement is correct.

2. A $\xrightarrow{\text{dil. } H_2SO_4/Hg^{2+}}$ 1-Methylcyclohexanol. Here A is

(*a*)  (*b*) 

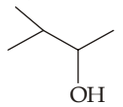
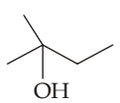
(*c*)  (*d*) 

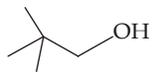
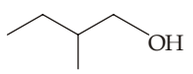
3. 2-Phenylbutanol-2 can be prepared by which of the following combinations ?
(*a*) $C_6H_5COCH_3 + C_2H_5MgBr$
(*b*) $C_2H_5COCH_3 + C_6H_5MgBr$
(*c*) $C_6H_5COC_2H_5 + CH_3MgBr$
(*d*) $C_6H_5COC_6H_5 + C_2H_5MgBr$

4. Which of the alcohol gives a positive iodoform test ?
(*a*) Benzylmethylcarbinol
(*b*) Phenylethylcarbinol
(*c*) Cyclopentylmethylcarbinol
(*d*) Isopropanol.

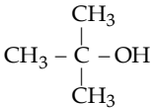
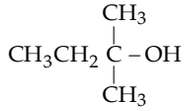
5. $C_6H_5COCH_2CH_2Br + LiAlD_4 \xrightarrow{H_2O}$ X, here X does not have
(*a*) $C_6H_5CD(OD)CH_2CH_2Br$
(*b*) $C_6H_5CD(OH)CH_2CH_2D$
(*c*) $C_6H_5CD(OH)CH_2CH_2Br$
(*d*) $C_6H_5CH(OH)CH_2CH_2D$.

6. Which of the following alcohol will mainly give the rearranged chloride, when treated with HCl?

(*a*)  (*b*) 

(*c*)  (*d*) 

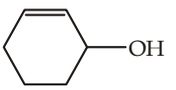
7. On treatment with a concentrated solution of zinc chloride in concentrated HCl at room temperature, an alcohol immediately gives, an oily product. The alcohol can be
(a) $C_6H_5CH_2OH$ (b) $CH_3CHOHCH_3$

(c)  (d) 

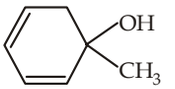
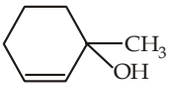
8. Which of the following are correct?
(a) ordinary ethyl alcohol is known as rectified spirit
(b) the alcohol sold in the market for polishing, etc., is known as methylated spirit
(c) absolute alcohol is 100% ethanol
(d) power alcohol is 100% ethanol

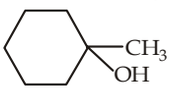
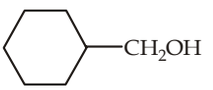
9. $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2 \xrightarrow{\text{reagent R}}$ alcohol

Which is/are true about alcohol and R?
(a) alcohol is $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2OH$ when reagent R is BH_3 / THF – H_2O_2 / OH^-
(b) alcohol is $CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-CH_3$ when reagent R is $Hg(OAc)_2/NaBH_4$ – H_2O
(c) alcohol is $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2-CH_3$ when reagent is H_3O^+
(d) none is correct

10. Chromic anhydride in H_2SO_4 is turned blue by :
(a) 1° alcohol (b) 2° alcohol
(c) 3° alcohol (d) 

11. Which gives turbidity with HBr?

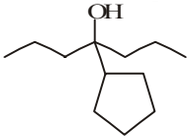
(a)  (b) 

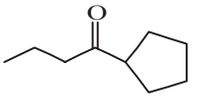
(c)  (d) 

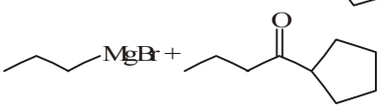
12. Which are correct statements?
(a) Rectified spirit is a binary azeotrope
(b) Denatured spirit contains CH_3OH ($\approx$ 5%)
(c) Ternary azeotrope is obtained when benzene is added to rectified spirit
(d) Pyrolegenous acid contains CH_3OH, CH_3COCH_3 and CH_3COOH

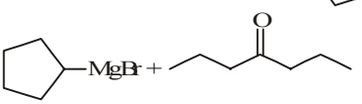
13. Which is/are correct statements?
(a) Oxidation product of 1, 2-ethanediol with HIO_4 is formaldehyde
(b) 1° alcohol turns $K_2Cr_2O_7/H^+$ solution green
(c) t-butyl alcohol is converted to isobutene on heating with Cu
(d) CH_3OH is also called wood spirit

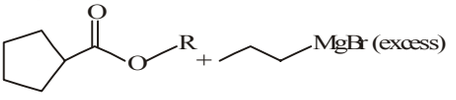
14. Which of the following combination of reactants can be used to prepare the following compound ?



(a) CH_3MgBr (excess) + 

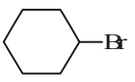
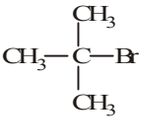
(b) 

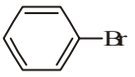
(c) 

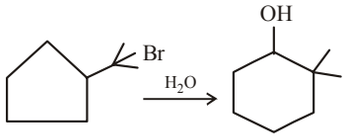
(d) 

EBD_7089

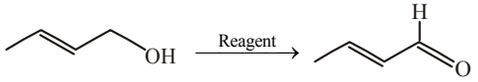
15. The following compounds are reacted with Mg/Ether followed by O_2 and then acidified. Lucas test is not positive with the final product of :

(a)  (b) 

(c)  (d) $CH_2 = CH - Br$

16. 

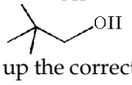
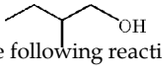
The above reaction involves
(a) Conversion of 2° to 3° carbocation
(b) Conversion of 3° to 2° carbocation
(c) Expansion of ring
(d) Conversion of 3° to the more stable benzylic carbocation

17. 

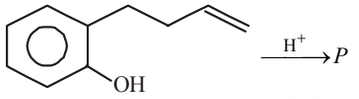
Reagent in the above reaction may be
(a) Collines reagent (b) Tollen's reagent
(c) PCC (d) PDC

18. Which of the following alcohol will mainly give the rearranged chloride, when treated with HCl?

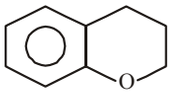
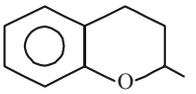
(a)  (b) 

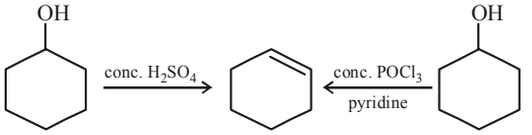
(c)  (d) 

19. Pick up the correct statements in the following reaction

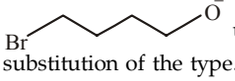


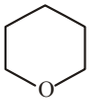
(a) protonation occurs at –OH
(b) protonation occurs at C = C linkage

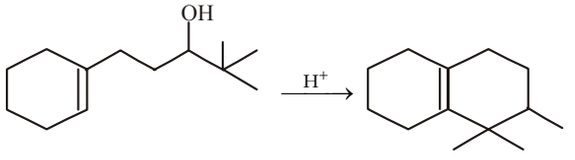
(c) *P* is  (d) *P* is 

20. 

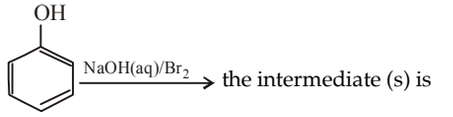
Which of the following statement is true regarding above reaction?
(a) Dehydration by conc. H_2SO_4 is slower than with $POCl_3$
(b) Both involve carbocation as intermediate
(c) Dehydration by $POCl_3$ involves elimination of $-OPOCl_2$ which is a better leaving group.
(d) Elimination of $-OPOCl_2$ and abstraction of proton by pyridine take place simultaneously.

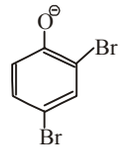
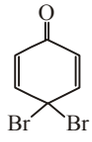
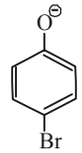
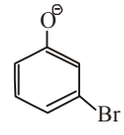
21.  undergoes intramolecular nucleophilic substitution of the type..... giving.....

(a) S_N1 (b) S_N2 (c)  (d) 

22. 

The above transformation involves
(a) protonation at the C = C linkage
(b) protonation at –OH group
(c) formation of 2° carbocation
(d) formation of 3° carbocation

23. In the reaction  the intermediate (s) is (are)

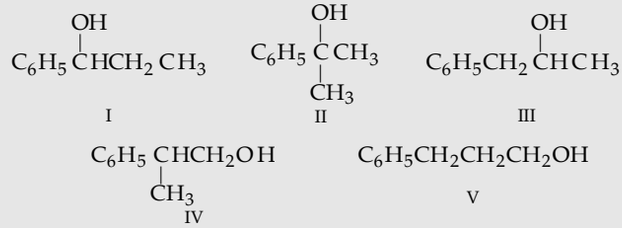
(a)  (b)  (c)  (d) 

DIRECTIONS for Q. 24 to Q. 35 : Read the following passages and answer the questions that follows :

PASSAGE 1

An organic compound **A** ($C_9H_{12}O$) exhibits following characteristics.
(a) It reacts with metallic sodium to give a colourless odorless gas
(b) It is oxidised by $KMnO_4$ to benzoic acid.
(c) It can be resolved.
(d) It does not give precipitate with iodine in presence of NaOH.
(e) It changes the colour of $Cr_2O_7^{2-}$ from orange to blue, and gives a chiral compound.

On the basis of the above reaction & the following 5 structures, answer the following questions :



I II III

IV V

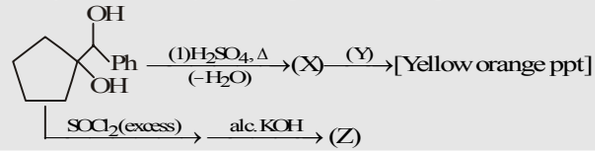
24. Which of the following given characteristics discard the possibility of compound V
(i) (b) (ii) (c) (iii) (d) (iv) (e)
(a) (i) and (ii) (b) (ii) and (iv)
(c) (i), (ii) and (iii) (d) all the four

25. The above characteristics establish the structure of A as
(a) I (b) II (c) III (d) IV

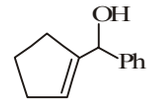
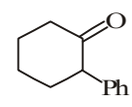
26. The total number of isomeric alcohols to IV would be
(a) 4 (b) 6 (c) 8 (d) 9

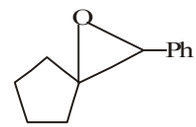
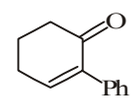
PASSAGE 2

Study the following road map and answer questions 16-18 :



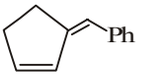
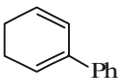
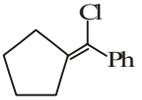
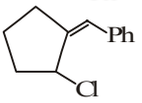
27. The compound (X), (the major product) is

(a)  (b) 

(c)  (d) 

28. The reagent Y can be
(a) Baeyer's reagent
(b) Lucas reagent
(c) I_2/NaOH
(d) 2, 4-Dinitrophenylhydrazine

29. The product Z is :

(a) 
(b) 
(c) 
(d) 

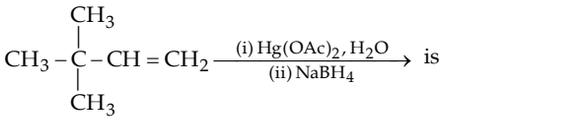
PASSAGE 3

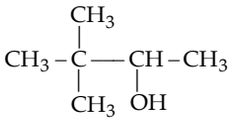
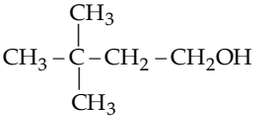
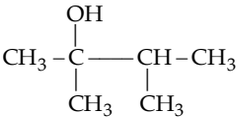
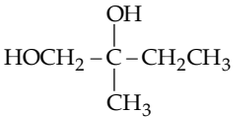
Hydration, hydroboration-oxidation and oxymercuration-demercuration are three important methods for the synthesis of alcohols from alkenes. The overall process in each case corresponds to the addition of elements of water (H^+, OH^-) to the alkenes. Whereas both hydration and oxymercuration-demercuration produce alcohols corresponding to Markovnikov's addition of water, hydroboration-oxidation produces alcohols corresponding to anti-Markovnikov's addition of water to the alkene with the only difference that hydration occurs through carbocation intermediate and thus often produces unexpected alcohols having rearranged carbon skeleton. In contrast, hydroboration-oxidation does not involve carbocation intermediate and produces only expected alcohols.

30. Hydration of 3-phenylbut--1-ene with dil. H_2SO_4 mainly gives
(a) 3-Phenylbutan-1-ol (b) 3-Phenylbutan-2-ol
(c) 2-Phenylbutan-1-ol (d) 2-Phenylbutan-2-ol

31. 2-Methylpropene upon hydroboration-oxidation gives
(a) 2-Methyl-1-propanol (b) 2-Methyl-2-propanol
(c) 2-propanol (d) 1-propanol

32. The product of the following reaction,



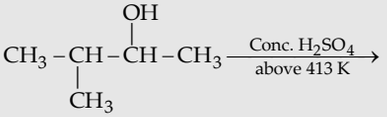
(a)  (b) 
(c)  (d) 

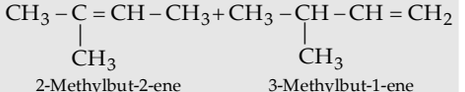
PASSAGE 4

Secondary and tertiary alcohols always give E1 reactions in dehydraton. Primary alcohols whose β-carbon is 3° or 4° also give E1 reactions. However, the primary alcohols whose β-carbon is 1° or 2° give E2 reactions. Dehydrating agents like conc. H_2SO_4, Al_2O_3, anhydrous $ZnCl_2$ are used.
The reactivity of alcohols for elimination reaction lies in following sequence :

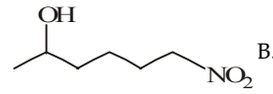
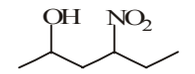
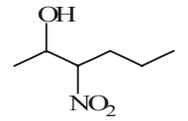
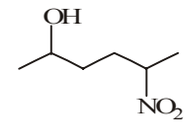
Tertiary alcohol > secondary alcohol > primary alcohol

Electron attracting groups present in alcohols increase the reactivity for dehydration. Greater is the –I effect of the group present in alcohol, more will be its reactivity. Both E1 and E2 mechanism give the product according to Saytzeff's rule, i.e., major product is the most substituted alkene.


1-Methylbutan-2-ol

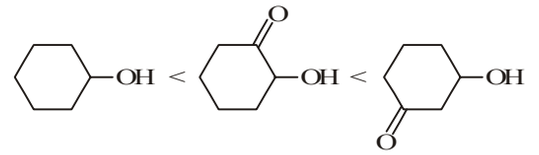

2-Methylbut-2-ene (Major product) 3-Methylbut-1-ene (Minor product)

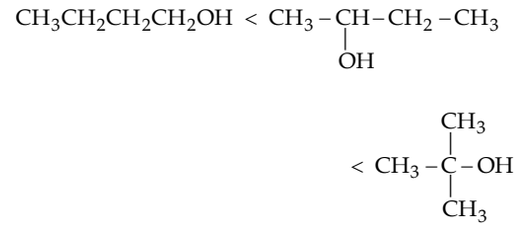
33. Arrange the reactivity of given four alcohols in decreasing order for dehydration.

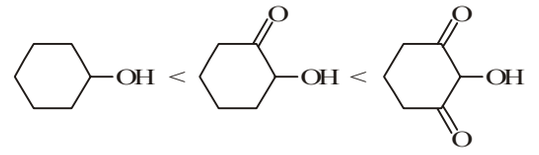
A.  B. 
C.  D. 

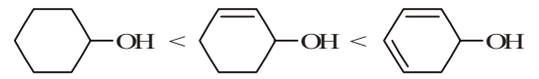
(a) A > B > C > D (b) D > C > B > A
(c) C > B > D > A (d) B > C > A > D

34. Which among the following sequences of reactivity for dehydration is incorrect ?

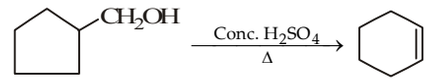
(a) 

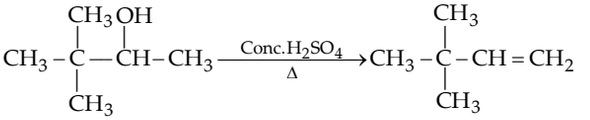
(b) 

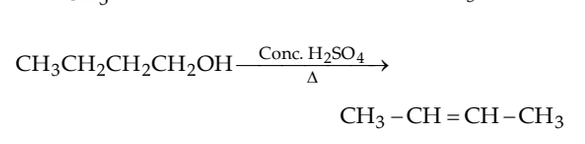
(c) 

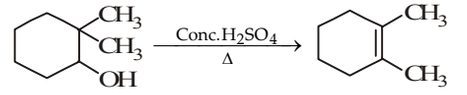
(d) 

35. Which of the following dehydration products is incorrect ?

(a) 

(b) 

(c) 

(d) 

DIRECTIONS for Q. 36 to Q. 40 : The following questions are matching type questions. Match Column I with Column II

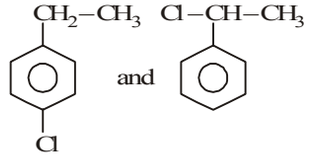
36.

Column I		*Column II*
(A)	Fuel	(a) Alkenes
(B)	Lewis acid	(b) Ammonical silver nitrate
(C)	Tollen's reagent	(c) Anhydrous $AlCl_3$
(D)	Yeast	(d) Ethanol

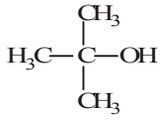
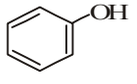
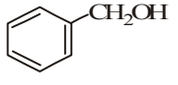
37. *Column I* *Column II*

(A)	Acid-catalysed hydration of alkenes	(a)	Markovnikov hydration
(B)	Oxymercuration-demercuration of alkenes	(b)	*anti*-Markovnikov hydration
(C)	Hydroboration-oxidation of alkenes	(c)	Stereoselective
(D)	Dehydration of alcohols to alkenes	(d)	Regioselective

38. Match the column :

Column-I (Compounds)	**Column-II (Can be differentiated by)**
A. $CH_3-\underset{\displaystyle OH}{\underset{\vert}{CH}}-CH_3$ and $CH_3-CH_2-CH_2-OH$	(p) Lucas reagent
B. $CH_2=CH-CH_2-OH$ and $CH_3-\underset{\displaystyle OH}{\underset{\vert}{\overset{\displaystyle CH_3}{\overset{\vert}{C}}}}-CH_3$	(q) Victor Meyer test
C. 	(r) Iodoform test
	(s) Aqueous $AgNO_3$

39. Match the following column :

Column-I	**Column-II**
A. CH_3-CH_2-OH	(p) No response to Victor Meyer's reagent
B. 	(q) Turbidity immediately when treated with Lucas reagent
C. 	(r) No response to Lucas reagent
D. 	(s) Red colour in Victor Meyer's test
	(t) Gives test with dil. $AgNO_3$

40.

Column-I	**Column-II**
A. Allyl alcohol	(p) Gives ppt with Lucas reagent immediately
B. Benzyl alcohol	(q) Reaction with sodium vigorously
C. Ter-butyl alcohol	(r) Reacts with sodium slowly
D. Ethyl alcohol	(s) Does not give precipitate with Lucas reagent at room temperature

Instructions for Q. 41 to 44 : Following questions are Assertion and Reasoning Type Questions :

Note : Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 5 choices (a), (b), (c), (d) and (e) out of which ONLY ONE is correct.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.

(c) Statement -1 is True, Statement-2 is False.

(d) Statement -1 is False, Statement-2 is True.

(e) Statement -1 is False, Statement-2 is False.

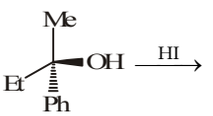
41. **Statement 1 :** Alcoholic fermentation involves conversion of sugar into ethyl alcohol by yeast.
Statement 2 : Fermentation involves the slow decomposition of complex organic molecules.

42. **Statement 1 :** Acid catalysed dehydration of *t*-butanol is slower than *n*-butanol.
Statement 2 : Dehydration involves formation of the protonated alcohol, ROH_2^+.

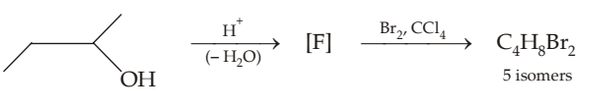
43. **Statement 1 :** The ease of dehydration of alcohols follows the order : Primary > Secondary > Tertiary.
Statement 2 : Dehydration proceeds through the formation of oxonium ions.

44. **Statement-1 :** Solubility of *n*-alcohols in water decreases with increase in its relative molar mass.
Statement-2 : The relative proportion of the hydrocarbon part in alcohols increases with increasing molar mass, which premits enhanced hydrogen bonding with water.

Instructions for Q. 45 to 46 : Following questions are Integer Type Questions :

45. 

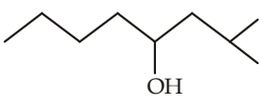
How many iodides are produced in more than 5% yield ?

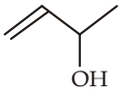
46. 

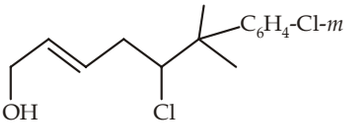
How many structures are possible for F ?

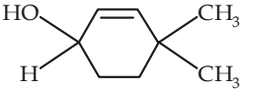
EXERCISE 11.3 (Subjective Problems)

1. Give IUPAC name of the following compounds.

(*a*) 

(*b*) 

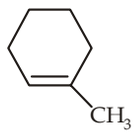
(*c*) 

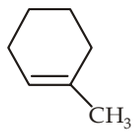
(*d*) 

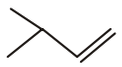
2. Write the structures and names of all isomeric cyclic alcohols of the formula C_4H_7OH. Indicate which one of the isomer is (are) chiral.

3. Arrange the following compounds in order of decreasing boiling point.
3-Hexanol, *n*-hexane, 2-methyl-2-pentanol, *n*-octyl alcohol and *n*-hexyl alcohol.

4. Predict the structure of the alcohol formed in each of the following cases.

(*a*)  $\xrightarrow[(ii)\ H_2O_2/OH^-]{(i)\ B_2H_6}$ [A]

(*b*)  $\xrightarrow[(ii)\ NaBH_4\ /\ OH^-]{(i)\ Hg(OAc)_2,\ H_2O}$ [B]

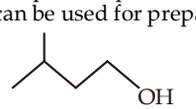
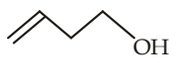
(*c*)  $\xrightarrow{\text{dil. } H_2SO_4}$ [C]

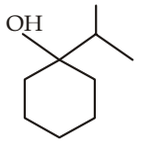
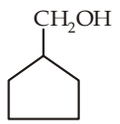
(*d*)  $\xrightarrow[(ii)\ NaBH_4/OH^-]{(i)\ Hg(OAc)_2,\ H_2O}$ [D]

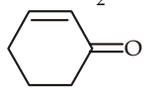
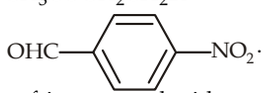
5. Explain the following :
(*a*) Reaction of *tert*-butyl chloride with OH^- gives no *tert*-butyl alcohol, while reaction with H_2O in dioxane gives appreciable amount of *tert*-butanol.
(*b*) Methanol and ethanol are reasonably good solvents for many ionic substances.
(*c*) Cyclohexanol is more soluble in water than 1-hexanol.
(*d*) Acid catalysed dehydration of *tert*-butanol is faster than that of *n*-butanol.

6. Give the synthesis of each of the following alcohols from an alkene with the same number of carbon atoms.
(*a*) 2-Butanol (*b*) Isobutanol
(*c*) Cyclopentylcarbinol (*d*) 2-methyl-2-butanol.

7. Give the possible pairs of Grignard reagent and other component that can be used for preparing following alcohols.

(*a*)  (*b*) 

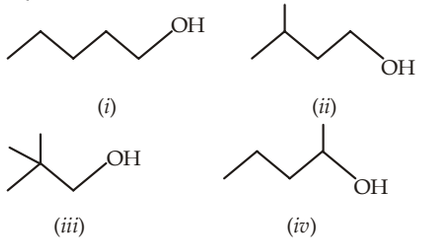
(*c*)  (*d*) 

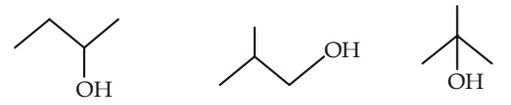
8. Give the expected product obtained by reducing following compounds with $LiAlH_4$.
(*a*) $CHO.CH_2COOCH_3$ (*b*) $CH_3COCH_2CH_2Br$
(c)  (*d*) 

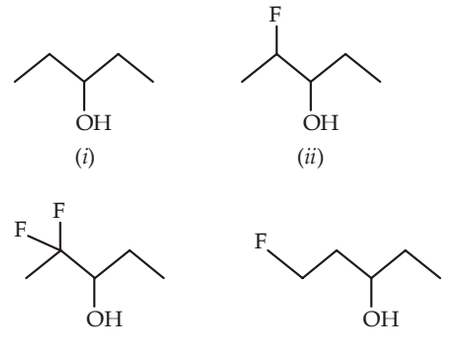
9. Give the products for the reaction of isopropanol with conc. H_2SO_4 at
(*a*) 0°C, (*b*) room temperature, (c) 130°C, and (*d*) 180°C.

10. How does the Lewis theory of acids and bases explain the functions of
(*a*) $ZnCl_2$ in the Lucas reagent, and
(*b*) ether as solvent in the Grignard reagent.

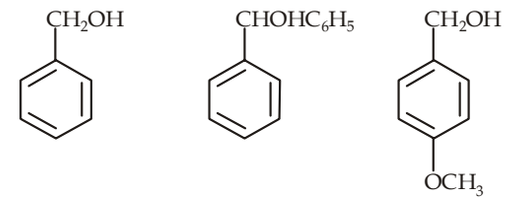
11. Arrange the following alcohols in order of their decreasing reactivity with HBr.

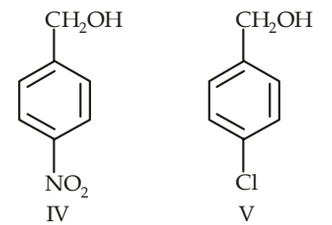
(*a*) 
(*i*) (*ii*) (*iii*) (*iv*)

(*b*) 
(*i*) (*ii*) (*iii*)

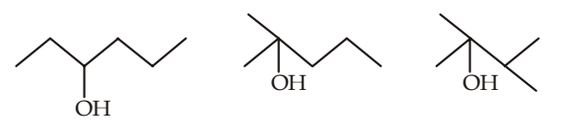
(*c*) 
(*i*) (*ii*) (*iii*) (*iv*)

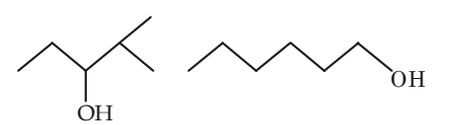
12. Arrange the following benzyl alcohols in order of their decreasing reactivity with HBr.


I II III


IV V

13. Arrange the following alcohols in decreasing order of dehydration with sulphuric acid.


I II III


IV V

14. Give structures and names of the main product expected from the reaction (if any) of isopropyl alcohol with
(*a*) C_2H_5MgBr (*b*) *aq*. NaOH
(*c*) cold. dil. $KMnO_4$
(*d*) CrO_3, H_2SO_4 (*e*) tosyl chloride, OH^-.

15. Give necessary steps involved in the conversions of
(*a*) 1- butanol to *n*-butane-1-deuterium
(*b*) 1-Butanol to *n*-butyraldehyde
(*c*) 1-Butanol to *n*-octane
(*d*) 2-Methyl-2-propanol to isobutane.

16. 3, 3-Dimethylbutan-2-ol loses a molecule of water in the presence of a concentrated sulphuric acid to give tetramethylethylene as a major product. Suggest a suitable mechanism.

EBD_7089

SOLUTIONS

EXERCISE 11.1

6	(d)	**11**	(a)	**16**	(d)	**21**	(d)	**26**	(a)	**31**	(c)	**36**	(d)	**41**	(c)
7	(c)	**12**	(c)	**17**	(c)	**22**	(d)	**27**	(a)	**32**	(b)	**37**	(b)	**42**	(b)
8	(d)	**13**	(c)	**18**	(b)	**23**	(c)	**28**	(c)	**33**	(b)	**38**	(c)	**43**	(c)
9	(d)	**14**	(c)	**19**	(d)	**24**	(c)	**29**	(c)	**34**	(c)	**39**	(c)		
10	(b)	**15**	(c)	**20**	(b)	**25**	(c)	**30**	(a)	**35**	(c)	**40**	(c)		

1. (*a*) Carbinol is CH_3OH, hence for $C_6H_5\overset{\beta}{C}H_2\overset{\alpha}{C}H_2CH_2OH$ option (*b*) is correct.

2. $CH \equiv C—CH_2—$ is propargyl group.

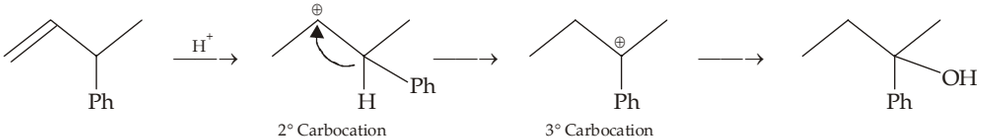
3. Isopropanol is used for rubdowns and its evaporation reduces fevers ; it is cheaper than ethanol hence replaced ethanol for this purpose.

4. Hydrogen bonding between ethanol and water permits the two unlike molecules to move close together in the solution than can ethanol to ethanol and water to water molecules.

5. *n*-$C_4H_9CH_2OH$ **(A)** ; $CH_3—\underset{\displaystyle OH}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}—CH_2CH_3$ **(B)** ; $CH_3—\underset{\displaystyle OH}{CH}—\underset{\displaystyle CH_3}{C}—CH_3$ **(C)**

With the increase in branching, the shape of the molecule becomes more compact and spherical ; hence less surface contact is available for van der Waals forces.

6.



2° Carbocation 3° Carbocation

7. Catalytic hydrogenation reduces double bond as well as carbonyl group.

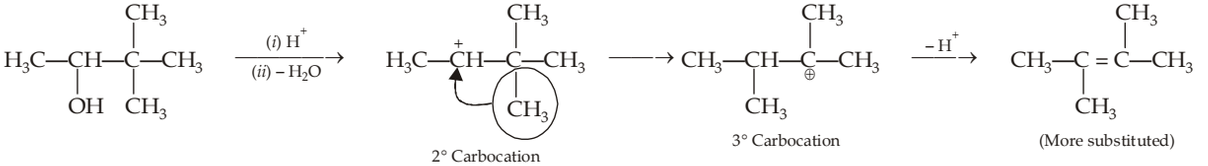
8. $\underset{\text{cis-or trans-Butene-2}}{CH_3CH=CHCH_3}$ or $\underset{\text{Butene-1}}{CH_3CH_2CH=CH_2} \xrightarrow{\text{Cold, Conc } H_2SO_4} CH_3CH_2\underset{\displaystyle OSO_3H}{\underset{|}{C}}HCH_3 \longrightarrow \underset{\text{rac–}}{CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3}$

9. Weaker a base better is the leaving group. Triflate (trifluoromethanesulphonate, $F_3CSO_2O^-$) anion is an extremely weak base because it has three powerful electron-withdrawing fluorine atoms which help to stabilize the triflate anion $F_3CSO_2O^-$ and thus make the parent acid F_3CSO_2OH (triflic acid) one of the strongest known Lowry-Bronsted acids, much stronger than H_2SO_4 or $HClO_4$.

10. For Lucas test, initially the alcohol must be soluble in the reagent. Alcohols having seven or more carbon atoms are not soluble, hence they form two layers at the start.

11. Remember that conjugated isomer is more stable than the non-conjugated ; neglecting the option (*c*) which is Saytzeff product. Out of *cis*- and *trans*-isomers, *trans*- is more stable and hence option (*a*) is main product.

12.



2° Carbocation 3° Carbocation (More substituted)

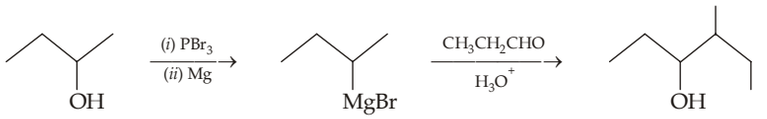
13. Jones reagent (chromic acid in aq. acetone solution) is a mild oxidizing agent and oxidizes alcohols without oxidising double bond.

14. Reaction of an alcohol with $SOCl_2$ does not cause rearrangement, while with HCl and HCl + $ZnCl_2$, rearranged product, $(CH_3)_2CClCH_2CH_3$ will be formed.

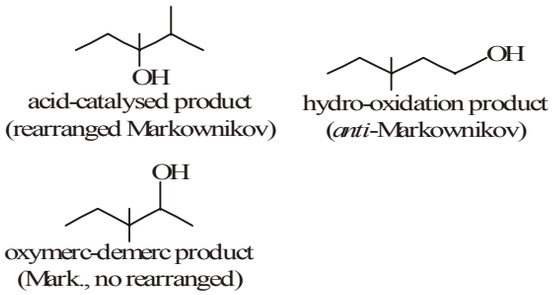
15. $\underset{\text{1–Phenyl–2–propanol}}{C_6H_5CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3} \xrightarrow{H^+} \underset{\substack{\text{1-Phenyl-1-propene}\\\text{(Major)}}}{C_6H_5CH=CHCH_3} + \underset{\text{1-Phenyl-2-propene}}{C_6H_5CH_2CH=CH_2}$

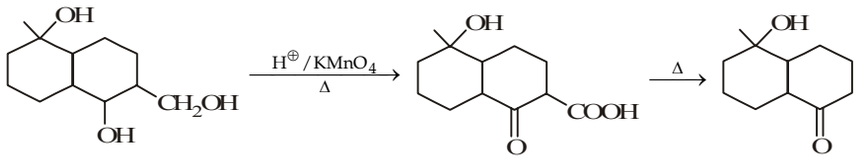
16. $NaBH_4$ does not reduce double bound, but only CHO to CH_2OH.

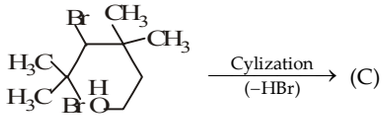
17. $\underset{[A]}{CH_3CH_2CH_2OH}$, $\underset{[B]}{CH_3CH=CH_2}$, $\underset{[C]}{CH_3CHBr.CH_2Br}$, $\underset{[D]}{CH_3C \equiv CH}$, $\underset{[E]}{CH_3.CO.CH_3}$

18. 

[A] [B]

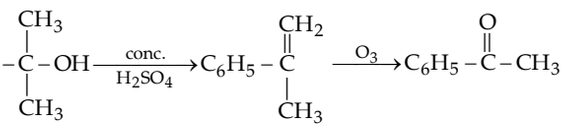
19. (d) 

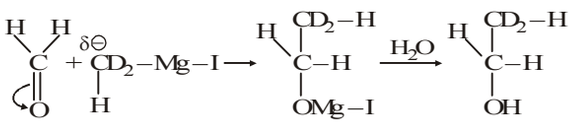
24. (c) 

25. (c) 

(C)

26. (a) $CH_2=\overset{+}{C}H-CH=CH-CH=CH-CH_3 \xrightarrow[(ii)-H^+]{(i)\,CH_3OH}$

27. (a) $\underset{S}{C_6H_5MgBr} + \underset{T}{CH_3COCH_3}$ 

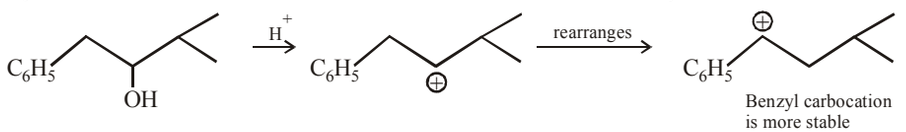
28. (c) 

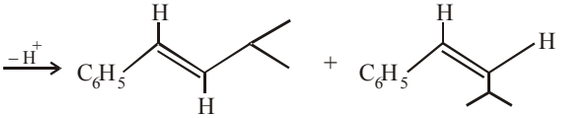
$\xrightarrow[\Delta]{\text{Conc. } H_2SO_4} D_2C=CH_2$ (Y)

29. (c) According to carbocation stability IV > III > II > I

30. (a) Option (a) will lead to conjugated ketone with highly substituted C = C.

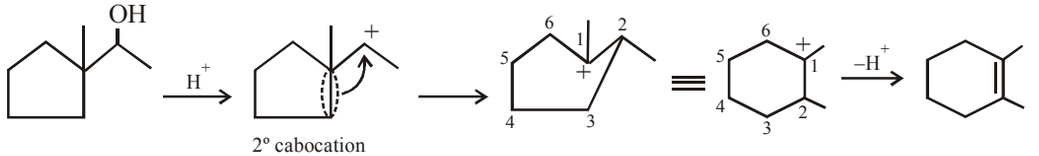
31. (c) Hydroboration – oxidation of alkenes leads to *anti*-Markownikoff's hydration.

32. **(b)** 



trans–(more stable due to steric relief) *cis*– (less stable due to bulky gps. lying on same side)

33. **(b)** Hydroboration – oxidation reaction of alkenes leads to anti-Markovnikov's hydration. Further addition of water adds in *syn*-manner, i.e., H and OH are added to the same face of the double bond leading *trans*-product. In short, hydroboration-oxidation of alkenes is regioselective as well as stereoselective.

34. **(c)** 

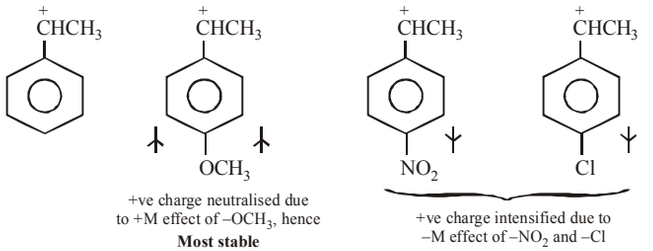
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35. (c) Higher is the stability of a species, more likely it is formed, hence lower will be the E_{act} for its precursor.

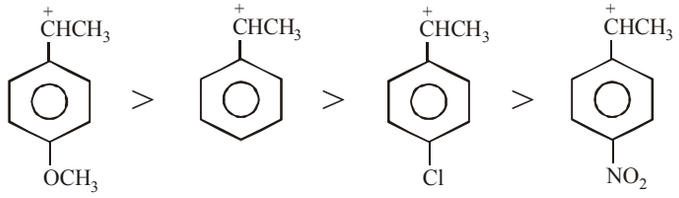
36. (d) $CH_3CH_2OH \xrightarrow[(\text{from } H_2SO_4)]{H^+} CH_3CH_2\overset{+}{O}H_2 \rightarrow CH_3\overset{+}{C}H_2 \xrightarrow[(\text{from } H_2SO_4)]{HSO_4^-} CH_2 = CH_2 + H_2SO_4$

Thus note that H_2SO_4 is acting as an acid in step (i), as a base in step (iii). Since it is regenerated back as such it also acts as a catalyst.

37. (b) The reaction involves the formation of carbocation as intermediate. Hence more the stability of the carbocation, more will be the rate of reaction. Let us draw the structure of the corresponding carbocation and observe the relative stability of the four benzyl carbocations.



The relative stability of the four carbocations is



38. (c) Zinc chloride is a Lewis acid and coordinates with the alcoholic group.

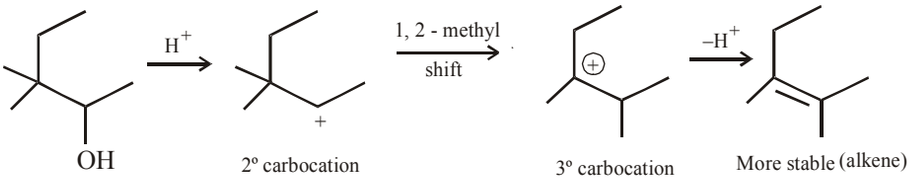
$$R-\ddot{O}H + ZnCl_2 \longrightarrow R-\overset{+}{O}(H)-\overset{\ominus}{Z}nCl_2 \longrightarrow R^+ + \underset{\text{Leaving group}}{HO-\overset{\ominus}{Z}nCl_2}$$

$$R^+ + Cl^- (\text{from HCl}) \rightarrow RCl + H^+$$

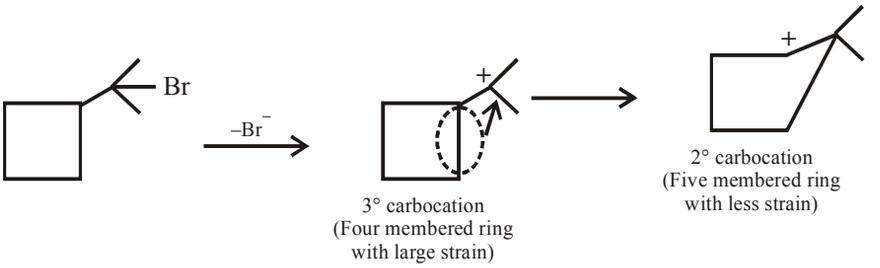
$$H^+ + HO^- - ZnCl_2 \rightarrow H_2O + ZnCl_2$$

39. (c) Step 2 involves the formation of carbonium ion by the loss of weakly basic H_2O molecule, hence it is slowest step. Step 4 involves the conversion of an unstable (or intermediate) species into a quite stable product, hence it is fastest step.

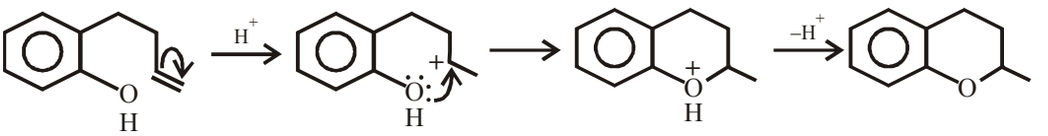
40. (c) It is an example of dehydration of alcohol. The 2° carbocation formed at first stage rearranges to the more stable 3°.



41. (c)



42. (b)



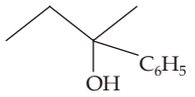
43. (c) $CH_2 = CH\overset{+}{C}H_2$ and $(CH_3)_3\overset{+}{C}$ are quite stable.

EXERCISE 11.2

>1 CORRECT OPTION	1	(a,c)	9	(a, b, c)	17	(a, c, d)
	2	(a,b)	10	(a, b, d)	18	(a, c, d)
	3	(a,b,c)	11	(a, b, c)	19	(b, d)
	4	(a,c,d)	12	(a, b, c, d)	20	(a, c, d)
	5	(a,c,d)	13	(a, b, c, d)	21	(a, c)
	6	(a,c,d)	14	(b, c, d)	22	(b, c, d)
	7	(c, d)	15	(c, d)	23	(a, c)
	8	(a, b, c)	16	(b, c)		
PASSAGE 1	24	(b)	25	(d)	26	(c)
PASSAGE 2	27	(b)	28	(d)	29	(c)
PASSAGE 3	30	(d)	31	(a)	32	(a)
PASSAGE 4	33	(c)	34	(c)	35	(b)
MATCH THE FOLLOWING	36	(A) – a, d; (B) – c; (C) – b; (D) – d				
	37	(A) - a, (B) - a, d, (C) - b, c, d, (D) - c, d				
	38	(A) - a,b,c (B) - b, (C) - b, c, d				
	39	(A) - c, d (B) - a, b, (C) - a, c; (D) - b, d				
	40	(A) - b,d (B) - a, b, (C) - a, c, (D) - b, d				
A/R	41	(a)	42	(d)	43	(d)
	44	(c)				
INTEGER	45	2	46	3		

1. If the aldehyde has a boiling point less than 100°C, it can be prepared by the oxidation of 1° alcohols with regular oxidising agents like acidic permanganate or dichromate. Since the aldehyde has a lower boiling point than the alcohol, it is distilled off as soon as it is formed ; so further oxidation to a carboxylic acid is minimized.

2. 

3. 

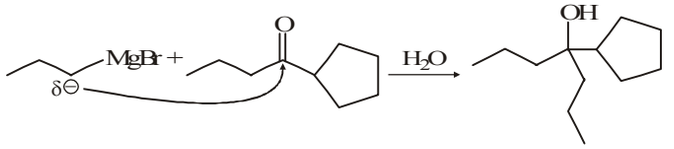
is a 3° alcohol ; the first three combinations can be applied for its preparation.

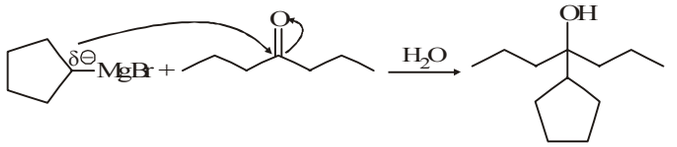
4. Phenylethylcarbinol, $PhCH(OH)CH_2CH_3$ does not have —$CHOHCH_3$ group, so does not respond haloform test.

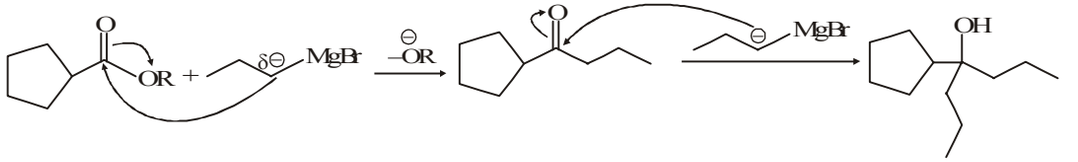
5. $LiAlH_4$ reduces —CO as well as Br group. Hydride ions from $LiAlH_4$ are transferred to carbonyl carbon and carbon bearing Br atom.

6. Option (*b*) will form the most stable (3°) carbocations, hence it does not rearrange.

14. (b, c, d)

(b) 

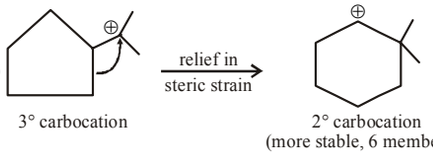
(c) 

(d) 

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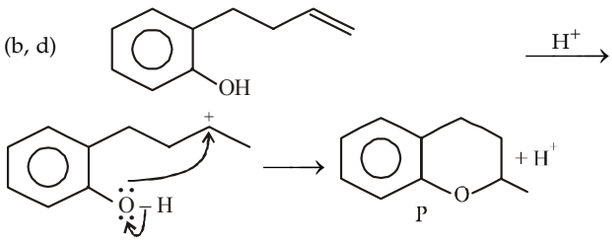
15. (c, d) (c) and (d) do not form RMgX, hence no alcohol; while (a) and (b) form alcohol which responds Lucas test.

16. (b, c)

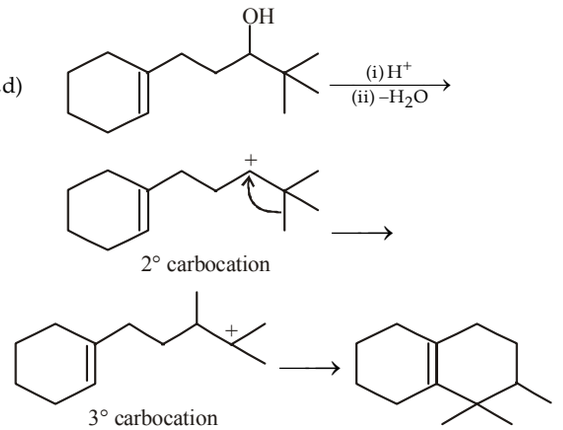


18. (a, c, d) Option (*b*) will form the most stable (3°) carbocation, hence it does not rearrange.

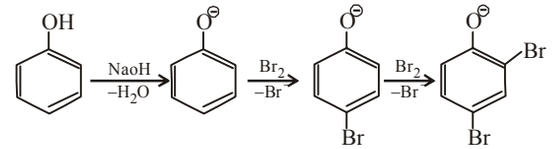
19. (b, d)

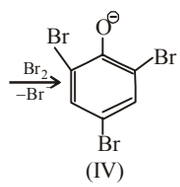


22. (b,c,d)



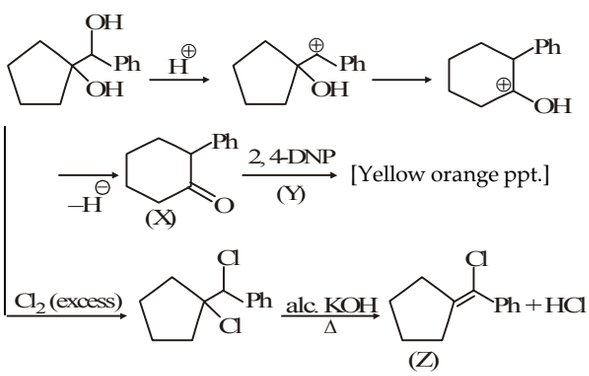
23. (a, c)



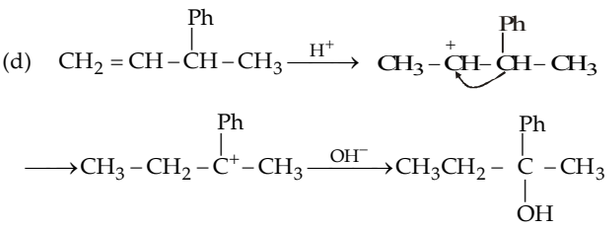


Product of reaction of phenol with NaOH/Br_2 is sodium salt of 2,4,6-tribromophenol. Hence, species (I), (II), (III) are formed as intermediate.

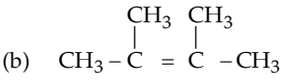
Sol. (27-29) :



30. (d)

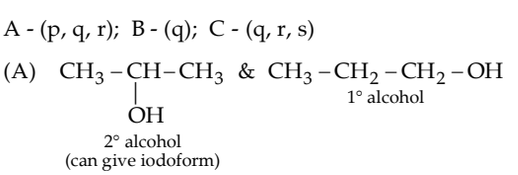


35. (b)



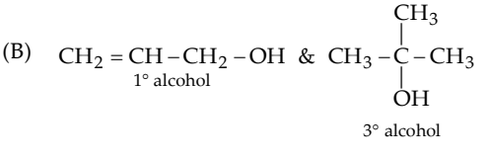
38. A - (p, q, r); B - (q); C - (q, r, s)

(A)



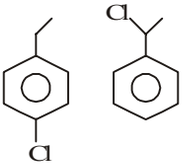
Lucas & Victor Meyer rest can also be used.

(B)



Lucas test can not be used since both give immediate turbidity. Victor Meyer test can be used.

(C)



Lucas test can not be used.

Victor Meyer, iodoform & $AgNO_3$ tests can be used.

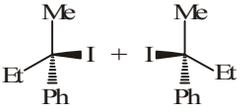
39. A - (r, s); B - (p, q); C - (p, r); D - (q, s)

40. A - (q, s); B - (p, q); C - (p, r); D - (q, s)

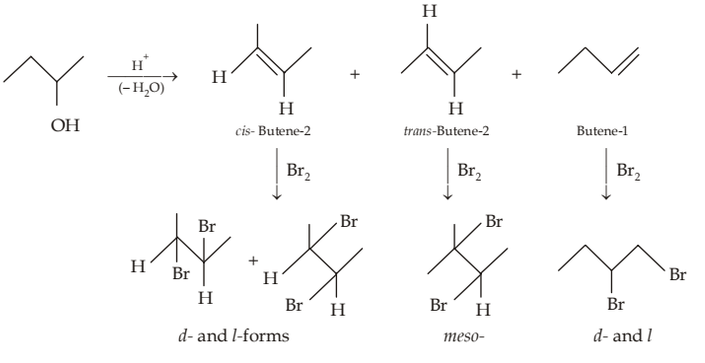
Though allyl alcohol reacts with Lucas reagent, the ppt reacts with HCl and dissolves in it.

44. (c) As hydrocarbon part increases, capacity to make hydrogen bonding decreases. So if molar mass increases, solubility decreases.

45. **Two**



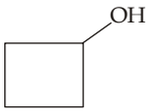
46. **3**

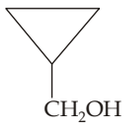


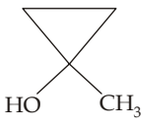
EXERCISE 11.3

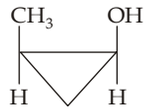
1. (*a*) 2-Methyl-4-octanol (*b*) 3-Buten-2-ol
(*c*) 5-Chloro-6-methyl-6-(3-chlorophenyl)-2-hepten-1-ol (*d*) 4, 4-Dimethyl-2-cyclohexen-1-ol.

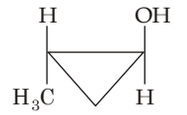
2.


Cyclobutanol


Cyclopropylmethanol

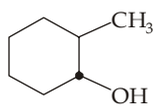

1-Methylcyclopropanol

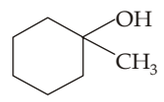

cis-2-Methylcyclopropanol **(Chiral)**

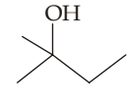

trans-2-Methylcyclopropanol **(Chiral)**

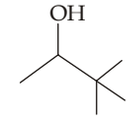
3. *n*-Octyl alcohol > *n*-Hexyl alcohol > 3-Hexanol > 2-Methyl-2-pentanol > *n*-Hexane.

4. In hydroboration-oxidation of alkenes, H_2O is added in *cis*– anti-Markovnikov's way. In oxymercuration-demercuration of alkenes, H_2O is added in Markovnikov's way without rearrangement. In acid-catalyzed hydration of alkenes, H_2O is added with rearrangement, if possible.


[A]
trans-2-Methylcyclohexanol (*cis*-Anti-Markovnikov's hydration)


[B]
1-Methylcyclohexanol (Markovnikov's hydration)


[C]
2-Methyl-2-butanol (Markovnikov's hydration with rearrangement)

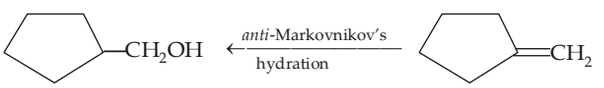

[D]
3, 3-Dimethyl-2-butanol (Markovnikov's hydration without rearrangement)

5. (*a*) 3° Halides react with bases to eliminate HCl forming alkenes ; they do not undergo S_N2 displacement to give alcohols. However, when heated with water in dioxane, 3° halides undergo S_N1 reaction forming 3° alcohols in good yield.
(*b*) Like water, methanol and ethanol form H-bond and have relatively high dielectric constant for organic compounds. They are able to insulate charges by solvation, minimizing attractions between unlike ions.
(*c*) The R in cyclohexanol is more compact than in 1-hexanol. Its OH group is more exposed and available for H-bonding with water. In addition, its small compact shape results in fewer water-water H-bonds being broken.
(*d*) Due to formation of more stable *tert*-butyl carbocation.

6. In such cases, first write down the structure of the required compound and then go backward for knowing the structure of the parent alkene. However, keep in mind that Markovnikov hydration can be achieved by dil. H_2SO_4 or by oxymercuration-demercuration ; while *anti*-Markovnikov's hydration is done by BH_3—THF followed by oxidation with H_2O_2 in *aq*. OH^-.

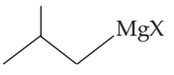
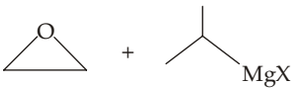
(*a*) $CH_3\underset{\text{2-Butanol}}{\overset{OH}{\overset{|}{C}}}HCH_2CH_3 \xleftarrow[\text{hydration}]{\text{Markovnikov's}} CH_3CH=CHCH_3$ or $CH_3CH_2CH=CH_2$

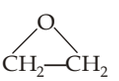
(*b*) $\underset{\text{Isobutyl alcohol}}{(CH_3)_2CHCH_2OH} \xleftarrow[\text{hydration}]{\textit{anti}\text{-Markovnikov's}} (CH_3)_2C=CH_2$

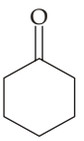
(*c*) 

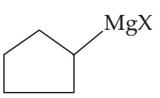
(*d*) $CH_3-\underset{OH}{\overset{CH_3}{\overset{|}{C}}}-CH_2CH_3 \xrightarrow[\text{hydration}]{\text{Markovnikov's}} (CH_3)_2C=CHCH_3$ *or* $H_2C=\overset{CH_3}{\overset{|}{C}}CH_2CH_3$

7. Observe the nature of alcohol (1°, 2° or 3°) and recall how these are prepared from Grignard reagents.

(*a*) $HCHO +$  or 

(*b*) $HCHO + CH_2=CHCH_2MgX$ or  $+ \; CH_2=CHX$

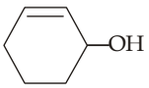
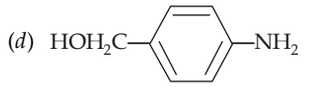
(*c*)  $+ \; (CH_3)_2CHMgX$

(*d*)  $+ \; CH_2O$

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8. In addition to carbonyl group, $LiAlH_4$ also reduces groups like —NO_2, —X, —NO_2, —COOH, —COOR, etc. $NaHB_4$ does not reduce either of these groups except carbonyl. Also remember that unsaturation present in α, β-position with respect to carbonyl group is neither reduced by $LiAlH_4$ nor by $NaBH_4$.

(*a*) $CH_2OH.CH_2CH_2OH$ (*b*) $CH_3CHOHCH_2CH_3$

(*c*)  (*d*) 

9. (*a*) $(CH_3)_2CHOH_2^+.HSO_4^-$ Isopropyloxoniumhydrogen sulphate (*b*) $(CH_3)_2CHOSO_3H$ Isopropylhydrogen sulphate

(*c*) $(CH_3)_2CH.O.CH(CH_3)_2$ Diisopropyl ether (*d*) $CH_3CH=CH_2$. Propene

10. (*a*) $\underset{\text{Lewis acid}}{ZnCl_2} + 2HCl \longrightarrow \underset{\text{(A stronger acid than HCl)}}{H_2ZnCl_4} \xrightarrow{ROH} ROH_2^+ \xrightarrow{Cl^-} RCl + H_2O$

(*b*) Magnesium of RMgX can coordinate with two molecules of ether *via* the electron pairs of their oxygen atoms to form an ether soluble addition compound.

11. In general, the order of reactivity is 3° > 2° > 1° < CH_3OH. Electronic factors are important except for 1° alcohols, for which steric factors are controlling.

(*a*) All are primary alcohols, greater the steric hindrance near the carbon of the alcoholic group, lesser will be its reactivity towards HBr. Thus

(*i*) > (*ii*) > (*iv*) > (*iii*)

(*b*) (*iii*) > (*i*) > (*ii*)
3° 2° 1°

(*c*) (*i*) > (*iv*) > (*ii*) > (*iii*)

All are 2°, rate decreases with the nearness and number of electron-withdrawing fluorines.

12. This is an S_N1 reaction and involves formation of carbocation as intermediate. Hence greater the stability of a carbocation, higher will be reactivity of its parent alcohol. Recall that

(*a*) electron withdrawing groups like NO_2 and Cl in the *para* position will destabilize the carbocation by intensifying the positive charge. Further NO_2 is more effective since it destabilizes by both resonance and induction, while Cl destabilizes only by induction.

(*b*) Electron releasing group like OCH_3 will stabilize the carbocation.

(*c*) More the number of phenyl groups on the benzylic carbon, more stable will be the carbocation.

III > II > I > V > IV.

13. Ease of dehydration of alcohols is 3° > 2° > 1°. Further among same type of alcohol (*viz*. 3°) the alcohol which gives a more substituted alkene will be dehydrated more easily than the other. Thus

III > II > IV > I > V

14. (*a*) $\underset{\text{Ethane}}{C_2H_6}$ (*b*) and (*c*) No reaction (*d*) $\underset{\text{Acetone}}{(CH_3)_2CO}$

(*e*) $(CH_3)_2CHOTs$ (Isopropyl tosylate)

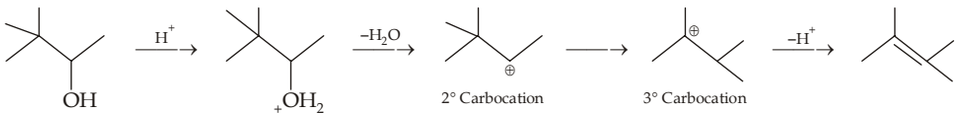
15. (*a*) $n\text{-}C_3H_7CH_2OH \longrightarrow n\text{-}C_3H_7CH_2Br \xrightarrow{Mg} n\text{-}C_3H_7CH_2MgBr \xrightarrow{D_2O} n\text{-}C_3H_7CH_2D$

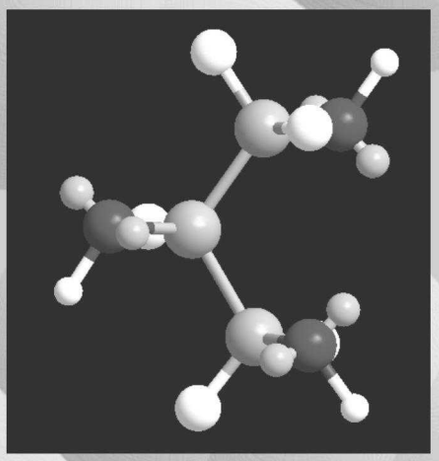
(*b*) $n\text{-}C_3H_7CH_2OH \xrightarrow{PCC,\ CH_2Cl_2} n\text{-}C_3H_7CHO$

(*c*) $n\text{-}C_3H_7CH_2OH \longrightarrow n\text{-}C_3H_7CH_2Br \xrightarrow{Li} n\text{-}C_3H_7CH_2Li \xrightarrow{CuI} (n\text{-}C_3H_7CH_2\text{–})_2\text{–}CuLi$

$\xrightarrow{n\text{-}C_3H_7CH_2Br} n\text{-}C_3H_7CH_2CH_2C_3H_7\text{-}n$

(*d*) $(CH_3)_3COH \xrightarrow{HBr} (CH_3)_3CBr \xrightarrow[(ii)\,H_2O]{(i)\,Mg} (CH_3)_3CH$

16. 



12

Ethers, Epoxides and Polyhydric Alcohols

CHAPTER HIGHLIGHTS

ETHERS

12.1 Nomenclature
12.2 Preparation of Ethers
12.3 Structure and Physical Properties
12.4 Chemical Properties

EPOXIDES (OXIRANES)

12.5 Nomenclature
12.6 Preparation
12.7 Properties
12.8 Illustrative Examples

GLYCOLS OR DIOLS

12.9 Preparation
12.10 Properties
12.11 Illustrative Examples

TRIHYDRIC ALCOHOLS OR TRIOLS

12.12 Preparation
12.13 Properties

EXERCISES
SOLUTIONS

ETHERS

12.1 Nomenclature

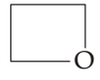
Ethers are compounds containing a C—O—C unit, hence their general formula is R—O—R (R may be alkyl or aryl). Ethers are named in radicofunctional way or IUPAC (substitutive) way.

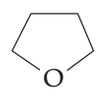
	$CH_3CH_2OCH_2CH_3$	$CH_3CH_2OCH_3$	$CH_3OCH_2CH_2Cl$
Radicofunctional name :	Diethyl ether	Ethyl methyl ether	2-Chloroethyl methyl ether
IUPAC name :	Ethoxyethane	Methoxyethane	1-Chloro-2-methoxyethane

If the two groups bonded to oxygen are identical, the ether is said to be **symmetrical or simple** (*e.g.* diethyl ether, diisopropyl ether) ; if these groups are different, then the ether is named as **unsymmetrical or mixed** (*e.g.* ethyl methyl ether, *tert*-butyl ethyl ether).

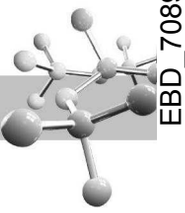
In cyclic ethers, oxygen is present inside the ring, they may be considered as heterocyclic compounds.


Oxirane
(Ethylene oxide)


Oxetane


Oxalone
(Tetrahydrofuran)


Oxane
(Tetrahydropyran)



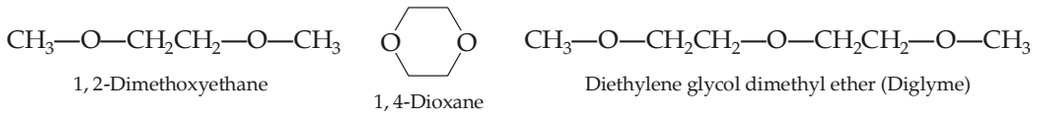
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Ethers are functional isomers of alcohols.

(*i*) CH_3OCH_3 and CH_3CH_2OH

(*ii*) $CH_3OCH_2CH_3$, $CH_3CH_2CH_2OH$ and $(CH_3)_2CHOH$

Examples of diethers and triethers (compounds containing two and three ether linkages) are



TEST YOUR UNDERSTANDING - 12.1

1. Give derived and IUPAC name for the following ethers.

(*a*) $C_6H_5OCH_2CH_3$ (*b*) $(CH_3)_2CHOCH(CH_3)CH_2CH_3$ (*c*) *p*-$NO_2.C_6H_4OCH_3$.

2. Write the structure of each of these ethers.

(*a*) Chloromethyl methyl ether (*b*) 2-(Chloromethyl) Oxirane (*c*) 3, 4-Epoxy-1-butene.

12.2 Preparation of Ethers

The first two methods given below are used for preparing simple ethers, while the rest for mixed ethers.

1. **By intermolecular dehydration of alcohols** *or* **acid catalysed condensation of alcohols.** (For details, consult properties of alcohols). This method is limited for the preparation of those *symmetrical ethers* in which both alkyl groups are primary because in 2° and 3° alcohols, alkenes will be formed in significant amount. This is industrial method for the preparation of symmetrical ethers.

2. **By treating alkyl halide with dry silver oxide.**

$$2(CH_3)_2CHCl + Ag_2O \longrightarrow (CH_3)_2CHOCH(CH_3)_2 + 2AgCl$$

3. **By the acid-catalyzed addition of alcohols to alkenes.**

$$\underset{\text{2-Methylpropene}}{(CH_3)_2C=CH_2} + CH_3OH \xrightarrow{H^+} \underset{\textit{tert}-\text{Butyl methyl ether*}}{(CH_3)_3C.O.CH_3}$$

Reaction involves the protonation of alkene to form carbocation followed by attack by alcohol (nucleophile) on the more stable carbocation to form ether as final product.

tert-**Butyl ethers as protecting group.** Reaction between isobutene and alcohol is of special significance, in the sense that the reactive alcoholic group is converted into non-reactive ether linkage, *i.e.* the alcoholic group is protected by *tert*-butyl group which can be easily removed by treating the ether with dil. aqueous acid, after carrying out the required reaction at other functional group. Consider the preparation of 4-pentyn-1-ol from 3-bromo-1-propanol and sodium acetylide. Direct reaction between them will not give the required product because the strongly basic acetylide will react first with the hydroxyl group and not with the bromine.

$$HC\equiv CH + NaOCH_2CH_2CH_2Br \xleftarrow{NaC\equiv CH} HOCH_2CH_2CH_2Br \xrightarrow{NaC\equiv CH} \underset{(\textit{Not formed})}{HOCH_2CH_2CH_2C\equiv CH}$$

However, the reaction at the carbon bearing Br can be achieved by protecting the —OH group in the form of —$OCMe_3$ and then carrying the reaction as usual.

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* *tert*-Butyl methyl ether is added to gasoline to increase octane number.

$$HOCH_2CH_2CH_2Br \xrightarrow[(ii)\ CH_2=C(CH_3)_2]{(i)\ H_2SO_4} (CH_3)_3COCH_2CH_2CH_2Br \xrightarrow{NaC\equiv CH} (CH_3)_3COCH_2CH_2CH_2C\equiv CH$$

$$\xrightarrow{H_3O^+/H_2O} \underset{\text{4-Pentyn-1-ol}}{HOCH_2CH_2CH_2C\equiv CH} + (CH_3)_3COH$$

4. By the use of diazomethane.

This method is used for preparing only methyl ethers..

$$n\text{-}C_4H_9OH + CH_2N_2 \xrightarrow{BF_3\ (Lewis\ acid)} \underset{n\text{-Butyl methyl ether}}{n\text{-}C_4H_9OCH_3} + N_2$$

$$C_6H_5OH + CH_2N_2 \xrightarrow{BF_3} \underset{\text{Anisole}}{C_6H_5OCH_3}$$

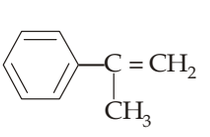
5. By solvomercuration-demercuration of alkenes.

We have studied oxymercuration-demercuration as a method of preparing alcohols from alkenes.

$$RCH=CH_2 \xrightarrow[(ii)\ NaBH_4/OH^-]{(i)\ Hg(OAc)_2—THF—H_2O} \underset{\text{Markovnikov orientation}}{\overset{\overset{\text{From water present in solvent (THF.}H_2O\text{)}}{\overset{OH}{|}}}{RCH—CH_2—H}}$$

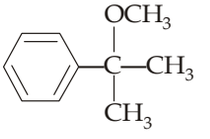
(from $NaBH_4$)

The above reaction can be modified for preparing ethers by taking an alcohol as solvent instead of aqueous tetrahydrofuran.



2-Phenylpropene

$$\xrightarrow[(ii)\ NaBH_4/OH^-]{(i)\ Hg(OAc)_2,\ CH_3OH}$$



2-Methoxy-2-phenylpropane

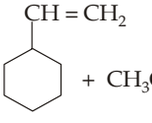
TEST YOUR UNDERSTANDING - 12.2

1. Reaction between allyl alcohol and isopropanol gives a good yield of a mixed ether. Write down its structure and explain its formation in quantitative yield.

2. Complete the reactions, giving the position of labelled oxygen in the product.

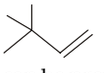
$$(CH_3)_3C^{18}OH + CH_3OH \xrightarrow{conc.H_2SO_4} \text{Ether + Water.}$$

3. Give mechanism involved in the following reaction.



$+\ CH_3OH \xrightarrow{H_2SO_4}$ A mixture of ethers

4. Complete the following reaction.



$\xrightarrow[H_2SO_4]{C_2H_5OH}$ Major product.

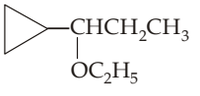
5. Show how each of the following ethers can be prepared by solvomercuration-demercuration process.

(*a*) $C_6H_5CH(CH_3)OCH_2CH_2CH_3$

(*b*) $CH_3CH(OCH_2CH_3)CH_2CH_2CH_2CH_3$

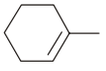
(*c*) $(CH_3)_3C.CH(OCH_3)CH_3$

(*d*)



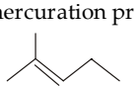
6. Write the structure of the ether obtained by solvomercuration-demercuration process ?

(*a*)



$\xrightarrow[(ii)\ NaBH_4/OH^-]{(i)\ Hg(OAc)_2,\ iso\text{-}C_3H_7OH}$

(*b*)



$\xrightarrow[(ii)\ NaBH_4/OH^-]{(i)\ Hg(OAc),\ C_6H_5OH}$

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6. Williamson synthesis. Williamson synthesis involves the reaction of a sodium alkoxide with an alkyl halide, alkyl sulphonate, or dialkyl sulphate.

$$R—ONa + X—R' \longrightarrow R—O—R' + Na—X$$

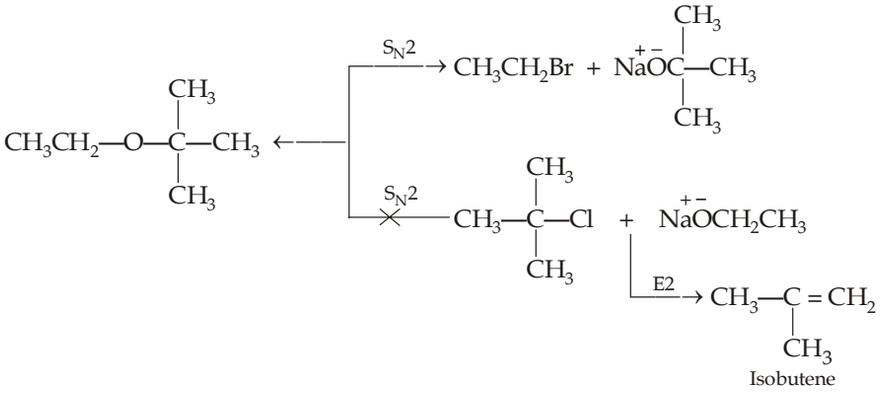
where X = Cl, Br, I, OSO_2R'', or OSO_2OR''

$$(CH_3)_2CHOH \xrightarrow{\text{Na or NaH}} (CH_3)_2CHO^-Na^+ \xrightarrow{CH_3CH_2I} \underset{\text{Ethyl isopropyl ether}}{(CH_3)_2CHOCH_2CH_3}$$

$$C_6H_5ONa + R'O_3S—C_6H_4—CH_3 \longrightarrow C_6H_5—O—R' + \overset{+\ -}{N}aO_3S—C_6H_4—CH_3$$

$$C_2H_5O^- + CH_3—OO_3SCH_3 \longrightarrow C_2H_5OCH_3 + CH_3OSO_3^-$$
(Dimethyl sulphate)

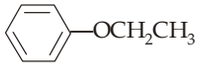
Williamson synthesis can be applied for the synthesis of symmetrical as well as unsymmetrical ethers. It follows S_N2 path, hence it is most successful when the alkyl halide, sulphonate, or sulphate is primary (or methyl). If the alkyl halide (substrate) is tertiary or secondary they react with alkoxide base by E2 elimination rather than by S_N2 substitution. Thus if we want to prepare *tert*-butyl ether, we must take *tert*-butyl group in the form of alkoxide rather than halide,



Note that the alkoxides as well as alkyl halides are prepared from alcohols, we can say that the Williamson synthesis ultimately involves the synthesis of an ether from two alcohols.

TEST YOUR UNDERSTANDING - 12.3

1. Choose the correct combination of alkyl halide and alkoxide for the preparation of each of the following ethers by the Williamson synthesis.

(*i*) $CH_2 = CHCH_2OCH(CH_3)_2$ (*ii*)  (*iii*) 

2. (*a*) Rank the following alkyl halides in decreasing order of reactivity in the Williamson synthesis.

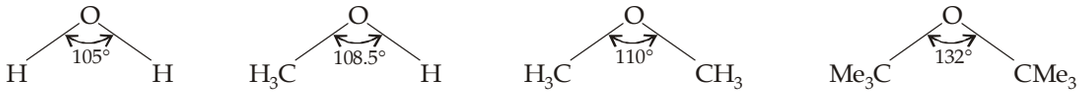
Me_3CCH_2Br (A), $ClCH_2CH=CH_2$ (B), $ClCH_2CH_2CH_3$ (C), $BrCH_2CH_2CH_3$ (D).

(*b*) Among the three methods for preparing ethers, *viz.* intermolecular dehydration, alkoxymercuration-demercuration and Williamson synthesis, which can best be used for preparing following ethers.

(*i*) Cyclohexyl ether (*ii*) $CH_3(CH_2)_2OCH_2CH_3$ (*iii*) $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HOC_3H_7$-*n*

12.3 Structure and Physical Properties

1. Like water, the central oxygen atom of ethers is sp^3 hybridised. Hence bonding in ethers can best be understood by comparing ethers (R—O—R) with water (H—O—H) and alcohols (R—O—H). In ether, van der Waals strain involving alkyl groups causes the bond angle at oxygen to be larger than in alcohols, which in turn is larger than in water. An extreme example is di-*tert*-butyl ether, where steric hindrance between the bulky *tert*-butyl groups increases the C—O—C bond angle to a larger extent.



Water Methanol Dimethyl ether Di-*tert*-butyl ether

2. Since the C—O—C bond angle is not 180°, the dipole moments of the two C—O bonds do not cancel each other, hence ethers possess a small net dipole moment, *e.g.* 1.18 D for diethyl ether.

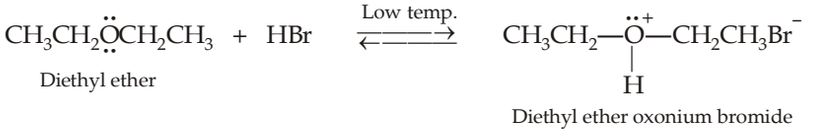
3. Boiling points of ethers are comparable with those hydrocarbons of the same molecular weight. However, boiling points of ethers are much lower than those of comparable alcohols, because alcohol molecules can associate with each other through H-bonding, while ether molecules cannot.

4. Although ethers are not able to form H-bond with themselves, they are able to form hydrogen bonds with water, hence ethers are nearly as much soluble, in water, as alcohols of comparable molecular weight.

12.4 Chemical Properties

Ethers are one of the least reactive functional groups. Dialkyl ethers react with very few reagents other than acids. Ethers resist attack by nucleophiles and by bases. This lack of reactivity, coupled with the ability of ethers to solvate cations, by donating an electron pair from their oxygen atom, makes ethers especially useful as solvents for many reactions. Diethyl ether, used as solvent in the preparation of Grignard reagent, must be free of traces of water and alcohol. This so-called **absolute ether** can be prepared by distilling ordinary ether over conc. H_2SO_4, which removes water, alcohol and peroxides, followed by storing over metallic sodium. The only reactive sites in a molecule of dialkyl ether are the C—H bonds of the alkyl groups and the —$\ddot{O}$— group of the ether linkage.

1. Due to the presence of unshared electron pairs on oxygen, ethers are basic and hence react with proton donors (*e.g.* HCl, HBr, H_2SO_4) to form oxonium salts.



Diethyl ether Diethyl ether oxonium bromide

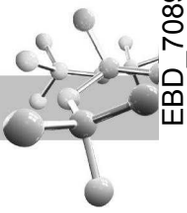
The oxonium salts are stable only at low temperature and in a strongly acidic medium. On dilution, they decompose to give back the original ether and acid.

2. **Formation of peroxides -** On standing in contact with air, ethers are converted into unstable peroxides *which are highly explosive* even in low concentrations. Hence *ether is always purified before distillation.* Purification (removal of peroxide) can be done by washing ether with a solution of ferrous salt (which reduces peroxide to alcohols, ROOH ⟶ ROH) or by distillation with conc. H_2SO_4 (which oxidises peroxides).

The presence of peroxides in ether is indicated by formation of red colour when ether is shaken with an aqueous solution of ferrors ammonium sulphate and potassium thiocyanate. The peroxide oxidises Fe^{2+} to Fe^{3+} which reacts with thiocyanate ion to give red colour of ferric thiocyanate.

$$\text{Peroxide} + Fe^{2+} \longrightarrow Fe^{3+} \xrightarrow{CNS^-} \underset{\text{Red}}{Fe(CNS)_3}$$

However, the formation of peroxide is prevented by adding a little Cu_2O to it.



EBD_7089

$$CH_3CH_2OCH_2CH_3 + O_2 \longrightarrow CH_3CH(OOH)OCH_2CH_3$$

1-Ethoxyethyl hydroperoxide

The reaction is free-radical, and oxidation occurs at the α-carbon atom.

Combustion of ethers gives CO_2 and H_2O.

$$CH_3CH_2OCH_2CH_3 + 6O_2 \longrightarrow 4CO_2 + 5H_2O$$

TEST YOUR UNDERSTANDING - 12.4

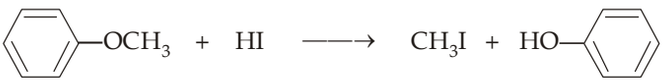
1. Does peroxide formation occur more rapidly with $(RCH_2)O$ or $(R_2CH)_2O$?
2. Why do free-radical substitution reactions of ethers occur preferentially on the α-carbon ?

3. **Acid-catalyzed cleavage of ethers.** As in alcohols, the carbon-oxygen bond of ethers is cleaved by reaction with hydrogen halides.

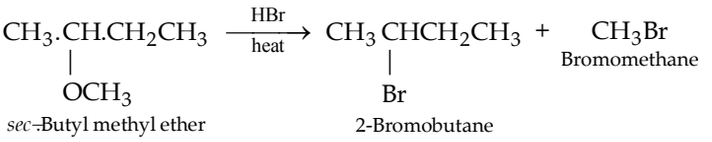
$$R—O—R' + HX \longrightarrow R—OH + R'—X$$

Reactivity of HX : HI > HBr >> HCl.

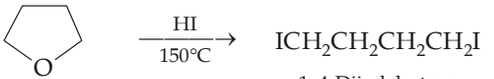
$$CH_3OCH_2CH_3 + HI \longrightarrow CH_3I + HOCH_2CH_3$$



However, when excess of HX is used, the alcohol formed as one of the products is subsequently converted into an alkyl halide, and thus the reaction typically leads to two alkyl halide molecules. Cleavage of ethers takes place only under vigorous conditions, *viz*. use of concentrated acids (HI or HBr) and at high temperature.



sec-Butyl methyl ether — 2-Bromobutane — Bromomethane



Tetrahydrofuran — 1, 4-Diiodobutane

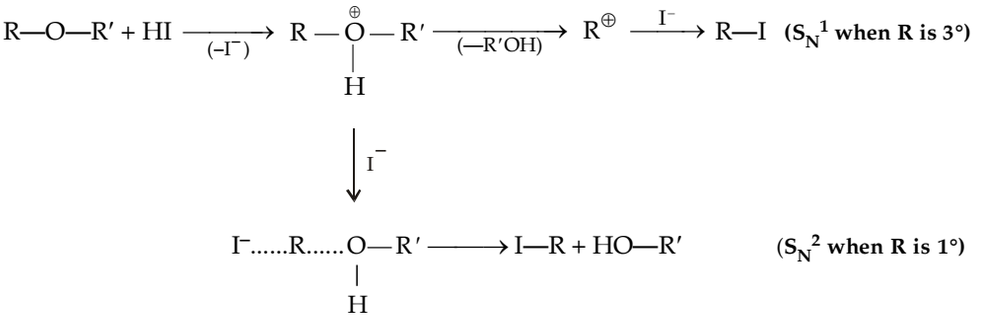
Reaction of ethers with HI forms the basis of **Zeisel method** for the detection and estimation of alkoxy group in a compound.

$$R'-O-CH_3 + HI \longrightarrow CH_3I \xrightarrow{AgNO_3} AgI + CH_3NO_3$$

Thus, moles of $-OCH_3$ = moles of AgI

$$\% \text{ of } -OCH_3 \text{ group} = \frac{31 \times \text{Wt. of AgI} \times 100}{\text{Mol. mass of AgI} \times \text{Wt. of ether}}$$

Mechanism. It is similar to reaction of alcohols with hydrogen halide in presence of acid to form alkyl halides (ROH + HX ⟶ RX), *i.e.* S_N1 or S_N2 depending upon the nature of the alkyl group.



On heating with sulphuric acid, ethers give alkyl hydrogen sulphate.

$$C_2H_5OC_2H_5 + H_2SO_4 \xrightarrow{\text{heat}} C_2H_5OH + C_2H_5HSO_4$$

4. **Hydrolysis of ethers**. Ethers, when treated with dil. aqueous acid, give alcohols.

$$R—O—R \xrightarrow{H_3O^+/H_2O} 2ROH$$

$$CH_3CH_2OC(CH_3)_3 \xrightarrow{H_3O^+/H_2O} CH_3CH_2OH + HOC(CH_3)_3$$

5. **Halogenation** (action of chlorine or bromine). In dark, substitution occurs at α-carbon atoms, while in presence of light all hydrogen atoms are substituted to form perhalo (fully halogenated) ether.

$$CH_3CH_2OCH_2CH_3 \xrightarrow[\text{dark}]{Cl_2} CH_3\overset{Cl}{\overset{|}{C}}HO\overset{Cl}{\overset{|}{C}}HCH_3 \xrightarrow[\text{light}]{Cl_2} \underset{\text{Perchlorodiethyl ether}}{CCl_3.CCl_2—O—CCl_2.CCl_3}$$

6. **Action of phosphorus pentachloride.**

$$R—O—R' + PCl_5 \longrightarrow RCl + R'Cl + POCl_3$$

TEST YOUR UNDERSTANDING - 12.5

1. (*i*) Why HI is considered as a better reagent that HBr for the reaction ?

$$R—O—R + HX \longrightarrow R—OH + RX$$

(*ii*) Di-*tert* butyl ether is rapidly cleaved by HCl and that too at room temperature.

2. Identify A in the following reaction.

(*a*) $B \xleftarrow[\text{HI, ether}]{\text{anhydrous}} CH_3OC(CH_3)_3 \xrightarrow{\text{aq. HI}} A$ (*b*) $C_6H_5—O—CH_3 + HI \longrightarrow C + D$

(*c*) $CH_3\overset{OCH_3}{\overset{|}{C}}HCH_2CH_3 \xrightarrow{\text{conc. HI}}$

3. Assign the structure to the three ethers, which when treated with excess of hydrogen bromide gave following results.

(*a*) One gave only benzyl bromide

(*b*) Other gave a mixture of bromocyclopentane and 1-bromobutne

(*c*) The third gave one mole of 1, 5-dibromopentane per mole of ether.

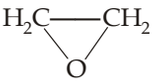
4. An ether A of the formula $C_6H_{14}O$ when treated with PCl_5 gives two chlorides which on treatment with aqueous NaOH give corresponding alcohols B and C. Both alcohols respond haloform test. B, when treated with sodium hypoiodite followed by acidic hydrolysis gives ethanoic acid. Give structures of the ether A and alcohols B and C.

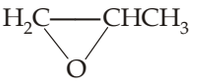
EBD_7089

EPOXIDES (OXIRANES)

12.5 Nomenclature

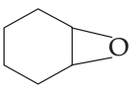
Epoxides are cyclic ethers with three-membered rings. At one time, these were named as oxides of alkenes. In IUPAC nomenclature. these are called **oxiranes,** while according to substitutive IUPAC nomenclature, these are named as *epoxy derivatives of alkanes.*



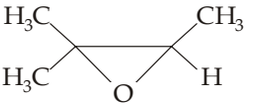


Common name	:	Ethylene oxide	Propylene oxide
IUPAC name	:	Oxirane	2-Methyloxirane
Substitutive IUPAC name	:	Epoxyethane	1, 2-Epoxypropane

However, substitutive IUPAC names are the widely used names.



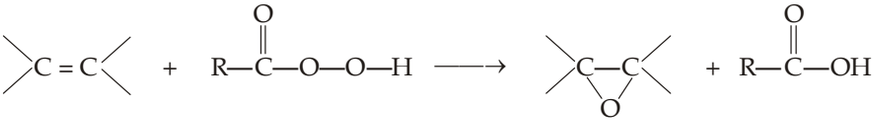
1, 2-Epoxycyclohexane



2-Methyl-2, 3-epoxybutane

12.6 Preparation

1. Epoxides are commonly prepared by the **oxidation of alkenes by peroxy acids** (also called per acid), *e.g.* peroxybenzoic acid ($C_6H_5CO_3H$), peroxyacetic acid (CH_3CO_3H), etc. This process is known as **epoxidation.**





1-Dodecene

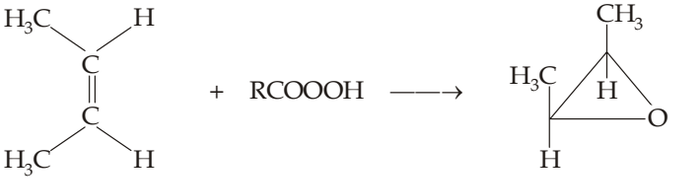
1, 2-Epoxydecane



Cyclopentene

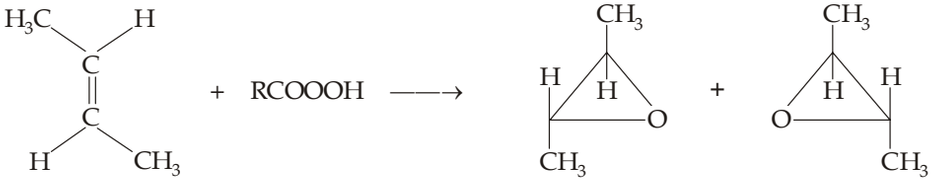
1,2-Epoxycyclopentane

(*i*) Epoxidation of alkenes with peroxy acids involves *syn* addition to the double bond.



cis-2-Butene

cis-2, 3-Dimethyloxirane
(a *meso* compound)



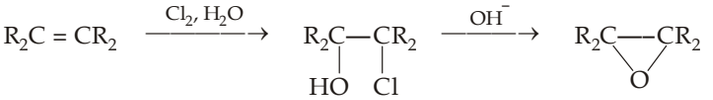
trans-2-Butene

trans-2, 3-Dimethyloxiranes (racemic)

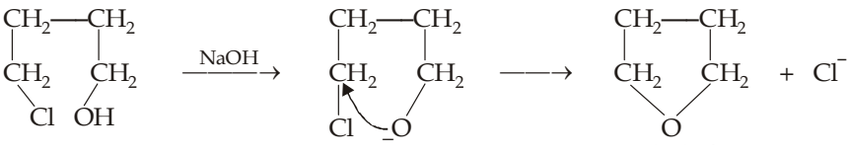
(*ii*) Presence of electron-releasing alkyl groups on the double bond increases the rate of epoxidation, suggesting that the peroxy acid acts as an electrophile towards he alkene.

$(CH_3)_2C = CHCH_3 > (CH_3)_2C = CH_2 > CH_3CH = CH_2 > CH_2 = CH_2$ **(Rate of epoxidation)**

2. Base catalysed cyclization of vicinal chlorohydrins



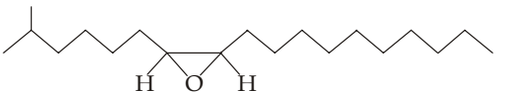
This method can be used for preparing 5- and 6-membered oxygen containing heterocyclic compounds.



Tetrahydrofuran

TEST YOUR UNDERSTANDING - 12.6

1. (*a*) Give IUPAC name of the following expoxide,



(*b*) also draw the structure of the alkene from which this important sex attractant (disparlure) can be prepared.

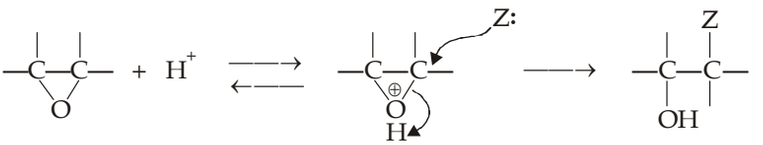
2. Give two methods for converting propylene to 1, 2-epoxypropane.

12.7 Properties

Epoxides react rapidly with nucleophiles under conditions in which ordinary ethers are inert. This enhanced reactivity is due to highly strained three membered ring which is opened up during reaction and thus strain is relieved.

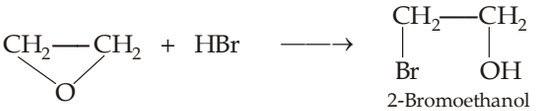
1. Acid-catalyzed cleavage of ethers.

These reactions either involve an acid as a reactant or occur under conditions of acid catalysis.

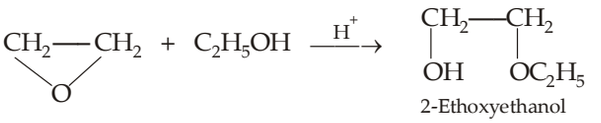


Protonated epoxide

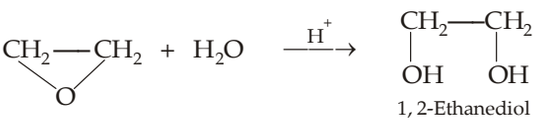
Where: Z is a nucleophile, *e.g.* Br^- or solvent like H_2O, CH_3OH, etc.



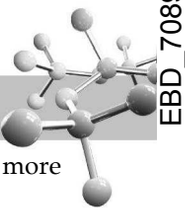
2-Bromoethanol



2-Ethoxyethanol

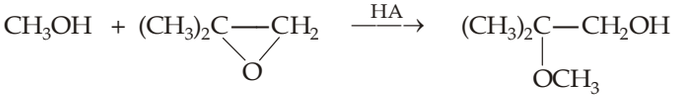


1, 2-Ethanediol

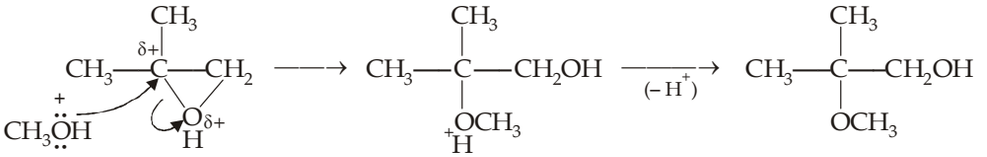


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In the acid-catalyzed ring opening of an unsymmetrical epoxide, the nucleophile attacks primarily at the more substituted carbon atom. For example,

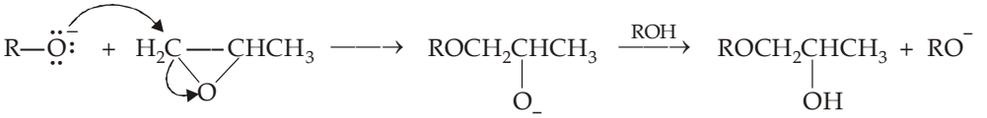


Attack of nucleophile on the more highly substituted carbon atom is because of the fact that such atom of the protonated epoxide acquires a considerable positive charge and thus resembles like a more stable 3° or 2° carbocation and hence the reaction is S_N1 like.

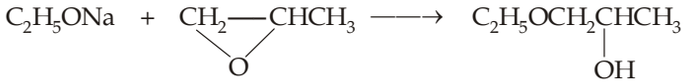


Thus alkenes can be easily converted to 1, 2,-diols by epoxidation followed by hydrolysis. This is a stereoselective reaction and the 1, 2-diols formed correspond to *anti*-addition to the carbon-carbon double bond (Similarity with the hydroxylation of alkenes by peroxyformic acid, but different with the hydroxylation of alkenes by permanganate or by osmium tetroxide which involves *syn*-addition).

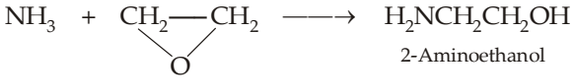
2. **Base-catalyzed cleavage of ethers.** Unlike ordinary ethers, epoxides can also undergo base-catalyzed ring opening, provided the attacking nucleophile is a strong base like alkoxide, phenoxide, ammonia, etc. Here the nucleophile attacks on the less substituted carbon atom which is least hindered to form alkoxide ion which is then protonated.



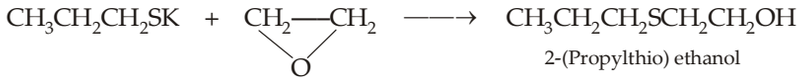
A strong nucleophile is able to open the strained epoxide ring in a direct S_N2 reaction.



1-Ethoxy-2-propanol

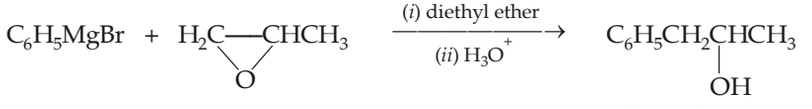


2-Aminoethanol



2-(Propylthio) ethanol

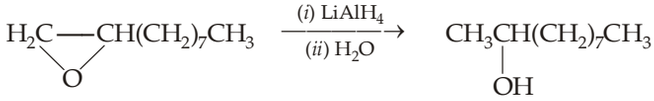
3. **Cleavage of ethers by Grignard reagents and lithium aluminium hydride.** In case of Grignard reagent, the nucleophilic end *i.e.* R part attacks on the carbon atom of the epoxide. This cleavage is also regioselective because here the nucleophile attacks at the less substituted ring carbon.



1-Phenyl-2-propanol

Thus this reaction is used for the preparation of alcohols having at least two carbon atoms more than the Grignard reagent.

Epoxides are reduced to alcohols on treatment with lithium aluminium hydride ; hydride ion is transferred to the less crowded carbon.

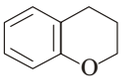
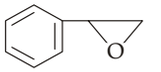


1, 2-Epoxydecane 2-Decanol

TEST YOUR UNDERSTANDING - 12.7

1. Which alkene, *cis*- or *trans*-2-butene, would give *meso*-2, 3-butanediol
(*a*) by epoxidation followed by acid-catalysed hydrolysis, and (*b*) by osmium tetroxide hydroxylation ?

2. Write down the product formed by treating each of the following epoxide with HI.

(*a*)  (*b*)  (*c*) 

3. What is the principal product formed in the reaction of ethylene oxide with each of the following ?

(*a*) NaOH in water (*b*) NaCN in water (*c*) NaN_3 (sodium azide) in water
(*d*) Phenyllithium in ether, followed by addition of dil. H_2SO_4 (*e*) 1-Butynylsodium in liq. NH_3.

4. Predict the chief product of each of the following reactions.

(*a*) Propylene oxide + NH_3 (*b*) Trimethylene oxide + HCl (*c*) Ethylene oxide in presence of acid.

5. Provide structure to the final product.

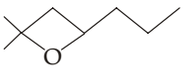
$$CH_3CH = CH_2 \xrightarrow{CF_3CO_3H} [A] \xrightarrow{DCl} [B] \xrightarrow{H_2O} [C].$$

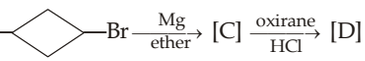
6. Give the second reactant for the following conversions.

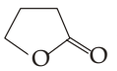
(*a*) 3-Methyl-1-butanol from ethylene oxide (*b*) 1-Phenylcyclohexanol from 1-phenylcyclohexene oxide.

7. Write down the structures of the alcohols obtained in the following reactions.

(*a*)  $+ CH_3MgBr \xrightarrow{H_3O^+}$ A

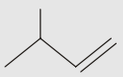
(*b*)  $\xrightarrow[H_3O^+]{CH_3MgBr}$ B

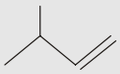
(*c*)  $\xrightarrow[ether]{Mg}$ [C] $\xrightarrow[HCl]{oxirane}$ [D]

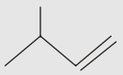
(*d*)  $\xrightarrow[(ii)\ H_3O^+]{(i)\ excess\ of\ CH_3MgBr}$ [E].

Example 1 :

3-Methylbutene is converted to ethers via following three different routes. Identify the ether in each case.

(a)  $\xrightarrow[(ii)\ CH_2N_2/HBF_4^-]{(i)\ H_3O^+}$ [A]

(b)  $\xrightarrow[(ii)\ H_2O_2/OH^-]{(i)\ BH_3\ .\ THF}$ [ ] $\xrightarrow[HBF_4^-]{CH_2N_2}$ [B]

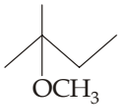
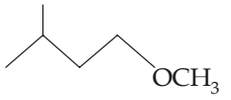
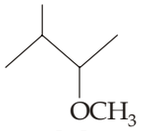
(c)  $\xrightarrow[(ii)\ NaBH_4/OH^-]{(I)\ Hg(OAc)_2/CH_3OH}$ [C].

Solution :

(*a*) Here alcohol is formed by simple hydration which leads to Markovnikov's product with rearranged carbocation; alcohol is then converted to methyl ether by diazomethane.

(*b*) Here alcohol is formed by hydroboration-oxidation method which leads to *anti*-Markovnikov addition without rearrangement, the alcohol so formed is then converted to methyl ether by diazomethane.

(*c*) Here ether is formed by solvomercuration-demercuration process according to Markovnikov addition without rearrangement.

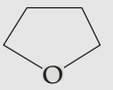
 ;  ; 

[A] [B] [C]

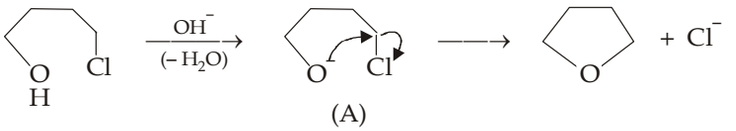
EBD_7089

Example 2 :

Give steps involved in the following reaction.

$$OHCH_2CH_2CH_2CH_2Cl \xrightarrow{OH^-}$$ 

Solution :



(A)

Note that the intermediate (A) acts both as an alkoxide group as well as a halide, hence intramolecular cyclization (Williamson synthesis) takes place forming cyclic compound.

Example 3 :

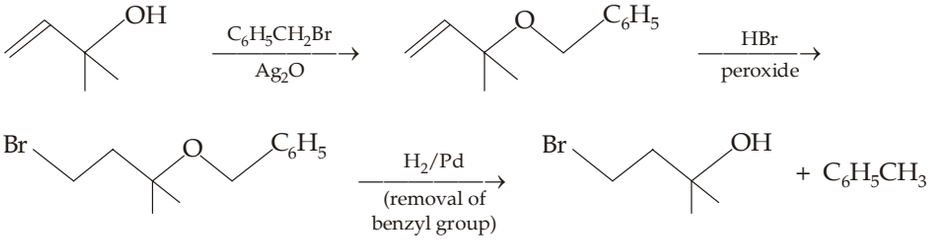
Give necessary steps involved in the following conversions.

(a) $CH_2 = CHC(CH_3)_2OH \longrightarrow BrCH_2CH_2C(CH_3)_2OH$ **(b)** $HOCH_2C \equiv CH \longrightarrow HOCH_2C \equiv CCH_3$

(c) $HOCH_2C(CH_3)_2CH_2Br \longrightarrow HOCH_2C(CH_3)_2CH_2D.$

Solution :

(*a*) Although the reaction involves simply addition of HBr in presence of peroxide, the direct reaction will also involve conversion of allylic —OH group to Br, so OH must first be protected.

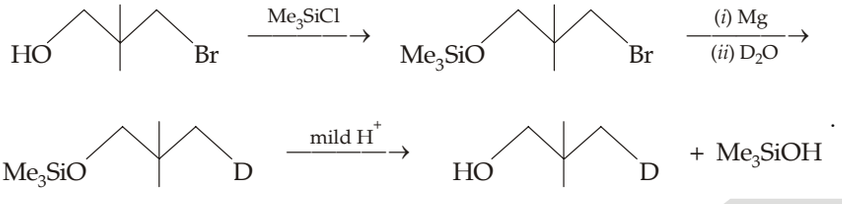


(*b*) Here also CH_3 group can't be directly introduced in place of acetylenic hydrogen atom, because this will lead to conversion of OH to reactive alkoxide ion. Hence OH group must first be protected, here benzyl group can't be used as protecting group because this will lead to reduction of the C ≡ C bond during catalytic hydrogenation required for removing the protecting benzyl group (as in above example). Hence trimethylsilyl group is used for protecting the OH group.

$$HOCH_2C \equiv CH + \underset{\text{Chlorotrimethylsilane}}{M_3SiCl} \xrightarrow{\text{amine base}} Me_3Si{-}OCH_2C \equiv CH$$

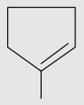
$$\xrightarrow[\text{(ii) } CH_3I]{\text{(i) BuLi}} Me_3Si{-}OCH_2C \equiv CCH_3 \xrightarrow{\text{mild } H^+} Me_3Si{-}OH + HOCH_2C \equiv CCH_3$$

(*c*) Here also OH group must first be protected to avoid its reaction with Grignard reagent formed during main reaction.

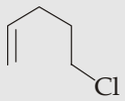


Example 4 :

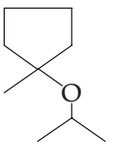
Identify A to D in the following reactions.

(a)  $\xrightarrow[NaBH_4/OH^-]{Hg(OAc)_2\,.\,(CH_3)_2CHOH}$ [A]

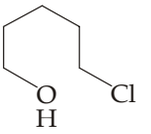
(b)  $\xrightarrow[NaBH_4/OH^-]{Hg(OAc)_2/Phenol}$ [B]

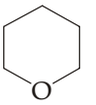
(c)  $\xrightarrow[H_2O_2/OH^-]{BH_3\,.\,THF}$ [C] $\xrightarrow[heat]{NaOH}$ [D]

Solution :


[A]


[B]


[C]

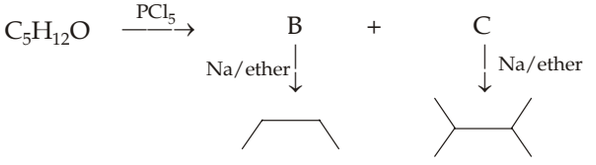

[D]

Example 5 :

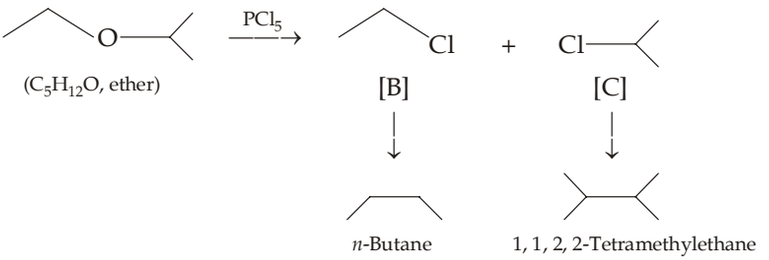
An ether of the molecular formula $C_5H_{12}O$ when treated with phosphorus pentachloride gives two compounds B and C. B when refluxed with metallic sodium in presence of ether gives *n*-butane, while C on similar treatment gives, 1, 1, 2, 2-tetramethylethane. Deduce the structure of A and, explain the formation of hydrocarbons from compounds B and C.

Solution :

In such cases, students are advised to sketch a map of the complete problem as below.



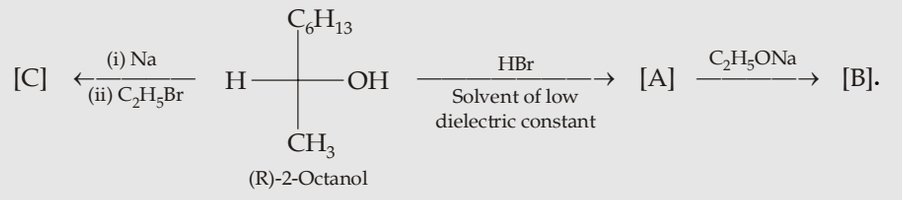
Structures of the hydrocarbons formed indicates that one alkyl group of ether is normal (unbranched) and the other is branched. Since products have 4 + 6 = 10 carbon atoms, it indicates that the chlorides B (having 2 carbon atoms) and C (having 3 carbon atoms) have undergone Wurtz reaction to form higher hydrocarbons. Hence the ether should be $CH_3CH_2OHC(CH_3)_2$.



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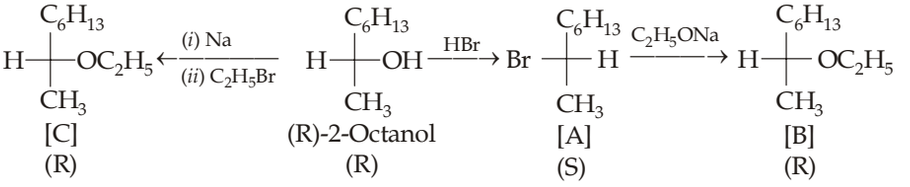
Example 6 :

Complete the following giving importance to configuration of the compounds A, B and C.



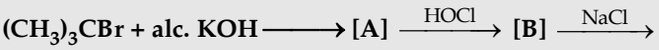
Solution :

In the reaction of alcohol with metallic sodium, since no bond to the chiral carbon is cleaved the product (C) will have R configuration. However, reaction of alcohol with HBr in solvent of low dielectric constant follows S_N2 mechanism, the chiral carbon is inverted, *i.e.* product will have S configuration. Further attack by $C_2H_5O^-$ is also an S_N2 reaction, again inverted product [B] will be obtained. Thus the net result of two inversions is retention of configuration.

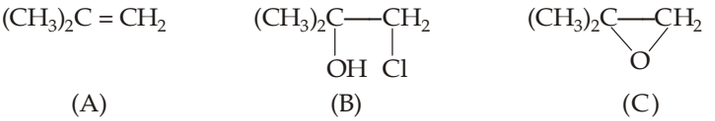


Example 7 :

Supply structures for compounds (A) to (C)

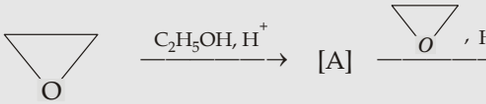


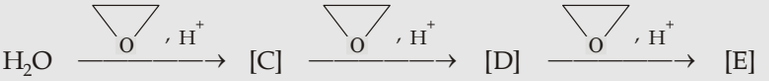
Solution :



Example 8 :

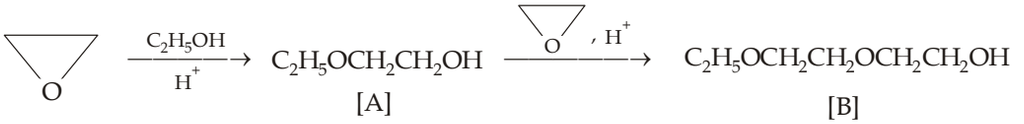
Complete the following reactions and identify the end product in each case ?

(a) 

(b) 

Solution :

All steps of these reactions involve acid-catalyzed cleavage of ethers.

(*a*) 

(*b*) $H_2O \xrightarrow{\text{O}, H^+} \underset{[C]}{HOCH_2CH_2OH} \longrightarrow \underset{[D]}{HOCH_2CH_2—O—CH_2CH_2OH}$

$\longrightarrow HOCH_2CH_2—O—CH_2CH_2—O—CH_2CH_2OH$

Triethylene glycol [E]

Example 9 :

Supply the missing reagent or organic compound in the following series of reactions.

$$CH_3CH—CH_2 \xrightarrow{[A]} [B] \xrightarrow{CH_3I} CH_3CHCH_2C \equiv CCH_3 \xrightarrow{H_2/Pd/BaSO_4} [C].$$

(O; OCH$_3$)

Solution :

Proceed backward from the given structure

$$CH_3CHCH_2C \equiv CCH_3 \xleftarrow{CH_3I} CH_3CHCH_2C \equiv CCH_3 \xleftarrow[[A]]{^-C \equiv CCH_3} CH_3CH—CH_2$$

(OCH$_3$; O$^-$; [B]; O)

$\downarrow H_2/Pd$

cis-$CH_3CHCH_2CH = CHCH_3$

(OCH$_3$)

[C]

Example 10 :

Propose mechanism for the following reaction.

$$ClCH_2 - \overset{14}{CH} - CH_2 \xrightarrow{C_2H_5ONa} H_2C - \overset{14}{CH} - CH_2 - OC_2H_5$$

(O; O)

Solution :

Ethoxide ion attacks the epoxide ring at the primary carbon because it is less hindered.

$$ClCH_2 - \overset{14}{CH} - CH_2 \xrightarrow{^-OC_2H_5} Cl - CH_2 - \overset{14}{CH} - CH_2OC_2H_5 \longrightarrow CH_2 - \overset{14}{CH} - CH_2 - OC_2H_5 + Cl^-$$

(O; O$^-$; O)

Example 11 :

Give necessary steps involved in the conversion of benzene to 1, 2-diphenylethanol through styrene.

Solution :

First, we will have to convert benzene to styrene, $C_6H_5CH = CH_2$

$$C_6H_6 + CH_3CH_2Cl \xrightarrow{AlCl_3} C_6H_5CH_2CH_3 \xrightarrow{NBS} C_6H_5CHBrCH_3 \xrightarrow{\text{alc. KOH}} \underset{\text{Styrene}}{C_6H_5CH = CH_2}$$

$$\xrightarrow{C_6H_5CO_3H} C_6H_5CH—CH_2 \xrightarrow[(ii)\ H_3O^+]{(i)\ C_6H_5MgBr} C_6H_5CH_2CHC_6H_5$$

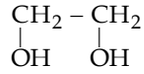
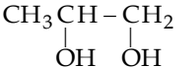
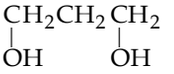
(O; OH)

1, 2-Diphenylethanol



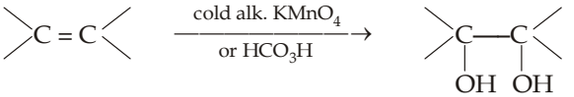
GLYCOLS OR DIOLS

Alcohols containing two hydroxyl groups are commonly called **glycols.** In IUPAC substitutive system, they are named as **diols.**

			
Common Name :	Ethylene glycol	Propylene glycol	Trimethylene glycol
IUPAC Name :	1, 2-Ethanediol	1, 2-Propanediol	1, 3-Propanediol

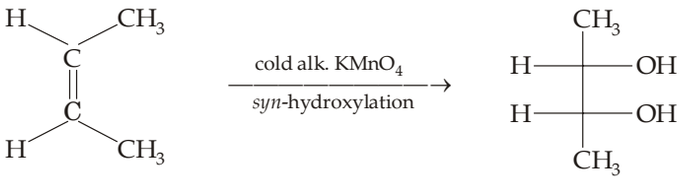
12.9 Preparation

1. Oxidation of alkenes. Of the numerous oxidizing agent that bring about hydroxylation, two of the most commonly used are (*a*) cold alkaline potassium permanganate (also known as *Baeyer's reagent*) and (*b*) peroxy acids, such as performic acid.

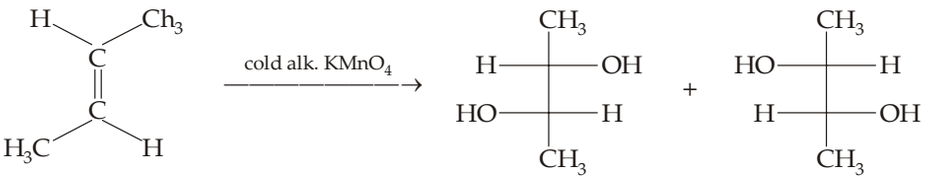


A 1, 2-diol

Hydroxylation with permanganate is carried out by stirring together the alkene and the aqueous permanganate solution, either neutral or better slightly alkaline at room temperature. Mild conditions are the key factors, and thus heat and addition of acid are avoided since these will promote further oxidation of the diol. Permanganate oxidation gives *syn*-hydroxylation. Thus

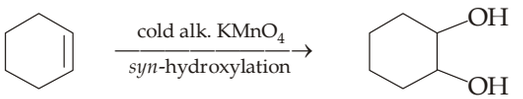


meso-2, 3-Butanediol (M.P. 34°C)



trans-2-Butene

Enantiomers
rac-2, 3-Butanediol (M.P. 19°C)



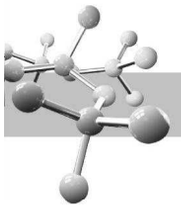
cis-1, 2-Cyclohexanediol

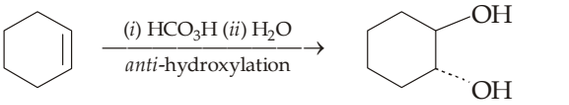
Hydroxylation of alkenes by **means of osmium tetroxide** in presence of hydrogen peroxide also takes place in *cis*-manner.

Hydroxylation with peroxy formic acids is carried out by allowing the alkene to stand with a mixture of hydrogen peroxide and formic acid, for a few hours, and then heating the product with water. Peroxy acids give *anti*-hydroxylation, and thus

$$\textit{cis}\text{-2-Butene} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } HCO_3H} \textit{rac}\text{-2, 3-Butanediol}$$

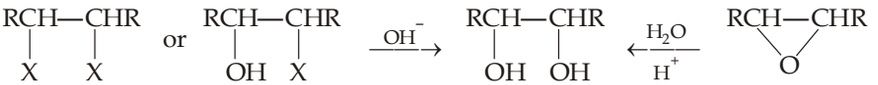
$$\textit{trans}\text{-2-Butene} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } HCO_3H} \textit{meso}\text{-2, 3-Butanediol}$$





trans-1, 2-Cyclohexanediol

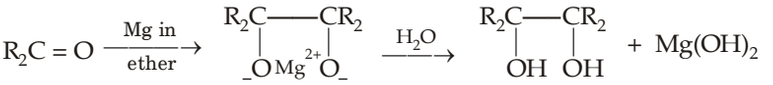
2. By the hydrolysis of alkylene dihalides, halohydrins and epoxides



Recall that hydrolysis of epoxides produces *anti*-hydroxylation.

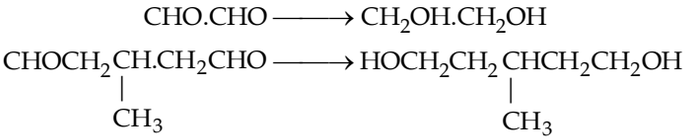
3. By the reduction of carbonyl compounds.

Symmetrical 1, 2-glycols, known as **pinacols,** are prepared by **bimolecular reduction** of aldehyddes or ketones.



A pinacol

Dicarbonyl compounds may be reduced easily to diols by catalytic hydrogenation, by reduction with $NaBH_4$ or $LiAlH_4$.



3-Methyl-1, 5-pentanediol

TEST YOUR UNDERSTANDING - 12.8

1. (*a*) Prepare ethylene glycol from ethanol.

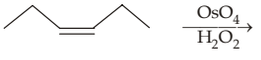
(*b*) Name the reagent used for preparing *cis*- and *trans*-cyclopentene glycol from cyclopentene.

(*c*) Give the structure of the glycol, called a pinacol, obtained by the reductive coupling of each of the following ketone using Mg in ether.

(*i*) CH_3COCH_3, (*ii*) $C_6H_5COCH_3$, (*iii*) $C_6H_5COC_6H_5$.

2. Identify the product obtained in each case.

(*a*) 

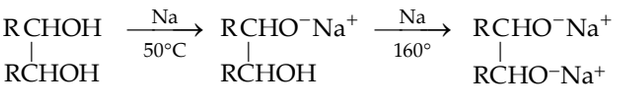
(*b*) 

12.10 Properties

Presence of two hydroxyl groups in glycols provides more sites for *intermolecular hydrogen bonding* than monohydric alcohols. Hence diols are more soluble in water and have much higher boiling and melting points as compared to monohydric alcohols of comparable molecular weights. Due to its very high boiling point and water solubility, ethylene glycol is used in automobiles as an antifreeze.

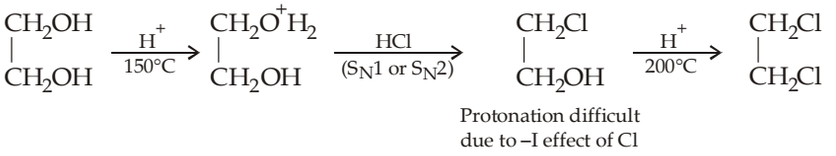
Chemical properties : Diols, *e.g.* ethylene glycol, are expected to exhibit chemical reactions similar to compounds containing two hydroxyl groups. However, when one hydroxyl group has undergone the chemical reaction, it modifies the reactivity of the other group.

1. Acidic nature. The two hydroxyl groups do not react simultaneously, but react one after the other, first —OH is very much reactive than the second. The electron-withdrawing inductive effect of one hydroxyl group makes the other more acidic than the —OH group of a monohydric alcohol ; hence diols react with the sodium metal more quickly. However, the alkoxide ion so formed makes the second —OH group less acidic because of its electron releasing effect, hence it requires higher temperature.

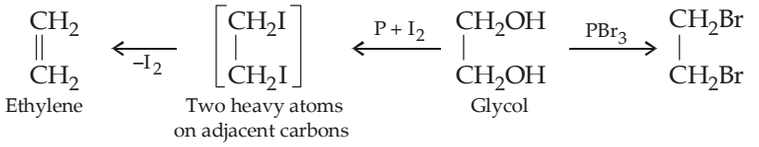


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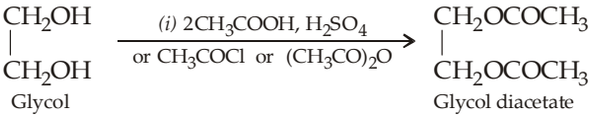
2. Reaction with hydrogen halides. Here also the displacement of the second —OH group by —X is more difficult than that of the first. The halogen atom introduced at first stage reduces electron density on the remaining oxygen due to strong electron withdrawing inductive effect with the result its protonation becomes difficult.



3. Other substitution reactions.



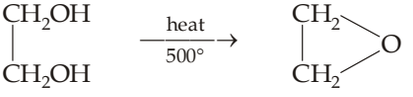
4. Esterification.



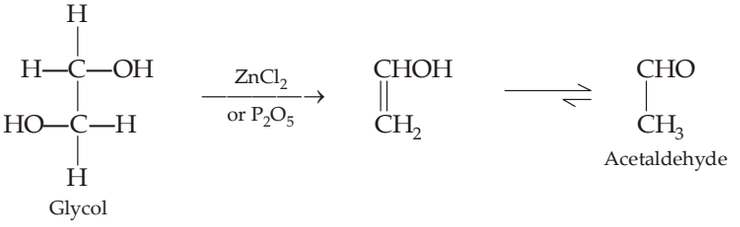
Esterification with terphthalic acid (*p*-HOOC.C_6H_4.COOH) produces a polyester synthetic fibre known as **terylene** or **dacron**, while with phthalic acid (*o*-HOOC.C_6H_4.COOH), polymer known as **glyptal** is produced.

5. Dehydration

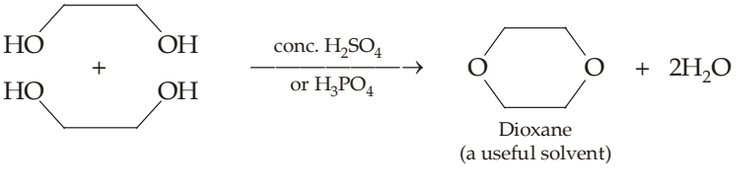
(*i*)



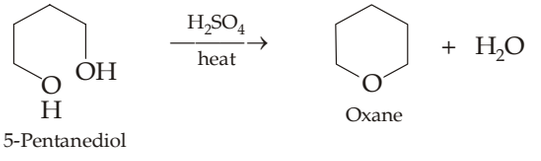
(*ii*)



(*iii*)

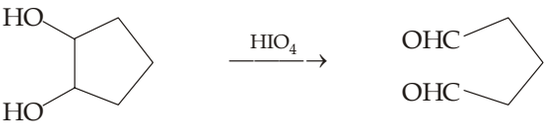


(*iv*) Diols easily undergo intramolecular dehydration to form cyclic ethers when a five-membered or six-membered ring is formed.



6. Oxidation involving carbon-carbon bond fission. 1, 2-Diols, when treated with an aqueous solution of **periodic acid** (H_5IO_6 or $HIO_4.2H_2O$), give aldehydes or ketones.



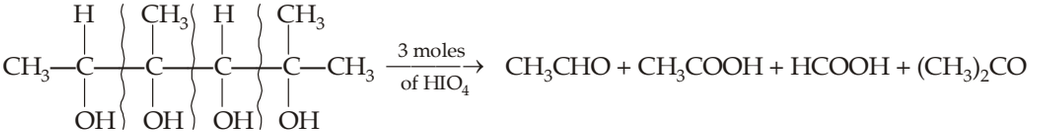


1, 2-Cyclopentanediol 1, 5-Pentanedial

(*i*) A 1° alcohol gives CH_2O, a 2° alcohol gives RCHO, a 3° alcohol gives a ketone.

(*ii*) In case of polyhydric alcohols, one mole of HIO_4 is consumed between every two adjacent hydroxy groups.

(*iii*) An alcholic group, attacked on both sides by HIO_4, is converted into carboxylic acid.

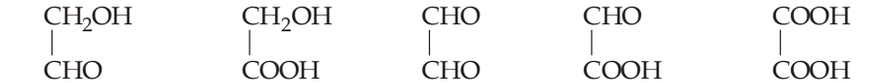


Thus periodic oxidation has been used for determining the structure of compounds by knowing the number of moles of HIO_4 consumed and nature of the product formed. The technique has found its widest application in carbohydrate chemistry.

Lead tetraacetate also oxidises 1, 2-diols to aldehydes and ketones.

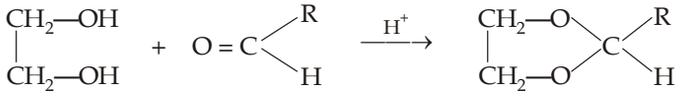


7. Oxidation in which carbon-carbon bond remains intact. Following products have been obtained depending upon the nature of the oxidising agent.

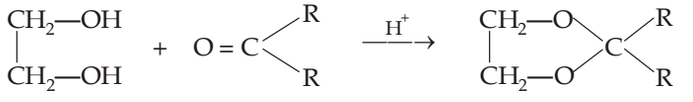


Glycollic aldehyde Glycollic acid Glyoxal Glyoxalic acid Oxalic acid

8. Formation of cyclic acetals (from aldehydes) and ketals (from ketones)

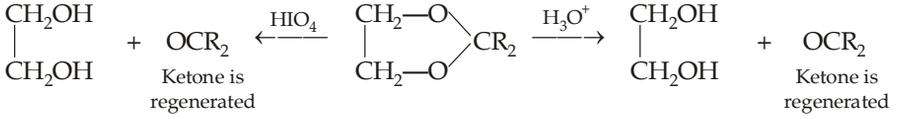


An acetal

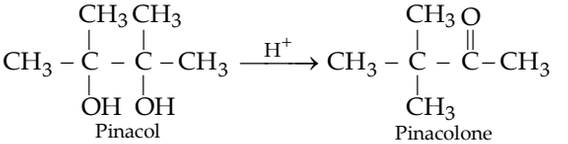


A ketal

These reactions are used in organic synthesis for protecting the carbonyl group. The acetals and ketals are stable in alkaline media whereas the ''rest'' of the molecule can be subjected to desired conversions under these conditions. The carbonyl group is regenerated in the final stage either by the addition of periodic acid to aqueous solution or by acidic hydrolysis.



9. Acid-catalyzed rearrangement of glycols. 1, 2-Diols on treatment with acids rearrange to form carbonyl compounds, the classic example being the acid catalyzed rearrangement of 2, 3-dimethyl -2, 3-butanediol **(pinacol)** into methyl *tert*-butyl ketone **(pinacolone)**. Thus the reaction is commonly known as **pinacol-pinacolone rearrangement.**



Pinacol Pinacolone

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TEST YOUR UNDERSTANDING - 12.9

1. Write down the chemical reactions between following compounds.

(*a*) 1, 3-Butanediol is heated with alumina at 350°C (*b*) 1, 2,-Dimethyl-1, 2-ethanediol is treated with $KMnO_4$

(*c*) 2, 3-Butanediol is treated with acetophenone (*d*) Ethane-1, 2-diol and ethylene oxide are treated in presence of acid

(*e*) 2-Methyl-3-phenylpropanediol is treated with periodic acid.

2. Write down the structures of cyclic acetals derived from

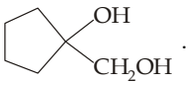
(*a*) 1, 2-Ethanediol and cyclopentanone (*b*) Ethylene glycol and isobutyl methyl ketone

(*c*) Benzaldehyde and 1, 3-propanediol (*d*) 2, 2-Dimethyl-1, 3-propanediol and isobutyl methyl ketone.

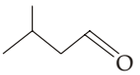
3. Give the products formed and the number of HIO_4 consumed in the reactions of each of the following glycols.

(*a*) $CH_3CHOHCH_2OH$ (*b*) $(CH_3)_2COHCHOHCH_3$

(*c*) $HOCH_2CH_2CH_2OH$ (*d*) $CH_3CHOHC(CH_3)OH.CHOH.COH(CH_3)_2$

(*e*) 

4. Deduce the structure of the following glycol which on oxidation gives following results.

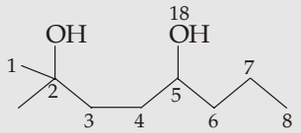
(*a*) $A \xrightarrow{1 \text{ mole } HIO_4}$  $+ \ CH_2O$

(*b*) $B \xrightarrow{2 \text{ moles } HIO_4} C_6H_5CHO + HCOOH + CH_3CHO.$

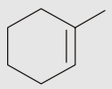
12.11 Illustrative Examples

Example 12 :

Identify the products [A] to [D], and explain your answer.

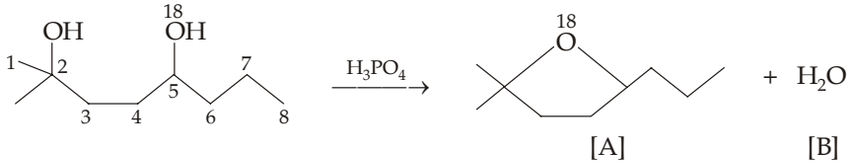
(a) 

$\xrightarrow{H_3PO_4}$ [A] + [B]

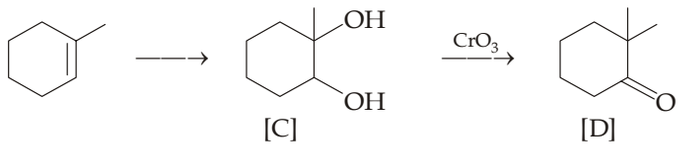
(b)  $\xrightarrow{\text{alk. } KMnO_4}$ [C] $\xrightarrow{CrO_3/\text{glacial } CH_3COOH}$ [D]

Solution :

(*a*) Note that the two OH groups are different, C_2—OH is 3° (more basic) and hence behaves as a base while C_5—OH is 2° (less basic than 3° alcoholic OH) and hence behaves as an acid. Thus during intramolecular dehydration H from C_5—OH and OH from C_2—OH will be eliminated as water. Consequently O^{18} will appear in the cyclic ether, and not in water.



(*b*)

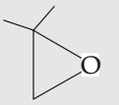
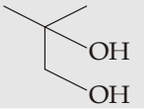


In compound [C], only 2° alcohol group is oxidised, the second OH group being 3° is resistant to oxidation.

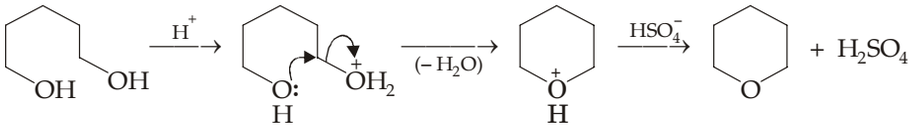
Example 13 :

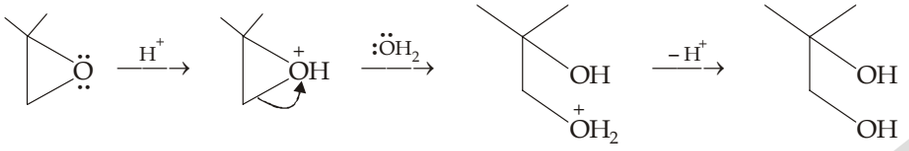
Give steps involved in the following reaction.

(a) $CH_2CH_2CH_2CH_2CH_2$ (OH, OH) $\xrightarrow[\text{heat}]{H_2SO_4}$ 

(b)  $\xrightarrow{H^+}$ 

Solution :

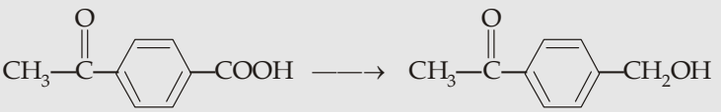
(*a*) 

(*b*) 

Example 14 :

How will you carry out following transformations ?

(a) $CH_3COCH_2CH_2C \equiv CH \longrightarrow CH_3COCH_2CH_2C \equiv CCH_3$

(b) 

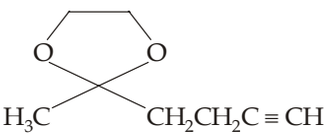
Solution :

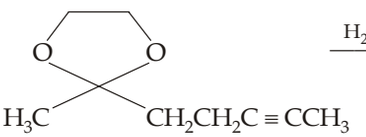
(*a*) Here it is not possible to directly convert —C ≡ CH to —C ≡ CCH_3 by means of $NaNH_2$ followed by CH_3I because of following reasons.

(*i*) The carbonyl group in the given acetylenic compound will not tolerate the strongly basic reagent ($NaNH_2$).

(*ii*) The carbonyl group will react with the carbanion, formed at first step.

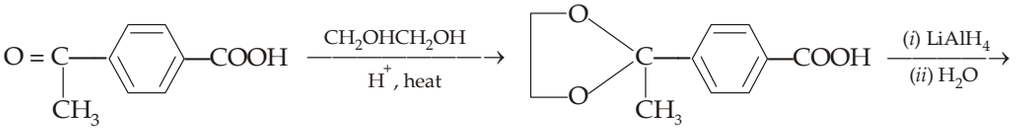
Hence it becomes necessary to protect the carbonyl group by acetal formation which can easily be removed at the desired stage by acidic hydrolysis.

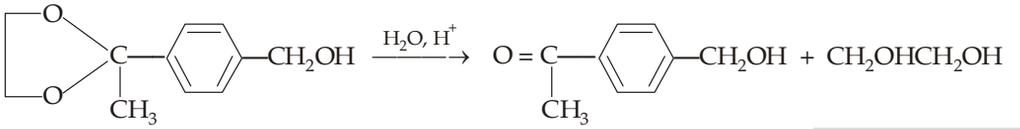
$CH_3COCH_2CH_2C \equiv CH \xrightarrow[H^+]{HOCH_2CH_2OH}$ 

$\xrightarrow[(ii)\ CH_3I]{(i)\ NaNH_2,\ NH_3}$  $\xrightarrow{H_2O,\ HCl}$ $CH_3COCH_2CH_2C \equiv CCH_3$

5-Heptyn-2-one

(*b*) Direct reduction of —COOH will also reduce —$COCH_3$ group, hence latter should first be protected by reaction with ethylene glycol.







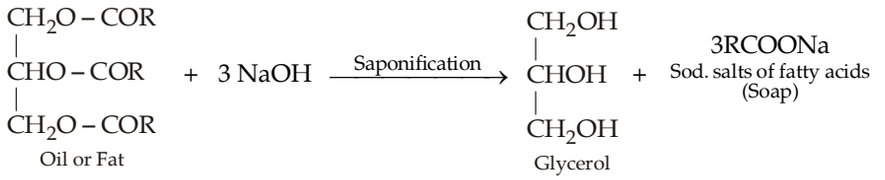
TRIHYDRIC ALCOHOLS OR TRIOLS

12.12 Glycerol

12.12.1 Preparation of Glycerol

The simplest and most important trihydric alcohol is **propane-1, 2, 3-triol,** commonly known as **glycerol.**

It is present in all oils and fats which are esters of glycerol (alcohol) with higher fatty acids, *e.g.* palmitic, stearic and oleic acids. Oils and fats are industrially used for the manufacture of **soaps** and **candles,** glycerol is obtained as a by product in each case. (*a*) In soap manufacture, oils are hydrolysed in presence of alkali (NaOH), (*b*) while in candle industry, oils are hydrolysed with steam.

(*a*)


(where R = $C_{15}H_{31}$, $C_{17}H_{33}$ or $C_{17}H_{35}$; R may be similar or different)

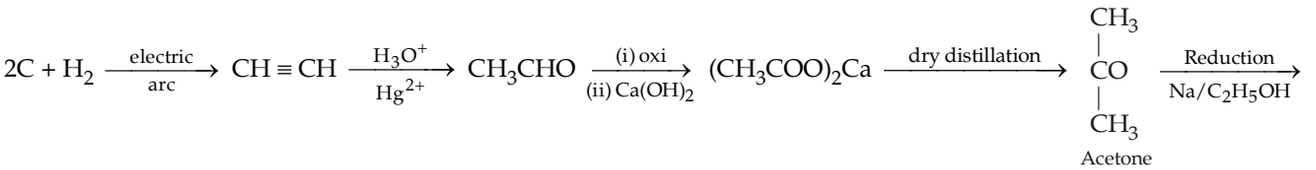
Filtrate after removing soap contains mainly glycerol and known as **spent lye** (app. 5% glycerol)

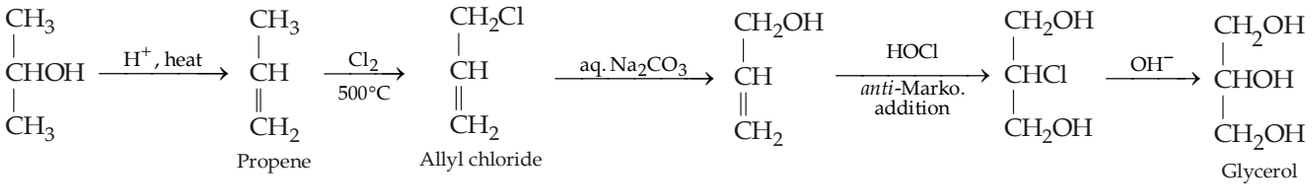
(*b*) Oil $\xrightarrow{\text{steam}}$ Fatty acids + Glycerol

Fatty acids are removed and mixed with paraffin wax to get candles. Product obtained after removing fatty acids mainly contains glycerol, and known as **sweet water.**

Glycerol from fermentation of sugars. Glycerol is also obtained as a by-product during alcoholic fermentation ; the yield of glycerol can be considerably improved by adding sodium sulphite.

Synthetic glycerol. Now-a-days, glycerol is mainly obtained from propene which is either synthesized from elements (carbon and hydrogen) or obtained as one of the products of cracking of petroleum.



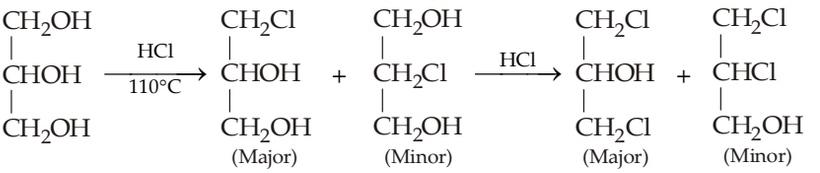


12.12.2 Properties of Glycerol

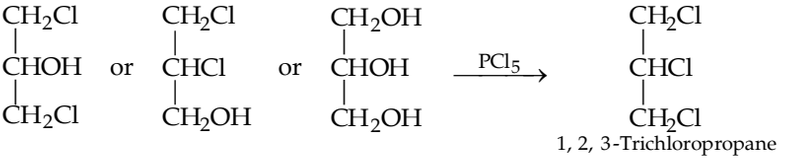
It is a colourless, viscous liquid boiling at 290° with decomposition. It is miscible, in all proportions, with water due to availability of three hydroxyl groups for H-bonding with water. Glycerol gives chemical reactions, typical to that of a primary and secondary alcohol.

1. **Reaction with metals.** At low temperature it forms monosodium salt, and at higher temperature it forms disodium salt (both 1° alcohols have reacted). Trisodium salt is generally not formed.

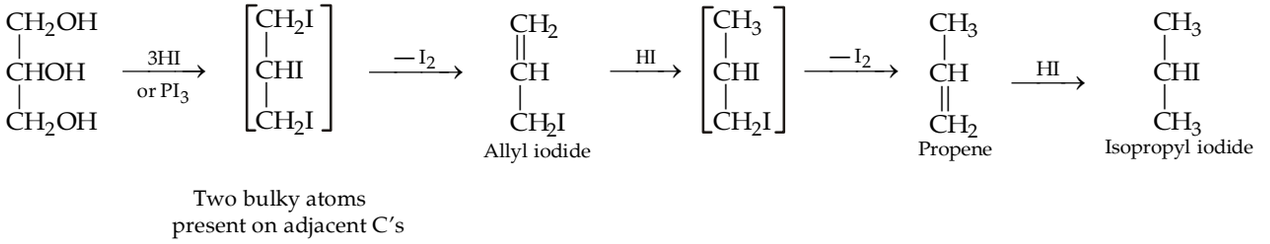
2. Reaction with hydrogen halides.



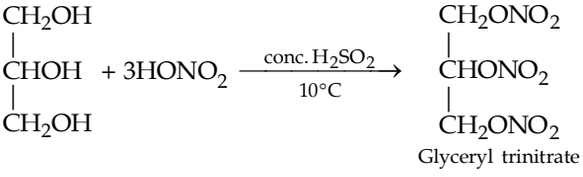
Low reactivity of the 2° alcoholic group is due to —I effect of the two 1° alcoholic group or chlorine and OH group which decrease the electron density on oxygen at 2-position, required for protonation. Either of the dichloro derivative or even glycerol, when treated with PCl_5 gives 1, 2, 3-trichloropropane.



3. Reaction with hydroiodic acid (a very strong acid).



4. Reaction with conc. HNO_3 in presence of conc. H_2SO_4

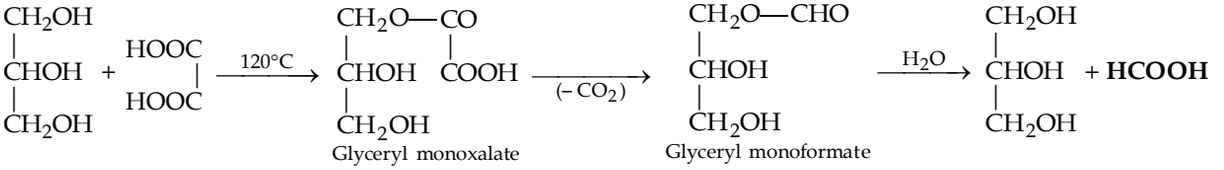


Remember that **glyceryl trinitrate is an ester,** and not a nitro compound, although commonly but wrongly named as trinitroglycerine, TNG. Glyceryl trinitrate is a highly poisonous oil and explodes violently when detonated. Due to its high sensitivity, its transportation is very hazardous task. However, Alfred Nobel discovered that this oil can be transported easily when adsorbed on keiselguhr ; glyceryl trinitrate adsorbed on keiselguhr was called **dynamite**, a patent registered by Alfred Nobel. **Cordite** (smokeless powder) is a mixture of glyceryl trinitrate, gun cotton (cellulose nitrate) and vaseline. **Blasting gelatine** is a mixture of glyceryl trinitrate with gum cotton.

Glycerol reacts with acetic anyhydride or acetyl chloride to form **glyceryl triacetate (triacetin).**

5. Reaction with oxalic acid

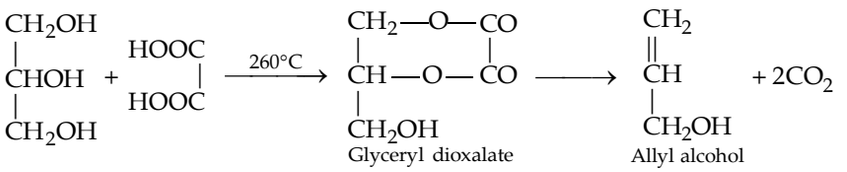
(*a*) *At low temperature (120°)*



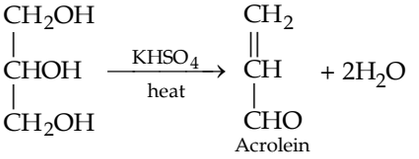
The overall reaction of glycerol with oxalic acid at low temperature (120°C) appears to be **conversion of oxalic acid to formic acid** with glycerol as a catalyst.

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(*b*) *At high temperature (260°C).* Allyl alcohol is the main product.

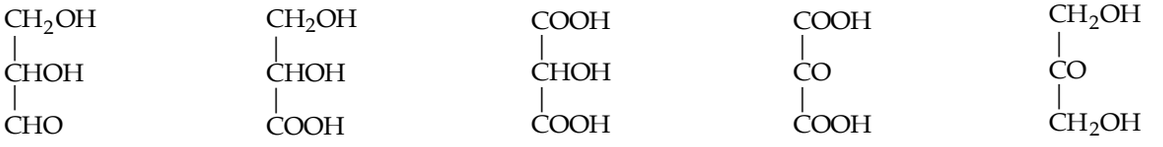


6. Dehydration



7. Oxidation

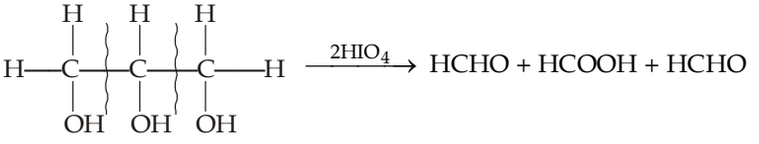
Various oxidation products of glycerol are



Glyceraldehyde | Glyceric acid | Tartronic acid | Mesoxalic acid | Dihydroxyacetone

Equimolar mixture of glyceraldehyde and dihydroxyacetone, called **glycerose,** is obtained by the oxidation of glycerol with bromine water or Fenton's reagent.

Periodic oxidation of glycerol forms two moles of formaldehyde and one mole of formic acid by consuming two mole of periodic acid.



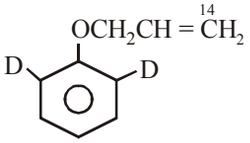
8. Reduction

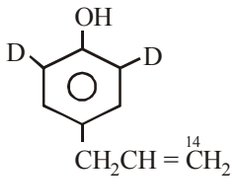
Glycerol when heated strongly with phosphorus and HI gives propane, $CH_3CH_2CH_3$.

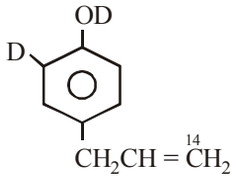
EXERCISE 12.1 (MCQ - ONE option correct)

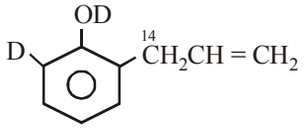
1. IUPAC name of the compound 

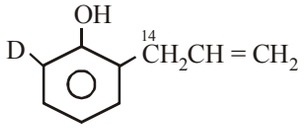
(*a*) 3-Cyclohexenyl isopropyl ether
(*b*) 2-Cyclohexenyl isopropyl ether
(*c*) Isopropoxycyclohexene-2
(*d*) Isopropoxycyclohexene.

2.  $\xrightarrow{heat}$ X ; X is

(a) 

(b) 

(c) 

(d) 

3. Identify the compound Y in the following reactions.

$CH_3CH_2CH_2CH_2OH \xrightarrow{conc.\ H_2SO_4} [X] \xrightarrow[H_2SO_4]{CH_3OH} Y$

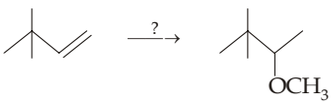
(*a*) $CH_3CHOHCH_2CH_3$ (*b*) $HOCH_2CH_2CH_2CH_3$
(*c*) $CH_3OCH_2CH_2CH_2CH_3$ (*d*) $CH_3CH(OCH_3)CH_2CH_3$.

4. Which of the following can be prepared by the typical Williamson reaction ?
(*a*) R_3COCR_3 (*b*) ArOAr
(*c*) RCH = CHOCH = CHR′ (*d*) none of the three.

5. Di-*tert*-butyl ether can be obtained by
(*a*) Williamson synthesis
(*b*) by dehydration of Me_3COH
(*c*) both (*a*) and (*b*)
(*d*) None of the two.

6. Benzyl ethyl ether can be prepared by which combination of components ?
(*a*) $C_6H_5CH_2Br + C_2H_5ONa$ (*b*) $C_6H_5CH_2ONa + C_2H_5Br$
(*c*) both (*a*) and (*b*) (*d*) $C_6H_5CH_2OH + C_2H_5OH$.

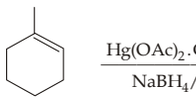
7. Following reaction can be carried out in three different ways

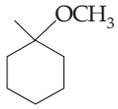
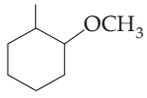


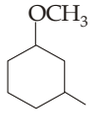
Use of which of the following reagents will give best result ?
(*a*) (*i*) H_3O^+, (*ii*) Na, (*iii*) CH_3Br
(*b*) $Hg(OAc)_2.THF.H_2O$, (*ii*) $NaBH_4/OH^-$, (*iii*) Na, (*iv*) CH_3Br
(*c*) (*i*) $BH_3.THF/H_2O_2$, OH^- (*ii*) Na (*iii*) CH_3Br
(*d*) None of the above.

8. Which of the following ether will form hydroperoxide easily ?
(*a*) *n*-propyl ether (*b*) *iso*-propyl ether (*c*)
Both (*d*) None.

9. Identify A in the following reactions

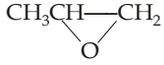


(*a*)  (*b*)  (*c*)

Both (*a*) and (*b*) (*d*) 

10. Identify the nature of (B)

$CH_3CH = CH_2 \xrightarrow{Cl_2, H_2O} [A] \xrightarrow{aq.\ NaOH} B$

(*a*) $CH_3CHOH.CH_2OH$ (*b*) $CH_2Cl.CHOH\,CH_2OH$
(*c*) $CH_2OH\,CHOHCH_2OH$ (*d*) 

11. Which of the following is an example of acid cleavage of ethylene oxide ?
(*a*) Reaction of ethylene oxide with methanol in presence of a little sulphuric acid
(*b*) Reaction of ethylene oxide with methanol in presence of a little amount of sodium methoxide.
(*c*) Reaction of ethylene oxide with methylamine
(*d*) None of the three.

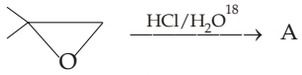
12. Following two compounds are isomers



(I) (II)

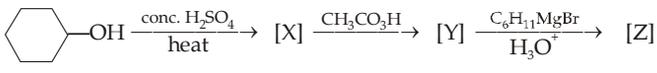
What is true about their enthalpies of combustion ?
(*a*) Both have equal enthalpies of combustion
(*b*) Enthalpy of combustion of I > II
(*c*) Enthalpy of combustion of II > I
(*d*) It can't be predicted.

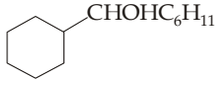
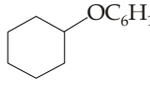
13. Identify the nature of the compound (A)

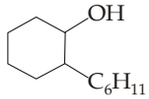


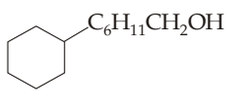
(*a*) $(CH_3)_2C(OH).CH_2O^{18}H$
(*b*) $(CH_3)_2C(O^{18}H)CH_2OH$
(*c*) $(CH_3)_2C(O^{18}H)CH_2O^{18}H$
(*d*) $(CH_3)_2C(OH)CH_2OH$.

14. Identify the end product in the following reaction.



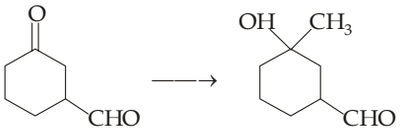
(*a*)  (*b*)  (*c*)



(*d*) 

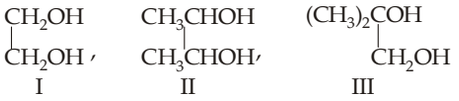
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15. Following conversion can be carried out by which sequence of reagents ?



(*a*) $1CH_3MgI, H_3O^+$
(*b*) $2CH_3MgI, H_3O^+$
(*c*) $(CH_2OH)_2, CH_3MgI, H_3O^+, H^+$
(*d*) Not possible.

16. Arrange the following glycols in order of decreasing rate of oxidation with periodic acid.



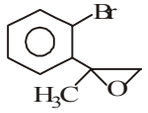
(*a*) I > II > III
(*b*) II > III > I
(*c*) III > II > I
(*d*) All will be oxidised at the same rate.

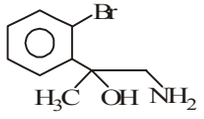
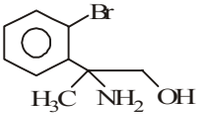
17. Identify the end product in the following reaction.

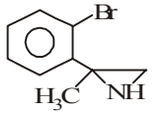
$$2(CH_3)_2CO \xrightarrow[(ii)\ H_3O^+]{(i)\ Mg} [A] \xrightarrow{HIO_4} [B]$$

(*a*) $(CH_3)_3COH$ (*b*) $(CH_3)_2C = CH_2$ (*c*) $2(CH_3)_2CO$ (*d*) Reaction not feasible.

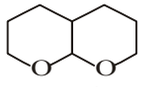
18. The compound which is not isomeric with diethyl ether is
(a) n-propylmethyl ether (b) butanol-1
(c) 2-methylpropanol (d) Butanone

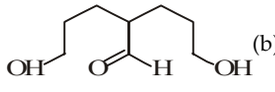
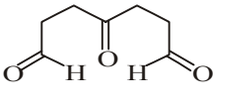
19.  $\xrightarrow{NH_3/CH_3OH}$ A, A is

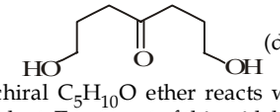
(a)  (b) 

(c)  (d) None of these

20. Hydrolysis product of given compound is

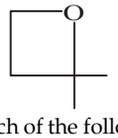


(a)  (b) 

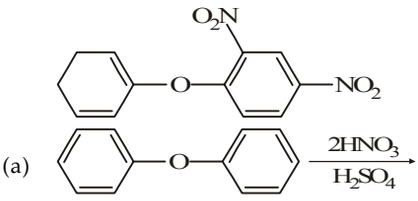
(c)  (d) No hydrolysis

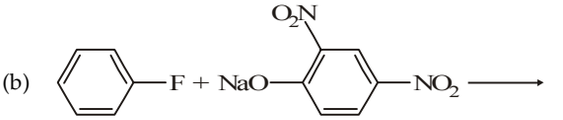
21. A chiral $C_5H_{10}O$ ether reacts with hot HI to give a $C_5H_{10}I_2$ product. Treatment of this with hot KOH in ethanol produces 1, 3-pentadiene. What is the structure of the original ether ?

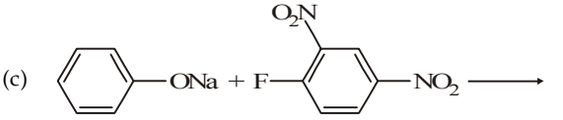
(a)  (b) 

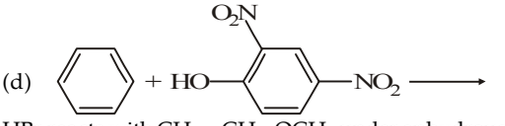
(c)  (d) 

22. Which of the following would work best for the synthesis of the ether shown below ?

(a) 

(b) 

(c) 

(d) 

23. HBr reacts with $CH_2 = CH - OCH_3$ under anhydrous conditions at room temperature to give
(a) $BrCH_2 - CH_2 - OCH_3$ (b) $H_3C - CHBr - OCH_3$
(c) CH_3CHO and CH_3Br (d) $BrCH_2CHO$ and CH_3OH

24. Anisole is treated with HI under two different conditions.

$$C + D \xleftarrow{HI(g)} C_6H_5OCH_3 \xrightarrow{conc.\ HI} A + B$$

The nature of A to D will be
(a) A and B are CH_3I and C_6H_5OH, while C and D are CH_3OH and C_6H_5I
(b) A and B are CH_3OH and C_6H_5I, while C and D are CH_3I and C_6H_5OH
(c) Both A and B as well as both C and D are CH_3I and C_6H_5OH
(d) A and B are CH_3I and C_6H_5OH, while there is no reaction in the second case.

25. $$Products(P_2) \xleftarrow{anhy.\ HI} (CH_3)_3C - O - CH_3 \xrightarrow{conc.\ HI} Products\ (P_1)$$

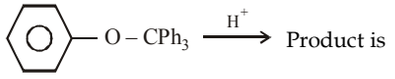
The products P_1 and P_2 respectively are
(a) $(CH_3)_3COH + CH_3I$ and $(CH_3)_3CI + CH_3OH$
(b) $(CH_3)_3CI + CH_3OH$ and $(CH_3)_3COH + CH_3I$
(c) $(CH_3)_3CCI + CH_3OH$ in both cases
(d) CH_3I and $(CH_3)_3COH$ in both cases

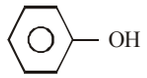
26. *tert*-Butyl ethyl ether can't be prepared by which reaction?
(a) *tert* – Butanol + ethanol $\xrightarrow{H^+}$
(b) *tert*-Butyl bromide + sodium ethoxide →
(c) Sodium *tert*-butoxide + ethyl bromide →
(d) Isobutene + ethanol $\xrightarrow{H^+}$

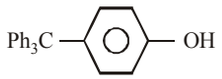
27. 

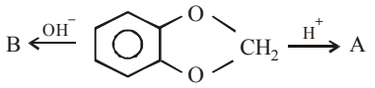
Here X and Y respectively are
(a) $CH_2 - CHCH_3$ (OCH$_3$, OH) and $HOCH_2 - CHCH_3$ (OCH$_3$)
(b) $HOCH_2 - CHCH_3$ (OCH$_3$) and $CH_2 - CHCH_3$ (OCH$_3$, OH)
(c) $CH_2 - CHCH_3$ (OCH$_3$, OH) in both cases
(d) $HOCH_2 - CHCH_3$ (OCH$_3$) in both cases

28. Predict the product in the following reaction



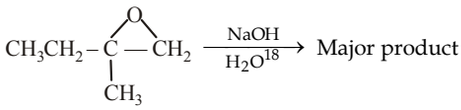
(a)  (b) Ph_3COH

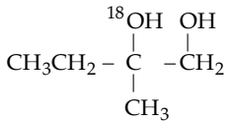
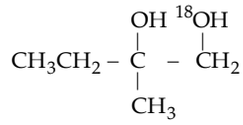
(c)  (d) All the three

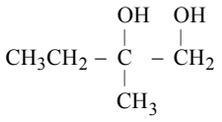
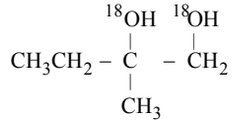
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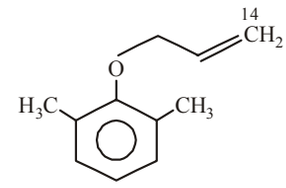
A and B are

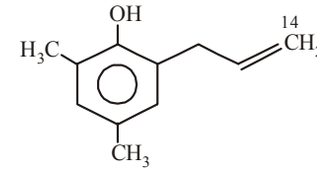
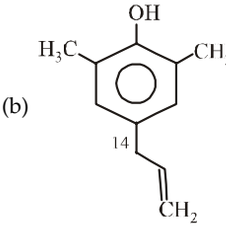
	A	B
(a)	Catechol + Methanal	Catechol + Methanal
(b)	Catechol + Methanal	Sodium salt of catechol + Methanal
(c)	No reaction	Catechol + Methanal
(d)	Catechol + Methanal	No reaction

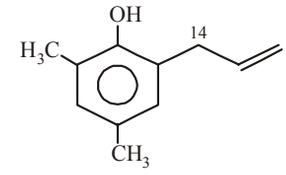
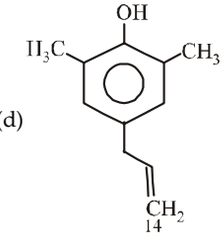
30. 

(a)  (b) 

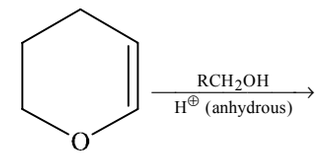
(c)  (d) 

31. 

(a)  (b) 

(c)  (d) 

32. The major product of the following reaction is



(a) a hemiacetal (b) an acetal

(c) an ether (d) an ester

EXERCISE 12.2 (MCQ 1 or >1 option correct, Passage based, Matching, A/R)

DIRECTIONS for Q. 1 to Q.15 : Multiple choice questions with one or more than one correct option(s).

1. Which of the following statement is true ?

(*a*) Ethers are soluble in water

(*b*) Ethers are soluble in alcohols

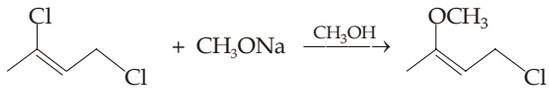
(*c*) Alcohols are soluble in ethers

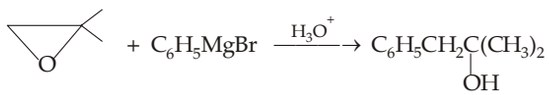
(*d*) All alcohols are soluble in water

2. Which of the following reaction is not possible ?

(*a*) $C_6H_5OH + HBr \longrightarrow C_6H_5Br + H_2O$

(*b*) $(CH_3)_3CCl + NaOCH_3 \longrightarrow (CH_3)_3COCH_3 + NaCl$

(*c*) 

(*d*) 

3. Which of the following statements about ethers are correct?

(a) Peroxide is obtained in the presence of air

(b) Ethers are weakly acidic

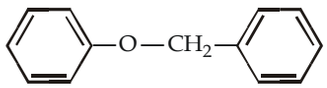
(c) Ethers form oxonium salts

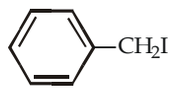
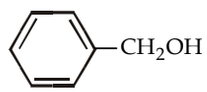
(d) Ethers form stable complexes with Lewis acids

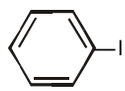
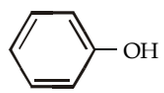
4. Diethyl ether reacts with

(a) sulphuric acid (b) hydrochloric acid

(c) acetic acid (d) hydroiodic acid

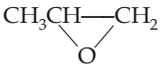
5. The ether  when treated with HI produces

(a)  (b) 

(c)  (d) 

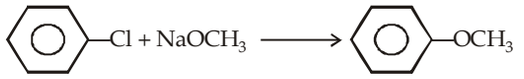
6. C_3H_6O(A) does not reduce Tollen's reagent, does not give iodoform test, but reacts with HI. A can be :

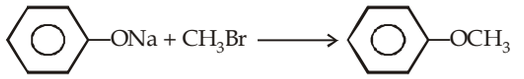
(a) CH_3COCH_3 (b) CH_3CH_2CHO

(c) $CH_2 = CH - O - CH_3$ (d) 

7. Which of the following reaction are feasible?

(a) $CH_3CH_2-C(CH_2CH_3)_2-Br + OH^- \xrightarrow[CH_3OH]{25^\circ C} CH_3CH_2-C(CH_2CH_3)_2-OH$

(b) 

(c) 

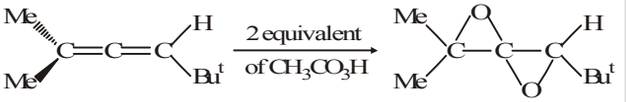
(d) $CH_3-C(CH_3)_2-ONa + CH_3Br \longrightarrow CH_3-C(CH_3)_2-O-CH_3$

8. The reaction products of $C_6H_5OCH_3 + HI \xrightarrow{\Delta}$ is :
(a) C_6H_5OH (b) CH_3I
(c) C_6H_5I (d) CH_3OH

9. Select the correct statement(s) :
(a) Methoxyethane gives iodoethane with one equivalent of anhydrous HI
(b) Order of basicity in aqueous medium is $MeNH_2 < Me_2NH < Me_3N$
(c) Optically active alkanol will show total retention of configuration during its reaction with $SOCl_2$
(d) S-2-Bromobutane gives R-2-methylbutane nitrile with AgCN as major product

10. Compound (x) C_3H_6O decolorises bromine water, with dil. H_2SO_4 it undergoes hydrolysis to give (y) and (z). The correct statements are :
(a) (x) is an ether
(b) (x) is an alkene
(c) (x) is cyclic compound
(d) Both (y) and (z) are crbonyl compounds

11. Choose the correct statement(s) regarding to the product formed in the reaction given below (–Bu^t stands for tertiary butyl group)



Epoxidation at double bond takes place one by one
(a) the final product formed does not contain plane of symmetry
(b) the initial attack takes place on more substituted double bond from the least hindered side
(c) the mono-epoxide obtained in (b) undergoes further epoxidation more rapidly than the first epoxidation.
(d) the final product contains two fold axis of symmetry

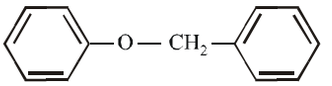
12. The reaction of $CH_3CH=CH-C_6H_4-OH$ with HBr gives

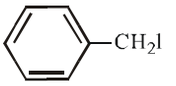
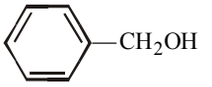
(a) $CH_3CHBrCH_2-C_6H_4-OH$

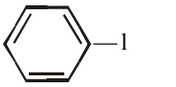
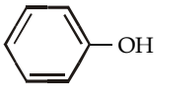
(b) $CH_3CH_2CHBr-C_6H_4-OH$

(c) $CH_3CHBrCH_2-C_6H_4-Br$

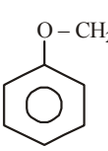
(d) $CH_3CH_2CHBr-C_6H_4-Br$

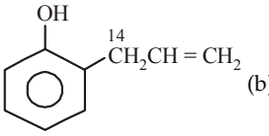
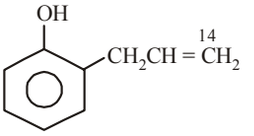
13. The ether  when treated with HI produces

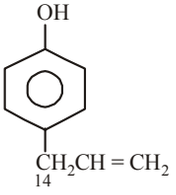
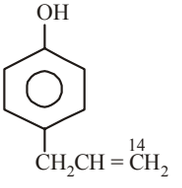
(a)  (b) 

(c)  (d) 

14. Which of the following combination can't be used for preparing an ether ?
(a) $C_6H_5OH + (CH_3)_2SO_4$
(b) $C_6H_5Br + CH_3CH_2OH$
(c) $p\text{-}NO_2C_6H_4Br + CH_3CH_2OH$
(d) $C_6H_5OH + (CH_3)_3CBr$

15.  $\xrightarrow{200^\circ}$ P. Product (P) may be

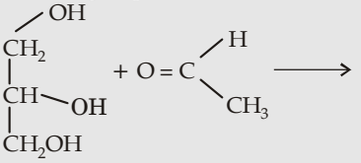
(a)  (b) 

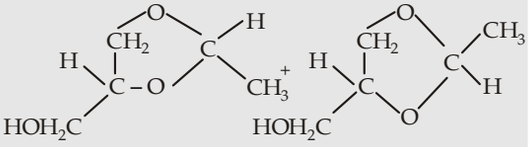
(c)  (d) 

DIRECTIONS for Q. 16 to Q. 30 : Read the following passages and answer the questions that follows :

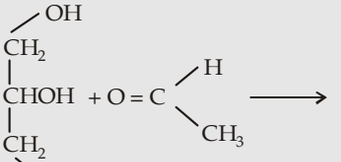
PASSAGE 1

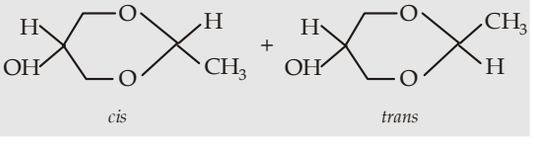
Cyclic acetal may be formed by the reaction of CH_3CHO (a) with the 1- and 2- OH groups, and (b) with 1- and 3- OH groups.





cis *trans*





cis *trans*

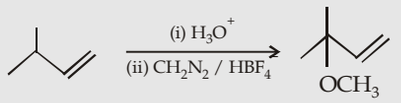
16. Total number of compounds formed in the first reaction is
(a) 1 (b) 2 (c) 3 (d) 4

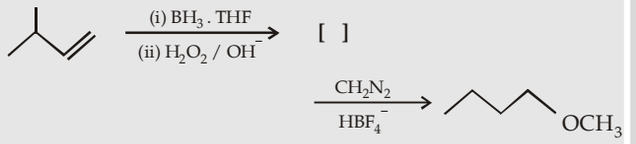
17. The total number of compounds formed in the second reaction is
(a) 1 (b) 2 (c) 3 (d) 4

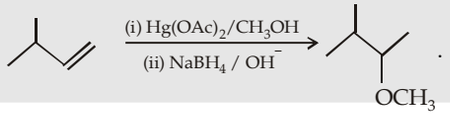
18. The mixture of both of the reactions can be separated to give ..... compounds.
(a) 3 (b) 4 (c) 5 (d) 6

PASSAGE 2

3-Methylbutene is converted to ethers via following three different routes.

(*a*) 

(*b*) 

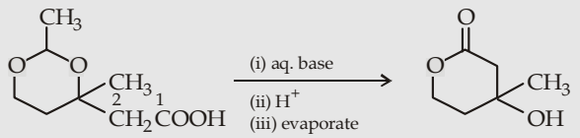
(*c*) 

19. The set of reactions in (a) involve
(a) Markownikoff addition
(b) Rearrangement of carbocation
(c) Both
(d) Oxidation

20. The set of reactions in (b) involve
(a) Anti-Markownikoff addition
(b) Hydroboration-oxidation
(c) No rearrangement
(d) All the three

21. The set of reactions in (c) involve
(a) Markownikoff addition (b) no rearrangement
(c) Both (d) None

PASSAGE 3



Acetals are resistant to base, while these are hydrolysed to acids to aldehydes and diols.

22. The functional groups present in the reactant and product are

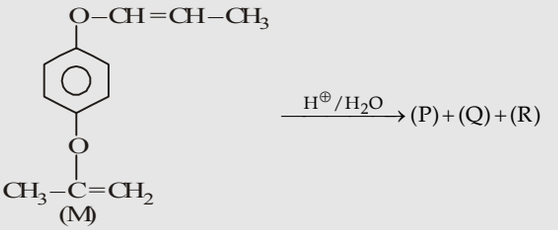
	Reactant	**Product**
(a)	ether, carboxylic acid	cyclic ketone, ether
(b)	hemiacetal, carboxylic acid	lactone, 3° alcohol
(c)	acetal, carboxylic acid	cyclic ester, 3° alcohol
(d)	diether, carboxylic acid	ether, ketone, 3° alcohol

23. Conversion of reactant to product involves
(a) hydrolysis and cyclisation
(b) hydrolysis and esterification
(c) Both (a) and (b)
(d) Hydrolysis and dehydration

24. What is the fate of C_1 of the reactant, when it converts into product?
(a) It will appear in the form of – C – OH
(b) It will appear in the form of C = O
(c) It will be removed as CO_2
(d) It will be appearing in the α-position to C = O group

PASSAGE 4

Observe the following reaction

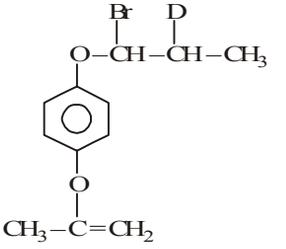


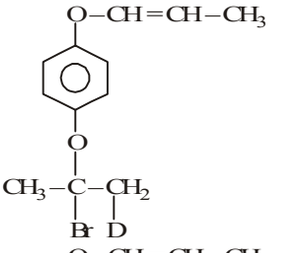
the product P shows positive test towards neutral $FeCl_3$, Q towards $I_2/\overset{\ominus}{O}H$ and R towards Fehling solution.

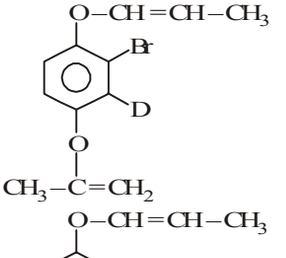
25. 'P' on reaction with bromine water followed by Zn dust gives a substituated benzene which was [X], number of halogens in X is
(a) 2 (b) 3
(c) 4 (d) 5

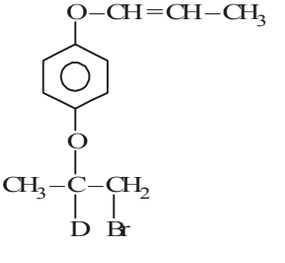
26. Q and R respectively are
(a) $CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$, CH_3COCH_3
(b) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$, CH_3CH_2CHO
(c) $CH_3-\overset{\overset{O}{\|}}{C}-C_2H_5$, CH_3CHO
(d) $CH_3-\overset{\overset{O}{\|}}{C}-H$, $CH_3\overset{\overset{O}{\|}}{C}CH_3$

27. M $\xrightarrow{DBr\ (Anhydrous)\ 1\ eq.}$ Product is

(a) 

(b) 

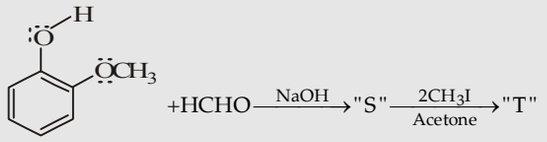
(c) 

(d) 

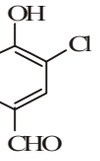
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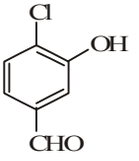
PASSAGE 5

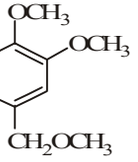
Read and observe the following sketch of organic transformation carefully and then answer the questions given below :

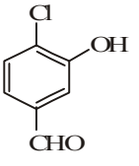


28. The structure of 'T' is :

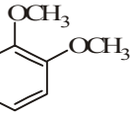
(a) 

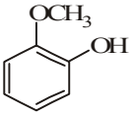
(b) 

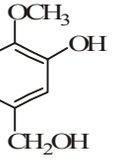
(c) 

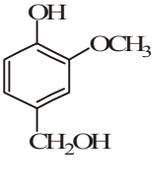
(d) 

29. The structure of 'S' is

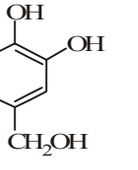
(a) 

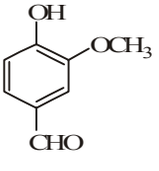
(b) 

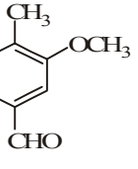
(c) 

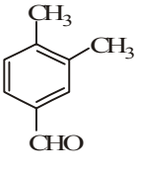
(d) 

30. If 'T' is treated with H_3O^+ the compound formed is

(a) 

(b) 

(c) 

(d) 

DIRECTIONS for Q. 31 & Q. 33 : The following questions are matching type questions. Match Column I with Column II

31.

Column I **(Reactant)**		*Column II* **(Product)**
(A) Glycerol	(a)	Glycerol
(B) Acetone	(b)	Acetone
(C) Dimethylcadmium	(c)	Chloroform
(D) Propene	(d)	Methanoic acid

32.

Column I **(Conversion of glycerol to)**		*Column II* **(Reagent required)**
(A) Methanal	(a)	Oxalic acid
(B) Formic acid	(b)	P + HI
(C) Propene	(c)	Periodic acid
(D) Propane	(d)	HI

33. Match the column :

Column-I		**Column-II**
A. $C_6H_5OCH_3 \xrightarrow{HI,\ 100°C}$	(a)	CH_3CH_2I
B. $C_6H_5CH_2OCH_3 \xrightarrow[100°C]{HI\ (1\ mole)}$	(b)	C_6H_5OH
C. $CH_3CH_2OCH_3 \xrightarrow[100°C]{HI\ (1\ mole)}$	(c)	$C_6H_5CH_2I$
D. $CH_3CH_2OCH_2CH_3 \xrightarrow{HI,\ 100°C}$	(d)	CH_3I

Instructions for Q. 34 to 41 : Following questions are Assertion and Reasoning Type Questions :

Note : Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 5 choices (a), (b), (c), (d) and (e) out of which ONLY ONE is correct.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement -1 is True, Statement-2 is False.
(d) Statement -1 is False, Statement-2 is True.
(e) Statement -1 is False, Statement-2 is False.

34. **Statement 1 :** Ethers behaves as bases in the presence of mineral acids.
Statement 2 : It is due to the presence of lone pair of electrons on the oxygen.

35. **Statement 1 :** The major products formed by heating $C_6H_5CH_2OCH_3$ with HI are $C_6H_5CH_2I$ and CH_3OH.
Statement 2 : Benzyl cation is more stable than methyl cation.

36. **Statement 1 :** t-butyl methyl ether is not prepared by the reaction of t-butyl bromide with sodium methoxide.
Statement 2 : Sodium methoxide is a strong nucleophile.

37. **Statement 1 :** Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method.
Statement 2 : Ethers cannot be prepared by the dehydration of secondary or tertiary alcohols.

38. **Statement-1 :** Ethers behave as bases in the presence of mineral acids.
Statement-2 : Due to the presence of lone pairs of electrons on oxygen.

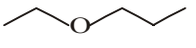
39. **Statement-1 :** High boiling point of glycerol is due to hydrogen bonding.
Statement-2 : Glycerol decomposes much below its boiling point and evaporation is carried in vacuum.

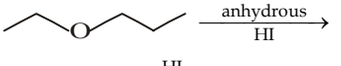
40. **Statement-1 :** With HI, anisole gives iodobenzene and methyl alcohol.
Statement-2 : Iodide ion combines with smaller group to avoid steric hindrance.

41. **Statement-1 :** With HI at 373 K, *ter*-butyl methyl ether gives *ter*-butyl iodide and methanol.
Statement-2 : The reaction occurs by S_{N^2} mechanism.

Instructions for Q. 42 to 43 : Following questions are Integer Type Questions :

42. Sum of molecular mass of iodides produced in following reaction is

(a) 

(b) 

(c) $Ph-O-Me \xrightarrow[excess]{HI}$

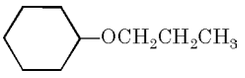
If answer of part (a) is x, part (b) is y and part (c) is z then present sum of x + y + z in the OMR sheet. For example : if answer (a) is 12, (b) is 13 and (c) is 3 you will fill 0028 in OMR sheet.

43. How many ethers will be formed when a mixture of C_2H_5OH and methyl alcohol are treated with conc. H_2SO_4 ?

EXERCISE 12.3 (Subjective Problems)

1. Give IUPAC name to each of the following compound :

(*a*) $ClCH_2CH_2OCH_3$ (*b*) $p\text{-}NO_2.C_6H_4OC_2H_5$

(*c*)  (*d*) $CH_2 = CHOCH_2C_6H_5$

(*e*) $CH_3CHOHCH_2CH_2CH_2OCH_3$.

2. Upon treatment with sulphuric acid, a mixture of ethyl alcohol and *n*-propyl alcohol gives a mixture of three ethers, while a mixture of *tert*-butyl alcohol and ethyl alcohol gives a single ether in quantitative yield. Explain.

3. How will you carry out following conversions ?

(*a*) Phenol to *p*-nitrophenyl ethyl ether

(*b*) Benzene to diphenyl ether

(*c*) Cyclohexanol to cyclohexyl methyl ether

(*d*) Toluene to dibenzyl ether

(*e*) Ethylene to divinyl ether.

4. Give the mechanism for the formation of hydroperoxide from ethers and oxygen.

5. Cleavage of optically active *sec*-butyl methyl ether by anhydrous HBr yields mainly methyl bromide and *sec*-butyl alcohol having same configuration and optical purity as the starting material. Can you suggest the mechanism (*i.e.* S_N2, or S_N1) involving in this reaction ?

6. Write the structures of the products when following ethers are exposed to oxygen.

(*a*) $CH_2 = CHCH_2OCH_2CH_2CH_3$

(*b*) $CH_3CH_2CH_2OCH_2C_6H_5$.

7. (*a*) Give a simple chemical test to distinguish an ether from a hydrocarbon of comparable molecular weight.

(*b*) Give chemical tests for distinguishing alcohols from ethers.

8. Explain the following :

(*a*) Ethers are soluble in conc. H_2SO_4 but separate out on addition of water.

(*b*) Ethers are used as solvents for BF_3 and Grignard reagent.

9. Give main products of (*a*) mononitration of *p*-methylanisole, and (*b*) monobromination of *p*-ethoxyphenol.

10. Give the products of the reactions of styrene oxide with

(*a*) *aq.* NaCN (*b*) *aq.* NaN_3

(*c*) dry HCl (*d*) excess NH_3

(*e*) $LiAlD_4$, then H_2O

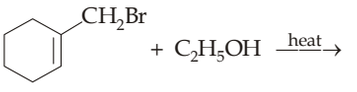
(*f*) CH_3CH_2SH followed by bases.

11. Give the products obtained by treating 1, 2-epoxypropane (propylene oxide) with the following reagents.

(*a*) Methanol in presence of HCl (*b*) Methanol

(*c*) Methanol in presence of sod. methoxide.

12. Give the various possible products that can be obtained from the following reaction.



13. What reagent will yield (*a*) *cis*- and (*b*) *trans*-cyclopentene glycol from cyclopentene ?

14. Predict the products in presence of periodic acid (or lead tetra acetate)oxidation of

(*a*) CH_2OHCH_2OH (*b*) $CH_3CHOHCH_2OCH_3$

(*c*) 1, 2-Cyclopentanediol.

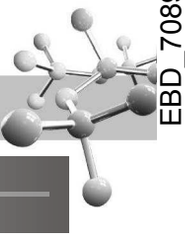
15. One mole of compound $C_6H_{14}O_5$ reacts with 4 moles of HIO_4. The moles of products formed are : $1CH_2O$, $1CH_3CHO$, and 3HCOOH. Suggest a possible structure for $C_6H_{14}O_5$.

16. Suggest the structure of the compound whose one mole on oxidation with one mole of periodic acid gives

(*a*) one mole each of CH_3COCH_3 and HCHO

(*b*) one mole of $CHO.(CH_2)_4.CHO$.

17. An alkene is treated with OsO_4 followed by aqueous sodium bisulphite to form compound X. The compound X is treated with periodic acid, it forms an unsubstituted cyclic ketone with molecular formula $C_6H_{10}O$. What is the structure of the alkene?



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SOLUTIONS

EXERCISE 12.1

1	(c)	**6**	(c)	**11**	(a)	**16**	(a)	**21**	(b)	**26**	(b)	**31**	(d)
2	(c)	**7**	(b)	**12**	(b)	**17**	(c).	**22**	(c).	**27**	(b).	**32**	(b)
3	(d)	**8**	(b)	**13**	(b)	**18**	(d)	**23**	(b)	**28**	(d)		
4	(d)	**9**	(a)	**14**	(c)	**19**	(a).	**24**	(c).	**29**	(d).		
5	(d)	**10**	(d)	**15**	(c)	**20**	(a)	**25**	(b)	**30**	(b)		

1. Double bond is the principal functional group.

2. (c) Remember that in migration to ortho position, allyl group rearranges only once, hence position of C^{14} is changed.

3. [X] is $CH_3CH = CHCH_3$, formed via 2° carbocation ; Y is $CH_3.\overset{OCH_3}{\overset{|}{C}}HCH_2CH_3$

4. *tert*- and *sec*-carbocations are liable to undergo elimination reaction in presence of strong alkoxide bases. Aryl and vinyl halides do not undergo nucleophilic substitution.

5. Williamson synthesis and dehydration of Me_3COH will lead to alkene (isobutene) as the main product because the *tert*-butyl cation will undergo dehydration readily than the attack of a bulkier nucleophile Me_3COH. However, di-*tert*-butyl ether can be prepared in low yield by following reaction.

$$2Me_3C{-}Cl \xrightarrow{Ag_2CO_3} Me_3C{-}O{-}CMe_3$$

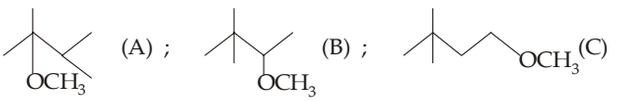
6. $C_6H_5CH_2Br + NaOC_2H_5$ or $C_6H_5CH_2ONa + C_2H_5Br \longrightarrow C_6H_5CH_2OC_2H_5$

7. (*a*) Acidic hydration leads to hydration according to Markovnikov addition, but with rearranged carbon skeleton.

(*b*) Oxymercuration-demercuration leads to hydration according to Markovnikov rule and without any rearrangement. This process will produce required ether.

(*c*) Hydroboration-oxidation leads to hydration in *anti*-Markovnikov's way without rearrangement.

Three respective main products are :



8. In isopropyl ether more stable (2°) intermediate is formed than in *n*-propyl ether which forms 1° intermediate.

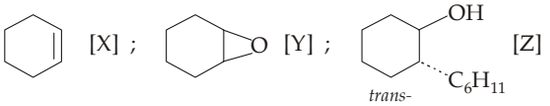
9. It is an example of solvomercuration and demercuration.

10. $CH_3CH = CH_2 \xrightarrow{Cl_2, H_2O} CH_3\underset{OH}{CH}{-}\underset{Cl}{CH_2} \xrightarrow{\text{aq. NaOH}} CH_3CH\text{—}CH_2$ (epoxide, O)

11. Only option (*a*) involves the use of an acid.

12. Epoxide has higher value of enthalpy of combustion because the three-membered ring is more strained.

13. In presence of acid, nucleophile H_2O^{18} attacks the more substituted carbon of the epoxide.

14. 

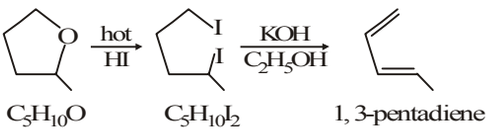
15. Here reaction is to be carried out only on —CO, so —CHO should be protected by ethylene glycol, otherwise Grignard reagent will react with both functional groups, *i.e.* —CO as well as CHO.

16. Greater the steric hindrance, slower is the oxidation.

17. Reaction is bimolecular reduction followed by oxidation

$$2CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}O \xrightarrow[(ii)\ H_3O^+]{(i)\ Mg} CH_3{-}\overset{CH_3}{\overset{|}{C}}{-}\overset{CH_3}{\overset{|}{C}}{-}CH_3 \xrightarrow{HIO_4} 2CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}O$$

(OH, OH)

21. (b) 

22. (c) In (b) aryl fluoride does not undergo S_N reaction.

23. (b) Methyl vinyl ether under anhydrous condition at room temperature undergoes addition reaction.

$$CH_2=CH-OCH_3 \xrightarrow{HBr} CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-O-CH_3$$

24. **(c)** Although in both cases products are CH_3I and C_6H_5OH; the two reactions follow different mechanism.

$$C_6H_5-O-CH_3 \xrightarrow[S_N2]{HI(g)} CH_3I + C_6H_5OH$$

$$C_6H_5-O-CH_3 \xrightarrow[S_N1]{conc.HI} CH_3I + C_6H_5OH$$

Remember that during S_{N1} reaction, CH_3^+ is formed because it is more stable than $C_6H_5^+$.

25. **(b)** When one of the alkyl groups is 3° and another is 1°, nature of reagent determines the type of mechanism (S_N1 or S_N2). A polar solvent or reagent capable of forming ions (viz. conc. HI) will cause S_N1 reaction, while a non-polar solvent or a reagent not capable of forming ions (anhydrous HI) will cause S_N2 reaction.

26. (b) $(CH_3)_3CBr + NaOC_2H_5$ can't be applied for synthesising the ether because sod. ethoxide, being a strong base, will preferentially cause elimination reaction.

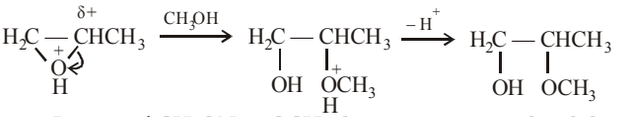
$$(CH_3)_3CBr \xrightarrow{-OC_2H_5} (CH_3)_2C=CH_2 + HBr$$

In isobutene + ethanol, isobutene will form *tert*-butyl cation which reacts with ethanol, a nucleophile to form ether.

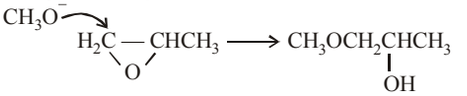
$$(CH_3)_2C=CH_2 \xrightarrow{H^+} (CH_3)_2\overset{+}{C}CH_3$$

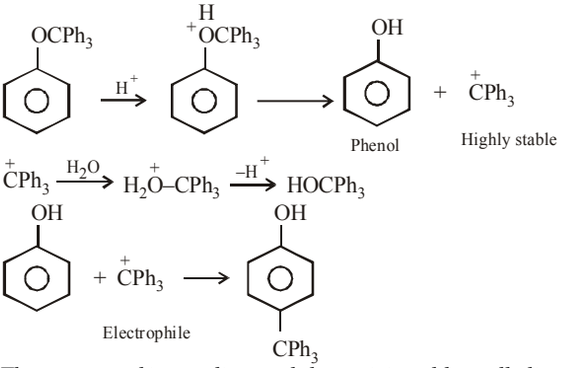
$$\xrightarrow[(ii)\ -H^+]{(i)\ CH_3CH_2OH} (CH_3)_3COCH_2CH_3$$

27. (b) In the acid-catalysed ring opening of an unsymmetrical epoxide, the nucleophile attacks primarily at the more substituted carbon atom because such carbon of the protonated epoxide acquires a considerable positive charge. This resembles like a more stable 2° or 3° carbocation and hence the reaction is S_{N1} like.



In case of CH_3ONa, $^-OCH_3$, being a strong nucleophile, opens the strained epoxide ring in a direct S_{N2} reaction, i.e. by attacking at the least hindered carbon atom.

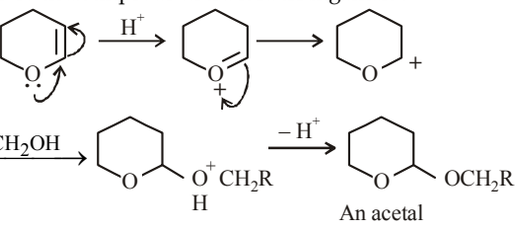


28. (d) 

29. (d) The compound is a cyclic acetal ; hence it is stable to alkalies and hydrolysed by acids.

30. (b) Base catalysed epoxide opening is a typical S_N2 reaction in which attack of the nucleophile takes place at the less hindered expoxide.

31. (d) It is an example of Claisen rearrangement.

32. (b) 

EXERCISE 12.2

MCQ >1 CORRECT OPTION	**1**	(a,b,c)	**2**	(a,b,c)	**3**	(a, c, d)
	4	(a, b, d)	**5**	(a, d)	**6**	(c, d)
	7	(c, d)	**8**	(a, b)	**9**	(a, b, d)
	10	(a, b)	**11**	(a, b, c)	**12**	(b)
	13	(a, d)	**14**	(b, b)	**15**	(a, d)
PASSAGE 1	**16**	(d)	**17**	(b)	**18**	(b)
PASSAGE 2	**19**	(c)	**20**	(d)	**21**	(c)
PASSAGE 3	**22**	(c)	**23**	(c)	**24**	(b)
PASSAGE 4	**25**	(c)	**26**	(b)	**27**	(b)
PASSAGE 5	**28**	(c)	**29**	(d)	**30**	(a)
Match the Following	**31**	(A)-d ; (B)-c ; (C)-b ; (D)-a				
	32	(A) - c, (B) - a, c, (C) - d, (D) - b				
	33	(A) - b, d; (B) - c; (C) - d, (D) - a, b				
A/R	**34**	(a)	**35**	(a)	**36**	(c)
	37	(b)	**38**	(a)	**39**	(b)
	40	(d)	**41**	(c)		
INTEGER	**42**	**454**	**43**	**3**		

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1. Ethers are capable of forming hydrogen bonds with water as well as alcohols. Alcohols too can form H-bonds with ethers and water. In higher alcohols alkyl group dominates, hence H-bond not possible.

2. (*a*) Phenol and HBr, both being acids, do not react with each other. Moreover, this reaction involves cleavage of the C—O bond which is difficult because C—O bond acquires double bond character due to resonance. Reaction (*b*) will lead to elimination reaction rather substitution. In reaction (*c*) vinylic chlorine will not be replaced, rather allylic chlorine will be replaced by —OCH_3.

9. (a, b, d)

(a) $Me-OCH_2-CH_3 \xrightarrow[(S_N2)]{\text{Anhydrous HI}} Me-I + Et-OH$

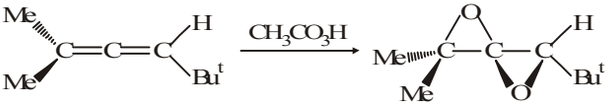
(b) Order of basicity in aqueous medium
$Me_2NH < Me-NH_2 < Me_3N$

(c) With $SOCl_2$ complete retention is obtained

(d) Isocyanide is major product not nitrile

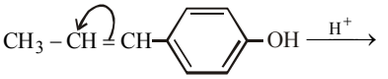
10. (a, b) $CH_2=CH-O-CH_3$

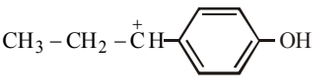
11. (a, b, c)



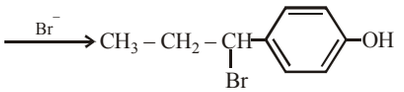
Second epoxidation is faster because of activation by the epoxy oxygen.

12. (b) The mechanism of this reaction is represented as follows.

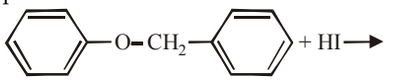


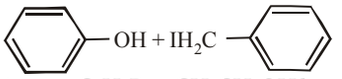


Benzylic carbocation (stable)



13. (a, d) The aromatic ethers are cleaved to give phenol as one of the products.



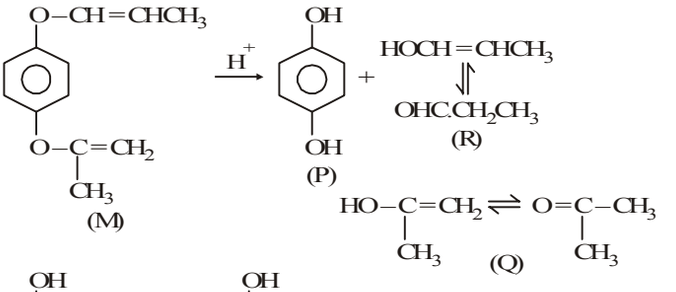


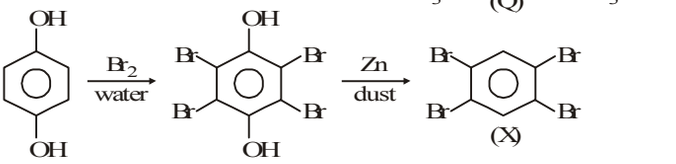
14. (b, d) The combination $C_6H_5Br + CH_3CH_2OH$ has non-reactive C_6H_5Br, while in the combination $C_6H_5OH + Me_3CBr$, Me_3CBr being *tert*-halide will undergo elimination reaction rather substitution. Hence, only combinations (*a*) and (*c*) can be used for preparing ether.

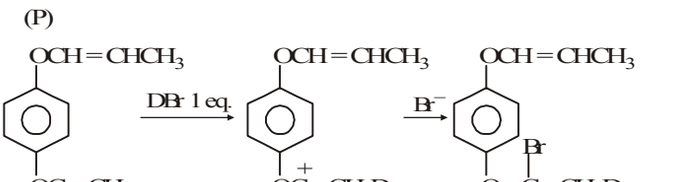
$C_6H_5OH + (CH_3)_2SO_4 \xrightarrow{S_N} C_6H_5OCH_3$;

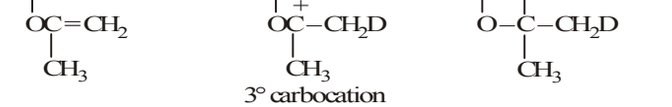
$p\text{-}NO_2C_6H_4Br + CH_3CH_2OH \xrightarrow{Ar\,S_N} p\text{-}NO_2C_6H_4OCH_2CH_3$

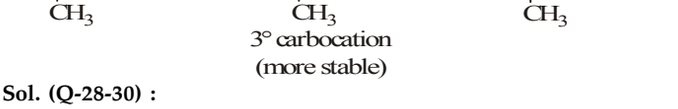
Sol. (Q-25-27) :





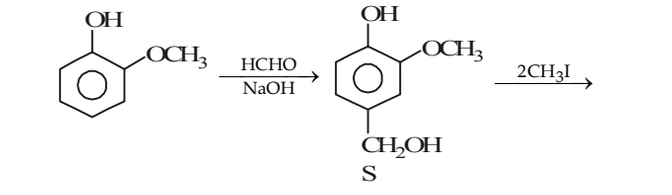


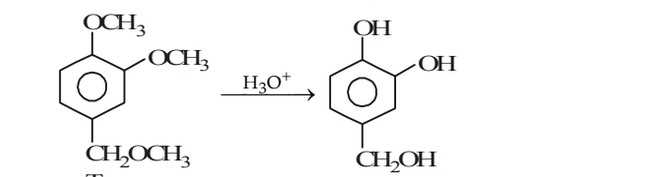




3° carbocation
(more stable)

Sol. (Q-28-30) :





28. (c) **29.** (d) **30.** (a)

42. 0454

(a)	156	I = 127	C_2H_5 = 29
(b)	156	I = 127	Me = 15
(c)	Me – I 142		

156 + 156 + 142 = 454

43. 3

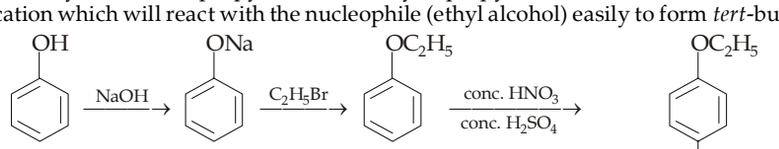
CH_3OCH_3, $CH_3OCH_2CH_3$, $C_2H_5OC_2H_5$.

EXERCISE 12.3

1. (*a*) 1-Chloro-2-methoxyethane (*b*) 4-Ethoxynitrobenzene (*c*) *n*-Propoxycyclohexane
(*d*) Benzyloxyethene (*e*) 5-Methoxy-2-pentanol.

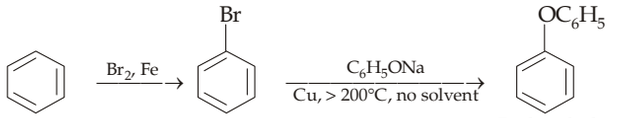
2. Ethyl alcohol and *n*-propyl alcohol, both are 1° alcohols ; hence they undergo S_N2 mechanism leading to the formation of three different ethers ; diethyl ether, di-*n*-propyl ether and ethyl *n*-propyl ether. On the other hand, *tert*-butyl alcohol may form quite stable *tert*-butyl carbocation which will react with the nucleophile (ethyl alcohol) easily to form *tert*-butyl ethyl ether.

3. (*a*)



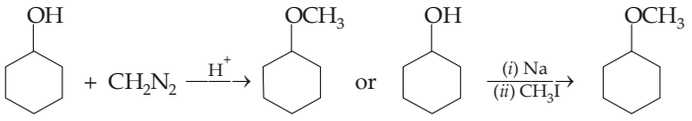
p-Nitrophenyl ethyl ether

In the preparation of aryl alkyl ether, halide component should be taken in the form of alkyl halide, because aryl halides do not readily undergo S_N2 reactions. Further note that since ArOH is much more acidic than ROH, it is converted to ArO^- by OH^- instead of by Na as in ROH.

(*b*) 

Diphenyl ether

Phenols do not undergo intermolecular dehydration. Although aryl halides can't be used as substrate in typical Williamson synthesis, they do undergo a modified Williamson-type synthesis at higher temperatures in presence of copper.

(*c*) 

(*d*) $C_6H_5CH_3 \xrightarrow[\text{light}]{Cl_2} C_6H_5CH_2Cl \xrightarrow[H_2O]{OH^-} C_6H_5CH_2OH \xrightarrow[(-H_2O)]{H_2SO_4} C_6H_5CH_2OCH_2C_6H_5$

(*e*) $CH_2=CH_2 \xrightarrow{HOCl} ClCH_2CH_2OH \xrightarrow[heat]{H_2SO_4} ClCH_2CH_2{-}O{-}CH_2CH_2Cl \xrightarrow{\text{alc. KOH}} \underset{\text{Divinyl ether}}{CH_2=CH{-}O{-}CH=CH_2}$

Remember that vinyl alcohol, $H_2C=CHOH$, can't be used as a starting material because it is not stable and rearranges to CH_3CHO. Hence, in the above preparation double bond must be introduced after the ether bond is formed.

4. Formation of hydroperoxide is a free-radical reaction, involving following steps.

Initiation step. $RCH_2OCH_2R + \cdot\ddot{O}{-}\ddot{O}\cdot \longrightarrow R\dot{C}HOCH_2R + H{-}\ddot{O}{-}\ddot{O}\cdot$

Propagation step. $R\dot{C}HOCH_2R + \cdot\ddot{O}{-}\ddot{O}\cdot \longrightarrow R{-}\underset{\displaystyle O{-}\dot{O}}{\overset{\displaystyle |}{CH}}OCH_2R$

$$R\underset{\displaystyle O{-}O.}{\overset{\displaystyle |}{C}}HOCH_2R + RCH_2OCH_2R \longrightarrow R\underset{\displaystyle O{-}OH}{\overset{\displaystyle |}{C}}HOCH_2R + R\dot{C}HOCH_2R$$
Hydroperoxide

5. $CH_3\underset{\displaystyle C_2H_5}{\overset{\displaystyle |}{C}}H{-}O{-}CH_3 \xrightarrow{H^+} CH_3\underset{\displaystyle C_2H_5}{\overset{\displaystyle |}{C}}H{-}\overset{+}{\underset{\displaystyle H}{O}}{-}CH_3$

The above protonated ether may react with Br^- either through S_N2 or S_N1. In case of S_N2, the attack of the Br^- will be at the least hindered methyl group to form CH_3Br and *sec*-butyl alcohol which is in accordance with the given product. Since bond to chiral carbon is not cleaved, configuration and optical purity of the product will be identical to that of the starting material. In case the mechanism were S_N1, carbocation would have been formed leading to racemic *sec*-butyl alcohol.

6. (*a*) $CH_2=CH\underset{\displaystyle OOH}{\overset{\displaystyle |}{C}}H{-}O{-}C_3H_7\text{-}n$ (*b*) $n\text{-}C_3H_7{-}O{-}\underset{\displaystyle OOH}{\overset{\displaystyle |}{C}}HC_6H_5$

Attack by oxygen on the given carbon will form more stable allylic radical in (*a*), and benzylic radical in (*b*).

7. (*a*) Like water and alcohols, ethers are basic, hence they dissolve in conc. H_2SO_4 with evolution of much heat.

$$\underset{\text{Base}_1}{ROR} + \underset{\text{Acid}_2}{H_2SO_4} \longrightarrow \underset{\text{Acid}_1}{[R_2OH]^+} + \underset{\text{Base}_2}{HSO_4^-}$$

(*b*) 1° and 2° alcohols are oxidizable and hence give positive tests with acidic potassium dichromate (orange colour turns green). 3° Alcohols give turbidity immediately on adding Lucas reagent. Ethers give negative results to these tests.

8. (*a*) Water is stronger base than ether and removes proton from protonated ether, R_2OH^+

$$\underset{\text{Acid}_1}{[R_2OH]^+} + \underset{\text{Base}_2}{H_2O} \longrightarrow \underset{\text{Base}_1}{R_2O} + \underset{\text{Acid}_2}{H_3O^+}$$

(*b*) Due to unshared electron pairs, ethers act as Lewis bases and hence easily react with Lewis acids like BF_3 and RMgBr to form coordinated compounds.

$$(C_2H_5)_2\ddot{O}: + BF_3 \longrightarrow (C_2H_5)_2\ddot{O} \longrightarrow \overset{+}{B}F_3$$

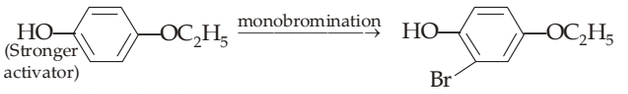
$$2(C_2H_5)_2\ddot{O}: + RMgBr \longrightarrow (C_2H_5)_2O \rightarrow \underset{\displaystyle Br}{\overset{\displaystyle R}{Mg}} \leftarrow O(C_2H_5)_2$$

Note that two molecules of ether coordinate tetrahedrally with one Mg^{2+}.

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9. (*a*) 

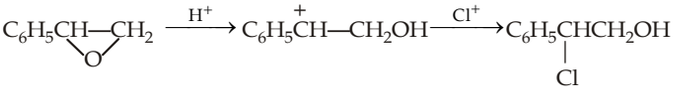
p-Methylanisole 2-Nitro-4-methylanisole

(*b*) 

p-Ethoxyphenol 2-Bromo-4-ethoxyphenol

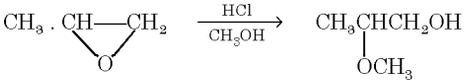
10. All are S_N2 reactions, except (*c*) which has S_N1 mechanism because of the stability of the intermediate benzyl carbocation, $C_6H_5\overset{+}{C}HCH_2OH$

(*a*) $C_6H_5CH(OH)CH_2CN$ (*b*) $C_6H_5CH(OH)CH_2N_3$

(*c*) 

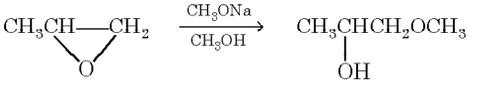
(*d*) $C_6H_5CH(OH)CH_2NH_2$ (*e*) $C_6H_5CH(OH)CH_2D$

(*f*) $C_6H_5CH(OH)CH_2SCH_2CH_3$.

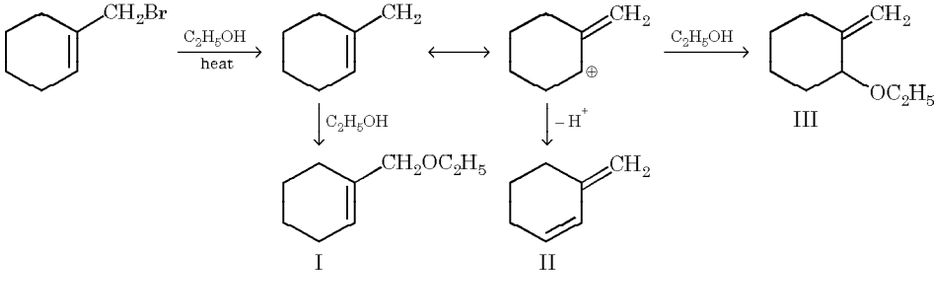
11. (*a*) 

(Acid-catalyzed cleavage)

(*b*) In the absence of acid, methanol (an *extremely weak base*) would have to displace the strongly basic alkoxy oxygen on ring-opening which cannot occur. However, in presence of acid, oxygen atom of the epoxide is displaced as weakly basic —OH group which is possible.

(*c*) 

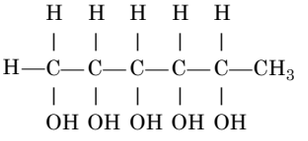
(Base-catalyzed cleavage)

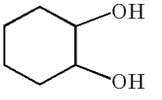
12. 

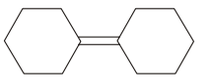
13. (*a*) Cold *aq*. $KMnO_4$ or OsO_4 containing H_2O_2 (*b*) Performic acid

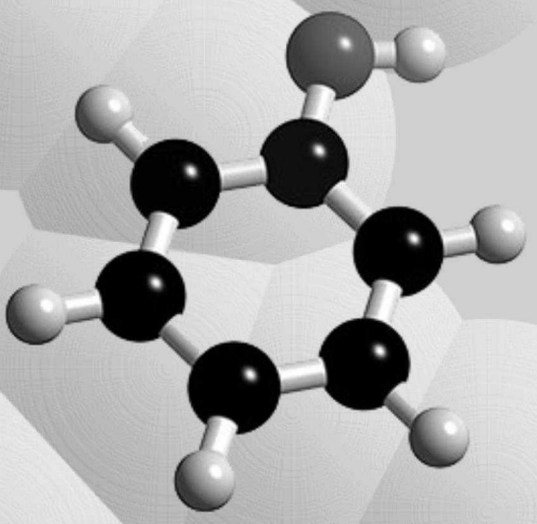
14. (*a*) CHO.CHO (*b*) No reaction (*c*) O = $CH(CH_2)_3CH$ = O.

15. There are four adjacencies, CH_2=O and CH_3CHO are formed by oxidation of the terminal C—OH groups, while 3HCOOH indicates the presence of three —CH—OH groups in the middle of the molecule.



16. (*a*) $(CH_3)_2CO + O = CH_2 \longleftarrow (CH_3)_2\underset{OH}{C}—\underset{OH}{CH_2}$ (*b*) $OHC(CH_2)_4CHO \longleftarrow$ 

17. 



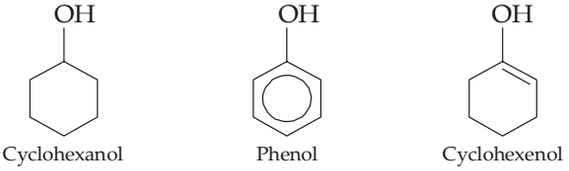
13 Phenols

CHAPTER HIGHLIGHTS

13.1 Nomenclature
13.2 Preparation of Phenols
13.3 Physical Properties
13.4 Acidity of Phenols
13.5 Chemical Properties of Phenols
13.6 Analysis of Phenols
13.7 Illustrative Examples
EXERCISES
SOLUTIONS

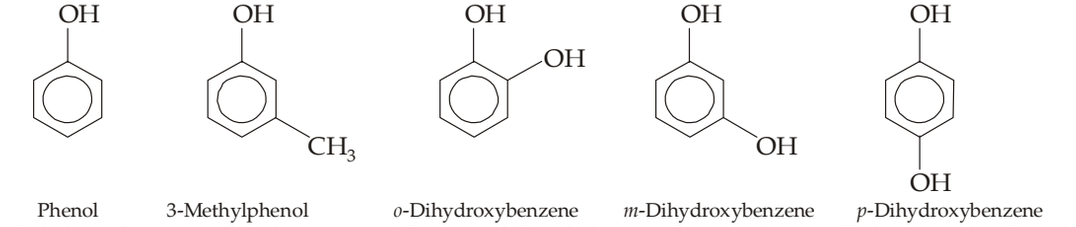
13.1 Nomenclature

Compounds in which hydroxyl group is directly attached to a benzene ring are called *phenols*. The parent compound of this group of compounds is simply called phenol, C_6H_5OH. Remember that phenols differ from alcohols in the respect that in the former the —OH group is directly attached to the carbon atom of an aromatic ring, *i.e.* to an sp^2 hybridised carbon, while in alcohols the —OH is attached to an sp^3 hybridised carbon ; however they resemble enols where —OH group is attached to an sp^2 hybridised carbon.



Cyclohexanol Phenol Cyclohexenol

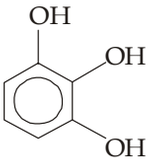
Although the systematic name for phenol is *benzenol*, phenol and hydroxybenzene are also acceptable IUPAC names. The three methylphenols and the three dihydroxybenzenes are generally named by their common names (given in bracket)



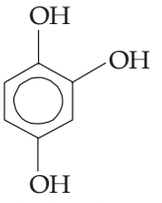
Phenol (Carbolic acid) | 3-Methylphenol (*m*–Cresol) | *o*-Dihydroxybenzene 1, 2-Benzendiol (Catechol) | *m*-Dihydroxybenzene (Resorcinol) | *p*-Dihydroxybenzene (Hydroquinone) or Quinol

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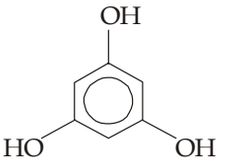
Like the dihydroxybenzenes, the isomeric trihydroxybenzenes have unique names.



1, 2, 3-Trihydroxybenzene
(Pyrogallol)

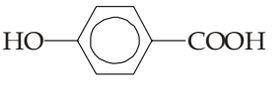


1, 2, 4-Trihydroxybenzene

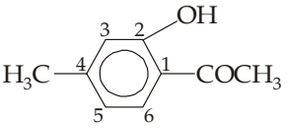


1, 3, 5-Trihydroxybenzene
(Phloroglucinol)

Carboxyl and acyl groups take precedence over the phenolic hydroxyl, and hence it is treated as a substituent in these cases.



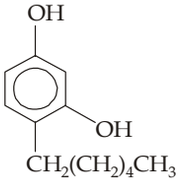
p-Hydroxybenzoic acid

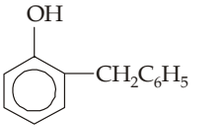


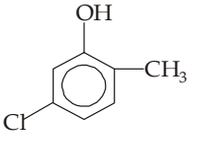
2-Hydroxy-4-methylacetophenone

TEST YOUR UNDERSTANDING - 13.1

1. Write IUPAC names for the following :

(*a*) 

(*b*) 

(*c*) 

2. Write the structure for the following compounds.

(*a*) Phenoxyacetic acid

(*b*) Phenyl acetate

(*c*) 2-Hydroxy-3-phenylbenzonic acid

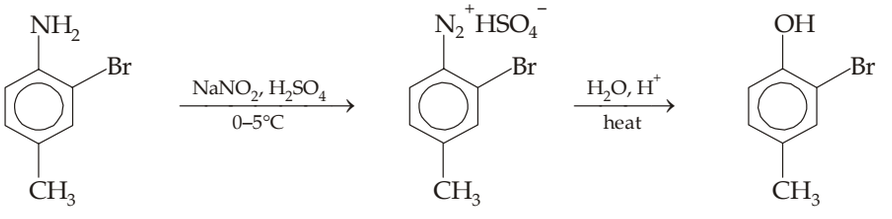
(*d*) *p*-Hydroxyanisole.

13.2 Preparation of Phenols

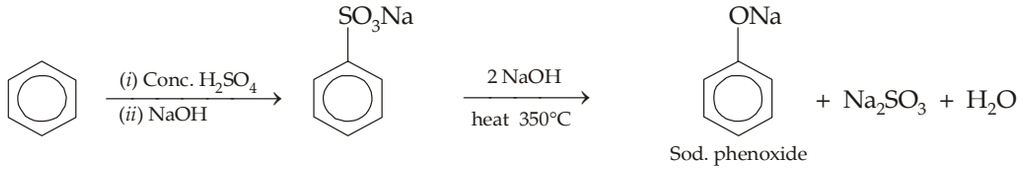
Phenol was first of all isolated from middle oil fraction of coal-tar distillation.

1. **By hydrolysis of arenediazonium salts.** This is a highly versatile method of making phenols because the conditions required for the preparation of diazonium salt (diazotization step) and its hydrolysis are mild. (Details are given in the chapter on diazonium salts).

$$ArNH_2 \xrightarrow[0-5°C]{HONO} ArN_2^+ \xrightarrow[heat]{H_2O} ArOH + N_2$$

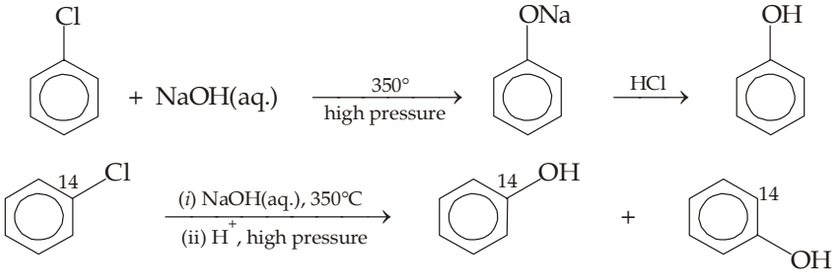


2. **By alkali fusion of sodium benzenesulphonates.** Sodium benzenesulphonate is melted (fused) with sodium hydroxide at 350°C to produce sodium phenoxide which is converted into phenol on acidification.

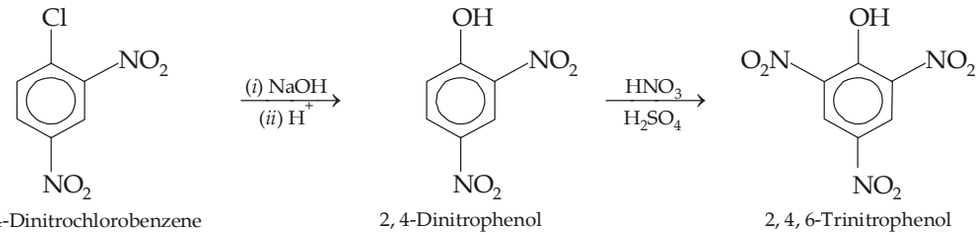


However, the condition required to bring about the reaction are so vigorous that this method cannot be used for the preparation of many phenols.

3. **By hydrolysis of chlorobenzene (Dow process).** Although chlorobenzene is inert to aq. NaOH under ordinary conditions, it can be converted quantitatively into phenol by heating at high temperature and under high pressure. Remember that conversion of chlorobenzene to phenol under these vigorous conditions takes place *via* benzyne mechanism (*elimination-addition mechanism*).

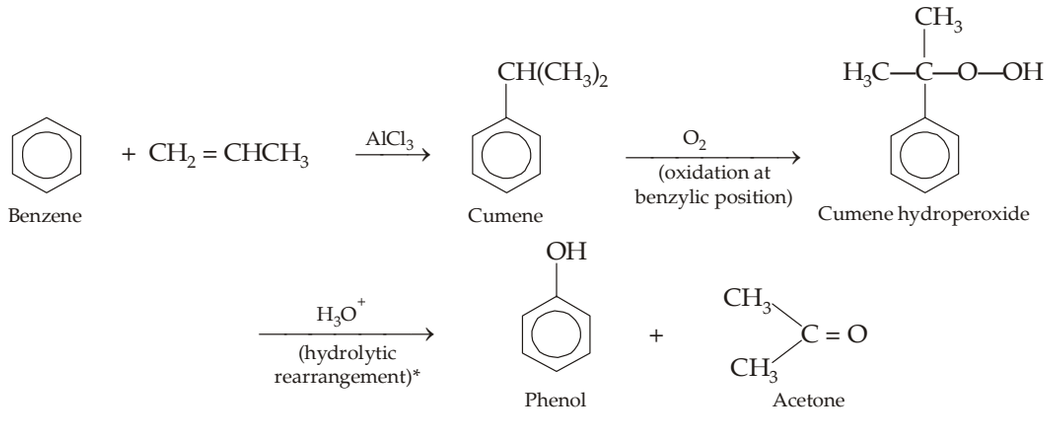


However, aryl halides containing strongly electron-withdrawing groups in *ortho* and *para* positions to the halogen easily undergo usual **(nucleophilic substitution)** reaction with aq. NaOH.



2, 4-Dinitrophenol can be easily converted into 2, 4, 6-trinitrophenol **(picric acid)** by nitration.

4. **From cumene hydroperoxide (Commercial method).** Commercially, nearly all phenol is made today from isopropylbenzene, commonly known as *cumene.* Cumene is converted by air oxidation into cumene hydroperoxide, which is converted by aqueous acid into phenol and acetone. Cumene, in turn, can be easily obtained by the Friedel-Crafts alkylation of benzene with propene.



Note that this method involves the conversion of two relatively inexpensive organic compounds (benzene and propene) into two valuable industrial chemicals, phenol and acetone.

---

* This step involves migration of phenyl group to electron-deficient oxygen.

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TEST YOUR UNDERSTANDING - 13.2

1. (*a*) Give mechanism involved in the conversion of *p*-toluenesulphonic acid to *p*-cresol.

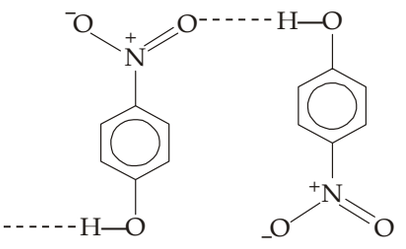
(*b*) Write a stepwise mechanism for the hydrolysis of chlorobenzene with aq. NaOH under high pressure and at high temperature (370°C).

2. Try to prepare (*a*) catechol (1, 2-dihydroxybenzene), and (*b*) resorcinol (1, 3-dihydroxybenezene) from benzene.

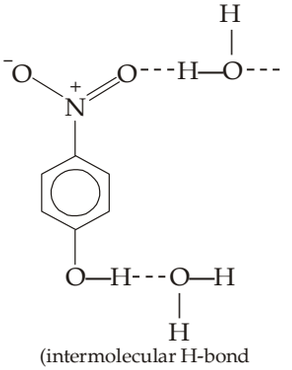
13.3 Physical Properties

Physical properties of phenols are strongly influenced by hydroxyl group, which permits phenols to form hydrogen bonds with other phenol molecules causing high melting and boiling points, and also with water, causing some (*partial*) solubility in water. This accounts why phenols have higher melting and boiling points and are more soluble in water than arenes and aryl halides of comparable molecular weight. Phenols, themselves, are colourless and the colour, if any, associated with phenols is either due to the presence of some other colour producing group, *viz*. —NO_2, or due to the presence of some oxidised product of phenol as impurity.

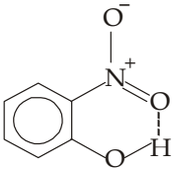
An interesting example of comparative solubility and boiling point is observed in the three isomeric (*o*-, *m*-, and *p*-) nitrophenols. *p*- Nitrophenol is capable of forming intermolecular H–bond between themselves and with water too, hence it has high higher m.p. and more solubility in water. *m*-Nitrophenol also behaves in the same way.



p-Nitrophenol (intermolecular H-bond between two *p*-nitrophenol molecules)



(intermolecular H-bond with water)



o-Nitrophenol (intramolecular H-bond restricts intermolecular H-bonds)

However, *o*-nitrophenol is capable of forming intramolecular H-bond because the newly formed ring will be 6-membered. Due to intramolecular H-bonding, it does not form intermolecular H-bond neither with its second molecule nor with water. Hence *o*-nitrophenol has low m.p. and low solubility in water than the corresponding *m*- and *p*-isomers.

TEST YOUR UNDERSTANDING - 13.3

1. Which of the following compounds is expected to have intramolecular hydrogen bonding ?

(*a*) *o*-Hydroxybenzaldehyde (*b*) *o*-Nitroaniline

(*c*) *o*-Hydroxybenzonitrile (*d*) Salicylic acid (*o*-Hydroxybenzoic acid)

(*e*) *o*-Fluorophenol (*f*) *o*-Cresol.

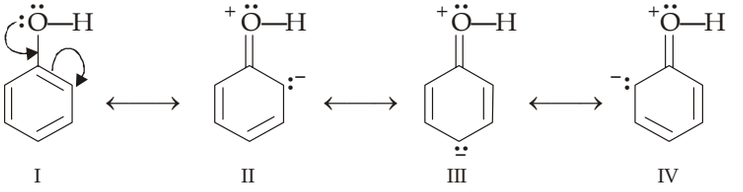
13.4 Acidity of Phenols

The most characteristic property of phenols is their acidity. Phenols are more acidic than alcohols which are even more weakly acidic than water, but phenols are less acidic than carboxylic acids.

R—COOH > Ar—OH > H—OH > R—OH **(Acidic character)**

Acidity of phenols has been discussed at large in the chapter on "Carboxylic Acids". However, a summary of acidic character of phenols is given here.

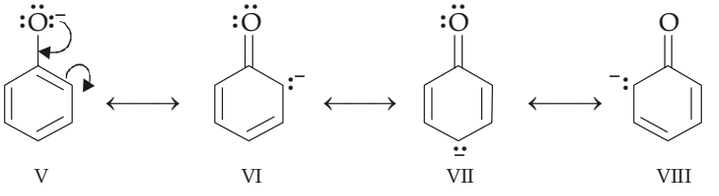
(*i*) Greater acidity of a phenol than an alcohol is due to possibility of resonance in phenol which leads to electron-deficient oxygen atom. Presence of electron-deficient oxygen atom (see structures II, III and IV) in turn weakens the $-\overset{+}{O}\longleftarrow H$ bond, and thus facilitates release of proton.



I II III IV

Such structures are not possible in alcohols.

(*ii*) Once hydrogen atom is removed from phenol, the ion (phenoxide) is very much stabilized due to delocalization of its negative charge.

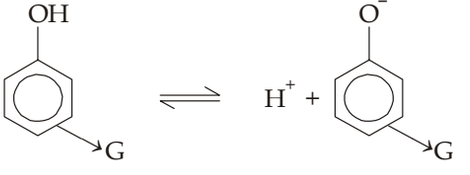


V VI VII VIII

Resonance in phenoxide ion (note that structures VI to VIII are equivalent)

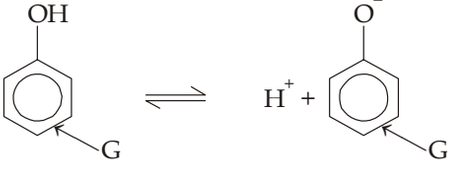
Remember that phenoxide ion is very much more stable than the parent compound phenol because phenoxide ion does not involve charge separation, while in phenol three equivalent resonanting structures (II to IV) involve charge separation.

(*iii*) Electron-withdrawing substituents increase the acidity of phenols ; while electron-releasing substituents decrease acidity. Thus substituents affect acidity of phenols in the same way as they affect acidity of carboxylic acids ; it is of course, opposite to the way these groups affect basicity of amines.



G withdraws electrons, thus disperses the –ve charge of the ion, stabilises it and hence increases ionization of the parent phenol.

(where G = —NO_2, —CN, —CHO, —COOH, —$\overset{+}{N}R_3$, —X)



G releases electrons, thus intensifies the -ve charge of the ion, destabilises it and hence decreases ionization of the parent phenol.

(where G = — R, —OR, —NR_2)

13.4.1 Relative Acidic Characters of *o*-, *p*- and *m*- Isomers

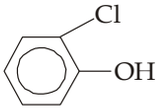
For assessing the comparative acidic character of an organic compound, always remember that the presence of an electron withdrawing group increases the acidity while that of an electron-releasing group decreases acidity mainly due to resonance effect and inductive effect ; although sometimes hyperconjugation and H–bonding also plays important role.

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(*i*) Since resonance operates from *ortho*- and *para*-positions (**not from meta**-), such group will affect acidity, nearly to equal extent, only when present in *o*- or *p*-position.

(*ii*) Since inductive effect operates from all the three positions (*o*-, *m*-, and *p*-), it will affect acidity of the compound from all positions. However, since the effect diminishes with the increase in distance between two groups, the effect will be maximum in *ortho*, then in *meta*- and least in *para*-.

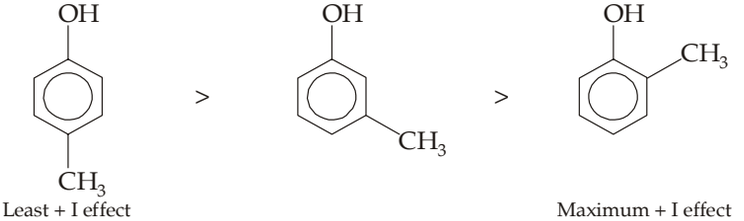
(*iii*) When the resonance and inductive effects operate in opposite directions, generally resonance effect predominates over inductive effect, except in some cases where the group is highly electronegative as in *o*-chlorophenol.



Here $-I_{of\ Cl} > +\ R_{of\ Cl}$

(*iv*) Whenever the acidic group is capable of forming H–bond with the *ortho*- substituent as in *o*-nitrophenol, *o*-fluorophenol, and *o*–nitrobenzoic acid, it becomes relatively difficult to remove acidic hydrogen as proton. Hence such compound will be less acidic than the corresponding *p*-isomer, although the —I effect (acid-strengthening effect) in the *o*-isomer is more than in the corresponding *p*-isomer.

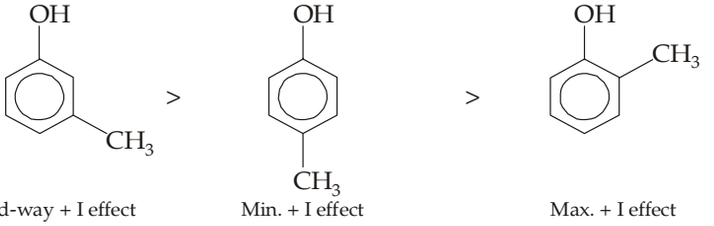
(*v*) In somes cases hyperconjugation also plays important role, *viz*. in cresols (*o*-, *m*- and *p*-) where acidic character is influenced by + I effect of the $-CH_3$ group. Since the + I (acid-weakening) effect is maximum in *ortho*-position, followed by *meta*- and least in *para*, the acidic character of the three cresols should follow the following order.



Least + I effect — Maximum + I effect

Theoretical relative acidic character, on the basis of + I effect.

However, in practice the order is found to be somewhat different.



Mid-way + I effect, No hyperconjugative effect | Min. + I effect, +ve Hyperconjugative effect | Max. + I effect, +ve Hyperconjugative effect

Hyperconjugation (no-bond resonance), which here is acid-weakening, is also possible in case of *o*- and *p*-isomers, but not in *m*-. Since in *m*-isomer, hyperconjugation does not operate, it will be stronger acid than the other two isomers where this effect operates and thus decreases their acidity.

TEST YOUR UNDERSTANDING - 13.4

1. In each of the following pairs, which is the stronger acid ?

(*a*) Phenol or *p*-hydroxybenzaldehyde

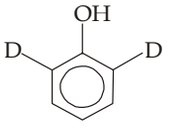
(*b*) *m*-Nitrophenol or *p*-nitrophenol

(*c*) *o*-Fluorophenol or *p*-fluorophenol

(*d*) *m*-Chlorophenol or *p*-chlorophenol

(*e*) *o*-Aminophenol or *m*-aminophenol.

(*f*) 

or


2. Arrange the following in increasing acidic character.

(*a*) Phenol, benzyl alcohol, benzenesulphonic acid and benzoic acid.

(*b*) Phenol, benzoic acid, *p*-nitrophenol and carbonic acid.

(*c*) Phenol, *p*-chlorophenol, *p*-nitrophenol and *p*-cresol.

(*d*) Phenol, *m*-chlorophenol, *m*-nitrophenol, and *m*-cresol.

3. Arrange the following compounds in decreasing order of acidity.

(*a*) Phenol (*A*), *o*-nitrophenol (*B*), *m*-nitrophenol (*C*), *p*-nitrophenol (*D*).

(*b*) Phenol (*A*), *o*-chlorophenol (*B*), *m*-chlorophenol (*C*), *p*-chlorophenol (*D*).

(*c*) Phenol (*A*), *o*-cresol (*B*), *m*-cresol (*C*), *p*-cresol (*D*).

13.4.2 Separation of Phenols from Alcohols and Carboxylic Acids

Since phenols are more acidic than water, phenol dissolves in sodium hydroxide according to the following reaction.

$$\underset{\substack{\text{Stronger acid}\\\text{(slighly soluble)}\\\text{in water}}}{C_6H_5OH} + \underset{\text{Stronger base}}{NaOH} \xrightleftharpoons{H_2O} \underset{\substack{\text{Weaker base}\\\text{(completely soluble)}\\\text{in water}}}{C_6H_5O^-Na^+} + \underset{\text{Weaker acid}}{H_2O}$$

The corresponding reaction of 1-hexanol with aqueous sodium hydroxide does not occur to a significant extent because 1-hexanol is a weaker acid than water.

$$\underset{\substack{\text{Weaker acid}\\\text{(very slightly soluble)}}}{CH_3(CH_2)_4CH_2OH} + NaOH \xleftarrow[H_2O]{\rightarrow} \underset{\text{Stronger base}}{CH_3(CH_2)_4CH_2O^-Na^+} + \underset{\text{Stronger acid}}{H_2O}$$

The fact that phenols dissolve in aqueous sodium hydroxide, whereas most alcohols with six or more carbon atoms do not, gives us a convenient means for distinguishing and separating phenols from most alcohols. (Note that alcohols with five or less carbon atoms are quite soluble in water, and hence they also dissolve in aqueous sodium hydroxide even though they are converted to sodium alkoxides in appreciable amounts, the solubility is actually due to H-bond with water molecules).

Opposite solubility properties of phenols and their salts (the salts being soluble in water and insoluble in organic solvents, while phenols are very less soluble in water and soluble in organic solvents) is applied in the isolation and separation of phenols. Aq. NaOH converts phenols into their salts which are converted back to phenols, on adding mineral acids.

$$\underset{\substack{\text{A phenol (acid)}\\\text{(Insoluble in water)}}}{ArOH} \xrightleftharpoons[H^+]{OH^-} \underset{\substack{\text{A phenoxide ion (salt)}\\\text{(soluble in water)}}}{ArO^-}$$

Most phenols are weaker acids than carbonic acid, hence, unlike carboxylic acids, which are stronger than carbonic acid, they (phenols) do not dissolve in aqueous bicarbonate solution. Indeed, phenols are conveniently liberated from their salts by the action of carbonic acid.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

$$\underset{\text{Stronger acid}}{H_2CO_3} + \underset{\text{(Soluble in water)}}{ArO^-Na^+} \longrightarrow \underset{\substack{\text{Weaker acid}\\\text{(Insoluble in water)}}}{ArOH} + HCO_3^-$$

Thus phenols can be separated (*i*) from non-acidic compounds by means of its solubility in base; and (*ii*) from carboxylic acids by means of its insolubility in bicarbonate.

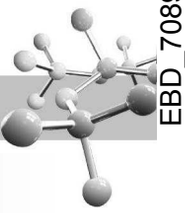
TEST YOUR UNDERSTANDING - 13.5

1. Account for the fact that

(*a*) unlike most phenols, 2, 4-dinitrophenol is soluble in aqueous sodium bicarbonate.

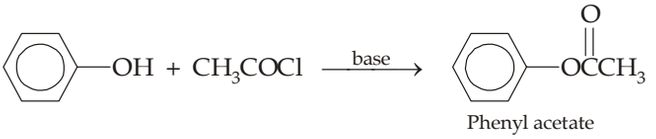
(*b*) Carboxylic acids are soluble in $NaHCO_3$ solution, while phenol not. Explain

2. Draw a flow sheet for the separation of a mixture of C_6H_5OH, $C_6H_5CH_2OH$ and C_6H_5COOH.

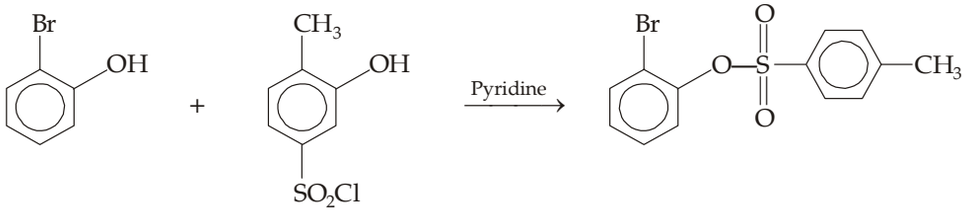


13.5 Chemical Properties of Phenols

1. Ester formation. Phenols react with acylating agents, such as acid chlorides and carboxylic acid anhydrides, *in the absence* of $AlCl_3$*, to form esters (O-acylation). These reactions are quite similar to those of alcohols.



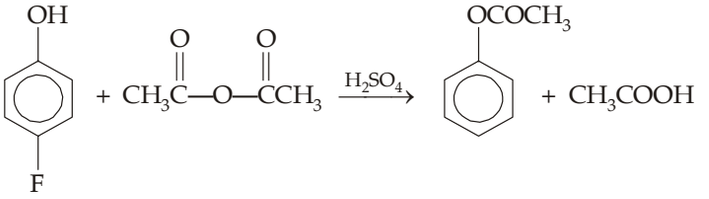
Phenyl acetate



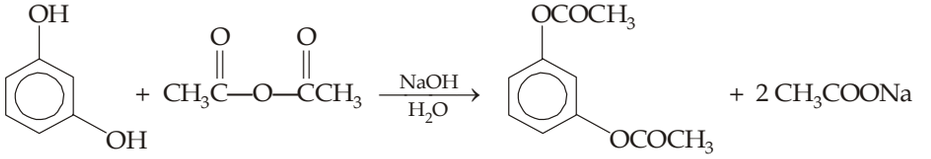
o-Bromophenol *p*-Toluenesulphonyl chloride *o*-Bromophenyl *p*-toluenesulphonate

The O-acylation of phenols with carboxylic acid anhydrides can be conveniently catalyzed in either of two ways.

(*a*) In one method, the acid anhydride is converted to more powerful acyl transfer agent, due to protonation of one of its carbonyl oxygens, by adding a few drops of sulphuric acid.

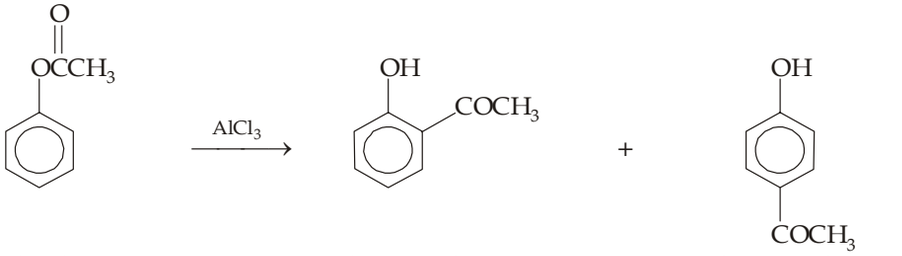


(*b*) In another method, the nucleophilicity of the phenol is increased by converting it to its phenoxide anion by adding base like aq. NaOH.



Resorcinol 1, 3-Diacetoxybenzene

When esters of phenols are heated with aluminium chloride, the acyl group migrates from the phenolic oxygen to an *ortho* or *para* position of the ring, thus forming a ketone. This reaction, called the **Fries rearrangement,** is often used instead of direct C–acylation leading to the synthesis of phenolic ketones.

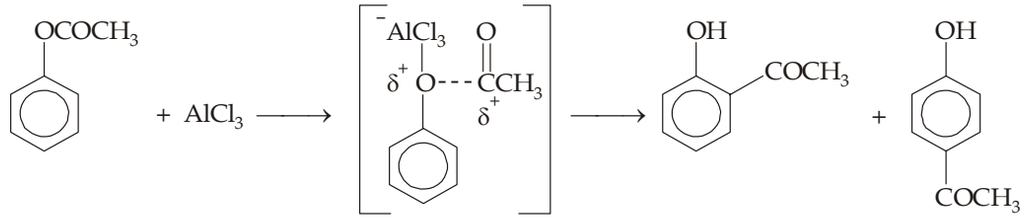


Phenyl acetate *o*-Hydroxyacetophenone (Volatile in steam) *p*-Hydroxyacetophenone (Non-volatile in steam)

* In presence of $AlCl_3$, phenols react with acid chlorides and carboxylic acid anhydrides to form *o*- and *p*-acyl phenols (Friedel-Crafts reaction, C–acylation).

Role of $AlCl_3$ in Fries rearrangement

$AlCl_3$ forms complex with the phenolic oxygen leading to the formation of acylium ion, RC^+O (an electrophile) which then attacks the ring as in Friedel Craft acylation.



TEST YOUR UNDERSTANDING - 13.6

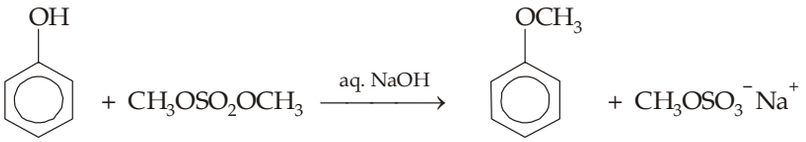
1. (*a*) Predict the product in the following reaction.

$$\text{Phenol} + C_6H_5COCl \xrightarrow{OH^-} [A] \xrightarrow{1 \text{ mole } Br_2 / Fe} \text{Product}$$

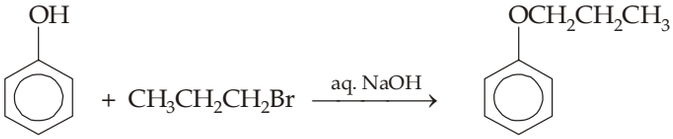
(*b*) *m*-Nitrophenyl acetate does not respond Fries rearrangement. Explain

2. **Ether formation (Williamson synthesis).** Phenols are converted into alkyl aryl ethers by treating its alkaline solution with 1° alkyl halides*. For preparing, aryl methyl ethers, methyl sulphate is frequently used because it is cheaper than methyl halides.

$$ArOH \xrightarrow{NaOH} ArONa \xrightarrow{R-X} ArOR + NaX \quad (\text{where, X = Cl, Br, I or } OSO_2OCH_3)$$

(*a*) 

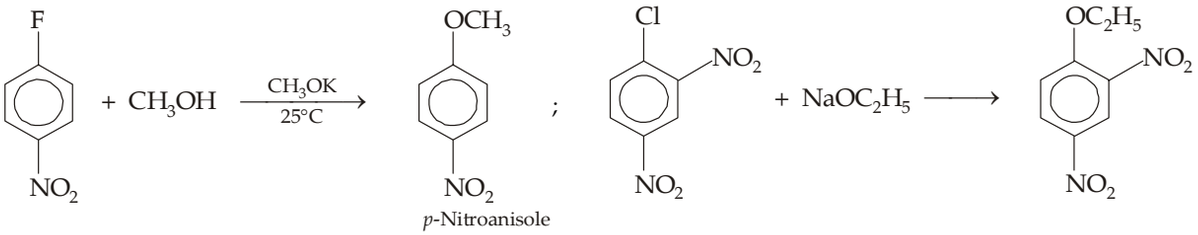
Phenol — Dimethyl sulphate (Methyl sulphate) — Anisole

(*b*) 

Remember that due to low reactivity of aryl halides toward nucleophilic substitution, they can't be used as one of the components of Williamson synthesis; *i.e.* the following pair can't be used for preparing ether.

$$CH_3CH_2CH_2ONa + \underset{\text{(low reactivity)}}{BrC_6H_5} \longrightarrow \text{No Reaction}$$

However, when the aryl halide has an electron-withdrawing substituent it can be applied for preparing ether with alcohols, *e.g.*

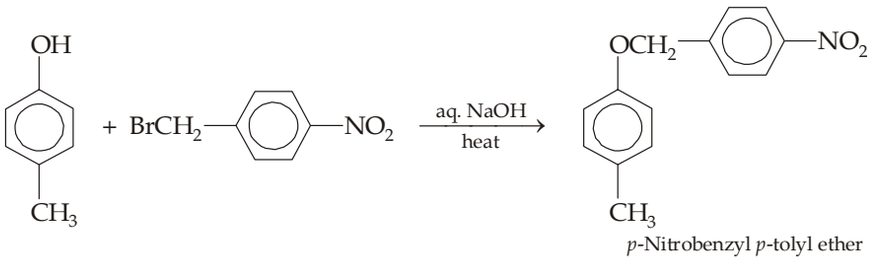


p-Nitroanisole

Recall that such aryl halides undergo nucleophilic aromatic substitution by the addition-elimination mechanism rather than S_N2 mechanism.

* 2° or 3° Alkyl halides may lead to elimination reactions.

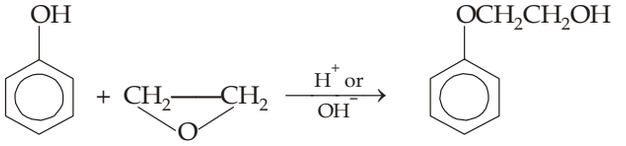
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(*c*) 

p-Nitrobenzyl *p*-tolyl ether

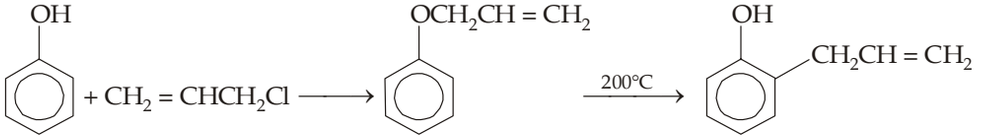
(*d*) $C_6H_5OH + ClCH_2COOH \xrightarrow[heat]{OH^-} C_6H_5OCH_2COONa \xrightarrow{HCl} C_6H_5OCH_2COOH$

Phenoxyacetic acid

(*e*) 

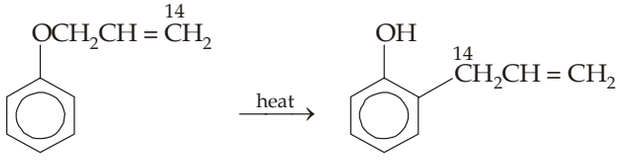
2-Phenoxyethanol

The last reaction is considered as a modification of the Williamson synthesis.

(*f*) 

Phenol Allyl chloride Allyl phenyl ether *o*-Allylphenol

Allyl aryl ethers, when heated, undergo rearrangement to form *o*-allylphenol. This reaction, known as *Claisen rearrangement,* involves migration of the allyl group from O to the ortho position of the ring. Remember that it is the C 3 (indicated by C^{14}) that becomes bonded to the benzene ring.



Like other ethers, alkyl aryl ethers are cleaved by hot conc. HBr or HI. Because of low reactivity at the bond between oxygen and an aromatic ring, alkyl aryl ethers undergo cleavage at the alkyl-oxygen bond and yields phenols and alkyl halides.

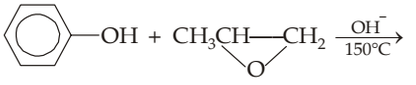
$$Ar—O—R + HI \xrightarrow{120-130^\circ C} Ar—OH + RI$$

Remember that the phenol does not react further with hydrogen halide to form aryl halide again due to strong nature of the bond between oxygen and the aromatic carbon.

TEST YOUR UNDERSTANDING - 13.7

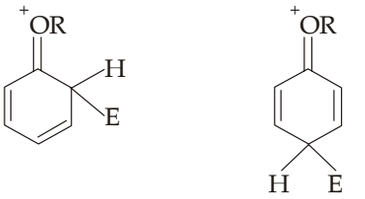
1. Why methyl sulphate is considered to be a good methylating agent ? Suggest another class of compounds that can be used in place of alkyl halides in the Williamson synthesis.

2. Predict the product of the following reaction.



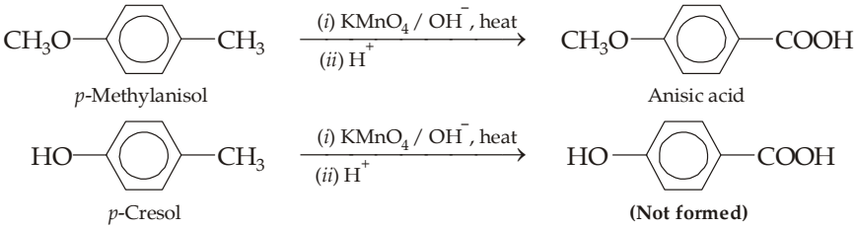
3. Alkylation of phenoxide ion with allyl chloride gives phenyl allyl ether along with some amount of *o*-allylphenol. Explain.

Other salient features of aryl alkyl ethers. Aryl alkyl ethers undergo electrophilic substitution in the *o*- and *p*-positions, because —OR groups are *o*-, *p*- directing with moderately activating effect. The alkoxy group is a much stronger activator than —R because the former involves the following especially stable intermediate oxonium ions where every atom (except hydrogen) has a complete set of electrons.

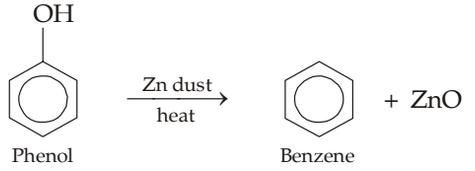


However, alkoxy group is much weaker electron-releasing than the —OH group, hence aryl ethers do not generally undergo those electrophilic substitution reactions which require the especially high reactivity of phenols, like coupling, Kolbe reaction, Reimer-Tiemann reaction, etc. This difference in reactivity is due to the fact that, unlike a phenol, an ether can't dissociate to form the extremely reactive phenoxide ion.

Due to lower reactivity of the ring, aromatic ethers are less sensitive to oxidation than a phenol, hence alkyl groups present on the ring of an ether can be easily oxidised to —COOH group.



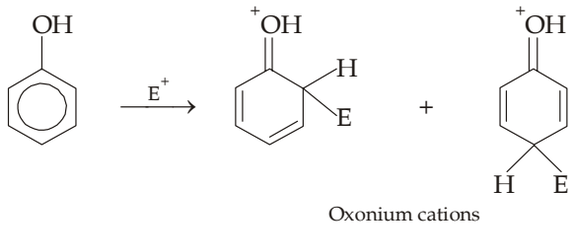
3. **Displacement of phenolic —OH group.** Like aryl halides, it is difficult to replace the —OH group of phenols. Thus, unlike ROH, phenols do not react with HX, $SOCl_2$ or phosphorus halides. However, phenols can be converted to hydrocarbons by distillation with zinc dust (replacement of —OH by H).



Displacement of phenolic —OH by —Cl. The —OH group attached to benzene ring is very less reactive, however when treated with PCl_5 it gives chlorobenzene, although in low yield because of formation of triphenyl phosphate.

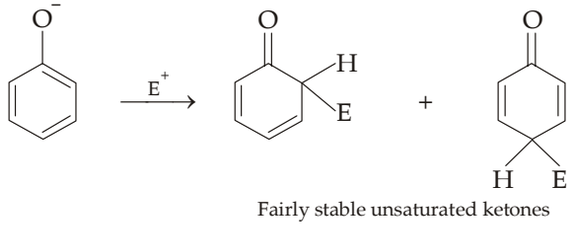
$$C_6H_5OH + PCl_5 \longrightarrow C_6H_5Cl + POCl_3 + HCl$$
$$3C_6H_5OH + PCl_5 \longrightarrow (C_6H_5)_3\,PO_3 + 3HCl$$

4. **Electrophilic aromatic substitution.** The —OH and even more so the —O^- (phenoxide) ion are strongly activating and *op*-directing. High reactivity of phenol can be attributed to exceptionally high stability of intermediates, which are oxocations, in which every atom (except hydrogen) has a complete octet of electrons. Hence they are formed tremendously faster than the carbocations derived from benzene itself.



Oxonium cations

Phenoxide ion forms even more stable, and hence more rapidly formed, intermediates—the unsaturated ketones.

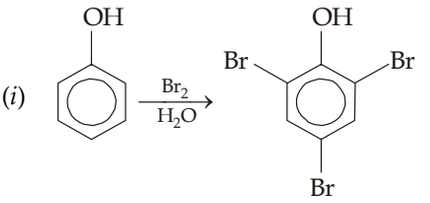


Fairly stable unsaturated ketones

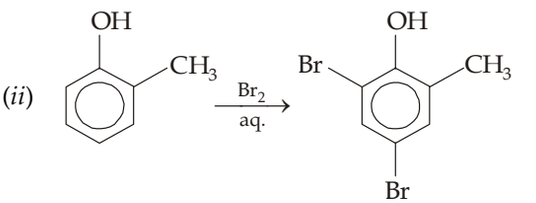
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Hence, like amines, special mild conditions are needed to achieve electrophilic monosubstitution in phenols because their high reactivity favours both polysubstitution and oxidation.

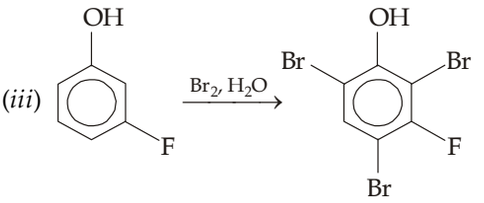
(*a*) **Halogenation.** Treatment of phenols with aqueous solution of bromine and even in absence of a catalyst results in replacement of every hydrogen *ortho*- or *para* to the —OH group, and may even cause displacement of certain groups, like —SO_3H (*bromodesulphonation*, see example *iv*).

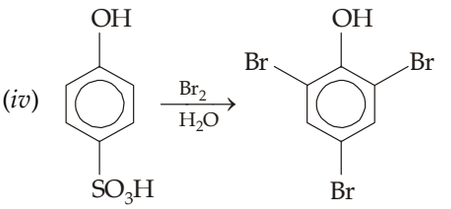


Phenol 2, 4, 6- Tribromophenol

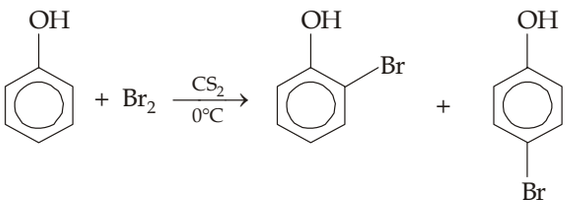


o-Crersol 4, 6-Dibromo-2-methylphenol



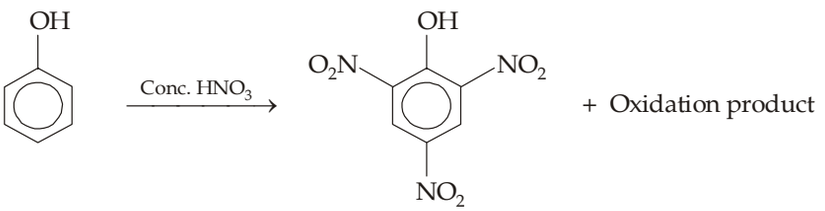


Monobromination can be achieved with non-polar solvents (like CS_2, $CHCl_3$, CCl_4 or CH_2ClCH_2Cl) to decrease the electrophilicity of Br_2 and also to minimize phenol ionization.



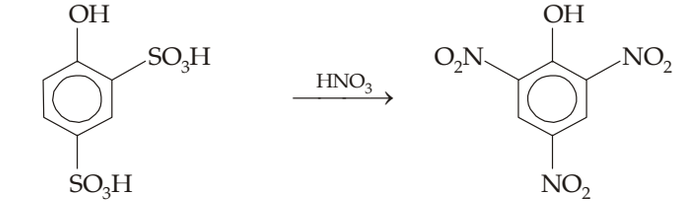
o-Bromophenol *p*-Bromophenol **(Major)**

(*b*) **Nitration**



2, 4, 6-Trinitrophenol **(Picric acid)**

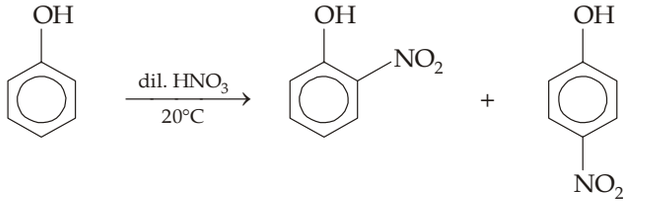
However, picric acid can quantitatively be prepared by treating phenol -2, 4-disulphonic acid with nitric acid.



Phenol -2, 4-disulphonic acid 2, 4, 6-Trinitrophenol

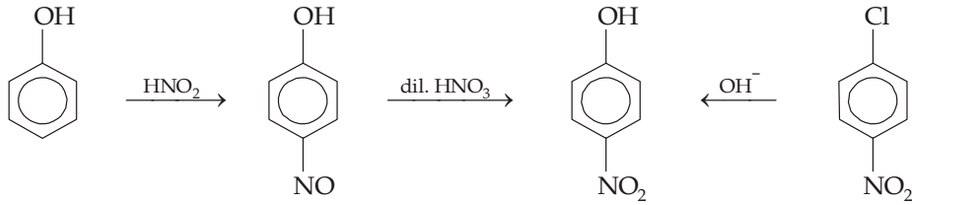
Two nitro groups (at position 2 and 4) are introduced by *nitrodesulphonation* (displacement of —SO_3H by electrophile, NO_2^+) while the third —NO_2 group at position 6 is introduced by direct nitration, note that this position (6) is favoured by all the three substituents already present in the molecule. Since, there is less destructive oxidation by the nitrating agent, this method gives a good yield.

Mononitro products, of course in poor yield, can be obtained by using dil nitric acid at a low temperature.



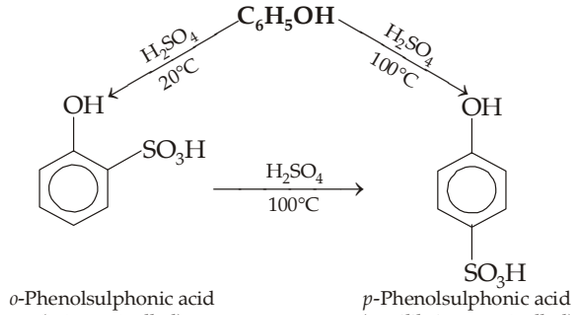
o-Nitrophenol *p*-Nitrophenol

Recall that the two isomeric nitrophenols can be easily separated because the *o*-isomer is steam volatile. Since direct nitration of phenol even under mild conditions gives low yield, these are better obtained *via* nitrosation or by hydrolysis of chloronitrobenzenes.



Phenol *p*-Nitrosophenol *p*-Nitrophenol *p*-Chloronitrobenzene

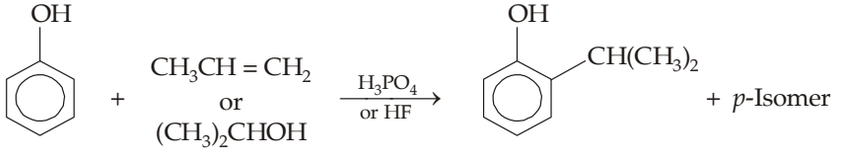
(*c*) **Sulphonation.** Phenol reacts with concentrated sulphuric acid to give mainly the *o*-sulphonated product at 20°C and mainly the *p*-sulphonated product at 100°C. This is another* example of thermodynamic (or equilibrium) versus kinetic (or rate) control of a reaction.

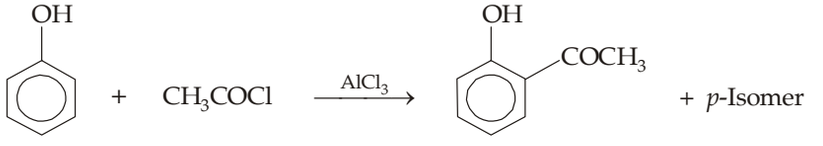


o-Phenolsulphonic acid (rate-controlled) *p*-Phenolsulphonic acid (equilibrium-controlled)

The reason for the formation of two different products at different temperatures is due to *reversible nature of sulphonation. The ortho isomer is formed more rapidly* and thus it will be the major product at low temperature, *while the para isomer is more stable* and thus it will be the major product at high temperature.

(*d*) **Friedel-Craft's alkylation and acylation.** Since RX and $AlCl_3$ give poor yields because $AlCl_3$ coordinates with oxygen of phenol, the latter is alkylated with the help of alkene or alcohol in presence of acid like H_2SO_4 or HF.





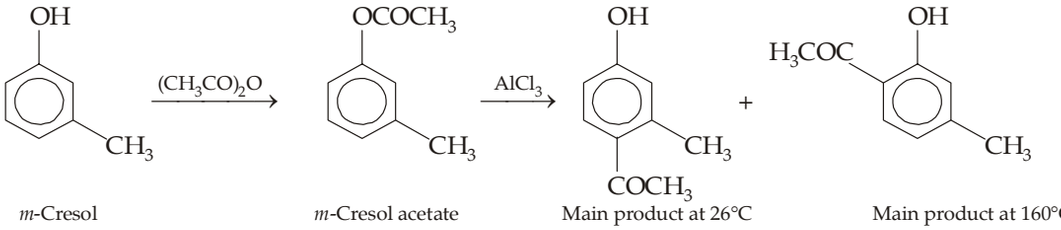
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* Addition of HBr on 1, 3-butadiene is also such example.

$$CH_2 = CHCH = CH_2 \xrightarrow{HBr} \underset{\substack{\text{1, 2-Product}\\ \text{(rate or kinetic controlled)}}}{CH_3CH(Br)CH = CH_2} + \underset{\substack{\text{1, 4-Product}\\ \text{(thermodynamic or equilibrium controlled)}}}{CH_3CH = CHCH_2Br}$$

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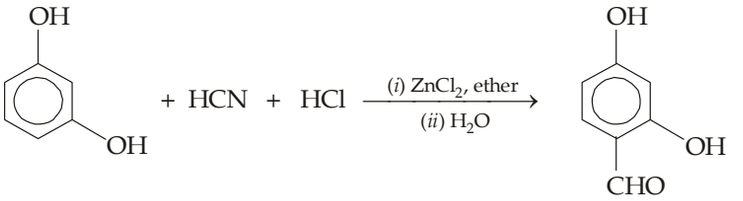
However, phenolic ketones are best prepared in two steps by means of Fries rearrangement (discussed earlier).



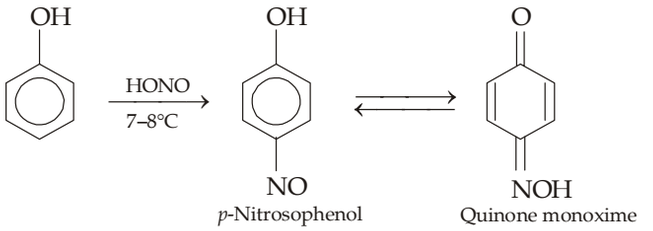
m-Cresol | *m*-Cresol acetate | Main product at 26°C | Main product at 160°C

(*e*) **Gattermann reaction**

$$C_6H_5OH + HCN + HCl \xrightarrow{ZnCl_2} p\text{-}CHO.C_6H_4.OH$$



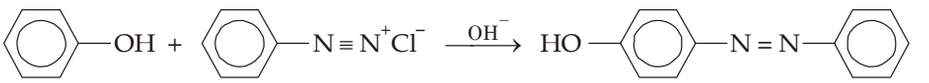
(*f*) **Nitrosation.** Since phenols are highly reactive, they also undergo electrophilic substitution by the weak electrophiles, like nitrosonium ion $(\overset{+}{N}O)$ and diazonium ions (ArN_2^+).



p-Nitrosophenol | Quinone monoxime

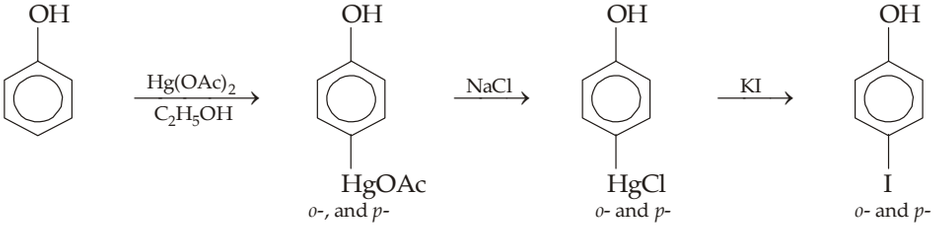
Since —NO group is readily oxidized to the $—NO_2$ group by nitric acid, nitrosation route is considered to be better way to synthesize *p*-nitrophenol than the direct nitration which may lead to oxidation of phenol.

(*g*) **Coupling with diazonium salts** with phenols gives azophenols.



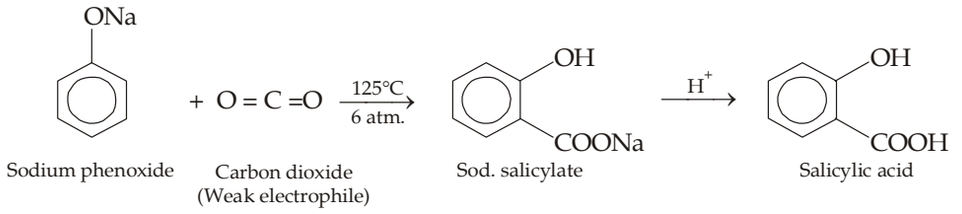
p-Hydroxyazobenzene

(*h*) **Mercuration.** Mercuriacetate cation, $\overset{+}{H}gOAc$ is another weak electrophile which substitutes in *ortho* and *para* positions of phenols. This reaction is used to introduce an –I on the ring.

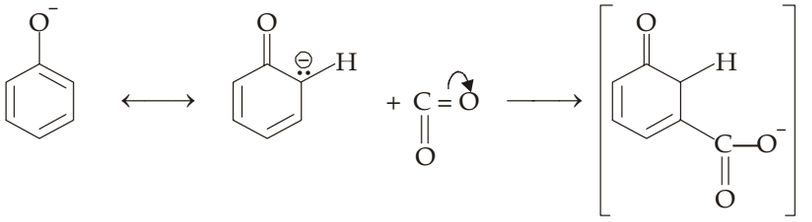


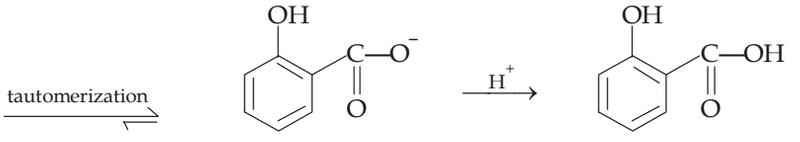
o-, and *p*- | *o*- and *p*- | *o*- and *p*-

(*i*) **Kolbe reaction** *or* **Kolbe-Schmidt reaction.** Treatment of sodium phenoxide phenol (activated toward electrophilic substitution) with carbon dioxide (a weak electrophile) at 125°C under pressure yields sodium salt of *o*-hydroxybenzoic acid. This reaction, known as *Kolbe reaction*, brings about substitution of the —COOH group for hydrogen of the ring.

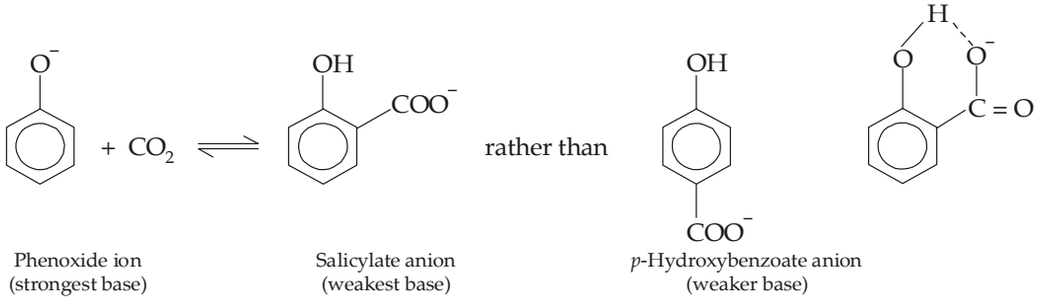


Mechanism.



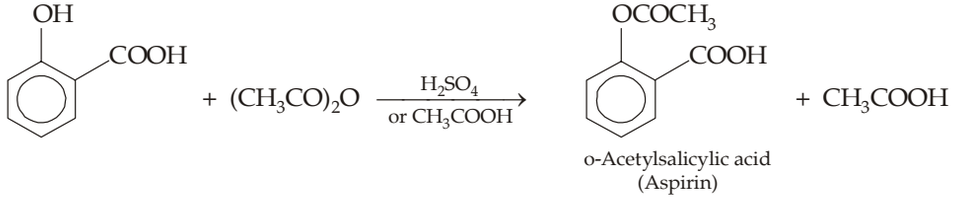


The Kolbe reaction is an equilibrium process governed by thermodynamic control. The position of equilibrium favours formation of the weaker base (salicylate ion) at the expense of the stronger one (phenoxide ion). Thermodynamic control is also responsible for the pronounced bias toward *ortho* over para substitution. Salicylate anion is a weaker base than *p*-hydroxybenzoate and so is the predominant species at equilibrium.



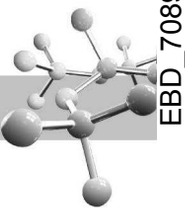
Weaker basic character of the salicylate anion than *p*-hydroxybenzoate anion is because of its stability due to intramolecular hydrogen bonding.

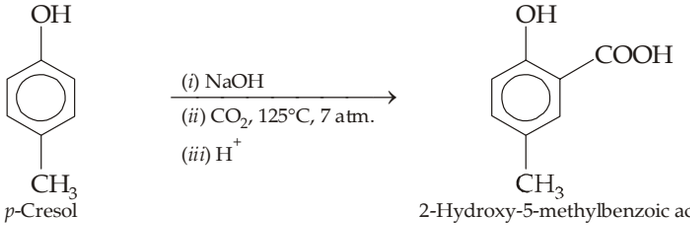
Salicylic acid is very important compound as it is used for preparing *o*-acetylsalicylic acid, also known as *aspirin*, by acetylation with acetic anhydride.



Aspirin has several medicinal properties, hence it is used as an *analgesic* (for relieving pain), *antipyretic* (for reducing fever) and *anti-inflammatory agent* (for relieving swelling associated with arthritis and minor injuries).

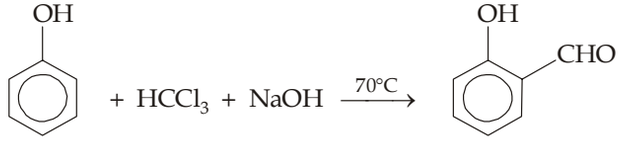
Phenols bearing alkyl groups behave very much like phenol, while phenols bearing strongly electron-withdrawing groups give low yields because their corresponding phenoxide anions are less basic.



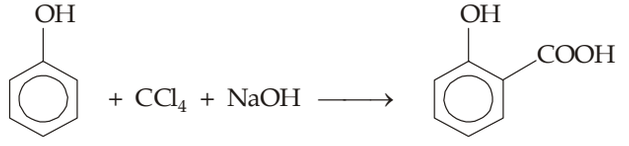


p-Cresol — 2-Hydroxy-5-methylbenzoic acid

(*j*) **Reimer-Tiemann reaction.** Treatement of a phenol with chloroform (or cabon tetrachloride) and aqueous hydroxide introduces an aldehyde (or —COOH) group in the *o*-position to the —OH group ; this reaction is known as *Reimer-Tiemann reaction.*



Salicylaldehyde

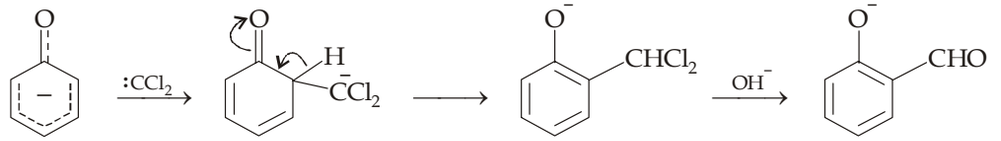


Salicylic acid

Mechanism. The reaction involves electrophilic substitution on the highly reactive phenoxide ring. Here the electrophile is dichlorocarbene, **:** CCl_2, generated from $CHCl_3$ (or CCl_4) by the action of a base

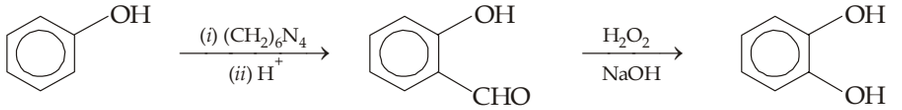
$$HCCl_3 + OH^- \longrightarrow H_2O + {}^-{:}CCl_3 \longrightarrow Cl^- + {:}CCl_2$$

Note that C has only a sextet of electrons



A benzal chloride

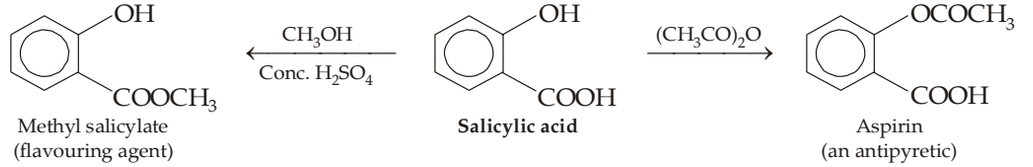
Salicylaldehyde can also be prepared by heating phenol with hexamethylenetetramine, glycerol and boric acid (**Duff reaction)**.



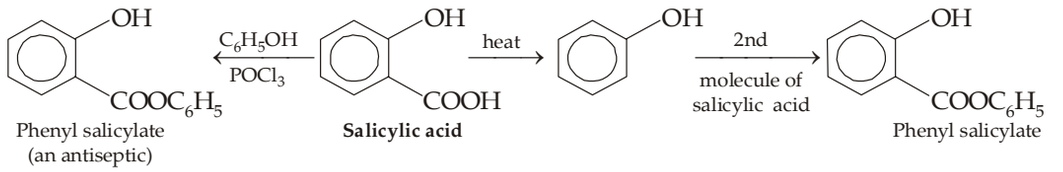
Phenol — Salicylaldehyde — Catechol

Salicylaldehyde, on oxidation with alkaline hydrogen peroxide is converted into 1, 2-dihydroxybenzene **(Dakin reaction).**

Three important derivatives of salicylic acid are **aspirin** (acetylsalicylic acid), **salol** (phenyl salicylate) and **methyl salicylate** (oil of wintergreen).

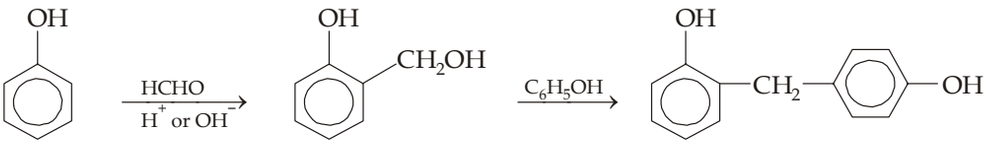


Methyl salicylate (flavouring agent) — **Salicylic acid** — Aspirin (an antipyretic)

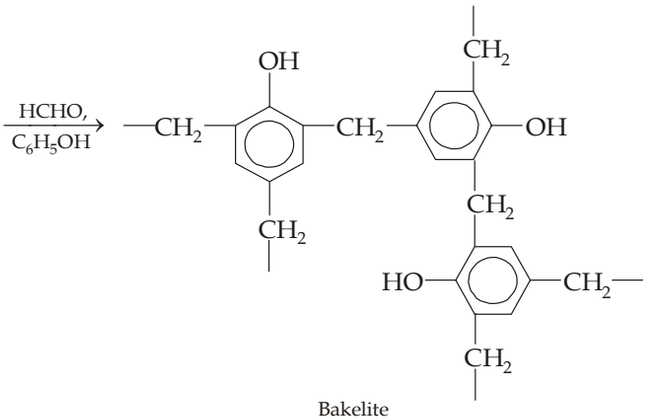


Phenyl salicylate (an antiseptic) — **Salicylic acid** — Phenyl salicylate

(*k*) **Condensation with formaldehyde.** When phenol is heated with formaldehyde (an electrophile) in presence of alkali or acid, a high-molecular-substanace (polymer), known as bakelite, is obtained in which many phenol rings are held together by —CH_2— groups.

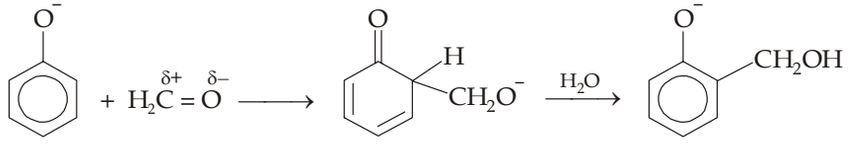


o-Hydroxymethylphenol



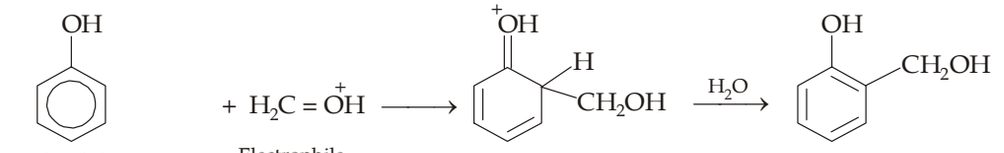
Bakelite

Base-catalysed mechanism. Base catalyzes reaction by converting phenol into the more reactive (more nucleophilic) phenoxide ion



Nucleophile Electrophile

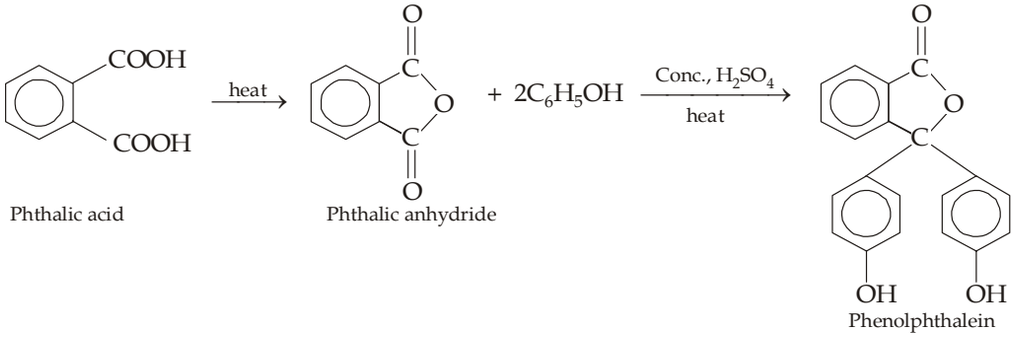
Acid-catalysed mechanism. Acid catalyzes reaction by protonating formaldehyde and thus increasing the electron deficiency of the carbonyl carbon



Nucleophile (weaker than $C_6H_5O^-$)

Electrophile (stronger than CH_2O)

(*l*) **Condensation of phenol with phthalic anhydride** in presence of conc. H_2SO_4 forms phenolphthalein (an acid-base indicator) which gives pink colour with NaOH



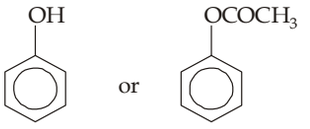
Phthalic acid Phthalic anhydride Phenolphthalein

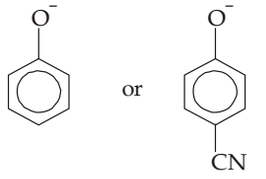
This reaction is used for detecting the presence of *o*-dibasic acid, *viz*. phthalic acid under the name of **phthalein test.** Condensation of resorcinol with phthalic anhydride in presence of conc. H_2SO_4 gives **fluorescein.**

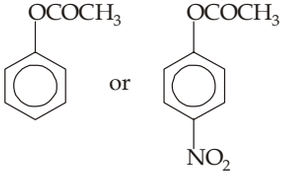
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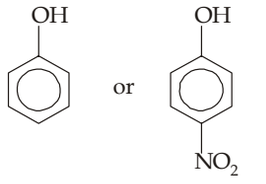
TEST YOUR UNDERSTANDING - 13.8

1. Which of the compound reacts faster, with the given reaction, in each of the following pairs ?

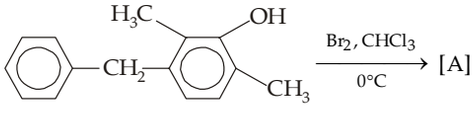
(*a*)  (for nitration)

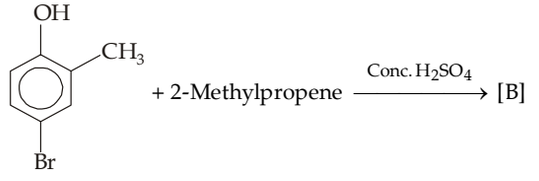
(*b*)  (for reaction with $C_6H_5CH_2Cl$)

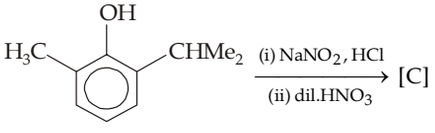
(*c*)  (for base-catalysed hydrolysis)

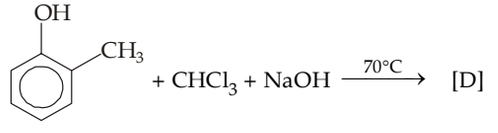
(*d*)  (for acid-catalysed esterification)

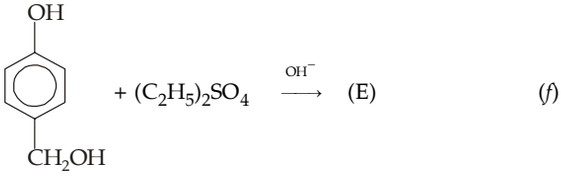
2. Give major product in each of the following reactions.

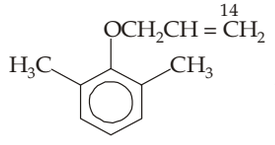
(*a*) 

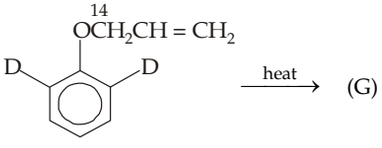
(*b*) 

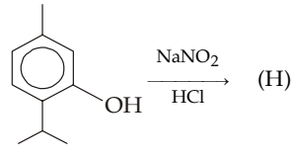
(*c*) 

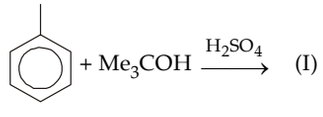
(*d*) 

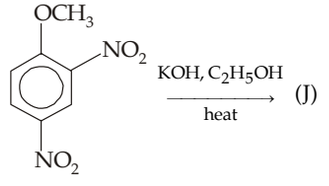
(*e*) 

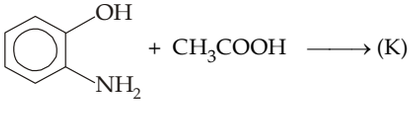
(*f*) 

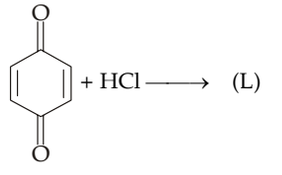
(*g*) 

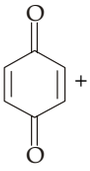
(*h*) 

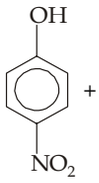
(*i*) 

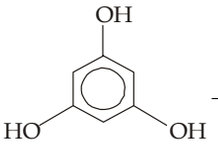
(*j*) 

(*k*) 

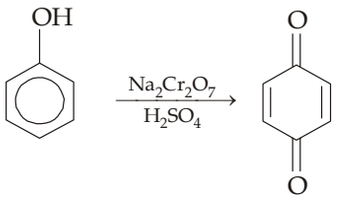
(*l*) 

(*m*)  + $H_2SO_3 + H_2O \longrightarrow$ (M)

(*n*)  + $CH_2(OC_2H_5)_2 \xrightarrow[H_2SO_4]{\text{Conc. HCl}}$ (N)

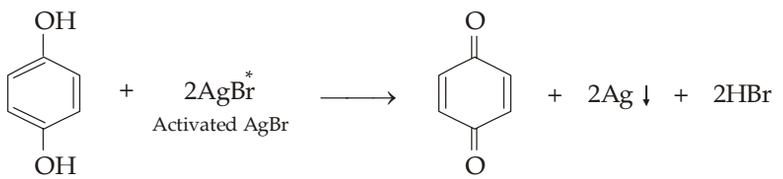
(*o*)  $\xrightarrow{NH_2OH}$ (O)

5. **Oxidation of phenols.** Phenols are more easily oxidized than alcohols. The oxidation can be brought by chromic acid to form conjugated dicarbonyl compounds, called **quinones.**

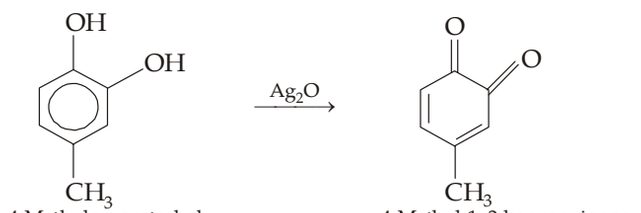


Phenol *p*-Benzoquinone

Hydroquinone is easily oxidised because it already has two oxygen atoms to the ring. Even very weak oxidants like silver bromide can oxidize hydroquinone.

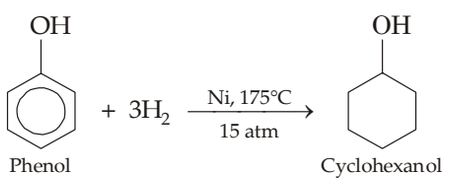


This reaction has been used in black-and-white photography. A film containing small grains of AgBr is exposed by a focussed image. When light strikes the film, AgBr grains are activated. The film is then treated with a hydroquinone solution (the developer) to reduce the activated AgBr to metallic black silver. This is the negative image, the dark (black) areas indicate the area exposed to light.



4-Methylpyrocatechol 4-Methyl-1, 2-benzoquinone

6. **Hydrogenation of phenols.**



Phenol Cyclohexanol

13.6 Analysis of Phenols

(*i*) Phenols have peculiar type of acidity. Most of them are stronger acids than water but weaker than carbonic acid. Hence, most of phenols dissolve in aqueous NaOH but not in aqueous $NaHCO_3$.

(*ii*) Many (*but not all*) phenols form coloured complexes, ranging from green through blue and violet to red, with ferric chloride. This test is also given by enols.

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TEST YOUR UNDERSTANDING - 13.9

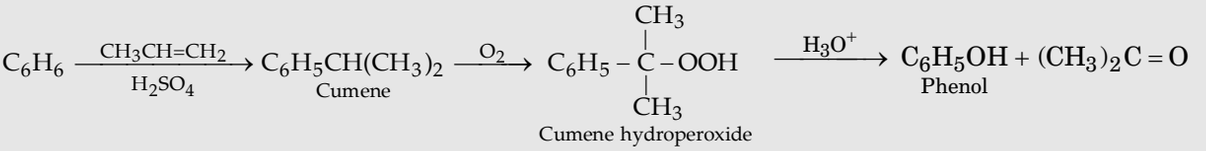
1. (*a*) Benzene ring of phenol is more easily oxdised than benzene itself. Explain.
(*b*) Give the method for the preparation of *p*-benzoquinone, other than direct oxidation.

2. Use simple chemical tests to differentiate between each member of the following pairs of compounds.
(*a*) Anisole and cresol
(*b*) Anisole and benzyl alcohol
(*c*) Salicylic acid and acetylsalicylic acid
(*d*) Ethyl salicylate and ethyl acetylsalicylate
(*e*) 2, 4, 6-Trimethylphenol and 2, 4, 6-trinitrophenol.

13.7 Illustrative Examples

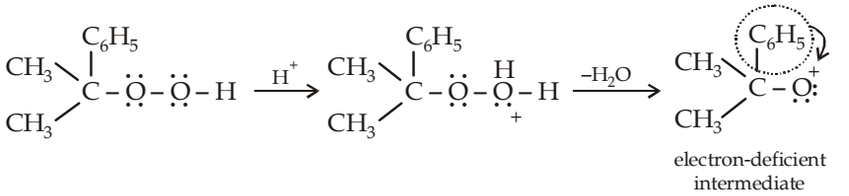
Example 1 :

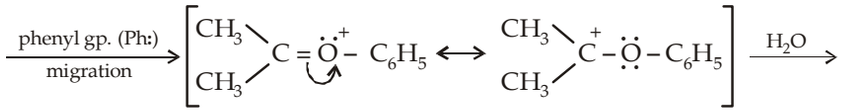
In industries phenol is prepared from cumene (isopropylbenzene) according to following steps.

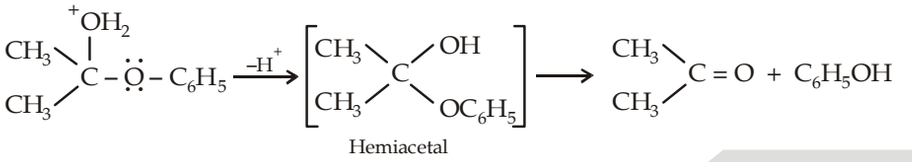


Suggest a mechanism for the acid-catalyzed decomposition of cumene hydroperoxide to phenol.

Solution :





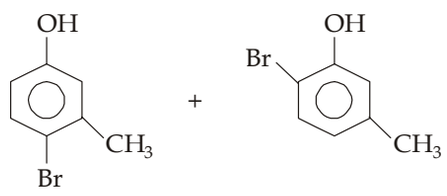


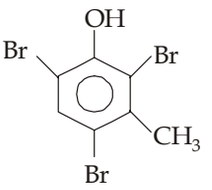
Example 2 :

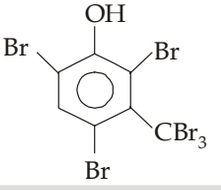
Give the structure of the products formed, when *m*-cresol is treated separately with each of the following reagent.

(a) Bromine in CCl_4 in the dark
(b) Excess of bormine in CCl_4 in the dark
(c) Excess of bromine in CCl_4 in the light

Solution :

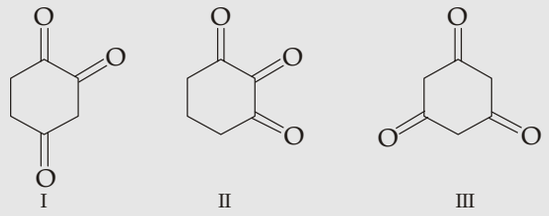
(a) 

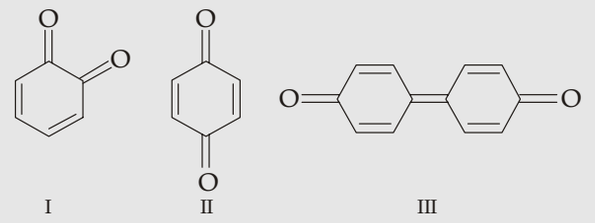
(b) 

(c) 

Example 3 :

Arrange the following three compounds in decreasing order of stability.

(a) 

(b) 

Solution :

(*a*) The keto group (C = O) has large resonance energy and therefore its presence imparts stability in the molecule. Since each of the three compounds has three keto groups, these should be quite stable. However, the compounds II and III have two or more C = O's on the adjacent carbon atoms, these are destabilized. Hence the order of stability will be

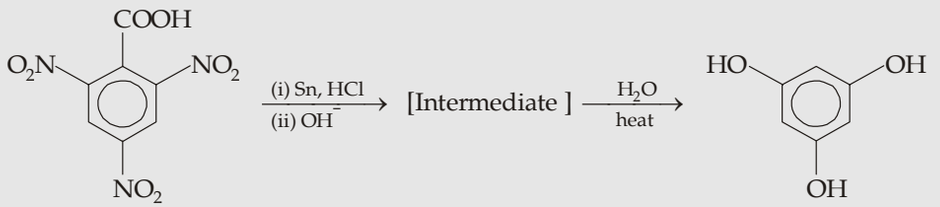
III > I > II

(*b*) The compound I has two adjacent C = O's which destabilize the *ortho* isomer relative to the para (II). Hence compound I is least stable. Relative stability between compounds II and III can be ascertained by the stability of their reduced products. Reduction of II will give a compound with a single benzene ring, while that of III gives a compound with two benzene rings, hence III will be more stable than II. Thus the stability order will be

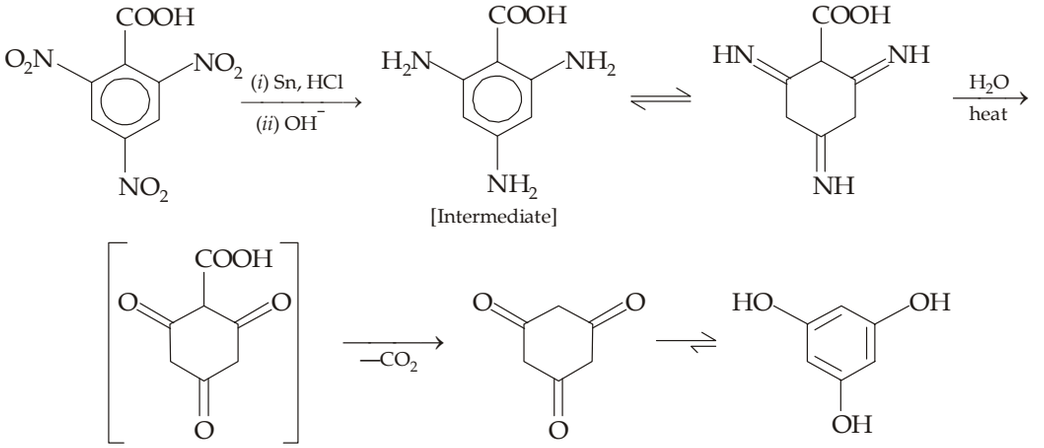
III > II > I

Example 4 :

Give steps involved in the following conversion.



Solution :

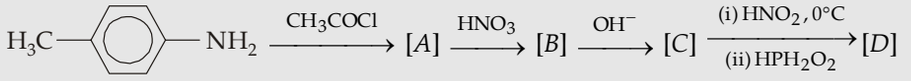


The intermediate undergoes hydrolysis through its triimino tautomer which gives corresponding triketo carboxylic acid. The latter, being a β-keto acid, readily decarboxylates to form triketo compound which readily tautomerizes to the more stable trihydric phenol. Higher stability of the phenol is due to presence of a very stable benzene ring.

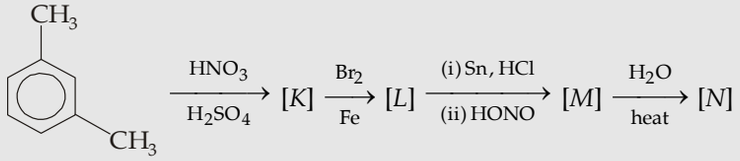
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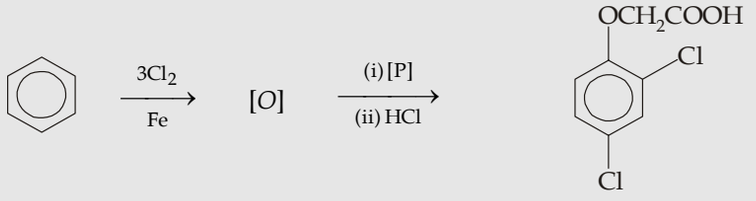
Example 5 :

Give structures of the bracketed products in each of the following reactions.

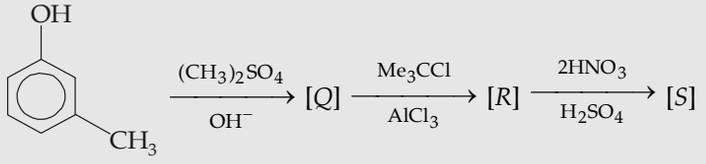
(*a*) 

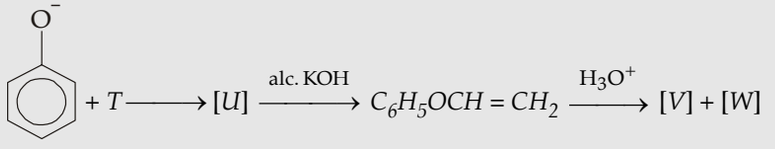
(*b*) $C_6H_5CH_3 \xrightarrow{HNO_3} [E] \xrightarrow[\text{heat}]{KMnO_4, H^+} [F] \xrightarrow[\text{(ii) } OH^-]{\text{(i) Sn, HCl}} [G] \xrightarrow[\text{(ii) heat}]{\text{(i) } HNO_2, 0°C} [H] \xrightarrow{SOCl_2} [I] \xrightarrow{LiAlH(OMe_3)_3} [J].$

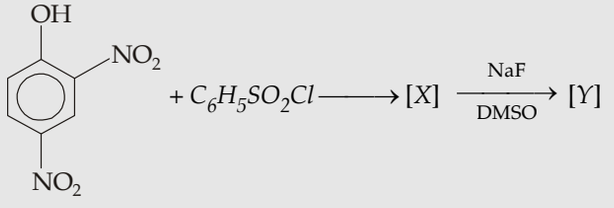
(*c*) 

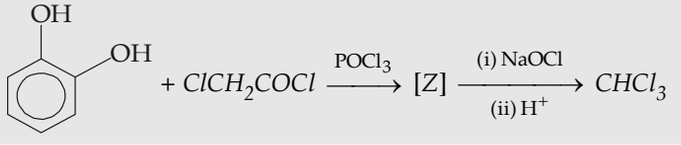
(*d*) 

2, 4-Dichlorophenoxyacetic acid (a sea weed)

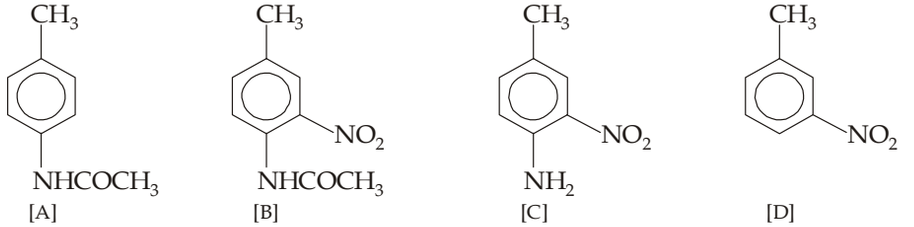
(*e*) 

(*f*) 

(*g*) 

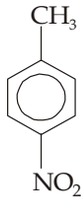
(*h*) 

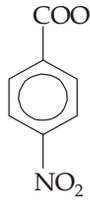
Solution :

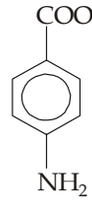
(*a*) 

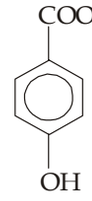
[A] [B] [C] [D]

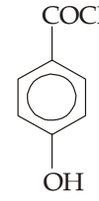
(*b*)

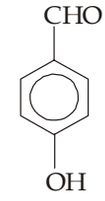

[E]


[F]

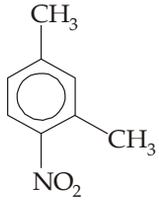

[G]

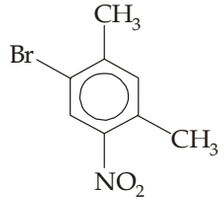

[H]

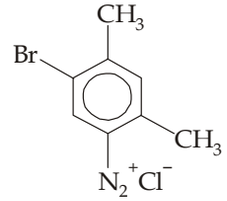

[I]

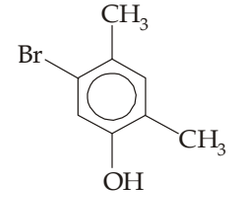

[J]

(*c*)

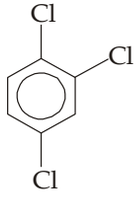

[K]

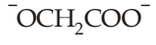

[L]


[M]

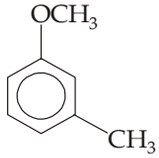

[N]

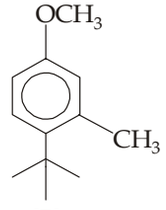
(*d*)

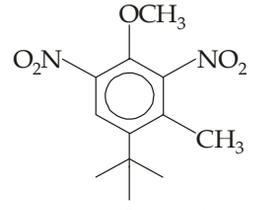

[O]


[P]

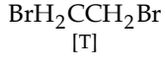
(*e*)


[Q]

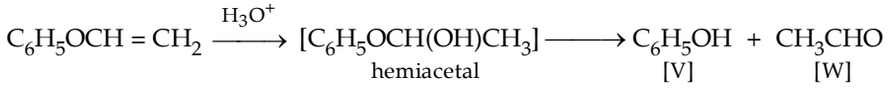

[R]


[S] A synthetic musk

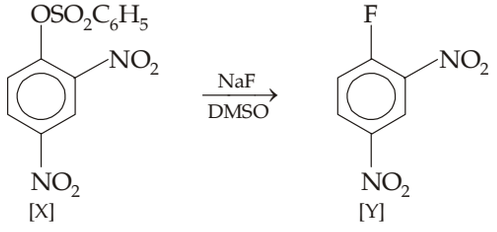
(*f*)


[T]


[U]

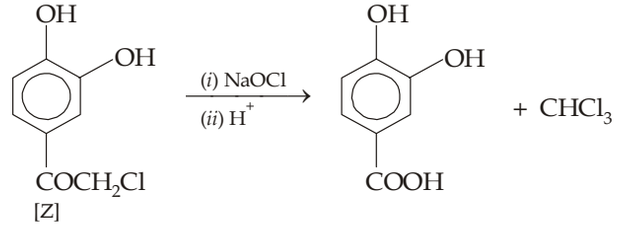

hemiacetal [V] [W]

(*g*)


[X] [Y]

Note that in the conversion of [X] to [Y], the very reactive unsolvated F^- displaces the good leaving group ($C_6H_5SO_3^-$) from the activated benzene ring.

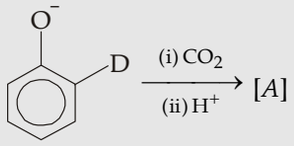
(*h*) Since Z undergoes haloform reaction, it must have —$COCH_2Cl$ grouping. Hence Z is acylated product of catechol.

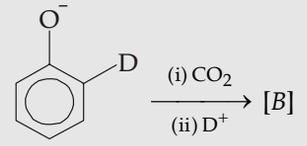

[Z]

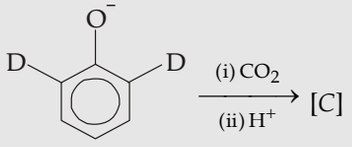
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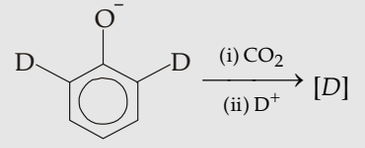
Example 6 :

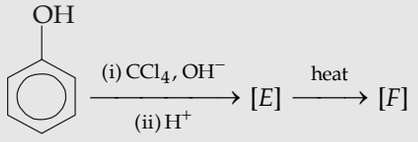
Give structures of the bracketed compounds, A to H.

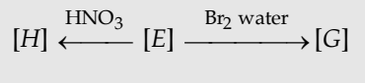
(*a*) 

(*b*) 

(*c*) 

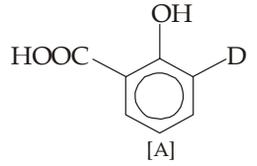
(*d*) 

(*e*) 

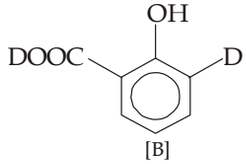
(*f*) 

Solution :

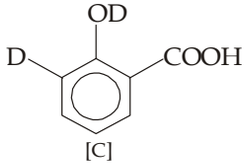
Note that reactions (*a*) to (*d*) are examples to Kolbe's reaction. For knowing the structure, students should know the mechanism of Kolbe reaction.

(*a*) 

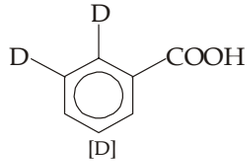
[A]
(C—D bond is stronger than C—H)

(*b*) 

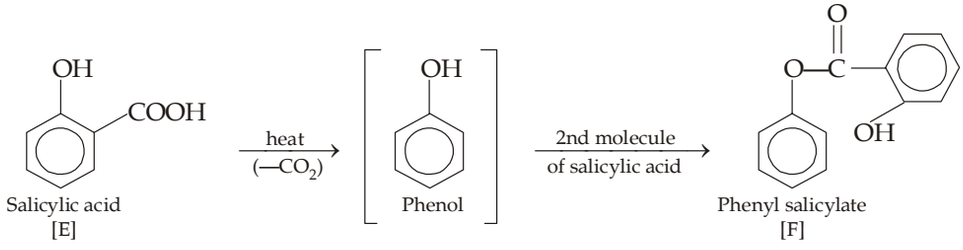
[B]

(*c*) 

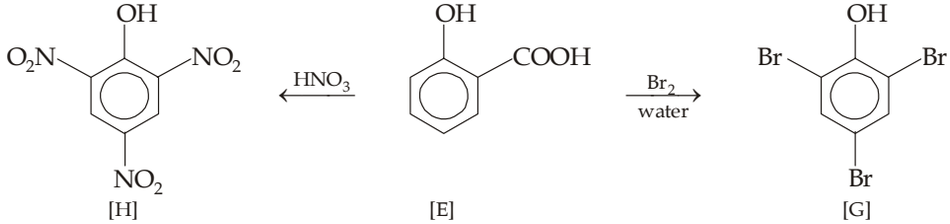
[C]

(*d*) 

[D]

(*e*) 

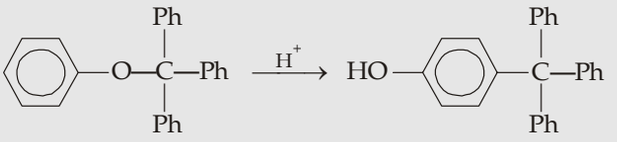
Salicylic acid [E] — Phenol — Phenyl salicylate [F]

(*f*) 

[H] — [E] — [G]

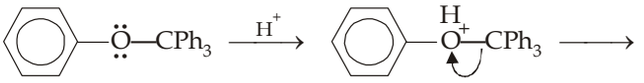
Example 7 :

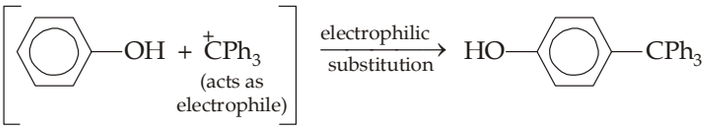
Give steps involved in following conversions.

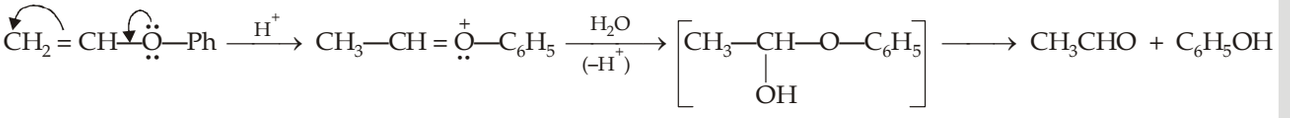
(*a*) 

(*b*) $CH_2 = CH—O—Ph \xrightarrow{H^+} CH_3CHO + C_6H_5OH$

Solution :

(*a*) 



(*b*) 

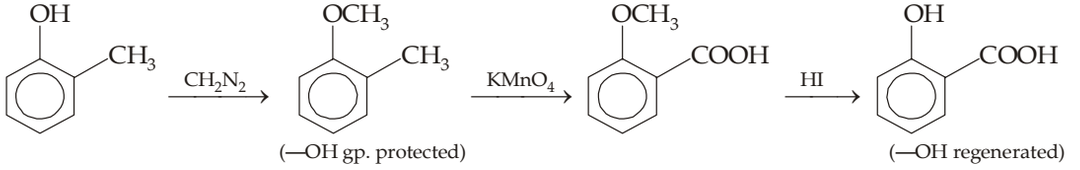
A hemiacetal

Example 8 :

Outline method for converting o-cresol to salicylic acid in quantitative yield.

Solution :

At first step, it seems that CH_3 group can directly be oxidised to —COOH group by $KMnO_4$, but this can cause damage to the benzene ring due to the presence of —OH (an activating) group. So, in order to get quantiative yield of the acid, —OH group must first be protected

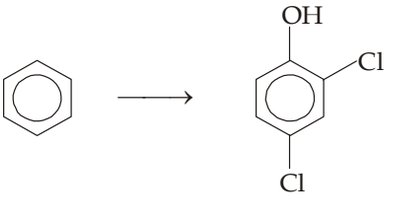


(—OH gp. protected) (—OH regenerated)

Example 9 :

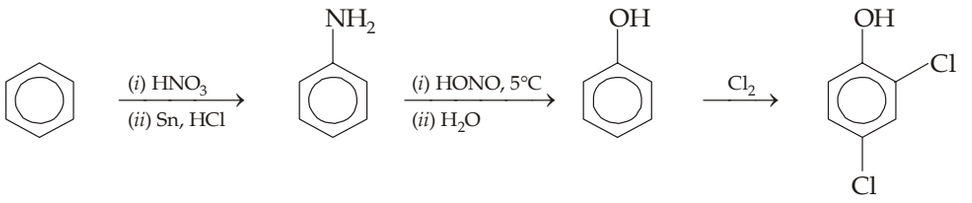
Prepare (a) 2, 4-dichlorophenol, and (b) 2, 4, 6-trinitrophenol from benzene.

Solution :

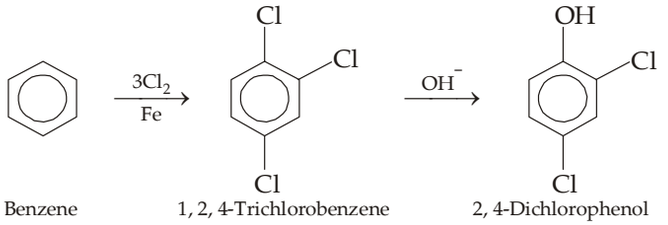
(*a*) 

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At first sight, it seems that the conversion can be affected by first converting benzene to phenol and then chlorinating the phenol.

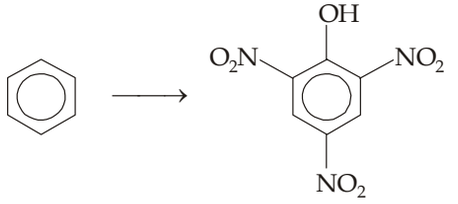


However, this method is not feasible because phenol is susceptible to oxidation by Cl_2. Hence the following scheme should be adopted.



Remember that ordinarily chlorine present on benzene nucleus is difficult to be replaced. However, when it has electron-withdrawing group in the *o*- and *p*-position it is easily replaced. Here chlorine present on C_1 is *ortho* to one chlorine (electronegative group) and para to other, hence it is replaced. Other two chlorines (at C_2 and C_4) are present at *meta* position to at least one chlorine, hence these are not replaced.

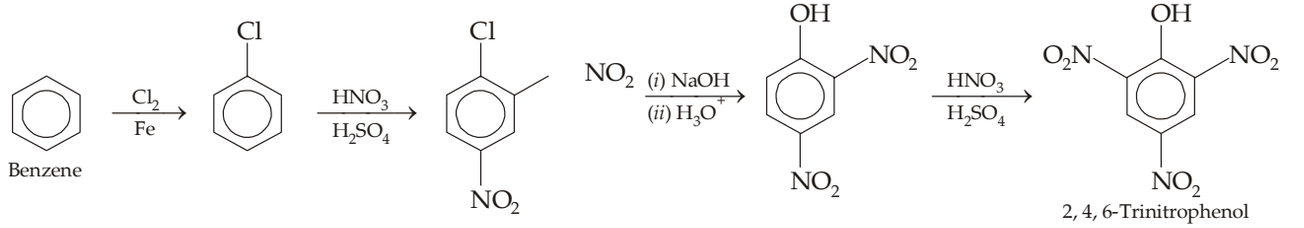
(*b*)



Here again following route is not feasible because of high susceptibility of phenol to oxidation by HNO_3.

$$C_6H_6 \longrightarrow C_6H_5OH \xrightarrow[H_2SO_4]{HNO_3} \text{Oxidised products}$$

Thus following scheme is adopted.



Note that :

(*i*) 2, 4-Dinitrochlorobenzene can't be nitrated further because the Cl and two NO_2's deactivate the ring toward further electrophilic substitution.

(*ii*) 2, 4-Dinitrophenol can be nitrated because the two deactivating NO_2's prevent ring oxidation. Moreover, the third NO_2 group is directed at the desired site by all the existing three groups.

Example 10 :

Devise laboratory synthesis for the following compounds from the given organic compound.

(a) ***m*-Iodophenol from benzene** **(b)** **3-Bromo-4-methylphenol from toluene**

(c) **2-Bromo-4-methylphenol from toluene** **(d)** ***m*-Aminophenol from benzene**

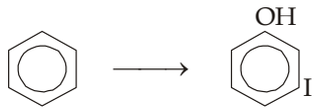
(e) **2-Hydroxy-5-methylbenzaldehyde from *p*-toluidine** **(f)** ***m*-Methoxyaniline from benzenesulphonic acid**

(g) **2, 4-Dinitrophenyl phenyl ether from chlorobenzene** **(h)** **4-Amino-2-hydroxybenzoic acid from nitrobenzene**

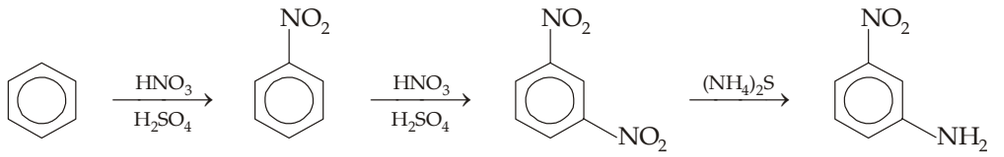
(i) **2, 4-Diaminophenol from chlorobenzene** **(j)** **5-Methylresorcinol from toluene.**

Solution :

(*a*)

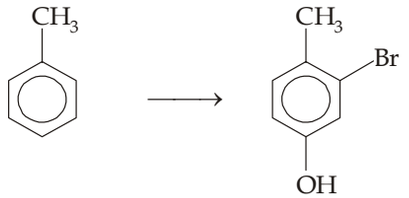


Either of the group can't be introduced directly at the required site, hence these are introduced indirectly through diazotisation.

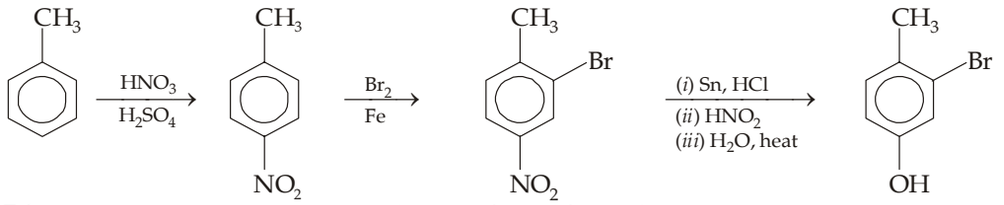


m-Iodophenol

(*b*)



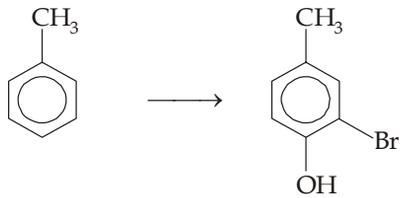
Here OH group in *para* position to CH_3 group can be easily introduced through nitration, reduction, diazotisation and heating the product. But note that Br is present in *m*-position to the —OH group, so it can not be introduced at the final stage. Hence it should be introduced at some intermediate step which is after nitration of $C_6H_5CH_3$ because in such case —Br at the required site will be directed by both of the existing groups (—CH_3 as well as —NO_2)



Toluene

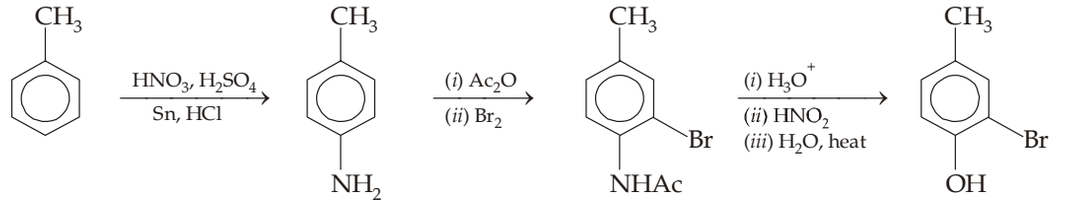
(Position of —Br is favoured by CH_3 as well as NO_2)

(*c*)



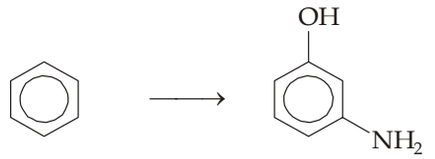
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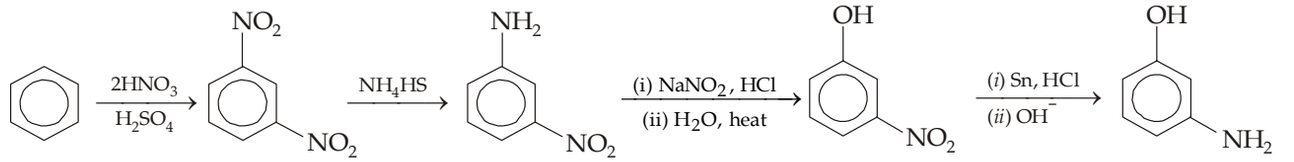
Note that here Br is present *ortho* to OH and *meta* to CH_3, so it must be introduced prior to OH and, of course, after the introduction of NH_2 which will give OH at the desired site because NH_2 is stronger activating group than CH_3.



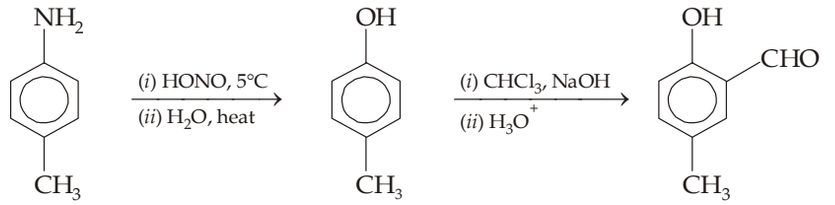
(NH_2 gp. is protected since Br_2 is oxidising agent)

(*d*)

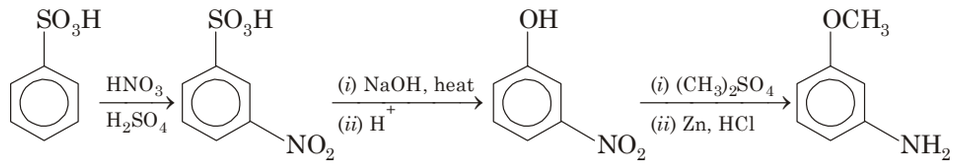




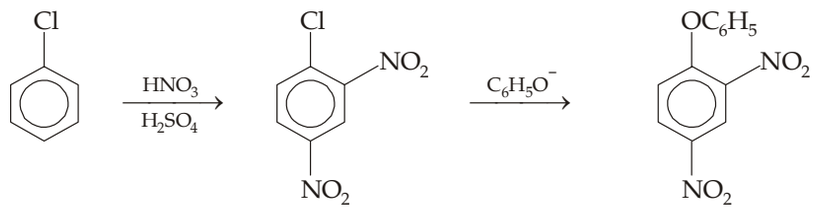
(*e*)



(*f*)

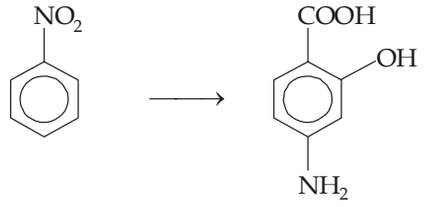


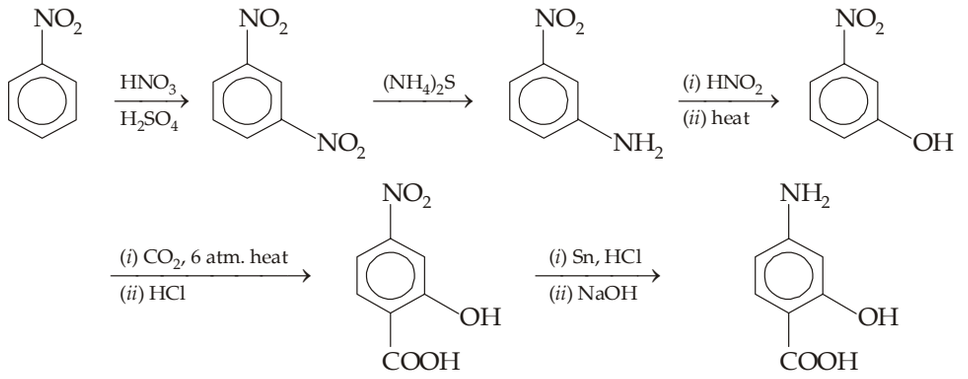
(*g*)



(–Cl activated by two —NO_2 gps.)

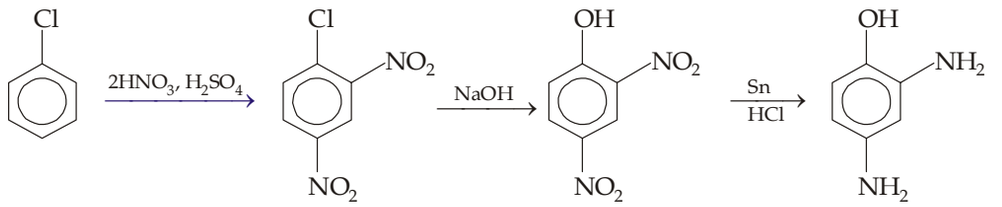
(*h*)





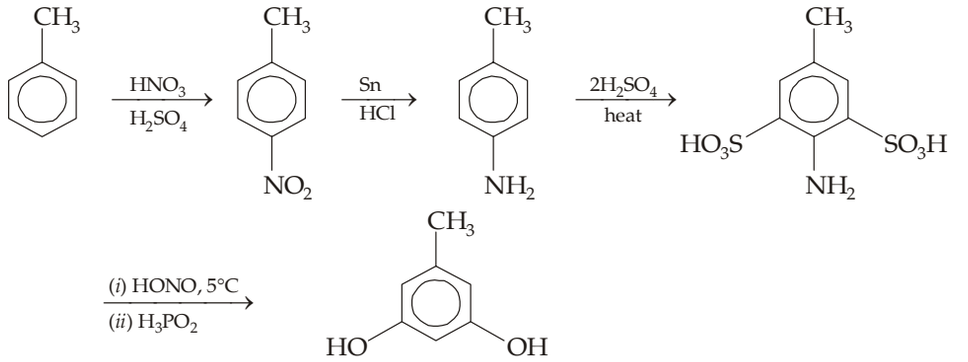
4-Amino-2-hydroxybenzoic acid

(*i*)



2, 4-Diaminophenol
(**Amidol,** a photographic developer)

(*j*)



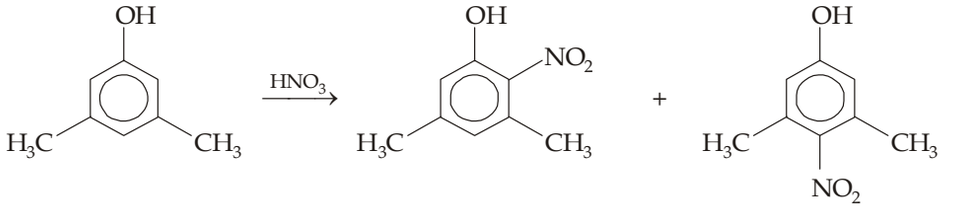
5-Methylresorcinol
(**Orcinol**, a constituent of litmus dye)

Example 11 :

A phenol ($C_8H_{10}O$) having two methyl groups as substituent, when treated with dilute nitric acid, gives two isomeric products. Give the structure of the isomers and the possible way for separating them.

Solution :

The phenol should have two CH_3 groups in 3 and 5 positions because only this can give two isomeric products.



3, 5-Dimethylphenol

Intramolecular H-bonding possible, hence it can be steam-distilled

(It is non-volatile)

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Example 12 :

(a) An organic compound (A) of the molecular formula C_7H_8O gives following reactions :

(i) It dissolves in NaOH but not in $NaHCO_3$ (ii) It reacts with Br_2 rapidly forming B, $C_7H_5OBr_3$. Give structures of A and B.

(b) What would be A, if it did not dissolve in NaOH ?

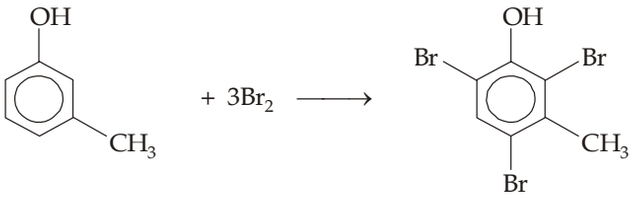
Solution :

(*a*) (*i*) Molecular formula of A (C_7H_8O) indicates 4° of unsaturation (molecular formula of saturated parent hydrocarbon with C_7 is $C_{17}H_{16}$). Since the compound A has very less hydrogen atoms, it must have a benzene ring which accounts for its 4° of unsaturation (three for 3 double bonds, and one for ring).

(*ii*) Solubility of A in NaOH and insolubility in $NaHCO_3$ indicates that A contains a phenolic group.

(*iii*) The seventh carbon atom of A can be present as CH_3 group ; hence A can be $CH_3C_6H_4OH$ (C_7H_8O).

(*iv*) Since A reacts with bromine to form tribromo product, the two substituents (CH_3 and OH) must be present in the *m*-position to each other.



A (C_7H_8O)
(—OH can direct Br to two *ortho* and one *para* positions)

B ($C_7H_5OBr_3$)

(*b*) The isomer of phenol that is insoluble in NaOH is ether, hence B should be anisole, $C_6H_5OCH_3$.

Example 13 :

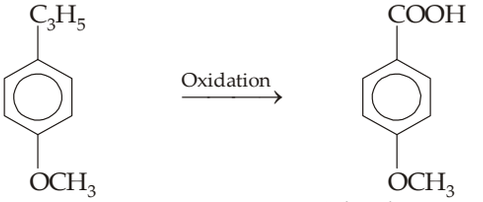
Two isomeric compounds A and B with the molecular formula $C_{10}H_{12}O$ are insoluble in aqueous NaOH and decolorize Br_2 in CCl_4. Each is vigorously oxidized to p-methoxybenzoic acid (p-anisic acid), and give the same products, on ozonolysis. Identify compounds A and B. Is any other isomer possible for the compounds A and B that too gives p-anisic acid on oxidation, if so give a chemical reaction to distinguish it from A and B ?

Solution :

(*i*) Molecular formula ($C_{10}H_{12}O$) of *A* and *B* indicates 5° of unsaturation, four of which can be accounted to benzene ring as indicated by relatively fewer H atoms, and the fifth to *C* = *C* bond as evidenced by positive test with Br_2.

(*ii*) Insolubility in aq. NaOH indicates that *A* and *B* are not having phenolic —OH group. Moreover, oxidation of *A* and *B* to form *p*-methoxybenzoic acid indicates that they are having —OCH_3 group and an alkenyl group in *para* position to each other.

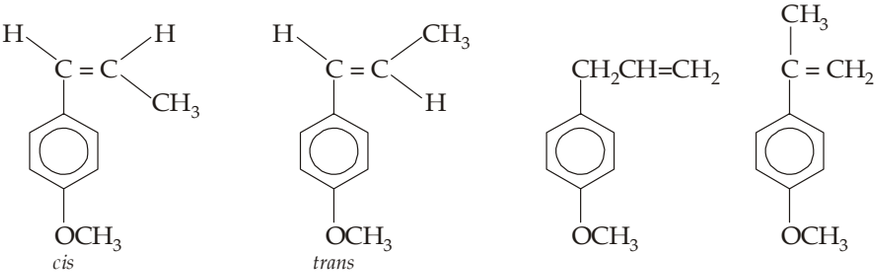
Since seven C's are accounted for by the ring and the C of OCH_3, the remaining three C's must be present in the form of alkenyl group (R).



[A] and [B]

p-Methoxybenzoic acid

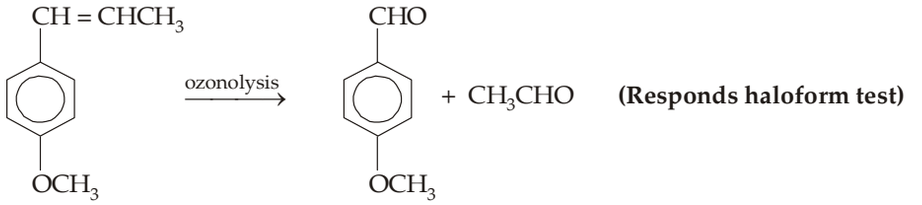
(*iii*) Since each gives the same ozonolysis products, they must have identical position of double bond. The isomerism, thus, may be *cis-trans* type; to exhibit this the side chain (R) should be —$CH = CHCH_3$.



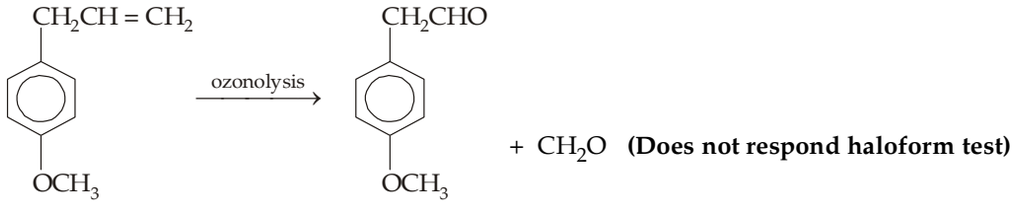
cis [A] and *trans* [B] [C] [D]

(*iv*) The structure of isomer of *A* and *B* should be *C* or *D* which explains all the given reactions.

Distinction between A/B and C

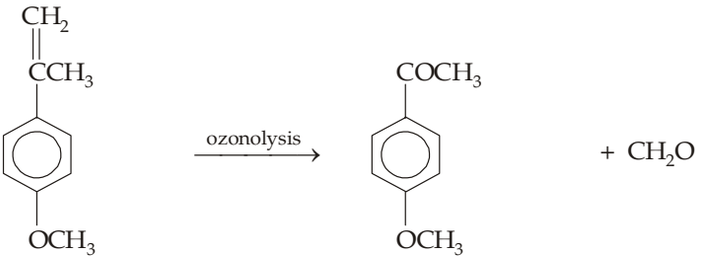


[A]/[B]



[C]

The isomer [D] can't be distinguished from A/B by ozonolysis followed by haloform test.



[D] (Responds haloform test)

Example 14 :

A sweet-smelling organic liquid A, $C_{10}H_{10}O_2$ gives the following reactions.

(a) It is insoluble in NaOH and does not give a colour with ferric chloride.

(b) On catalytic hydrogenation, it adds one equivalent of hydrogen.

(c) On ozonolysis it gives methanal and a compound B ($C_9H_8O_3$) which responds Tollen's reagent.

(d) On oxidation with $KMnO_4$, it gives a monocarboxylic acid C (N.E. = 166) which does not give colour with $FeCl_3$. However, acid C gives 3, 4-dihydroxybenzoic acid and methanal, when refluxed with conc. HI.

Identify compounds A, B, and C and explain the concerned reactions.

Solution :

(*i*) Molecular formula of A ($C_{10}H_{10}O_2$) indicates 6° of unsaturation, four of which must be due to benezene ring.

(*ii*) Since A does not dissolve in NaOH or give a colour with $FeCl_3$, it is not a phenol.

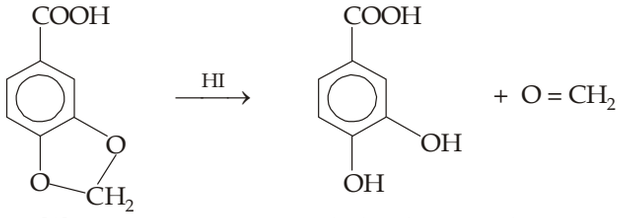
(*iii*) Ozonolysis product, methanal ($CH_2 = O$), of A indicates that A has a chain with a terminal $= CH_2$ grouping. Since the second ozonolysis product (B) responds Tollen's reagent, it has an —CHO group and hence A has $—CH = CH_2$ grouping.

$$\underset{\text{(A)}}{—CH = CH_2} \xrightarrow{O_3} \underset{\text{(B)}}{—CHO} + \underset{\text{Methanal}}{O = CH_2}$$

Note that the double bond accounts for the fifth degree of unsaturation.

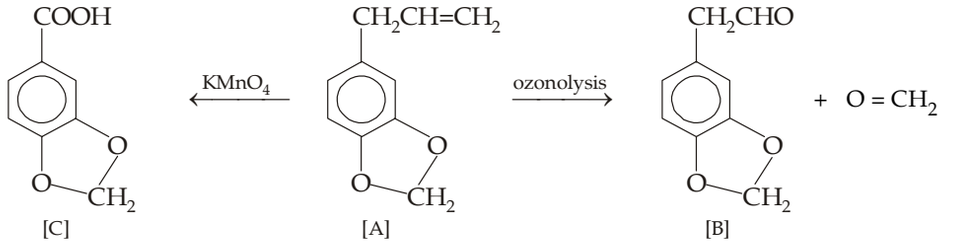
EBD_7089

(*iv*) Since the oxidation product (C) is a monocarboxylic acid, it indicates that no other carbon is directly linked to the ring, had it been so a dicarboxylic acid should have been the oxidation product. This leads to the thought that the two oxygen's must be prsent as ether linkages probably present as a ring to explain the sixth degree of unsaturation. This is confirmed by isolating $CH_2 = O$ and 3, 4-dihydroxybenzoic acid on cleavage with HI. Formation of $CH_2 = O$ indicates that the two oxygen's are linked together through CH_2, hence acid C has following structure.



[C] 3, 4-Dihydroxybenzoic acid

Thus compounds (A) and (B) should have following respective structures.



[C] [A] [B]

Example 15 :

Give structural formula for the dicarboxylic acids with the molecular formula $C_6H_{10}O_4$ which satisfies following conditions.

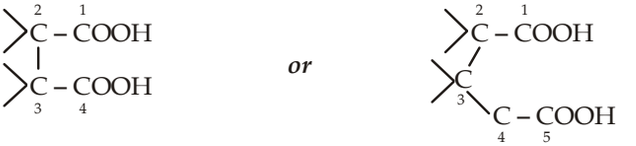
(a) They are chiral, form anhydride easily but not decarboxylated easily.

(b) They are achiral, do not form anhydride easily, but decarboxylated easily.

Solution :

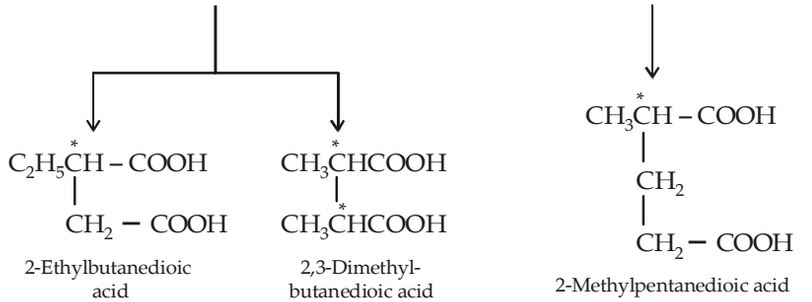
The dicarboxylic acids, $C_6H_{10}O_4$, should have structure as $HOOC(C_4H_8)COOH$. Now we know that 1,4- and 1,5-dicarboxylic acids on heating form anhydride, while 1,2- and 1,3-dicarboxylic acids form monocarboxylate and CO_2 on heating. Thus

(a) the acid capable of forming anhydride should have following part structure.



It needs two carbon and for being chiral it can have a C_2H_5 on C_2 (or C_3) and H on C_3 (or C_2); or it can have a CH_3 each on C_2 and C_3

It needs only one C, and for being chiral it can have $-CH_3$ group at C_2 or C_4

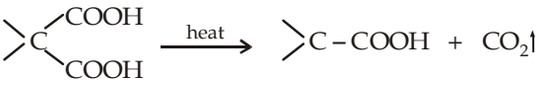


2-Ethylbutanedioic acid

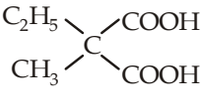
2,3-Dimethyl-butanedioic acid

2-Methylpentanedioic acid

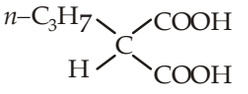
(b) Since the dicarboxylic acids, HOOC (C_4H_8)COOH evolve CO_2 on heating, two acidic groups must be on same carbon atom, i.e. these are 1,3-dicarboxylic acids



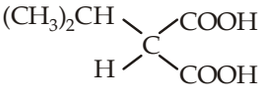
The three carbon fraction can be present as C_2H_5 and CH_3, or *n*-C_3H_7 and H, or *iso*-C_3H_7 and H. Thus here also three isomeric dicarboxylic acids are possible.



Ethylmethylpropane-dioic acid



Propylpropanedioic acid



Isopropylpropanedioic acid

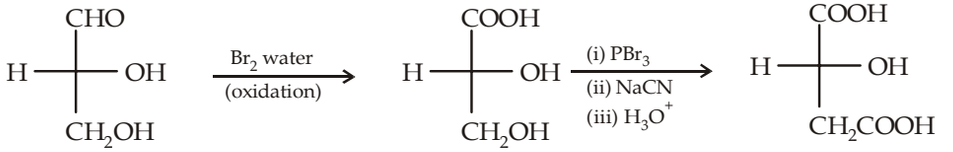
Example 16 :

Give steps involved in the conversion of (*R*)-(+)-glyceraldehyde to

(i) (*R*)-(+)-malic acid, (ii) (*S*)-(–)-malic acid

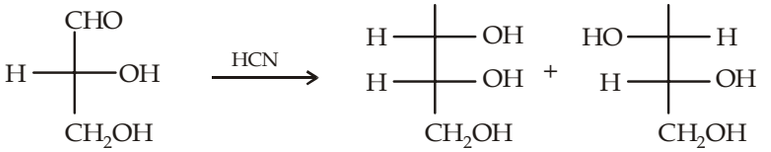
Solution :

(i)

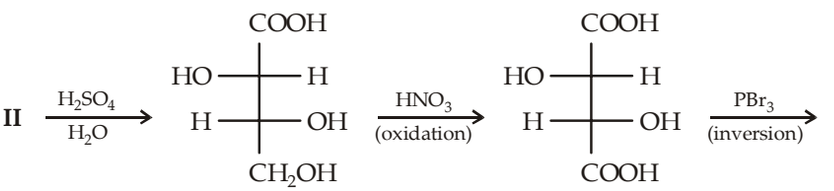


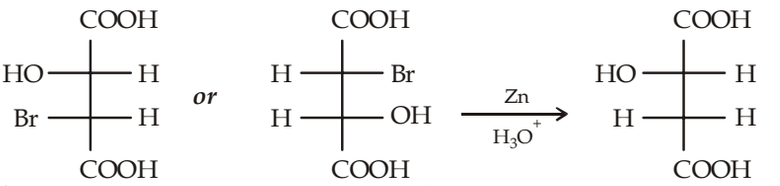
(R)-(+)-Glyceraldehyde (R)-(+)-Malic acid

(ii)



(R)-(+)-Glyceraldehyde I II



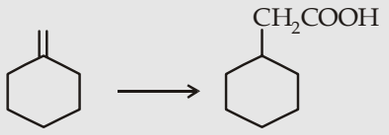


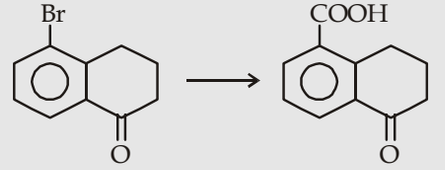
Both are same stereoisomer (S)-(–)-Malic acid

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Example 17 :

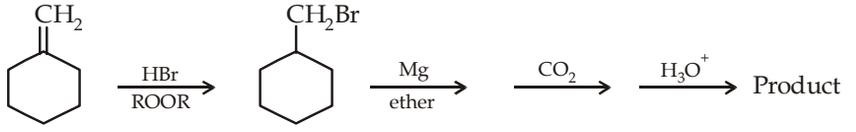
Carry out the following conversions in not more than four steps.

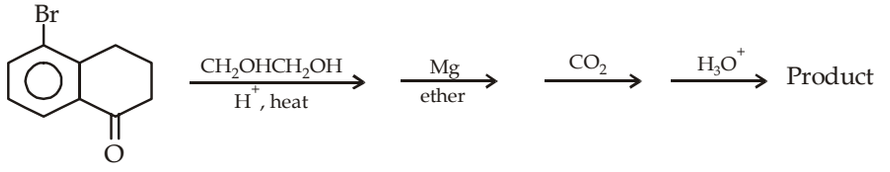
(a) 

(b) 

(c) $(CH_3)_3CCOOH \longrightarrow (CH_3)_3CCN$

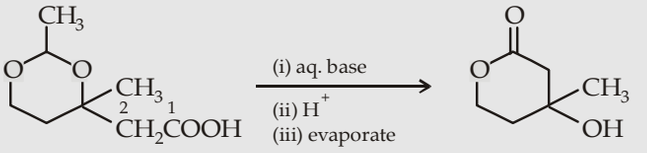
Solution :

(a) 

(b) 

(c) $(CH_3)_3CCOOH \xrightarrow{SOCl_2} \xrightarrow{NH_3} \xrightarrow{P_4O_{10}}$ Product

Example 18 :



Answer the following questions regarding above reaction :

(a) Name the functional groups in the reactant and product

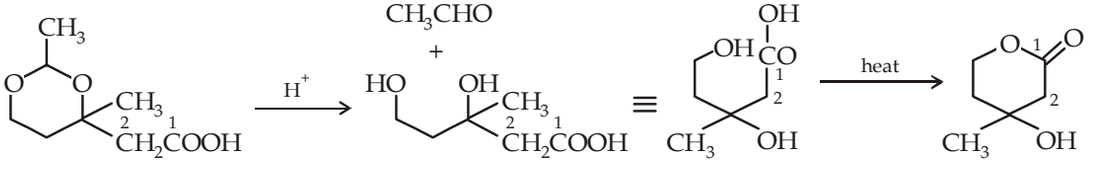
(b) What is the effect of aq. base and acid in the reaction?

(c) Label the positions of C_1 and C_2 of reactant into product.

Solution :

(a) Reactant has acetal and –COOH groups, while the product has a lactone and alcoholic group.

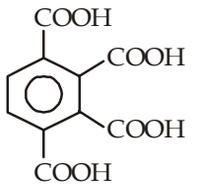
(b) and (c) Since acetals are resistant to base, hence the compound will not undergo any significant change except that –COOH will be converted to $-COO^-Na^+$. Acids decompose acetals to CH_3CHO and a diol; the latter on heating undergo esterification to form cyclic ester, commonly called lactone.



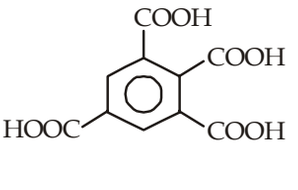
Example 19 :

Benzene tetracarboxylic acids have three isomeric structures. Write their structures and show how these can be distinguished by anhydride formation?

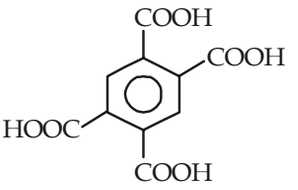
Solution :



1,2,3,4– **(A)**

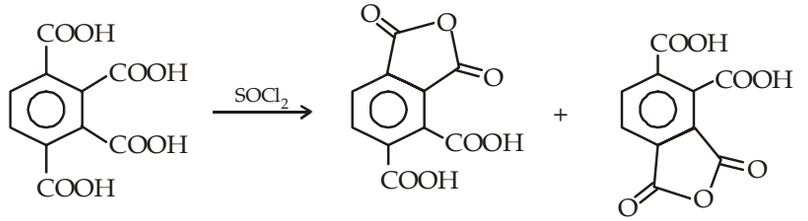


1,2,3,5– **(B)**

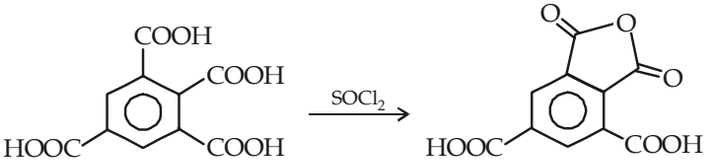


1,2,4,5– **(C)**

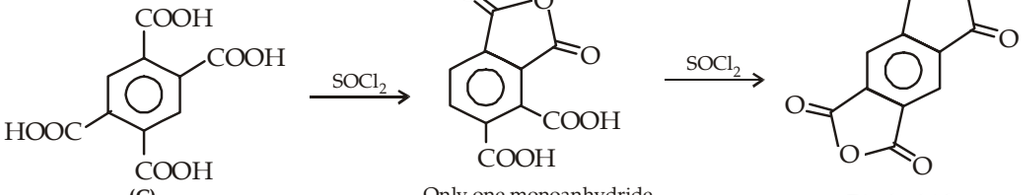
The three isomers can be distinguished by adding *an equivalent* amount of $SOCl_2$, when (**A**) gives two isomeric anhydrides, while (**B**) and (**C**) form one anhydride each; (**B**) and (**C**) can further be distinguished by adding second equivalent of $SOCl_2$ when only the monoanhydride from (**C**) will form a dianhydride.



(A) Two isomeric anhydrides



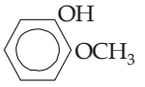
(B) Only one mono-anhydride



(C) Only one monoanhydride Dianhydride

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EXERCISE 13.1 (MCQ - ONE option correct)

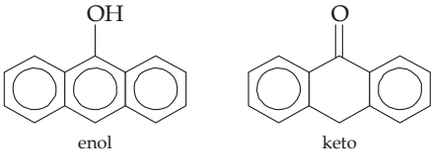
1. The compound,  can be named as

(*a*) 2-hydroxyanisole (*b*) catechol monomethyl ether
(*c*) Guaiacol (*d*) by all the three names.

2. The least accepted name for  is

(*a*) 2-mercaptophenol (*b*) 2-hydroxythiophenol
(*c*) monothiocatechol (*d*) *o*-meraptophenol.

3. 9-Hydroxyanthracene (anthranol) shows keto-enol tautomerism, which of the tautomer is more stable ?



(*a*) Keto (*b*) Enol
(*c*) Both are equally stable (*d*) It can't be predicted.

4. Which of the following isomer of nitrophenol is steam volatile?

(*a*) *ortho* (*b*) *meta*
(*c*) *para* (*d*) none.

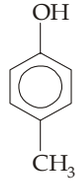
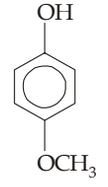
5. Cumene (isopropylbenzene) is obtained by two cheap hydrocarbons, namely

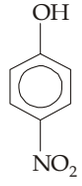
(*a*) Benzene + *n*-Propane (*b*) Toluene + Ethylene
(*c*) Benzene + Propene (*d*) Benzene + Propyne.

6. Well-known antiseptic 4- *n*-hexylresorcinol is prepared most easily from which of the phenol ?

(*a*) Catechol (*b*) Resorcinol
(*c*) Quinol (*d*) From all the three.

7. Which of the following phenol will give lower yield during Kolbe-Schmidt reaction ?

(*a*)  (*b*) 

(*c*)  (*d*) All will give good yield.

8. Which of the following method gives better yield of *p*-nitrophenol?

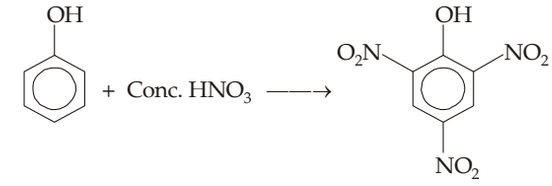
(*a*) Phenol $\xrightarrow[20°C]{\text{dil. } HNO_3}$ *p*-Nitrophenol

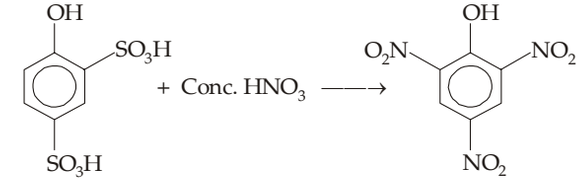
(*b*) Phenol $\xrightarrow[\text{(ii) } HNO_3]{\text{(i) } NaNO_2 + H_2SO_4,\ 7-8°C}$ *p*-Nitrophenol

(*c*) Phenol $\xrightarrow[\text{(ii) Conc. } HNO_3]{\text{(i) NaOH}}$

(*d*) None of the three.

9. Which of the following method is preferred for preparing 2, 4, 6-trinitrophenol ?

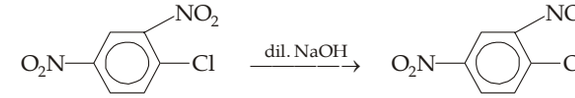
(*a*) 

(*b*) 

(*c*) Both (*a*) and (*b*) give similar result
(*d*) None of the two.

10. What happens when, 2, 4, 6-trinitrochlorobenzene is just warmed with water ?

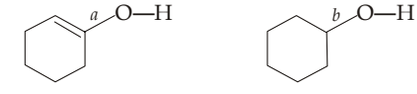
(*a*) No reaction takes place
(*b*) A hydrate is formed
(*c*) 2, 4- Dinitrophenol is formed
(*d*) Picric acid is formed.

11. 

Which one is ture about the above representation ?

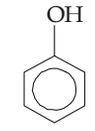
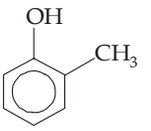
(*a*) It is an example of electrophilic substitution
(*b*) It is an example of substitution through benzyne intermediate
(*c*) It is an example of activated nucleophilic substitution
(*d*) Above reaction is not possible since C—Cl bond is very strong.

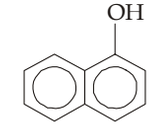
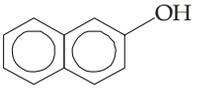
12. Which is true about the C—O bond lengths in the following compounds ?



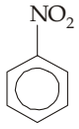
(*a*) $a = b$ (*b*) $a > b$
(*c*) $a < b$ (*d*) all the three.

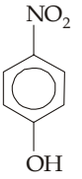
13. Which of the following has minimum pK_a value ?

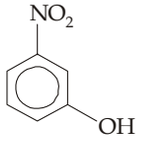
(*a*)  (*b*) 

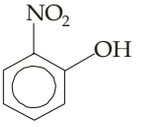
(*c*)  (*d*) 

14. Which one of the following has highest dipole moment ?

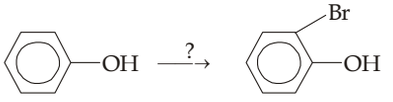
(*a*) 

(*b*) 

(*c*) 

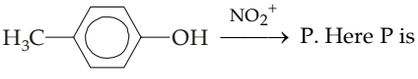
(*d*) 

15. Choose the reagent to carry out following reaction :

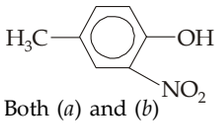


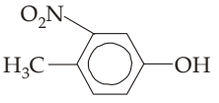
(*a*) Br_2 water (*b*) Br_2 in CCl_4

(*c*) Either of the two (*d*) Reaction not possible.

16. 

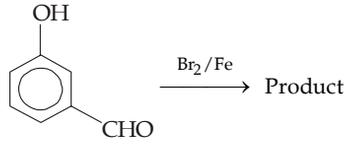
P. Here P is

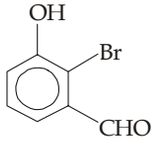
(*a*) 

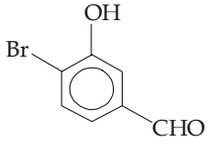
(*b*) 

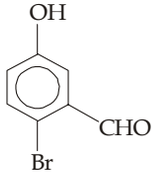
(*c*) Both (*a*) and (*b*) (*d*) Reaction not possible.

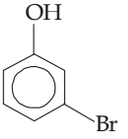
17. What should be the product in the following reaction ?



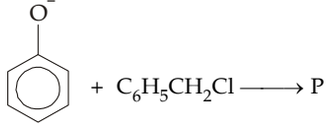
(*a*) 

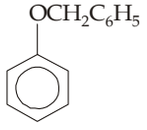
(*b*) 

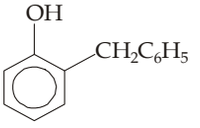
(*c*) 

(*d*) 

18. Predict the nature of P in the following reaction.

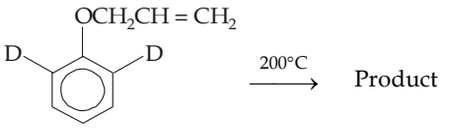


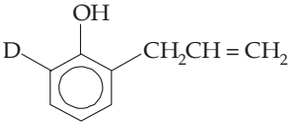
(*a*) 

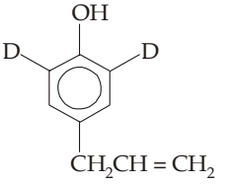
(*b*) 

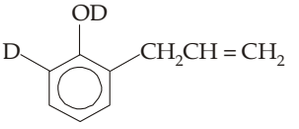
(*c*) Both (*a*) and (*b*) (*d*) Reaction is not possible.

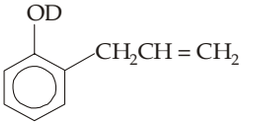
19. Direct the nature of the product in the following reaction :



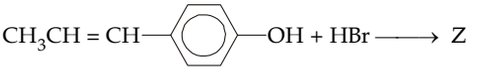
(*a*) 

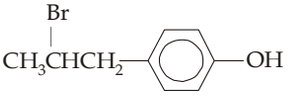
(*b*) 

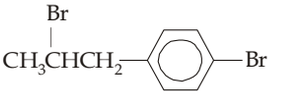
(*c*) 

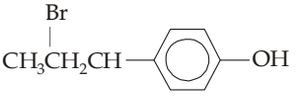
(*d*) 

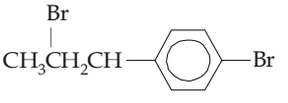
20. Predict the product *Z* in the following reaction :



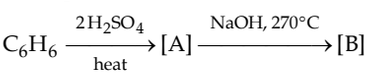
(*a*) 

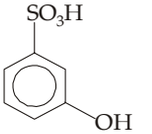
(*b*) 

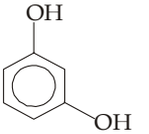
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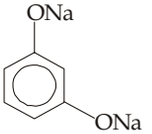
(*d*) 

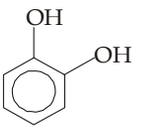
21. Identify the end product



(*a*) 

(*b*) 

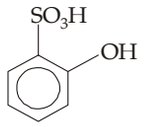
(*c*) 

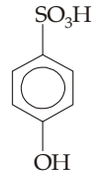
(*d*) 

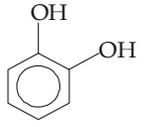
EBD_7089

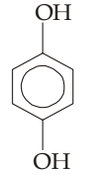
22. Identify the end product in the following series of reactions :

$$C_6H_5NO_2 \xrightarrow[\text{(ii) NaOH}]{\text{(i) Sn, HCl}} [A] \xrightarrow[H_2SO_4]{Na_2Cr_2O_7} [B] \xrightarrow[H_2O]{SO_2} [C]$$

(*a*) 

(*b*) 

(*c*) 

(*d*) 

23. Phenol is

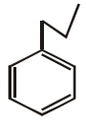
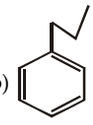
(a) a base weaker than ammonia
(b) an acid stronger than carbonic acid
(c) an acid weaker than carbonic acid
(d) a neutral compound

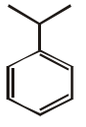
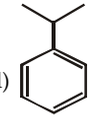
24. $-NO_2$ group is acid-strengthening group ; when present in *para*-position of phenol and benzoic acid. Which statement is true about this ?

(*a*) It increases acidity of both to the same extent.
(*b*) It increases acidity of phenol more than that of benzoic acid.
(*c*) It increases acidity of benzoic acid more than that of the phenol.
(*d*) It does not increase acidity of any of the compound.

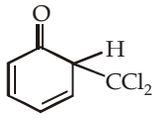
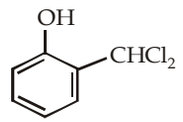
25.  $+Cl-CH_2CH_2-CH_3 \xrightarrow{AlCl_3} P \xrightarrow[(ii)\ H_3O^+]{(i)\ O_2/\Delta} Q + \text{Phenol}$

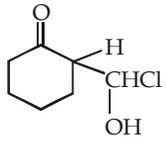
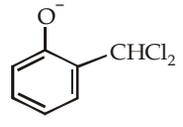
The major products P and Q are

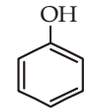
(a)  and CH_3CH_2CHO (b)  and CH_3COCH_3

(c)  and CH_3COCH_3 (d)  and CH_3CH_2CHO

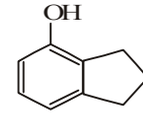
26. When phenol is reacted with $CHCl_3$ and NaOH followed by acidification, salicyladehyde is obtained. Which of the following species are involved in the above mentioned reaction as intermediates?

(a)  (b) 

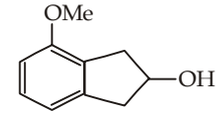
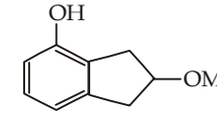
(c)  (d) 

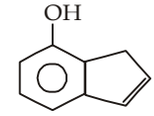
27.  $+ C_2H_5I \xrightarrow[\text{Anhydrous } (C_2H_5OH)]{^-OC_2H_5} ?$

(a) $C_6H_5OC_2H_5$ (b) $C_2H_5OC_2H_5$
(c) $C_6H_5OC_6H_5$ (d) C_6H_5I

28.  $\xrightarrow[2.\ MeBr]{1.\ One\ eq.\ NaOH} (A);$

Product (A) is :

(*a*)  (*b*) 

(*c*)  (*d*) None of these

29. $\text{Phenol} \xrightarrow[\text{distillation}]{\text{Zinc}} (A) \xrightarrow[\text{Conc.}H_2SO_4\text{ at }60°C]{\text{Conc.}HNO_3} (B) \xrightarrow[NaOH]{Zn} (C)$

In the above reaction compounds (A), (B) and (C) are :

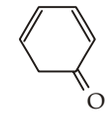
(*a*) benzene, nitrobenzene and aniline
(*b*) benzene, dinitrobenzene and *m*-nitroaniline
(*c*) toluene, *m*-nitrobenzene and *m*-toluidine
(*d*) benzene, nitrobenzene and hydrazobenzene

30. Salol can be used as

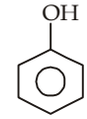
(*a*) Antiseptic (*b*) Antipyretic
(*c*) Both (*a*) and (*b*) (*d*) None of these

31. Which of the following compounds have higher enol content as per conditions given in paranthesis:

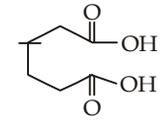
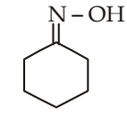
(*a*) $CH_3-CO-CH_3$ (at higher temperature)
(*b*) $CH_3-CO-CH_2-COOC_2H_5$ (in polar solvent)

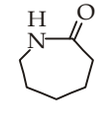
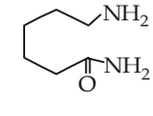
(*c*)  (non polar solvent)

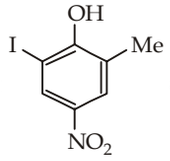
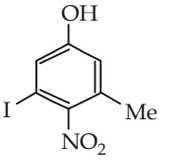
(*d*) All of the above

32.  $\xrightarrow{Ni/H_2} (P) \xrightarrow[250°C]{Cu} (Q) \xrightarrow{NH_2OH} (R) \xrightarrow{H^+} (S)$

In the above sequence, the product (S) is :

(*a*)  (*b*) 

(*c*)  (*d*) 

33. Among  and 

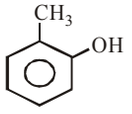
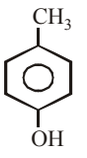
(I) (II)

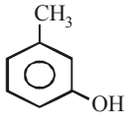
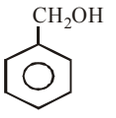
the acidic strength is

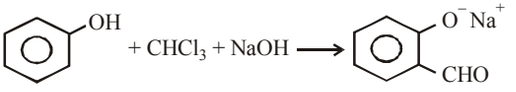
(*a*) I > II (*b*) II > I

(*c*) I = II (*d*) Cannot be predicted

34. The structure of the compound that gives a tribromo derivative on treatment with bromine water is

(*a*)  (*b*) 

(*c*)  (*d*) 

35. 

The electrophile involved in the above reaction is

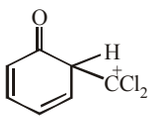
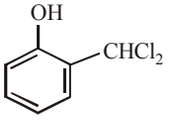
(*a*) trichloromethyl anion ($\overset{\ominus}{C}Cl_3$)

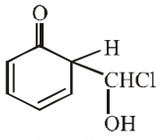
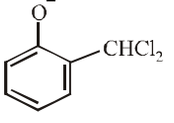
(*b*) formyl cation ($\overset{\oplus}{C}HO$)

(*c*) dichloromethyl cation ($\overset{\oplus}{C}HCl_2$)

(*d*) dichlorocarbene ($:CCl_2$)

36. When phenol is reacted with $CHCl_3$ and NaOH followed by acidification, salicylaldehyde is obtained. Which of the following species are involved in the above mentioned reaction as intermediate?

(*a*)  (*b*) 

(*c*)  (*d*) 

37. Arrange the following in the decreasing order of acidic strength

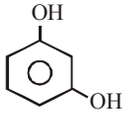
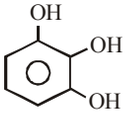
Phenol, *p* - nitrophenol, *m* - cresol, *p* - cresol

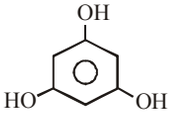
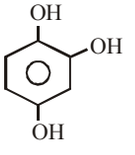
I II III IV

(*a*) II > III > IV > I (*b*) II > I > III > IV

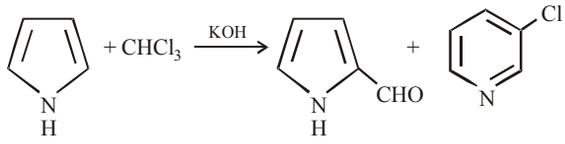
(*c*) II > I > IV > III (*d*) III > IV > II > I

38. Which of the following compound can react with hydroxylamine?

(*a*)  (*b*) 

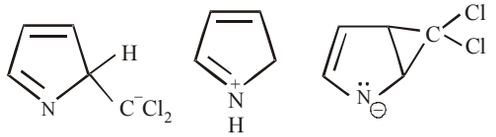
(*c*)  (*d*) 

39. Pyrrole is treated with alkaline chloroform to form two products A and B

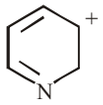


A B

Which of the following intermediate is likely to be formed?



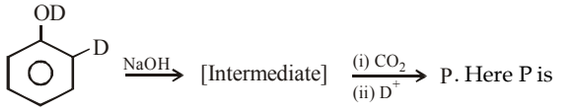
I II III

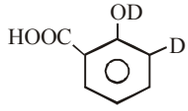
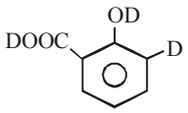


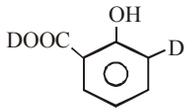
IV

(*a*) I and IV (*b*) I and III

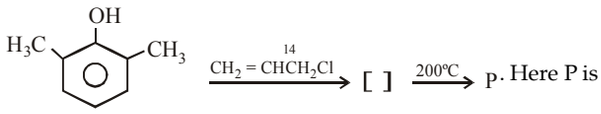
(*c*) III and IV (*d*) I, III and IV

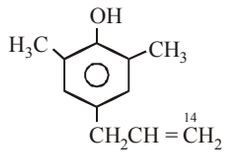
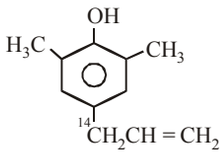
40.  P. Here P is

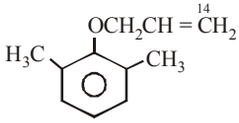
(*a*)  (*b*)  (*c*)



(*d*) Reaction not possible

41.  P. Here P is

(*a*)  (*b*) 

(*c*) Both (*d*) 

42. Phenol is converted into bakelite by heating it with formaldehyde in presence of alkali or acid. Which statement is true regarding this reaction ?

(*a*) The electrophile in both cases is $CH_2 = O$

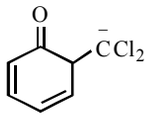
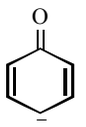
(*b*) The electrophile in both cases is $CH_2 = \overset{+}{O}H$

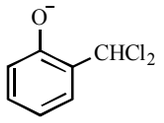
(*c*) The electrophile is $CH_2 = O$ in presence of alkali and $CH_2 = \overset{+}{O}H$ in presence of acid

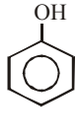
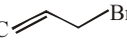
(*d*) It is a nucleophilic substitution reaction

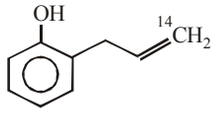
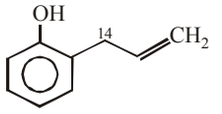
EBD_7089

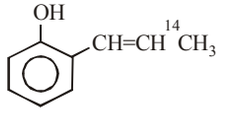
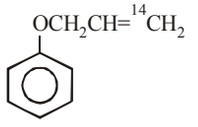
43. Which of the following is not formed as an intermediate in the Reimer-Tiemann reaction between phenol and alkaline chloroform?

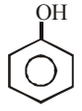
(*a*)  (*b*) 

(*c*)  (*d*) $:CCl_2^{2-}$

44.  $+ H_2{}^{14}C$  $\xrightarrow[\text{(ii) heat}]{\text{(i) } K_2CO_3}$ Z. Here Z is

(*a*)  (*b*) 

(*c*)  (*d*) 

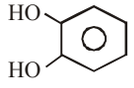
45.  $\xrightarrow{NaOH}$ [X] $\xrightarrow{CH_2=CHCH_2Cl}$ [Y]. Here [Y] is a

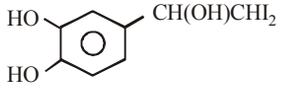
(*a*) single compound
(*b*) mixture of two compounds
(*c*) mixture of three compounds
(*d*) no reaction is possible

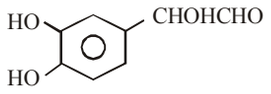
46. Phenol undergoes electrophilic substitution more easily than benzene because

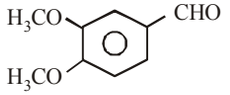
(*a*) –OH group exhibits +M effect and hence increases the electron density on the *o*- and *p*-positions.
(*b*) oxocation is more stable than the carbocation
(*c*) both (a) and (b)
(*d*) –OH group exhibits acidic character

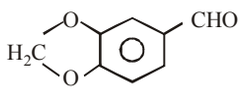
47. Identify the prodcut [B] in the following reaction

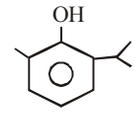
 $\xrightarrow[\text{(ii) } H^+]{\text{(i) } CHCl_3 / NaOH}$ [A] $\xrightarrow[NaOH]{CH_2I_2}$ [B]

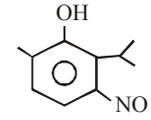
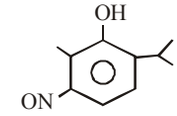
(*a*) 

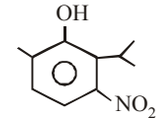
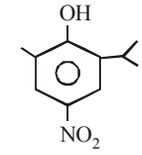
(*b*) 

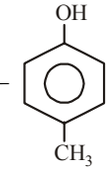
(*c*) 

(*d*) 

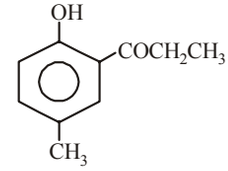
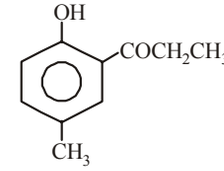
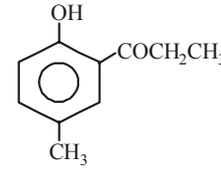
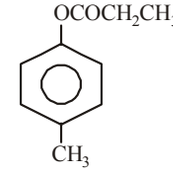
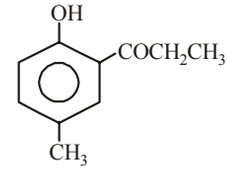
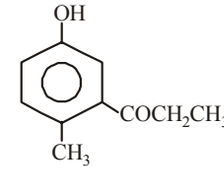
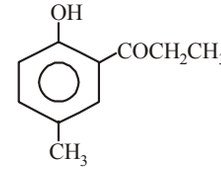
48.  $\xrightarrow[\text{(ii) dil. } HNO_3]{\text{(i) } NaNO_2, HCl}$ Z. Here Z is

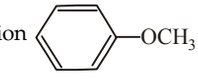
(*a*)  (*b*) 

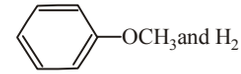
(*c*)  (*d*) 

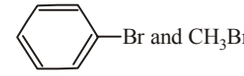
49. $Y \xleftarrow[\text{absence of } AlCl_3]{CH_3CH_2COCl}$  $\xrightarrow[\text{anhy. } AlCl_3]{CH_3CH_2COCl} X$

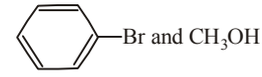
X and *Y* respectively are

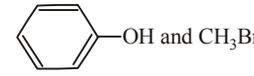
	X	*Y*
(*a*)		
(*b*)		
(*c*)		
(*d*)		No reaction

50. In the reaction  the products are

(a) 

(b) 

(c) 

(d) 

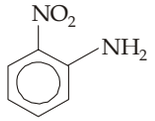
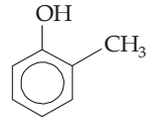
EXERCISE 13.2 (MCQ 1 or >1 option correct, Passage based, Matching, A/R)

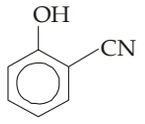
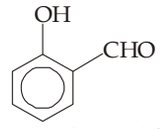
DIRECTIONS for Q. 1 to Q. 14 : Multiple choice questions with one or more than one correct option(s).

1. Which of the following is correct name for 

(*a*) Hydroquinone (*b*) *p*-Benzenediol
(*c*) Quinol (*d*) Resorcinol

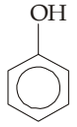
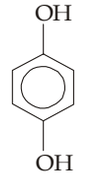
2. Which of the following can't form intramolecular hydrogen bonding?

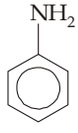
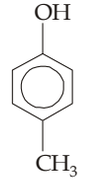
(*a*)  (*b*) 

(*c*)  (*d*) 

3. Which of the following combination can't be used for preparing an ether ?
(a) $C_6H_5OH + (CH_3)_2SO_4$
(b) $C_6H_5Br + CH_3CH_2OH$
(c) $p\text{-}NO_2C_6H_4Br + CH_3CH_2OH$
(d) $C_6H_5OH + (CH_3)_3CBr$

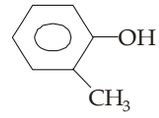
4. Which of the following gives *p*-benzoquinone on oxidation ?

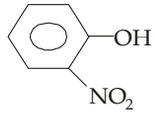
(*a*)  (*b*) 

(*c*)  (*d*) 

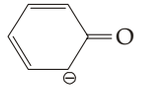
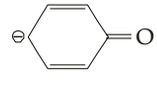
5. Phenol is less acidic than :
(a) acetic acid (b) p-methoxyphenol
(c) p-nitrophenol (d) ethanol

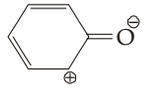
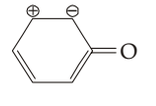
6. Which is/are less acidic than phenol?

(a) CH_3OH (b) 

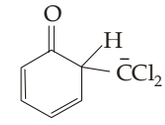
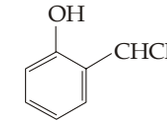
(c)  (d) H_2O

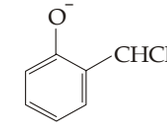
7. Resonating forms of phenoxide ion is/are :

(a)  (b) 

(c)  (d) 

8. When phenol is reacted with $CHCl_3$ and NaOH followed by acidification, salicyaldehyde is obtained. Which of the following species are involved in the above mentioned reaction as intermediates?

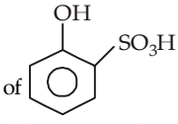
(a)  (b) 

(c) $CHCl_3$ (d) 

9. Which are the sources of phenol?
(a) Middle oil of coal-tar distillation
(b) Cumene
(c) Hydrolysis of benzene diazonium salts
(d) Reaction of diazonium salt with H_3PO_2

10. These reagents find application in photography :
(a) Hypo (b) Quinol
(c) Hydrazine (d) $AgNO_3$

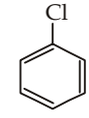
11. Select the incorrect statement(s) from the following :
(*a*) Rate of sulphonation of C_6H_6 & C_6D_6 will be equal

(*b*) On treatment of  with Br_2 / water (in excess) it results in a dibromo product.

(*c*) When HCOOEt is treated with MeMgBr in excess followed by hydrolysis it will results in the formation of tertiary alcohol.

(*d*) $MeCH_2\underset{\text{Optically pure}}{-CH(Me)-CH(Cl)-Me} \xrightarrow[S_N2]{\text{aq. KOH}}$ Product. Product is enantiomer of the reactant

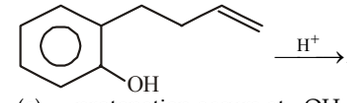
12. In the Dow's process for the manufacture of phenol, chlorobenzene is fused with NaOH at high temperature under pressure.

 $\xrightarrow[\text{high pressure}]{\text{NaOH, 360°C}}$ [intermediate]

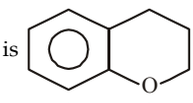
$\xrightarrow{H_2O}$ Phenol + $\underbrace{(A) + (B)}_{\text{Side products}}$

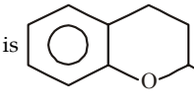
Which of the following statements is/are correct for the above set of transformations ?
(*a*) Phenol is formed via an intermediate that is aromatic
(*b*) Diphenyl ether is also formed as by-product
(*c*) *p*-Phenylphenol is also formed as by-product
(*d*) Biphenylene is also formed as by-product

13. Pick up the correct statements in the following reaction



(*a*) protonation occurs at –OH
(*b*) protonation occurs at C = C linkage

(*c*) *P* is 

(*d*) *P* is 

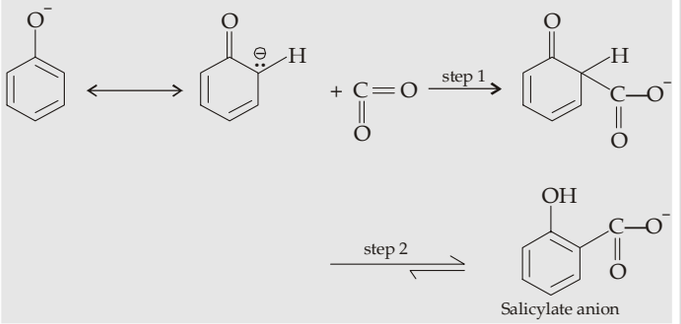
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14. 2, 4, 6 -Tribromophenol can be prepared by the bromination of
(*a*) phenol
(*b*) salicylic acid
(*c*) *p*-hydroxybenzenesulphonic acid
(*d*) *p*-bromophenol

INSTRUCTION for Q. 15 to 31 : Read the passages given below and answer the questions that follow.

PASSAGE 1

Treatment of sodium peroxide with carbon dioxide at 125°C under pressure yields sodium salt of o-hydroxy benzoic acid, commonly known as salicylate ion. This reaction, known as Kolbe-Schmidt reaction, proceeds as below.



15. Which of the following statement is true ?
(a) Carbon dioxide is a strong nucleophile so requires a strong electrophile, the phenoxide ion.
(b) Carbon dioxide is a strong electrophile so requires strong nucleophile, the $C_6H_5O^-$
(c) Carbon dioxide is a weak electrophile, hence it requires a strong nucleophile like $C_6H_5O^-$
(d) Sodium phenoxide can be replaced by parent phenol.

16. Step 2 of the reaction involves
(a) addition of H^+ (b) tautomerization
(c) resonance (d) None of these

17. Which of the following is correct explanation for the formation of *o*-hydroxybenzoate rather than the *p*-isomer.
(a) *o*-Hydroxybenzoate anion is a weaker base than phenoxide ion.
(b) *o*-Hydroxybenzoate anion is a weaker base than the *p*-hydroxybenzoate anion.
(c) Both of the two
(d) None of the two

PASSAGE 2

Two isomeric compounds A and B with the molecular formula $C_{10}H_{12}O$ are insoluble in aqueous NaOH and decolorize Br_2 in CCl_4. Each is vigorously oxidized to p-methoxybenzoic acid (p-anisic acid), and give the same products, on ozonolysis.

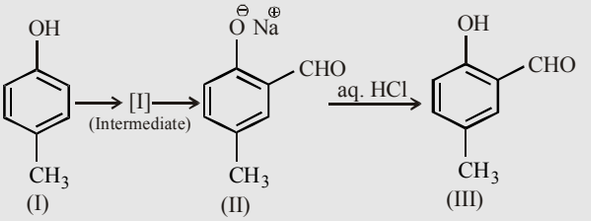
18. The degree of unsaturation and their nature in compound B are
(a) 5-benzene, two C = C double bonds
(b) 5-benzene, an aldehydic group
(c) 4-benzene, a carboxylic group
(d) 5-benzene, one carbon-carbon double bond

19. The isomers A and B show ..... isomerism.
(a) Optical (b) Geometrical
(c) Conformational (d) Two of the three

20. The ozonolysis product of A undergoes haloform reaction, which is due to the formation of
(a) CH_3COCH_3 (b) CH_3CHO
(c) CH_3CH_2OH (d) $C_6H_5COCH_3$

PASSAGE 3

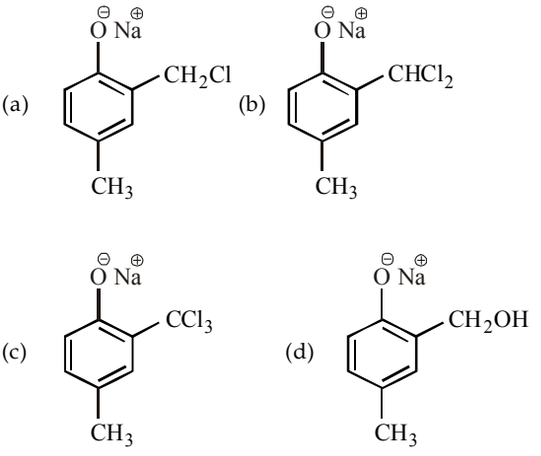
Riemer-Tiemann reaction introduces an aldehyde group, on to the aromatic ring of phenol, ortho to the hydroyl group. This reaction involves electrophilic aromatic substitution. This is a general method for the synthesis of substituted salicylaldehyde as depicted below.



21. Which one of the following reagents is used in the above reaction?
(a) aq.NaOH + CH_3Cl (b) aq.NaOH + CH_2Cl_2
(c) aq.NaOH + $CHCl_3$ (d) aq.NaOH + CCl_4

22. The electrophile in the reaction is
(a) : CHCl (b) $^+CHCl_2$
(c) : CCl_2 (d) CCl_3

23. The structure of the intermediate I is



PASSAGE 4

Although chlorobenene is inert to nucleophilic substitution, it gives quantitative yield of phenol when heated with aq. NaOH at high temperature and under high pressure. Phenol, so formed, is a weaker acid than the carboxylic acid; hence it dissolves only in strong bases like NaOH, but not weak like $NaHCO_3$. It reacts with acid chlorides and acid anhydrides in the absence of $AlCl_3$ to form esters. As far as electrophilic substitution in phenol is concerned, the –OH is an activating group, hence its presence enhances the electrophilic substitution in the *o*- and *p*-positions.
Condensation with formaldehyde is one of the important property of phenol. The condensation may take place in presence of acids or alkalis and leads to the formation of bakelite, an important industrial polymer.

24. Conversion of chlorobenzene into phenol involves
(*a*) modified S_N1 mechanism
(*b*) modified S_N2 mechanism
(*c*) both (*a*) and (*b*)
(*d*) elimination - addition mechanism

25. The *o*-acylation of phenols with acid anhydrides can be catalyzed by
(*a*) sulphuric acid (*b*) NaOH
(*c*) both (*d*) none

26. Phenol undergoes electrophilic substitution more readily than benzene because
(*a*) the intermediate carbocation is a resonance hybrid of more resonanting structures than that from benzene
(*b*) the intermediate is more stable as it has positive charge on oxygen, which can be better accommodated than on carbon
(*c*) in one of the canonical structures, every atom (except hydrogen) has complete octet
(*d*) the –OH group is *o, p*–directing which like all other *o,p*-directing groups is activating

27. Phenol undergoes electrophilic substitution more readily in presence of alkali than the phenol itself because
(*a*) of the formation of a more stable carbocation as an intermediate
(*b*) of the formation of a more stable carbanion as an intermediate
(*c*) of the formation of a more stable neutral intermediate
(*d*) in presence of alkali, a stronger electrophile is produced

28. Condensation of phenol with formaldehyde is an electrophilic substitution, in which
(*a*) $CH_2 = O$ as such is the electrophile in both acidic as well as basic medium
(*b*) $CH_2 = O$ is the real electrophile in acidic medium while in basic medium $\overset{+}{C}H_2 - O^-$ is the real electrophile
(*c*) $CH_2 = \overset{+}{O}H$ and $CH_2 = O$ are the electrophiles in acidic and basic medium respectively.
(*d*) $CH_2 = O$ and $\overset{+}{C}H_2 - O^-$ are the electrophiles in acidic and basic medium respectively

PASSAGE 5

Most of phenols are less acidic than carbonic and carboxylic acids and hence do not decompose $NaHCO_3$ evolving CO_2. Presence of electron-withdrawing group in the benzene ring increases acid strength, while electron donating group decreases the acid strength of phenols. The relative acid strength of *o*-, *m*- and *p*-substituted phenols, however, depends upon a combination of inductive and resonance effect of the substituent.

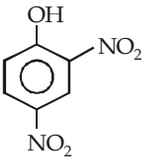
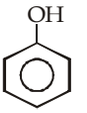
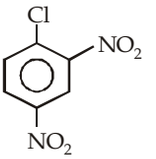
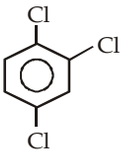
29. Increasing pK_a values of *o, m* and *p*-cresols is
(*a*) $o < p < m$ (*b*) $m < p < o$
(*c*) $m < o < p$ (*d*) $p < o < m$

30. Which of the following compounds decomposes $NaHCO_3$ solution?
(*a*) Phenol (*b*) 2-Nitrophenol
(*c*) Methoxyphenol (*d*) 2,4,6-Trinitrophenol

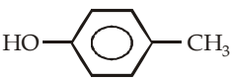
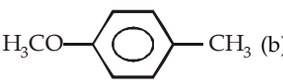
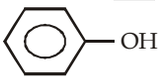
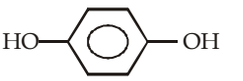
31. Choose the correct acidity order of the following phenols :
(*a*) *p*-nitrophenol > *p*-chlorophenol > *p*-cresol > phenol
(*b*) *p*-nitrophenol > *p*-cresol > *p*-chlorophenol > phenol
(*c*) *p*-nitrophenol > *p*-chlorophenol > phenol > *p*-cresol
(*d*) *p*-nitrophenol > phenol > *p*-chlorophenol > *p*-cresol

Instructions for Q. 32 & Q. 34 : Following questions are Multiple Matching type Questions :

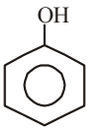
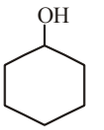
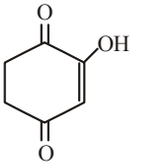
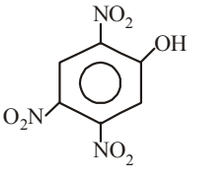
32.

	Column I	*Column II*
(A)		(a) Oxidation of the ring by HNO_3
(B)		(b) Nitration of the ring possible
(C)		(c) Nitration of the ring not possible
(D)		(d) Reaction with OH^- possible

33.

	Column I	*Column II*
(A)		(a) Coupling with $C_6H_5N_2Cl$ in presence of NaOH
(B)		(b) Oxidation with AgBr
(C)		(c) $KMnO_4$ oxidises $–CH_3$ to –COOH
(D)		(d) $KMnO_4$ does not oxidise $–CH_3$ group to –COOH

34.

	Column I	*Column II*
(A)		(a) Reacts with sodium acetylide, $HC \equiv \bar{C}\,Na^+$
(B)		(b) Reacts with sodium hydroxide, NaOH
(C)		(c) Reacts with sodamide, $NaNH_2$
(D)		(d) Reacts with sodium bicarbonate, $NaHCO_3$

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Instructions for Q. 35 to 43 : Following questions are Assertion and Reasoning Type Questions :

Note : Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 5 choices (a), (b), (c), (d) and (e) out of which ONLY ONE is correct.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.

(c) Statement -1 is True, Statement-2 is False.

(d) Statement -1 is False, Statement-2 is True.

(e) Statement -1 is False, Statement-2 is False.

35. **Statement 1 :** *p*-nitrophenol boil at high temperature than *o*-nitrophenol

Statement 2 : In *p*-nitrophenol, the – OH group of one molecule forms hydrogen bonds with the $-NO_2$ group of the neighbouring p-nitrophenol molecule

36. **Statement 1 :** *o*-nitrophenol has much lower solubility in water than *m*- or *p*-isomers.

Statement 2 : In *o*-nitrophenol both the groups, –OH and $-NO_2$, are involved in intramolecular hydrogen bonding.

37. **Statement 1 :** ortho-nitrophenol more acidic than ortho-methoxyphenol.

Statement 2 : Nitro group ($-NO_2$) is an electron-withdrawing group while methoxy group ($-OCH_3$) is an electron releasing group.

38. **Statement 1 :** The –OH group attached to a carbon of benzene ring activates it towards electrophilic substitution

Statement 2 : The –OH group is an electron-releasing group.

39. **Statement 1 :** Resorcinol turns $FeCl_2$ solution purple.

Statement 2 : Resorcinol have phenolic group.

40. **Statement 1 :** *p*-Nitrophenol is a weaker acid than *o*-nitrophenol.

Statement 2 : Intramolecular H-bonding is present in ortho isomer. Intermolecular H-bonding is present in para isomer.

41. **Statement 1 :** Phenol on chlorination in presence of $FeCl_3$ and CS_2 gives *o*-chlorophenol as a major product.

Statement 2 : *o*-Chlorophenol is thermodynamically more stable than *p*-chlorophenol due to intramolecular hydrogen bonding in the former.

42. **Statement-1 :** Reimer-Tiemann reaction of phenol with CCl_4 in NaOH at 340 K gives salicyclic acid as the major product.

Statement-2 : The reaction occurs through intermediate formation of dichlorocarbene.

43. **Statement-1 :** Phenol is more reactive than benzene towards electrophilic substitution reaction.

Statement-2 : In the case of phenol, the intermediate carbocation is more resonance stabilized.

EXERCISE 13.3 (Subjective Problems)

1. (*a*) Distinguish among alcohols, enols and phenols.
(*b*) Why phenols are more stable than enols ?
(*c*) Draw and name the two structures of phenol.

2. Give the structural formula and (*i*) IUPAC, (*ii*) common, and (*iii*) CA names of the phenyl isomers of C_7H_8O.

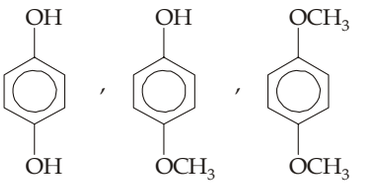
3. Explain the following :
(*i*) The C—O bond length in phenol is shorter than in alcohol.
(*ii*) The dipole moments of phenol (1.7 D) and methanol (1.6 D) are in opposite directions.
(*iii*) The dipole moment of *p*-nitrophenol (5.0 D) is greater than that of phenol or nitrobenzene (4.0 D).
(*iv*) Benzenol (C_6H_5OH) has a higher boiling point than benzenethiol.
(*v*) 1, 4-Dihydroxybenzene (quinol) has a higher melting point than 1, 2-dihydroxybenzene (catechol).

4. (*a*) What do you mean by the term steam distillation ?
(*b*) What physical property most influences the ability of a compound to be steam distilled ?
(*c*) Why only *o*-nitrophenol is distilled, but *m*- and *p*- not ?

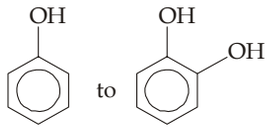
5. Use chemical equations to compare the reactions of
(*a*) RCOOH and C_6H_5OH with aq. $NaHCO_3$.
(*b*) RCOOH and C_6H_5OH with aq. Na_2CO_3.
(*c*) RCOONa and C_6H_5ONa with CO_2.
Predict which reaction is possible, and which not.
Given pK_a for RCOOH, C_6H_5OH, H_2CO_3, and HCO_3^- are 5, 10, 6.4 and 10.3 respectively.

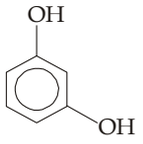
6. Give the structural formula and name of the principal compound formed (if any) from the reaction of *p*-cresol with
(*a*) hot conc. HCl (*b*) C_6H_5Cl, aq. NaOH
(*c*) $C_6H_5CH_2Cl$, aq. NaOH
(*d*) SO_2Cl (*e*) $C_6H_5SO_2Cl$
(*f*) phthalic anhydride (*g*) 2, 4-dinitrochlorobenzene
(*h*) $NaNO_2$ and dil . H_2SO_4, followed by HNO_3
(*i*) Cold dil . HNO_3 (*j*) H_2SO_4 at 15°C
(*k*) H_2SO_4, 100°C (*l*) Bromine water
(*m*) Br_2, CS_2
(*n*) *p*-Nitrobenzenediazonium chloride
(*o*) CO_2, NaOH, 125°C, 5 atm.

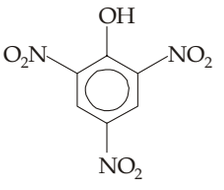
7. Arrange the compounds of each set in order of acidity.
(*a*) Carbonic acid, phenol, sulphuric acid, water
(*b*) *m*-Bromophenol, *m*-cresol, *m*-nitrophenol, phenol
(*c*) Benzenesulfonic acid, benzoic acid, benzyl alcohol, phenol
(*d*) *p*-Chlorophenol, 2,4-dichlorophenol, 2, 4, 6-trichlorophenol.

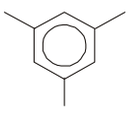
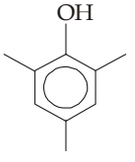
8. Arrange the compounds of each set in order of reactivity toward bromine.
(*a*) Anisole, benzene, chlorobenzene, nitrobenzene, phenol
(*b*) Anisole, *m*-hydroxyanisole, *o*-methylanisole, *m*-methylanisole.
(*c*) 

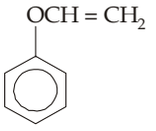
9. Outline steps involved in the following conversions :

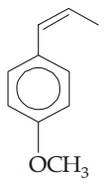
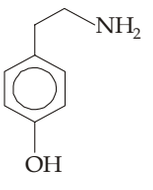
(*a*)  to

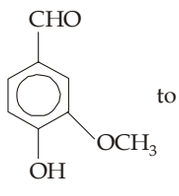
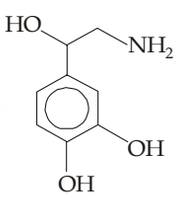
(*b*)  to 

(*c*)  to 

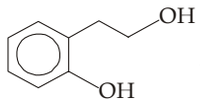
(*d*)  to 

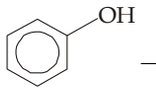
(*e*)  to 

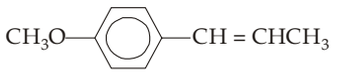
(*f*)  to 

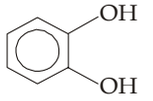
(*g*)  to 

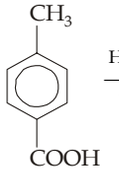
10. Complete the following :

(*a*) 

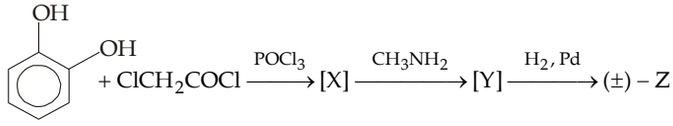
(*b*) 

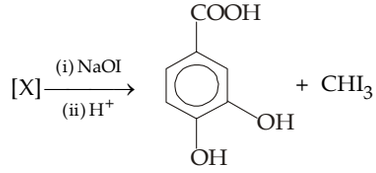
(*c*) 

(*d*) 

(*e*) 

11. Deduce the structure of the compound *Z* from the following reactions.





12. An organic compound (*A*) of the formula $C_{10}H_{12}O_3$ is insoluble in water, dil. HCl, and dil. aqueous $NaHCO_3$ but soluble in dil. NaOH. Its solution in dil. NaOH is distilled and distillate is collected in an alkaline solution of iodine, when a yellow precipitate is formed. The alkaline residue in the distillation flask when acidified with dil. H_2SO_4 gives a solid residue (*B*) of the formula $C_7H_6O_3$. When this acidified mixture is boiled, the compound *B* is collected as steam distillate. The compound (*B*) is soluble in aqueous $NaHCO_3$ with the evolution of a gas. Give structures of (*A*) and (*B*) and explain the reactions involved.

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SOLUTIONS

EXERCISE 13.1

1	(d)	**6**	(b)	**11**	(c)	**16**	(a)	**21**	(c)	**26**	(d)	**31**	(c)	**36**	(d)	**41**	(b)	**46**	(c)
2	(b)	**7**	(c)	**12**	(c)	**17**	(b)	**22**	(d)	**27**	(b)	**32**	(c)	**37**	(c)	**42**	(c)	**47**	(d)
3	(a)	**8**	(b)	**13**	(c)	**18**	(c)	**23**	(c)	**28**	(a)	**33**	(b)	**38**	(c)	**43**	(d)	**48**	(d)
4	(a)	**9**	(b)	**14**	(d)	**19**	(c)	**24**	(b)	**29**	(d)	**34**	(c)	**39**	(b)	**44**	(b)	**49**	(b)
5	(c)	**10**	(d)	**15**	(b)	**20**	(c)	**25**	(c)	**30**	(a)	**35**	(d)	**40**	(c)	**45**	(c)	**50**	(d)

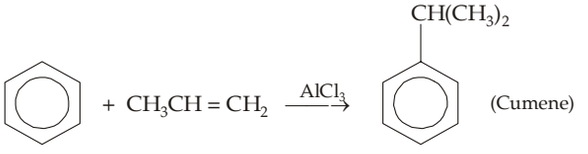
1. All are correct name for the given structure.

2. —OH has priority over —SH.

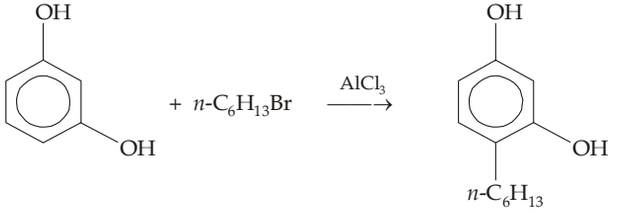
3. The keto tautomer (anthrone) has two distinct intact aromatic rings in addition to the C = O, making it more stable than the enol tautomer (anthranol) which suffers a loss of aromaticity per ring because its three rings are fused.

4. *ortho*-Nitrophenol has low b.p. and low water solubility than the *m*- and *para*-isomers.

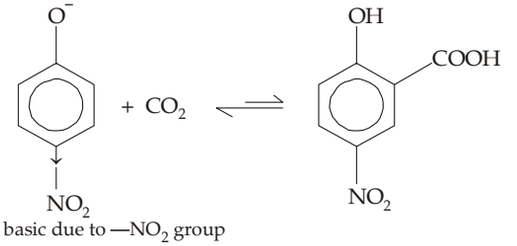
5.



6. In resorcinol, the two —OH groups in the *meta*-positions reinforce each other in electrophilic substitution.

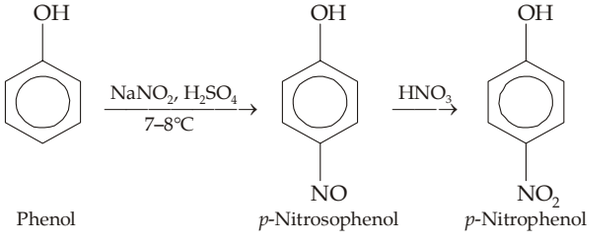


7. The corresponding phenoxide ion will be less basic, hence equilibrium will not lie favourably toward carboxylation.



Less basic due to —NO_2 group

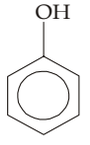
8.



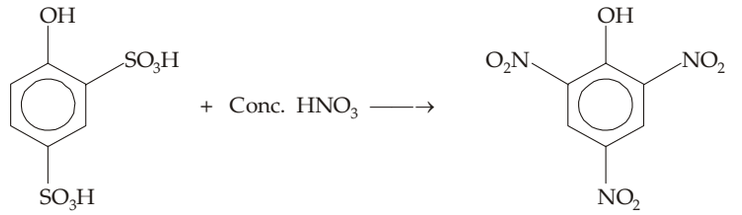
Phenol *p*-Nitrosophenol *p*-Nitrophenol

Thus here, oxidation of phenol is minimised by forming *p*-nitrosophenol.

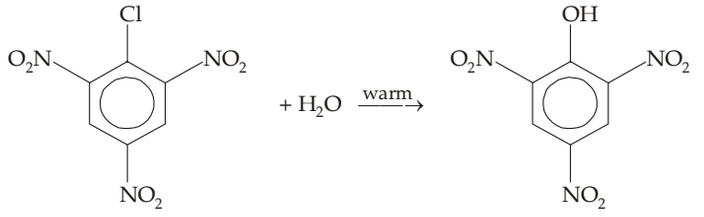
9. (*a*)



+ Conc. HNO_3 ⟶ Oxidised product formed

(*b*) 

Two electron-withdrawing —SO_3H groups deactivate phenol toward oxidation
(an example of electrophilic reaction)

10. 

2, 4, 6 Trinitrophenol (Picric acid)

Three —NO_2 groups present in *ortho*- and *para*-positions strongly activate —Cl toward nucleophilic substitution.

11. Same as above.

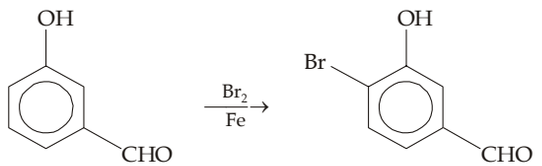
12. In enols, carbon atom bonded to O is sp^2 hybridized, hence its bond length will be less than that in alcohols, where carbon atom bonded to O is sp^3 hybridized.

13. Phenoxide from α-naphthol has more resonating structures than that from β-naphthol and phenol.

14. Recall that dipole moment is an additive property.

15. Bromine water will cause polybromination, because phenol is a highly reactive molecule.

16. —OH group is more electron-releasing due to mesomeric effect than the —CH_3 group, hence electrophilic substitution is governed by —OH. Remember that nitric acid is not used, hence oxidation of phenol does not occur.

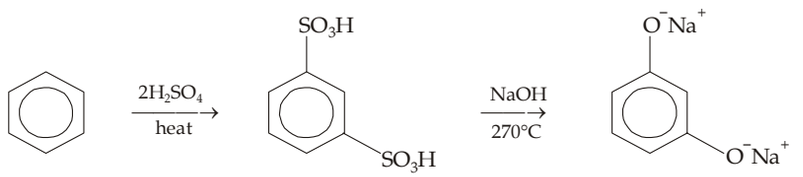
17. 

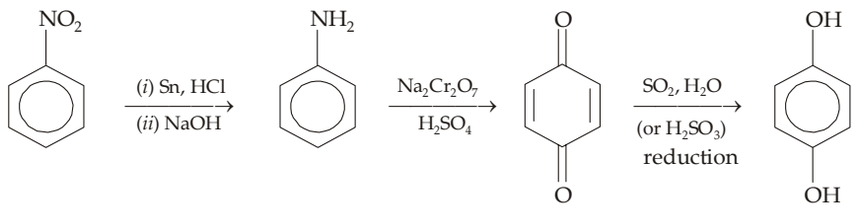
Position of Br is in accordance with the —OH group ; other two possible positions for Br are not observed due to steric factor.

18. $C_6H_5O^-$ is actually an ambident anion with a negative charge on O and on the *o, p*-ring positions. Hence attack by O^- gives the ether $C_6H_5OCH_2C_6H_5$ while attack by the *ortho* carbanion gives *o*-benzylphenol.

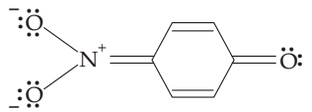
19. Consult mechanism of Claisen rearrangement.

20. It is an electrophilic addition reaction and involves the formation of carbocation, hence more stable is the cation more easily it will be formed. Recall that benzylic carbocation is very stable. Since phenols are very less reactive toward nucleophilic substitution, —OH will not be replaced by —Br.

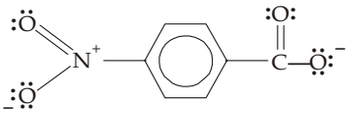
21. 

22. 

24. Charge delocalization in the *p*-nitrophenate ion is much more effective because of direct interaction between O^- and NO_2, which is not possible in the *p*-nitrobenzoate anion.



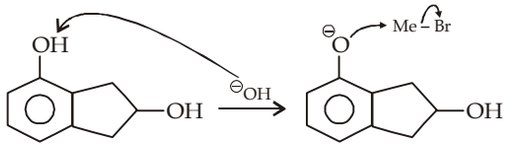
p-Nitrophenate anion
(direct extended π bonding)

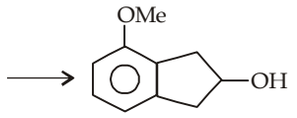


p-Nitrobenzoate anion
(no direct extended π bonding)

EBD_7089

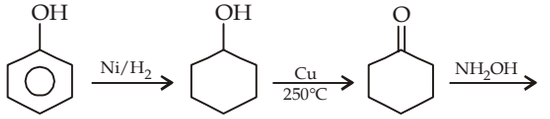
28. (*a*)

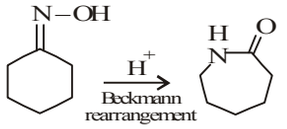




31. (*c*) Enolic form is benzenoid.

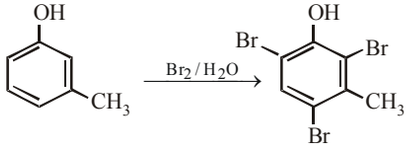
32. (*c*)



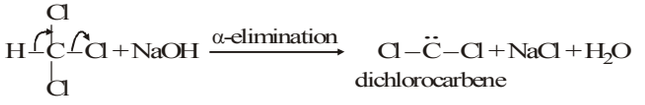


33. (*b*) In (I) steric inhibition is available.

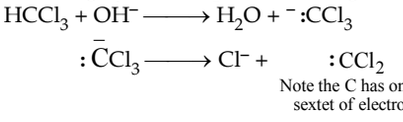
34. (*c*) *Note :* OH group activates the benzene nucleus.

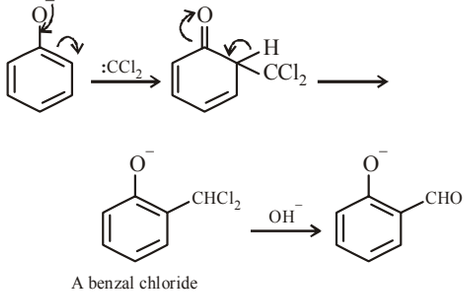


35. (*d*) *Note :* This is Riemer-Tiemann reaction and the electrophile is dichlorocarbene.



36. (*d*) Riemer-Tiemann reaction involves electrophilic substitution on the highly reactive phenoxide ring.

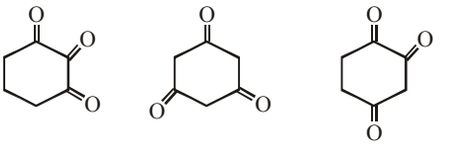


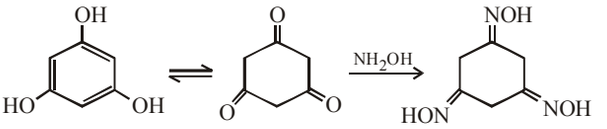


37. (*c*) Recall that $-NO_2$ group increases, while $-CH_3$ decreases acidity of the phenol. Further, in case of $-CH_3$ group acid-weakening effect is due to +I effect, *m*-methyl will exert powerful +I effect than the *p*-methyl. Hence the acidic order will be

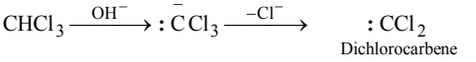
p – nitrophenol > phenol > *p* – cresol > *m* – cresol
II I IV III

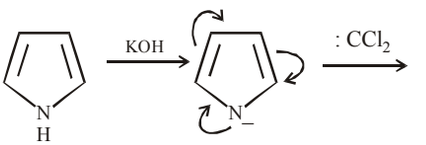
38. (*c*) We know that phenols show keto-enol tautomerism and the stability of the keto form depends upon the number of keto group (more the number of keto groups, higher will be stability of the keto tautomer). Thus trihydric phenols should exist in keto form in considerable amount but only when the two keto groups are not on adjacent carbon atoms which decreases stability due to positive charge on adjacent carbon atoms.

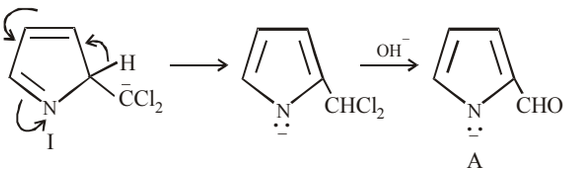


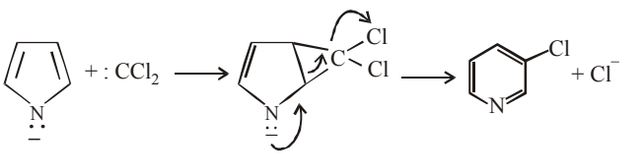


39. (*b*) It is an example of Reimer-Tiemann reaction



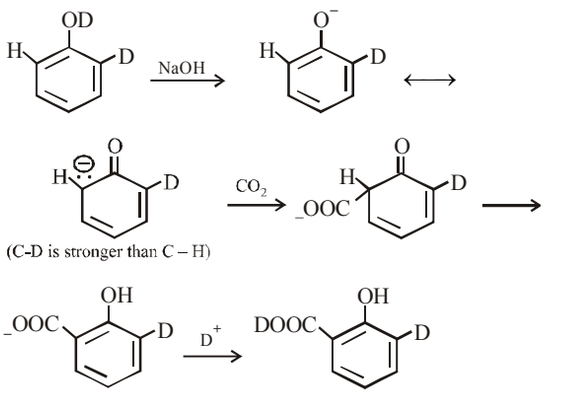






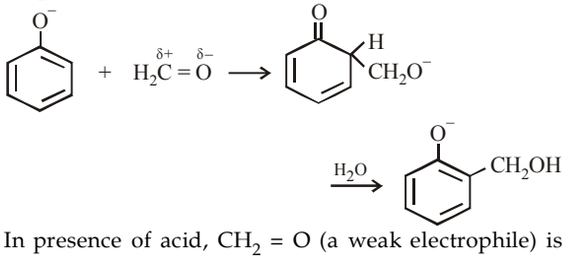
III

40. (*c*)

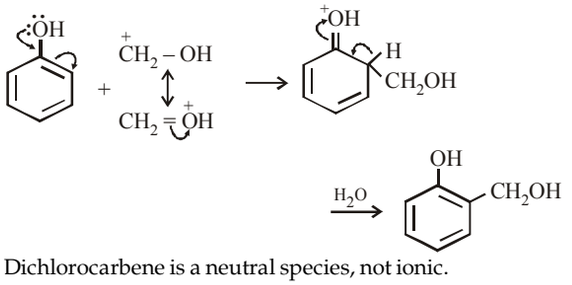


41. (*b*) The reaction is an example of Claisen rearrangement in which allyl phenyl ethers, on heating, is forming *p*-allylphenol because *o*-positions are not free. Further, in the formation of *p*-product allyl group migrates twice, the labelled C^{14} comes to its original position.

42. (*c*) Condensation of phenol with formaldehyde is an electrophilic substitution reaction. Base converts phenol into phenoxide ion which, being more reactive, reacts easily with $CH_2 = O$ (a weak electrophile).

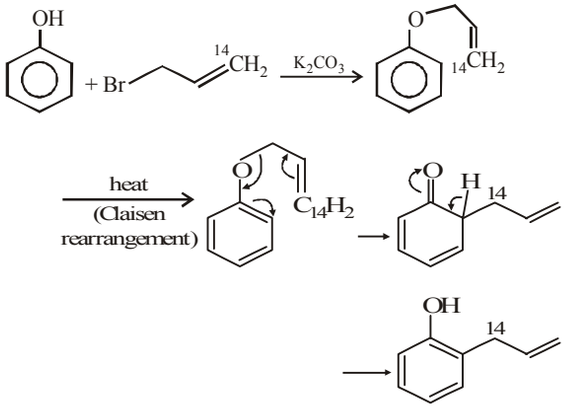


In presence of acid, $CH_2 = O$ (a weak electrophile) is protonated to $CH_2 = \overset{+}{O}H$ (a strong electrophile) which easily reacts with phenol (a weak nucleophile).

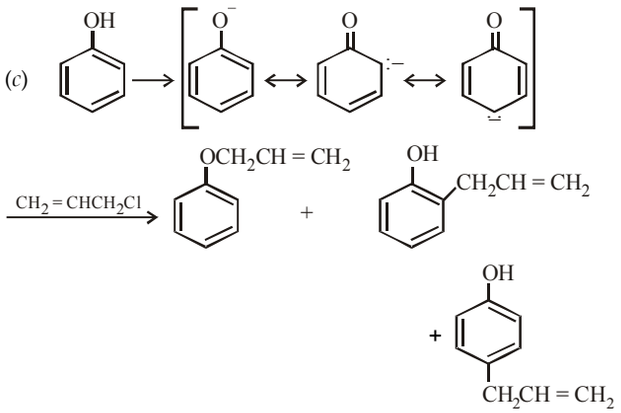


43. (*d*) Dichlorocarbene is a neutral species, not ionic.

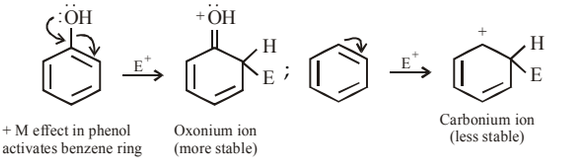
44. (*b*)



45. (*c*)



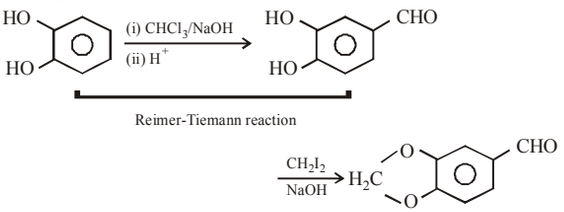
46. (*c*)



+ M effect in phenol activates benzene ring — Oxonium ion (more stable) — Carbonium ion (less stable)

High stability of oxonium ion (oxocation) is because here every atom (except H) has a complete octet of electrons, while in carbocations, carbon bearing positive charge is having six electrons.

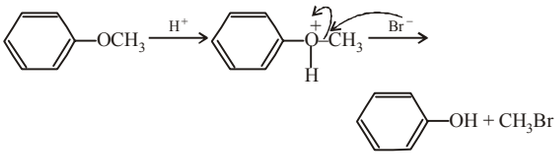
47. (*d*)



Reimer-Tiemann reaction

48. (*d*) Nitrosonium ion will go to *p*-position with respect to –OH group. Further dil. HNO_3 oxidises –NO group to $-NO_2$ group.

50. (d)



EXERCISE 13.2

MCQ > 1 CORRECT OPTION	**1**	(a,b,c)	**2**	(b,c)	**3**	(b,d)	**4**	(a,b,c)
	5	(a, c, d)	**6**	(a, b, d)	**7**	(a, b)	**8**	(a, d)
	9	(a, b, c)	**10**	(a, b)	**11**	(a, b, c, d)	**12**	(a, b, c)
	13	(b, d)	**14**	(a, b, c, d)				
PASSAGE 1	**15**	(c)	**16**	(b)	**17**	(b)		
PASSAGE 2	**18**	(d)	**19**	(b)	**20**	(b)		
PASSAGE 3	**21**	(c)	**22**	(c)	**23**	(b)		
PASSAGE 4	**24**	(d)	**25**	(c)	**26**	(c)		
	27	(c)	**28**	(c)				
PASSAGE 5	**29**	(b)	**30**	(d)	**31**	(c)		
Match the	**32**	(A) - b, (B) - a, c, (C) - c, d, (D) - c, d						
Following	**33**	(A) - a, d, (B) - a, c, (C) - a, (D) - a, b						
	34	(A) - a, b, c; (B) - a, b, c; (C) - a, b, c, d; (D) - a, b, c, d						
A/R	**35**	(a)	**36**	(a)	**37**	(a)	**38**	(a)
	39	(c)	**40**	(d)	**41**	(a)	**42**	(c)
	43	(a)						

EBD_7089

1. All are correct name for the given structure, resorcinol is 1,3-isomer.

2. Compound II has —CH_3 group in the *ortho* position to —OH, hence it can't form H-bond ; although III has —C ≡ N group which can form H–bond but due to its *sp* hybridized character, its carbon keeps N away from —OH group, hence here —C ≡ N can't form intramolecular H-bond.

3. The combination $C_6H_5Br + CH_3CH_2OH$ has non-reactive C_6H_5Br, while in the combination $C_6H_5OH + Me_3CBr$, Me_3CBr being *tert* will undergo elimination reaction rather substitution. Hence, only combinations I and III can be used for preparing ether.

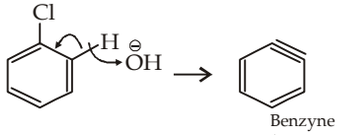
$$C_6H_5OH + (CH_3)_2SO_4 \xrightarrow{S_N} C_6H_5OCH_3$$

$$p\text{-}NO_2C_6H_4Br + CH_3CH_2OH \xrightarrow{Ar\,S_N} p\text{-}NO_2C_6H_4OCH_2CH_3$$

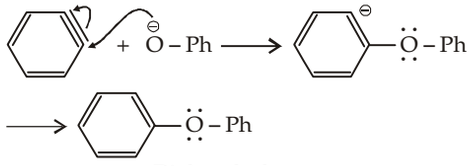
4. Aniline as well as phenol are highly activated compounds towards electrophilic reactions (oxidation), hence all the three will be easily oxidised to *p*-benzoquinone, but not (d).

11. (*a,b,c,d*)
(a) Isotopic effect is observed in sulphonation.
(b) Salicyclic acid gives 2,4,6-tribromophenol (i.e. decarboxy -bromination takes place)
(c) Product is sec. alcohol.
(d) Products are diastereomers.

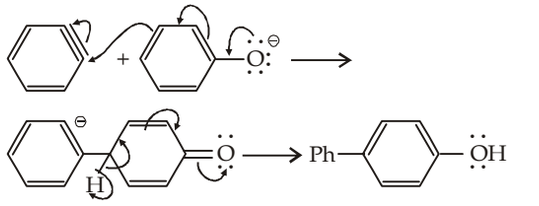
12. (*a,b,c*) The nucleophilic substitution of chlorobenzene by OH under drastic condition takes place via benzyne itermediate.



Benzyne
(Aromatic)

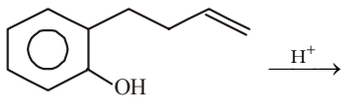


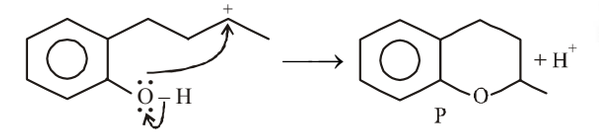
Diphenyl ether

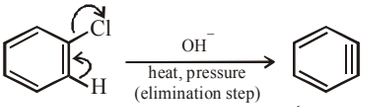


p-Phenylphenol

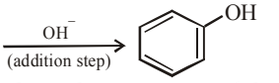
13. (*b,d*)





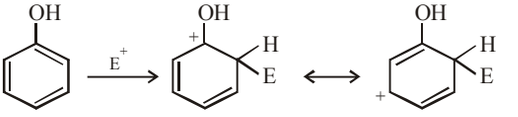


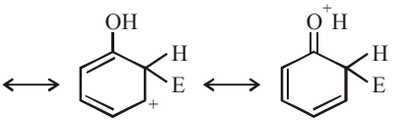
benzyne



25. Acid (H_2SO_4) converts acid anhydride to the more powerful electrophile, $CH_3\overset{+}{C}=O$ group. On the other hand, base (NaOH) converts phenol to the more powerful nucleophile, phenoxide ion.

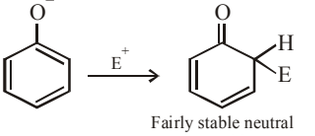
26.





Oxonium cation
(every atom has octet)

27.



Fairly stable neutral
conjugated ketone

28. In presence of acids, $CH_2 = O$ is protonated to form $CH_2 = \overset{+}{O}H$ in which carbon is more electron deficient than that in $CH_2 = O$. In presence of OH^-, phenol is converted into phenoxide, $C_6H_5O^-$ which being a stronger nucleophile is easily attacked by weaker nucleophile, the unprotonated $CH_2 = O$.

34. (A)-a, b, c; (B)-a, b, c; (C)-a, b, c, d; (D)-a, b, c, d

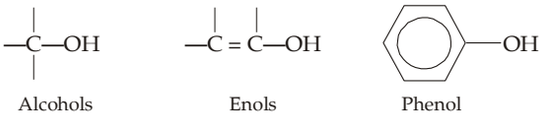
40. Due to intra molecular H-bonding in ortho isomer H^+ ion may not release easily, so ortho isomer is weak acidic than para isomer. Here Statement 1 is wrong and Statement 2 is correct.

42. The correct reason is : Nucleophilic attack of phenolate ion through the *ortho*-carbon atom occurs on CCl_4 (a neutral electrophile) to form an intermediate which on hydrolysis gives salicylic acid (ArSE reaction).

43. Due to +M effect of $-\ddot{O}H$, its intermediate carbocation is more stable than the one in benzene.

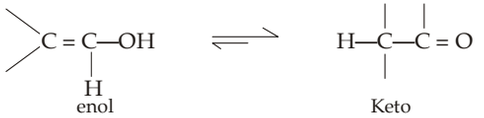
EXERCISE 13.3

1. (*a*) In alcohols, —OH group is attached to an sp^3 hybridized carbon, while enols have —OH group attached to sp^2 hybridized carbon. Further, when the —OH group is attached to a vinyl group, the compound is called enol, while when it is attached to a carbocylic aromatic ring it is called phenol.



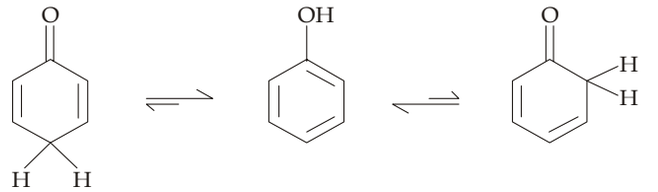
Alcohols Enols Phenol

(*b*) Both phenols and enols are considered as tautomers of a keto structure. The large resonance energy of C = O usually causes the keto tautomer to be much more stable than the enol.



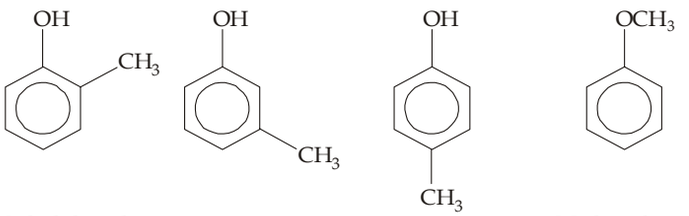
However, the keto form of phenol can be attained only with loss of the stable aromatic ring, hence it is very much stable than enol.

(*c*)



2, 5-Cyclohexadienone *para*-keto form | Phenol *enol* form | 2, 4-Cyclohexadienone *ortho*-keto form

2.



1UPAC name	*o*-Methylphenol	m-	p-	Methoxybenzene
Common name	*o*-Cresol	m-Cresol	p-Cresol	Anisole
CA name	2-Methylbenzeneol	3-	4-	Methoxybenzene

Although the CA name for C_6H_5OH is phenol, substituted phenols are considered as derivatives of *benzeneol*.

3. (*i*) Remember that the bond lengths in C—X decreases with the increase in *s* character of the carbon.

	sp^3 C—OH	=	sp^2 C—OH
	Alcohols		Enols (Phenols)
% of *s* character of C	25		33.3

Thus the C—O bond of ArOH's (having 33.3% *s* character) will be shorter than the C—O bond of ROH's (having 25% *s* character).

(*ii*) The delocalization of electron density from O to the ring causes the O of phenol to be positive end of the molecular dipole. In alcohols, delocalization of electrons is not possible and hence it is electronegativity of O atom that produces negative end of the dipole.

(*iii*) The electron-donation of —OH reinforces the electron-withdrawal of $—NO_2$.

(*iv*) Sulphur forms weak hydrogen bonding than O, hence intermolecular attraction (association) in C_6H_5SH is weaker than in C_6H_5OH.

(*v*) Molecules of *p*-isomer fit closer in the solid state causing it to have the higher melting point.

4. (*a*) When a compound is mixed (*but not soluble*) with boiling water and thus carried by steam, the compound is said to be steam distilled.

(*b*) The steam-distilled compound must have an appreciable vapour pressure at the boiling point of water.

(*c*) Attraction to water greatly lowers the vapour pressure, preventing steam distillation. Since the chelated *o*-isomer has a minimal attraction with water, it is steam distilled.

5. The equilibria of Bronsted acid-base reactions favour the side with the weaker acid and base. In each case, write the ionic equation as if it occurs and place the pK_a values under each acid. If the weaker acid is on the right-side, the reaction occurs but if the weaker acid is on the left-side, the reverse reaction occurs.

(*a*) $RCOOH + HCO_3^- \longrightarrow RCOO^- + H_2CO_3\ (H_2O + CO_2)$

$pK_a = 5$ $\qquad$ $pK_a = 6.4$ (weaker acid)

$C_6H_5OH + HCO_3^- \longrightarrow\!\!\!\!\!\!\times\ C_6H_5O^- + H_2CO_3\ (H_2O + CO_2)$

$pK_a = 10$ $\qquad$ $pK_a = 6.4$ (stronger acid)

(*b*) $RCOOH + CO_3^{2-} \longrightarrow RCOO^- + HCO_3^-$

$pK_a = 5$ $\qquad$ $pK_a = 10.3$ (weaker acid)

$C_6H_5OH + CO_3^{2-} \rightleftharpoons C_6H_5O^- + HCO_3^-$

$pK_a = 10$ $\qquad$ $pK_a = 10.3$ (weaker acid)

The last reaction occurs, however the result is borderline and any substituted phenol that has $pK_a > 10.5$ may not react.

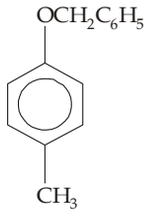
(*c*) $RCOO^- + \underbrace{H_2O + CO_2}_{pK_a = 6.4} \longrightarrow\!\!\!\!\!\!\times\ \underset{\text{(stronger acid)}}{\underset{pK_a = 5}{RCOOH}} + HCO_3^-$

$C_6H_5O^- + \underbrace{H_2O + CO_2}_{pK_a = 6.4} \longrightarrow \underset{\text{(weaker acid)}}{\underset{pK_a = 10}{C_6H_5OH}} + HCO_3^-$

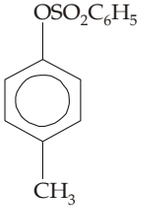
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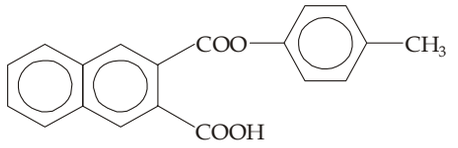
6. (*a*) No reaction

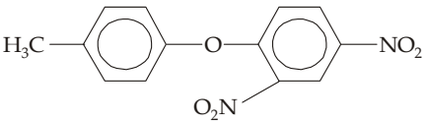
(*b*) No reaction. Aryl halides, unless activated, are inert toward S_N.

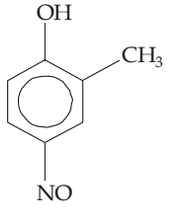
(*c*) 

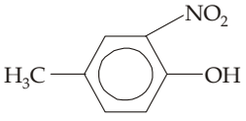
(*d*) No reaction

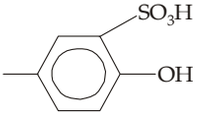
(*e*) 

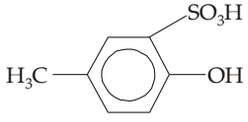
(*f*) 

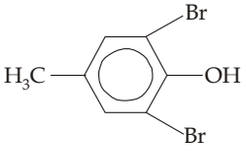
(*g*) 

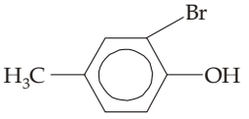
(*h*) 

(*i*) 

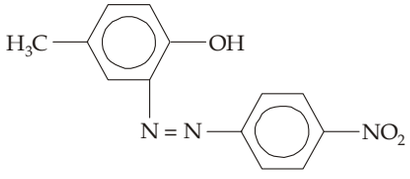
(*j*) 

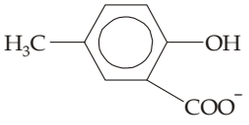
(*k*) 

(*l*) 

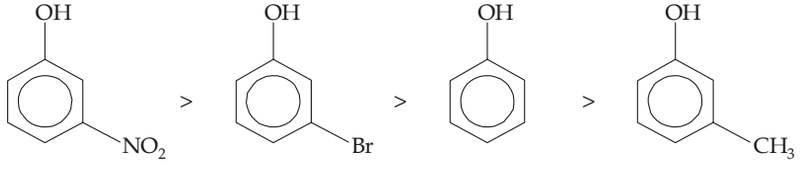
(*m*) 

(Note *p*-position is not free)

(*n*) 

(*o*) 

7. (*a*) $H_2SO_4 > H_2CO_3 > C_6H_5OH > H_2O$

(*b*) 

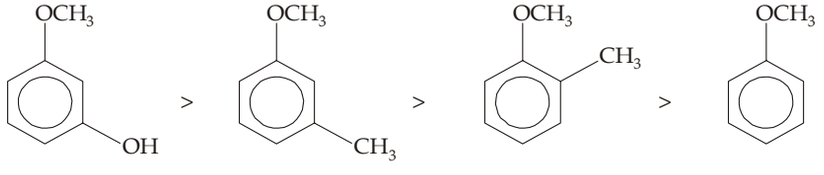
(*c*) $C_6H_5SO_3H > C_6H_5COOH > C_6H_5OH > C_6H_5CH_2OH$

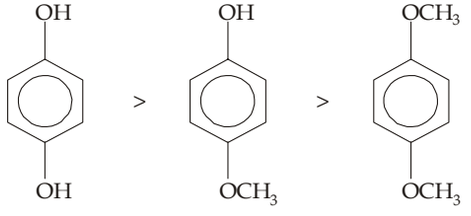
(*d*) 2, 4, 6-Trichlorophenol > 2, 4-Dichlorophenol > *p*-Chlorophenol

8. Relative activating effect of the substituents toward electrophilic substitution :

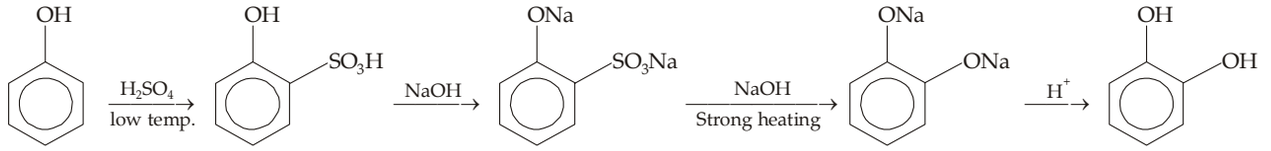
$$—OH > —OCH_3 > —CH_3 > —H > —Cl > —NO_2$$

(*a*) $C_6H_5OH > C_6H_5OCH_3 > C_6H_6 > C_6H_5Cl > C_6H_5NO_2$

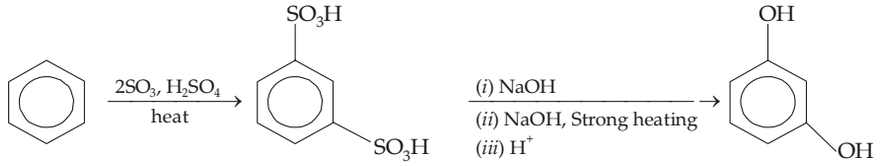
(*b*) 

(*c*) 

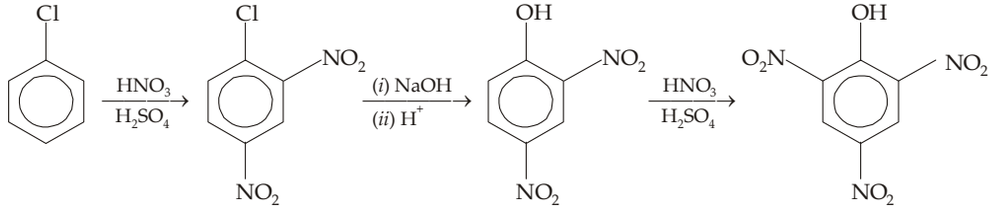
9. (*a*)



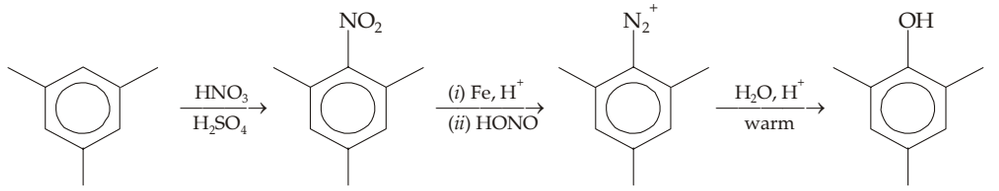
(*b*)



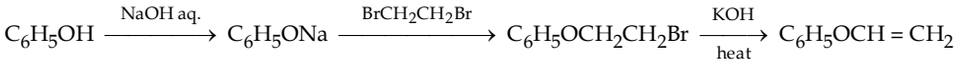
(*c*)



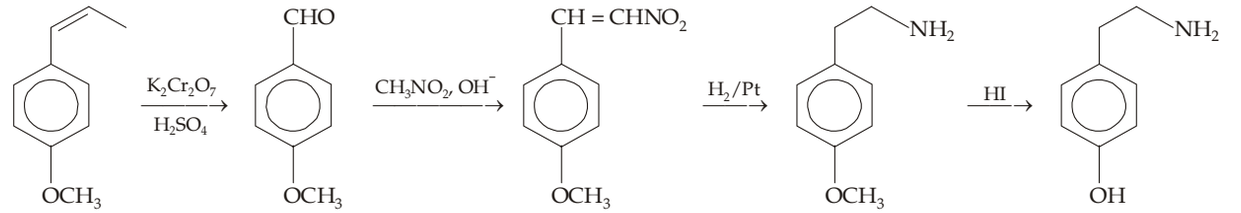
(*d*)



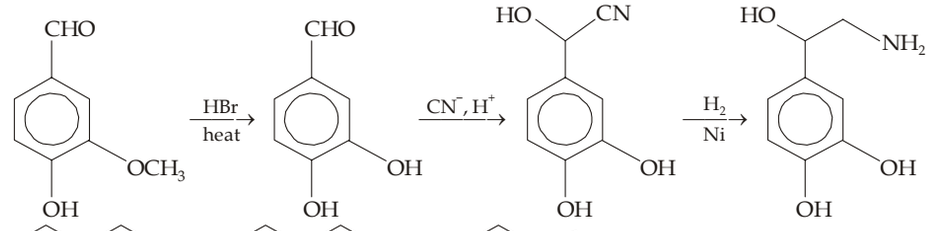
(*e*)



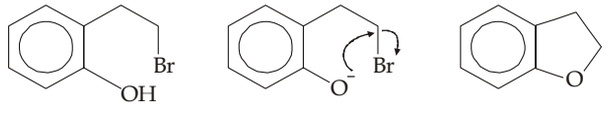
(*f*)



(*g*)

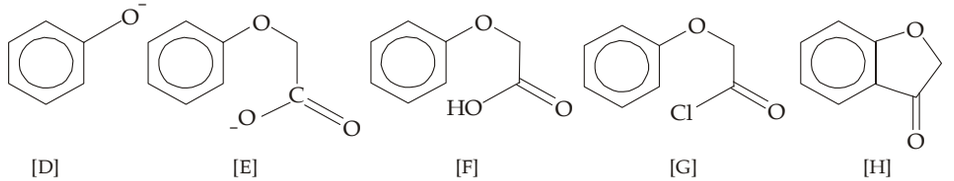


10. (*a*)



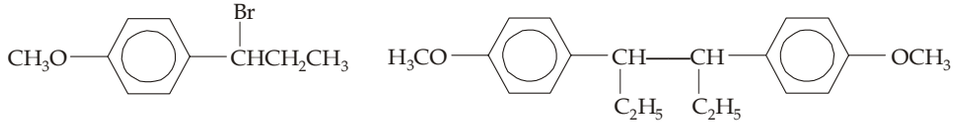
[A] [B] [C]

(*b*)

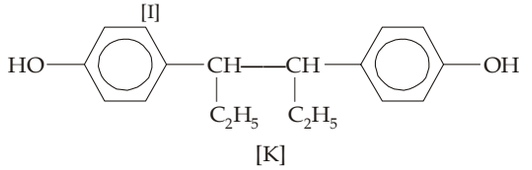


[D] [E] [F] [G] [H]

(*c*)



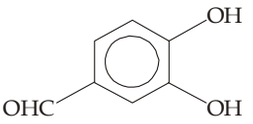
[I] [J]



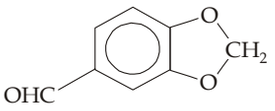
[K]

EBD_7089

(*d*)

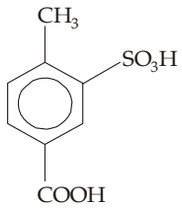


[L]

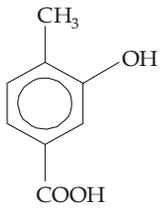


[M]

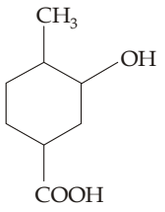
(*e*)



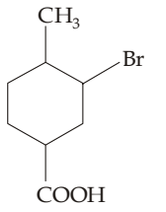
[N]



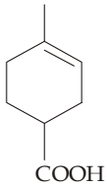
[O]



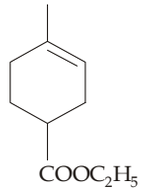
[P]



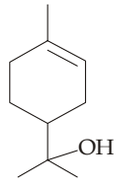
[Q]



[R]

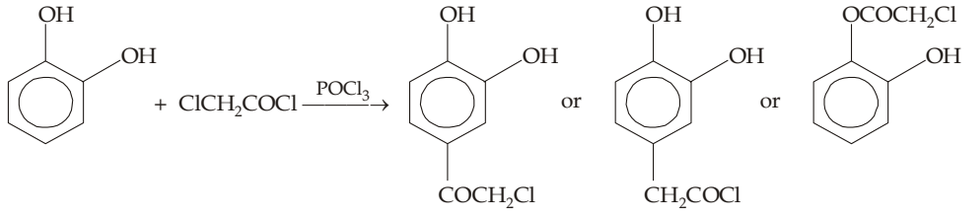


[S]



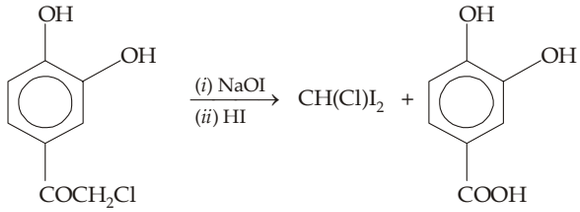
[T]

11. There are three possible products for the reaction between catechol and chloroacetyl chloride.



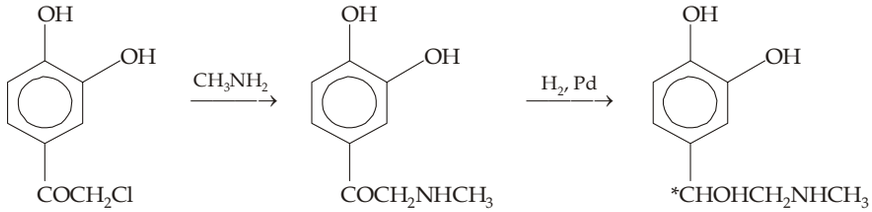
(X_1) By ring acylation (X_2) By ring alkylation (X_3) By esterification

However, the compound [X] so obtained undergoes haloform reaction which is possible only in case of (X_1).



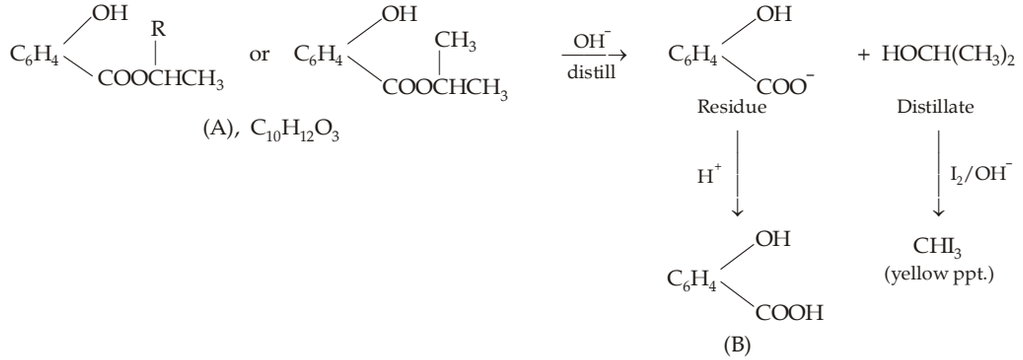
(X_1)

Hence the compound [X] should be $[X_1]$ and thus the various reactions can be written as below.



(X) (Y) (±)-Z

12. Solubility of the compound A indicates it to be a phenol. Alkaline hydrolysis of A also indicates presence of an ester group. Further since the distillate undergoes haloform test, alcoholic part of the ester should be $RCHOHCH_3$. Thus the structure of A can be written as below.



(A), $C_{10}H_{12}O_3$ (B)

Among the three hydroxybenzoic acids, only the *ortho* isomer (salicylic acid) is steam-volatile, hence B must be salicylic acid and A isopropyl salicylate.

ALCOHOLS, PHENOLS AND ETHERS

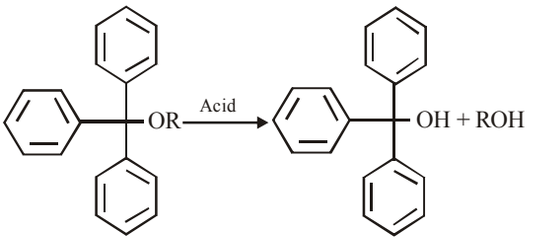
PAST YEAR QUESTIONS JEE ADVANCED/IIT-JEE (2013 - 2017)

MCQs with One Correct Answer

1. For the identification of β-naphthol using dye test, it is necessary to use **[JEE Adv. 2014]**

(a) Dichloromethane solution of β-naphthol
(b) Acidic solution of β-naphthol
(c) Neutral solution of β-naphthol
(d) Alkaline solution of β-naphthol

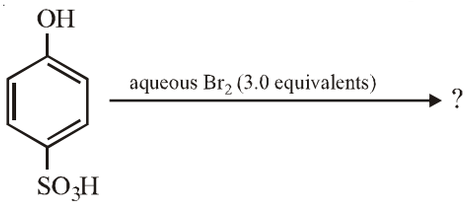
2. The acidic hydrolysis of ether (X) shown below is fastest when **[JEE Adv. 2014]**

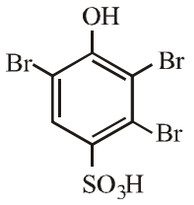


(a) One phenyl group is replaced by a methyl group
(b) One phenyl group is replaced by a *para*-methoxyphenyl group
(c) Two phenyl groups are replaced by two *para*-methoxyphenyl groups
(d) No structural change is made to *X*

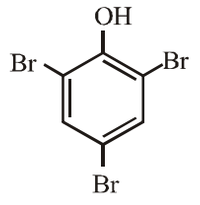
MCQs with One or More Than One Correct

1. The major product(s) of the following reaction is(are) **[JEE Adv. 2013]**

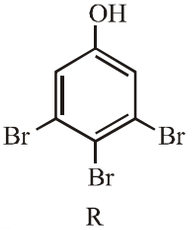




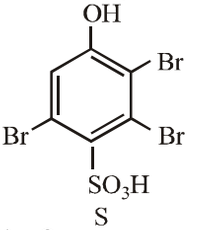
P



Q



R



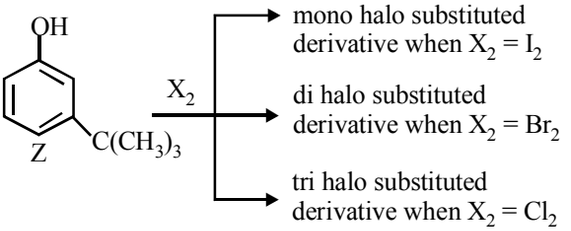
S

(a) P (b) Q
(c) R (d) S

2. The correct combination of names for isomeric alcohols with molecular formula $C_4H_{10}O$ is/are **[JEE Adv. 2014]**

(a) Tert-butanol and 2-methylpropan-2-ol
(b) Tert-butanol and 1, 1-dimethylethan-1-ol
(c) n-butanol and butan-1-ol
(d) Isobutyl alcohol and 2-methylpropan-1-ol

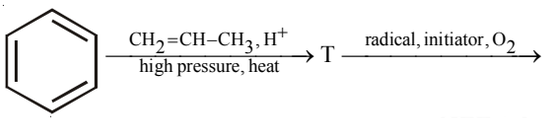
3. The reactivity of compound Z with different halogens under appropriate conditions is given below: **[JEE Adv. 2014]**



The observed pattern of electrophilic substitution can be explained by

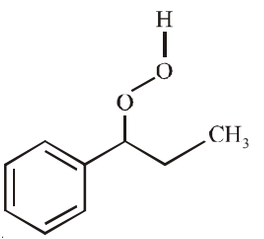
(a) The steric effect of the halogen
(b) The steric effect of the *tert*-butyl group
(c) The electronic effect of the phenolic group
(d) The electronic effect of the *tert*-butyl group

4. The major product U in the following reactions is

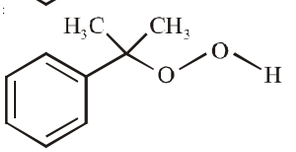


[JEE Adv. 2015]

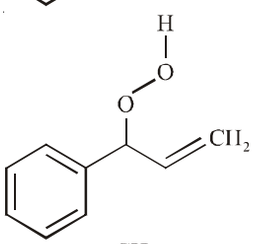
(a)



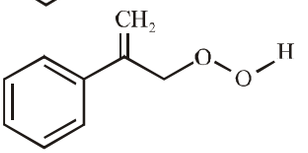
(b)



(c)



(d)

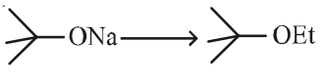


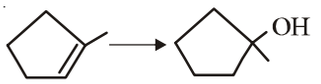
Match the Following

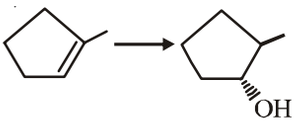
1. Match the chemical conversions in List I with the appropriate reagents in List II and select the correct answer using the code given below the lists : ***(JEE Adv. 2013)***

List I **List II**

P  1. (i) $Hg(OAc)_2$; (ii) $NaBH_4$

Q.  2. NaOEt

R.  3. Et-Br

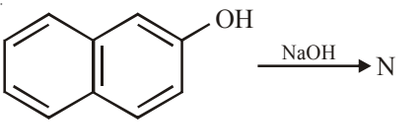
S.  4. (i) BH_3; (ii) H_2O_2/NaOH

Codes :

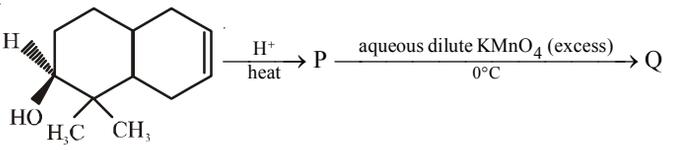
	P	Q	R	S
(a)	2	3	1	4
(b)	3	2	1	4
(c)	2	3	4	1
(d)	3	2	4	1

Integer Value Correct Type

1. The number of resonance structures for N is ***(JEE Adv. 2015)***

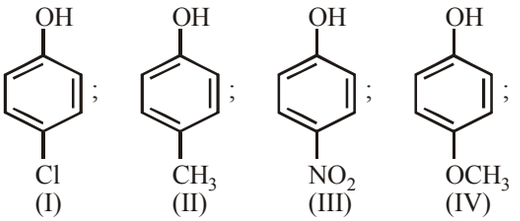


2. The number of hydroxyl group(s) in Q is ***(JEE Adv. 2015)***



PAST YEAR QUESTIONS JEE MAIN/AIEEE (2013 - 2017)

1. Arrange the following compounds in order of decreasing acidity : **[JEE M 2013]**



(I) (II) (III) (IV)

(a) II > IV > I > III (b) I > II > III > IV

(c) III > I > II > IV (d) IV > III > I > II

2. An unknown alcohol is treated with the "Lucas reagent" to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism : **[JEE M 2013]**

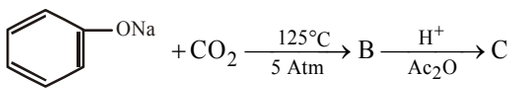
(a) secondary alcohol by S_N1

(b) tertiary alcohol by S_N1

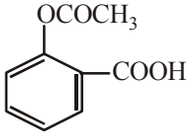
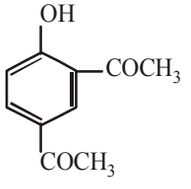
(c) secondary alcohol by S_N2

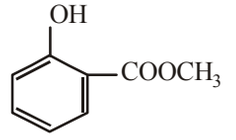
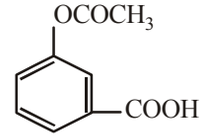
(d) tertiary alcohol by S_N2

3. Sodium phenoxide when heated with CO_2 under pressure at 125°C yields a product which on acetylation produces C.



The major product C would be **[JEE M 2014]**

(a)  (b) 

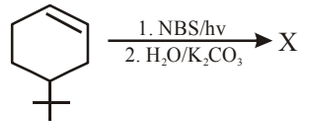
(c)  (d) 

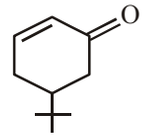
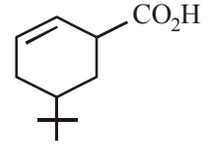
4. Thiol group is present in : **[JEE M 2016]**

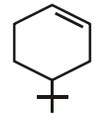
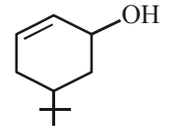
(a) Cysteine (b) Methionine

(c) Cytosine (d) Cystine

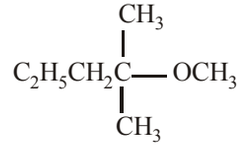
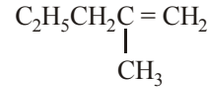
5. The product of the reaction given below is: **[JEE M 2016]**

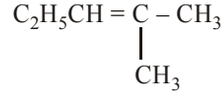


(a)  (b) 

(c)  (d) 

6. 2-chloro-2-methylpentane on reaction with sodium methoxide in methanol yields: **[JEE M 2016]**

(1)  (2) 

(3) 

(a) (3) only (b) (a) and (b)

(c) All of these (d) (a) and (c)

SOLUTIONS

PAST YEAR QUESTIONS JEE ADVANCED/IIT-JEE (2013 - 2017)

MCQs with One Correct Answer

1. (d) In dye test, phenolic — OH group is converted to — O^- which activates the ring towards electrophilic aromatic substitution

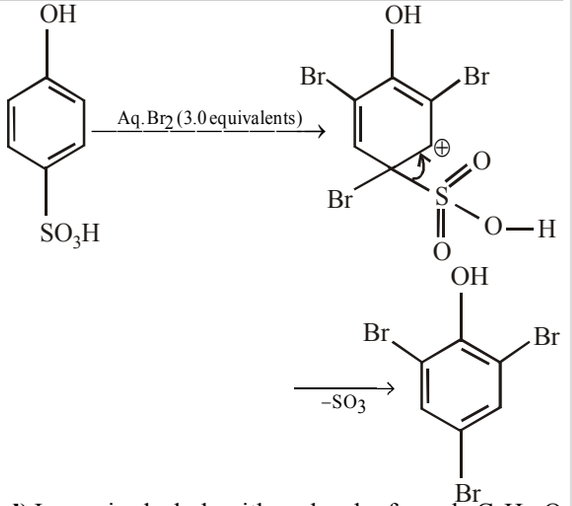
2. (c) The given reaction proceeds through S_N1 mechanism which involves carbocation as intermediate.

$$Ph_3C-O-R \xrightleftharpoons{H^+} Ph_3C-\overset{+}{\underset{H}{O}}-R \rightleftharpoons Ph_3C^+ + ROH$$

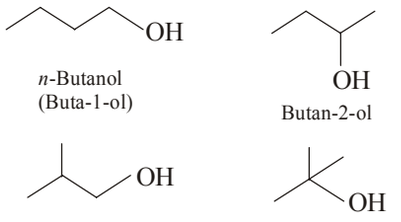
Thus, higher the stability of the carbocation, greater will be reactivity. Presence of electron releasing group (e.g., — OCH_3) in *p*-position of the phenyl group will disperse the positive charge of the carbocation by +M effect, hence stabilizes the carbocation.

MCQs with One or More Than One Correct

1. (b)

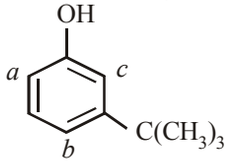


2. (a, c, d) Isomeric alcohols with molecular formula $C_4H_{10}O$ are

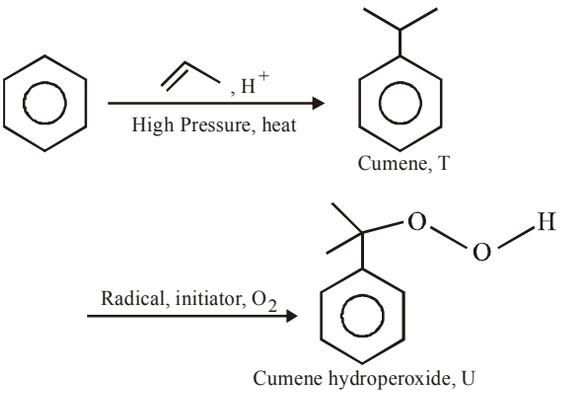


n-Butanol (Buta-1-ol) | Butan-2-ol | Isobutyl alcohol (2-methylpropan-1-ol) | *tert*-Butanol (2-methylpropan-2-ol)

3. (a, b, c) —OH group is strongly activating and *o*, *p*-directing due to +M effect. Thus positions *a*, *b* and *c* are the sites for attack by an electrophile. However, sites *b* and *c* are not preferred by bulky electrophile due to steric crowding. Thus more bulky electrophile (like I_2) can attack only site *a*, which is least sterically hindered, a bit smaller electrophile (Br_2) can attack at sites *a* and also *b* (relatively less sterically hindered site) and the smallest electrophile (Cl_2) can attack all the three sites, viz., *a*, *b* and *c* (most sterically hindered site).



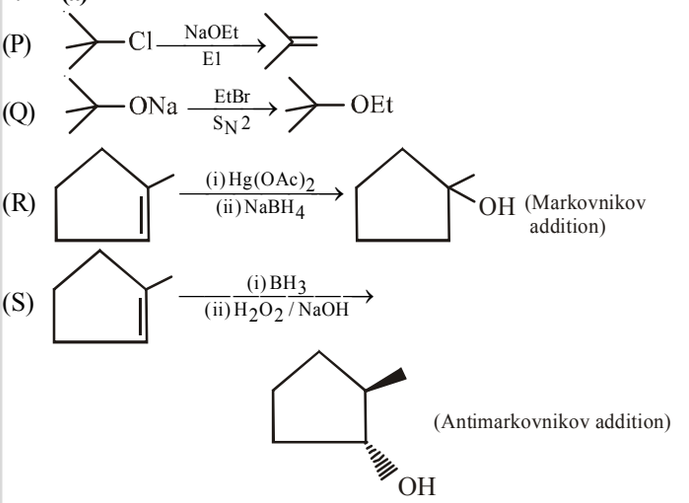
4. (b)



Cumene hydroperoxide, U

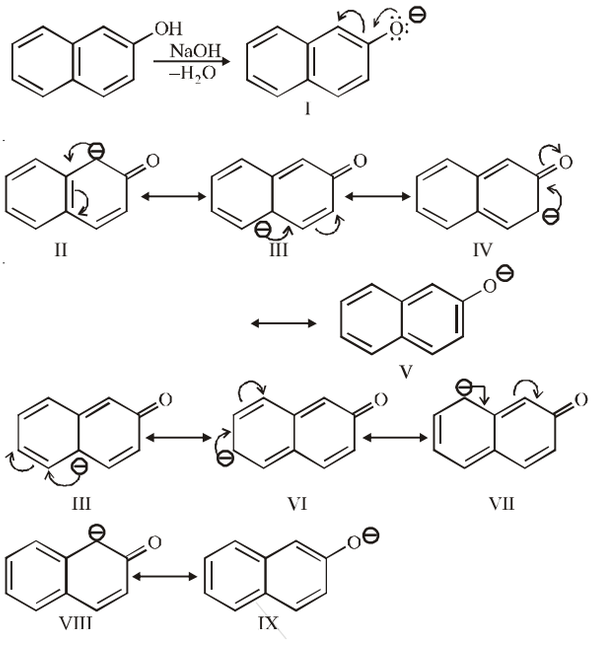
Match the Following

1. (a)

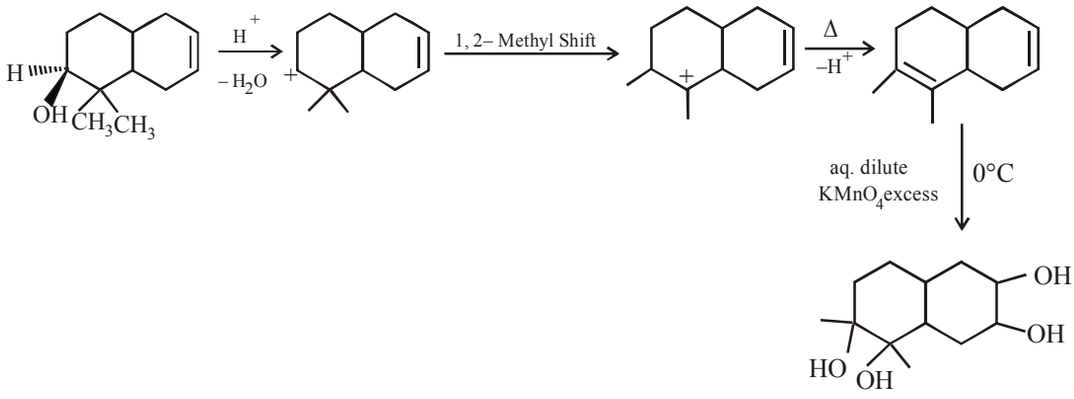


Integer Value Correct Type

1. (9)

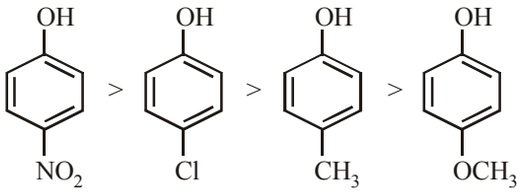


2. (4)



PAST YEAR QUESTIONS JEE MAIN/AIEEE (2013 - 2017)

1. (c) Electron withdrawing substituents like $-NO_2$, Cl increase the acidity of phenol while electron releasing substituents like $-CH_3$, $-OCH_3$ decreases acidity. hence the correct order of acidity will be



Further $(-I)\ NO_2 > (-I)$ Cl and $(+I)\ CH_3 > (+I)\ OCH_3$

2. (b) Tertiary alchols reacts fastest with lucas reagnet as the rate of reaction is directly proportional to the stability of carbocation formed in the reaction. Since most stable 3° carbocation is formed in the reaction hence it will react fastest further tetriary alcohols appears to react by S_N1 mechanism.

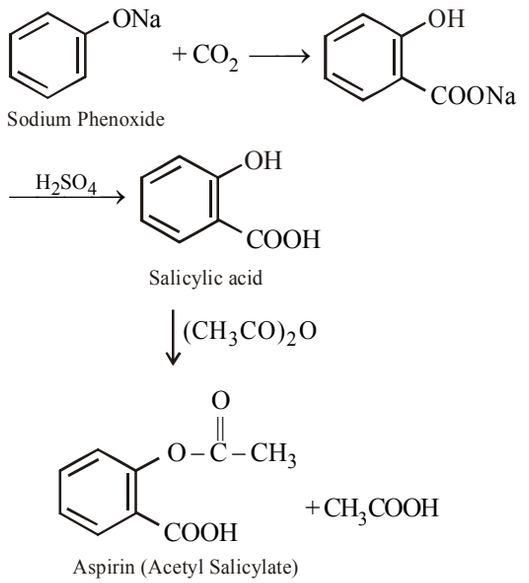
Step 1. $(CH_3)_3C-OH+H-Cl \rightleftharpoons (CH_3)_3-\overset{+}{O}H_2+Cl^-$

Step 2. $(CH_3)_3C-\overset{+}{O}H_2 \rightleftharpoons (CH_3)_3C^+ + H_2O$

Setp 3. $(CH_3)_3C^+ + Cl^- \longrightarrow (CH_3)_3C-Cl$

tert-Butyl chloride

3. (a)

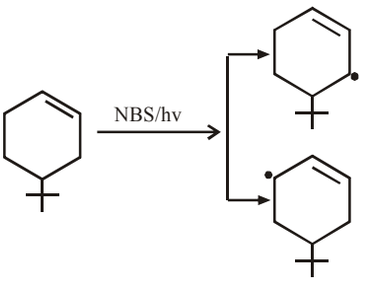


4. (a) Among 20 naturally occuring amino acids "Cysteine" has '– SH' or thiol functional group.

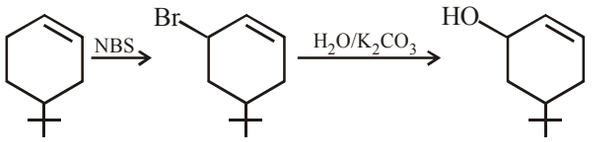
$\Rightarrow$ General formula of amino acid $\rightarrow$ R–CH–COOH
|
NH_2

$\Rightarrow$ Value of R = $-CH_2-SH$ in Cysteine.

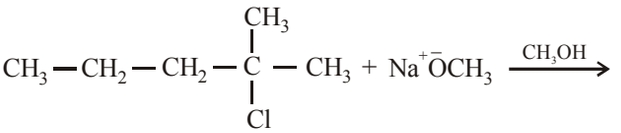
5. (d) N – bromosuccinimide results into bromination at allylic and benzylic positions



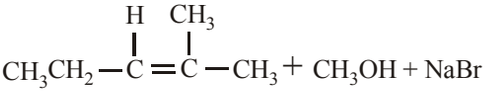
More stable



6. (a) When *tert* -alkyl halides are used in Williamson synthesis elimination occurs rather than substitution resulting into formation of alkene. Here alkoxide ion abstract one of the β-hydrogen atom along with acting as a nucleophile.



2-Chloro-2-methylpentane



2-Methyl-pent-2-ene

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PREFACE

REVISED EDITION

It gives us immense pleasure and satisfaction to bring out the thoroughly revised and updated edition of the book **"Disha's Carbonyl Compounds"** The book has been designed to give a better look & feel and to make the text more lucid. The new pattern of JEE Main & Advanced has been kept in mind throughout.

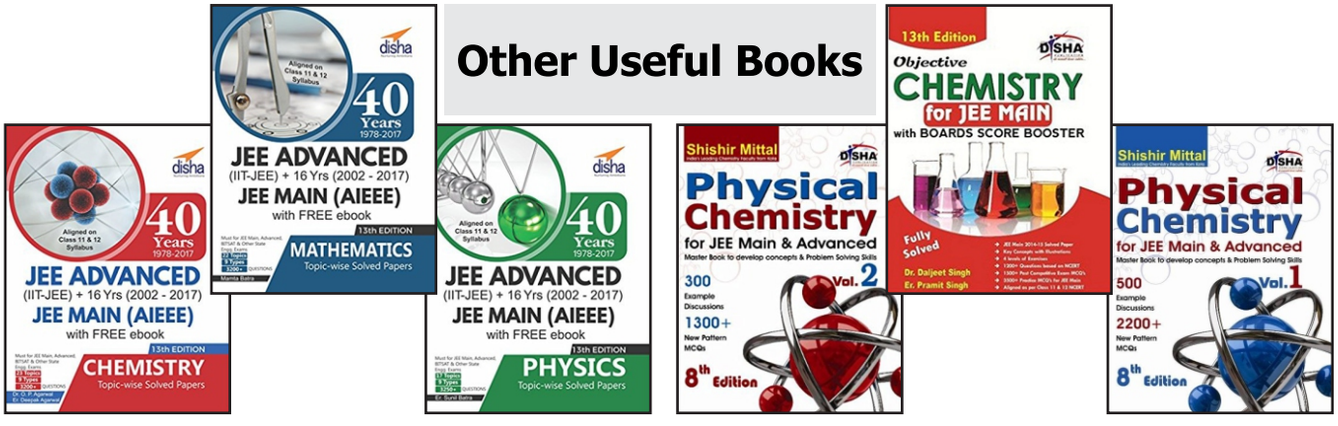
The exercises at the end of each chapter have been designed in the flavour of the new pattern of JEE Main & Advanced. The questions from the previous JEE papers have been incorporated in the different exercises. A separate section having past JEE questions is also provided at the end.

1. **Exercise 1 - MCQ with One correct option :** This exercise contains a collection of question, which has been very carefully selected and it is ensured that there is no repetition. The exercise contains a collection of questions, which has been very carefully selected and it is ensured that there is no repetition. The exercise has been designed so as to cover all the concepts involved in the chapter.
2. **Exercise 2 :** This exercise contains all the four new variety of questions which have been asked in the last 3-4 JEE examinations. These variety of questions are-
   - **(i) MCQ's with one or more than one correct answers :** Around 20-30 well selected problems introduced in each chapter.
   - **(ii) Comprehension based questions :** More than 50 passages which tests the student's comprehension and analytical ability have been added. All these are newly framed problems.
   - **(iii) Matching type question :** Match the following type of question with multiple matching have been introduced in each chapter. These are unique and newly framed problems which will definitely pose a big challenge to the student. I feel that this type of problem is the best way to check a student's concepts.
   - **(iv) Assertion & Reason type questions :** Assertion and Reason type of questions have been incorporated in each and every chapter.
3. **Exercise 3 - Subjective Problems :** This exercise contains a unique collection of subjective problems which will not only give practice to the students but will also help in revising the complete chapter.

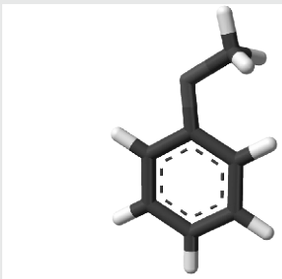
In the end, We would like to request all readers to highlight the printing errors and come forward with suggestions for further improvement of the book.

DR. O.P. AGARWAL

Other Useful Books



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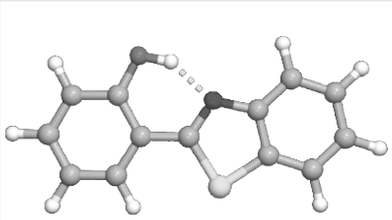


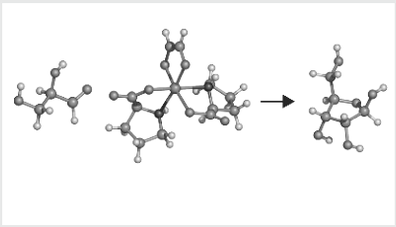
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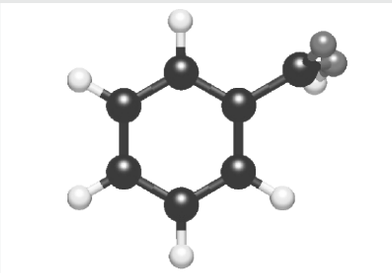


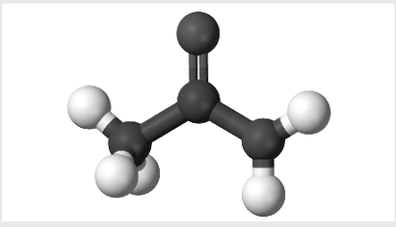
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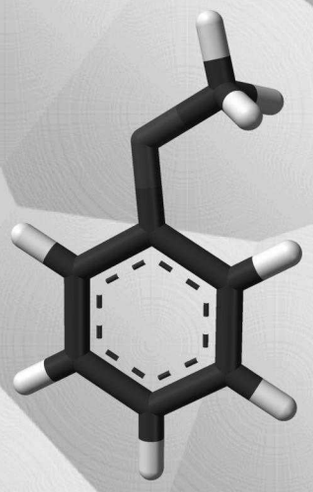




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14

Aldehydes and Ketones

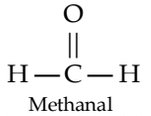
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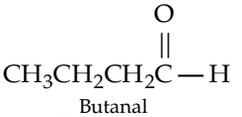
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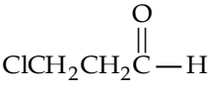
14.1 Nomenclature and Isomerism

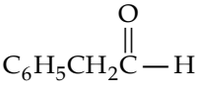
Aldehydes and ketones are the compounds containing a carbonyl group, > C=O. They have the same general formula, $C_nH_{2n}O$. The general structure of aldehydes is R—CHO, except for formaldehyde where R=H ; and that of ketones is RR'CO ; the groups R and R' may be aliphatic, aromatic or alicyclic.

The *common names of aldehydes* are derived from the names of the corresponding carboxylic acids by replacing *-ic acid* by *-aldehyde*. In IUPAC system, aliphatic aldehydes are named as **alkanals**.

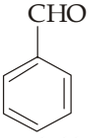

Methanal
(Formaldehyde)

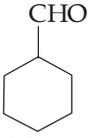

Butanal
(*n*-Butyraldehyde)

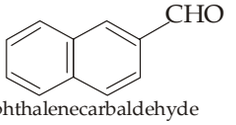

3-Chloropropanal
(β-Chloropropionaldehyde)


Phenylethanal
(Phenylacetaldehyde)

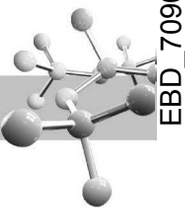
Aldehydes in which the —CHO group is attached to a ring system are named as substitutively by adding the suffix *carbaldehyde*.

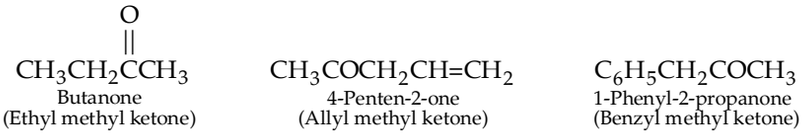

Benzenecarbaldehyde
(Common name : Benzaldehyde)


Cyclohexane-
carbaldehyde

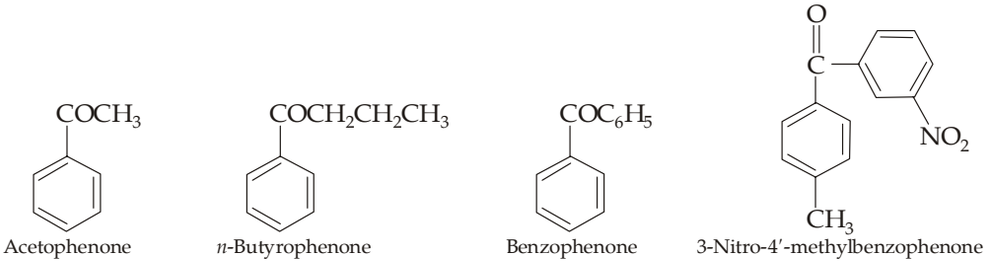

2-Naphthalenecarbaldehyde

Common name for ketones are obtained simply by adding the word ketone to the name of the two alkyl groups. In IUPAC system, these are named as **alkanones**.





A ketone in which the carboxyl group is attached to a benzene ring is named as a - *phenone*.

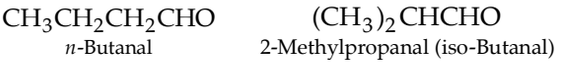


When it is necessary to name the —CHO and —COR groups as prefix, these are named as **methanoyl (or formyl) and alkanoyl (or acyl) groups** respectively.

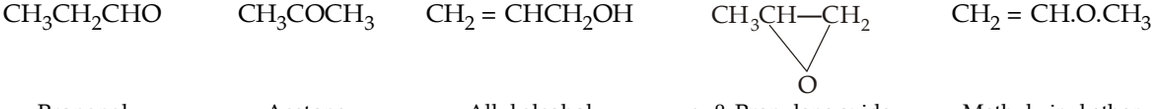


Aldehydes show **chain** and **functional isomerism.**

Chain isomers.



Functional isomers.



Ketones show **chain, functional and metamerism.** *Examples of functional isomerism is given above in aldehydes.*

Chain isomers.

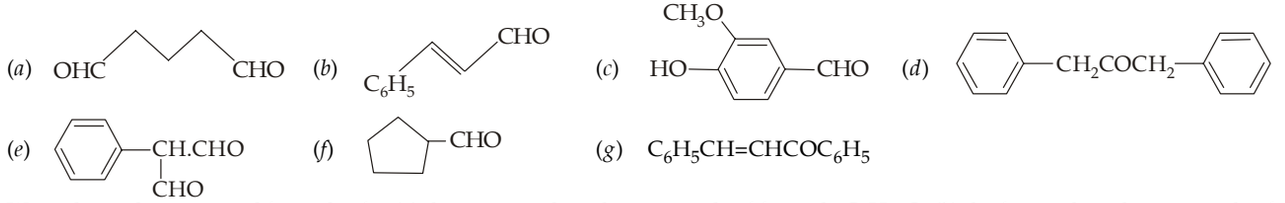


Metamers.



TEST YOUR UNDERSTANDING - 14.1

1. Give IUPAC names of the following compounds :

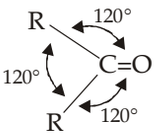


2. Write down the structural formulas for (*a*) the seven carbonyl compounds of formula $C_5H_{10}O$, (*b*) the five carbonyl compounds of formula C_8H_8O having a benzene ring.

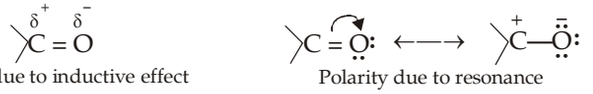
14.2 Structure of the Carbonyl Group (*Cf. carbon-carbon double bond*)

Like the carbon-carbon double bond of alkenes, the carbon-oxygen double bond of the carbonyl group is composed of one σ and one π bond.

In the carbonyl group, carbon atom is in a state of sp^2 hybridisation. The C—O σ bond is produced by overlap of an sp^2 orbital of carbon with a *p* orbital of oxygen. On the other hand, the C—O π bond is formed by the sideways overlap of *p* orbitals of carbon and oxygen. The remaining two sp^3 orbitals of carbon form σ bonds with the *s* orbital of hydrogen or sp^2 orbital of carbon of the alkyl group. Now since the three σ bonds of the carbonyl carbon utilize sp^2 orbitals, they lie in one plane and are 120° apart (*similarity with* C = C).



However, it is important to note that the carbon-oxygen double bond is different from carbon-carbon double bond. Due to greater electronegativity of oxygen atom, the π electron cloud is attracted towards oxygen. Consequently, oxygen attains a partial negative charge and carbon a partial positive charge. This polar nature of the carbonyl group causes intermolecular attraction in aldehydes or ketones and hence accounts for their higher boiling points than that of hydrocarbons and ethers of comparable molecular weight. Moreover, polar nature of the carbonyl group also explains the dipole moment in aldehyde and ketones. However, the high values of dipole moments (2.3 – 2.8 D) of aldehydes and ketones can't be accounted for only by inductive effect ; this can be accounted for if carbonyl group is a resonance hybrid of the two structures.

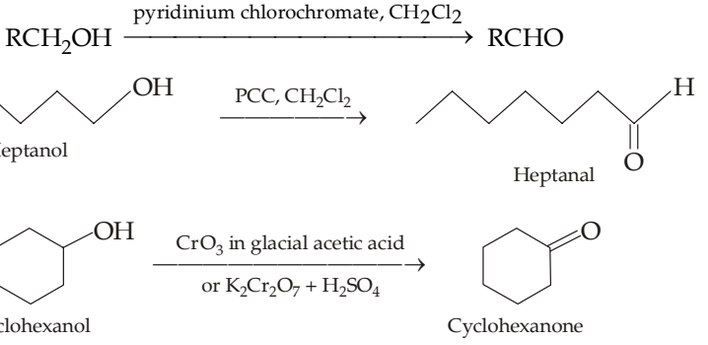


Polarity due to inductive effect Polarity due to resonance

Other important difference in carbon-oxygen and carbon-carbon double bonds lies in the fact that the carbonyl group undergoes nucleophilic addition reactions, while olefinic bond undergoes electrophilic addition reactions.

14.3 Preparation of Aldehydes and Ketones

1. By oxidation of primary and secondary alcohols. Discussed in the chapter on "Monohydric Alcohols".

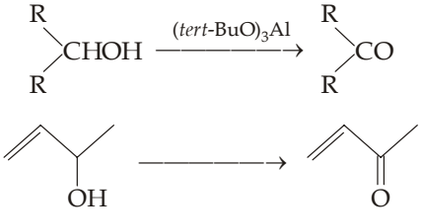


Since ketones are oxidised with difficulty, so these can be easily prepared by oxidizing 2° alcohols with acidic dichromate (difference from aldehyde preparation).

Recall that solution of chromic anhydride in pyridine is known as **Sarett's reagent**, while solution of chromic anhydride in water, acetone and sulphuric acid is known as **Jone's reagent**.

Primary and secondary alcohols may also be oxidised to aldehyde and ketones respectivley by heating with copper at about 250–300°C (dehydrogenation of alcohol).

Ketones can also be prepared by oxidizing 2° alcohols with aluminium *tert*-butoxide (**Oppenauer oxidation).**



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TEST YOUR UNDERSTANDING - 14.2

1. Can an aldehyde be prepared by oxidation of a 1° alcohol with acid dichromate ? If, yes mention the condition.

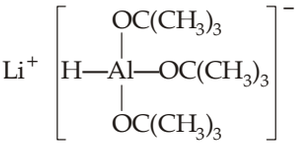
2. **By reduction of acid chlorides, esters, and nitriles (only for aldehydes).** Theoretically, we may think that aldehydes can be prepared by reducing carboxylic acids with lithiumaluminium hydride ($LiAlH_4$ or LAH). However, LAH is a very powerful reducing agent and hence aldehydes formed as intermediate are very readily further reduced to primary alcohols.

$$RCOOH \xrightarrow{LiAlH_4} [RCHO] \xrightarrow{LiAlH_4} RCH_2OH$$

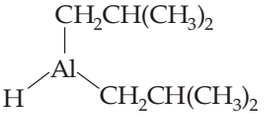
However, a modified version of the reaction is used for preparing aldehydes. For this,

(*i*) a derivative of a carboxylic acid, which is more easily reduced than the carboxylic acid itself is taken as a starting material. Three such acid derivatives are acid chlorides, esters and nitriles ; which in turn are easily prepared from carboxylic acids.

(*ii*) a less reactive aluminium hydride derivative than $LiAlH_4$ is used. Two such derivatives are lithium tri-*tert*-butoxyaluminium hydride (**LBAH**) and diisobutylaluminium hydride (**DBAH**).

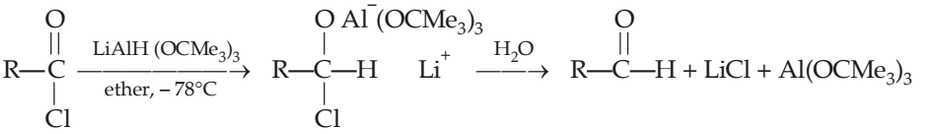


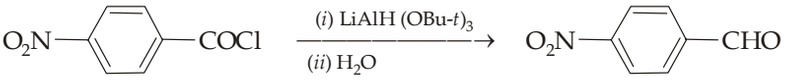
Lithium tri-*tert*-butoxyaluminium hydride



Diisobutylaluminium hydride

These two hydrides are less reactive than $LiAlH_4$ as they are much more sterically hindered and, therefore, face difficulty in transferring hydride ions. Reduction by these reagents is brought about by the transfer of a hydride ion from the aluminium atom to the carbonyl carbon (in case of acid chlorides and esters) or the nitrile carbon (in case of nitriles). Subsequent hydrolysis of the intermediate liberates the aldehyde.

(*a*)




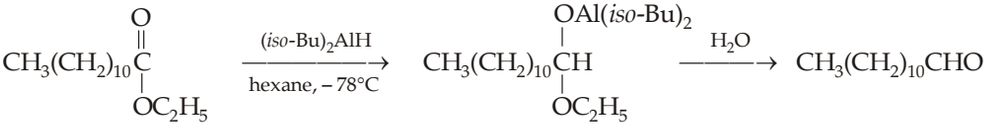
Acid chlorides may also be reduced to aldehydes by catalytic hydrogenation (H_2/Pd)

$$RCOCl + H_2 \xrightarrow{Pd/BaSO_4} RCHO + HCl$$

over deactivated (by sulphur or quinoline) palladized barium sulphate or carbonate. (**Rosenmund reduction**).

$$RCOCl + H_2 \xrightarrow[S \text{ or quinoline}]{Pd/BaSO_4} RCHO$$

Partial deactivation of the catalyst is necessary to check further reduction of the product aldehyde.

(*b*)


(*c*)


Ketones can't be prepared by this method.

3. By hydration of alkynes (Discussed in alkynes).

$$HC \equiv CH \xrightarrow{H_2SO_4, Hg^{2+}} CH_2 = CHOH \rightleftharpoons CH_3CHO$$

$$CH_3CH_2C \equiv CH \xrightarrow{H_2SO_4, Hg^{2+}} CH_3CH_2COCH_3$$

4. Hydroboration of alkynes (Discussed in alkynes). Hydroboration of terminal alkynes followed by oxidation of the intermediate (vinylboranes) with alkaline hydrogen peroxide gives aldehydes.

$$\underset{\text{Propyne}}{CH_3C \equiv CH} \xrightarrow{BH_3.THF} \underset{\text{Vinylborane}}{[CH_3CH = CH]_3B} \xrightarrow{H_2O_2/OH^-} CH_3CH = CHOH \rightleftharpoons \underset{\text{Propanal}}{CH_3CH_2CHO}$$

Similar reaction with non-terminal alkynes gives ketones

$$\underset{\text{Butyne-2}}{CH_3C \equiv CCH_3} \xrightarrow{BH_3.THF} [CH_3CH=\underset{\displaystyle CH_3}{\underset{|}{C}}]_3B \xrightarrow[OH^-]{H_2O_2} CH_3CH = \underset{\displaystyle CH_3}{\underset{|}{C}}OH \longrightarrow \underset{\text{Butanone-2}}{CH_3CH_2COCH_3}$$

To get good yield of vinylboranes and hence aldehydes, sterically hindered alkylboranes should be used instead of borane itself.

$$CH_3C \equiv CH \xrightarrow{R_2BH.THF} (CH_3CH = CH)BR_2 \xrightarrow{H_2O_2/OH^-} CH_3CH = CHOH \rightleftharpoons CH_3CH_2CHO$$

TEST YOUR UNDERSTANDING - 14.3

1. Write structures for A and B in the following reactions :

$$B \xleftarrow[0°C]{LBAH} CH_3CH(CH_3)COCl \xrightarrow{LAH} A$$

2. Prepare $CH_3CH_2CH_2CHO$ from (*a*) an ester, (*b*) a nitrile, and (*c*) an acid chloride.

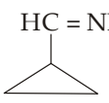
3. Give an outline of the scheme for preparing 3-phenylpropanal from benzene and oxirane.

4. Use hydroboration method for preparing following aldehydes or ketones.

(*a*) Pentanal (*b*) Cyclohexanone (*c*) *n*-Butyl cyclopentyl ketone (*d*) Dicyclohexyl ketone.

5. From organometallic compounds.

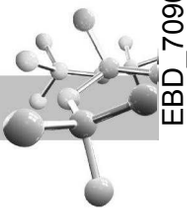
(*a*) Aldehydes are obtained by the reaction of (*i*) Grignard reagent with hydrogen cyanide, or (*ii*) Grignard reagent with alkyl formate in equimolar amounts. For details, consult chapter on Grignard reagents.

(*i*) $HC \equiv N +$  $\xrightarrow{\text{ether}}$  $\xrightarrow{H_2O}$  $+ MgBrNH_2$

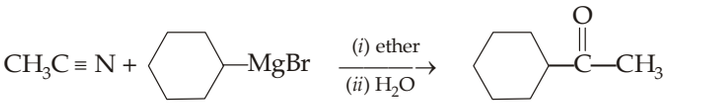
(*ii*) $H-\underset{\displaystyle O}{\underset{\|}{C}}-OC_2H_5 + CH_3MgBr \longrightarrow H-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle O^-}{\overset{|}{C}}}}-OC_2H_5 \xrightarrow{H_3O^+} CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-H + C_2H_5O^-$

(*b*) **Ketones from Grignard reagents** (Details discussed earlier).

(*i*) $\underset{\text{A nitrile}}{R-C \equiv N} + R'MgX \xrightarrow{\text{ether}} R-\underset{\displaystyle R'}{\underset{|}{C}} = NMgX \xrightarrow{H_2O} R-\underset{\displaystyle R'}{\underset{|}{C}} = O$



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Cyclohexyl methyl ketone

(*ii*) $RCOCl + CH_3MgBr \xrightarrow[(ii)\ H_3O^+]{(i)\ \text{ether}} RCOCH_3 + MgBrCl$

An acid chloride

(*iii*) $(RCO)_2O + CH_3MgBr \xrightarrow{-70°C} RCOCH_3 + RCOOMgBr$

An acid anhydride

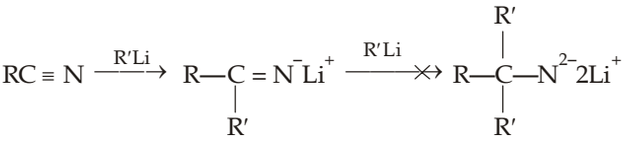
(*iv*) $CH_3COOC_2H_5 + C_2H_5MgBr \xrightarrow[(ii)\ H_3O^+]{(i)\ \text{ether}} CH_3COC_2H_5$

Ethyl ethanoate

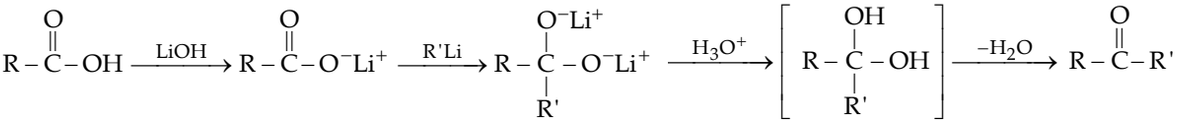
(*c*) **Ketones from organolithium compounds**

$$CH_3C \equiv N + CH_3CH_2CH_2Li \xrightarrow[(ii)\ H_3O^+]{(i)\ \text{ether}} CH_3COCH_2CH_2CH_3$$

Even though a nitrile has a triple bond, addition of the Grignard or lithium reagent takes place only once because addition of second molecule of the reagent would place a double negative charge on the nitrogen.



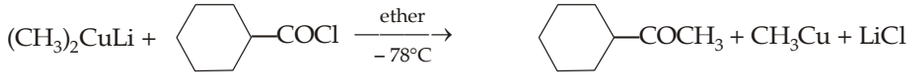
Alternatively, organolithium reagents react with carboxylic acids in the following way to form ketones.



Or $RCOOH + 2R'Li \longrightarrow R-\underset{\displaystyle R'}{\overset{\displaystyle O^-Li^+}{\overset{|}{\underset{|}{C}}}}-O^-Li^+ \xrightarrow{H_3O^+} \left[R-\underset{\displaystyle R'}{\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}-OH\right] \xrightarrow{-H_2O} R-\overset{\displaystyle O}{\overset{\|}{C}}-R'$

(*d*) **Ketones from lithium dialkylcuprates**, also known as **Gilman reagent** (*Organocopper compounds*).

$$\underset{\text{Lithium dialkylcuprate}}{R_2CuLi} + R'COCl \xrightarrow[-78°C]{\text{ether}} R'COR + RCu + LiCl$$



Cyclohexyl methyl ketone

$$n\text{-}C_4H_9Br \xrightarrow{Li} n\text{-}C_4H_9Li \xrightarrow{CuI} \underset{\text{Lithium di-}n\text{-butylcuprate}}{(n\text{-}C_4H_9)_2CuLi} \xrightarrow{2(CH_3)_2CHCOCl} \underset{\text{2–Methyl-3-heptanone}}{2\ n\text{-}C_4H_9COCH(CH_3)_2}$$

Organocopper reagents (lithium dialkylcuprate) are less reactive than Grignard reagents and organolithium compounds toward the carbonyl group of ketones, hence the reaction stops at the ketonic stage whereas in other reagents, *tert*-alcohols are usually formed because ketones are more reactive than acid chlorides. Although organocopper compounds are more reactive than Grignard reagents toward alkyl halides, however, these do not react with many of the functional groups (*e.g.* —NO_2, —CN, —CO—, —COOR, etc.) with which Grignard reagents and organolithiums do react. In short, organocopper compounds are highly selective toward different functional groups.

$CH_3OOC.CH_2CH_2COCl + [(CH_3)_2CHCH_2CH_2]_2CuLi \rightarrow CH_3OOC.CH_2CH_2COCH_2CH_2CH(CH_3)_2$

Lithium diisopentylcuprate — Methyl-4-oxo-7-methyloctanoate

(*e*) **Ketones from organocadmium compounds**

$$RCOCl + R'—Cd—R' \longrightarrow RCOR' + R'CdCl$$

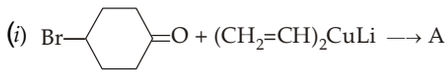
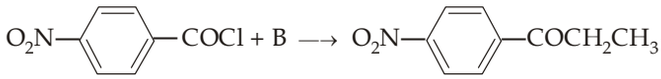
Dialkyl cadmium

Like organocopper compounds, organocadmium compounds are also less reactive than Grignard reagents and organolithiums.

TEST YOUR UNDERSTANDING - 14.4

1. Account for the difference in behaviour of RMgX and R_2CuLi.

2. (*a*) Identify the compounds A and B.

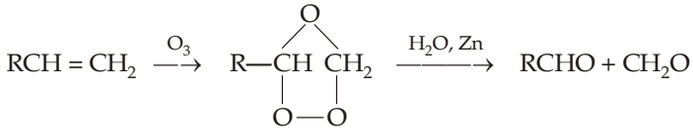
(*i*)  (*ii*) 

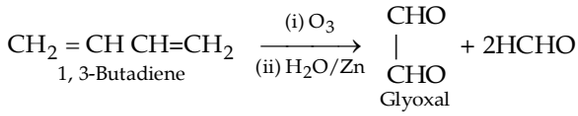
(*b*) Would it be feasible to prepare *p*-nitroacetophenone in the following way ?



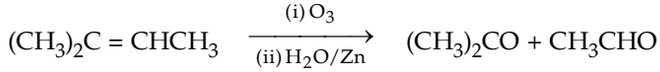
Lithium di (-*p*-nitrophenyl) cuprate — *p*-Nitroacetophenone

6. **Ozonolysis of alkenes.** Alkenes and ozone react readily at low temperatures to yield ozonides which on decomposition with a reducing agent yield aldehydes or ketone depending upon the structure of the alkene.



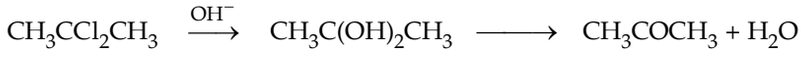


1, 3-Butadiene — Glyoxal

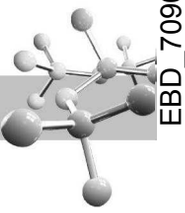


7. **By the hydrolysis of *gem*-dihalides.**





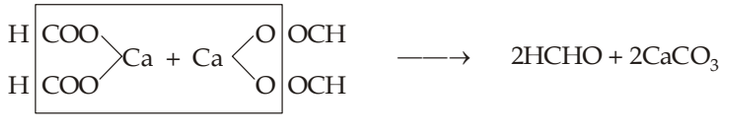
8. **By the reduction of nitriles.** This method is used only for aldehydes.



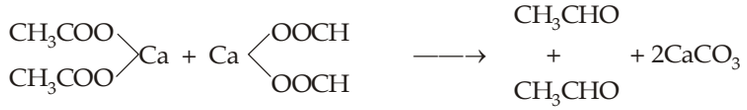
(*a*) $CH_3C \equiv N \xrightarrow[HCl]{SnCl_2} CH_3CH = NH \xrightarrow{H_2O} CH_3CHO$ (**Stephen reduction**)

(*b*) $CH_3C \equiv N \xrightarrow[(ii)\ H_3O^+]{(i)\ (iso\text{-}Bu)_2AlH_2,\ -40°C} CH_3CHO$

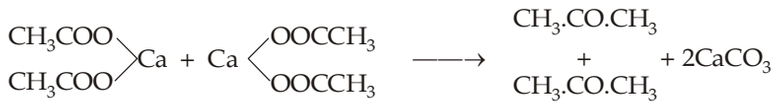
9. By dry distillation of calcium salts of fatty acids. Calcium formate, on pyrolysis, gives formaldehyde ; calcium formate mixed with calcium salt of any other fatty acid gives aldehydes; calcium salts of fatty acids other than calcium formate yield ketones.



Calcium formate (2 moles) Formaldehyde (2 moles)

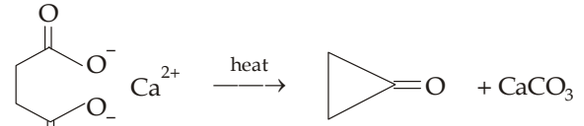


Cal. acetate Cal. formate Acetaldehyde

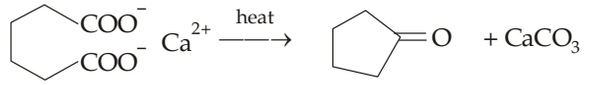


Calcium acetate (2 moles) Acetone (2 moles)

When calcium salts of dicarboxylic acids are heated, cyclic ketones are formed.



Calcium succinate Cyclopropanone



Calcium adipate Cyclopentanone

Instead of using calcium salts of an acid, vapours of acid or mixture of acids can be passed over heated MnO at 300°C.

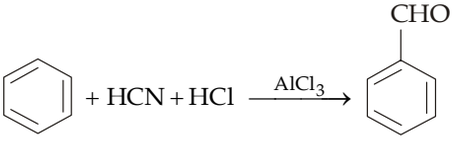
$$CH_3COOH + HCOOH \xrightarrow[300°C]{MnO} CH_3CHO + CO_2 + H_2O$$

$$2CH_3COOH \longrightarrow CH_3COCH_3 + CO_2 + H_2O$$

$$CH_3COOH + CH_3CH_2COOH \longrightarrow CH_3COCH_2CH_3 + CO_2 + H_2O$$

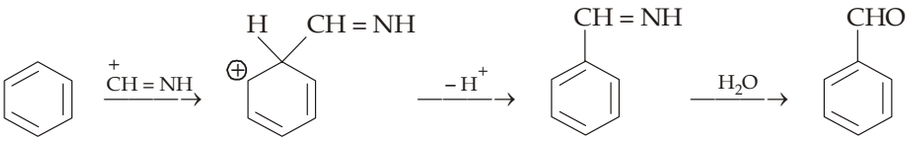
PREPARATION OF AROMATIC ALDEHYDES

1. Gattermann aldehyde synthesis.

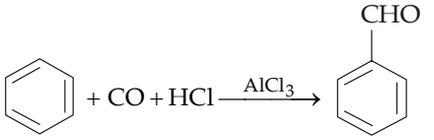


Mechanism

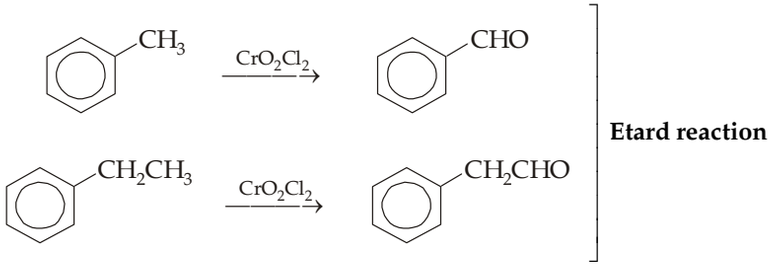
$$H-C\equiv N+HCl \longrightarrow ClCH\equiv NH \xrightarrow{AlCl_3} \underset{\text{Electrophile}}{\overset{+}{C}H=NH} + AlCl_4^-$$



2. Gattermann Koch aldehyde synthesis.



3. Oxidation of toluene.



Industrial methods.

(*a*) Formaldehyde, a starting material for a number of plastics, is prepared by oxidation of methanol over a silver or iron oxide-molybdenum oxide catalyst at elevated temperature.

$$CH_3OH + \frac{1}{2}O_2 \xrightarrow[500°C]{\text{Catalyst}} HCHO + H_2O$$

(*b*) Acetaldehyde can be prepared by (*i*) hydration of acetylene, or (*ii*) more economically by aerial oxidation of ethylene in presence of palladium chloride and copper (II) chloride as catalysts (**Wacker process**).

$$CH_2=CH_2 + \frac{1}{2}O_2 \xrightarrow[H_2O]{PdCl_2, CuCl_2} CH_3CHO$$

Similarly, $$CH_3CH=CH_2 \xrightarrow[H_2O]{PdCl_2, CuCl_2} CH_3CH_2CHO$$

$$CH_3CH=CHCH_3 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_3$$

(*c*) Aldehydes can also be prepared by **hydroformylation**, a reaction in which alkenes are converted to aldehydes containing an additional carbon atom by reaction with carbon monoxide and hydrogen in presence of a suitable cobalt– or rhodium-based catalyst.

$$RCH=CH_2 + CO + H_2 \xrightarrow{Co_2(CO)_8} \underset{\text{(Major)}}{RCH_2CH_2CHO} + R-\underset{\underset{\text{(Major)}}{CH_3}}{\underset{|}{CH}}.CHO$$



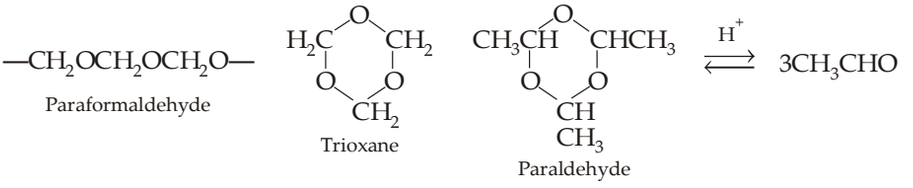
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14.4 Physical Properties

(*i*) The carbonyl group is a polar group, therefore, the dipole-dipole attractive forces between molecules are stronger and hence aldehydes and ketones have higher boiling points than hydrocarbons (non-polar) of comparable molecular weight. However, aldehydes and ketones cannot have strong hydrogen bonds between their molecules, hence they have lower boiling points than the corresponding alcohols.

(*ii*) The carbonyl oxygen atom of aldehydes and ketones form hydrogen bonds to water molecules, hence lower aldehydes and ketones show appreciable solubility in water.

(*iii*) Formaldehyde is a gas (b.p. – 21°C), and is handled either as an aqueous solution (**formalin**), or as one of its solid polymers : **paraformaldehyde**, $(CH_2O)_n$, or **trioxane**, $(CH_2O)_3$. When dry formaldehyde is desired (as in reaction with a Grignard reagent), it is obtained by heating paraformaldehyde or trioxane. Similarly, acetaldehyde is usually generated by heating its higher-boiling trimer with acid.



TEST YOUR UNDERSTANDING - 14.5

1. Identify A to C in the following reactions :

(*a*) [B] $\xleftarrow{CO,\ H_2}$ $CH_3CH = CH_2$ $\xrightarrow[CuCl_2,\ H_2O]{O_2,\ PdCl_2}$ A (*b*) $(CH_3)_2C = C(CH_3)_2$ $\xrightarrow{CO,\ H_2}$ C

2. Which of the components of each of the following pair has higher boiling point ?

(*a*) Hexane or hexanal (*b*) Hexanal or 1-hexanol (*c*) 2-Pentanol or 2-pentanone

(*d*) Benzaldehyde or benzyl alcohol (*e*) 2-Phenylethanol or acetophenone.

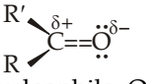
3. *n*-Butanol boils at 118°C and *n*-butanal boils at 76°C, although their molecular weights are nearly similar. Explain.

14.5 Chemical Properties

The carbonyl group, C = O governs the chemistry of aldehydes and ketones in two ways : (*a*) by providing a site for nucleophilic addition, and (*b*) by increasing the acidity of the hydrogen atoms attached to the alpha carbon. Both of these effects is due to the ability of oxygen to accommodate a negative charge.

(A) Carbonyl group as a site for nucleophilic addition

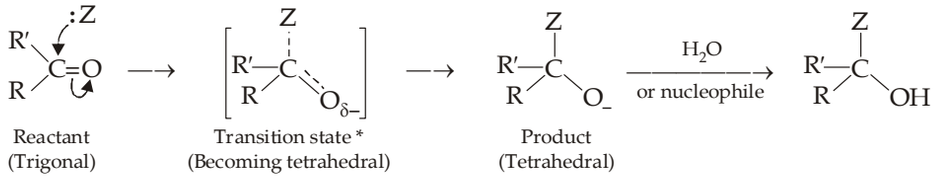
The mobile π electrons of the carbon-oxygen double bond are pulled strongly towards oxygen, which makes carbonyl oxygen electron-rich and carbonyl carbon electron-deficient. Further, since carbonyl group is flat, it is relatively open to attack from above or below.



The positive charge on the carbonyl carbon atom means that it is especially susceptible to attack by a nucleophile. On the other hand, the negative charge on the carbonyl oxygen atom means that nucleophilic addition is susceptible to acid catalysis.

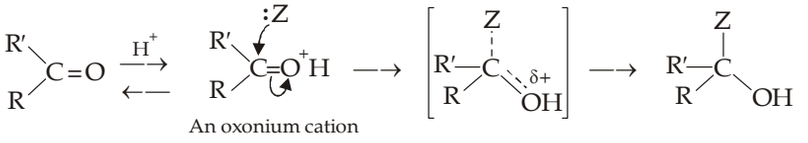
Thus nucleophilic addition to the carbon-oxygen double bond occurs in either of two general ways.

1. When the reagent is a *strong nucleophile*, addition usually takes place in the following way, in which trigonal planar aldehyde or ketone is converted into a tetrahedral product.



Note that as the nucleophile is forming a bond through its electron pair with the carbonyl carbon atom, the electron pair of the carbon-oxygen π bond shifts out to the carbonyl oxygen (as indicated by full negative charge on oxygen) and thus oxygen gets a negative charge which it can accommodate easily. Thus **the ability of oxygen to carry a negative charge is the real cause of reactivity of carbonyl group toward nucleophiles.** (The polarity of the carbonyl group is not the cause of the reactivity, it is simply another manifestation of the electronegativity of oxygen).

2. When the reaction is acid-catalysed, nucleophilic addition on carbonyl group takes place in the following way.

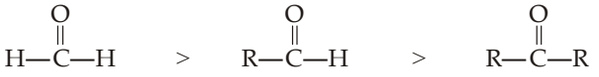


(*i*) The oxonium cation is highly reactive toward nucleophilic attack at the carbonyl carbon atom because the carbonyl carbon atom carries more positive charge than it does in the unprotonated compound.

(*ii*) Prior protonation of the carbonyl group lowers the E_{act} for nucleophilic attack, because it permits oxygen to acquire the π electrons without having a negative charge.

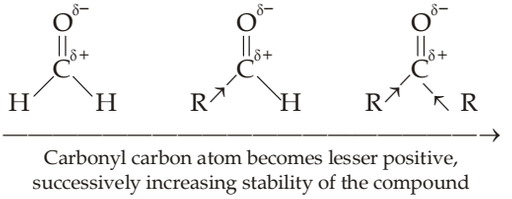
(*iii*) This mechanism operates when carbonyl compounds are treated with *strong acids* (sometimes Lewis acids) in presence *weak nucleophiles*.

Relative reactivity of aldehydes and ketones toward nucleophilic addition. The reactivity of the carbonyl group toward the nucleophilic addition reactions depends upon the magnitude of the positive charge on the carbonyl carbon atom (**electronic factor**) and also on the crowding around the carbonyl carbon atom in the transition state (**steric factor**). Both these factors predict the following order



(*i*) Formaldehyde has no alkyl group, whereas other aldehydes and ketones contain one and two alkyl groups respectively. Since an alkyl group is larger than the hydrogen atom, greater the number of alkyl or aryl group more will be crowding in the transition state which has four groups on C (sp^3) and lesser will be its stability.

(*ii*) Aldehydes have only one electron-releasing group to partially neutralize, and thereby stabilize, the positive charge at their carbonyl carbon atom. Ketones have two electron-releasing groups and are thus stabilized more. Greater stabilization of the ketone (the reactant) relative to the product means lesser reactivity.



In short, any substituent in the carbonyl compound that decreases the positive charge on the carbonyl carbon will increase the stability (or decrease the reactivity) of the molecule toward nucleophilic addition and *vice versa*. Thus, the decreasing order of reactivity of certain carbonyl compounds is

(*a*) $NO_2CH_2CHO > ClCH_2CHO > CH_3CHO > CH_3CH_2CHO$

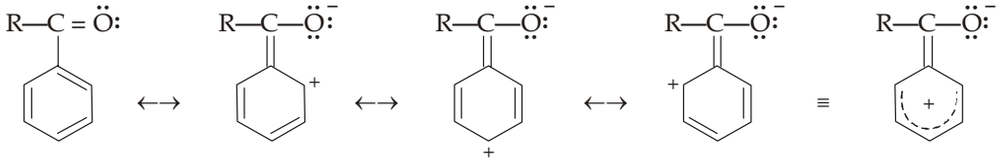
(*b*) $CH_3COCH_3 > CH_3-\overset{O}{\overset{\|}{C}}-C_2H_5 > CH_3-\overset{O}{\overset{\|}{C}}-CH(CH_3)_2 > CH_3-\overset{O}{\overset{\|}{C}}-C(CH_3)_3$

* Note that this transition state is relatively roomy as compared to the transition state for an S_N2 reaction in which carbon is pentavalent.

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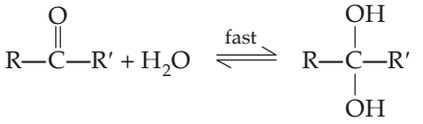
(*iii*) An alkyl group releases electrons, and thus destabilizes the transition state by intensifying the negative charge developing on oxygen.

(*iv*) An aryl group has an electron-withdrawing inductive effect, and thus it is expected to destabilize the reactant or stabilize the transition state and thus should speed up the reaction. However, it seems to stabilize the reactant even more, by resonance and thus causes net deactivation.



Addition of water, alcohols, hydrogen cyanide, sodium bisulphite, ammonia derivatives, hydride ion (in the form of $LiAlH_4$ and $NaBH_4$), organometallic compounds, etc. are examples of nucleophilic addition on carbonyl group.

1. Addition of water (***gem*-diol formation**). Aldehydes and ketones react with water in presence of acid or base in a rapidly reversible equilibrium.



Like the general nucleophilic additions, hydrate formation follows the following order :

	$HCHO$	>	CH_3CHO	>	$(CH_3)_3CCHO$	>	CH_3COCH_3
% of hydrate formed	99.96		50		19		0.14

TEST YOUR UNDERSTANDING - 14.6

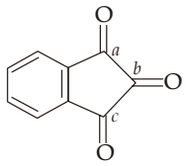
1. Arrange the following compounds in decreasing order of reactivity toward nucleophilic addition.

(*a*) RCHO, CH_2O, R_2CO and RCOY **:** (*b*) R_2CO, Ar_2CO, ArCOR and $ArCH_2COR$.

2. In contrast to negligible hydration of acetone, hexafluoroacetone is completely hydrated. Explain.

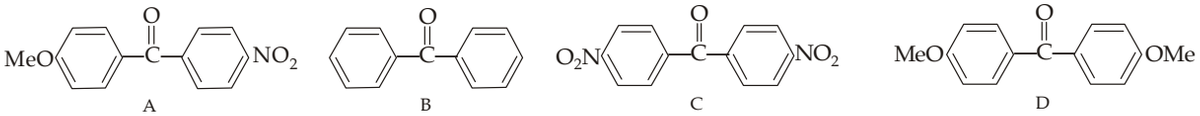
3. Account for the isolation of $CH_3CO^{18}CH_3$ from a solution of $CH_3CO^{16}CH_3$ in excess of H_2O^{18}.

4. Ninhydrin has three ketonic groups, which one of them is likely to be hydrated easily ?



5. Arrange the following in decreasing ease of hydration to form *gem*-diol.

(*a*)

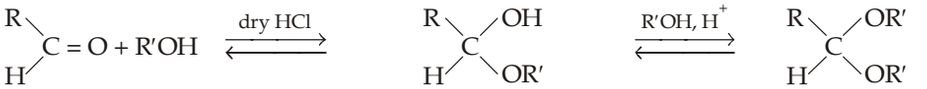


A B C D

(*b*) CH_3CH_2CHO $CH_3CHFCHO$ $CH_3CHClCHO$ CH_2ClCH_2CHO

A B C D

2. Addition of alcohols (*Acetal formation*). Anhydrous alcohols add to the carbonyl group of aldehydes in the presence of anhydrous hydrogen chloride to form **acetals** via **hemiacetals**.



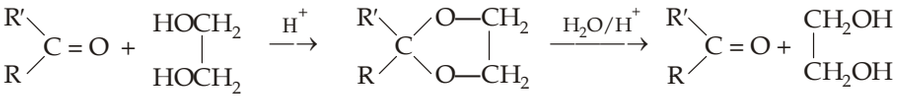
Hemiacetal (an alcohol, as well as an ether)

Acetal (an ether) (stable to alkalies)

(*i*) With a few exceptions, open-chain hemiacetals are too unstable to be isolated. However, cyclic hemiacetals with five- or six-membered rings are usually much more stable.

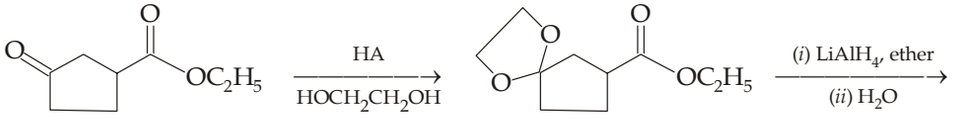
(*ii*) All steps in the formation of an acetal from an aldehyde are reversible.

(*iii*) Acetal formation is not favoured when ketones are treated with simple alcohols and gaseous HCl (remember that the usuage of hemiketals and ketals have been replaced by hemiacetals and acetals respectively). However, cyclic acetal formation is favoured when a ketone is treated with an excess of a 1, 2-diol and a trace of acid.

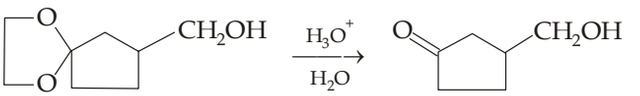


(*iv*) Like ethers, acetals are cleaved by acids and are stable toward bases. However, acetals differ from ethers, in the extreme ease with which they undergo acidic cleavage, actually acetals are rapidly converted into aldehydes and alcohols by dilute mineral acids even at room temperature. Thus acetal formation may be used to protect the aldehydic and ketonic group against undesired reactions in basic solutions.

Thus we can reduce only ester group in the following group by protecting ketonic group.

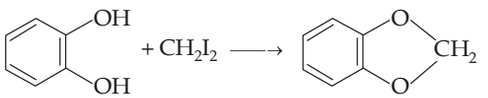


Ketonic group protected



Several other examples have been discussed in ethylene glycol in the chapter on "Polyhydric Alcohols".

TEST YOUR UNDERSTANDING - 14.7

1. 

Answer the following with reference to above reaction.

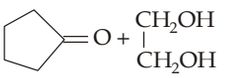
(*a*) The above reaction is an example of which familiar synthesis ?

(*b*) To what family of compounds does the product belong ?

(*c*) Give the reaction of the product with acid, and base.

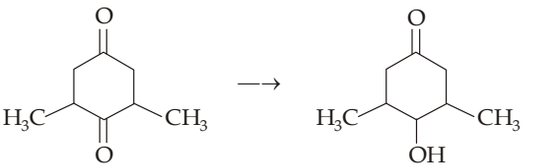
2. Account for the fact that anhydrous acids bring about formation of acetals while aqueous acids bring about hydrolysis of acetals.

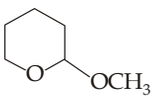
3. Give the structure of the acetal formed in each of the following reactions.

(*a*) 

(*b*) Butanal + 1, 3-propanediol (*c*) $BrCH_2CH_2COCH_3 + CH_2OH.CH_2OH$.

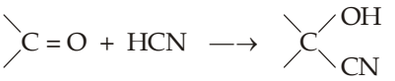
4. Give steps involved in the conversion of each of the following.

(*a*) CH_2=CHCHO ⟶ CH_2(OH)CH(OH)CHO (*b*) 

(*c*) $HOCH_2CH_2CH_2CH_2CHO$ ⟶ 

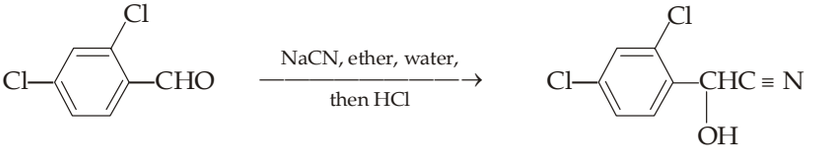
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3. Addition of hydrogen cyanide. Hydrogen cyanide adds to the carbonyl groups of aldehydes and *most ketones* to form **cyanohydrins.** Ketones in which carbonyl group is highly hindered do not undergo this reaction.

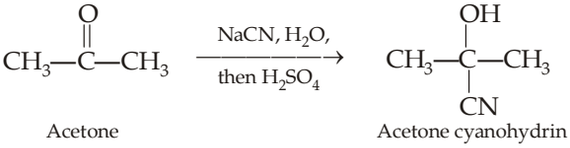


(*i*) Addition of hydrogen cyanide itself takes place very slowly because HCN is a poor source of the nucleophile, CN^-. However, addition of potassium cyanide, or any base that can generate cyanide ions from the weak acid HCN, causes a dramatic increase in the rate of reaction. The cyanide ion, being a stronger nucleophile, is able to attack the carbonyl carbon atom much more rapidly than HCN itself, and this is the source of its catalytic effect. Bases stronger than cyanide ion catalyze reaction by converting HCN (pK_a = 9) to cyanide ion.

(*ii*) Liquid hydrogen cyanide can be used for this reaction (HCN is a gas at room temperature), but since HCN is a very toxic and volatile, it is generally produced in the reaction mixture for which an acid (generally H_2SO_4) is added to a solution of the aldehyde or ketone and aqueous sodium or potassium cyanide.

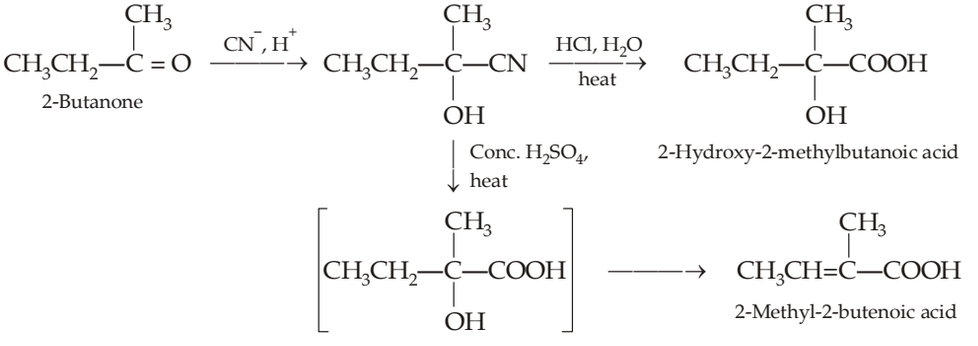


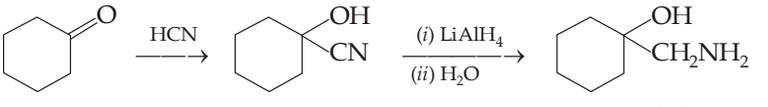
2, 4-Dichlorobenzaldehyde — 2, 4-Dichlorobenzaldehyde cyanohydrin



Acetone — Acetone cyanohydrin

Cyanohydrins are useful intermediates in organic synthesis. A cyano group may be hydrolysed to an α-hydroxy carboxylic acid or to an α, β-unsaturated acid (depending upon the condition used) or may be reduced to a primary amine.

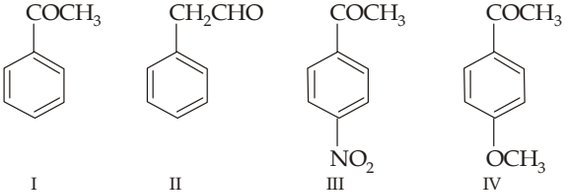




A β-amino alcohol

TEST YOUR UNDERSTANDING - 14.8

1. Arrange the following compounds in decreasing ease of formation of cyanohydrin.



I II III IV

2. Can you draw a scheme for converting acetone to methacrylonitrile, $CH_2=C(CH_3)CN$, an industrial chemical used in the production of plastics and fibres ?

3. Following compounds are converted into their corresponding cyanohydrins. Predict the number of fraction and their optical activity status in each case.

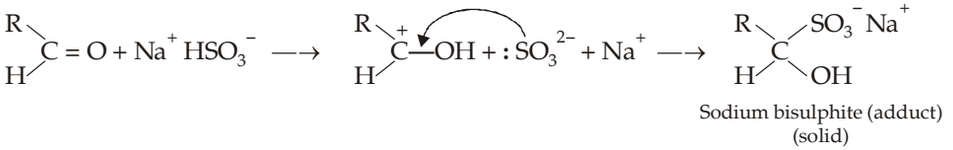
(*a*) CH_3CHO (*b*) $(CH_3)_2CO$ (*c*) R –(+)– $CH_2OHCHOHCHO$ (*d*) (±)– $CH_2OHCHOHCHO$.

4. (*a*) In cyanohydrin formation, an optimum pH of 9—10 is recommended. Explain.

(*b*) Which is the more favourable equilibrium situation for cyanohydrin formation ?

RCHO + NaCN or RCHO + HCN (both in water).

4. Addition of sodium bisulphite. Aldehydes, methyl ketones and cyclic ketones (not aromatic) react with sodium bisulphite in presence of ethanol to give solid adduct.

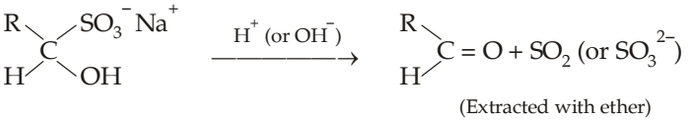


NOTE.

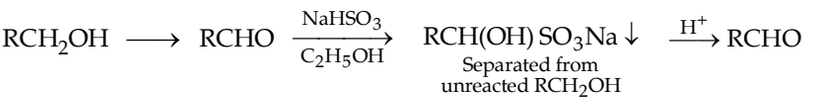
(*i*) A C—S bond is formed rather than C—O because S has more nucleophilic site than O.

(*ii*) Sulphite ion, SO_3^{2-} is a large ion and hence reacts only if C = O is not sterically hindered ; as in the case for RCHO, $RCOCH_3$, and cyclic ketones.

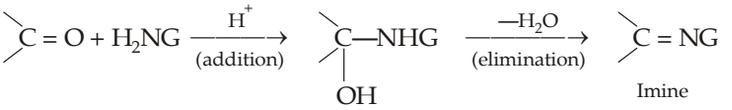
The solid adduct is filtered from the ethanolic solution and then decomposed by acid or base to regenerate the carbonyl compound. Hence *this reaction is used for the purification and separation of carbonyl compounds*.



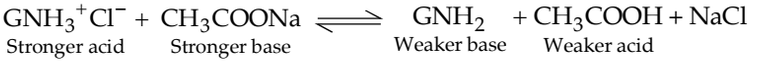
Separation of RCHO from unreacted RCH_2OH.



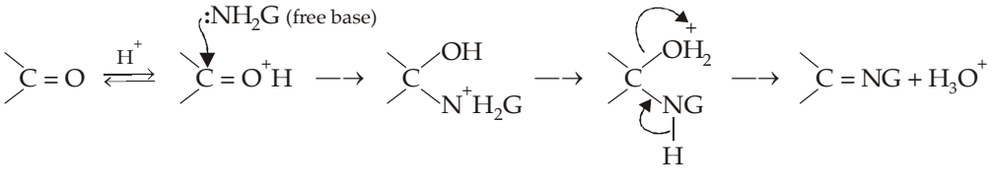
5. Addition of derivatives of ammonia. Certain compounds related to ammonia (such as hydroxylamine, NH_2OH; phenylhydrazine, $H_2NNHC_6H_5$; and semicarbazide $H_2NNHCONH_2$, etc.) react with carbonyl compounds to form compounds, having carbon-nitrogen double bond, known as **imines**. The reaction is acid catalyzed and involves two stages : addition of the ammonia derivative to form *carbinolamine* followed by dehydration to yield imine which is a mixture of *E*- and *Z*-isomers

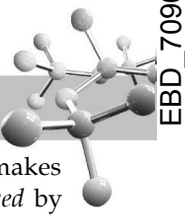


Like ammonia, these derivatives of ammonia are basic and hence form salts with acids, viz. hydroxylamine hydrochloride $N^+H_3OHCl^-$, phenylhydrazine hydrochloride, $C_6H_5NHNH_3^+Cl^-$; and semicarbazide hydrochloride, $NH_2CONHNH_3^+Cl^-$. These salts are less easily oxidized by air than the free bases, and hence these ammonia derivatives are best used in the form of their salts. When used, the parent reagents are liberated from their salts in the presence of the carbonyl compound by adding a base, generally sodium acetate.



Imine formation requires a moderate pH (between 4–5), because very low as well as very high pH retards the reaction. To know why it is so, we must know the steps involved during the reaction

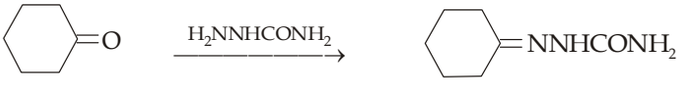




From the above steps, it is obvious that an acid is essential to protonate the carbonyl oxygen which makes carbonyl carbon more susceptible to nucleophilic attack. Hence *protonation of the carbonyl group is favoured* by *high acidity*. However, in presence of strong acid, the ammonia derivative ($H_2\ddot{N}$—G) can also undergo protonation to form the ion, H_3N^+—G lacking the unshared electrons which thus will no longer be nucleophilic. Hence *the addition of reagent* (H_2NG) *will be favoured by low acidity*. Thus optimum acidity is the compromise between the two steps to carry out the reaction successfully, *i.e.* the solution must be acidic enough for an appreciable fraction of the carbonyl compound to be protonated, but not so acidic that the concentration of the free nitrogen compound is too low. The exact conditions used depend upon the basicity of the reagent, and upon the reactivity of the carbonyl compound.

Reaction of aldehydes and ketones with derivatives of ammonia, (H_2NG)

$$>C=O + H_2N—G \longrightarrow >C=NG$$

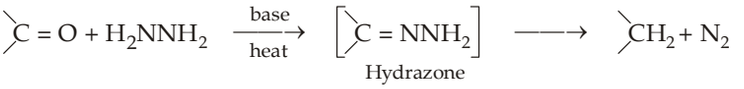
Reagent H_2NG and its name	Name of product with specific example
H_2NR, 1° Amine	$(C_2H_5)(CH_3)C=O \xrightarrow{H_2NC_2H_5} (C_2H_5)(CH_3)C=NC_2H_5$ An **Imine** (A Schiff 's base)
H_2NOH, Hydroxylamine	$(CH_3)(H)C=O \xrightarrow{H_2NOH} (CH_3)(H)C=NOH$ Acetaldoxime **oxime**
H_2NNH_2, Hydrazine	$(CH_3)_2C=O \xrightarrow{H_2NNH_2} (CH_3)_2C=NNH_2$ Acetone **hydrazone**
$H_2NNHC_6H_5$, Phenylhydrazine	$(C_6H_5)(CH_3)C=O \xrightarrow[H_3O^+,\ CH_3COOH]{H_2NNHC_6H_5} (C_6H_5)(CH_3)C=NNHC_6H_5$ Acetophenone **phenylhydrazone**
H_2NHN—(2,4-NO_2)—C_6H_3, 2, 4-Dinitrophenylhydrazine	$(CH_3)(H)C=O \xrightarrow[\text{phenylhydrazine}]{\text{2, 4-Dinitro-}} (CH_3)(H)C=NNH$—(2,4-$NO_2$)—$C_6H_3$ Acetaldehyde **2, 4-dinitrophenylhydrazone**
$H_2NNHCONH_2$, Semicarbazide	 Cyclohexanone s**emicarbazone**

The products of the reaction of aldehydes and ketone with hydroxylamine, phenylhydrazine, 2, 4-dinitrophenylhydrazine and semicarbazide are usually insoluble solids with sharp characteristic melting points. Moreover, oximes and hydrazones when refluxed with dil HCl, they regenerate the parent aldehyde or ketone. Hence, formation of oximes and hydrazones is used for the detection and purification of aldehydes and ketones

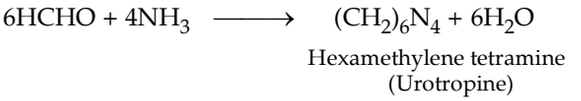
$$>C=O + H_2NOH \longrightarrow >C=NOH \xrightarrow[\text{reflux}]{HCl} >C=O + NH_2OH.HCl$$

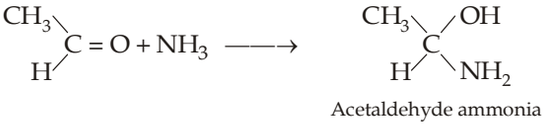
$$>C=O + H_2NNHPh \longrightarrow >C=NNHPh \xrightarrow[\text{reflux}]{HCl} >C=O + H_2NNHPhHCl$$

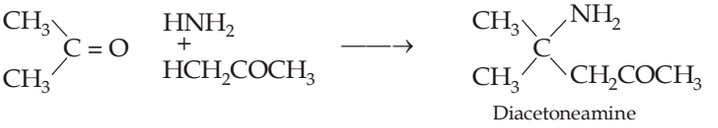
Unlike, 2, 4-dinitrophenylhydrazones, simple hydrazones have low melting points and are hence occasionally used to identify carbonyl compounds. However, they form the basis for a useful method to reduce carbonyl group to methylene group (**Wolf-Kishner reduction**).



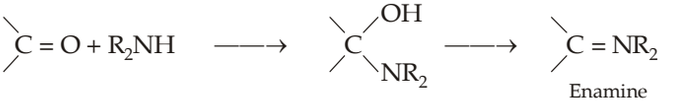
Ammonia reacts with formaldehyde, other aldehydes and ketones in different ways.

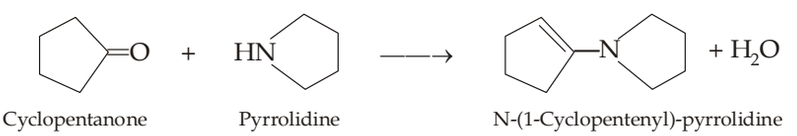




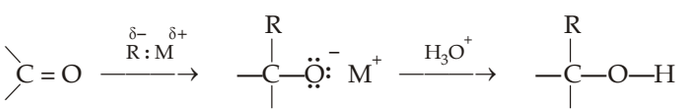


Secondary amines, R_2NH add to aldehydes and ketones to form carbinolamines which are dehydrated easily to form **enamines**





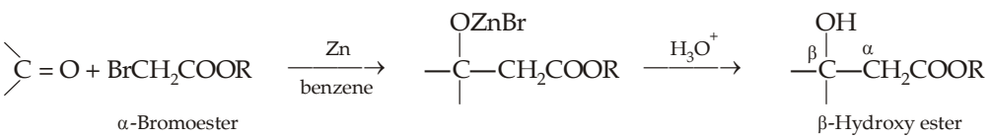
6. **Addition of organometallic compounds.** Organometallic compounds, such as Grignard reagents, alkyllithiums and organozinc compounds provide nucleophile which add on carbonyl group to form alcohols.



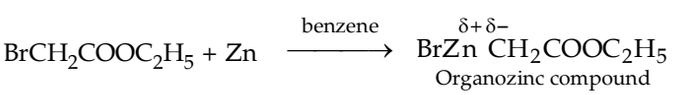
Such reactions with Grignard reagents and alkyllithiums have already been discussed at length, so here we will confine only to addition of organozinc compounds.

In short, it can be summarised that *Grignard reagents (*M = MgX*) or alkyllithium (*M = Li*) react with formaldehyde, other aldehydes and ketones to form 1°, 2° and 3° alcohols respectively.*

Addition of organozinc compounds (The Reformatsky reaction). Reformatsky reaction involves the reaction of an aldehyde or ketone with an α-bromoester in presence of zinc metal to form β-hydroxy ester.



Actually an organozinc compound is first formed as an intermediate which then adds to the carbonyl group in a manner analogous to that of a Grignard reagent.



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Since organozinc reagent is less reactive than a Grignard reagent, it does not add to the ester group.

$$CH_3CH_2CH_2CHO + BrCH_2COOC_2H_5 \xrightarrow[(ii)\ H_3O^+]{(i)\ Zn} \underset{\beta\text{-Hydroxy ester}}{CH_3CH_2CH_2\overset{\overset{OH}{|}}{C}HCH_2COOC_2H_5}$$

The β-hydroxy esters produced in the reaction are easily dehydrated to α, β-unsaturated esters because the resulting product contains a more stable conjugated system.

$$CH_3CH_2CH_2\overset{\overset{OH}{|}}{C}HCH_2COOC_2H_5 \xrightarrow[heat]{H_3O^+} CH_3CH_2CH_2CH = CH-\overset{\overset{O}{||}}{C}-OC_2H_5 + H_2O$$

TEST YOUR UNDERSTANDING - 14.9

1. What are Schiff bases. Give the structure of the product of the following reactions :

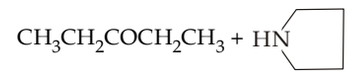
(*a*) Cyclohexanone + *tert*-Butyl amine

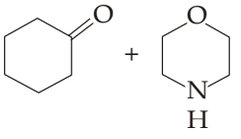
(*b*) $CH_3COCH_3 + H_2NCONHNH_2$

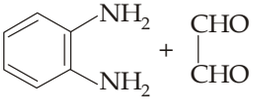
(*c*) 2-Butanone + $[H_3N^+OH]Cl^-$, CH_3COONa

(*d*) Acetophenone + Cyclohexyl amine

(*e*) $CH_3COCH_2C_6H_5$ and 

(*f*) $CH_3CH_2COCH_2CH_3$ + 

(*g*) 

(*h*) 

2. Explain the following :

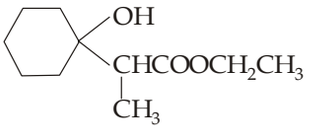
(*i*) Reaction of hydroxylamine with acetone gives a single oxime, while similar reaction with an aldehyde or a methyl ethyl ketone forms two isomeric oximes.

(*ii*) Oximes are more acidic than hydroxylamine.

(*iii*) Although semicarbazide has two NH_2 groups, only one of them reacts with an aldehyde or ketone.

3. (*a*) How would you prepare following compounds using Reformatsky reaction ?

(*i*) $(CH_3)_2\overset{\overset{OH}{|}}{C}CH_2COOCH_2CH_3$

(*ii*) 

(*b*) Why is Mg or Cd not used in place of Zn in the Reformatsky reaction ?

7. **Cannizzaro reaction.** *Aldehydes containing no α-hydrogen atom, when treated with concentrated alkali, (aqueous or alcoholic), undergo self oxidation-reduction* (also known as disproportionation) *to yield a mixture of an alcohol and a salt of a carboxylic acid*. This reaction, known as **Cannizzaro reaction**, is carried out at room temperature ; remember that under these conditions, aldehydes having α-hydrogen atom undergo aldol condensation.

$$\underset{}{2HCHO} \xrightarrow{50\%\ NaOH} \underset{\text{Methanol}}{CH_3OH} + \underset{\text{Sodium formate}}{HCOONa}$$

$$2(CH_3)_3CCHO \xrightarrow{50\%\ NaOH} (CH_3)_3CCH_2OH + (CH_3)_3CCOONa$$

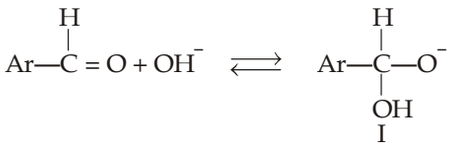
In general, a mixture of two aldehydes (each having no α-hydrogen atom) undergo Cannizzaro reaction to form a mixture of all possible products. However, if one of the aldehydes is formaldehyde, reaction always yields sodium formate as one of the products and the alcohol (second product) corresponding to the other aldehyde. Cannizzaro reaction between different aldehyde molecules is known as **crossed Cannizzaro reaction**.

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Formaldehyde}}{HCHO} \xrightarrow{conc.\ NaOH} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Sod. formate}}{HCOONa}$$

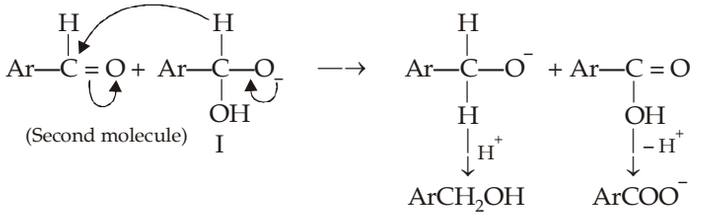
Mechanism.

The reaction involves two successive nucleophilic addition, of course at different carbonyl groups.

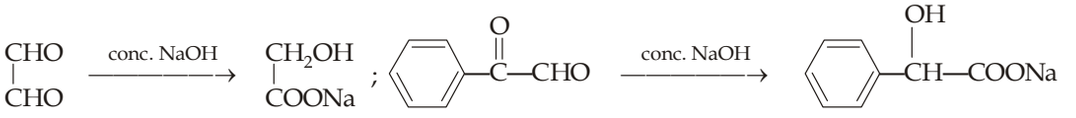
Step 1.



Step 2.

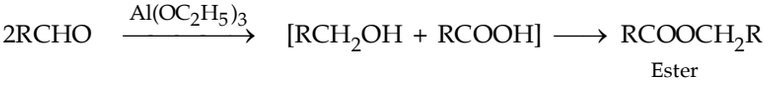


Intramolecular or Internal Cannizzaro reaction



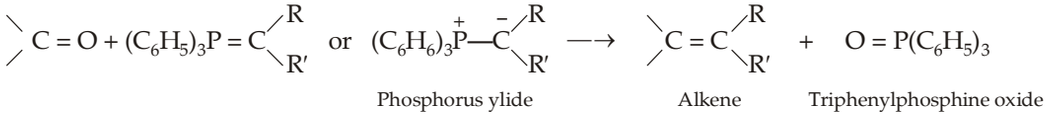
Remember that keto group can only be reduced, not oxidised, in internal Cannizzaro reaction.

Although aldehydes having α-hydrogen atom do not undego Cannizzaro reaction, they along with all their aldehydes can be made to undergo such reactions in presence of aluminium ethoxide. The reaction is now known as **Tischenko reaction** and here esters are isolated instead of alcohol and carboxylic acids.



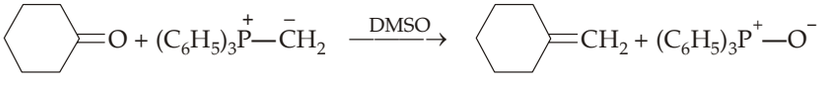
Ester

8. **Addition of ylides (The Wittig reaction).** An ylide is a neutral molecule having a negative carbon adjacent to a positive hetero atom (*e.g.* P or S), each atom has an octet of electrons and directly bonded to each other. Aldehydes and ketones react with phosphorus ylides to yield *alkenes* and triphenylphosphine oxide. The reaction, known as Wittig reaction, has proved to be a valuable method for synthesizing alkenes.



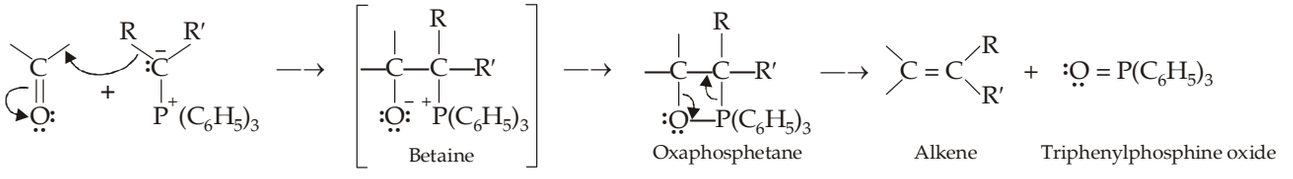
Phosphorus ylide Alkene Triphenylphosphine oxide

Thus the net result of the reaction is the replacement of carbonyl oxygen, = O, by the group = CRR′. The reaction is carried out under mild conditions and in presence of solvents like tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO).



Wittig reaction has a great advantage over most other alkene syntheses in that *no ambiguity exists as to the location of the double bond in the product*.

Mechanism. The ylide acting as a nucleophile attacks the carbonyl carbon of the aldehyde or ketone to form an unstable intermediate *betaine* followed by *oxaphosphetane* which then spontaneously loses triphenylphosphine oxide to form an alkene. The driving force for the Wittig reaction is the formation of the very strong P—O bond ($DH° = 540$ kJ mol^{-1}).

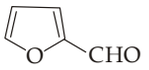


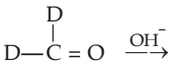
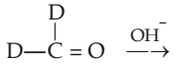
Betaine Oxaphosphetane Alkene Triphenylphosphine oxide

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TEST YOUR UNDERSTANDING - 14.10

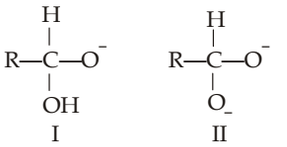
1. Give the structure of the product(s) obtained in each of the following reactions.

(*a*)  $\xrightarrow{\text{conc. NaOH}}$ (*b*) $C_6H_5COCHCl_2 \xrightarrow{\text{conc. NaOH}}$ (*c*) ArCDO $\xrightarrow{\text{conc. NaOH}}$

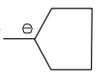
(*d*)  (*e*) 

2. In the crossed Cannizzaro reaction, formaldehyde is always oxidised. Explain.

3. Which of the following intermediate (I or II) is considered as a better hydride donor to an aldehyde ?

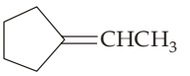


4. Identify the alkene produced in each of the following Wittig reactions :

(*a*) Benzaldehyde +  (*b*) Butanal + $Ph_3P^+\ddot{C}HCH=CH_2$

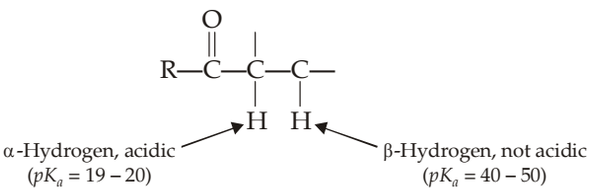
(*c*) Cyclohexyl methyl ketone + $Ph_3P^+=\ddot{C}H_2$

5. Give the structure of an ylide and a carbonyl compound from which each of the following could be prepared.

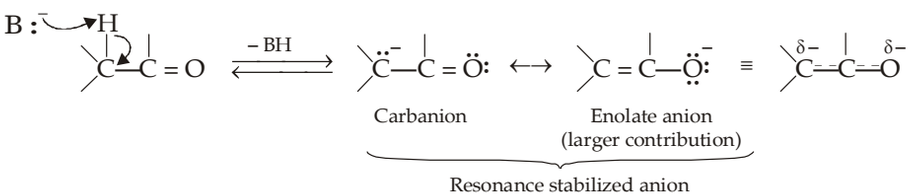
(*a*) $CH_3CH_2CH_2CH=C(CH_3)CH_2CH_3$ (*b*) $C_6H_5CH=CHC_6H_5$ (*c*) 

(B) Acidity of α-hydrogens of carbonyl compounds

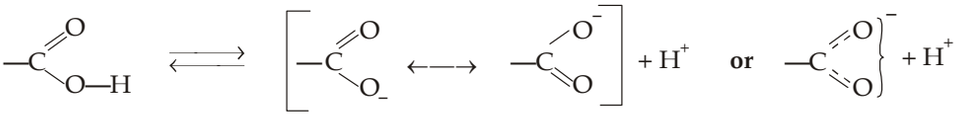
In addition to nucleophilic addition reactions, carbonyl compounds exhibit the unusual acidity of α-hydrogen atoms. Actually, in the first type of properties carbonyl group acts as a functional group, while in the second type carbonyl group acts as a substituent and exerts its effect on the adjacent (alpha) carbon atoms.



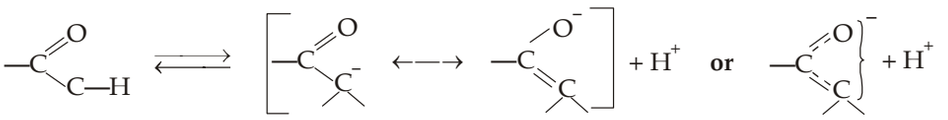
The unusual acidity of the α-hydrogens of carbonyl compounds is due to its strong electron-withdrawing nature which in turn makes α-carbon also electron-withdrawing. Hence in presence of base, it easily loses hydrogen as proton and itself converted into carbanion. Once the anion (carbanion) is formed, it is stabilized by resonance.



Thus the carbonyl group affects the acidity of α-hydrogens in just the same way it affects the acidity of carboxylic acids, *i.e.* by helping to accommodate the negative charge of the anion.



Resonance stabilized carboxylate anion
(Equivalent contributing structures)



Resonance stabilized enolate anion
(Non-equivalent contributing structures)

Although α-hydrogen atoms of an aldehyde or ketone are very weakly acidic than the hydrogen atom of a —COOH group, they are considerably more acidic than hydrogen atoms anywhere else in the molecule and they are acidic enough for producing carbanions in significant concentration. It is interesting to note that the two important properties of a carbonyl group : (*a*) susceptibility to nucleophilic attack, and (*b*) acidity of α-hydrogens, is due to the *ability of oxygen to accommodate the negative charge*.

TEST YOUR UNDERSTANDING - 14.11

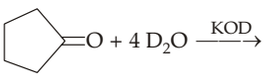
1. Account for the following facts.

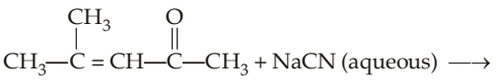
(*a*) (+) $—C_6H_5CH(CH_3)CHO$ undergoes reacemization, when treated with base.

(*b*) The diketone 2, 4-pentanedione is almost as acidic as phenol, and much more acidic than acetone.

(*c*) γ-Hydrogens of α, β-unsaturated carbonyl compounds are acidic.

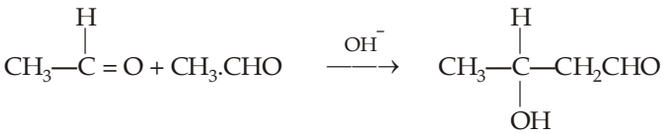
2. Write down the structure of the product in the following reactions.

(*a*) 

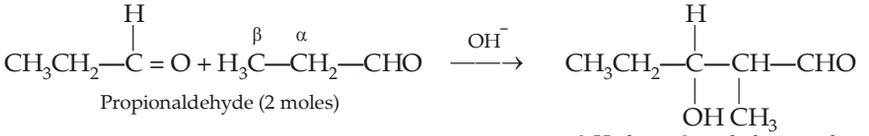
(*b*) 

Reactions of carbonyl compounds due to acidic hydrogen atom, i.e. *due to enols and enolate anions.*

9. **Aldol condensation.** Two molecules of an aldehyde or a ketone, containing at least one α-hydrogen atom, when treated *with dilute base* (like NaOH, $Ba(OH)_2$, K_2CO_3, etc.) at room temperature (or below) combine to form a β-hydroxyaldehydes or β-hydroxyketones. This reaction is called **aldol condensation**. In every case, it is the α-carbon and α-hydrogen atoms of one molecule that add to the carbonyl carbon and oxygen atoms respectively of the second molecule.

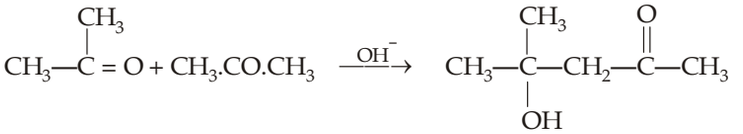
(*i*) 

3-Hydroxybutanal

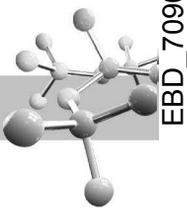
(*ii*) 

Propionaldehyde (2 moles)

3-Hydroxy-2-methylpentanal

(*iii*) 

4-Hydroxy-4-methyl-2-pentanone



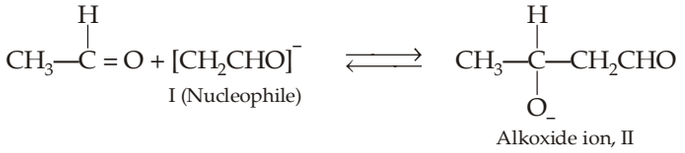
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Mechanism.

Step 1. $CH_3CHO + OH^- \rightleftharpoons [CH_2CHO]^- + H_2O$

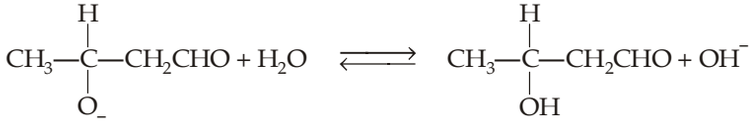
Carbanion, I

Step 2.



I (Nucleophile) Alkoxide ion, II

Step 3.

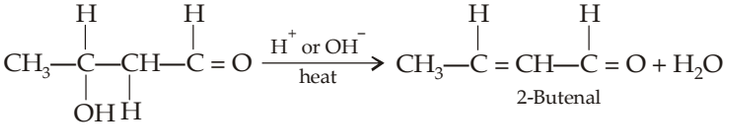


Remember that presence of α-hydrogen in aldehyde or ketone is the essential condition for aldol condensation, since only such carbonyl compounds can form carbanions, the actual nucleophile, which then attacks the carbonyl carbon to form the product. Hence, aldehydes or ketones, not having α-hydrogen atom, do not undergo aldol condensation.

$$ArCHO, HCHO, (CH_3)_3CCHO, ArCOAr, \text{ or } ArCOCR_3 \xrightarrow[OH^-]{\text{dilute}} \text{No reaction}$$

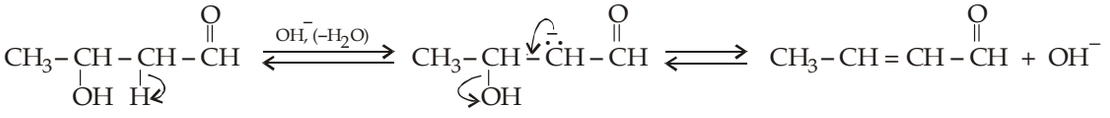
However, in presence of concentrated base, above compounds undergo Cannizzaro reaction.

Dehydration of aldol products. The β-hydroxy aldehydes and β-hydroxy ketones obtained from aldol condensation are very easily dehydrated, on heating, to form α, β-unsaturated carbonyl compound (conjugated system).



Aldol 2-Butenal

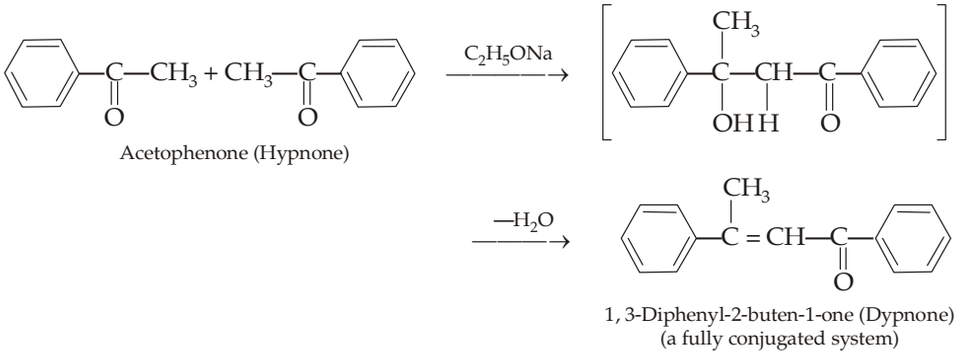
Dehydration under acidic conditions follows a mechanism similar to those of other acid-catalyzed alcohol dehydration. The steps involved in *base-catalyzed dehydration* of aldol are summarised below.



Enolate ion Conjugated system

Note that in the second step, **hydroxide ion which is not a good leaving group in an E2 elimination is removed.** However, here OH^- can serve as a leaving group in a strongly exothermic step leading to a highly stable (conjugated) compound.

In some cases, especially when the double bond produced is conjugated with an aromatic ring, dehydration of the aldol product occurs so readily that we cannot isolate the product in the aldol form.



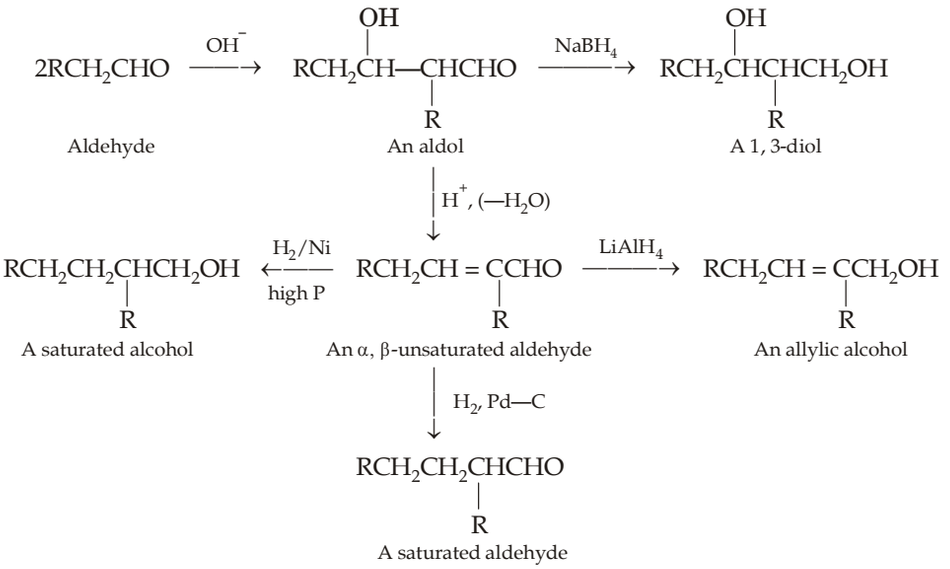
Acetophenone (Hypnone)

1, 3-Diphenyl-2-buten-1-one (Dypnone)
(a fully conjugated system)

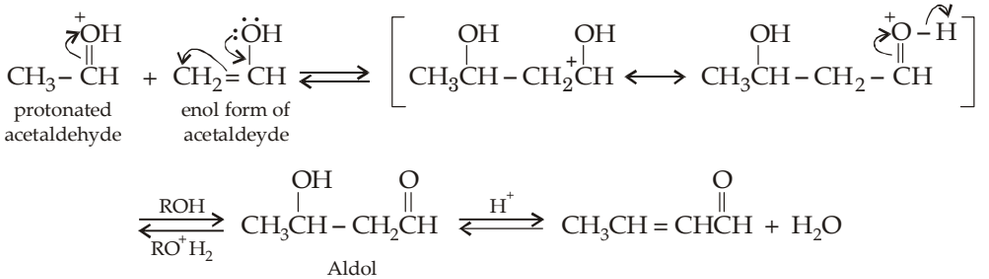
Synthetic applications. (*i*) Aldol reaction is a general reaction given by aldehydes and ketones having an α-hydrogen atom.

(*ii*) Further, aldol reaction gives us a product by introducing a new carbon-carbon bond between two molecules.

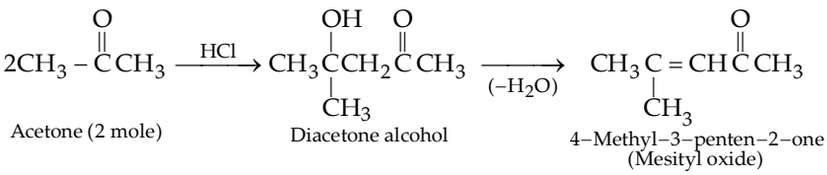
(*iii*) Aldol products contain two functional groups, —OH and —CHO, each of which can be used to carry out a number of subsequent reactions.



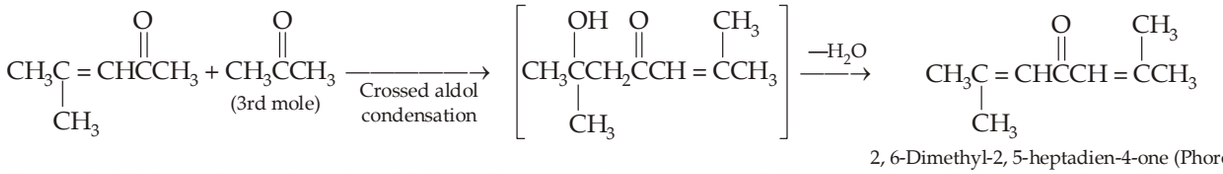
Acid-catalyzed aldol condensations. Aldol condensation can also be brought about with acid catalysts. The enol serves as a weak nucleophile to attack an activated (protonated) carbonyl group. Steps involved in the acid-catalyzed aldol condensation of acetaldehyde are given below.



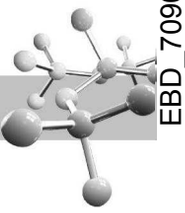
Similarly acetone, when treated with hydrogen chloride gives 4-methyl-3-penten-2-one. Here, the aldol formed undergoes dehydration to form 4-methyl-3-penten-2-one.

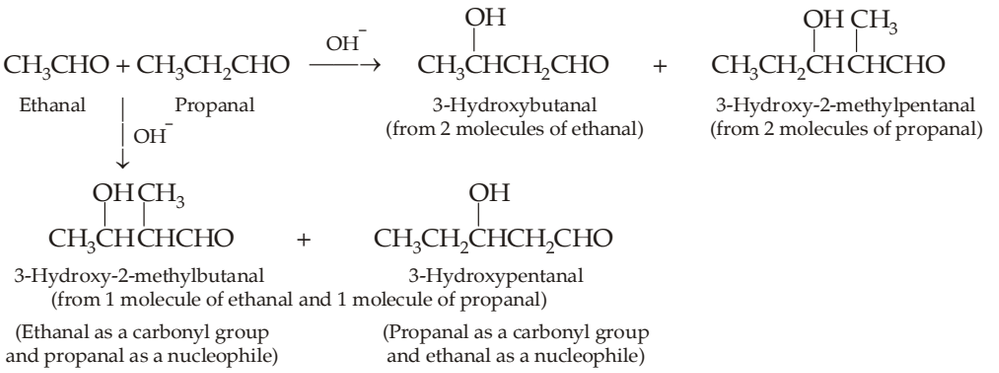


Mesityl oxide may further undergo crossed aldol condensation to form phorone as final product.

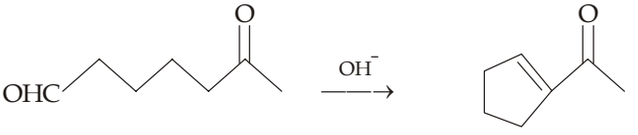


Crossed aldol condensation. An aldol condensation between two different carbonyl compounds each having at least one α-hydrogen atom (**crossed aldol condensation**) gives a mixture of the four possible products, hence it is not always feasible in the laboratory. For example, reaction of acetaldehyde and propanal in presence of dilute NaOH gives a mixture of four products.





Intramolecular aldol condensation (*Cyclization via aldol condensation*). A dialdehyde, a keto aldehyde, or a diketone undergoes aldol condensation to form five and six-membered (sometimes even longer) cyclic compounds, *e.g.*

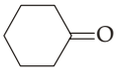


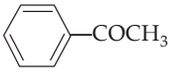
1-Cyclopentenyl methyl ketone

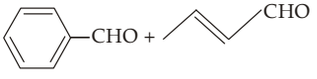
In the above keto aldehyde, three different enolates are possible, however it is the enolate from the ketone side of the molecule that adds to the aldehyde group leading to the product. The reason being greater reactivity of aldehydes toward nucleophilic addition than the ketones due to electronic as well as steric factors.

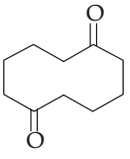
TEST YOUR UNDERSTANDING - 14.12

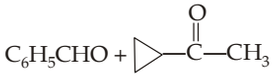
1. Write structural formulas for the products obtained by the aldol condensation of following compounds:

(*a*) 

(*b*) 

(*c*) 

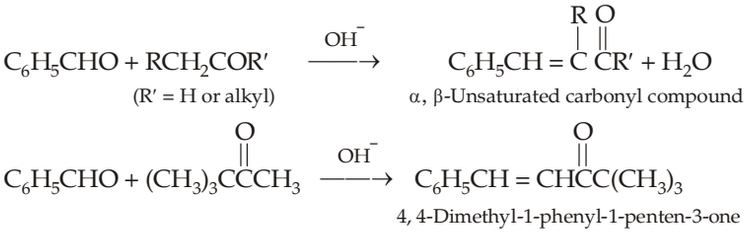
(*d*) 

(*e*) 

Other reactions related to aldol condensation

There are large number of condensations that are closely related to the aldol condensation, each of these reactions has its own name, viz. Claisen-Schmidt, Knovenagel, Perkin (given only by aromatic aldehydes), etc. At first glance each may seem to quite different from the others, closer examination shows that each of these involves attack by a carbanion on a carbonyl group. In each case carbanion is generated like that in aldol condenstion, *i.e.*, hydrogen α-to the carbonyl group is abstracted by base.

(*a*) **Claisen-Schmidt reaction.** A crossed aldol condensation in which an aromatic aldehyde reacts with an enolizable aldehyde, ketone or ester, eg $CH_3COOC_2H_5$ to form α, β-unsaturated carbonyl compound is known as **Claisen-Schmidt reaction**.



(*b*) **Knoevenagel reaction.** Condensation between an aldehyde or ketone with compound containing active methylene group* in the presence of ammonia, amines, pyridine, piperidine etc. to form α, β-unsaturated compound is known as **Knoevenagel reaction.**

(*i*) $CH_3CHO + H_2C(COOH)_2 \longrightarrow CH_3CH = C(COOH)_2 \xrightarrow[-CO_2]{\text{heat}} CH_3CH = CHCOOH$

Malonic acid — Crotonic acid

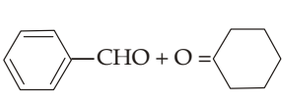
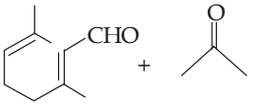
(*ii*) $C_6H_5CHO + H_2C(COOH)_2 \xrightarrow[\text{(ii)}\ -CO_2]{\text{(i) heat}} C_6H_5CH = CHCOOH$

Cinnamic acid

Note that in Knoevenagel reaction, enol (or enolate ion) is provided by molonic acid and not by aldehyde.

TEST YOUR UNDERSTANDING - 14.13

1. Give the structure of the mixed aldol condensation product of the following.

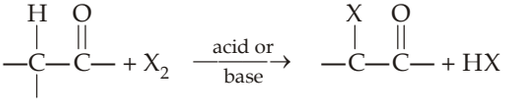
(*a*) $C_6H_5CHO + C_6H_5COCH_3$ (*b*)  (*c*) 

2. Give the final product in each case.

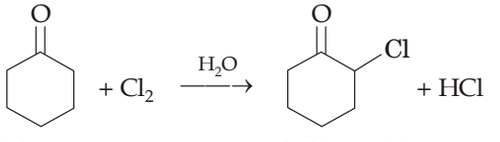
(*a*) $CH_3CHO + CH_3NO_2 \xrightarrow{KOH}$ (*b*) $C_6H_5CHO + C_6H_5CH_2CN \xrightarrow{C_2H_5ONa}$

(*c*) $C_6H_5CHO + CH_3COCH_2COOC_2H_5 \xrightarrow{NH_3}$

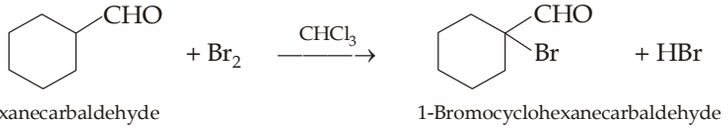
10. α-Halogenation of aldehydes and ketones. Aldehydes and ketones having α-hydrogen atom react with halogens to form α-haloaldehyde or ketone.



The reaction is *regiospecific* for substitution of an α-hydrogen.



Cyclohexanone — 2-Chlorocyclohexanone



Cyclohexanecarbaldehyde — 1-Bromocyclohexanecarbaldehyde

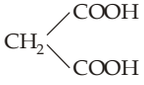
$C_6H_5COCH_3 + Cl_2 \longrightarrow C_6H_5COCH_2Cl$

Acetophenone — Phenacyl chloride

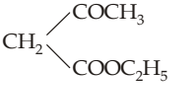
Phenacyl chloride is a relatively harmless but powerful **lachrymator** or *tear gas* and is used by police to disperse mobs.

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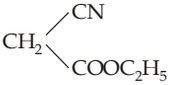
* A methylene group flanked on both sides by negative groups is known as active methylene group, *e.g.*,



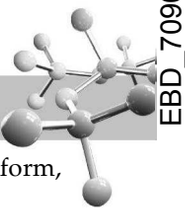
Malonic acid



Ethyl acetoacetate



Ethyl cyanoacetate

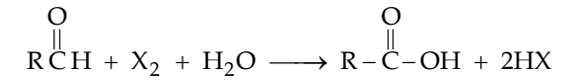


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(*i*) α-Halogenation of aldehydes and ketones can be carried out in a variety of solvents like water, chloroform, acetic acid and diethyl ether.

(*ii*) The reaction is quite different from the free-radical halogenation of alkanes and involves the formation of resonance stabilized enols.

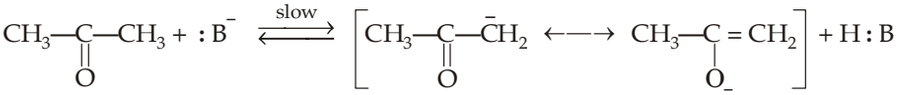
(*iii*) Unlike ketones, aldehydes are easily oxidized, and since halogens are strong oxidizing agents, halogenation of aldehydes usually results in oxidation to carboxylic acids.



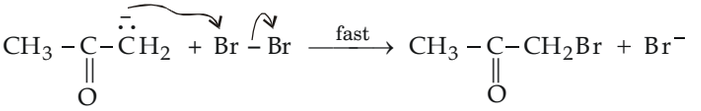
(*iv*) Since one of the reaction products is hydrogen halide, the process when catalyzed by acids is said to be **auto-catalytic**. However, halogenation promoted by base is more important and discussed here.

Mechanism. The rate of reaction depends upon the concentration of acetone and of base, but is independent of bromine concentration.

Step 1.



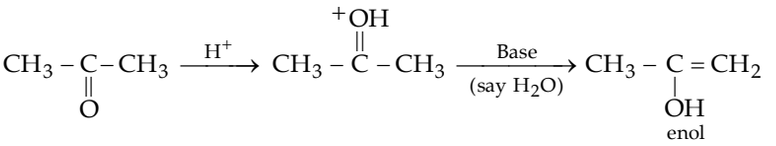
Step 2.

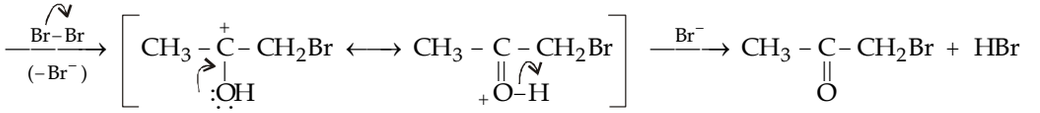


Since base is not regenerated during the reaction, halogen of ketones in presence of base is called **base-promoted**, rather than *base-catalyzed reaction*. As we will discuss below in haloform reaction, multiple halogenation of aldehydes and ketones having more than one α – H occurs.

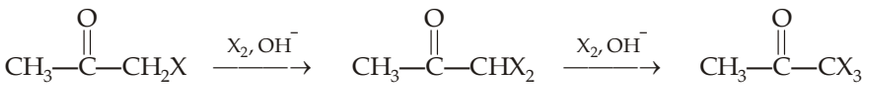
Mechanism of acid catalyzed α-halogenation of ketones. The ketone is dissolved in acetic acid, which serves as both the solvent and the acid catalyst. In contrast with basic halogenation, acidic halogenation can selectively replace just one hydrogen or more than one if appropriate amounts of the halogen are used.

In the first step, the carbonyl oxygen is protonated to form enol which reacts with the halogen (electrophile).

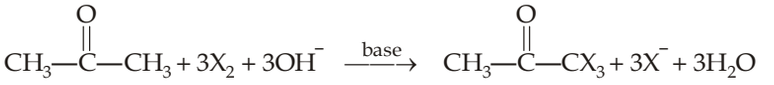




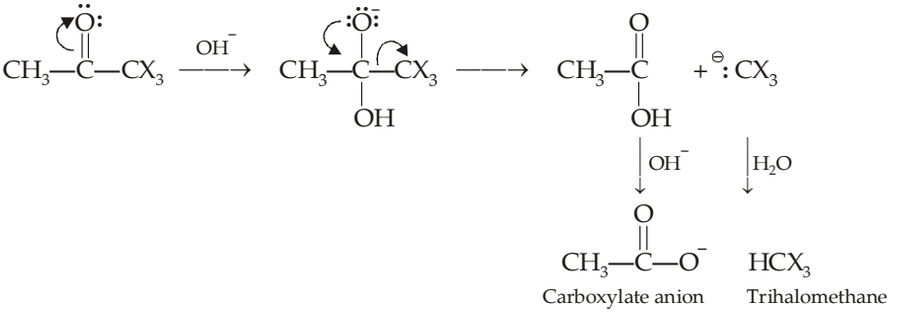
11. Haloform reaction. When methyl ketones (or acetaldehyde) react with halogen in the presence of base, multiple halogenation of the α-methyl group takes place because introduction of the first halogen (due to its electronegativity) makes the remaining α hydrogens on the methyl carbon more acidic. Actually, introduction of the first halogen is slowest, while that of last (*i.e.* third) is fastest.



In short,



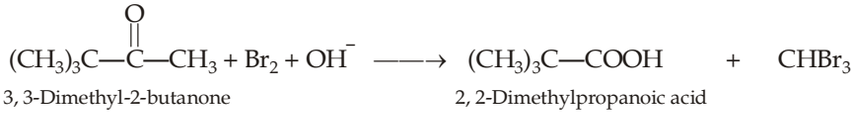
When methyl ketones react with halogens in aqueous sodium hydroxide (*i.e.* hypohalite solutions), an additional reaction takes place. Hydroxide ion attacks the carbonyl carbon atom of the trihaloketone (*nucleophilic addition*) and causes a cleavage of the carbon-carbon bond between the carbonyl group and the trihalomethyl group ($:CX_3^-$), the latter, being a *good leaving group**, departs easily forming a carboxylic acid and the trihalomethyl anion.



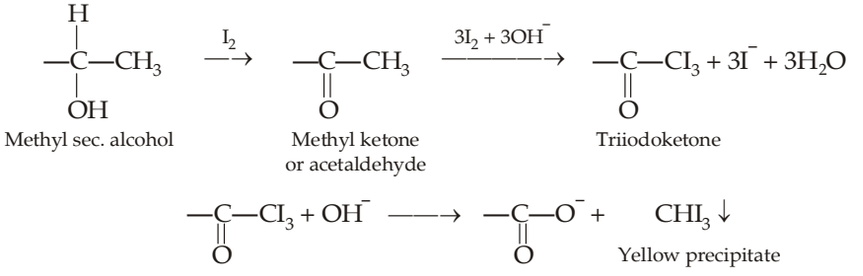
Since haloform ($CHCl_3$, $CHBr_3$ or CHI_3) is produced in the reaction, it is known as **haloform reaction** (*reaction of methyl ketones with alkaline halogen to form haloform, CHX_3*).

Importance of haloform reaction.

1. Haloform reaction is used as a means of preparing carboxylic acids from methyl ketones. For this, chlorine and bromine are most commonly used as the halogen component because resulting haloform (chloroform and bromoform) are water immiscible liquids and hence are easily separated from the aqueous solution containing the carboxylate anion.



2. Haloform reaction, particularly iodoform reaction is used as a laboratory test for identifying methyl ketones, acetaldehyde and methyl secondary alcohols which are first oxidized to methyl ketones under the reaction conditions.



TEST YOUR UNDERSTANDING - 14.14

1. Give the product of the reaction of 1 equivalent of Br_2 in H_3O^+ with

(*a*) propanal (*b*) acetophenone (*c*) cyclopentanone.

2. Arrange the following in decreasing ease of bromination.

CH_3COCH_3, CH_3COCH_2Br, CH_3COCH_2Cl, $CH_3COCHBr_2$.

3. Explain the following.

(*a*) Ketone I undergoes racemization in basic solution, but ketone II does not.

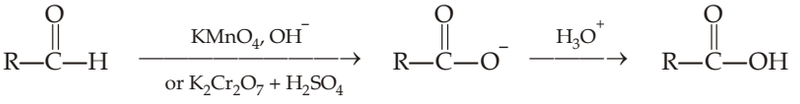


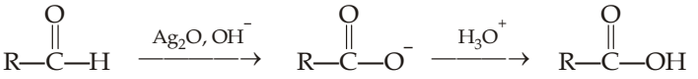
(*b*) ArCHO, HCHO and RCH_2CHO ($R \neq H$) do not undergo haloform reaction.

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(C) Other reactions of aldehydes and ketones.

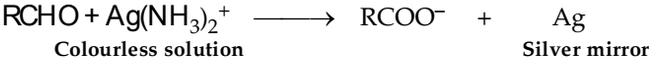
12. Oxidation. Aldehydes are much more easily oxidized, than ketones, to carboxylic acids. Aldehydes are oxidized not only by the same reagents that oxidize primary and secondary alcohols, viz. permanganate and dichromate, but also by the very mild oxidizing agent as silver ion. Oxidation by silver ion requires an alkaline medium under which conditions it forms insoluble silver oxide, hence to dissolve this oxide a complexing agent ammonia is added, which brings silver ion as diamminosilver (I) ion, $Ag(NH_3)_2^+$. This alkaline solution of silver nitrate in presence of ammonia is commonly known as **Tollen's reagent**.



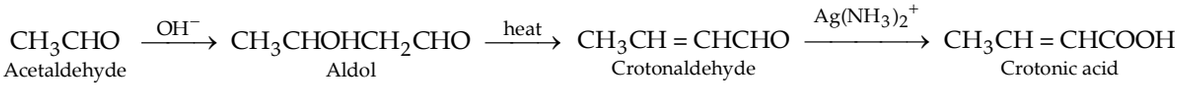


Note that in the above reactions, aldehydes lose the hydrogen that is attached to the carbonyl carbon atom, and since ketones do not have such hydrogen, they are resistant to oxidation.

Oxidation by Tollen's reagent is accompanied by colour change (due to reduction of Ag^+ ion to metallic silver), hence the reagent is commonly used for detecting the presence of an aldehyde in laboratory.



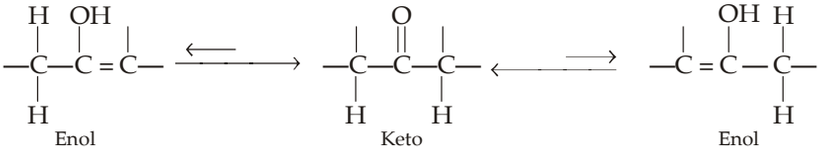
Since Tollen's reagent is a mild oxidising agent, it does not attack carbon-carbon double bond, hence it is used for the synthesis of unsaturated acids from unsaturated aldehydes which are easily obtained from aldol condensation.

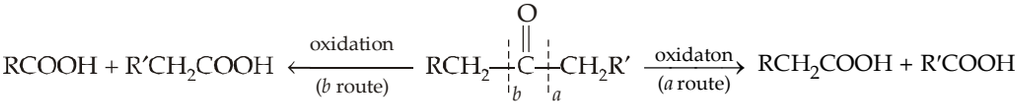


Aldehydes (except benzaldehyde) also reduce Fehling's solution (an alkaline solution of cupric ion complexed with tartarate ion) and Benedict's solution, in which complexing agent is citrate ion.

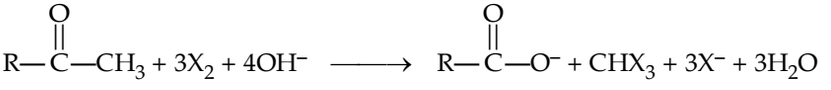


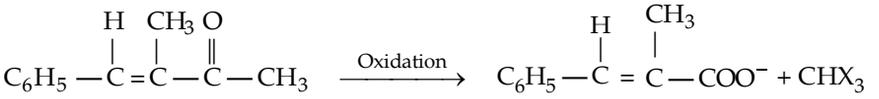
Oxidation of ketones requires breaking of carbon-carbon bonds, and hence (**except for haloform reaction**) takes place only under vigorous conditions. It is the double bond of the enol form that is cleaved during oxidation of ketones, thus where structure permits oxidation may occur on either end of the carbonyl group to form a mixture of carboxylic acids.





Methyl ketones are oxidized smoothly by means of hypohalite (NaOH or KOH + halogen) to form carboxylate ion and haloform, and hence the reaction is commonly known as **haloform reaction**. (Details discussed earlier).

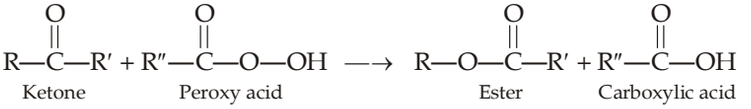




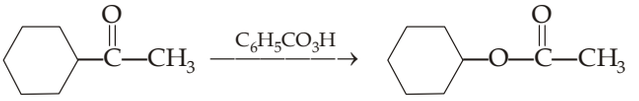
Aldehydes and ketones having a methyl or methylene group adjacent to the carbonyl group are oxidised by selenium dioxide.

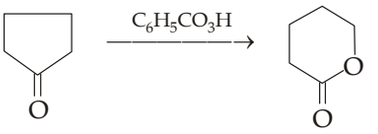
$$\underset{\text{Ethanal}}{CH_3CHO} \xrightarrow{SeO_2} \underset{\text{Glyoxal}}{CHO.CHO} ; \underset{\text{Propanone}}{CH_3COCH_3} \xrightarrow{SeO_2} \underset{\text{Methylglyoxal}}{CH_3COCHO}$$

Baeyer-Villiger oxidation. Both aldehydes and ketones are oxidised by peroxy acids. This reaction, called Baeyer-Villiger oxidation, is however especially useful with ketones, because it converts them to carboxylic esters.

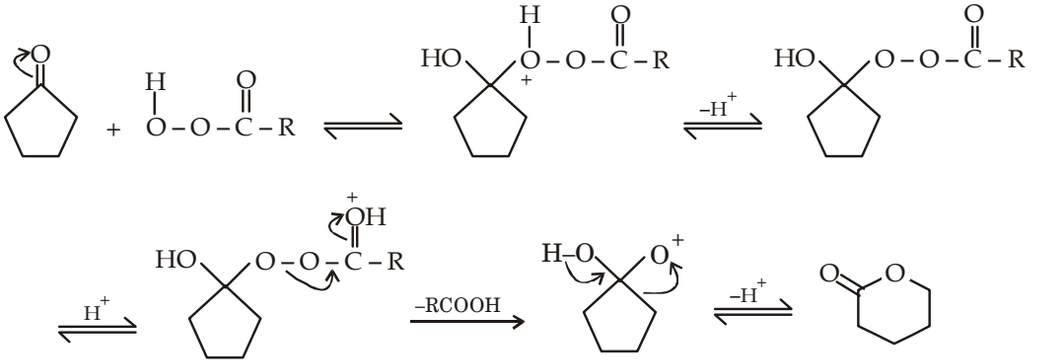


Note that an oxygen from the peroxy acid is inserted between the carbonyl carbon and carbon atom of one the alkyl groups of the ketone. In case of mixed ketones, oxygen insertion occurs between the carbonyl carbon and the larger of the two alkyl groups of the ketone





Mechanism, taking the example of cyclopentanone.



The tendency of a group to migrate (migratory aptitude) in all reactions where the group migrates with its electron pairs (i.e. as anions) follows the order :

H > phenyl > 3° alkyl > 2° alkyl > 1° alkyl > methyl

TEST YOUR UNDERSTANDING - 14.15

1. Give the products of reaction for

(*a*) Benzaldehyde + Tollen's reagent (*b*) CH_3CHO + dil. $KMnO_4$

(*c*) 3-Hexanone + Strong oxidant (*d*) Cyclohexanone + HNO_3, heat

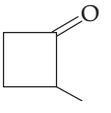
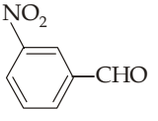
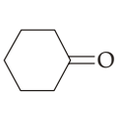
(*e*) Propanol + $Ag(NH_3)_2^+$ (*f*) Methyl ethyl ketone + HNO_3, heat

2. Give the products of the reaction of I_2 in KOH

(*i*) CH_3CH_2CHO (*ii*) CH_3CH_2OH (*iii*) C_6H_5CHO (*iv*) $C_6H_5CH_2COCH_3$

(*v*) $Me_3C.COCH_3$ (*vi*) $CH_3CH_2COCH_2CH_2COCH_3$ (*vii*) $C_6H_5CH_2OH$.

3. What is the product of the reaction of each of the following ketones with peroxybenzoic acid ?

(*a*) $C_6H_5COC_6H_5$ (*b*)  (*c*)  (*d*) 

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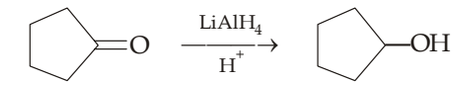
13. Reduction.

(*a*) Aldehydes and ketones can be reduced to primary and secondary alcohols respectively by a variety of reagents. Catalytic hydrogenation over a metal catalyst and reduction with lithium aluminium hydride or sodium borohydride are common methods and have been discussed in detail in the chapter on "Monohydric Alcohols". Sodium in ethanol is useful for reduction of ketones.

$$>C=O \xrightarrow[LiAlH_4 \text{ or } NaBH_4]{H_2/Ni \text{ or}} >CHOH$$

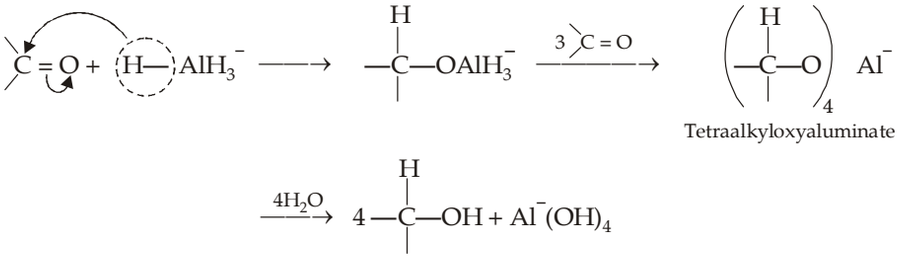
Benzaldehyde undergoes coupling reaction with Na/C_2H_5OH, so it can be reduced into alcohol by Na/C_2H_5OH.

$$CH_3CH=CHCH_2OH \xleftarrow[(ii)\ H^+]{(i)\ LiAlH_4,\ or\ NaBH_4} CH_3CH=CHCHO \xrightarrow{H_2/Ni} CH_3CH_2CH_2CH_2OH$$



Cyclopentanone Cyclopentanol

Remember that reduction of carbonyl compounds to alcohols by $LiAlH_4$ or $NaBH_4$ is an example of **nucleophilic addition** reactions in which hydride ion, $H:^-$ (from $LiAlH_4$ or $NaBH_4$) is transferred from the metal to the carbonyl carbon.

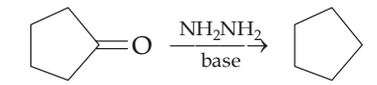


Tetraalkyloxyaluminate

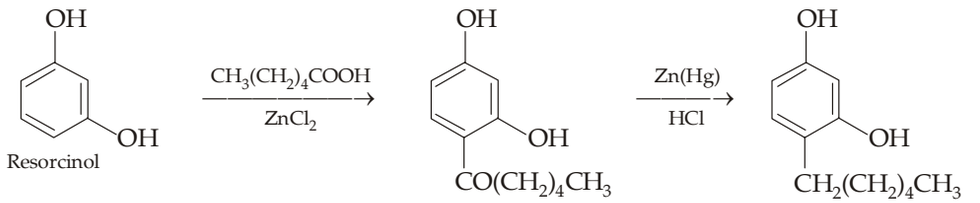
(*b*) Aldehydes and ketones can be reduced to hydrocarbons by the action (*i*) of amalgamated zinc and concentrated hydrochloric acid (**Clemmensen reduction**), or (*b*) of hydrazine (NH_2NH_2) and a strong base like NaOH, KOH or potassium *tert*-butoxide in a high-boiling alcohol like ethylene glycol or triethylene glycol (**Wolf-Kishner reduction**).

$$>C=O \xrightarrow[\text{or } NH_2NH_2, KOH, \text{ glycol}]{Zn(Hg),\ HCl} >CH_2$$

Both these methods reduce neither carboxylic acid nor the carbon-carbon double or triple bonds (however, remember that Zn and HCl reduces $—NO_2$ to $—NH_2$ group).



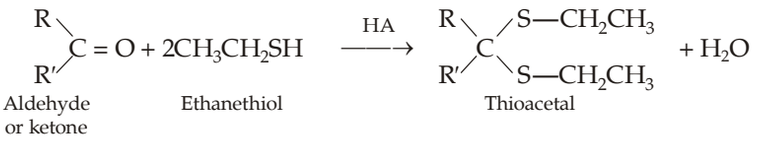
Cyclopentanone Cyclopentane

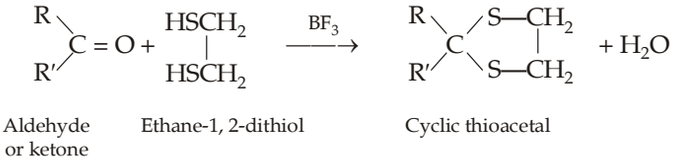


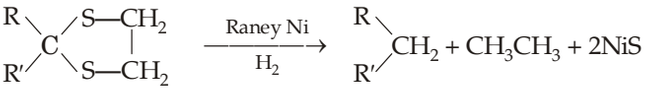
Resorcinol

4-*n*-Hexylresorcinol
(a constituent of **dettol**)

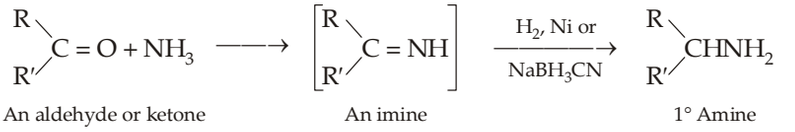
(*c*) Aldehydes and ketones can be reduced to hydrocarbons through thioacetal formation too.



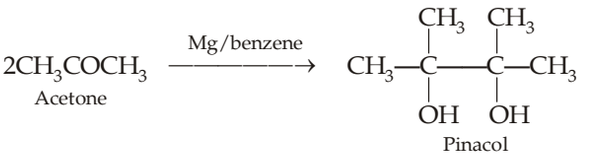




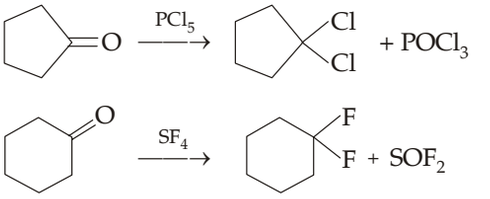
(*d*) Many aldehydes and ketones are converted into amines by **reductive amination** (reduction in presence of ammonia). Reduction can be done catalytically or by sodium cyanohydridoborate, $NaBH_3CN$. Reaction involves reduction of an intermediate *imine*.



(*e*) Reduction of ketones to pinacols in presence of magnesium has already been discussed in the chapter on "Polyhydric Alcohols"



14. Formation of dihalides. Aldehydes and ketones react with PCl_5 and sulphur tetrafluoride to form corresponding dihalide.



TEST YOUR UNDERSTANDING - 14.16

1. Write down the structure and IUPAC name of the products in each of the following reactions.

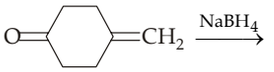
(*a*) 4, 4-Dimethylcyclohexanone + NH_2NH_2, OH^- (*b*) Pent-3-enal + NH_2NH_2, OH^-

(*c*) Acetylacetic acid + Zn(Hg) and HCl (*d*) Pent-2-enal + Zn(Hg) and HCl.

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2. Give structures of the compounds A to D.

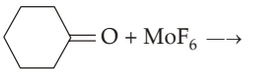
(*a*) $C_6H_5CHO + HSCH_2CH_2SH \xrightarrow{\text{dry HCl}} [A] \xrightarrow[Ni]{\text{Raney}} [B]$

(*b*) [D] $\xrightarrow[(ii)\ H_2O_2, OH^-]{(i)\ BH_3/THF}$  $\xrightarrow{NaBH_4}$ [C].

3. (*a*) Write structures for the products of the reaction of PCl_5 with

(*i*) propanal (*ii*) propanone (*iii*) benzophenone

(*b*) Give the products in the following reactions :

(*i*) $C_6H_5CHO + SF_4 \xrightarrow{\text{heat}}$ (*ii*)  $+ MoF_6 \longrightarrow$

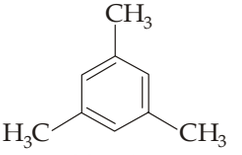
15. Polymerisation. Lower aldehydes undergo polymerisation to form different products under different conditions.

nHCHO (n = 6 to 50) $\xrightleftharpoons{\text{evaporate to dryness}}$ $(CH_2O)_n$ Paraformaldehyde

3HCHO $\xrightleftharpoons{\text{room temp.}}$ $(CH_2O)_3$ Metaformaldehyde (6-membered cyclic compound)

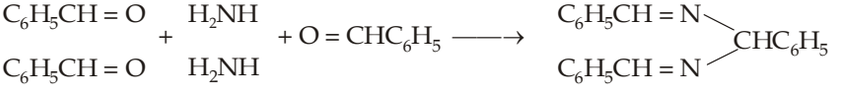
$3CH_3CHO \xrightleftharpoons{\text{conc. } H_2SO_4}$ $(CH_3CHO)_3$ Paraldehyde (6-membered cyclic compound)

$4CH_3CHO \xrightleftharpoons{\text{conc. } H_2SO_4,\ 0°C}$ $(CH_3CHO)_4$ Metaldehyde (8-membered cyclic compound)

$3CH_3COCH_3 \xrightarrow[\text{heat}]{\text{conc. } H_2SO_4}$  Mesitylene

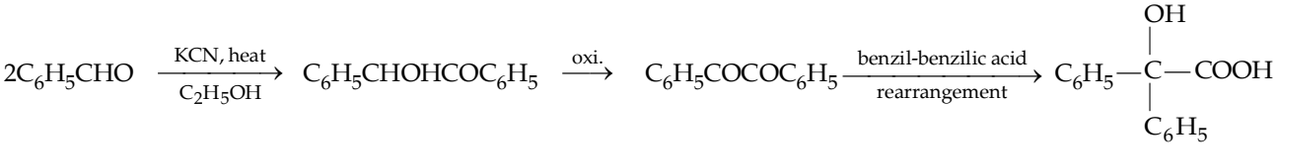
14.6 Special Reactions Given by Aromatic Aldehydes and Ketones

1. **Reaction with ammonia.** Benzaldehyde reacts with ammonia to form hydrobenzamide, recall that aldehydes other than formaldehyde give aldehyde ammonia, while formaldehyde forms hexamethylenetetramine, commonly known as **urotropine**, an important urinary antiseptic.



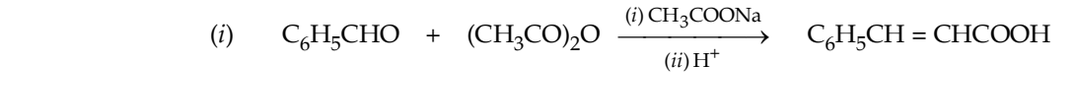
Hydrobenzamide

2. **Benzoin condensation.** Aromatic aldehydes, when heated with aqueous ethanolic NaCN or KCN, undergoes self condensation to form **benzoins**. For example,



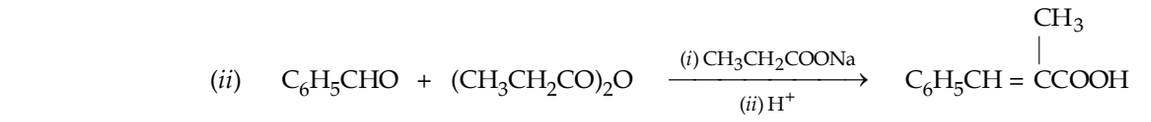
Benzoin (An α-hydroxyketone) Benzil Benzilic acid

3. **Perkin reaction.** Condensation of an aromatic aldehyde with an acid anhydride in presence of sodium salt of the same acid to form α, β-unsaturated acid is known as Perkin reaction.



(*i*) $C_6H_5CHO + (CH_3CO)_2O \xrightarrow[(ii)\ H^+]{(i)\ CH_3COONa} C_6H_5CH = CHCOOH$

Benzaldehyde Acetic anhydride Cimmanic acid



(*ii*) $C_6H_5CHO + (CH_3CH_2CO)_2O \xrightarrow[(ii)\ H^+]{(i)\ CH_3CH_2COONa} C_6H_5CH = \overset{CH_3}{\overset{|}{C}}COOH$

Benzaldehyde Propanoic anhydride α-Methylcinnamic acid

Remember that it is the α-carbon atom of the anhydride that reacts with the aldehydic group, observe (*ii*) example.

4. **Reaction with benzene nucleus.** Aromatic aldehydes and ketones undergo electrophilic substitutions in the *meta* position. However, these reactions are slow because of deactivating influence of the carbonyl group. Moreover, certain side reactions like oxidation make the yield poor.

14.7 Analysis of Aldehydes and Ketones

1. Aldehydes and ketones can be differentiated from non-carbonyl compounds through their reactions with semicarbazide, 2, 4-dinitro-phenylhydrazine, and hydroxylamine with which they form precipitates. Semicarbazones and oximes are colourless, while 2, 4-dinitrophenylhydrazones are usually orange. The melting points of these derivatives can also be used in indentifying specific aldehydes and ketones.
2. Aldehydes are differentiated from ketones through their ease of oxidation. They give a positive test with Tollen's reagent, while ketones do not. However, a positive Tollen's test is also given by few other easily oxidisable compounds, *e.g.* α-hydroxy ketones, certain phenols and hydroxylamines.
3. **Schiff's test** is a highly sensitive test for aldehydes. An aldehyde reacts with the fuchsin-aldehyde reagent to form a characteristic megenta colour.
4. Aldehydes are easily oxidised by cold, dilute, neutral $KMnO_4$ and by CrO_3 in sulphuric acid.
5. Aliphatic aldehydes and ketones having α-hydrogen react with bromine in CCl_4 (*caution* this is also a test for unsaturation).
6. Methyl ketones, acetaldehyde, ethyl alcohol and methyl secondary alcohols give positive iodoform test. In general, iodoform test is given by following groupings.

(*a*) $-\overset{O}{\overset{\|}{C}}-CH_3$ present in ethanal, $H-\overset{O}{\overset{\|}{C}}-CH_3$ and all methyl ketones

(*b*) $-\overset{OH}{\overset{|}{\underset{H}{\underset{|}{C}}}}-CH_3$ present in ethanol and all secondary methyl ketones.

(*c*) $R-\overset{O}{\overset{\|}{C}}-CH_2X$ since these products are formed during holoform reaction.

(*d*) $R-\overset{X}{\overset{|}{C}}H-CH_3$ since these on hydrolysis with aq. NaOH give 2° alcohols having methyl group.

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TEST YOUR UNDERSTANDING - 14.17

1. What happens when an aldehyde or a ketone is treated with the following reagents ?
Conc. H_2SO_4, cold dil., neutral $KMnO_4$, CrO_3 in H_2SO_4, and Br_2 in CCl_4.

2. By rapid test tube reactions distinguish between

(*a*) 2-Pentanol and 2-pentanone (*b*) Pentanal and diethyl ketone

(*c*) $C_6H_5COCH_2CH_3$ and $C_6H_5CH(OH)CH_2CH_2CH_3$ (*d*) $C_6H_5CH = CHCH_2OH$ and $C_6H_5CH = CHCHO$.

14.8 Illustrative Examples

Example 1 :

Give various steps involved in the following conversions :

$C_6H_5CH = CHCHO$ to $C_6H_5CHBrCHBrCH_2Cl$.

Solution :

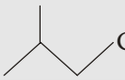
Conversion involves two main reactions, viz. addition of Br_2 on C = C and conversion of —CHO to —CH_2Cl. Since bromine oxidizes —CHO to —COOH, so —CHO first be converted to CH_2Cl before adding bromine.

$$C_6H_5CH = CHCHO \xrightarrow[(ii)\ H_2O]{(i)\ NaBH_4} C_6H_5CH = CHCH_2OH \xrightarrow{PCl_5} C_6H_5CH = CHCH_2Cl \xrightarrow{Br_2} C_6H_5CHBrCHBrCH_2Cl.$$

Example 2 :

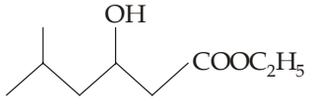
Write structures of the compounds from A to I.

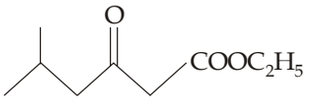
(a) $$C_6H_6 + CH_2 = CHCH_2OH \xrightarrow{HF} [A] \xrightarrow[(ii)\ H_2O_2/OH^-]{(i)\ BH_3/HF} [B] \xrightarrow[Pyridine]{CrO_3} [C] \xrightarrow[(ii)\ H_3O^+]{(i)\ CN^-} [D]$$

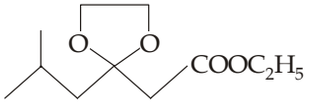
(b)  $+ BrCH_2COOC_2H_5 \xrightarrow{Zn} [E] \xrightarrow[Pyridine]{CrO_3} [F] \xrightarrow{HOCH_2CH_2OH} [G] \xrightarrow{LiAlH_4} [H] \xrightarrow{H_3O^+} [I].$

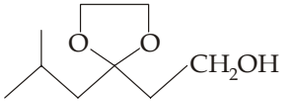
Solution :

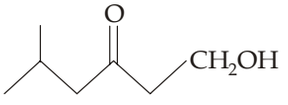
(*a*) [A] is $C_6H_5CH_2CH = CH_2$,
(obtained by Friedel-craft alkylation)
[B] is $C_6H_5CH_2CH_2CH_2OH$,
(obtained by *anti*-Markovnikov hydration)
[C] is $C_6H_5CH_2CH_2CHO$;
[D] is $C_6H_5CH_2CH_2CHOHCOOH$

(*b*) 
[E] (Perkin reaction)


[F]


[G] (Protection of keto group)


[H] (Reduction of ester)

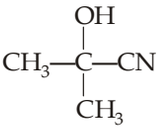

[I] (Regeneration of keto group)

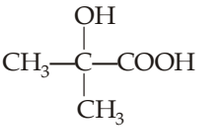
Example 3 :

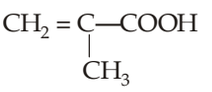
Write structures for A to D in the following.

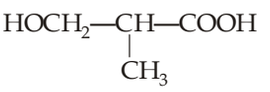
$$(CH_3)_2CO \xrightarrow{CN^-} \textbf{[A]} \xrightarrow{H_3O^+} \textbf{[B]} \xrightarrow[\text{heat}]{H_2SO_4} \textbf{[C]} \xrightarrow[(ii)\,H_2O_2,\,OH^-]{(i)\,BH_3\,/\,THF} \textbf{[D].}$$

Solution :


[A]


[B]


[C]


[D]

Example 4 :

Identify A to C in the following :

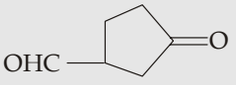
$$C_6H_5CH_2CH_3 \xrightarrow{2NBS} \textbf{[A]} \xrightarrow{H_3O^+} \textbf{[B]} \xrightarrow{NaOCl} \textbf{[C] + [D]}$$

Solution :

$C_6H_5CBr_2CH_3$, [A] $C_6H_5COCH_3$, [B] $C_6H_5COO^-Na^+ + CHCl_3$ [C] and [D]

Example 5 :

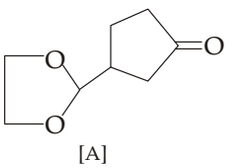
Identify A to C in the following reactions.



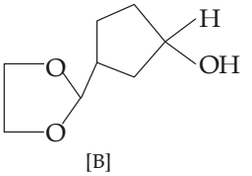
$$\xrightarrow[H^+]{CH_2OHCH_2OH} \textbf{[A]} \xrightarrow[CH_3OH]{NaBH_4} \textbf{[B]} \xrightarrow{H_3O^+} \textbf{[C]}$$

Solution :

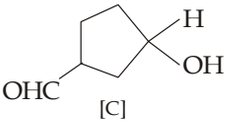
Aldehydes are more reactive than ketones, hence acetal formation at first step will be with the —CHO group ; this is done to protect the aldehydic group.



[A]



[B]



[C]

Example 6 :

Complete the following reactions.

(a) $\textbf{CH} \equiv \textbf{CH} \xrightarrow{C_2H_5MgBr} \textbf{[A]} \xrightarrow[(ii)\,H^+]{(i)\,CO_2} \textbf{B} \xrightarrow{H_2SO_4,\,Hg^{2+}} \textbf{C} \xrightarrow[H_2SO_4]{CrO_3} \textbf{[D]}$

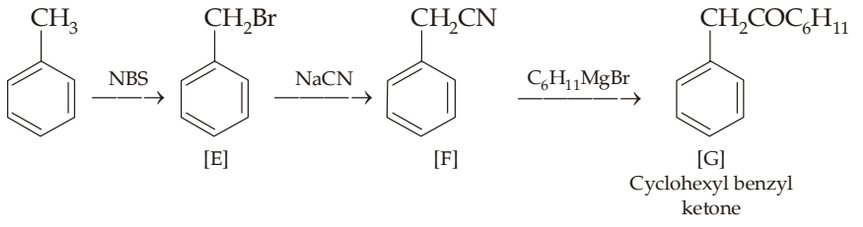
(b) $C_6H_5CH_3 \xrightarrow{NBS} \textbf{E} \xrightarrow{NaCN} \textbf{F} \xrightarrow[(ii)\,H_3O^+]{(i)\,C_6H_{11}MgBr} \textbf{G}$

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Solution :

(*a*) $CH \equiv CH \xrightarrow[(-C_2H_6)]{C_2H_5MgBr} \underset{[A]}{HC \equiv CMgBr} \xrightarrow[(ii)\ H^+]{(i)\ CO_2} \underset{[B]}{HC \equiv C\!\rightarrow\! COOH} \xrightarrow{H_2SO_4,\ Hg^{2+}}$

$\underset{\substack{\textit{anti}\text{-Markownikov hydration}\\ \text{due to } -\text{I effect of } -\text{COOH}}}{HOCH = CHCOOH} \xrightarrow{\text{tautomerises}} \underset{[C]}{OHCCH_2COOH} \xrightarrow{CrO_3} \underset{[D]}{HOOCCH_2COOH}$

(*b*) 

[E] [F] [G] Cyclohexyl benzyl ketone

Example 7 :

Give steps involved in the following conversions.

(a) Acetaldehyde to 2, 3-dibromopentanoic acid

(b) Acetaldehyde to α-hydroxypropanoic acid (lactic acid)

(c) Benzene to *p*-chlorobenzaldehyde

(d) Cyclopentane to cyclopentanecarbaldehyde.

Solution :

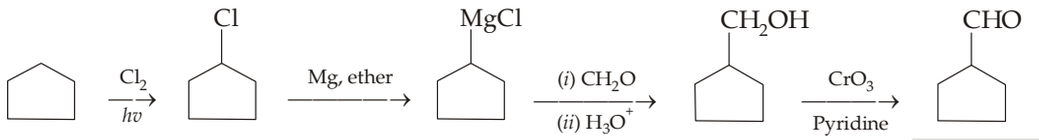
(*a*) $2H_3CHO \xrightarrow{OH^-} CH_3CHOHCH_2CHO \xrightarrow{heat} CH_3CH = CHCHO$

$\xrightarrow{[Ag(NH_3)_2]^+} CH_3CH = CHCOOH \xrightarrow{Br_2} CH_3\underset{Br}{\underset{|}{C}}H\underset{Br}{\underset{|}{C}}HCOOH$

(*b*) $CH_3CHO \xrightarrow{NaCN} CH_3CHOHCN \xrightarrow{H^+} \underset{\text{Lactic acid}}{CH_3CHOHCOOH}$

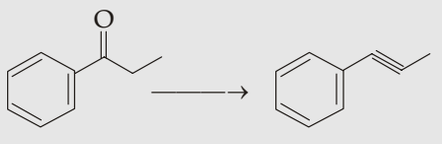
(*c*) $C_6H_6 \xrightarrow[(ii)\ Mg,\ ether]{(i)\ Br_2,\ Fe} C_6H_5MgBr \xrightarrow[(ii)\ H_3O^+]{(i)\ CH_2O} C_6H_5CH_2OH \xrightarrow{Cl_2,\ Fe} p\text{-}Cl.C_6H_4CH_2OH$

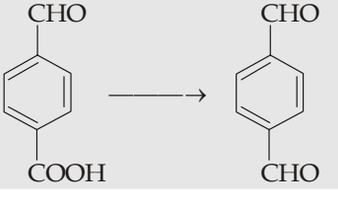
$\xrightarrow{CrO_3,\ Pyridine} p\text{-}ClC_6H_4CHO$

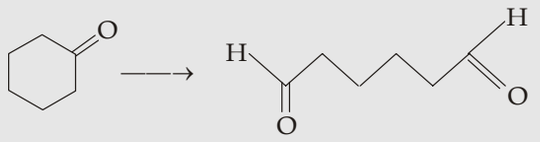
(*d*) 

Example 8 :

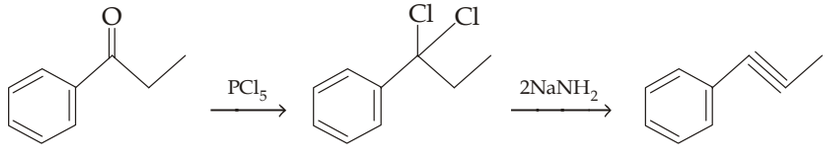
Perform each of the following transformations :

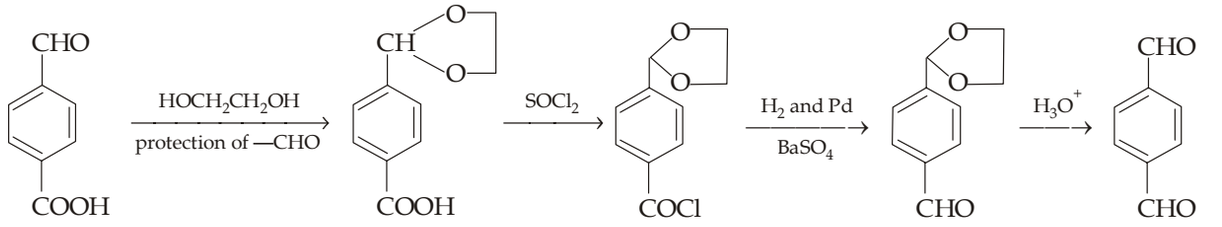
(a) 

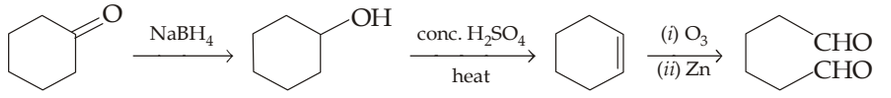
(b) 

(c) 

Solution :

(*a*) 

(*b*) 

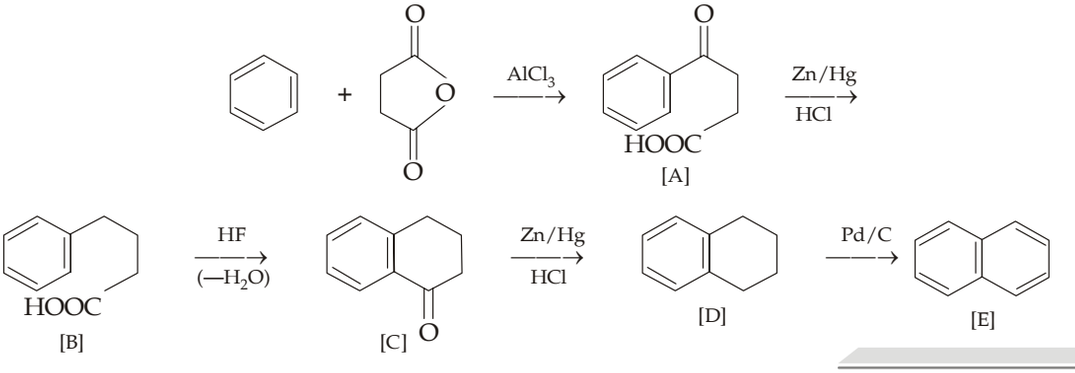
(*c*) 

Example 9 :

Illustrate the following series of reactions by providing structure to each of the intermediate.



Solution :



Example 10 :

Give steps involved in the following conversions.

(a) $^{14}CH_3OH$ **to** $CH_3{}^{14}CH_2OH$

(b) $^{14}CH_3OH$ **to** $^{14}CH_3CH_2OH$

(c) $^{14}CH_3CH_2OH$ **to** $^{14}CD_3CHO$

(d) $^{14}CH_3CHO$ **to** $^{14}CH_3CHDOH$.

Solution :

(*a*) $^{14}CH_3OH \xrightarrow[300°C]{Cu} H_2{}^{14}C = O \xrightarrow[(ii)\ H_3O^+]{(i)\ CH_3MgBr} CH_3{}^{14}CH_2OH$

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(*b*) $^{14}CH_3OH \xrightarrow{HBr} {}^{14}CH_3Br \xrightarrow[ether]{Mg} {}^{14}CH_3MgBr \xrightarrow[(ii)\,H_3O^+]{(i)\,CH_2O} {}^{14}CH_3CH_2OH$

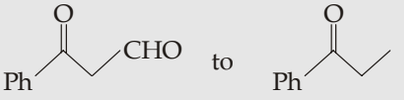
(*c*) $^{14}CH_3CH_2OH \xrightarrow{Cu} {}^{14}CH_3CHO \xrightarrow{D_2O,\ OD^-\ (trace)} {}^{14}CD_3CHO$

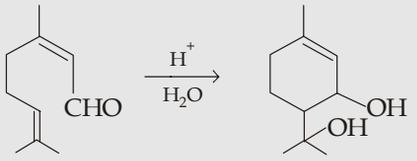
(*d*) $^{14}CH_3CHO \xrightarrow[LiAlD_4]{D_2\,/\,Pt\ or} {}^{14}CH_3CHDOD \xrightarrow{H_2O} {}^{14}CH_3CHDOH.$

Example 11 :

How will you carry out following transformations ?

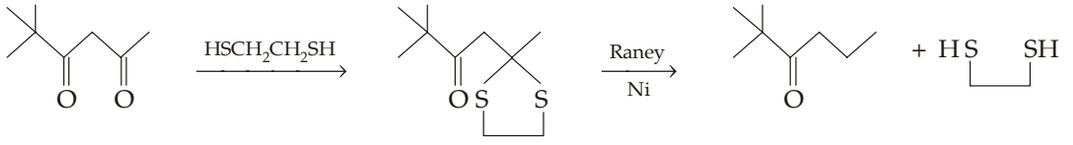
(a) 

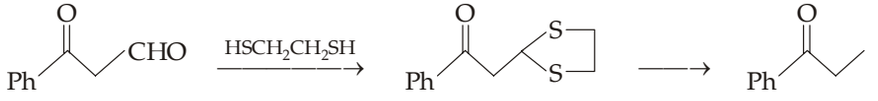
(b) 

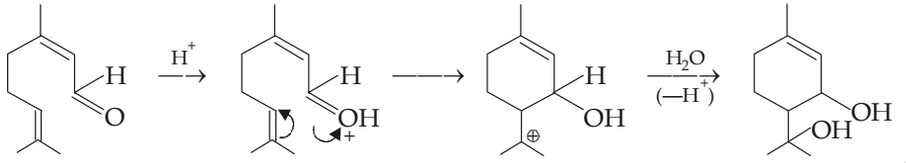
(c) 

Solution :

The sterically unhindered keto group in (*a*) and the more reactive aldehyde group in (*b*) are more easily effected.

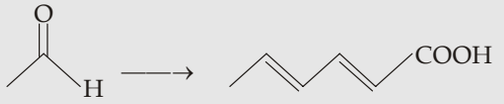
(*a*) 

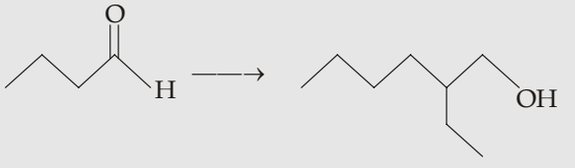
(*b*) 

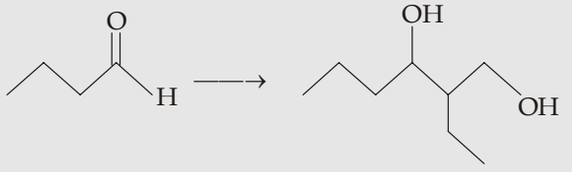
(*c*) 

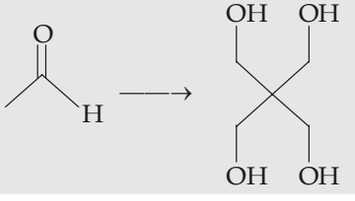
Example 12 :

Write down the steps involved in the following reactions, each involves aldol condensation.

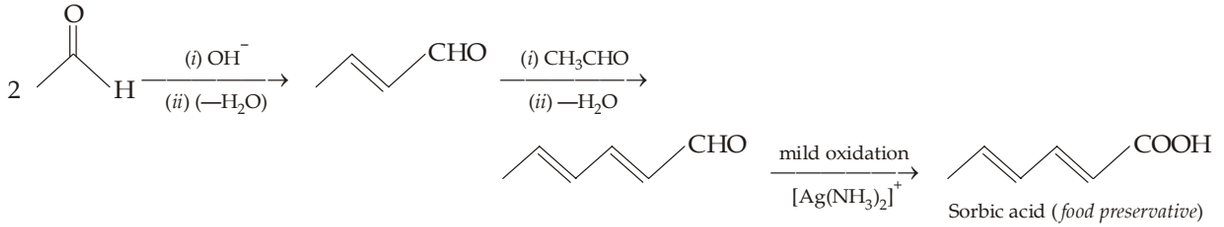
(a) 

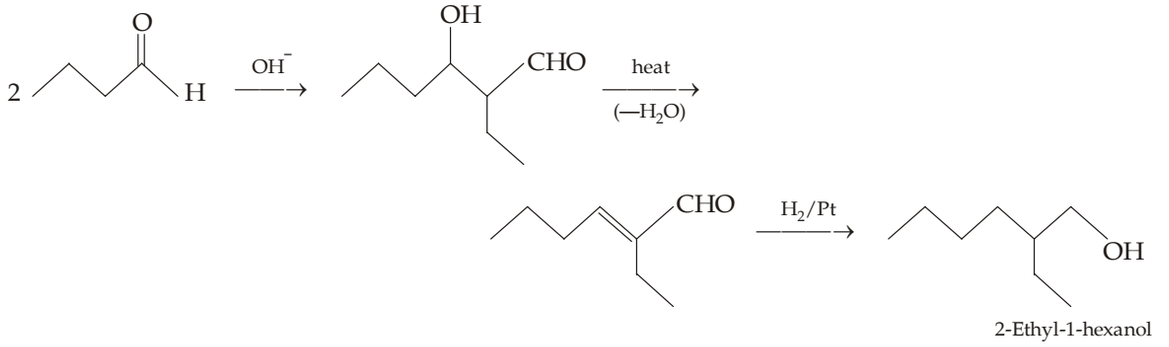
(b) 

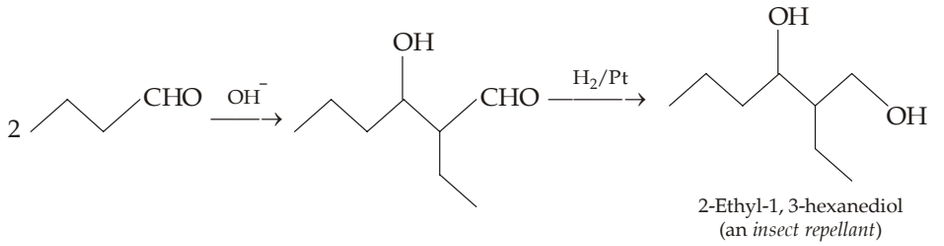
(c) 

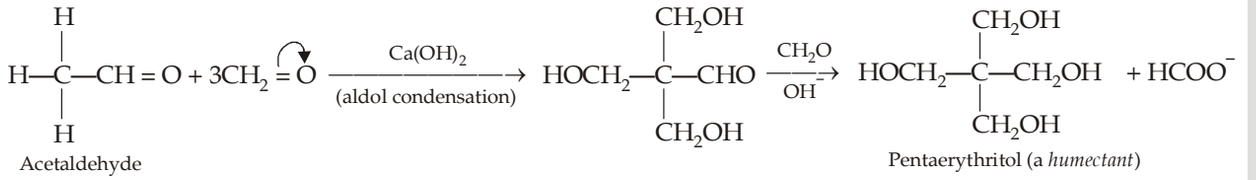
(d) 

Solution :

(*a*) 

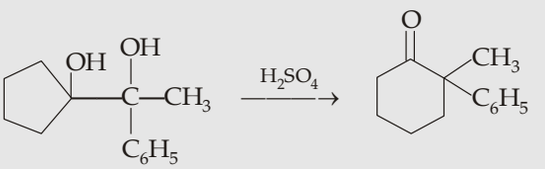
(*b*) 

(*c*) 

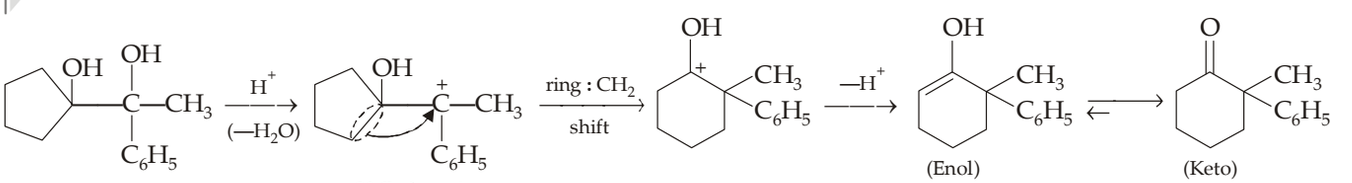
(*d*) 

Example 13 :

Give steps involved in the following conversion.



Solution :



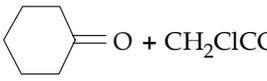
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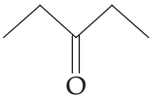
Example 14 :

Identify the final product formed in each case and explain its formation.

(a) $CH_3COCH_3 + CH \equiv CH \xrightarrow[(ii)\ H^+]{(i)\ NaNH_2}$

(b) $(CH_3)_2C(OH)CH_2OH \xrightarrow{H^+}$

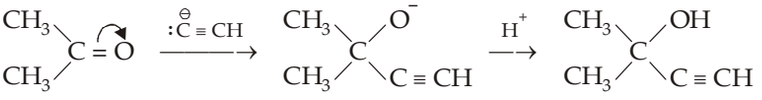
(c)  $+ CH_2ClCOOCH_2CH_3 \xrightarrow{Me_3COK}$

(d)  $+ NH_3 \xrightarrow{CN^-}$

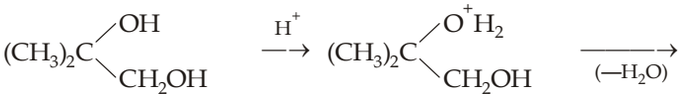
Solution :

(*a*)

$$HC \equiv CH \xrightarrow{NaNH_2} {}^{\ominus}:C \equiv CH$$



(*b*)

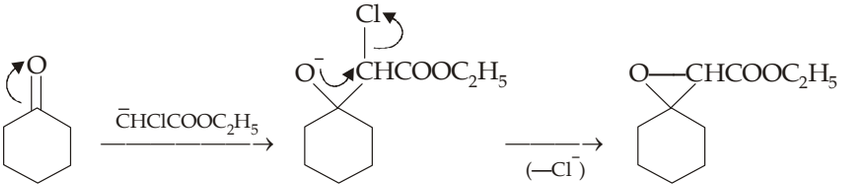


3° alcohol is more basic than 1°

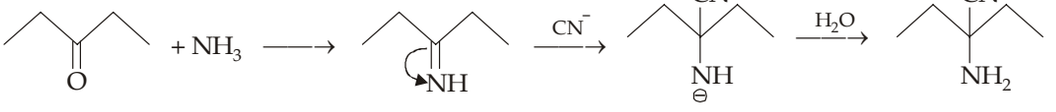
$$(CH_3)_2\overset{+}{C}CH_2OH \xrightarrow{-H^+} [(CH_3)_2C{=}CHOH] \xrightarrow{\text{tautomerization}} (CH_3)_2CHCHO$$

(*c*)

$$CH_2ClCOOCH_2CH_3 \xrightarrow{Me_3CO^-} \bar{C}HClCOOCH_2CH_3$$

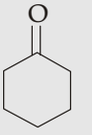


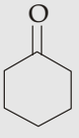
(*d*)



Example 15 :

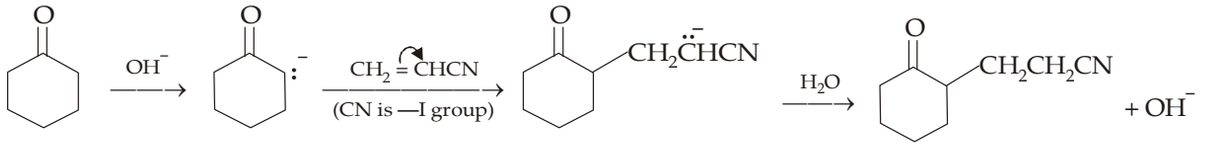
Predict the product and explain its formation in each of the following reactions.

(a)  $+ CH_2 = CHCN \xrightarrow{OH^-}$

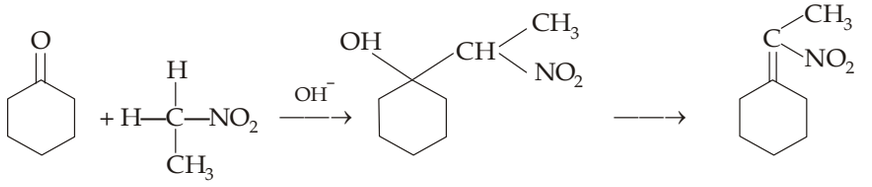
(b)  $+ CH_3CH_2NO_2 \xrightarrow{OH^-}$

Solution :

(*a*)



(*b*)

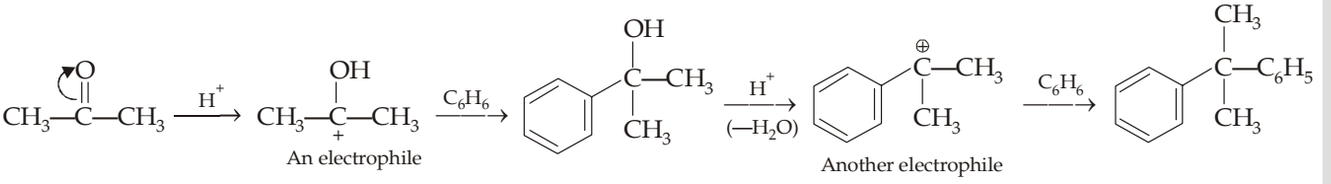


Example 16 :

Can you suggest a proper mechanism for the following reaction ?

$$2C_6H_6 + (CH_3)_2CO \xrightarrow{H^+} (C_6H_5)_2C(CH_3)_2.$$

Solution :



Example 17 :

Semicarbazide (1 mol) is added to a mixture of cyclohexanone (1 mol) and benzaldehyde (1 mol). If the product is isolated immediately, it consists almost entirely of the semicarbazone of cyclohexanone, if the product is isolated after several hours, it consists almost entirely of the semicarbazone of benzaldehyde. Explain.

Solution :

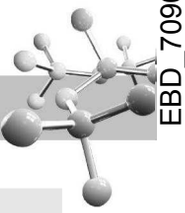
Semicarbazone formation is reversible. Cyclohexanone reacts more rapidly because its C = O group is not sterically hindered (its R groups are tied back into a ring), but benzaldehyde gives the more stable product, $C_6H_5CH = NNHCONH_2$, because of conjugation. Hence, initially the rate controlled product (cyclohexanone semicarbazone) is formed ; later, after equilibrium is established the equilibrium controlled product (*i.e.* the more stable benzaldehyde semicarbazone) is formed.

Example 18 :

An organic compound of the formula $C_5H_8O_2$ reduces Tollen's reagent and also responds iodoform test. It reacts with hydroxylamine hydrochloride to form a dioxime and can be reduced to *n*-pentane. Deduce the structure of the compound.

Solution :

Positive test with Tollen's reagent indicates the presence of —CHO group, while positive iodoform test indicates the presence of $—COCH_3$ grouping. Two carbonyl groups is also indicated by the formation of dioxime. Reduction of the compound to *n*-pentane indicates the presence of 5 carbon atoms in a continuous chain. Hence the compound should be $CH_3—\overset{\overset{O}{\|}}{C}CH_2CH_2CHO$.



Example 19 :

Compound X, $C_9H_{10}O$, is inert to Br_2 in CCl_4. Vigorous oxidation with hot alkaline permanganate yields benzoic acid. X gives a precipitate with semicarbazide hydrochloride and with 2, 4-dinitrophenylhydrazine (DNPH). Write all possible structures for X. How can these isomers be distinguished by using simple chemical tests ?

Solution :

Formation of benzoic acid, on oxidation of the compound X, indicates that X is having only one side chain. The formula reveals five degree of unsaturation, four for the benzene ring indicated by the formation of benzoic acid and hence fifth must be present in the side chain. The side unsaturation must be due to C = O group, indicated by reaction with DNPH. Thus the possible structures for the compound X are

$$\underset{\text{I}}{C_6H_5COCH_2CH_3} \qquad \underset{\text{II}}{C_6H_5CH_2COCH_3} \qquad \underset{\text{III}}{C_6H_5CH_2CH_2CHO} \qquad \underset{\text{IV}}{C_6H_5\overset{\overset{CH_3}{|}}{C}HCHO}$$

Difference between I, II, III and IV. Aldehydes III and IV undergo oxidation by cold $KMnO_4$ and CrO_3 in H_2SO_4; while compound II undergoes iodoform reaction.

Example 20 :

The Grignard reagent of an alkyl halide (I) reacts with propanal to give a secondary alcohol (II). II is converted into another alkyl halide (III), Grignard reagent of (III) is hydrolyzed to form an alkane (IV). Compound IV can be produced by coupling alkyl halide (I). Establish the structure of I and explain the reactions involved.

Solution :

Let us translate the given description into chemical equations.

$$\underset{\text{I}}{RBr} \xrightarrow[\text{ether}]{Mg} RMgBr \xrightarrow[(ii)\,H_3O^+]{(i)\,CH_3CH_2CHO} \underset{\text{II}}{CH_3CH_2CH(OH)R} \xrightarrow{HBr} \underset{\text{III}}{CH_3CH_2\overset{\overset{R}{|}}{C}HBr} \xrightarrow{Mg,\ ether} \underset{\text{IV}}{CH_3CH_2\overset{\overset{R}{|}}{C}HMgBr} \xrightarrow{H_2O} CH_3CH_2CH_2R$$

Since IV is formed by coupling of I, it must be symmetrical, *i.e.* R should be $CH_3CH_2CH_2$—. Hence compound I is $CH_3CH_2CH_2Br$ and thus the various reactions can be written as below.

$$\underset{\text{I}}{CH_3CH_2CH_2Br} \xrightarrow{Mg,\ ether} \underset{\text{II}}{CH_3CH_2CH_2MgBr} \xrightarrow[(ii)\,H_3O^+]{(i)\,CH_3CH_2CHO} CH_3CH_2CH_2\overset{\overset{CH_2CH_3}{|}}{C}HOH$$

$$\xrightarrow{HBr} CH_3CH_2CH_2\overset{\overset{CH_2CH_3}{|}}{C}HBr \xrightarrow{Mg,\ ether} \underset{\text{III}}{CH_3CH_2CH_2\overset{\overset{CH_2CH_3}{|}}{C}HMgBr} \xrightarrow{HOH} CH_3CH_2CH_2\overset{\overset{CH_2CH_3}{|}}{C}H_2 \xleftarrow[\text{(coupling)}]{Na} \underset{\text{I}}{2BrCH_2CH_2CH_3}$$

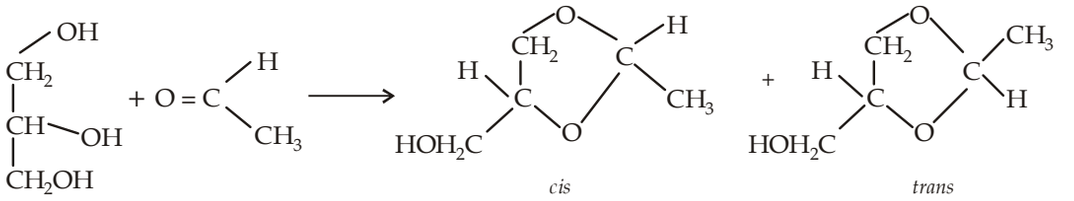
Example 21 :

Glycerol and ethanal are treated in equivalent amounts. Predict the number of isomeric acetals formed.

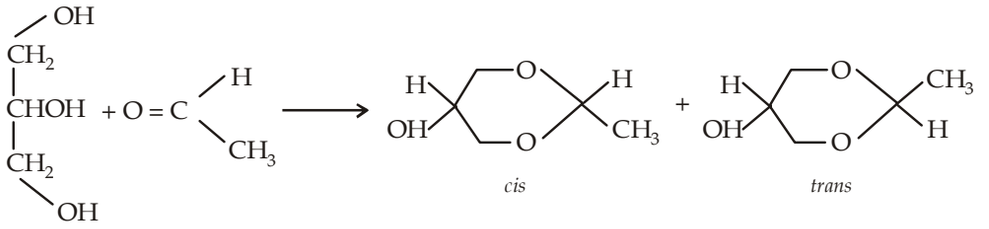
$$CH_2OHCHOHCH_2OH + CH_3CHO \longrightarrow$$

Solution :

Cyclic acetal may be formed by the reaction of CH_3CHO (a) with the 1- and 2- OH groups, and (b) with 1- and 3- OH groups. The former possibility creates two chiral centers, hence two pairs of enantiomers will be formed, one pair is the *cis*- and the other is *trans.*



Reaction of CH_3CHO with 1- and 3- OH groups will give *cis*- and *trans*- isomers, none of which is chiral. These isomers are diastereomers.

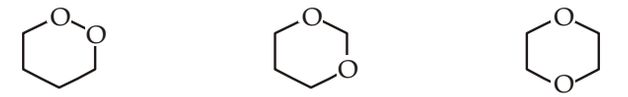


Thus, on the whole six isomers will be formed.

Example 22 :

The three isomeric dioxanes; 1,2-dioxane, 1,3-dioxane and 1,4-dioxane; behave differently. One of these acts like an ether and is used as an excellent solvent for Grignard reactions, the other isomer when heated explodes, and the third quickly hydrolyzes in dil. acid. Predict which one is which, and explain the difference.

Solution :



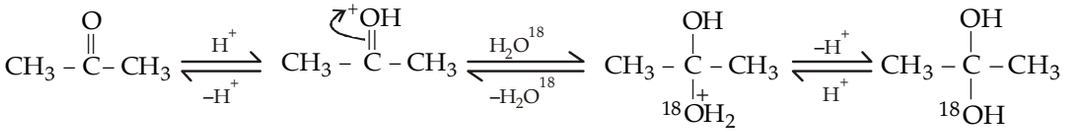
The isomer I has an peroxide linkage (–O–O–) which decomposes on heating to give radicals. In the presence of organic compounds, radical reactions can be explosive. The isomer II behaves like an acetal which hydrolyzes in dil. acid to alcohol and HCHO, while the III isomer behaves like a simple ether, the two oxygens are far enough apart to act independently.

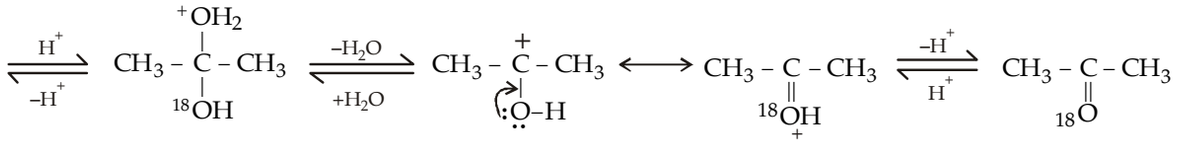
Example 23 :

Acetone, when dissolved in water having labelled oxygen (O^{18}) gives $CH_3CO^{18}CH_3$, and this conversion is catalyzed by traces of strong acids and strong bases. Devise a mechanism for this.

Solution :

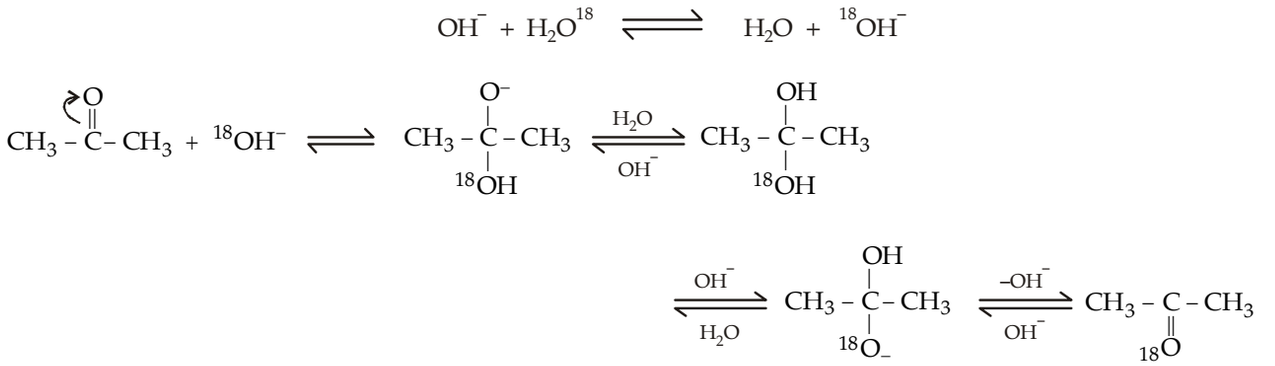
Acid catalyzed reaction :





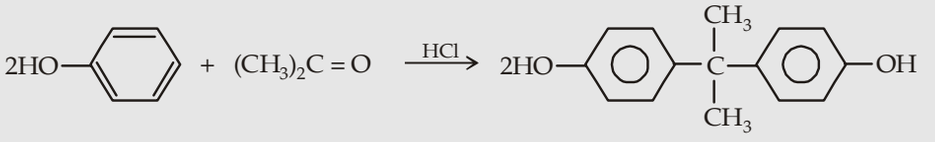
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Base-catalyzed reaction :



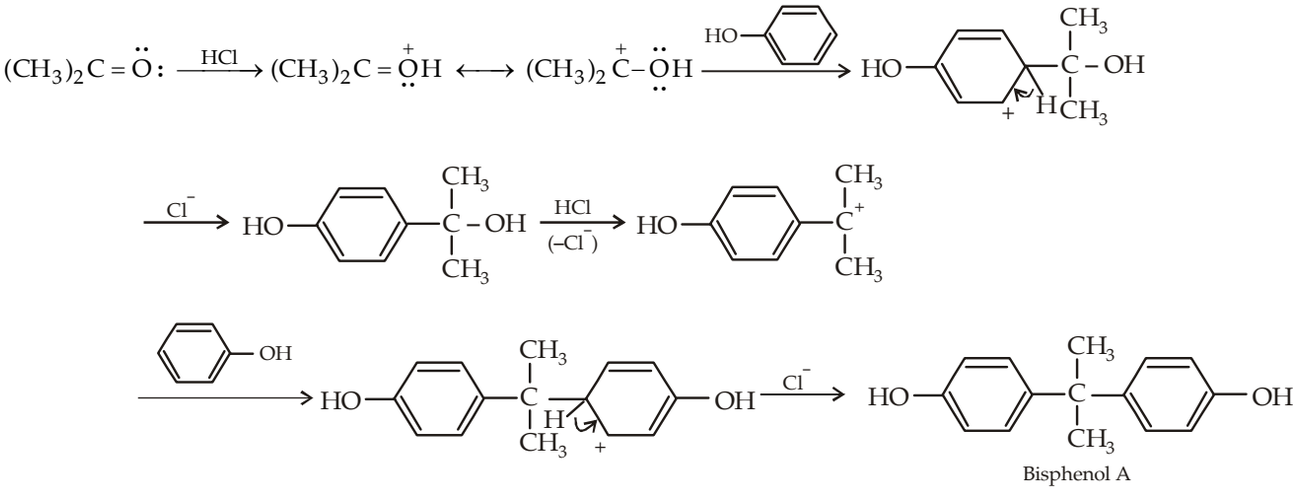
Example 24 :

Bisphenol A, an important constituent of many polymers like polyurethanes, polycarbamates, and epoxy resins, is synthesized from phenol and acetone in presence of HCl. Propose a mechanism for this reaction.



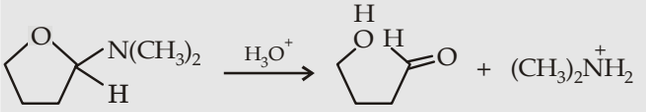
Bisphenol A

Solution :



Bisphenol A

Example 25 :

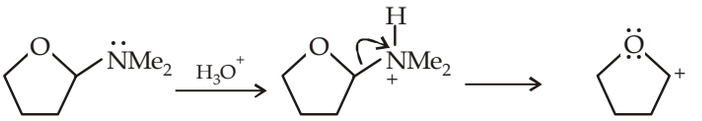


(a) Propose a mechanism for the above hydrolysis of aminoacetals.

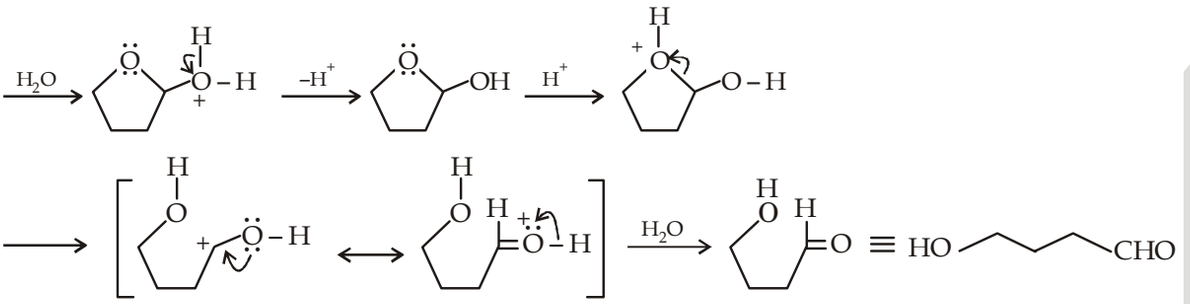
(b) Although aminoacetals are easily and quickly hydrolyzed by dilute acids, the nucleosides (having an aminoacetal functional group) which are building blocks of DNA are not easily hydrolysed. Explain.

Solution :

(a)



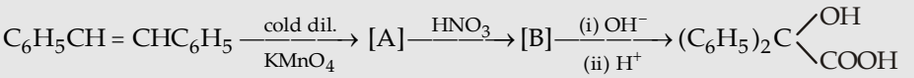
Resonance stabilized carbocation



(b) In the nucleosides the lone pair of electrons on nitrogen (forming a part of aminoacetal functional group) is involved in aromatic sextet, hence not easily available for protonation with dilute acids. Protonation may occur with extremely strong acids.

Example 26 :

Complete the following by supplying structures to compounds A and B

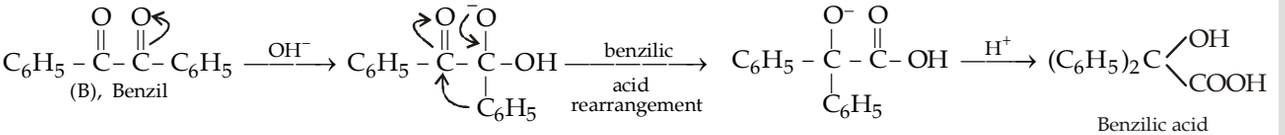


Propose mechanism for the conversion of compound (B) to the final product.

Solution :



(A) (B)

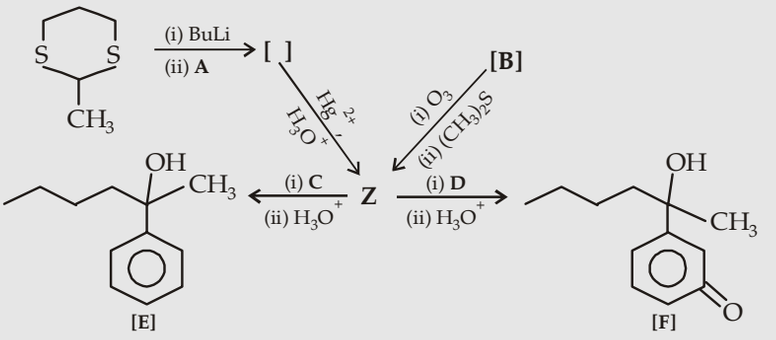


(B), Benzil

Benzilic acid

Example 27 :

Identify compounds A, B, C and D through the structure of the compound Z.



[E] [F]

EBD_7090

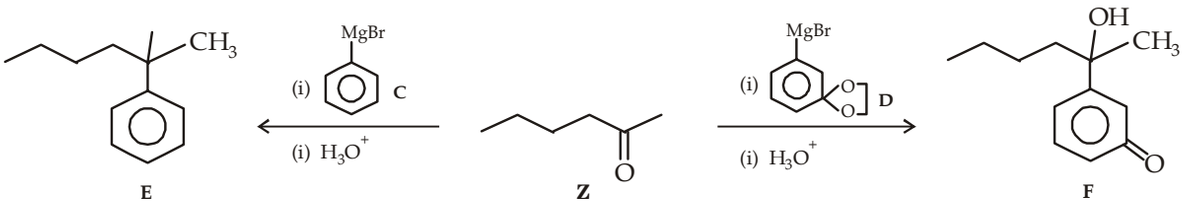
Solution :

The structure of compound Z can be established with the help of the known structure of the compounds E and F with the help of following facts.

(a) Both are 3° alcohols and formed by identical reaction which seems to be Grignard reagent. Further both E and F have $CH_3CH_2CH_2CH_2-$ group as common, so the compound Z can be a Grignard reagent or a ketone with *n*-butyl group as one alkyl group.

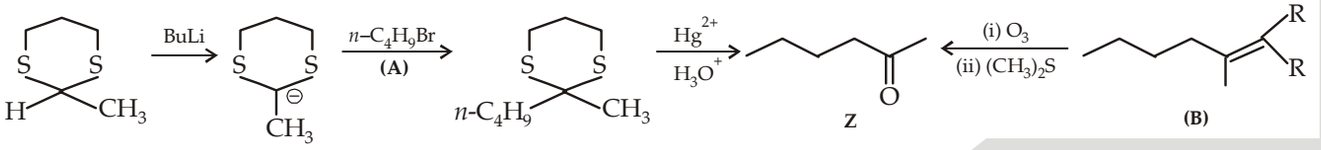
(b) Further the formation of Z from A and B suggests that Z is a ketone rather than the Grignard reagent.

Thus the compound Z is hexa-2-one which explains all reactions.



E **Z** **F**

Formation of Z from A and B separately :

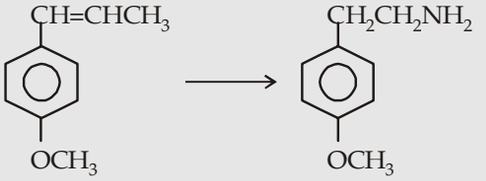


Z **(B)**

Example 28 :

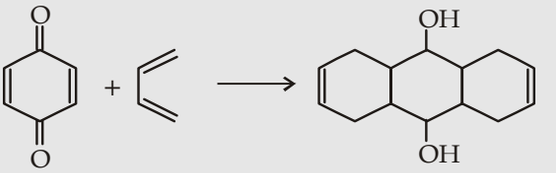
Give steps involved in each of the following conversions.

(a)



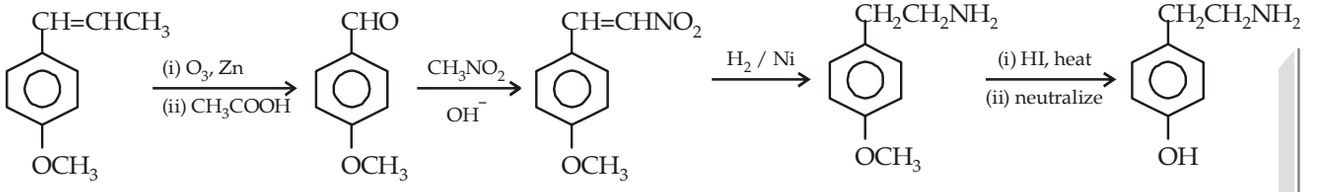
Anethole Tyramine

(b)

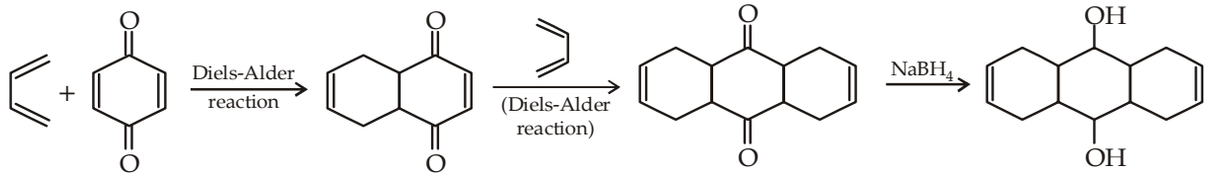


Solution :

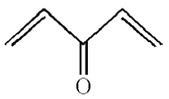
(a)



(b)



EXERCISE 14.1 (MCQ - ONE option correct)

1.  has its IUPAC name as

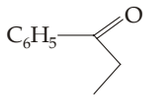
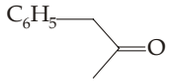
(*a*) divinyl ketone (*b*) 1, 4-pentdien-3-one (*c*) 1, 3-penten-2-one (*d*) 1, 4-pentandione-3.

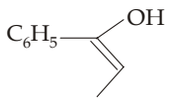
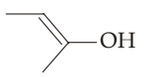
2. In the following reaction, the compound A is

$$[A] \xrightarrow{H_2SO_4,\ HgSO_4} CH_3CH_2COCH_3$$

(*a*) $HC \equiv CCH_2CH_3$ (*b*) $CH_3C \equiv CCH_3$
(*c*) Either of the two (*d*) $CH_3CH_2CH = CH_2$

3. $C_6H_5C \equiv CCH_3 \xrightarrow{Hg^{2+}/H^+}$ A. Here A is

(*a*)  (*b*) 

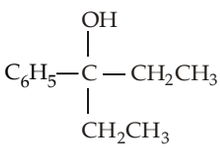
(*c*)  (*d*) 

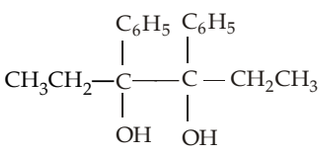
4. Carbonyl compounds show two types of important properties : nucleophilic addition and acidity of α-hydrogen atoms. Which factor is most useful in explaining these two ?
(*a*) Presence of carbon-oxygen double bond
(*b*) Resonance in carbonyl group
(*c*) Ability of oxygen to accommodate negative charge
(*d*) All are equally important.

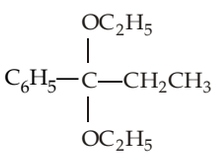
5. Identify the end product in the following series of reactions

$$C_6H_6 + CH_3CH_2COCl \xrightarrow{AlCl_3} [B] \xrightarrow[ether]{Mg} \text{End product}$$

(*a*) $C_6H_5COCH_2CH_2Mg$

(*b*) 

(*c*) 

(*d*) 

6. Identify the nature of the compound (Z).

$$\underset{\text{n-Butyl alcohol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow{CrO_3/\text{Pyridino}} [X] \xrightarrow{(CH_3)_2CHCH_2MgBr} [Y] \xrightarrow[\text{Pyridine}]{CrO_3} [Z]$$

(*a*) $2CH_3CH_2CH_2COOH$
(*b*) $CH_3CH_2CH_2COOH + (CH_3)_2CHCOOH$
(*c*) $CH_3CH_2CH_2COCH_2CH(CH_3)_2$
(*d*) $CH_3CH_2CH_2CHOHCH_2CH(CH_3)_2$.

7. An organic compound A of the molecular formula $C_5H_{10}Cl_2$ is hydrolyzed to compund B, $C_5H_{10}O$ which gives an oxime with hydroxylamine and yellow precipitate with a mixture of iodine and sodium hydroxide. The compound A should be
(*a*) $CH_3CH_2CCl_2CH_2CH_3$
(*b*) $CH_3CH_2CH_2CCl_2CH_3$
(*c*) $CH_3CH_2CH_2CH_2CHCl_2$
(*d*) $CH_3CH_2CH_2CHClCH_2Cl$.

8. Identify the nature of the reagent in the following reaction.

$$C_6H_5CH = C(CH_3)COCH_3 \xrightarrow{?} C_6H_5CH = C(CH_3)COOH$$

(*a*) alk. $KMnO_4$ (*b*) conc. HNO_3
(*c*) NaOI, H^+ (*d*) any of the three.

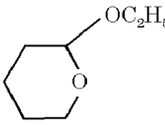
9. Identify the compound X in the following reaction.

$$C_6H_5COCHO \xrightarrow{OH^-} X$$

(*a*) $C_6H_5COCH_2OH$ (*b*) $C_6H_5CHOHCH_2OH$
(*c*) $C_6H_5CHOHCOO^-$ (*d*) $C_6H_5COO^- + CH_3OH$.

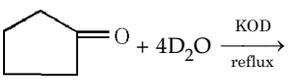
10. $CH_3CHO + H_2O^{18} \xrightarrow{HCl}$ Acetaldehyde. The structure of the product acetaldehyde is
(*a*) CH_3CHO (*b*) CH_3CHO^{18}
(*c*) A mixture of (*a*) & (*b*) (*d*) Reaction is not possible.

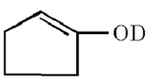
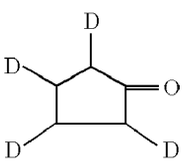
11. Observe the following two reactions, here the products (A) and (B) are
(*i*) $CH_3CHO + LiAlD_4 \longrightarrow [A]$
(*ii*) $CH_3CHO + D_2 \xrightarrow{Pt} [B]$
(*a*) CH_3CD_2OD (*b*) CH_3CHDOD
(*c*) CH_3CH_2OD (*d*) CH_3CHDOH.

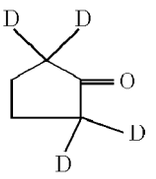
12. Identify P in the reaction,  $\xrightarrow{H_2O,\ H^+}$ P

(*a*) $HOCH_2CH_2CH_2CH_2CH_2CH_2OH + C_2H_5OH$
(*b*) $OHC.CH_2CH_2CH_2CH_2CHO$
(*c*) $HOCH_2CH_2CH_2CH_2CHO + C_2H_5OH$
(*d*) No reaction.

13. Identify the product, if any, in the following chemical equation

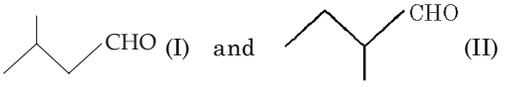


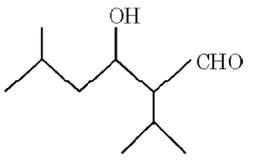
(*a*)  (*b*) 

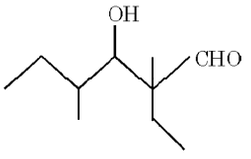
(*c*)  (*d*) No reaction takes place.

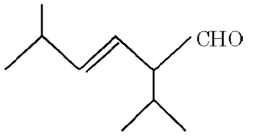
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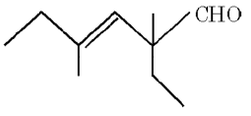
14. The most likely acid-catalysed aldol condensation products of each of the two aldehydes I and II will respectively be

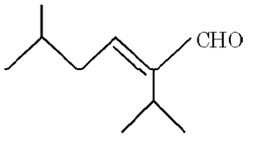


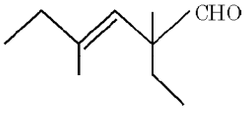
(*a*) 

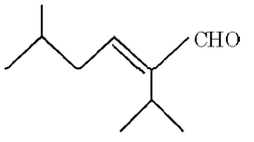
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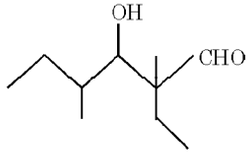
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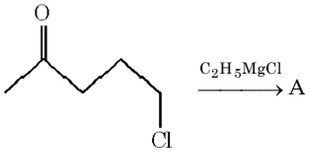
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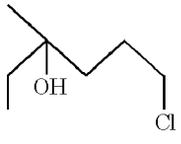
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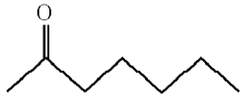
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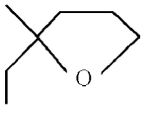
(*d*) 

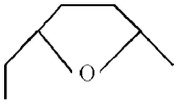
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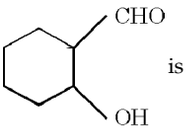
15. Identify A : 

(*a*) 

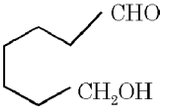
(*b*) 

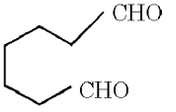
(*c*) 

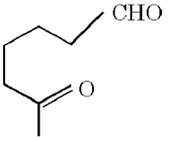
(*d*) 

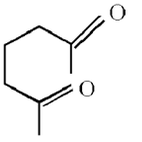
16. 

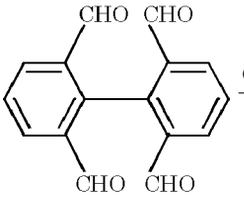
is formed by intramolecular aldol condensation of

(*a*) 

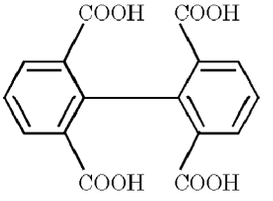
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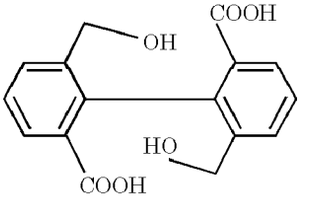
(*c*) 

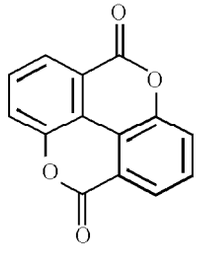
(*d*) 

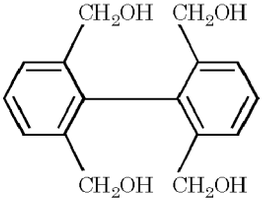
17. 

Major product is

(*a*) 

(*b*) 

(*c*) 

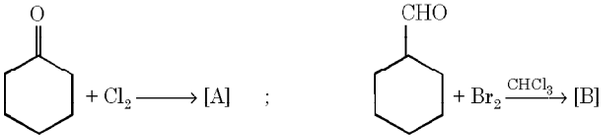
(*d*) 

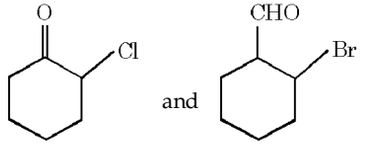
18. Which of the following will undergo hydration most readily ?

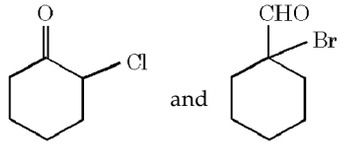
(*a*) CH_3COCH_3 (*b*) CH_3COCCl_3

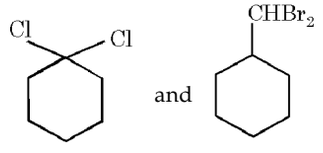
(*c*) CCl_3COCCl_3 (*d*) CF_3COCF_3.

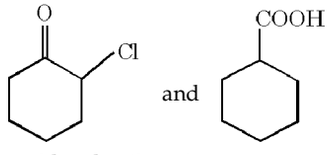
19. In the following reactions [A] and [B] respectively are



(*a*) 

(*b*) 

(*c*) 

(*d*) 

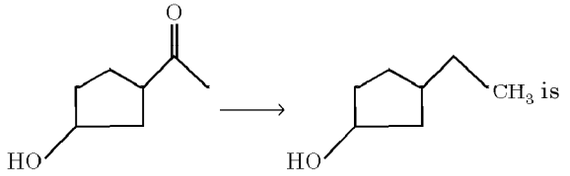
20. Acetic acid on heating gives
(*a*) methane (*b*) ethane
(*c*) methyl radical (*d*) ketene.

21. Which one is the best method for reducing 3-bromopropanal to 1-bromopropane ?

$$BrCH_2CH_2CHO \longrightarrow BrCH_2CH_2CH_3$$

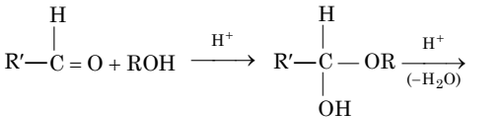
(*a*) Wolf-Kishner reduction
(*b*) Clemmensen reduction
(*c*) Either of the two
(*d*) None of the two.

22. The appropriate reagent for the following transformation

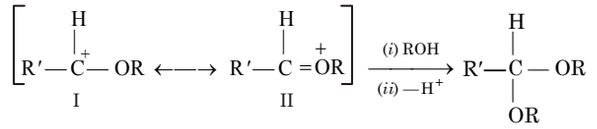


(*a*) Zn (Hg), HCl (*b*) NH_2NH_2, OH^-
(*c*) H_2/Ni (*d*) $NaBH_4$.

23. Aldehydes when treated with alcohols form first hemiacetals and then acetals in the following way



A hemiacetal



In the above reaction, which of the two cations is more stable?
(*a*) I (*b*) II
(*c*) Both are equally stable (*d*) None is stable.

24. The enol form of acetone, after treatment with D_2O gives

(*a*) $CH_3-\overset{\overset{OD}{|}}{C}=CH_2$ (*b*) $CD_3-\overset{\overset{O}{\|}}{C}-CD_3$

(*c*) $CH_2=\overset{\overset{OH}{|}}{C}-CH_2D$ (*d*) $CD_2=\overset{\overset{OD}{|}}{C}-CD_3$

25. How many α hydrogens are present in benzyl methyl ketone,
(*a*) 3 (*b*) 4 (*c*) 5 (*d*) No

26. In the Cannizzaro reaction, given below,

$$2C_6H_5CHO \xrightarrow{OH^-} C_6H_5CH_2OH + C_6H_5COO^-$$

the slowest step is
(*a*) the attack of OH^- at the carbonyl group
(*b*) the transfer of hydride to the carbonyl group
(*c*) the abstraction of proton from the carboxylic acid
(*d*) the deprotonation of $C_6H_5CH_2OH$.

27. Among the following compounds, which will react with acetone to give product containing >C = N –.
(*a*) $C_6H_5NHCOCH_3$ (*b*) $(CH_3)_3N$
(*c*) $C_6H_5NHC_6H_5$ (*d*) $C_6H_5NHNH_2$.

28. $C_6H_5CH(OH)CH(OH)CH_3 \xrightarrow{H^+}$ [A]. Here [A] is
(*a*) $C_6H_5CH=CHCH_3$ (*b*) $C_6H_5CH=C(OH)CH_3$
(*c*) $C_6H_5COCH_2CH_3$ (*d*) $C_6H_5CH_2COCH_3$.

29. $C_6H_{11}Cl \xrightarrow[(ii)\ Li,\ (iii)\ CuLi]{(i)\ Mg,\ ether}$ [A] $\xrightarrow{CH_3CH_2COCl}$ [B].

The compund B is

(*a*) $C_6H_{11}-\overset{\overset{OH}{|}}{\underset{\underset{CH_2CH_3}{|}}{C}}-CH_2CH_3$ (*b*) $C_6H_{11}COCH_2CH_3$

(*c*) $C_6H_{11}CH_2COCH_3$ (*d*) $C_6H_{11}CH_2CH_2CHO$.

30. Which of the following compunds is oxidised to prepare methyl ethyl ketone ?
(*a*) 2-Propanol (*b*) 1-Butanol
(*c*) 2-Butanol (*d*) *tert*-Butyl alcohol.

31. The product formed by the reaction of chlorine with C_6H_5CHO in the absence of catalyst is
(*a*) chlorobenzene (*b*) benzyl chloride
(*c*) benzoyl chloride (*d*) *o*-chlorobenzaldehyde.

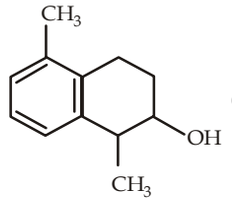
32. Which alkene is formed from the following ylide carbonyl pair ?
$CH_3CH_2CH_2CH=PPh_3$ + 2-Butanone
(*a*) 3-Methyl-3-heptene (*b*) 4-Methyl-3-heptene (*c*) 5-Methyl-3-heptene (*d*) 1-Methyl-5-heptene.

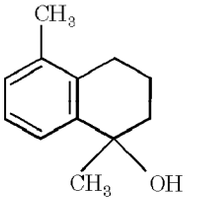
33. An organic compound A has the molecular formula C_3H_6O. It undergoes iodoform test. When saturated with HCl it gives B of molecular formula $C_9H_{14}O$; A and B respectively are
(*a*) propanal and mesitylene
(*b*) propanone and mesityl oxide
(*c*) propanone and 2, 6-dimethyl-2, 5-heptadien-4-one
(*d*) propane and mesitylene oxide.

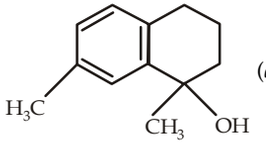
34. Compound A (molecular formula C_3H_8O) is treated with acidified dichromate to form a product B (molecular formulae C_3H_6O). B forms a shining silver mirror on warming with ammonical silver nitrate.B when treated with an aqueous solution of $H_2NCONHNH_2HCl$ and sodium acetate gives a product C. Identify the structure of C
(*a*) $CH_3CH_2CH=NNHCONH_2$
(*b*) $(CH_3)_2C=NNHCONH_2$
(*c*) $(CH_3)_2C=NCONHNH_2$
(*d*) $CH_3CH_2CH=NCONHNH_2$.

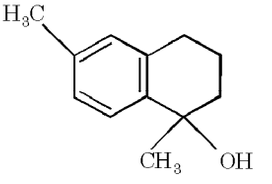
35. Identify the final product (D).

$$C_6H_5CH_3 + (CH_2CO)_2O \xrightarrow{AlCl_3} [A] \xrightarrow[HCl]{Zn/Hg} [B] \xrightarrow{HF} [C] \xrightarrow[(ii)\ H_3O^+]{(i)\ CH_3MgI} [D]$$

(*a*) 

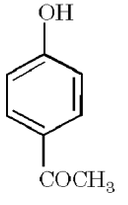
(*b*) 

(*c*) 

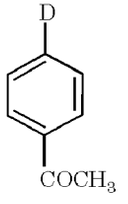
(*d*) 

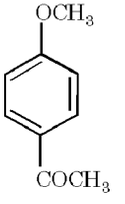
36. Identify the final product [E]

$$C_6H_6 \xrightarrow{Br_2/Fe} [A] \xrightarrow{(CH_3CO)_2O, AlCl_3} [B] \xrightarrow{CH_3OH/HCl} [C] \xrightarrow[(ii)\ D_2O]{(i)\ Mg} [D] \xrightarrow{H_3O^+} [E]$$

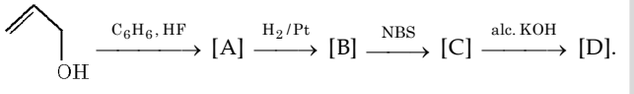
(*a*) 

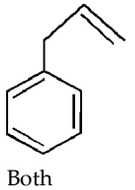
(*b*) 

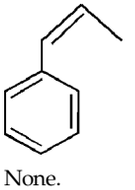
(*c*) 

(*d*) 

37. Identify the final product D in the following reaction.



(*a*) 

(*b*) 

(*c*) Both (*d*) None.

38. Which compound(s) does(do) not undergo **Cannizzaro condensation**?

(*a*) Methanal (*b*) Trichloroacetaldehyde
(*c*) Benzaldehyde (*d*) Ethanal

39. Treatment of propionaldehyde with dil. NaOH solution gives

(*a*) $CH_3CH_2COOCH_2CH_2CH_3$

(*b*) $CH_3CH_2CH(OH).CH(CH_3).CHO$

(*c*) $CH_3CH_2CHOHCH_2CH_2CHO$

(*d*) $CH_3CH_2COCH_2CH_2CHO$

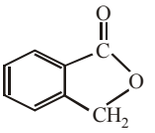
40. Which of the following forces explain the boiling point of aldehydes and ketones?

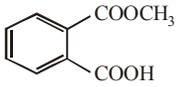
(*a*) Hydrogen bonding (*b*) Vander waal
(*c*) Dipole-dipole attraction (*d*) Any other

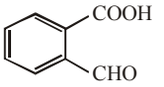
41. Which of the following will give yellow precipitate with I_2/NaOH?

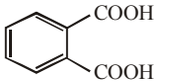
(*a*) $ICH_2COCH_2CH_3$ (*b*) $CH_3COOCOCH_3$
(*c*) CH_3CONH_2 (*d*) $CH_3CH(OH)CH_2CH_3$

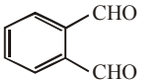
42. Which of the following reactants on reaction with conc. NaOH followed by acidification gives adjacent lactone as the product?



(*a*) 

(*b*) 

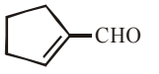
(*c*) 

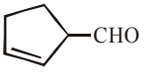
(*d*) 

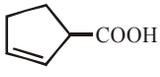
43. The smallest ketone and its next homologue are reacted with NH_2OH to form oxime

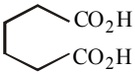
(*a*) Two different oximes are formed
(*b*) Three different oximes are formed
(*c*) Two oximes formed are optically active
(*d*) All oximes formed are optically active

44. Cyclohexene on ozonolysis followed by reaction with zinc dust and water gives compound **E**. Compound **E** on further treatment with aqueous KOH yields compound **F**. Compound **F** is

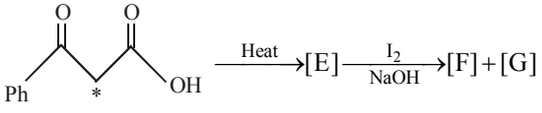
(*a*) 

(*b*) 

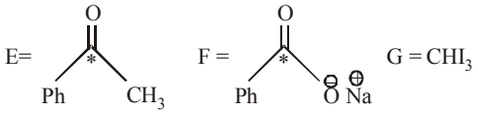
(*c*) 

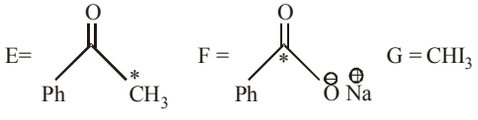
(*d*) 

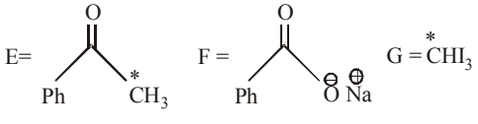
45. In the following reaction sequence, the correct structures of E, F and G are

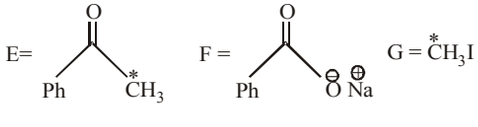


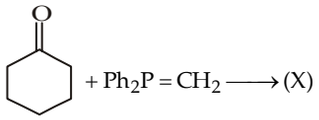
[* implies ^{13}C labelled carbon)

(*a*) 

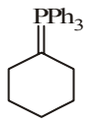
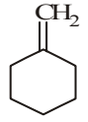
(*b*) 

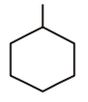
(*c*) 

(*d*) 

46.  $+ Ph_2P=CH_2 \longrightarrow (X)$

Product (X) is

(a)  (b) 

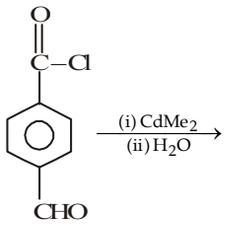
(c)  (d) 

47. $HC \equiv CH \xrightarrow[H_2SO_4]{HgSO_4} (A) \xrightarrow[5^\circ C]{dil.\ OH^\ominus} (B)$

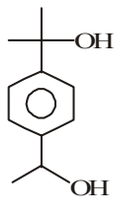
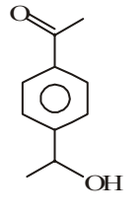
Give the IUPAC name of "B" is

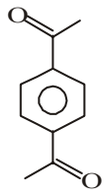
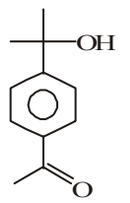
(a) 2-butenal (b) 3-hydroxybutanal

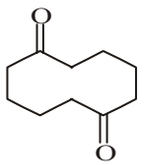
(c) 3-formyl-2-propanol (d) 4-oxo-2-propanol

48.  $\xrightarrow[(ii)\,H_2O]{(i)\,CdMe_2}$

Product is

(a)  (b) 

(c)  (d) 

49.  $\xrightarrow[H_2O]{Mg/Hg} A \xrightarrow[\Delta]{H_3/PO_4} B$

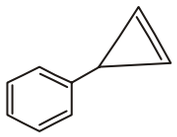
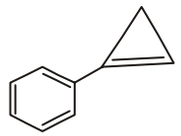
B is

(a) Bicyclo-[4, 4, 0] deca-1, 6-diene

(b) Cyclodecanone

(c) Spiro-[4, 5]-decan-6-one

(d) Bicyclo-[4, 4, 0] deca-1, 5-diene

50.  

To distinguish between the above isomeric hydrocarbons molecules, which will work best ?

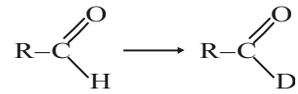
(a) Bromine water test

(b) O_3/H_2O, heating and passing evolved gas through lime water

(c) O_3/H_2O, Δ, $I_2/NaOH$

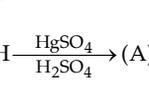
(d) Tollen's test

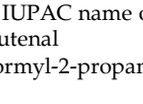
51. Which of the following sequence of reagents can best be utilized for the given transformation ?



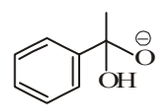
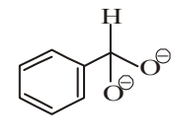
(a) Cl_2, AcOH; D_2O; $LiAlH_4/H_2O$

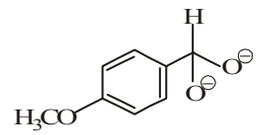
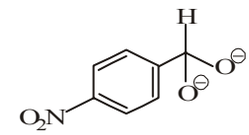
(b) D_2O/D_3O^+, Cl_2, AcOH; $NaBH_4/H_2O$

(c)  , base; D_2O and then $HgCl_2/CdCO_3 - H_2O$

(d) Base,  , $HgCl_2/CdCO_3 - H_2O$ and then D_2O

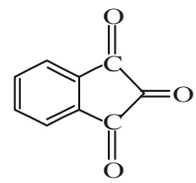
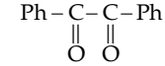
52. In a Cannizzaro reaction, the intermediate that will be the best hydride donor is

(a)  (b) 

(c)  (d) 

53. Which will form(s) stable gem-diol ?

I.  II. CCl_3CHO

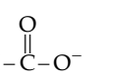
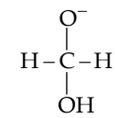
III.  IV. 

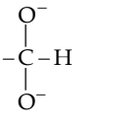
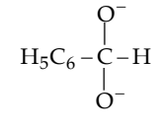
V. 

(a) I, II, III, V only (b) I, II, III, IV only

(c) II, III, IV only (d) II, III,

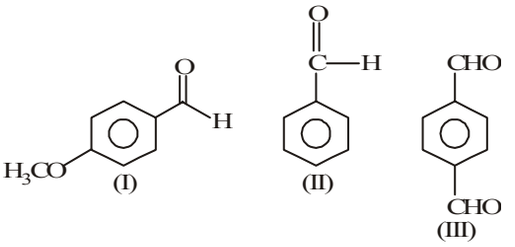
54. In Cannizaro reaction which species is best hydride donor (in conc. alkaline medium)

(a)  (b) 

(c)  (d) 

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55. The $K_{eq.}$ value in HCN addition to the following aldehydes are in the order :



(I) (II) (III)

(a) I > II > III (b) III > II > I
(c) III > I > II (d) II < I > III

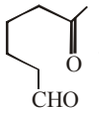
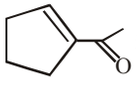
56. The major product obtained in the reaction :

$$H_5C_6-\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{CH}-CH_3 + D_2O \xrightarrow[\text{room temp.}]{OD^-}$$

is

(a) $H_5C_6-\overset{\overset{O}{\|}}{C}-\overset{\overset{CD_3}{|}}{CH}CH_3$ (b) $H_5C_6-\overset{\overset{O}{\|}}{C}-\overset{\overset{CD_3}{|}}{CD}-CD_3$

(c) $H_5C_6-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CD}-CH_3$ (d) None of these

57. The reacion  $\xrightarrow{OH^-}$  is an example of

(a) oxidation reaction (b) reduction
(c) both (d) aldol condensation

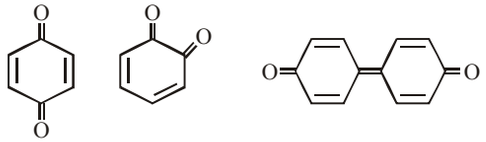
58. A new carbon - carbon bond is formed in

Aldol condensation (I) Kolbe's reaction (II)

Reimer-Tiemann reaction (III) Wurtz-Fittig reaction (IV)

(a) I, III (b) II, III
(c) I, III, IV (d) All the four

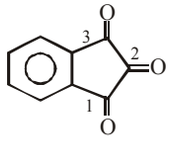
59. The correct stability order of the following three quinones is



I II III

(a) I > III > II (b) I = III > II
(c) I = II > III (d) III > I > II

60. Ninhydrin has three keto groups, which of the keto group is expected to be hydrated most easily?



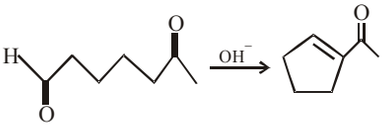
(a) 2 (b) 3
(c) 1 (d) all equal

61. $2\ \underset{\underset{COOH}{|}}{\overset{\overset{CHO}{|}}{}} \xrightarrow{OH^-} \underset{\underset{CH_2OH}{|}}{\overset{\overset{COO^-}{|}}{}} + \underset{\underset{COO^-}{|}}{\overset{\overset{COO^-}{|}}{}}$

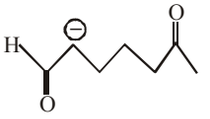
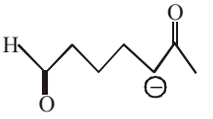
The above reaction can said be to an example of
(a) intramolecular Cannizzaro reaction
(b) intermolecular Cannizzaro reaction
(c) crossed Cannizzaro reaction
(d) Tischenko reaction

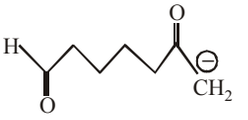
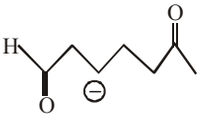
62. Which of the following complex hydride is a stronger reducing agent ?

(a) $Li^+[AlH_4]^-$ (b) $Li^+[Al(OCMe_3)_3H]^-$
(c) $Al(CH_2CHMe_2)_2H$ (d) All are equal

63. 

The above reaction involves

(a)  (b) 

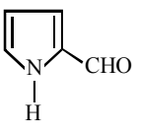
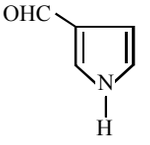
(c)  (d) 

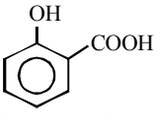
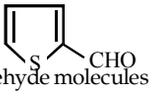
64. $CH_3CHO + 4HCHO \xrightarrow{Ca(OH)_2}$

$$C(CH_2OH)_4 + \frac{1}{2}(HCOO)_2Ca$$

the above reaction is an example of
(a) aldol condensation (b) Cannizzaro reaction
(c) both (d) none

65. Which of the following can't be prepared by the direct of Reimer –Tiemann reaction ?

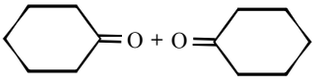
(a)  (b) 

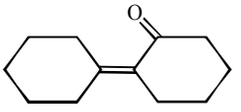
(c)  (d) 

66. Cannizzaro reaction between formaldehyde molecules involves the formation of

(a) $H-\underset{\underset{O^-}{|}}{\overset{\overset{OH}{|}}{C}}-H$ (b) $H-\underset{\underset{O^-}{|}}{\overset{\overset{O^-}{|}}{C}}-H$

(c) Both (a) and (b) (d) none

67.  $\xrightarrow{OH^-}$



This reaction is an example of
(a) Aldol condensation (b) Cannizzaro reaction
(c) Claisen condensation (d) Wittig reaction

EXERCISE 14.2 (MCQ 1 or >1 option correct, Passage based, Matching, A/R)

DIRECTIONS for Q. 1 to Q. 50 : Multiple choice questions with one or more than one correct option(s).

1. Which of the following statement is true regarding the following chemical reaction ?

$$CH_3CHO \xrightarrow{HCN} CH_3CHOHCN$$

(*a*) The product on hydrolysis gives a mixture of two compounds :
(*b*) The product is a mixture of two compounds which can be separated by fractional distillation.
(*c*) The product is a mixture of two compounds which can't be separated by fractional distillation.
(*d*) The product on hydrolysis gives a single compound.

2. One mole of $C_6H_5COCH_2CH_3$ is treated with one mole of Br_2 in basic solution, the product(s) formed is (are)
(*a*) 1 mole of $C_6H_5COCBr_2CH_3$
(*b*) 1 mole of $C_6H_5COCHBrCH_2Br$
(*c*) 0.5 mole of $C_6H_5COCBr_2CH_3$
(*d*) 0.5 mole of unreacted $C_6H_5COCH_2CH_3$.

3. Pentaerythritol, an important industrial chemical, is prepared by the following reaction

$$4CH_2O + CH_3CHO \xrightarrow{Ca[OH]_2} CH_2OH-\underset{\text{Pentaerythritol}}{\overset{\overset{CH_2OH}{|}}{\underset{CH_2OH}{\underset{|}{C}}}}-CH_2OH$$

This reaction involves
(*a*) Cannizzaro reaction (*b*) aldol condensation
(*c*) Crossed Cannizzaro (*d*) crossed aldol condensation

4. A mixture of cinnamaldehyde and crotonaldehyde is treated with concentrated alkali,

$$C_6H_5\overset{\beta}{C}H=\overset{\alpha}{C}HCHO + \overset{\gamma}{C}H_3\overset{\beta}{C}H=\overset{\alpha}{C}HCHO \xrightarrow{OH^-}$$

which statement is not true about the above reaction ?
(*a*) Aldol condensation takes place and α-carbon atom of crotonaldehyde provides the carbanion,
(*b*) Aldol condensation takes place and β-carbon atom of crotonaldehyde provides the carbanion.
(*c*) Aldol condensation takes place and γ-carbon atom of crotonaldehyde provides the carbanion.
(*d*) Aldol condensation takes place and α-carbon atom of cinnamic aldehyde provides the carbanion.

5. Which of the following undergoes Cannizzaro reaction ?
(*a*) $(CH_3)_3C.CHO$ (*b*) $(CH_3)_3CCDO$
(*c*) $C_6H_5CH_2Cl$ (*d*) CH_3CHO

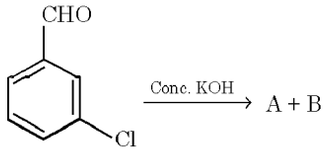
6. Each of the following two ketones is treated with a base (KOH)

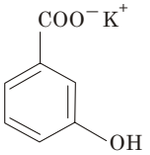
$$(+)-C_6H_5-\underset{\text{I}}{\overset{O}{\overset{||}{C}}-\overset{CH_3}{\overset{|}{CH}}-C_6H_5} \xrightarrow{OH^-} P_I;$$

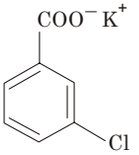
$$(+)-C_6H_5-\underset{\text{II}}{\overset{O}{\overset{||}{C}}-\overset{CH_3}{\overset{|}{\underset{C_2H_5}{\underset{|}{C}}}}-C_6H_5} \xrightarrow{OH^-} P_{II}$$

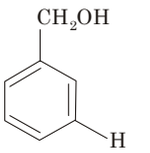
Which of the following statement is false regarding above reactions?
(*a*) Both P_I as well as P_{II} are racemic mixtures
(*b*) Both P_I as well as P_{II} are optically pure enantiomers
(*c*) P_I is optically pure while P_{II} is a racemic mixture
(*d*) P_I is a racemic mixture while P_{II} is optically pure.

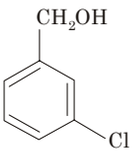
7. Predict the nature of products



(*a*) 

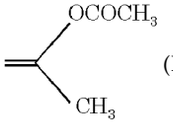
(*b*) 

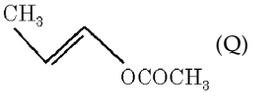
(*c*) 

(*d*) 

8. Which of the following can be used for the preparation of chloroform?
(a) $C_6H_5CHCl_2$ (b) CH_3CHO
(c) CD_3COCH_3 (d) CCl_3CHO

9. The product of acid hydrolysis of P and Q can't be distinguished by



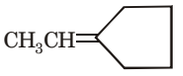
(P)


(Q)

(*a*) Lucas reagent (*b*) 2, 4-DNP
(*c*) Fehling solution (*d*) $NaHSO_3$.

10. Acetaldehyde is obtained in the reactions

(a) $CH_2=CH-CH_2-CH=CH_2 \xrightarrow[2.\ Zn,\ H_2O]{1.\ O_3}$

(b) 

(c) $HC\equiv CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4}$

(d) $CH_3COCl + H_2O \xrightarrow{Pd-BaSO_4}$

11. Which of the following statements are correct about a carbonyl group?
(a) The carbonyl carbon is sp^2–hybridized
(b) The carbonyl carbon is sp^3–hybridized
(c) The three groups attached to the carbonyl carbon lie in different planes
(d) The three groups attached to the carbonyl carbon lie in the same plane

12. Phosphorus pentachloride reacts with
(a) alcohols (b) ketones
(c) ethers (d) amines

13. Which of the following aldehydes undergo aldol condensation?
(a) CH_3CHO (b) C_6H_5CHO
(c) $C_6H_5CH_2CHO$ (d) *p*–ClC_6H_4CHO

14. Which of the following do not undergo base catalysed aldol condensation?
(a) Benzaldehyde
(b) 2,2, dimethyl propionaldehyde
(c) 2-methyl propionaldehyde
(d) p-methylbenzaldehyde

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15. Which of the following statements are correct about the C = O bond?
(a) It is made up of one π-bond and one σ-bond
(b) It is used the sp^2-hybrid orbital of carbon for its formation
(c) It is planar in nature
(d) It undergoes addition reactions

16. Which compound(s) undergoes (undergo) aldol condensation?
(a) Acetaldehyde (b) Benzaldehyde
(c) Phenylacetaldehyde (d) Ethylmethyl ketone

17. Dry distillation of a mixture of calcium acetate and calcium formate can form
(a) acetone (b) formaldehyde
(c) acetaldehyde (d) propanone

18. Which of the following are generally used for preparing derivatives of aldehydes and ketones?
(a) Hydroxylamine hydrochloride
(b) 2,4-Dinitrophenylhydrazine
(c) Phenylhydrazine hydrochloride
(d) Hydrogen cyanide

19. Base catalysed aldol condensation occurs with :
(a) propionaldehyde
(b) benzaldehyde
(c) 2-Methyl propionaldehyde
(d) 2, 2-Dimethyl propionaldehyde

20. Which of the following compounds will give a yellow precipitate with iodine and alkali?
(a) 2-Hydroxy propane (b) Acetophenone
(c) Methyl acetate (d) Acetamide

21. Which of the following compounds will react with ethanolic KCN?
(a) Ethyl chloride (b) Acetyl chloride
(c) Chlorobenzene (d) Benzaldehyde

22. Keto-enol tautomerism is observed in

(a) $H_5C_6-\overset{O}{\overset{\|}{C}}-H$ (b) $H_5C_6-\overset{O}{\overset{\|}{C}}-CH_3$

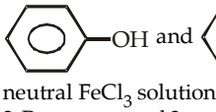
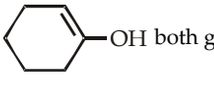
(c) $H_5C_6-\overset{O}{\overset{\|}{C}}-C_6H_5$ (d) $H_5C_6-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_3$

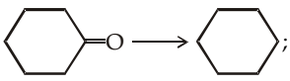
23. Which of the following are the examples of aldol condensation?
(a) $2CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3CHOHCH_2CHO$
(b) $2CH_3COCH_3 \xrightarrow{\text{dil. NaOH}} (CH_3)_2COHCH_2COCH_3$
(c) $2HCHO \xrightarrow{\text{dil. NaOH}} CH_3OH$
(d) $C_6H_5CHO + HCHO \xrightarrow{\text{dil. NaOH}} C_6H_5CH_2OH$

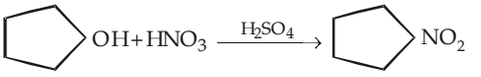
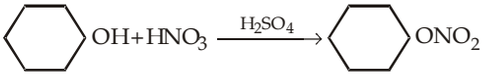
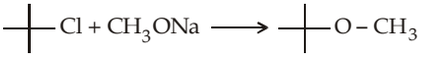
24. A new carbon-carbon bond formation is possible in
(a) Cannizzaro reaction (b) Friedel–Crafts alkylation
(c) Clemmensen reduction (d) Reimer–Tiemann reaction

25. Which of the following will undergo aldol condensation?
(a) Acetaldehyde (b) Propanaldehyde
(c) Benzaldehyde (d) Trideuteroacetaldehyde

26. Among the following compounds, which will react with acetone to give a product containing > C = N –bond ?
(a) $C_6H_5NH_2$ (b) $(CH_3)_3N$
(c) $C_6H_5NHC_6H_5$ (d) $C_6H_5NHNH_2$.

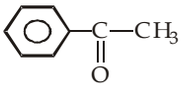
27. Select correct statements :
(a)  and  both give colour with neutral $FeCl_3$ solution
(b) 2-Pentanone and 3-pentanone are position isomers as well as metamers
(c) When benzaldehyde reacts with hydroxylamine product formed shows geometrical isomerism
(d) 1, 2-Dibromocyclohexane shows geometrical and optical isomerism

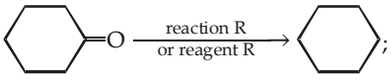
28.  ; This change can be carried out using:
(a) NH_2NH_2, glycol/OH^- (b) Sn(Hg)/conc. HCl
(c) P/HI (d) $NH_3/LiAlH_4$

29. In which cases products formed are not according to reaction?
(a) 
(b) 
(c) $CH_2=CH-CHO + LiAlH_4 \longrightarrow CH_3CH_2CH_2OH$
(d) 

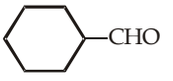
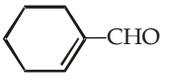
30. Which of the following compounds will give haloform test?

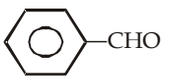
(a) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2I$ (b) $CH_3-\underset{Cl}{\underset{|}{CH}}-CH_3$

(c)  (d) CH_3CH_2Br

31.  ; R can be :
(a) Wolf Kischner reduction (b) Clemmensen reduction
(c) (P + HI) mixture (d) Rosen mund reduction

32. Cannizzaro reaction will be given by :

(a)  (b) 

(c)  (d) CCl_3CHO

33. $CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{SeO_2} A$; A will :
(a) reduce Tollens reagent (b) give iodoform test
(c) form dioxime (d) give Cannizzaro reaction

34. $3CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{\text{conc. } H_2SO_4} A$; which is/are correct statement(s) about A :
(a) A is an aromatic compound
(b) A can be oxidised to carboxylic acid
(c) A can undergo free radical as well as electrophilic substitution reaction
(d) A contains two carbonyl group

35. Identify the set from the following which contains the two compounds each of which can form acetone in a single-step reaction:
(a) $CH_3CH(OH)CH_3$, $(CH_3)_2C=CH_2$
(b) $(CH_3COO)_2Ca$, $(CH_3)_2C=CH_2$
(c) $(CH_3COO)_2Ca$, $CH_3C\equiv CH$
(d) $CH_3C\equiv CH$, $CH_3C(Cl)_2CH_3$

36. $CH\equiv CH \xrightarrow{HgSO_4/H_2SO_4} B \xleftarrow{\text{reaction R}} A$. A, B and reaction R are :

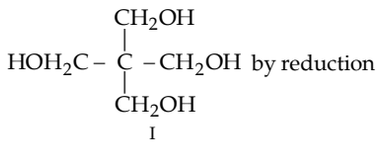
(a) $CH_3-\overset{O}{\overset{\|}{C}}-Cl$, CH_3CHO, Rosenmund ($Pd/BaSO_4$, H_2)

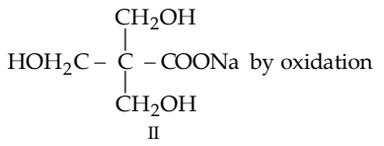
(b) CH_3COOH, $LiAlH_4$, hydroboration oxidation
(c) CH_3CN, CH_3CHO, Stephen ($SnCl_2$ / HCl)
(d) $CH\equiv CH$, CH_3CHO, hydroboration oxidation

37. Which is/are correct statement(s)?
(a) In presence of conc. H_2SO_4, CH_3CHO changes to cyclic trimer-paraldehyde which is a *hypnotic*
(b) At room temperature, HCHO forms cyclic trimer-trioxan
(c) In presence of $Ba(OH)_2$, HCHO forms hexose
(d) Bakelite is the polymer of HCHO and urea

38. $3HCHO + CH_3CHO \xrightarrow{NaOH} A$; A formed can :
(a) reduce Tollen's reagent
(b) give Cannizzaro reaction
(c) react with Na
(d) give green colour with $Cr_2O_7^{2-} / H^+$

39. A formed in previous question further reacts with NaOH to give:

(a)  by reduction
I

(b) 
II

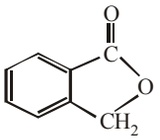
(c) only I (d) only II

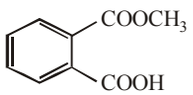
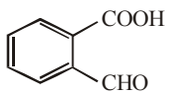
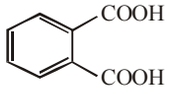
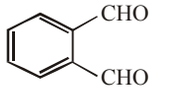
40. Which are correct statements :
(a) Cannizzaro reaction is proton-hydride transfer reaction
(b) Hofmann-degradation of acid amide involves intramolecular migration of alkyl/aryl group from C to N
(c) Fries migration is intramolecular
(d) Cannizzaro reaction is disproportionation

41. m-Chlorobenzaldehyde on reaction with conc. KOH at room temperature gives
(a) potassium m-chlorobenzoate
(b) m-hydroxy benzaldehyde
(c) m-chlorobenzyl alcohol
(d) m-hydroxybenzyl alcohol

42. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives
(a) benzyl alcohol (b) sodium benzoate
(c) sodium formate (d) methyl alcohol

43. Which of the following reactants on reaction with conc. NaOH followed by acidification gives following lactone as the product?



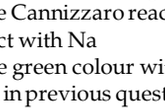
(a)  (b) 
(c)  (d) 

44. The smallest ketone and its next homologue are reacted with NH_2OH to form oxime
(a) Two different oximes are formed
(b) Three different oximes are formed
(c) Two oximes formed are optically active
(d) All oximes formed are optically active

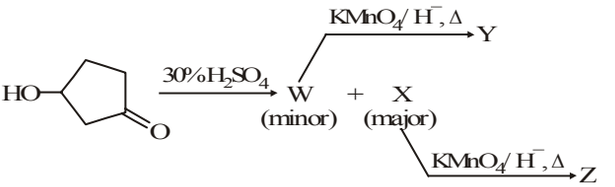
45. MeCHO and PhCHO will give different type of reaction with
(a) NaOI (b) Brady's reagent
(c) MeMgBr (d) KOH, Δ

46. $HCHO \xrightarrow[\Delta]{conc.\ NaOH} MeOH + HCOONa$
True about the above reaction is/are :
(a) it is Cannizzaro reaction
(b) it is redox reaction
(c) it is a bimolecular reaction
(d) it is a disproportionation reaction

47. Which of the following will give yellow precipitate with $NaOH/I_2$

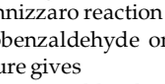
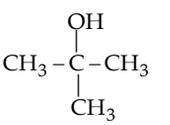
(a)  (b) CH_3CHO

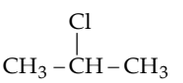
(c) (d) EtOH

48. 

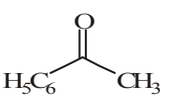
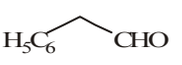
Of the 4 compounds listed above, more than one will :
(a) exhibit resonance due to conjugation in their structure
(b) show $NaHCO_3$ test
(c) have a cyclic structure
(d) show 2, 4-DNPH precipitation

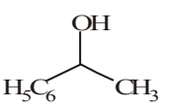
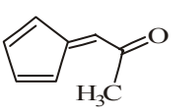
49. Which of the following compounds will give yellow crystals of iodoform on reaction with aq. NaOH + I_2 ?

(a)  (b) 

(c) $Ph-CO-CH_3$ (d) 

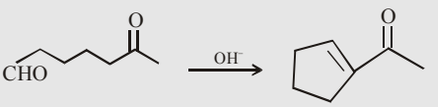
50. Compound (X), molecular formula C_8H_8O, is water insoluble and gives yellow ppt. with I_2/NaOH. It reacts with H_2NOH in presence of NH_4Cl/NH_4OH to give two geometrical isomers, which do not undergo dehydration but can go for rearrangement with acids. Compound (X) can be

(a)  (b) 

(c)  (d) 

INSTRUCTION for Q. 51 to 82 : Read the passages given below and answer the questions that follow.

PASSAGE 1



EBD_7090

51. The reaction is an example of
(a) aldol condensation
(b) crossed aldol condensation
(c) intramolecular aldol condensation
(d) none of the three

52. How many carbanions are possible in this case ?
(a) 1 (b) 2
(c) 3 (d) 4

53. Which of the functional group is acting as nucleophile ?
(a) Aldehyde (b) Ketone
(c) Either of the two (d) None of the two

PASSAGE 2

The carbonyl group C = O governs the chemistry of aldehydes and ketones in two ways (a) : by providing a site for nucleophilic addition, and (b) by increasing the acidity of the hydrogen atoms attached to the alpha carbon.

The mobile π electrons of the carbon-oxygen double bond are pulled strongly towards oxygen, which makes carbonyl oxygen electron-rich and carbonyl carbon electron-deficient. Further, since carbonyl group is flat, it is relatively open to attack from above or below. The positive charge on the carbonyl carbon atom means that it is especially susceptible to attack by a nucleophile. On the other hand, the negative charge on the carbonyl oxygen atom means that nucleophilic addition is susceptible to acid catalysis.

In addition to nucleophilic addition reactions, carbonyl compounds exhibit the unusual acidity of alpha-hydrogen atoms. The unusual acidity of the alpha-hydrogen of carbonyl compounds is due to its strong electron-withdrawing nature which in turn makes alpha-carbon also electron-withdrawing. Hence in presence of base it easily loses hydrogen as proton and itself converted into carbanion.

54. The carbonyl carbon is more reactive toward the nucleophile
(a) in presence of acids
(b) in absence of acids
(c) equally reactive in both cases
(d) in presence of base

55. The yield of hydrate is maximum in
(a) CH_3CHO (b) HCHO
(c) O_2NCH_2CHO (d) CH_3COCH_3

56. Which of the following reactions of aldehydes is due to nucleophilic addition on carbonyl group as well as due to acidic nature of the α-carbon atom?
(a) Reformatsky reaction (b) Aldol condensation
(c) Cannizzaro reaction (d) Wittig reaction

57. The final product obtained during aldol condensation of propanal is reduced in two ways.

$$[B] \xleftarrow{H_2,\ Pd/C} CH_3CH_2CH=\overset{CH_3}{\overset{|}{C}}CHO \xrightarrow{LiAlH_4} [A]$$

Which of the above reactions is a nucleophilic addition?
(a) Reaction leading to [A] (b) Reaction leading to [B]
(c) Both (d) None

58. The compounds A and B in the above question are

(a) $CH_3CH_2CH=\overset{CH_3}{\overset{|}{C}}CH_2OH$, $CH_3CH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_2OH$

(b) $CH_3CH_2CH=\overset{CH_3}{\overset{|}{C}}CH_2OH$, $CH_3CH_2CH_2\overset{CH_3}{\overset{|}{C}}HCHO$

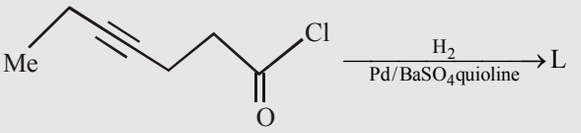
(c) $CH_3CH_2CH=\overset{CH_3}{\overset{|}{C}}CH_2OH$, $CH_3CH_2CH=\overset{CH_3}{\overset{|}{C}}OH$

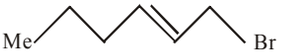
(d) $CH_3CH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_2OH$, $CH_3CH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_2OH$

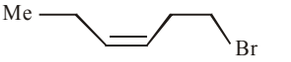
PASSAGE 3

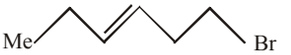
In the following reaction sequence, product I, J and L are formed. K represents a reagent.

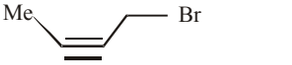
$$Hex-3-ynal \xrightarrow[2.PBr_3]{1.NaBH_4} I \xrightarrow[3.H_3O^+]{\substack{1.Mg/ether\\2.CO_2}} J \xrightarrow{K}$$

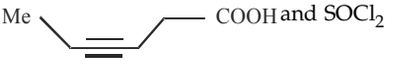


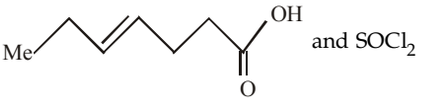
59. The structure of the product I is –
(a) 

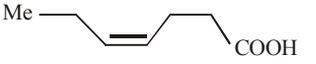
(b) 

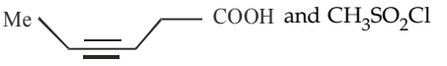
(c) 

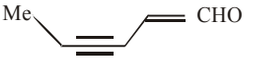
(d) 

60. The structures of compound J and K, respectively, are
(a) 

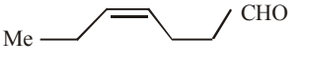
(b) 

(c) 

(d) 

61. The structure of product L is
(a) 

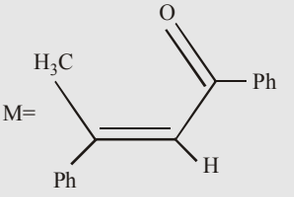
(b) 

(c) 

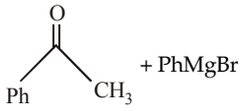
(d) 

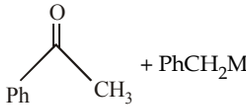
PASSAGE 4

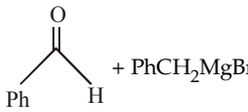
A tertiary alcohol H upon acid catalysed dehydration gives a product I. Ozonolysis of I leads to compounds J and K. Compound J upon reaction with KOH gives benzyl alcohol and compound L, whereas K on reaction with KOH gives only M.

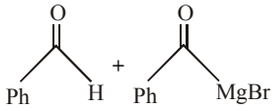


62. Compound H is formed by the reaction of

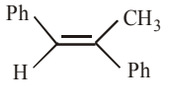
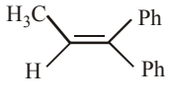
(a)  + PhMgBr

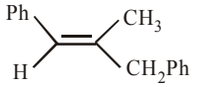
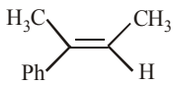
(b)  + $PhCH_2MgBr$

(c)  + $PhCH_2MgBr$

(d) 

63. The structure of compound I is

(a)  (b) 

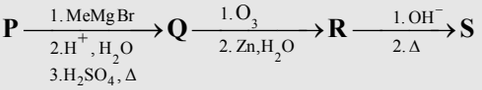
(c)  (d) 

64. The structure of compounds J, K and L respecitvely, are –

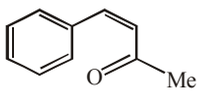
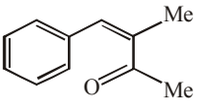
(a) $PhCOCH_3$, $PhCH_2COCH_3$ and $PhCH_2COO^-K^+$
(b) PhCHO, $PhCH_2CHO$ and $PhCOO^-K^+$
(c) $PhCOCH_3$, $PhCH_2CHO$ and $CH_3COO^-K^+$
(d) PhCHO, $PhCOCH_3$ and $PhCOO^-K^+$

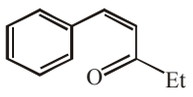
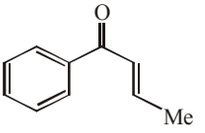
PASSAGE 5

A carbonyl compound **P**, which gives positive iodoform test, undergoes reaction with MeMgBr followed by dehydration to give an olefin **Q**. Ozonolysis of **Q** leads to a dicarbonyl compound **R**, which undergoes intramolecular aldol reaction to give predominantly **S**.

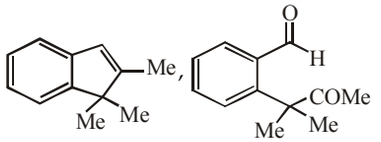


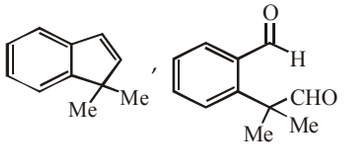
65. The structure of the carbonyl compound **P** is

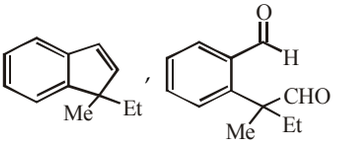
(a)  (b) 

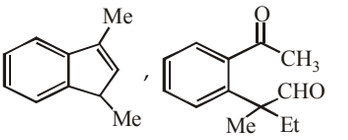
(c)  (d) 

66. The structures of the products **Q** and **R**, respectively, are

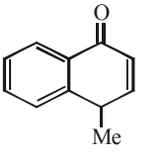
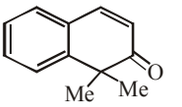
(a) 

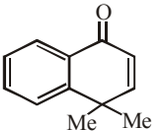
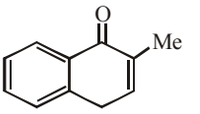
(b) 

(c) 

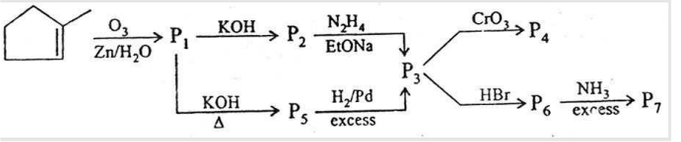
(d) 

67. The structure of the product **S** is

(a)  (b) 

(c)  (d) 

PASSAGE 6



68. Which of the following statement is correct about P_4 ?

(a) It will not give yellow/orange or red colour with 2, 4-DNP
(b) It will give red colour with ceric ammonia nitrate
(c) It will not give Fehling test
(d) It will give Bielstien test

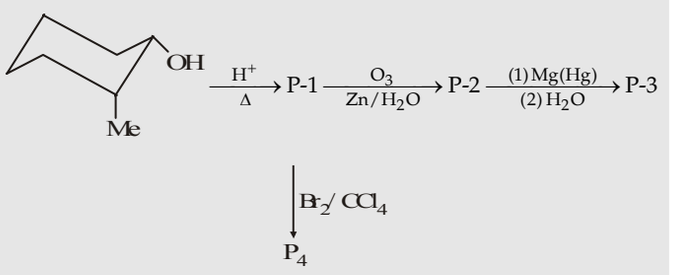
69. Which of the following statement is correct abot P_7 ?

(a) It will not give mustard oil reaction
(b) It will not give carbylamine test or isocyanide test
(c) It will decolourize bromine water
(d) It will give base soluble product with Hinsberg reagent

70. Which of the following reaction will be useful for conversion of P_3 to P_4.

(a) Clemmensen's reduction
(b) Oppenauer oxidation
(c) Meerwin Pondorff Verely reduction
(d) Tischenko reaction

PASSAGE 7



71. If methyl group is in axial position in product (P-4), then what is the position of Br atoms on C_1 and C_2 respectively.

(a) axial, equatorial (b) equatorial, axial
(c) axial, axial (d) equatorial, equatorial

EBD_7090

72. Correct sequence of reagents to convert P-4 into P-3.

(a) (i) Zn, Δ; (ii) dil. H_2SO_4

(b) (i) Na/Et_2O; (ii) B_2H_6; (iii) NaOH, H_2O_2

(c) (i) Mg (excess)/Et_2O; (ii) O_2 (excess); (iii) NH_4Cl (excess)

(d) (i) Mg (1 eq.); (ii) $Hg(OAc)_2 + H_2O$; (iii) $NaBH_4$

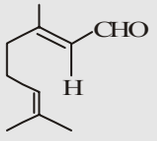
73. Which of the following will produce same visual change as P-1 with Br_2 water ?

(a)  (b) 

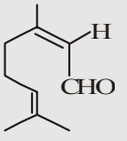
(c)  (d) None of these

PASSAGE 8

Citral or 3, 7-dimethyl-2, 6-octadienal is a mixture of a pair of terpenoids having molecular formula $C_{10}H_{16}O$. The two compounds are double bond isomers. The E-isomer is known as geranial (citral – *a*). The Z-isomer is known as neral (citral – *b*), whereas geranial has a strong lemon odour, neral enjoys a mild lemony fragrance. Citral therefore finds applications in making deodorants and soaps.



Citral - *a*



Citral - *b*

Citral, when subjected to reductive ozonolysis forms three compounds – X, Y and Z (decreasing molar mass, X > Y = Z)

74. Identify the 'false' statement :

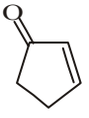
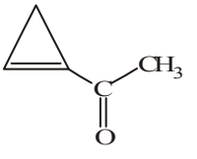
(a) Citral – *a* and *b* are diastereomers

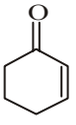
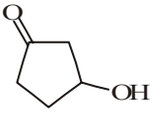
(b) All fragments obtained on reductive ozonolysis of reduced citral (Wolf-Kishner reduction) undergo haloform reaction

(c) Y and Z cannot be distinguished by Fehling's reagent

(d) Citral is an isoprene – based natural polymer (dimer)

75. X when reacted with 5% hot and dilute baryta water will form which major product;

(a)  (b) 

(c)  (d) 

76. 100 ml of an aqueous sample of Z when successfully titrated with $Ag(NH_3)_2^+$ followed by rapid and excess addition of hot and conc. H_2SO_4 evolves a mixture of gases which when passed over red hot charcoal occupy a volume of 6.72 ml at NTP. The molarity of the initial sample is

(a) 10^{-1} (b) 10^{-2}

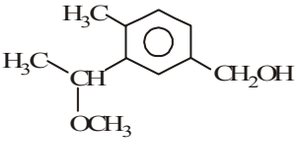
(c) 10^{-3} (d) 10^{-4}

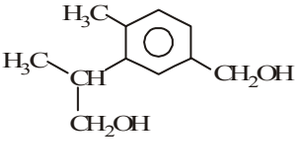
PASSAGE 9

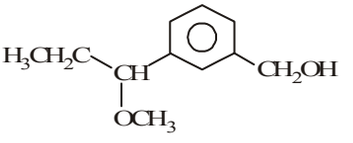
An optically active organic compound 'A' has molecular formula $C_{11}H_{16}O_2$ and it neither forms salt with NaOH nor decolourises bromine water, but evolves a gas on treatment with CH_3MgBr. A on treatment with HI gives another optically active compound $B(C_9H_{10}I_2)$. B on treatment with aqueous KOH yields another optically active compound $C(C_9H_{12}O_2)$. C on treatment with PCC yields $D(C_9H_8O_2)$ which gives positive iodoform test as well as positive Tollen's test. D is optically inactive and on treatment with $Cl_2/AlCl_3$ gives one and only one possible monochloro derivative $E(C_9H_7O_2Cl)$

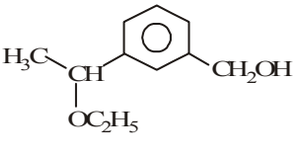
Based on the above information answer the fllowing questions :

77. The compound (A) is

(a) 

(b) 

(c) 

(d) 

78. Conversion of B into C mainly follows

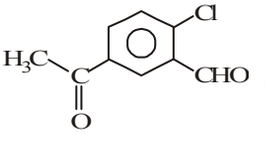
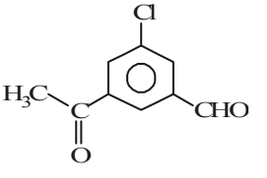
(a) S_N1 mechanism only

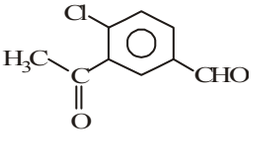
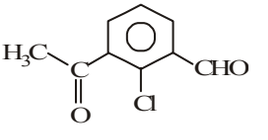
(b) S_N2 mechanism only

(c) S_N1 at one site and S_N2 at other site

(d) S_N^i only

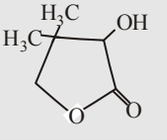
79. The compound 'E' is

(a)  (b) 

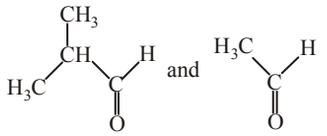
(c)  (d) 

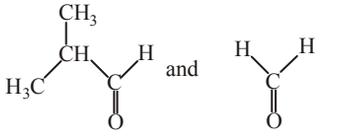
PASSAGE 10

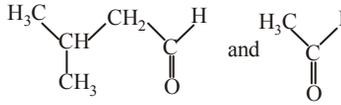
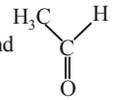
Two aliphatic aldehydes P and Q react in the presence of aqueous K_2CO_3 to give compound R, which upon treatment with HCN provides compound S. On acidification and heating, S gives the product shown below.

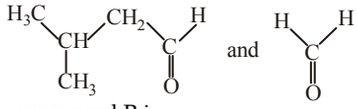
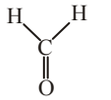


80. The compounds P and Q respectively are :

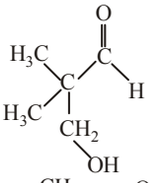
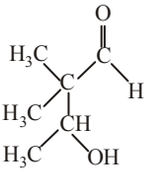
(a)  and

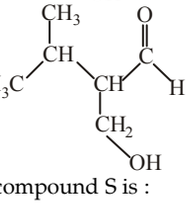
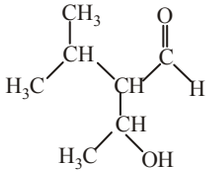
(b)  and

(c)  and 

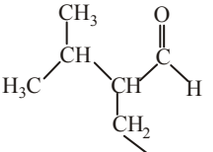
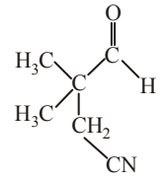
(d)  and 

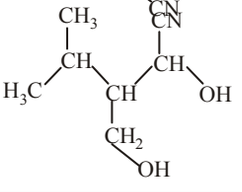
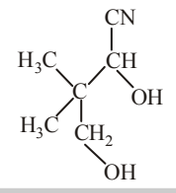
81. The compound R is :

(a)  (b) 

(c)  (d) 

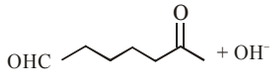
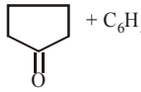
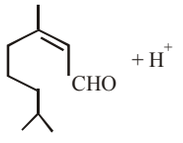
82. The compound S is :

(a)  (b) 

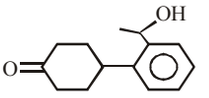
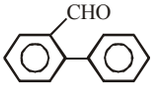
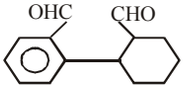
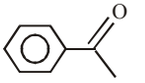
(c)  (d) 

Instructions for Q. 83 to Q. 88 : Following questions are Multiple Matching type Questions :

53. $\boxed{-CHO > C=O}$

	Column I		*Column II*
(A)		(a)	Cyclization
(B)		(b)	Aldol condensation
(C)		(c)	Ring expansion
(D)	$HOCH_2CH_2CH_2CH_2Cl + OH^-$	(d)	Williamson synthesis

84.

	Column I		*Column II*
(A)		(a)	aldol condensation
(B)		(b)	Cannizzaro reaction
(C)		(c)	haloform reaction
(D)		(d)	reaction with chlorine

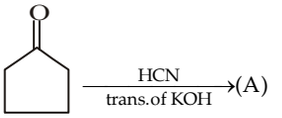
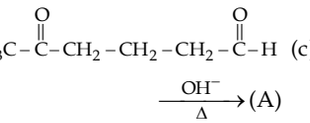
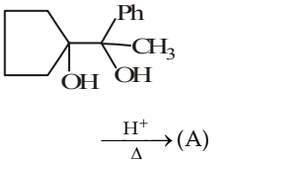
85.

	Column I		*Column II*
(A)	Schiff's reagent	(a)	Elimination reaction
(B)	Alcoholic KOH	(b)	colourless solution due to SO_2
(C)	Ammonical $AgNO_3$	(c)	Aldehydes
(D)	Benedict solution	(d)	Chloroform

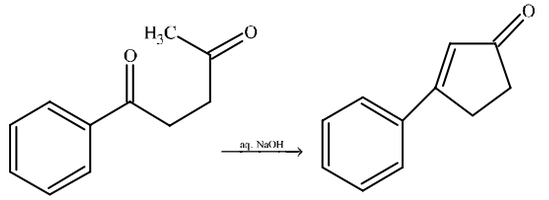
86.

Column - I	**Column - II**	**Column - III**
A. $CH_3CHO \xrightarrow{Zn/Hg.HCl}$	p.	w. Clemmensen reduction
B. $CH_3COCH_3 \xrightarrow{[H]}$	q. 	x. $LiAlH_4$ reduction
C. CH_3COCH_3	r. $CH_3CH_2CH_3$	y. Pinacol reduction
D. $CH_3COCH_3 \xrightarrow{Mg/HCl}$	s. CH_3CH_3	z. Wolf-Kishner reduction

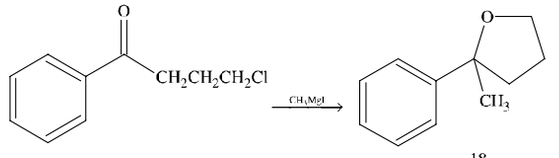
87. Match the column :

Column-I (Reactions)	**Column-II (products)**
A.  $\longrightarrow$ (B) $\longrightarrow$ (C)	(a) Formation of six membered ring takes place
B. 	(b) Final product is ketone or α, β-unsaturated ketone.
C. 	(c) Final product formed will give positive Tollen's test.
D. 	(sd) Final product formed will react with 2, 4-DNP
	(e) Ring expansion takes place

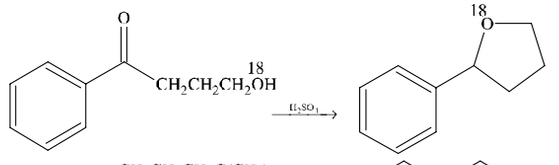
88. **Column I** **Column II**

(A) 

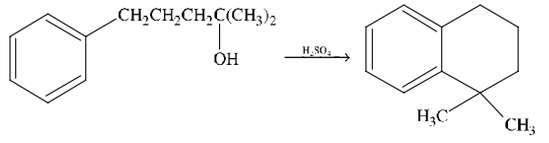
(a) Nucleophilic substitution

(B) 

(b) Electrophilic substitution

(C) 

(c) Dehydration

(D) 

(d) Nucleophilic addition

Instructions for Q. 89 to 100 : Following questions are Assertion and Reasoning Type Questions :
Note : Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 5 choices (a), (b), (c), (d) and (e) out of which ONLY ONE is correct.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement -1 is True, Statement-2 is False.
(d) Statement -1 is False, Statement-2 is True.
(e) Statement -1 is False, Statement-2 is False.

89. **Statement 1 :** Acetaldehyde on treatment with alkali gives aldol.
Statement 2 : Acetaldehyde molecule contains hydrogen atom.

90. **Statement 1 :** Acetylene on treatment with alkaline $KMnO_4$ produce acetaldehyde.
Statement 2 : Alkaline $KMnO_4$ is a reducing agent.

91. **Statement 1 :** Hydroxyketones are not directly used in Grignard reaction.
Statement 2 : Grignard reagents react with hydroxyl group.

92. **Statement 1 :** Isobutanal does not give iodoform test.
Statement 2 : It does not have α-hydrogen

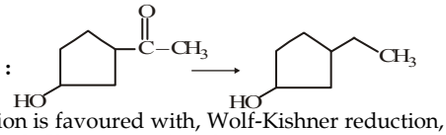
93. **Statement 1 :** Cyclohexanone forms cyanohydrin in good yield but 2, 4, 6-trimethyl cyclohexanone does not.
Statement 2 : The formation of cyanohydrin involves the nucleophilic attack by CN^- ion on the carbonyl carbon.

94. **Statement 1 :** There are two $-NH_2$ groups in semicarbazide.
Statement 2 : One group is involved in the formation of semicarbazones.

95. **Statement-1 :** Acetoacetic ester, $CH_3-\overset{O}{\overset{\|}{C}}-CH_2\overset{O}{\overset{\|}{C}}OC_2H_5$ will give iodoform test
Statement-2 : It contains $CH_3-\overset{O}{\overset{\|}{C}}-$group.

96. **Statement-1 :** Crossed Cannizzaro reaction between formaldehyde and benzaldehyde gives benzyl alcohol and formate ion.
Statement-2 : Formaldehyde is a better hydride donor than benzaldehyde.

97. **Statement-1 :** Protonation of a carbonyl group increases its electrophilic character.
Statement-2 : Protonation of a carbonyl group involves addition of an electrophile on nucleophilic oxygen.

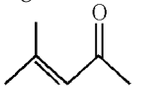
98. **Statement-1 :** 
This conversion is favoured with, Wolf-Kishner reduction, but unfavoured with Clemmensen's reduction.
Statement-2 : Clemmenson reduction is base sensitive reaction, whereas Wolf-Kishner reduction is acid sensitive.

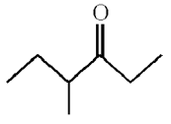
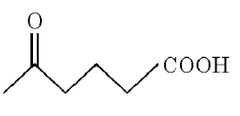
99. **Statement-1 :** Formaldehyde can't be prepared by Rosenmund's reduction method.
Statement-2 : Formyl chloride is unstable

100. **Statement-1 :** The aldol condensation product is $C_6H_5-\underset{OH}{CH}-\underset{CH_3}{CH}-CHO$ whcn propanal is slowly added to excess of benzaldehyde.
Statement-2 : On slow addition self aldol condensation of propanal can be prevented.

EXERCISE 14.3 (Subjective Problems)

1. Give IUPAC names for the following :

(*a*) $C_6H_5CH = CHCHO$ (*b*) 

(*c*)  (*d*) 

2. Give the structural formula of
(*a*) Trimethylacetaldehyde
(*b*) α, γ-Dimethylcaproaldehyde
(*c*) *p*, *p*′-Dimethylbenzophenone.

3. What are the expected H—C—O and H—C—H bond angles in CH_2O ?

4. Compare the polarities of the C = O and C = C bonds. How does this difference influence the reactivity of each bond as a nucleophilic site for reaction ?

5. Account for the following :
(*a*) The boiling points of 2-propanol, propanone, and 2-methylpropene differ very much, although they have approximately same molecular weight.
(*b*) Carbonyl compounds are more soluble in water than the corresponding alkanes but less than the corresponding alcohols.
(*c*) 2-Butanone has a lower $\Delta H°$ of combustion than butanol.

6. What is a ketene ? Give the structural formula and atomic orbital representation of ketene.

7. (*a*) How will you prepare an aldehyde by the reduction of a carboxylic acid ester ?
(*b*) Give the product of the reaction of *cis*-1, 2-cyclohexanediol with periodic acid. Why is the *trans*-glycol almost inert to this reagent ?

8. Give reagent(s) used for preparing $(CH_3)_2CHCH_2COCH_3$ from
(*a*) an alkyne (*b*) an alcohol
(*c*) an acid chloride + organocopper compound
(*d*) a carboxylic acid
(*e*) an acid chloride + organocadmium compound
(*f*) a nitrile.

9. Write the organometallic compound and other chemical compound (a carbonyl compound) used for preparing following alcohols.
(*a*) 1-Phenyl-1-propanol (*b*) 2-Phenyl-2-propanol
(*c*) 1-Phenyl-2-propanol (*d*) 3-Phenyl-1-propanol
(*e*) 1-Methylcyclohexanol (*f*) Cyclohexylmethanol
(*g*) 1-Cyclohexylethanol (*h*) 1-Pentyn-3-ol
(*i*) 3-Pentyn-2-ol (*j*) 1-(*p*-tolyl) ethanol.

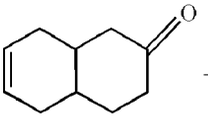
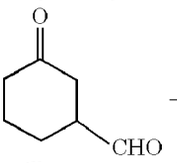
10. Write down the structure of the compound obtained when phenyl acetaldehyde or cyclohexanone is treated with each of the following reagents ?
(*a*) Tollen's reagent (*b*) CrO_3/H_2SO_4
(*c*) Cold dil. $KMnO_4$ (*d*) Acidic $KMnO_4$, heat
(*e*) H_2, Ni, pressure (*f*) $NaBH_4$
(*g*) C_6H_5MgBr, H_2O (*h*) $Me_2CHMgCl$, H_2O
(*i*) $HC \equiv CLi$, H_2O (*j*) Semicarbazide
(*k*) ethyl alcohol, dry HCl (gas) (*l*) *tert*-Butyl amine
(*m*) C_2H_5SH, H^+.

11. Convert propanal into following
(*a*) *n*-Propanol (*b*) α-Hydroxybutanoic acid
(*c*) *sec*-Butyl alcohol (*d*) 1-Phenyl-1-propanol
(*e*) 2-Methyl-3-pentanol.

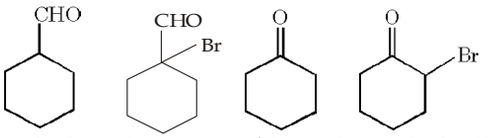
12. Name the reagent used to convert 2-methyl-2-pentenal to
(*a*) 2-methyl-2-pentenol (*b*) 2-methylpentanol
(*c*) 2-methylpentane (*d*) 2-methylpentanal.

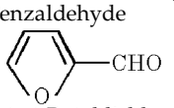
13. A carbonyl group can be reduced to methylene group by three methods : Clemmensen, Wolf-Kishner and Raney Ni desulphurization. How would you decide which method should be applied for a particular carbonyl compound?

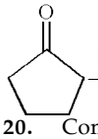
14. Select the best way for reducing the carbonyl group to methylene in each of the following :
(*a*) $BrCH_2CH_2CHO$ (*b*) $(CH_3)_2C(OH)CH_2CH_2COCH_3$
(*c*) $C_6H_5CHOHCH_2COC_2H_5$ (*d*) 

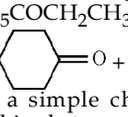
15. Identify the reduced product.
(*a*)  $\xrightarrow{Pt,\ 1\ eq.\ H_2}$ [A]
(*b*)  $\xrightarrow[CH_3OH]{1\ eq.\ NaBH_4}$ [B]

16. How will you convert $C_6H_5CH = CHCOCH_3$ to
(*a*) $C_6H_5CH = CHCOOH$ (*b*) $C_6H_5CH = CHCHOHCH_3$
(*c*) $C_6H_5CH_2CH_2COCH_3$ (*d*) $C_6H_5CH = CHCH_2CH_3$
(*e*) $C_6H_5CH_2CH_2CH_2CH_3$.

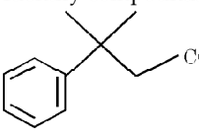
17. Arrange the following in decreasing ease of hydration :
(*a*) CH_3CHO, $(CH_3)_2CO$, HCHO, $CH_2ClCOCH_3$, CH_2ClCHO
(*b*) 

18. (*a*) Write down the structure of the product(s) obtained by treating each of the following aldehyde with conc. OH^-
(*i*) Benzaldehyde (*ii*) Trimethylacetaldehyde
(*iii*)  (*iv*) Benzal chloride
(*v*) *tert*-Butyldichloromethane
(*b*) Write down the structure of the product(s) obtained by treating each of the following with conc. NaOH.
(*i*) $C_6H_5CH_2CHO$ (*ii*) $CH_3CH = CHCHO$
(*iii*) $C_6H_5CH = CHCHO + CH_3CH = CHCHO$
(*iv*) CH_3CHO + 4 HCHO.

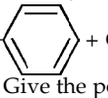
19. Identify A to D in the following series of reactions :
 $\xrightarrow[(ii)\ H_2O]{(i)\ CH_3MgI}$ [A] $\xrightarrow[heat]{H_2SO_4}$ [B] $\xrightarrow{(i)\ O_3/H_2O/Zn}$ [C] $\xrightarrow{OH^-}$ [D]

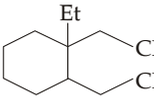
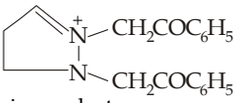
20. Complete the following reactions :
(*a*) $C_6H_5COCH_2CH_3 + SO_2Cl_2 \longrightarrow$
(*b*) Me_2  $+ NBS \longrightarrow$

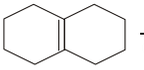
21. Describe a simple chemical test that can be applied for distinguishing between
(*a*) phenylacetaldehyde and benzyl alcohol
(*b*) 2-pentanone and 3-pentanone
(*c*) cyclohexanone and cyclohexyl methyl ether
(*d*) diethyl acetal and *n*-valeraldehyde
(*e*) diethyl acetal and di-*n*-propyl ether
(*f*) methyl *m*-tolyl ketone and propiophenone
(*g*) 2-pentanone and 2-pentanol
(*h*) paraldehyde and diisobutyl ether
(*i*) dioxane and trioxane.

22. Identify compounds [A] to [D] and explain their formation.
 $\xrightarrow{PCl_3}$ [A] $(C_{11}H_{13}OCl)$ $\xrightarrow{AlCl_3}$ [B] $(C_{11}H_{12}O)$
$\xrightarrow[heat]{NH_2NH_2, OH^-}$ [C] $(C_{11}H_{14})$ $\xleftarrow[\text{or Conc. } H_2SO_4]{AlCl_3}$ [D] $(C_{10}H_{13}CH_2OH)$

23. Identify the compounds [A] to [E] in the following reactions.
$n\text{-}C_5H_{11}C \equiv CH \xrightarrow{LiNH_2}$ [A] $\xrightarrow{CH_2ClCH_2CH_2Br}$ [B] $\xrightarrow[(ii)\ R'CHO]{(i)\ Mg}$
[C] $\xrightarrow[catalyst]{H_2,\ Lindlar}$ [D] $\xrightarrow{CrO_3}$ [E]

24. Identify [A] in the following reaction.
Cl—  $+ CCl_3CH(OH)_2 \xrightarrow{H^+}$ [Intermediate] $\xrightarrow[H^+]{C_6H_5Cl}$ [A]

25. Give the possible product(s) obtained in each of the following reactions.
(a)  $\xrightarrow{base}$ (b) 

26. Complete the following explaining each step
(*a*)  $\xrightarrow{CH_3OCH=PPh_3}$ [A] $\xrightarrow{H^+, H_2O}$ [B]
(*b*)  $\xrightarrow[(ii)\ Zn,\ CH_3COOH]{(i)\ O_3}$ [C] $\xrightarrow{base}$ [D]

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SOLUTIONS

EXERCISE 14.1

6	(c)	**11**	(b)	**16**	(b)	**21**	(b)	**26**	(b)	**31**	(c)	**36**	(c)	**41**	(d)	**46**	(b)	**51**	(c)	**56**	(c)	**61**	(b)	**66**	(c)
7	(b)	**12**	(c)	**17**	(c)	**22**	(b)	**27**	(d)	**32**	(a)	**37**	(b).	**42**	(d)	**47**	(b)	**52**	(c)	**57**	(d)	**62**	(a)	**67**	(a)
8	(c)	**13**	(c)	**18**	(d)	**23**	(b)	**28**	(c)	**33**	(c)	**38**	(d)	**43**	(b)	**48**	(b)	**53**	(a)	**58**	(d)	**63**	(b)		
9	(c)	**14**	(d)	**19**	(b)	**24**	(b)	**29**	(b)	**34**	(a)	**39**	(b)	**44**	(a)	**49**	(c)	**54**	(c)	**59**	(d)	**64**	(c)		
10	(b)	**15**	(c)	**20**	(d)	**25**	(c)	**30**	(c)	**35**	(c)	**40**	(c)	**45**	(c)	**50**	(c)	**55**	(b)	**60**	(a)	**65**	(b)		

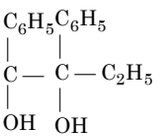
1. Theoretical

2. $HC \equiv CCH_2CH_3$ or $CH_3C \equiv CCH_3 \xrightarrow[Hg^{2+}]{H_2SO_4} CH_3CH_2COCH_3$

3. $C_6H_5C \equiv CCH_3 \xrightarrow{H^+} \underset{\substack{\text{Benzylic type carbocation}\\(\text{more stable})}}{C_6H_5\overset{+}{C} = CHCH_3} \longrightarrow$

$$C_6H_5\overset{\overset{+}{O}H_2}{\underset{|}{C}} = CHCH_3 \xrightarrow{-H^+} C_6H_5\overset{OH}{\underset{|}{C}} = CHCH_3 \xrightarrow{\text{tautomerises}} \underset{(a)}{C_6H_5COCH_2CH_3}$$

4. Theoretical

5. $C_6H_6 + C_2H_5COCl \xrightarrow{AlCl_3} C_6H_5COC_2H_5 \xrightarrow[\text{(bimolecular reduction)}]{\text{Mg, ether}}$ 

6. $n\text{-}C_3H_7CH_2OH \xrightarrow[\text{Pyridine}]{CrO_3} n\text{-}C_3H_7CHO \xrightarrow{Me_2CHCH_2MgBr} n\text{-}C_3H_7CH(OH)CH_2CHMe_2 \xrightarrow{CrO_3/\text{Pyridine}} n\text{-}C_3H_7COCH_2CHMe_2$

7. $CH_3CH_2CH_2CCl_2CH_3 \longrightarrow \underset{\text{unstable}}{[CH_3CH_2CH_2C(OH)_2CH_3]} \longrightarrow CH_3CH_2CH_2COCH_3 \xrightarrow{I_2/OH^-} \mathbf{CHI_3}\downarrow$

8. Alk. $KMnO_4$ and conc. HNO_3 can't be used because they oxidize the C = C bond too. Since the compound has —$COCH_3$ grouping, it can easily be oxidised by alkaline halogen (NaOX) ; **haloform reaction.**

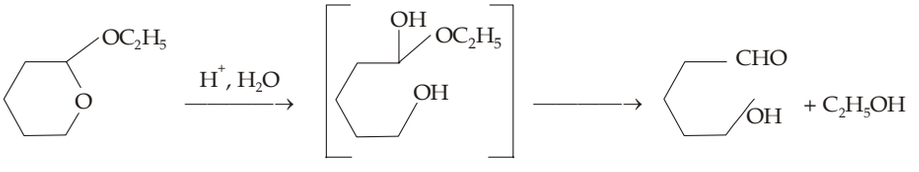
9. It is an example of internal crossed—Cannizzaro reaction.

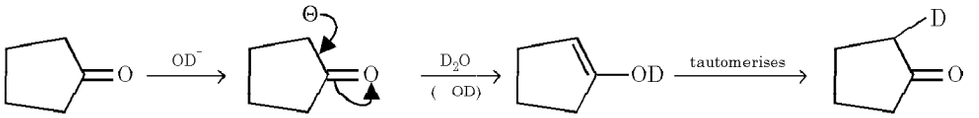
$$C_6H_5COCHO \xrightarrow{OH^-} C_6H_5CH(OH)COO^-\,Na^+$$

10. $CH_3CHO + H_2O^{18} \underset{}{\overset{H^+}{\rightleftharpoons}} \underset{\text{Hydrate}}{\left[CH_3\underset{OH}{\underset{|}{C}}HO^{18}H\right]} \underset{H^+}{\rightleftharpoons} CH_3CHO^{18} + H_2O$

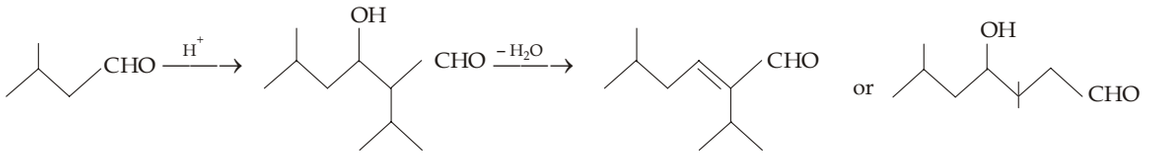
The unstable half-labelled hydrate loses H_2O but not H_2O^{18} because C—O^{18} bond is strong as compared to C—O^{16}, hence relatively difficult to cleave.

11. $>C = O + D_2/Pt$ (or $LiAlD_4$) $\longrightarrow >CDOD$

12. 

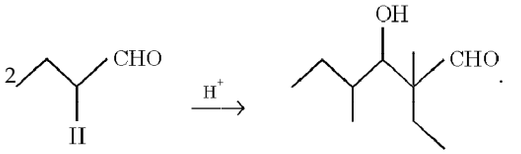
13. 

Reaction is repeated till all other α-hydrogen atoms are replaced.

14. 

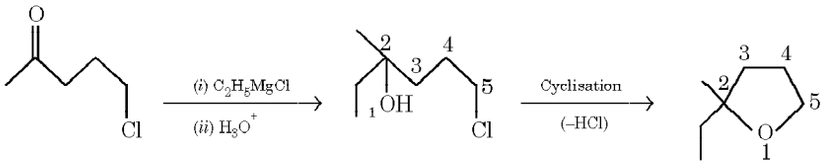
I

Conjugated system (stable)



It does not lose water because the double bond so formed will be isolated.

It does not lose water because the double bond so formed will be isolated.

15. 

3° alcohol

16. Since the product is having an aldehydic group, the reactant should be a dialdehyde because —CHO are more reactive than ketones so in a ketoaldehyde the final product should have a ketonic group.

17. It is an example of intramolecular Cannizzaro reaction followed by cyclization.

18. Presence of electron-withdrawing group on the carbonyl carbon atom increases nucleophilic addition.

19. Halogenation of carbonyl compounds takes place in α-position ; since aldehydes are easily oxidisable so here $CHCl_3$ is used and not water.

20. $CH_3COOH \xrightarrow{\text{heat}} CH_2 = C = O + H_2O$. This is an industrial method for the preparation of ketene, another method is

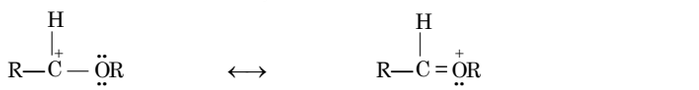
$CH_3COCH_3 \xrightarrow{700°} CH_2 = C = O + CH_4$.

21. $BrCH_2CH_2CHO \xrightarrow[HCl]{Zn\ (Hg)} BrCH_2CH_2CH_3$

Wolf-Kishner reduction will cause dehydrobromination (—HBr) because it involves alkaline conditions.

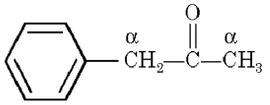
22. Zn(Hg), HCl is not used here, because the acidic medium of the reagent may cause dehydration.

23. II cation (oxonium ion) is more stable because here every atom has an octet of electrons



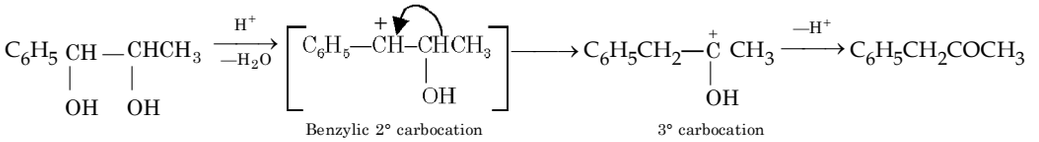
I (+vely charged C has six electrons) ⟷ II (each atom, except H, has eight electrons)

24. Recall that α H's of carbonyl compounds are easily replaced by D of D_2O.

25. 

26. Consult mechanism of Cannizzaro reaction.

27. Only $C_6H_5NHNH_2$ has —NH_2 group.

28. 

Benzylic 2° carbocation — 3° carbocation

29. $C_6H_{11}Cl \xrightarrow[(ii)\ Li,\ (iii)\ CuCl]{(i)\ Mg,\ ether} [C_6H_{11}]_2\ LiCu \xrightarrow{CH_3CH_2COCl} C_6H_{11}COCH_2CH_3$

[A] [B]

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30. Methyl ethyl ketone (a C_4 compound) can't be prepared from 2-propanol (a C_3 compound) ; *tert*-butyl alcohol, being 3° alcohol, is not oxidised easily, 1-butanol, a 1° alcohol will form aldehyde. Thus 2-butanol should be the answer.

$$CH_3\underset{|}{\overset{OH}{C}}HCH_2CH_3 \xrightarrow{\text{Oxidation}} CH_3COCH_2CH_3$$

31. $C_6H_5CHO \xrightarrow{Cl_2,\ h\nu} C_6H_5COCl$

32. $CH_3CH_2CH_2CH = PPh_3 + CH_3COCH_2CH_3 \xrightarrow[\text{reaction}]{\text{Wittig}} CH_3CH_2CH_2CH = \underset{\text{3-Methyl-3-heptene}}{\overset{CH_3}{\underset{|}{C}}CH_2CH_3}$

33. Since the compound A has the molecular formula C_3H_6O and undergoes iodoform test, it should be CH_3COCH_3. Further reaction of A with HCl gives $C_9H_{14}O$ having three times the number of carbon atoms in A, hence B should be trimer of acetone, *i.e.*, it should be *phorone*.

$$\underset{\text{Acetone (3 moles)}}{(CH_3)_2C = O + H_3CCOCH_3 + O = C(CH_3)_2} \longrightarrow \underset{\text{2, 6-Dimethyl-2, 5-heptadien-4-one (phorone)}}{(CH_3)_2C = CHCOCH = C(CH_3)_2}$$

34.

$$\underset{(A)}{C_3H_8O} \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{(B)}{C_3H_6O} \xrightarrow[CH_3COONa]{H_2NCONHNH_2\ HCl} C$$

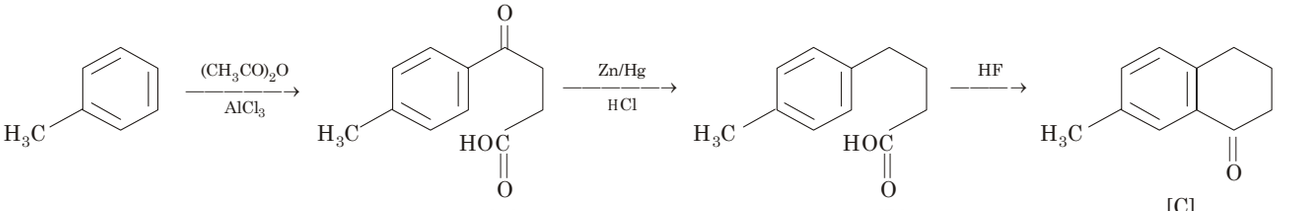
$$\downarrow \text{ Ammonical } AgNO_3$$

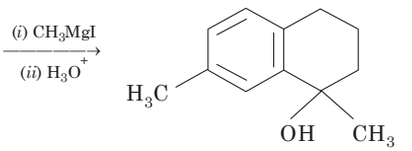
Silver mirror

Since B reduces ammonical silver nitrate, it should be an aldehyde and hence A is primary alcohol, which should be $C_2H_5CH_2OH$. Hence

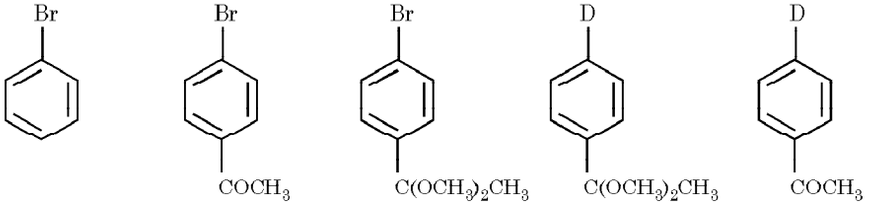
$$\underset{(A)}{CH_3CH_2CH_2OH} \xrightarrow{K_2Cr_2O_7,\ H_2SO_4} \underset{(B)}{CH_3CH_2CHO} \xrightarrow{H_2NCONHNH_2} \underset{(C)}{CH_3CH_2CH = NNHCONH_2}$$

35.

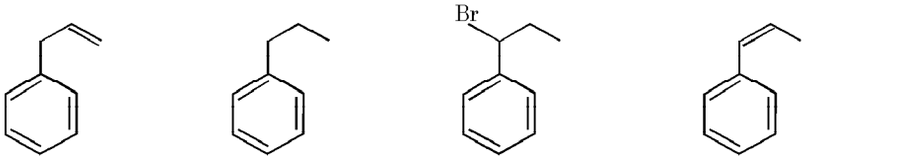


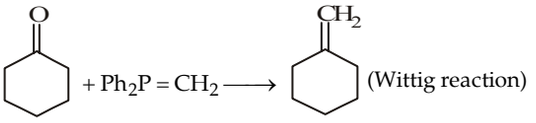


36.



37.

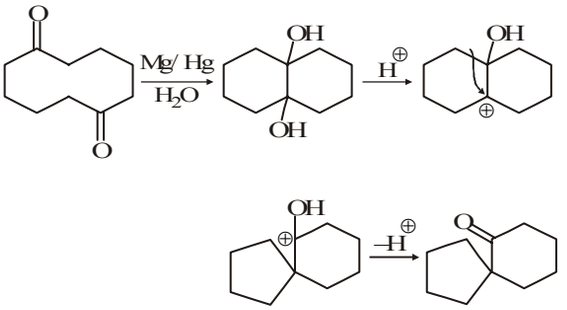


46. (b) 

47. (b) $CH \equiv CH \xrightarrow[H_2SO_4]{HgSO_4} CH_3 - CHO \xrightarrow[5°C]{dil.NaOH}$

$CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_2 - CHO$ (3-hydroxybutanal)

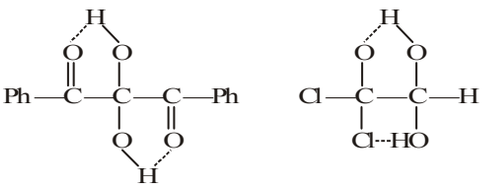
48. (b)

49. (c) 

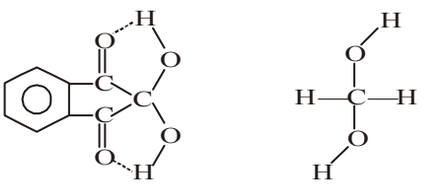
50. (c) Both molecules will respond to A and B; neither will respond to D.

51. (c) Aldehyde is first converted into cyclic thioacetal and then strong base like PhLi is used to generate carbanion and then treated with D_2O. Finally, the aldehyde is regenerated.

52. (c) The methoxy group being electron-releasing group makes the release of hydride group more easy.

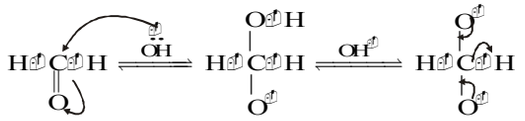
53. (a) 

(I) (I)



(III)

(V)

54. (c) 

The dianion will clearly be a much powerful hydride donor.

55. (b) III > II > I

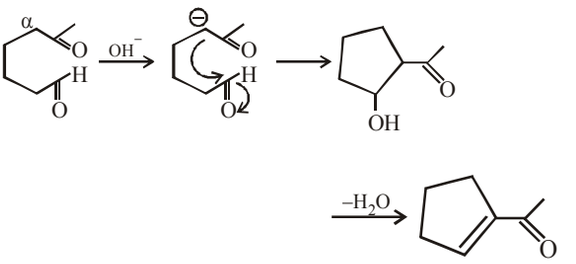
In I, $-OCH_3$ is electron donating group (+M) so will decrease the electron deficiency of carbonyl carbon to the most.

In II, there is no electron donating group.

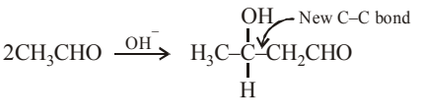
In III, electron withdrawing group is present which will increase electron deficiency at carbonyl carbon.

56. (c) Under basic conditions only the protons at carbon atom $\propto$ to the carbonyl group are replaced by deuterium.

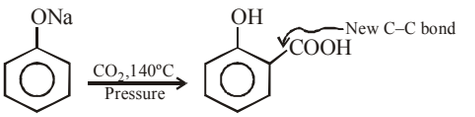
57. **(d)** It is an example of intramolecular aldol condensation. The carbon atom labelled as α acts as a nucleophile.



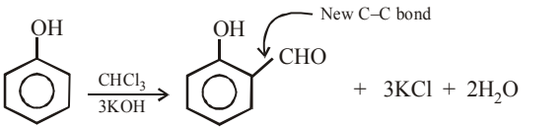
58. **(d)** Aldol condensation :



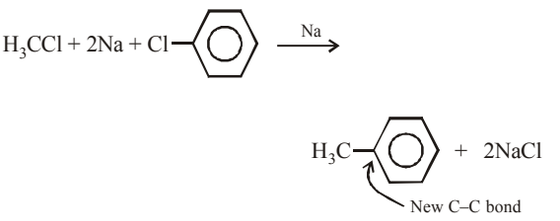
Kolbe reaction :



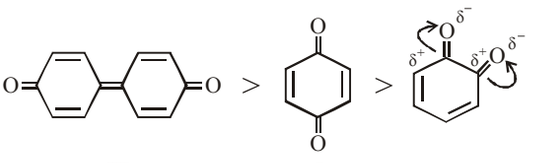
Reimer-Tiemann reaction :



Wurtz-Fittig reaction :



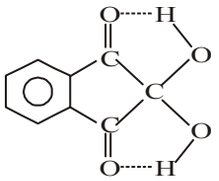
59. **(d)** The keto group has considerable resonance energy ; hence more the number of keto groups in a compound, higher is its stability. However, here all the three compounds have same (two) number of keto groups. Compound II is least stable because two adjacent keto groups destabilize the molecule due to positive charge on the adjacent carbon atoms. Relative stability of I and III can be ascertained by the stability of their fully reduced forms (phenols), since fully reduced form of III has two benzene rings, it will be more stable than the I whose reduced form has only one benzene ring. Thus



III I II

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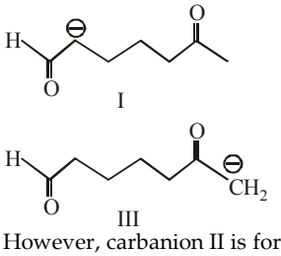
60. **(a)**



61. **(b)** **Two molecules of the same aldehyde** are reacting in presence of alkali to form sodium salt of the acid and an alcohol, hence it is an example of intermolecular Cannizzaro reaction.

62. **(a)** Lithium tri-tert-butoxyaluminium hydride (LBAH) and diisobutyl-aluminium hydride (DBAH) are less reactive than LAH because they are much more sterically hindered and hence face difficulty in transferring their hydride ions.

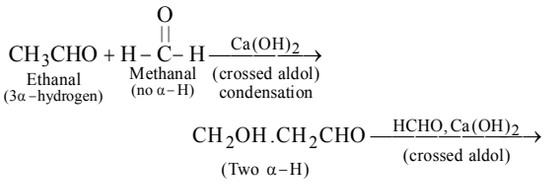
63. **(b)** The reaction is an example of intramolecular aldol condensation. In this keto aldehyde, three different enolates are possible corresponding to the following three carbanions.

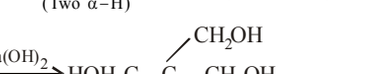


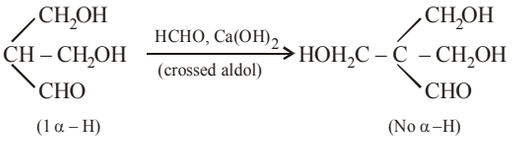
I II III

However, carbanion II is formed preferentially because aldehydes are more reactive towards nucleophilic addition than the ketones due to electronic as well as steric factors.

64. **(c)** First three HCHO molecules react with acetaldehyde via crossed aldol condensation, while the fourth HCHO molecule reacts via crossed Cannizzaro reaction.





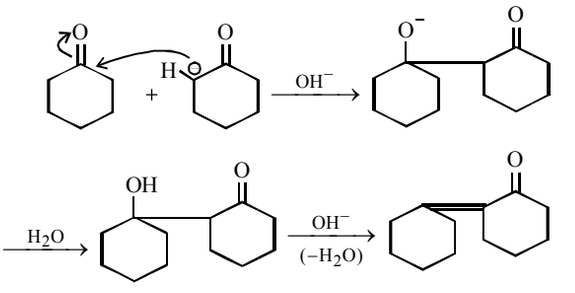




65. **(b)** Reimer-Tiemann reaction develops – CHO or – COOH group in *ortho* position to the OH group in phenols or to the hetero atom in pyrrole and thiophene.

66. **(c)** Consult mechanism of Cannizzaro reaction.

67. **(a)** Condensation of aldehydes/ketones having $\alpha - H$ in presence of base to form α, β-unsaturated carbonyl compound (aldol condensation).

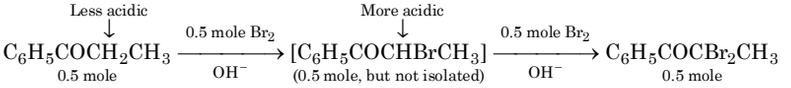


EXERCISE 14.2

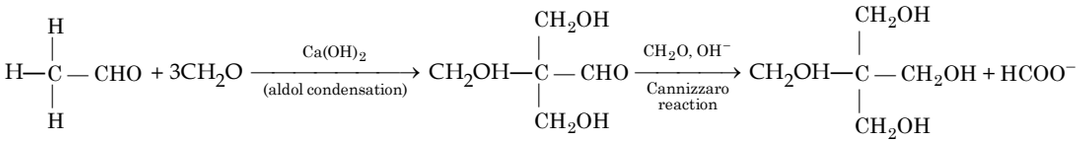
>1 CORRECT OPTION	1	(a,c)	2	(c,d)	3	(a,b)	4	(a,b,d)	5	(a,b,c)	6	(a,b,c)	7	(b,d)	8	(b,c,d)
	9	(a,b,d)	10	(b, c, d)	11	(a, d)	12	(a, b, c)	13	(a, c)	14	(a, b, d)	15	(a,b,c,d)	16	(a, c, d)
	17	(a, b, c)	18	(a, b, c)	19	(a,c)	20	(a, b)	21	(a, b, d)	22	(b, d)	23	(a, b)	24	(b, d)
	25	(a, b, d)	26	(a, d)	27	(a,b,c,d)	28	(a, b, c)	29	(a, c, d)	30	(a,b,c,d)	31	(a, b, c)	32	(b, c, d)
	33	(a,b,c,d)	34	(a, b, c)	35	(a,b,c,d)	36	(a, c, d)	37	(a, b, c)	38	(a,b,c,d)	39	(a, b)	40	(a,b,c,d)
	41	(a, c)	42	(a, c)	43	(d)	44	(b)	45	(a, d)	46	(a, b, c, d)	47	(a, b, c, d)	48	(a, c, d)
	49	(a, c, d)	50	(a, d)												
PASSAGE 1	51	(c)	52	(c)	53	(b)										
PASSAGE 2	54	(a)	55	(b)	56	(b)	57	(a)	58	(b)						
PASSAGE 3	59	(d)	60	(a)	61	(c)										
PASSAGE 4	62	(b)	63	(a)	64	(d)										
PASSAGE 5	65	(b)	66	(a)	67	(b)										
PASSAGE 6	68	(c)	69	(d)	70	(b)										
PASSAGE 7	71	(d)	72	(c)	73	(b)										
PASSAGE 8	74	(c)	75	(a)	76	(c)										
PASSAGE 9	77	(d)	78	(a)	79	(b)										
PASSAGE 10	80	(b)	81	(a)	82	(d)										
MATCH THE FOLLOWING	83	(A)- a, b ; (B) –c ; (C) - a ; (D) - a, d														
	84	(A)-a, c, d ; (B)-b ; (C)- a, b, d ; (D)- a, c, d														
	85	(A) – b, c; (B) – a; (C) – c, d; (D) – c														
	86	(A) – s, w; (B) – p, x; (C) – r, z; (D) – q, y														
	87	(A) – a, b, d, e; (B) – a, e; (C) – a, b, d; (D) – a, b, d, e														
	88	(A) – c, d, e; (B) – a, d; (C) – c, d; (D) – b, e														
A/R	89	(a)	90	(e)	91	(e)	92	(c)	93	(a)	94	(b)				
	95	(d)	96	(a)	97	(b)	98	(a)	99	(a)	100	(d)				

1. Since the product, $CH_3CHOHCN$ has a chiral carbon and is a mixture of two enantiomers (racemic mixture) which can't be separated by fractional distillation. By fractional crystallisation from a suitable solvent they can be separated.

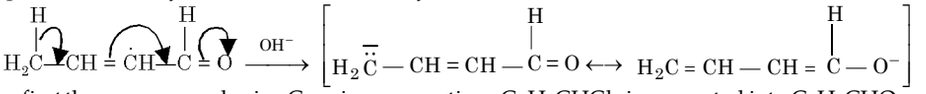
2. Substitution by one mole of Br gives $C_6H_5COCHBrCH_3$; the electron-withdrawing Br increases the acidity of the remaining α hydrogen which *reacts more rapidly* than the hydrogens on the unsubstituted ketones.



3. Acetaldehyde having three α-hydrogen atoms undergo aldol condensation with three moles of CH_2O. The product formed now undergoes intermolecular Cannizzaro reaction with the fourth mole of CH_2O to form pentaerythritol.



4. Removal of γ-hydrogen of crotonaldehyde provides more stable allylic carbanion, hence here γ-carbon (not α) provides the carbanion (nucleophile) for carbonyl carbon of cinnamaldehyde.



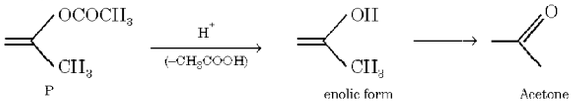
5. Only the first three compounds give Cannizzaro reaction ; $C_6H_5CHCl_2$ is converted into C_6H_5CHO, under the Cannizzaro conditions, hence it also responds the reaction.

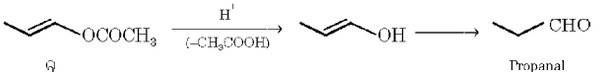
6. Carbonyl compounds having αH form carbanion on treatment with a base, carbanion being flat can be attacked by proton on either side of the face forming racemic mixture. Only ketone I has α H, so it will form carbanion while ketone II does not form such carbanion.

7. It is an example of Cannizzaro reaction.

8. Only b, c and d will undergo haloform reaction, but not a because on hydrolysis by alkali it gives C_6H_5CHO, having no αH.

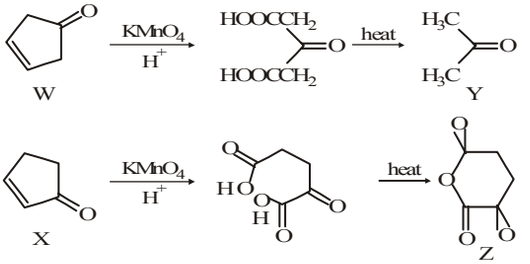
9.





Acetone and propanal can be distinguished by Fehling solution, and not by others.

48. (a, c, d)



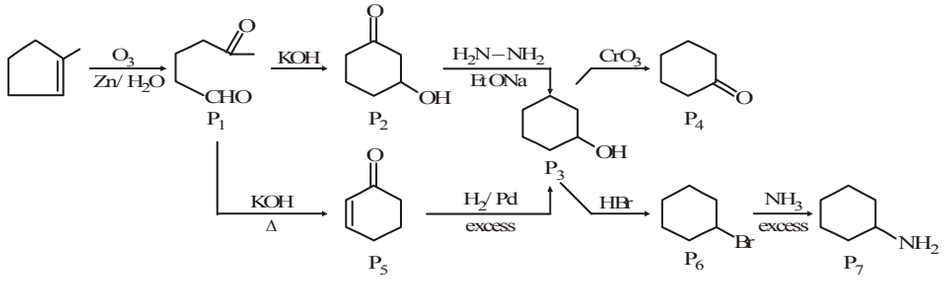
49. (a, c, d)

(a) and (c) have methyl keto $\left(CH_3-\overset{\overset{O}{\|}}{C}-\right)$ group.

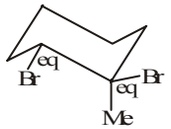
(d) forms $CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$, on reaction with aq. NaOH, which then gives iodoform test.

50. (a, d) Compound (X) gives positive haloform test. Hence [X should be (a), (c) and (d).] However, c does not react with NH_2OH to give two oximes.

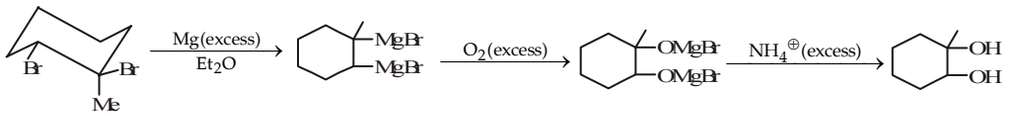
Sol. (68-70) :



71. (d)

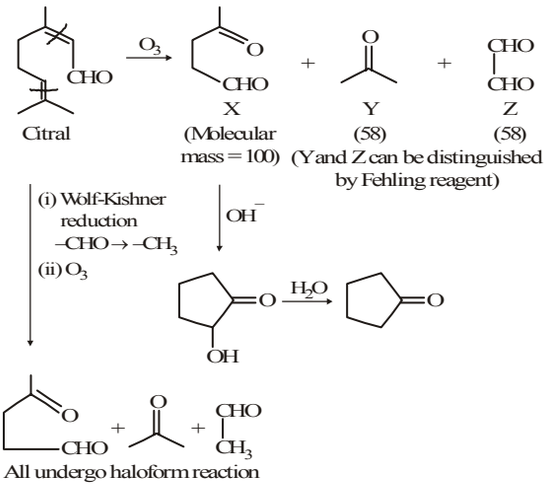


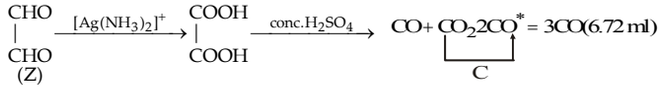
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72. (c) 

73. (b)  gives addition reaction and decolourises Br_2 water.

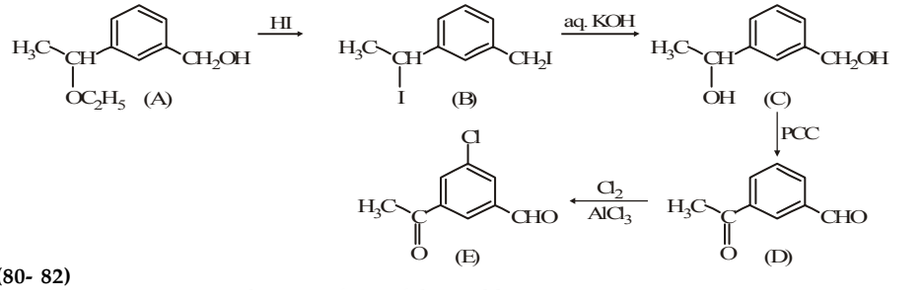
Sol. (74-75) :



76. (c) 

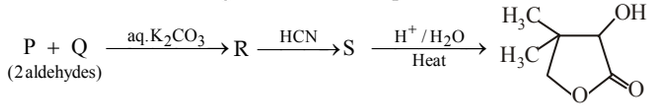
$$\text{Moles} = \frac{6.72}{22400} = 3\times10^{-4} \qquad \therefore \text{ Moles of } \begin{matrix}\text{CHO}\\|\\\text{CHO}\end{matrix} = 10^{-4} \text{ (in 100 ml)} = 10^{-3}\ \text{M}$$

Sol. (77-79) :

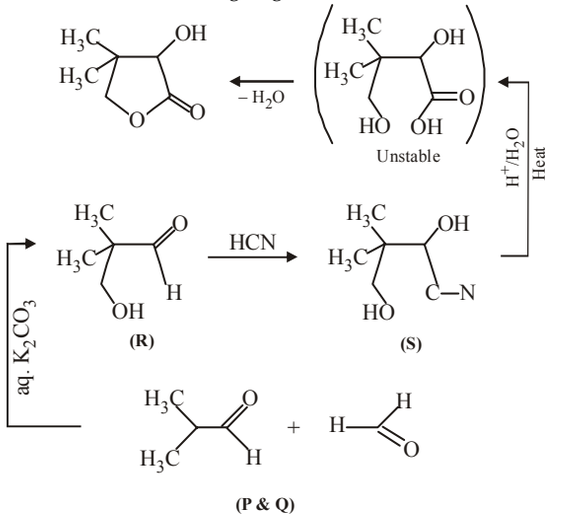


Sol. (80- 82)

Let us summarize the given facts of the problem.

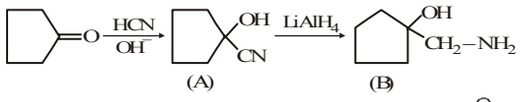


Structures of P, Q, R and S can be established on going backward from the known final product.

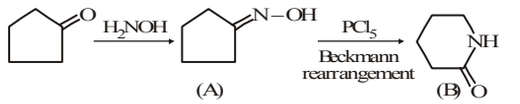


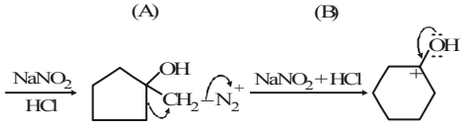
87. A - (p, q, s, t); B - (p, t); C - (p, q, s); D - (p, q, s, t)

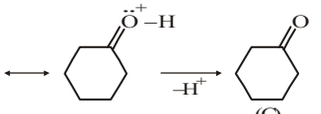
(A)



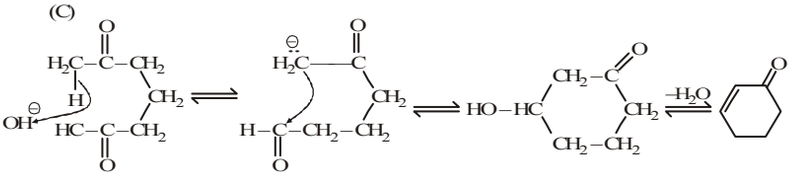
(B)



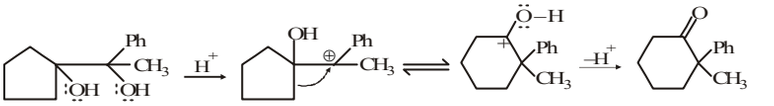




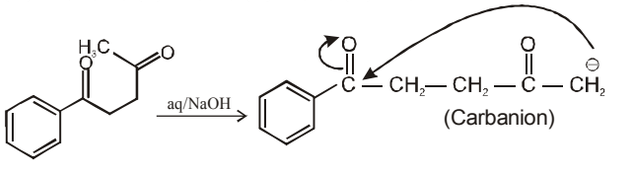
(C) Intramolecular aldol condensation

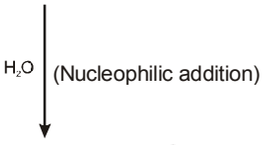


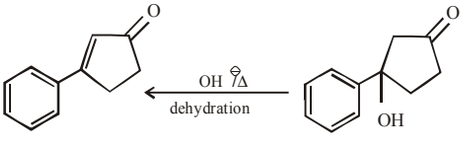
(D) Pinacol – Pinacolone rearrangement



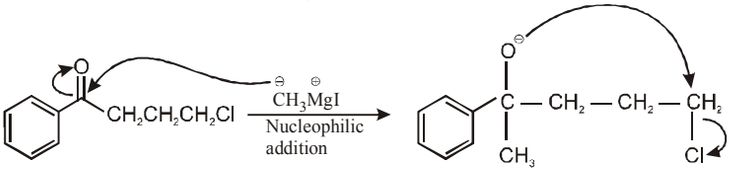
88. (A) – c, d, e ; (B) – a, d ; (C) - c, d; (D) – b, c

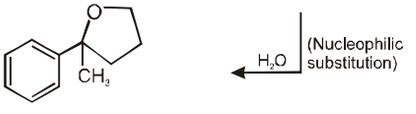




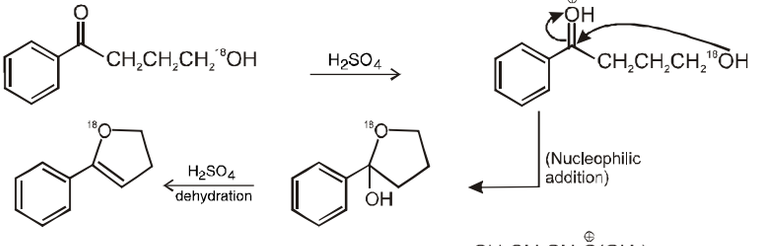


(B)

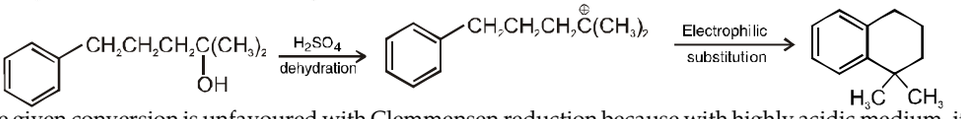




(C)



(D)



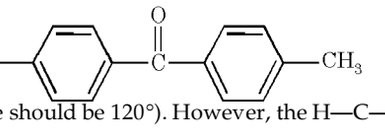
97. (a) The given conversion is unfavoured with Clemmensen reduction because with highly acidic medium, it will attack on –OH group of the given compound.

100. (d) $C_6H_5-CH=\underset{\displaystyle CH_3}{\overset{|}{C}}-CHO$ is the condensation product.

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EXERCISE 14.3

1. (*i*) 3-Phenylpropenal (*ii*) 4-Methyl-3-penten-2-one (*iii*) 4-Methyl-3-hexanone
(*iv*) 4-Ketopentanoic acid (—COOH group has a higher priority over —CO group).

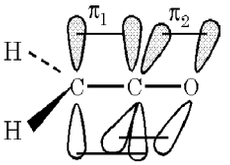
2. (*a*) $(CH_3)_3CCHO$ (*b*) $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCHO$ (*c*) 

3. $H_2C = O$ is a planar molecule, *i.e.*, its C is sp^2 hybridised (theoretically, its bond angle should be 120°). However, the H—C—O bond angle is slightly greater (121.8°) than the expected 120°, while the H—C—H angles are 116.5°, slightly less than 120°.

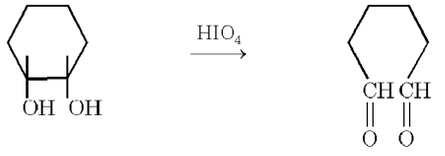
4. The C = O bond is polarised ($\overset{\delta+}{C} = \overset{\delta-}{O}$) due to more electronegative nature of oxygen, while the C = C bond is nearly non-polar. The π bond of C = C is an electron source, and is a nucleophilic site, while in C = O, the nucleophilic site is O.

5. (*a*) 2-Propanol has highest boiling point due to intermolecular H—bonding, since propanone and 2-methylpropene have no hydrogen on oxygen, they can't undergo association. However, the dipole-dipole attractive forces of carbonyl compounds are responsible for their higher boiling point than those of alkenes.
(*b*) Oxygen of C = O forms H—bond with the H of water making the former to dissolve in the latter (water) ; such hydrogen bond formation is not possible in an alkene as it has no oxygen. However, carbonyl group has no H atom which can form H—bond with the O of H_2O, hence these are less water soluble than alcohols.
(*c*) Alkyl substituents stabilize C = O as they do C = C by releasing electrons towards the sp^2 hybridized C. The enthalpy of the ketone is lower because it has two R groups, while the aldehydes have only one.

6. Ketenes have the general formula, $R_2C = C = O$. Structural formula for the ketene is $H_2C = C = O$,



7. (*a*) Reduction of RCOOR with $LiAlH_4$ gives RCH_2OH, since the intermediate aldehyde RCHO is generally susceptible to further reduction. Hence one equivalent of the less reactive diisobutyllithium aluminium hydride (DBAH) is used at —70°C followed by hydrolysis ; when aldehyde is obtained in good yield.

(*b*) 

cis-1, 2-Cyclohexanediol Hexan-1, 6-dial

The corresponding *trans*-form does not form transition state easily, hence it is not oxidised by periodic acid.

8. (*a*) $(CH_3)_2CHCH_2C \equiv CH + H_2O$ in $HgSO_4$, H_2SO_4
(*b*) $(CH_3)_2CHCH_2CHOHCH_3 + KMnO_4$ or a Cr(VI) reagent
(*c*) $(CH_3)_2CHCH_2COCl + (CH_3)_2CuLi$ (from $CH_3MgI + Li$, then Cu)
(*d*) $(CH_3)_2CHCH_2COOH + 2CH_3Li$
(*e*) $(CH_3)_2CHCH_2COCl + (CH_3)_2Cd$ (from $CH_3MgI + CdCl_2$)
(*f*) $(CH_3)_2CHCH_2C \equiv N + CH_3MgI$ or CH_3Li.

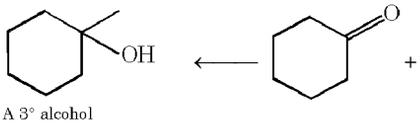
9. In such cases, proceed backward *i.e.*, first write down the structure of the required compound and then apply your memory for getting the two required components for its preparation.

(*a*) $C_6H_5\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CH_3 \longleftarrow C_6H_5MgBr + CH_3CH_2CHO$ **or** $C_6H_5CHO + CH_3CH_2MgBr$
A 2° alcohol

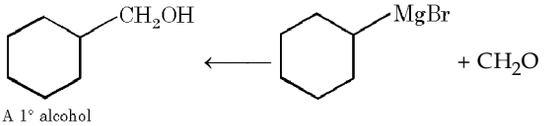
(*b*) $C_6H_5-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}}}}-CH_3 \longleftarrow C_6H_5MgBr + (CH_3)_2CO$ **or** $C_6H_5COCH_3 + CH_3MgBr$
A 3° alcohol

(*c*) $C_6H_5CH_2CHOHCH_3 \longleftarrow C_6H_5CH_2CHO + CH_3MgBr$
1-Phenyl-2-propanol, a 2°alcohol

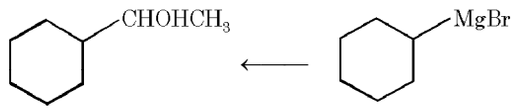
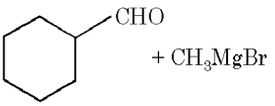
(*d*) $C_6H_5CH_2CH_2CH_2OH \longleftarrow C_6H_5CH_2CH_2MgBr + HCHO$
3-Phenylpropanol, a 1° alcohol

(*e*) 

A 3° alcohol

(*f*) 

A 1° alcohol

(*g*)  + CH_3CHO or  + CH_3MgBr

A 2° Alcohol

(*h*) $CH_3CH_2CHOHC \equiv CH$ ⟵ $CH_3CH_2CHO + HC \equiv CLi$

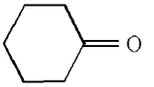
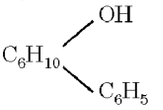
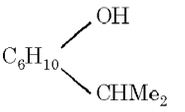
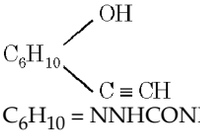
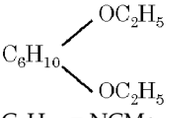
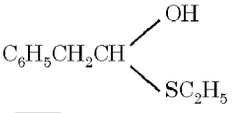
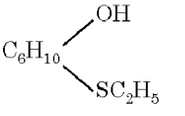
A 2° alcohol

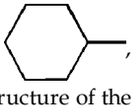
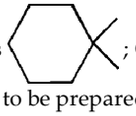
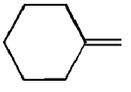
(*i*) $CH_3CHOHC \equiv CCH_3$ ⟵ $CH_3CHO + CH_3C \equiv CLi$

A 2° alcohol

(*j*) $p\text{-}CH_3C_6H_4CHOHCH_3$ ⟵ $p\text{-}CH_3C_6H_4MgBr + CH_3CHO$ **or** $p\text{-}CH_3C_6H_4CHO + CH_3MgBr$

10.

Reagent	Product from $C_6H_5CH_2CHO$	*Product from* 
(*a*) Tollen's reagent	$C_6H_5CH_2COO^-Ag^+$	No reaction
(*b*) CrO_3/H_2SO_4	$C_6H_5CH_2COOH$	No reaction
(*c*) Cold dil $KMnO_4$	$C_6H_5CH_2COOH$	No reaction
(*d*) $KMnO_4$, H^+, heat	C_6H_5COOH	$HOOC(CH_2)_4COOH$
(*e*) H_2, Ni, Pressure	$C_6H_5CH_2OH$	$C_6H_{11}CHOH$
(*f*) $NaBH_4$	$C_6H_5CH_2OH$	$C_6H_{11}CHOH$
(*g*) C_6H_5MgBr, H_2O	$C_6H_5CH_2CHOHC_6H_5$	
(*h*) $Me_2CHMgCl$, H_2O	$C_6H_5CH_2CHOHCHMe_2$	
(*i*) $HC \equiv CLi$, H_2O	$C_6H_5CH_2CHOHC \equiv CH$	
(*j*) $NH_2CONHNH_2$	$C_6H_5CH_2CH = NNHCONH_2$	$C_6H_{10} = NNHCONH_2$
(*k*) C_2H_5OH, HCl	$C_6H_5CH_2CH(OC_2H_5)_2$	
(*l*) Me_3CNH_2	$C_6H_5CH = NMe_3$	$C_6H_{10} = NCMe_3$
(*m*) C_2H_5SH, H^+		

Where C_6H_{11}— is  , C_6H_{10}– is  ; C_6H_{10} = is 

11. Write down the structure of the compound to be prepared.

(*a*) $CH_3CH_2CH_2OH \xleftarrow[\text{or } H_2, \text{Ni}]{LiAlH_4} CH_3CH_2CHO$

(*b*) $CH_3CH_2\underset{\underset{OH}{|}}{C}HCOOH \xleftarrow{H_2O,\ H^+} CH_3CH_2\underset{\underset{OH}{|}}{C}HCN \xleftarrow[H^+]{CN^-} CH_3CH_2CHO$

(*c*) $CH_3CH_2\underset{\underset{OH}{|}}{C}HCH_3 \longleftarrow CH_3CH_2CHO + CH_3MgBr$

(*d*) $CH_3CH_2\underset{\underset{OH}{|}}{C}HC_6H_5 \longleftarrow CH_3CH_2CHO + C_6H_5MgBr$

(*e*) $CH_3CH_2\underset{\underset{OH}{|}}{C}HCH(CH_3)_2 \longleftarrow CH_3CH_2CHO + (CH_3)_2CHMgBr$

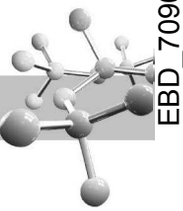
12. 2-Methyl-2-pentenal, $CH_3CH_2CH = C(CH_3)CHO$ to

(*a*) $CH_3CH_2CH = \underset{\underset{CH_3}{|}}{C} - CH_2OH$
(reduction of only —CHO to $—CH_2OH$, hence $NaBH_4$ is used)

(*b*) $CH_3CH_2CH_2\underset{\underset{CH_3}{|}}{C}HCH_2OH$
(reduction of —CHO to $—CH_2OH$ as well as C = C, hence H_2/Pt is used)

*(*c*) $CH_3CH_2CH_2\underset{\underset{CH_3}{|}}{C}HCH_3$
(reduction of —CHO to $>CH_2$ and also of C = C)

**(*d*) $CH_3CH_2CH_2\underset{\underset{CH_3}{|}}{C}HCHO$
(reduction only C = C, hence —CHO must be first protected)



*(*c*) $CH_3CH_2CH=\overset{\overset{CH_3}{|}}{C}CHO \xrightarrow[\text{Wolf-Kishner reduction}]{NH_2NH_2, OH^-, \text{heat}} CH_3CH_2CH=\overset{\overset{CH_3}{|}}{C}CH_3 \xrightarrow{H_2/Pt} CH_3CH_2CH_2\overset{\overset{CH_3}{|}}{C}HCH_3$

**(*d*) $CH_3CH_2CH=\overset{\overset{CH_3}{|}}{C}CHO \xrightarrow[HCl]{CH_3OH} CH_3CH_2CH=\overset{\overset{CH_3}{|}}{C}CH(OCH_3)_2 \xrightarrow[(ii)\ HCl,\ H_2O]{(i)\ H_2/Pt} CH_3CH_2CH\overset{\overset{CH_3}{|}}{C}HCHO$

13. If a carbonyl compound has some other functional group which is stable to acids but react with strong base, then Clemmensen method (Zn/Hg + HCl) should be used. In case, the carbonyl compound is sensitive to acid but stable in base, then Wolf-Kishner method (NH_2NH_2, OH^-) should be used. Raney Ni desulfurization occurs under neutral conditions : however it can't be used with reactants with good leaving groups because —SH is an excellent nucleophile.

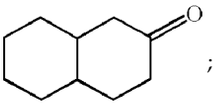
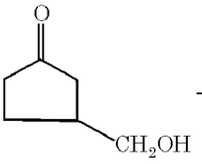
14. (*a*) $BrCH_2CH_2CHO \longrightarrow BrCH_2CH_2CH_3$. It should be carried out by Clemmensen reduction because strong base (used in Wolf-Kishner method) causes dehydrohalogenation. Desulfurisation by Raney Ni can't be used because $HSCH_2CH_2SH$, used for converting C = O into thioacetal, can displace Br^- (a good leaving group), hence thioacetal will not be formed.

$$BrCH_2CH_2CHO + HSCH_2CH_2SH \longrightarrow HSCH_2CH_2SCH_2CH_2CHO + Br^-$$

(*b*) $Me_2C(OH)\ CH_2CH_2COCH_3 \longrightarrow Me_2C(OH)CH_2CH_2CH_2CH_3$. It can be carried out by Wolf-Kishner reduction or desulphurisation. Clemmensen method, using HCl, is not suitable because 3° alcohol is easily dehydrated in presence of acid.

(*c*) $C_6H_5CH(OH)CH_2COCH_2CH_3 \longrightarrow C_6H_5CH(OH)CH_2CH_2CH_2CH_3$.
Here again acid causes dehydration of an alcohol which is although 2° but produces quite stable alkene because its double bond is conjugated with the benzene. Hence either of the other two methods can be used.

(*d*) Epoxides are very reactive, hence these are opened up by the reagents used in either of the three methods used for reducing carbonyl group. Thus none of the three methods give good result for reducing a carbonyl group.

15. (*a*) [A] is  ; [B] is  —CHO group is reduced earlier than keto.

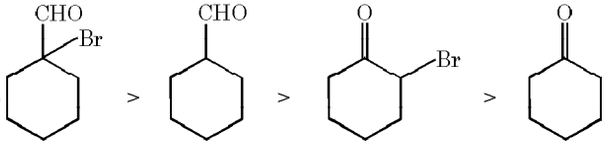
16. (*a*) $C_6H_5CH=CHCOCH_3 \xrightarrow[\text{(haloform reaction)}]{Cl_2, OH^-} C_6H_5CH=CHCOOH$ (*b*) $C_6H_5CH=CHCOCH_3 \xrightarrow{LiAlH_4} C_6H_5CH=CHCHOHCH_3$

(*c*) $C_6H_5CH=CHCOCH_3 \xrightarrow[\text{Birch reduction}]{Li,\ liq.NH_3,\ ether} C_6H_5CH_2CH_2COCH_3$ (*d*) $C_6H_5CH=CHCOCH_3 \xrightarrow{NH_2NH_2,\ OH^-} C_6H_5CH=CHCH_2CH_3$

(*e*) $C_6H_5CH=CHCOCH_3 \xrightarrow[(ii)\ H_2/Pt]{(i)\ NH_2NH_2,\ OH^-} C_6H_5CH_2CH_2CH_2CH_3$

17. Aldehydes are more easily hydrated than ketones. Further, presence of electron–withdrawing group increases hydration.

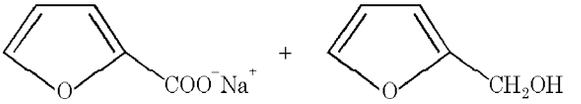
(*a*) $HCHO > CH_2ClCHO > CH_3CHO > CH_2ClCOCH_3 > CH_3COCH_3$

(*b*) 

18. (*a*) All these compounds undergo Cannizzaro reaction (a characteristic reaction of aldehydes lacking α-hydrogen atom). Note that compounds (*iv*) and (*v*) although do not have an aldehydic group, however, in presence of OH^- these are converted into aldehydes lacking α-hydrogen atom, hence they also undergo Cannizzaro reaction.

$$C_6H_5CHCl_2 \xrightarrow{OH^-} C_6H_5CH(OH)_2 \longrightarrow C_6H_5CHO;\quad Me_3CCHCl_2 \xrightarrow{OH^-} Me_3CCH(OH)_2 \longrightarrow Me_3CCHO$$

Thus the products in these compunds will be

(*i*) and (*iv*) $C_6H_5COO^-Na^+ + C_6H_5CH_2OH$ (*iii*) 

(*ii*) and (*v*) $Me_3CCOO^-Na^+ + Me_3CCH_2OH$

(*b*) All these compounds have α-hydrogen, so they will undergo aldol condensation.

(*i*) $2C_6H_5CH_2CHO \xrightarrow{OH^-} C_6H_5CH_2\underset{\underset{C_6H_5}{|}}{\overset{\overset{OH}{|}}{C}}HCHO \xrightarrow{-H_2O} C_6H_5CH_2CH=\underset{\underset{C_6H_5}{|}}{C}CHO$

Highly conjugated system
(C = C is conjugated with —CHO as well as benzene ring)

(*ii*) In $CH_3CH = CHCHO$, since the —CHO group is conjugated with the double bond, hydrogen atom of the methyl group (allylic hydrogen) becomes acidic, *i.e.*, it is the allylic carbanion that will be formed rather than vinylic, hence in such cases aldol condensation involves allylic hydrogen atom which is, of course, not the α-hydrogen atom.

$$2\,CH_3CH=CHCHO \longrightarrow CH_3CH=CH\underset{\displaystyle OH}{\underset{|}{C}}HCH_2\,CH=CHCHO \xrightarrow[-H_2O]{} CH_3CH=CHCH=CHCH=CHCHO$$

(*iii*) $$C_6H_5CH=CHCHO + CH_3CH=CHCHO \xrightarrow{OH^-} C_6H_5CH=CH\underset{\displaystyle OH}{\underset{|}{C}}HCH_2\,CH=CHCHO \xrightarrow[(-H_2O)]{heat} C_6H_5CH=CHCH=CHCH=CHCHO$$

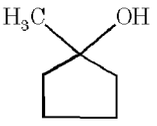
(*iv*) $$H-\underset{\displaystyle H}{\underset{|}{C}}=O + HCH_2CHO \longrightarrow H-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}}-CH_2CHO$$

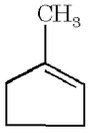
Here only CH_3CHO has α-hydrgoen atom so it will be forming carbanion which then adds on carbonyl carbon of formaldehyde. The process repeats till all the three hydrogen atoms of CH_3CHO are replaced by $—CH_2OH$ group.

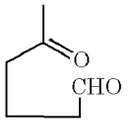
$$H-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}}-CHO \xrightarrow[\text{(aldol condensation)}]{CH_2O,\ OH^-} H-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle CH_2OH}{\overset{|}{C}}}}-CHO \xrightarrow[\text{(aldol condensation)}]{CH_2O} CH_2OH-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle CH_2OH}{\overset{|}{C}}}}-CHO \xrightarrow[\text{(aldol condensation)}]{CH_2O}$$

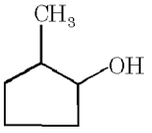
$$CH_2OH-\underset{\displaystyle CH_2OH}{\underset{|}{\overset{\displaystyle CH_2OH}{\overset{|}{C}}}}-CHO \xrightarrow[\text{(Cannizzaro reaction)}]{CH_2O} CH_2OH-\underset{\displaystyle CH_2OH}{\underset{|}{\overset{\displaystyle CH_2OH}{\overset{|}{C}}}}-CH_2OH + HCOO^-$$

19.

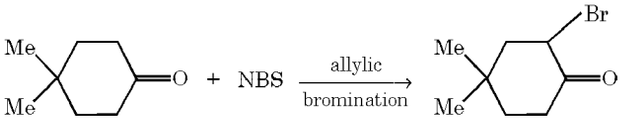

[A]


[B]

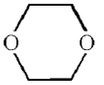

[C]


[D]

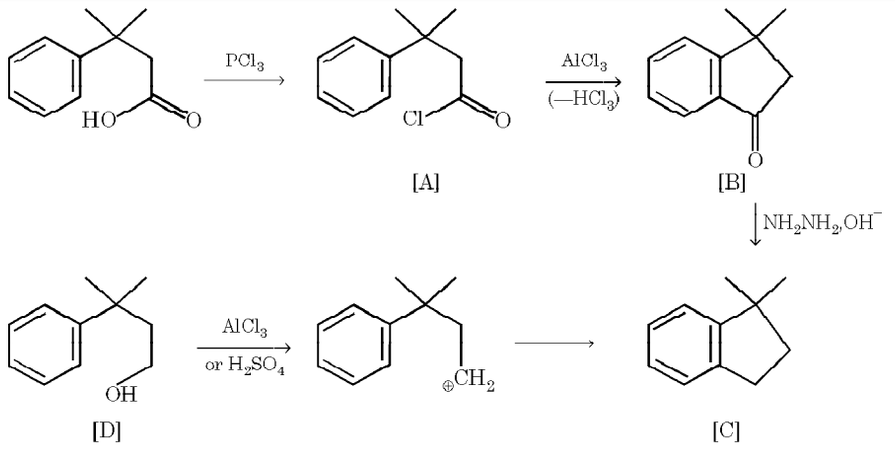
20. (*a*) Halogenation occurs at the α-position to the C = O group under free radical conditions, hence product will be $C_6H_5COCHClCH_3$.

(*b*) 

21. (*a*) Only phenylacetaldehyde, $C_6H_5CH_2CHO$ responds Tollen's reagent.
(*b*) Only 2-pentanone, $CH_3COCH_2CH_2CH_3$ responds iodoform test
(*c*) Only cyclohexanone gives crystals with 2, 4-dinitrophenylhydrazine
(*d*) Only *n*-valeraldehyde responds Tollen's reagent.
(*e*) Diethyl acetal on treatment with acid regenerates aldehyde which responds Tollen's reagent.
(*f*) Only propiophenone, $C_6H_5CH_2COCH_3$ responds iodoform test
(*g*) Only 2-pentanone responds 2, 4-dinitrophenylhydrazine, while 2-pentanol gives colour reaction with CrO_3/H_2SO_4.
(*h*) Paraldehyde, a cyclic trimer of acetaldehyde, $(CH_3CHO)_3$, on treatment with acid gives CH_3CHO which responds Tollen's or Schiff's reagent.
(*i*) Trioxane, $(CH_2O)_3$ on treatment with acid followed by heating gives CH_2O which responds Tollen's reagent or Schiff's test.

Dioxane is a cyclic ether 

22. First step involves the conversion of —COOH to —COCl [A]. Conversion of [A] to [B] involves loss of HCl but without any change in carbon number, it indicates that the reaction is intramolecular Friedel Crafts acylation. Thus conversion of [A] to [C] can be represented as below.

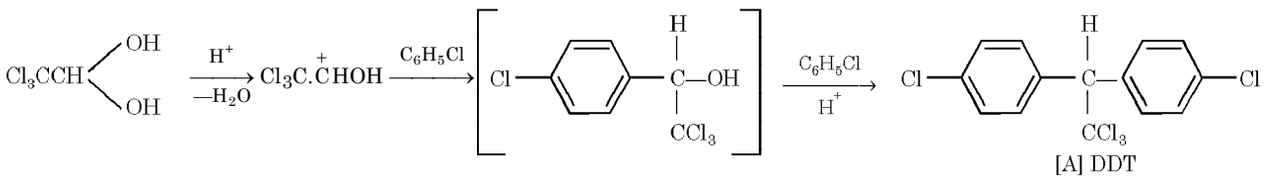


23. $n\text{-}C_5H_{11}C \equiv CLi$ $n\text{-}C_5H_{11}C \equiv CCH_2CH_2CH_2Br$ $n\text{-}C_5H_{11}C \equiv CCH_2CH_2CH_2CHR'$ (OH)

[A] [B] [C]

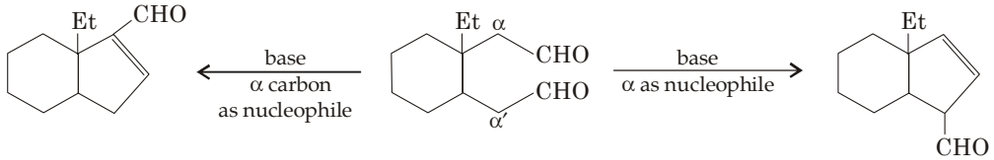


24.

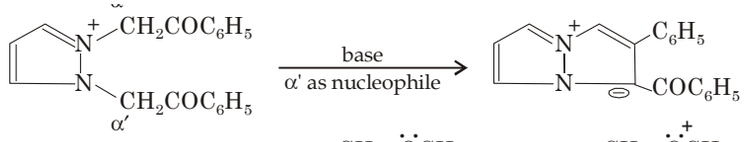


[A] DDT

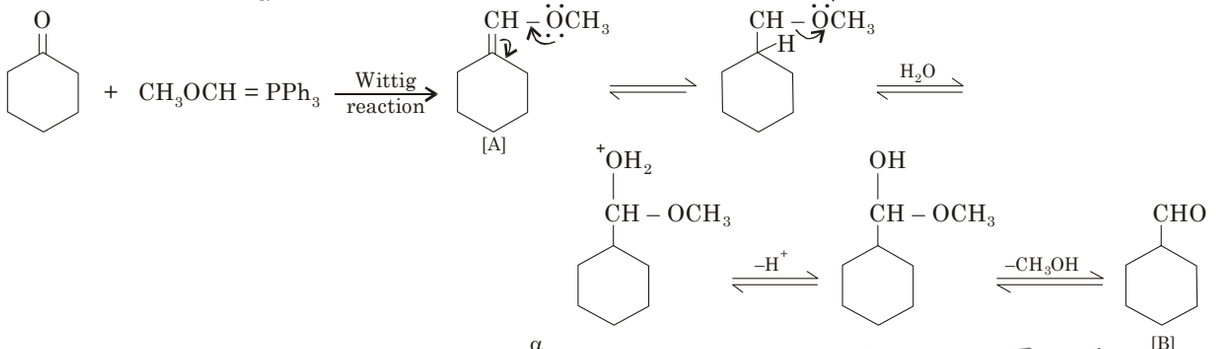
25. (a) Here either of the α-carbon can act as a nucleophile to form two possible compounds by intramolecular aldol condensation.



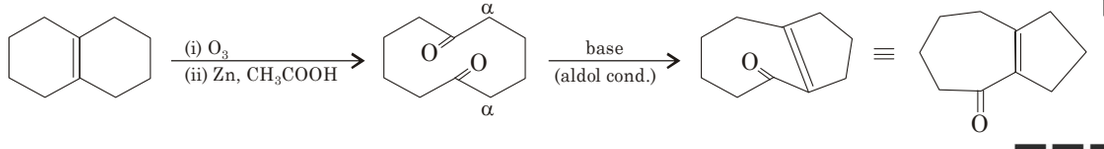
(b) Here only one product will be formed by the aldol condensation since here only one α carbon (α' carbon) can form a stable carbanion; in the second case (α carbon) +ve and –ve charges will be present an adjacent atoms causing unstability.

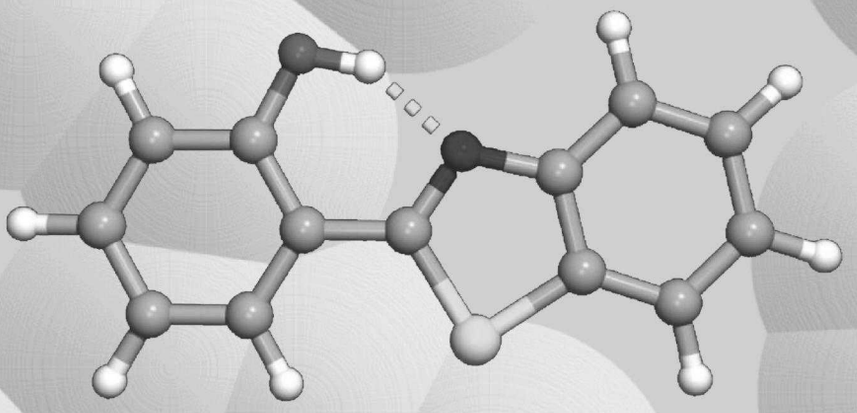


26. (a)



(b)





15 Carbanions

CHAPTER HIGHLIGHTS

15.1 Reactions Involving Carbanions

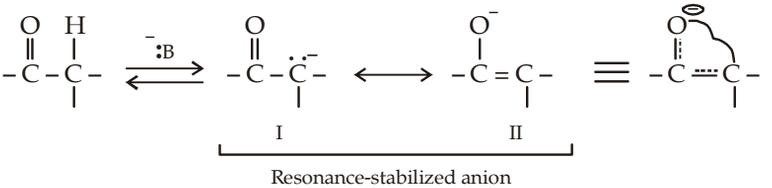
15.2 Reactions *via* Enols and Enolate Ions

15.3 Illustrative Examples

EXERCISES

SOLUTIONS

In the preceding chapter we found nucleophilic addition to the carbonyl group as one of the important characteristics of aldehydes and ketones. However, another important characteristic of carbonyl compounds is the unusual acidity of its α hydrogen atom; i.e. such hydrogens are far more acidic than a hydrogen in an alkane. The reason for the unusual acidity of the α hydrogens of carbonyl compounds is due to stability of its corresponding enolate anion (carbanion).

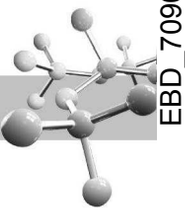


Resonance-stabilized anion

Note that of the above two resonating structures, II is more stable because negative charge is present on oxygen (an electronegative element). Since the structure II (an enolate ion) makes a greater contribution to the hybrid, such carbanions are commonly known as **enolate ions** rather than carbanions.

15.1 Reactions Involving Carbanions

The carbonyl group occurs in compounds other than aldehydes and ketones and thus the α-hydrogens of such compounds should also be acidic. Such compounds (acids) in which proton is lost from carbon are called **carbon acid**, and hence the conjugate base of a carbon acid is known as carbanion. However, note that different carbon acids differ in their acidic property, e.g. aldehydes and ketones are more acidic than esters because the lone pair of electrons of the carbanions of an ester is not as readily delocalized as the carbanion of an aldehyde or ketone.





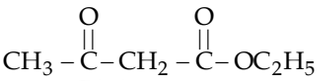
Electron pair on C is delocalised



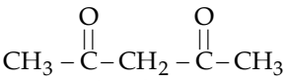
Electron pair on C is localised — Electron pair on C is delocalised

Note that in esters two pairs of electrons compete for delocalization onto carbonyl oxygen.

Nitroalkanes, nitriles and N,N-disubstituted amides also have relatively acidic α-hydrogens because in each case, the electrons left after the removal of the proton can be delocalized onto an atom that is more electronegative than carbon. Further, if the α-carbon is in between two carbonyl groups, the acidity of an α-hydrogen is even greater. Thus ethyl acetoacetate (a β-keto ester) and acetylacetone (a β-diketone) are more acidic than the corresponding ordinary ketone.

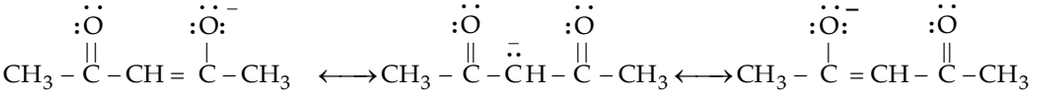


Ethyl acetoacetate
(Ethyl 3–oxobutyrate)



Acetylacetone
(2, 4-Pentanedione)

Higher acidity of α-hydrogens bonded to two electronegative groups ($>C=O$, $-NO_2$, $-C\equiv N$) is because the electrons left after the removal of proton can be delocalized onto two oxygen atoms.



Resonance stabilization of 2,4-pentanedione anion

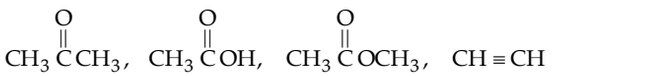
TEST YOUR UNDERSTANDING - 15.1

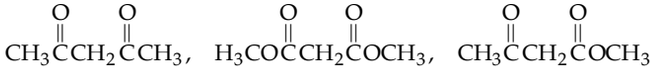
1. How many acidic hydrogens are present in each of the following?

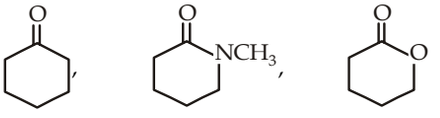
(a) 3,3-Dimethyl-2-butanone (b) Benzyl methyl ketone

(c) 2,2-Dimethylpropanal (d) Cyclohexane-1,3-dione

2. Arrange the listed compounds in each of the following groups in order of decreasing acidity.

(a) 

(b) 

(c) 

The pK_a values of some carbon acids

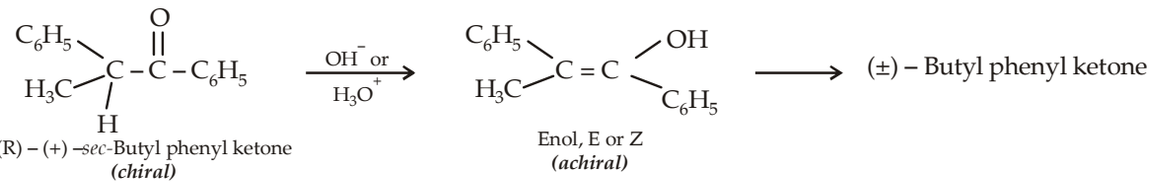
	pK_a		pK_a
$CH_3\overset{O}{\overset{\|}{C}}NMe_2$	30	$N\equiv CCH_2CN$	11.8
$CH_3\overset{O}{\overset{\|}{C}}OCH_2CH_3$	25	$CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OC_2H_5$	10.7
$CH_3C\equiv N$	25	$C_6H_5-\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}CH_3$	9.4
$CH_3\overset{O}{\overset{\|}{C}}CH_3$	20	$CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}CH_3$	8.9
$CH_3\overset{O}{\overset{\|}{C}}H$	17	$CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}H$	5.9
$CH_3CH_2NO_2$	8.6	$O_2NCH_2NO_2$	3.6

15.2 Reactions *via* Enols and Enolate Ions

Although in majority of cases, enolates are carbanions, in some cases ordinary carbanions (not enolates) serve as carbanions.

15.2.1 Racemization

When a solution of (+)-*sec*-butyl phenyl ketone in aqueous ethanol solution is treated with either acids or bases, a racemic mixture of the ketone is formed after some time.

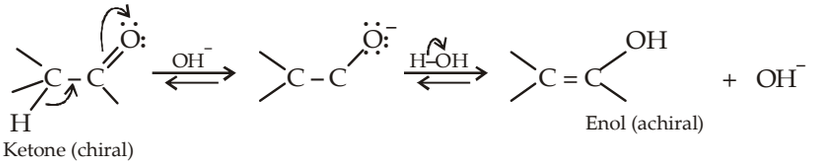


(R) – (+) –*sec*-Butyl phenyl ketone ***(chiral)*** Enol, E or Z ***(achiral)***

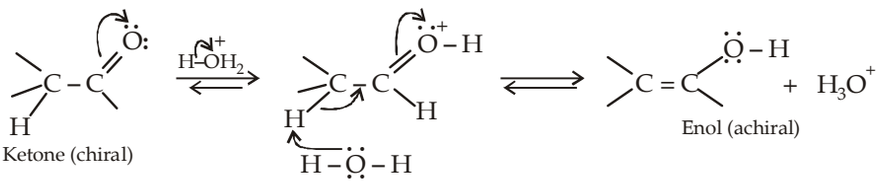
In the acyclic ketone, the enol or enolate anion formed can be E or Z. Protonation on one face of the E isomer and protonation on the same face of the Z isomer produces enantiomers.

Mechanism

Base-catalyzed enolization.



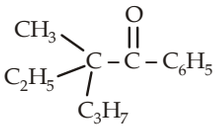
Acid-catalyzed enolization

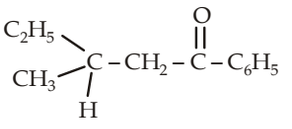


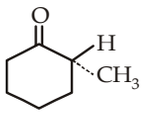
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TEST YOUR UNDERSTANDING - 15.2

1. What do you expect when each of the following optically active ketone is treated with a base?

(a) 

(b) 

(c) 

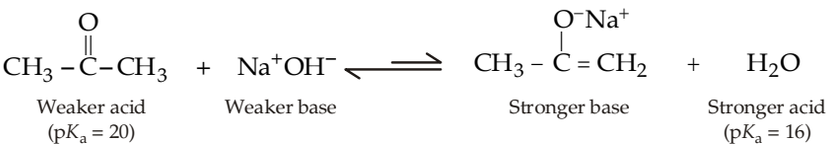
2. Explain with mechanism what happens when *sec*-butyl phenyl ketone is treated with D_3O^+ in the presence of D_2O.

3. Predict which form (*keto* or *enol*) will present in the larger concentration at equilibrium in each of the following. Suggest the reason for the predominant form.

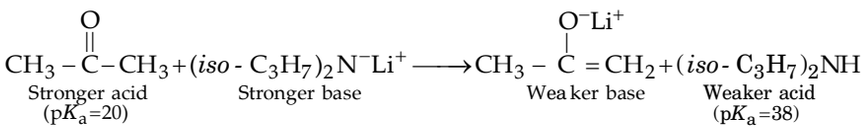
(a) 2, 4-Pentanedione (b) 2,4-Cyclohexadien-1-one

15.2.2 Formation of Lithium Enolates

The amount of carbonyl compound converted to enolate depends on the pK_a of the carbonyl compound and the base used to remove the α-hydrogen. For example, when OH^- is used to remove an α-proton from acetone ($pK_a = 20$), only a small amount of the carbonyl group is converted into enolate because OH^- is a weaker base than the base being formed.

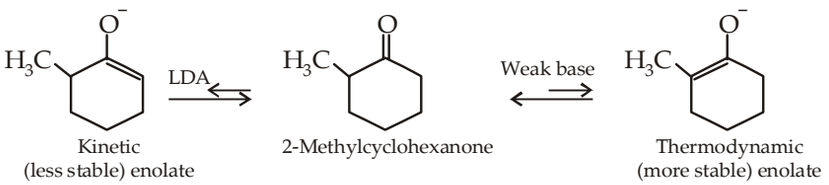


On the other hand, if a very strong base is used, the equilibrium lies far to the right. **Lithium diisopropylamide (LDA*)** is a very strong base used for converting ketones completely to the corresponding enolate form.



Regioselective formation of enolate anion : An unsymmetrical ketone can form two possible enolates. Which of the two enolates predominates depends upon the nature of the base used and on the conditions employed.

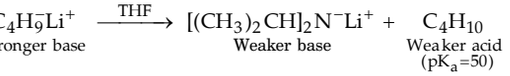
(a) As in the formation of alkenes, the *enolate with the more highly substituted double bond is the* ***thermodynamically more stable enolate.*** The thermodynamic enolate is formed predominantly under conditions that permit the establishment of an equilibrium i.e., by using a relatively weak base in a protic solvent.



(b) *The enolate with the less substituted double bond is usually formed faster* because here hydrogen is removed from the less sterically hindered and slightly more acidic position. This enolate, called the **kinetic enolate** is formed predominantly when the reaction is kinetically controlled (or rate controlled), i.e. by using a very strong base like LDA. LDA, being a strong and sterically hindered base rapidly removes proton from the less hindered α-carbon of the ketone. The notable feature of LDA is that although it is a strong base, it is a poor nucleophile hence it does not attack the carbonyl carbon. The poor nucleophilic character of LDA is again due to the presence of two bulky alkyl substituents on the N which make difficult for the N to come close enough to the carbonyl carbon.

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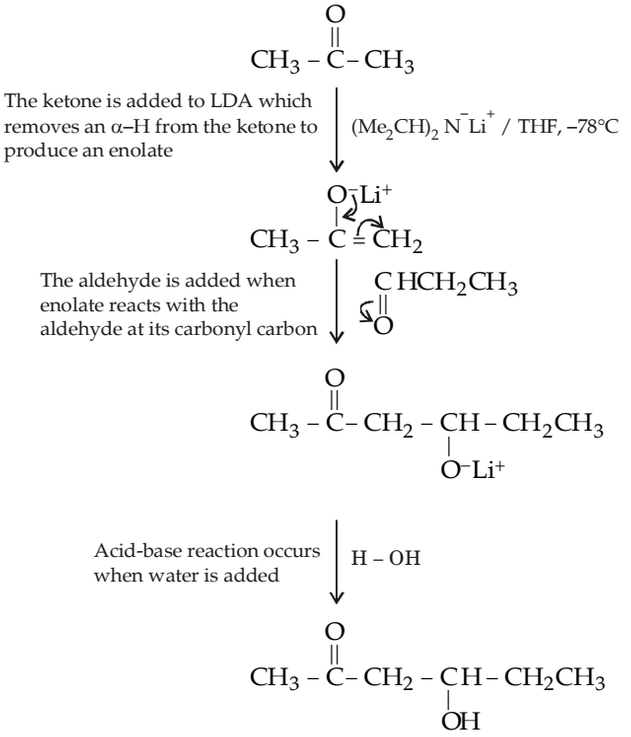
* LDA is easily prepared by adding an alkyllithium to diisopropylamine in THF at –78°C.



Lithium enolate in desired aldol reaction : One of the important applications of lithium enolate is to carry out (i) aldol condensation in unsymmetrical ketone, and (ii) mixed (crossed) aldol condensation between two different aldehydes/ ketones, each capable of undergoing aldol condensation itself, in a **desired direction**. For example, aldol condensation between CH_3COCH_3 and CH_3CH_2CHO gives rise to three aldol products;

$$CH_3COCH_3 + CH_3CH_2CHO \xrightarrow{OH^-} \text{Three products}$$

However, the desired aldol can be obtained by taking ketone in the form of lithium enolate and adding another aldehyde or ketone to this lithium enolate.

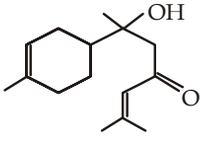


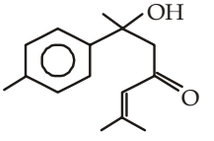
TEST YOUR UNDERSTANDING - 15.3

1. Give the starting materials used for preparing following aldol products.

(a) $CH_3CH(CH_3)COCH_2CH(OH)CH_2CH_3$

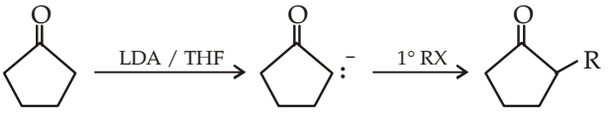
(b) $CH_3CH=CHCOCH_2CH(OH)CHCH_3$

(c) 

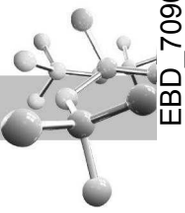
(d) 

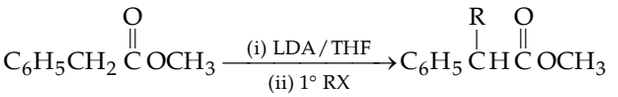
15.2.3 Alkylation of the α-Carbon of Carbonyl Compounds *via* Lithium Enolates

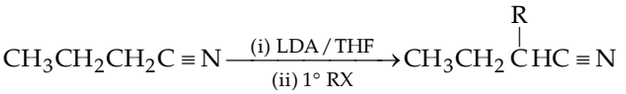
Alkylation of the α-carbon of carbonyl compounds (ketones*, esters and nitriles) gives us another important way to form a new carbon-carbon bond.



* Aldehydes are not suitable for direct alkylation because they are more reactive (strong electrophiles) than ketones, hence they will undergo aldol condensation with enolate ion (formed from another molecule of the aldehyde) very readily.

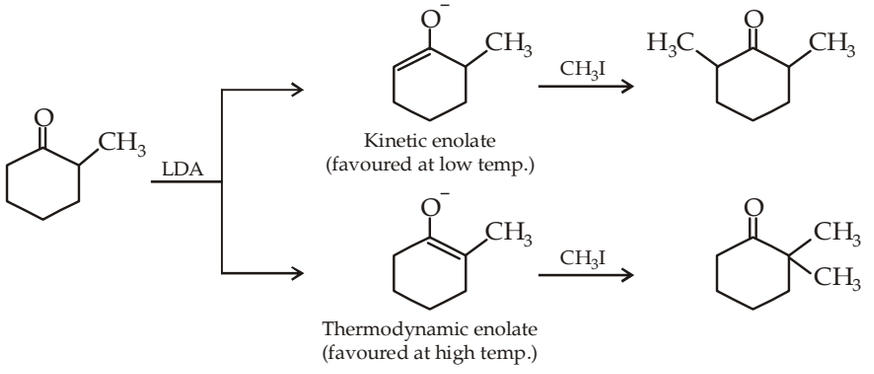






Since enolate ions are strong bases, *successful alkylations occur only when primary alkyl, primary benzylic, and primary allylic halides are used;* with secondary and tetiary halides, elimination becomes the main course of the reaction.

In case the ketone is unsymmetrical, two different products can be formed.

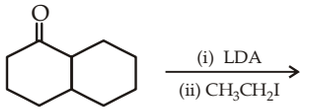


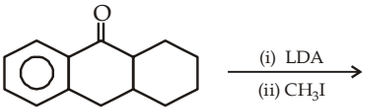
TEST YOUR UNDERSTANDING - 15.4

1. Predict the product(s) in each of the following reactions.

(a) $CH_3COCH_3 \xrightarrow[(ii)\ CH_2{=}CHCH_2Br]{(i)\ LDA}$

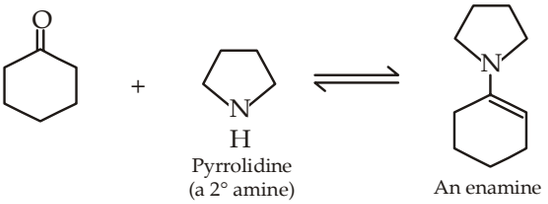
(b) $CH_3CH_2CN \xrightarrow[(ii)\ C_6H_5CH_2Br]{(i)\ LDA}$

(c) 

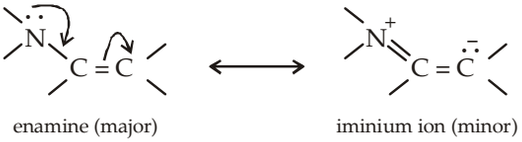
(d) 

15.2.4 Alkylation and Acylation of the α-Carbon *via* Enamine

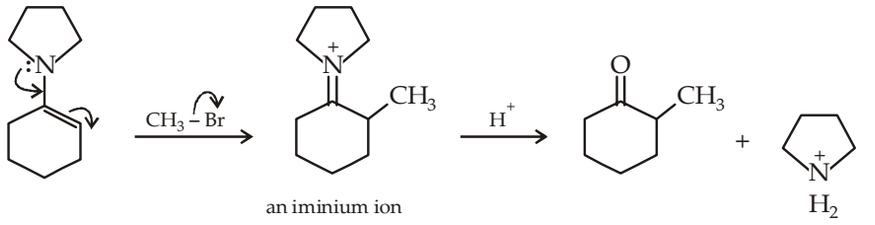
An *enamine* (a vinyl amine), the nitrogen analogue of an enol, is formed when an aldehyde or a ketone reacts with a secondary amine.



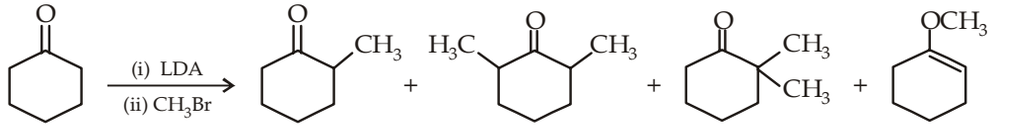
The resonance of an enamine shows that it has some carbanions character. Although, an enamine is a stronger nucleophile than an enol, it is quite selective in its alkylation reactions.



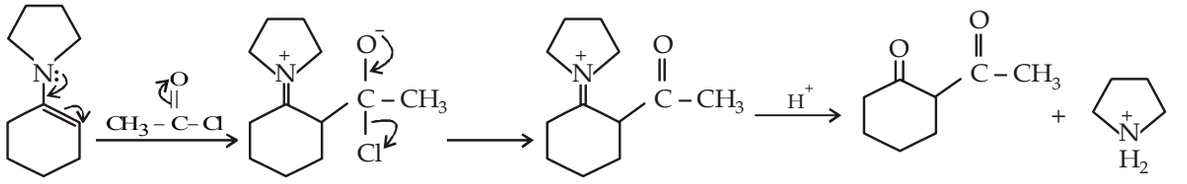
Like enolates, enamines react with electrophiles and thus they help in introducing an electrophile to the α-carbon of an aldehyde or a ketone.



Since, alkylation step is an S_N2 reaction, only primary alkyl halides or methyl halides should be used. Note that the iminium ions are unreactive toward further alkylation, so only one alkyl group can be introduced via enamine route (advantage over enolate route which may lead to monoalkylated, dialkylated and O–alkylated products).



Aldehydes and ketones can also be acylated *via* an enamine intermediate.



The enamine alkylation/acylation is sometimes called **Stork reaction**. Note that β-diketones are easily alkylated, hence they serve as useful intermediates in the synthesis of more complicated molecules.

TEST YOUR UNDERSTANDING - 15.5

1. Give the expected product of the following acid-catalyzed reactions.

(a) Acetophenone + Dimethylamine (b) Acetophenone + Methylamine

(c) Cyclohexanone + Aniline (d) Cyclohexanone + Piperidine

2. Give steps involved in the following conversions through enamine formation.

(a) Cyclopentanone ⟶ 2-Allylcyclopentanone (b) 3-Pentanone ⟶ 2-Methyl-1-phenyl-3-pentanone

(c) Acetophenone ⟶ Dibenzoylmethane

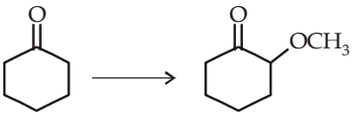
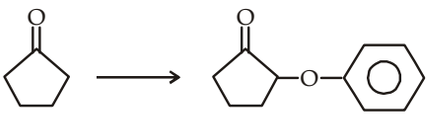
15.2.5 α-Halogenation of Aldehydes and Ketones

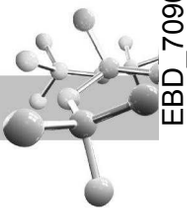
Discussed in the chapter on **'Aldehydes and Ketones'**.

TEST YOUR UNDERSTANDING - 15.6

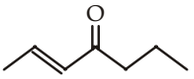
1. How would you accomplish the following conversions?

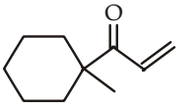
(a) $CH_3CH_2CHO \longrightarrow CH_3CH(NMe_2)CHO$ (b) $CH_3CH_2CHO \longrightarrow CH_3CH(OH)CHO$

(c)  (d) 

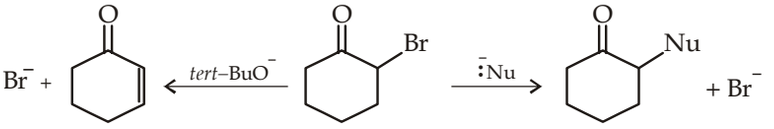


2. How will you prepare the following compounds from a carbonyl compound with no carbon-carbon double bonds?

(a) 

(b) 

α-Brominated carbonyl compounds are useful in synthetic chemistry, because such compounds easily undergo reactions of alkyl halides.



15.2.6 α-Halogenation of Carboxylic Acids (The HVZ Reaction)

Carboxylic acids do not undergo substitution reactions at the α-carbon (of course except halogenation through the HVZ reaction) because the OH group is much more acidic than the α-carbon. However, if a carboxylic acid is treated with PBr_3 and Br_2 (or red phosphorus and excess Br_2), then bromination occurs at the α-carbon; the reason being the fact that here the α-substitution occurs on an acyl bromide rather than the parent carboxylic acid. For details, consult chapter on **'Carboxylic Acids'**.

15.2.7 Nucleophilic Addition of Enolates to Carbonyl Compounds

Under this heading following reactions are covered.

(a) **Aldol condensations :** Discussed earlier in the chapter on **'Aldehydes and Ketones'**.

(b) **Reactions related to aldol condensation :** There are other important reactions which involve the attack by a carbanion (provided by compounds other than aldehydes and ketones) on a carbonyl group. These reactions are Perkin, Knoevenagel, Claisen, Dieckmann etc. These reactions may also be grouped in **nucleophilic acyl substitution**.

(i) **Perkin reaction :**

$$C_6H_5CHO + (CH_3CO)_2O \xrightarrow{CH_3COONa} C_6H_5CH = CHCOOOH$$

Here the carbanion is provided by $(CH_3CO)_2O$.

(ii) **Knoevenagel reaction :**

$$C_6H_5CHO + H_2C(COOC_2H_5)_2 \xrightarrow{\text{piperidine}} C_6H_5CH = CHCOOH$$

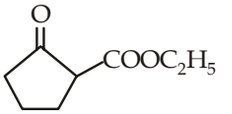
Here the carbanion (nucleophile) is provided by $H_2C(COOC_2H_5)_2$.

(iii) **Claisen condensation :**

$$CH_3COOC_2H_5 + H_3CCOOC_2H_5 \xrightarrow{C_2H_5ONa} CH_3COCH_2COOC_2H_5$$

Here the carbanion is provided by $CH_3COOC_2H_5$.

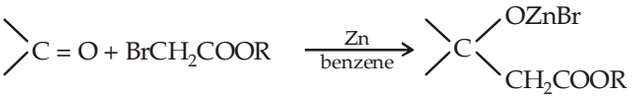
(iv) **Dieckmann condensation :**

$$COOC_2H_5(CH_2)_4COOC_2H_5 \xrightarrow{C_2H_5ONa}$$ 

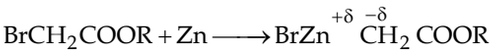
Here the carbanion is provided by α-carbon of the ester.

All these reactions are discussed in appropriate chapters on **Aldehydes and Ketones** or **Functional Derviatives of Carboxylic Acids**.

(c) Reformatsky reaction :

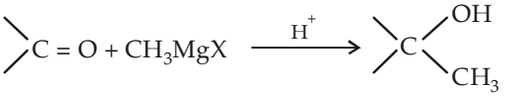


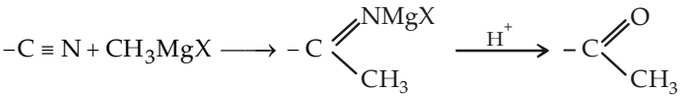
Here the carbanion is provided by the carbon atom attached to halogen (Br).



For details, consult chapter on **"Aldehydes and Ketones"**.

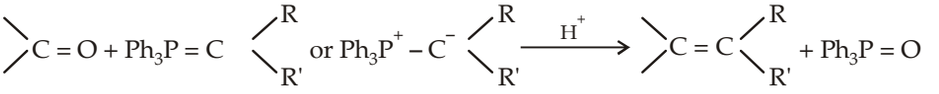
(d) Addition of Grignard reagents :





Here the carbanion (nucleophile) is provided by alkyl or aryl group of the Grignard reagent. For details, consult chapter on **"Organometallic Compounds"**.

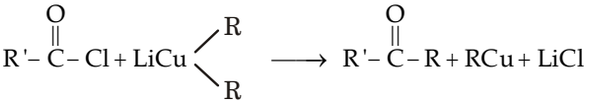
(e) Wittig reaction :



Details are given in the chapter on **"Aldehydes and Ketones"**.

15.2.8 Nucleophilic Acyl Substitution

Here the nucleophilic attack finally gives substituted product (*the typical reaction of acyl compounds*), while in aldol condensation, the nucleophilic attack leads to addition (*the typical reaction of aldehydes and ketones*). Examples of this type are Claisen condensation, Dieckmann condensation (both discussed in esters) and acylation of organocopper compounds (discussed in the preparation of ketones in the chapter on **'Aldehydes and Ketones'**).



Here the carbanion is provided by alkyl group.

15.2.9 Nucleophilic Aliphatic Substitution (Substitution on an sp^3 Carbon by a Nucleophile)

(a) Coupling of alkyl halides with organometallic compounds : Discussed in the preparation of alkanes, in the chapter on **'Aliphatic Hydrocarbons–I'**. Here, carbanion is provided by alkyl group of the organometallic compound.

(b) Alkylation of malonic ester, ethyl acetoacetate and related compounds.

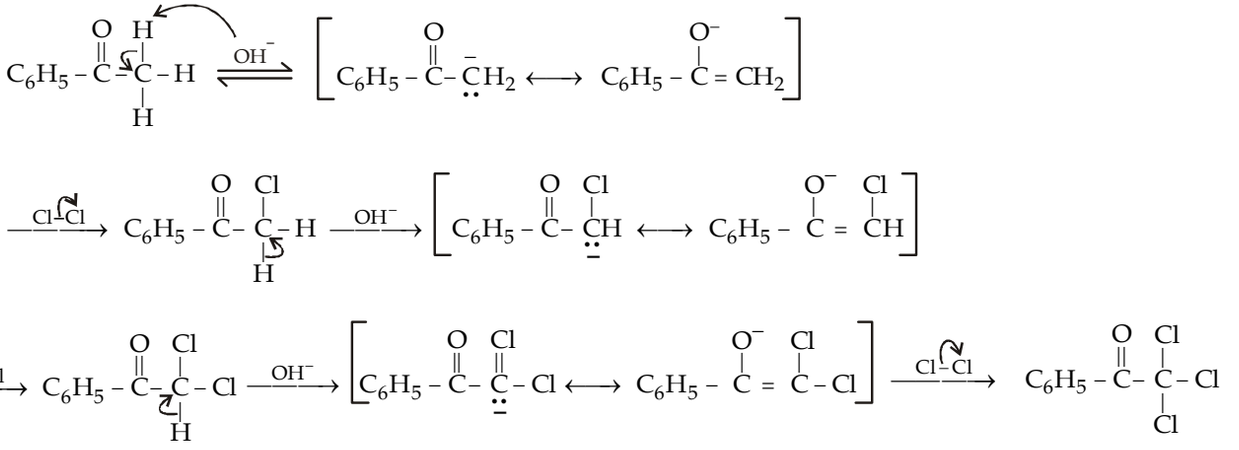
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15.3 ILLUSTRATIVE EXAMPLES

Example 1 :

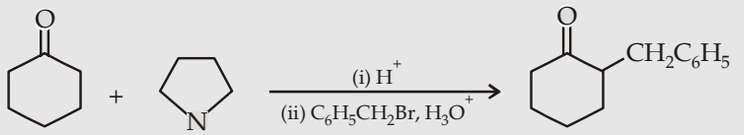
Propose a mechanism to show how acetophenone undergoes *base-promoted* bromination to form tribromoacetophenone.

Solution :

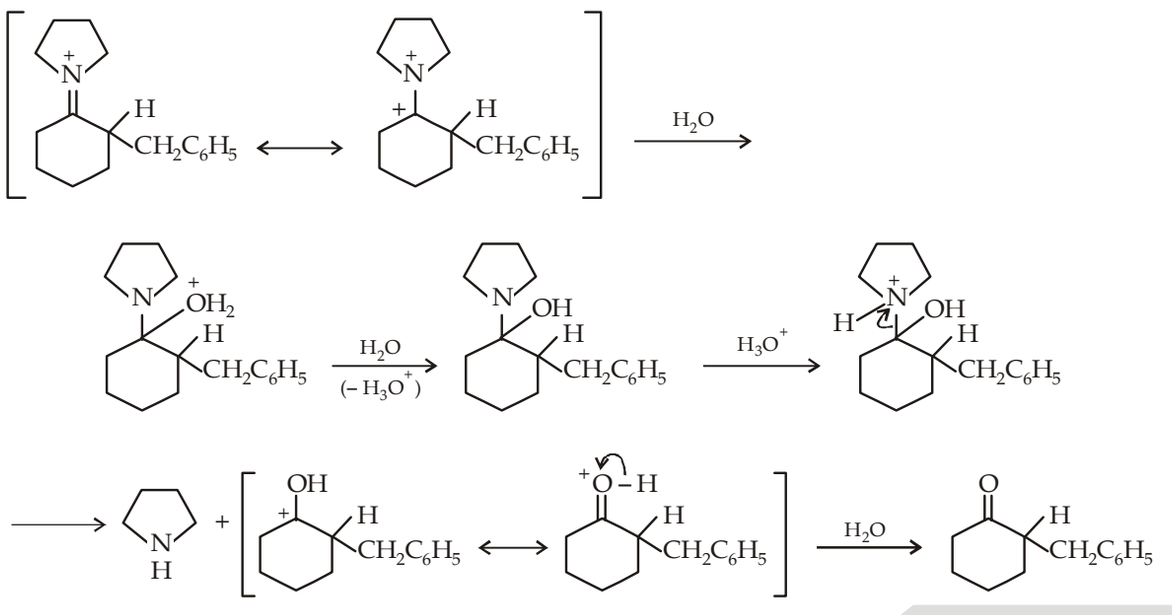


Example 2 :

Propose mechanism for the following conversion.



Solution :



Example 3 :

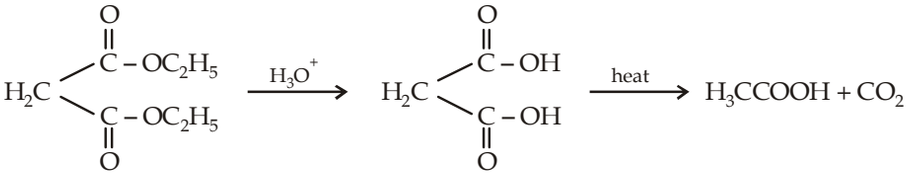
Give steps for preparing following compounds using malonic ester synthesis.

(a) 3-Phenylpropanoic acid **(b) 2-Benzylbutanoic acid**

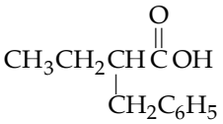
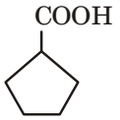
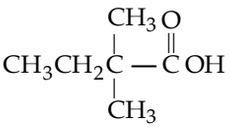
(c) Cyclopentanecarboxylic acid **(d) 2,2-Dimethylbutanoic acid**

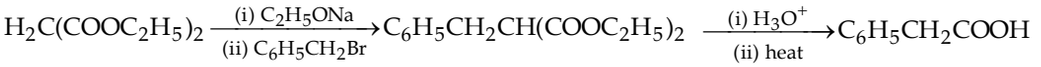
Solution :

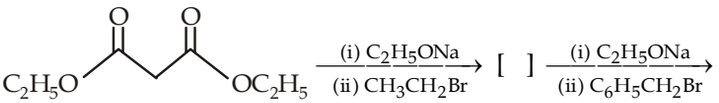
In malonic ester synthesis, the $-CH_2COOH$ or $-\overset{|}{C}HCOOH$ part of the product is coming from malonic ester itself, so the other substituent(s) should be introduced by alkylation of malonic ester before the final steps of hydrolysis and decarboxylation.

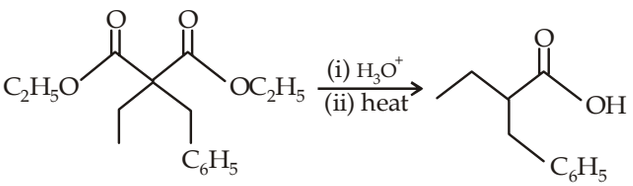


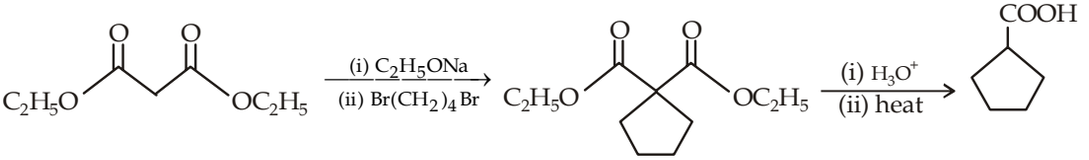
Further note that malonic ester synthesis can be applied for synthesising carboxylic acids having either one or two substituents on the α-carbon (not three), i.e. either $-CH_2COOH$ or $-\overset{|}{C}HCOOH$ type and not R_3CCOOH type. For getting the right route for synthesis of such questions, first write down the structure of the product and know the nature of alkyl group to be introduced.

(a)  (b)  (c)  (d) 

(a) 

(b) 



(c) 

(d) 2,2-Dimethylbutanoic acid has three alkyl groups on the α-carbon atom, but malonic ester has only two α-hydrogen atoms so only two alkyl groups (sbstituents) can be introduced in malonic ester. Thus the compound (d) can't be prepared through malonic ester synthesis.

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Example 4 :

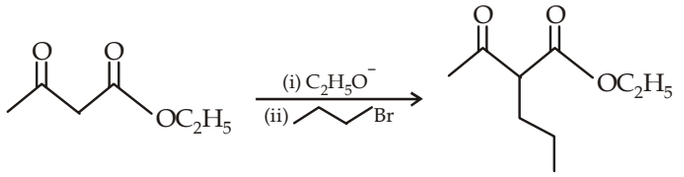
Give steps involved in the conversion of ethyl acetoacetate into

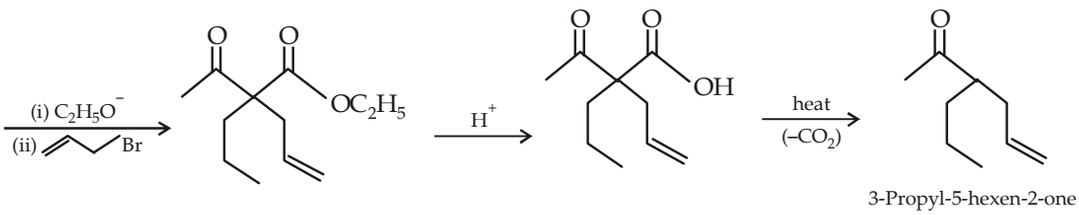
(a) 3-propyl-5-hexen-2-one **(b) cyclopropyl methyl ketone**

(c) 4-phenylbut-3-en-2-one **(d) benzyl *sec*-2-propenylphenyl ketone**

Solution :

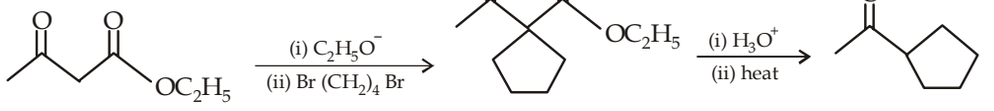
(a)



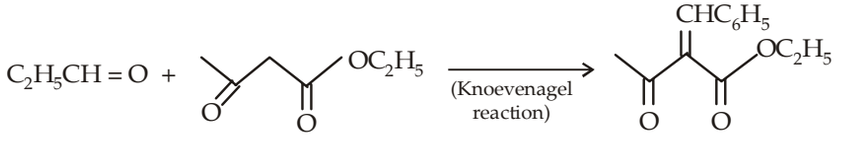


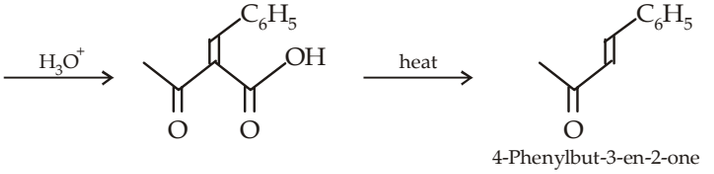
3-Propyl-5-hexen-2-one

(b)



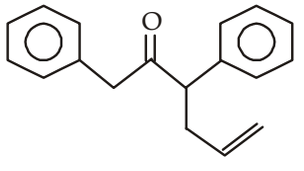
(c)



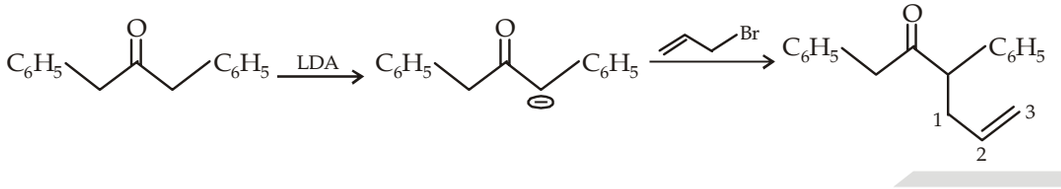


4-Phenylbut-3-en-2-one

(d)



This compound can't be prepared from ethyl acetoacetate because here ketonic group is having substituents on both $-CH_2-$ groups which is not possible because in acetoacetic ester only one $-CH_2-$ is activated. However, this can be prepared from dibenzyl ketone in the following way.

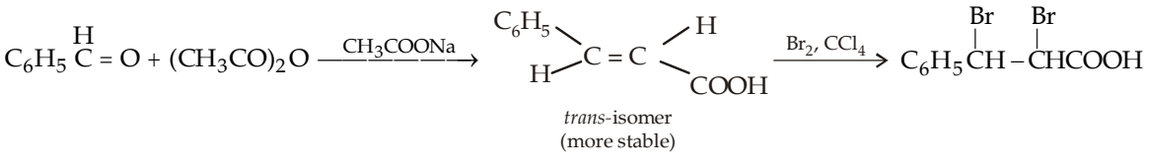


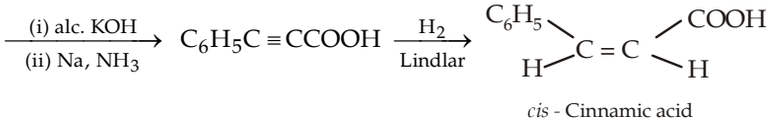
Example 5 :

Perkin condensation between benzaldehyde and ethanoic anhydride in presence of sodium ethanoate leads to the more stable *trans*-cinnamic acid. Suggest a method for preparing the *cis*-cinnamic acid (*cis*-3-phenylpropenoic acid).

Solution :

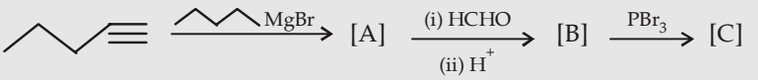
Remember that a *cis*-alkene can often be prepared from an alkyne by hydrogenation of a triple bond over Lindlar's catalyst.

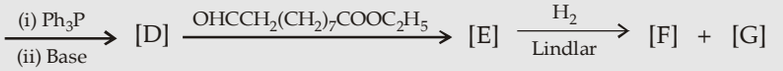




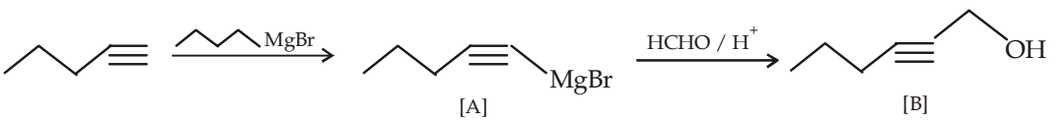
Example 6 :

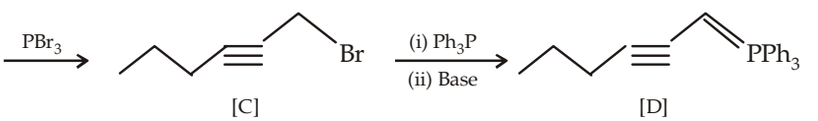
Complete the following and comment on the reaction of each step.

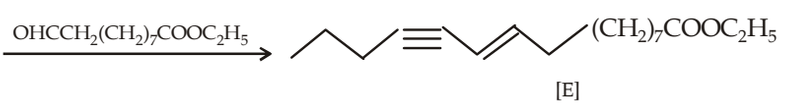


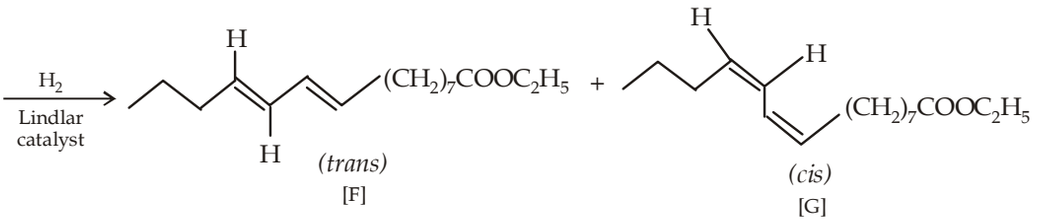


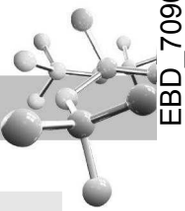
Solution :











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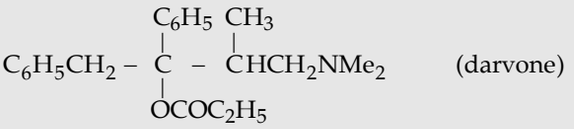
Example 7 :

Give steps involved in the conversion of

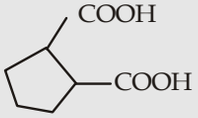
(a) ethyl cyanoacetate to valproic acid (2-propylpentanoic acid), an antiepileptic compound.

(b) benzaldehyde to acetophenone involving 1,3-dithiane as an intermediate.

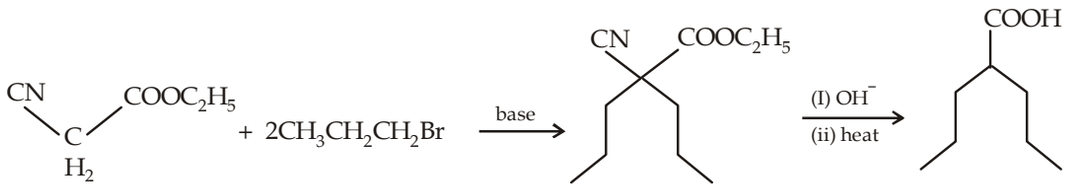
(c) Ethyl phenyl ketone to darvone, an analgesic using $(CH_3CH_2CO)_2O$, $C_6H_5CH_2MgBr$, HCHO and $(CH_3)_2NH$ as reagents.

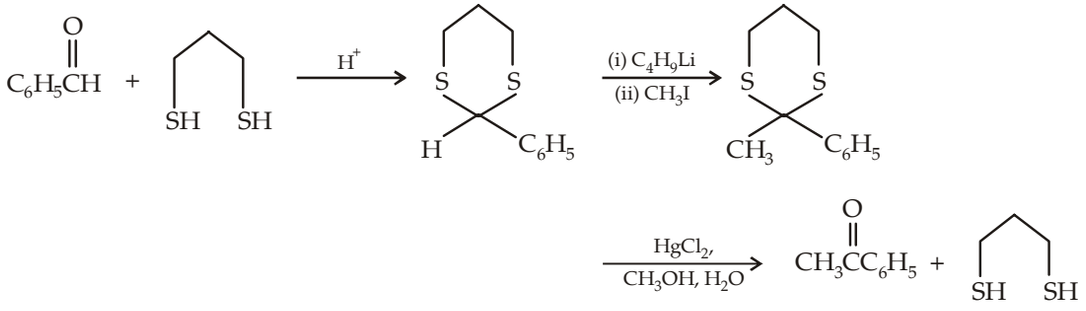


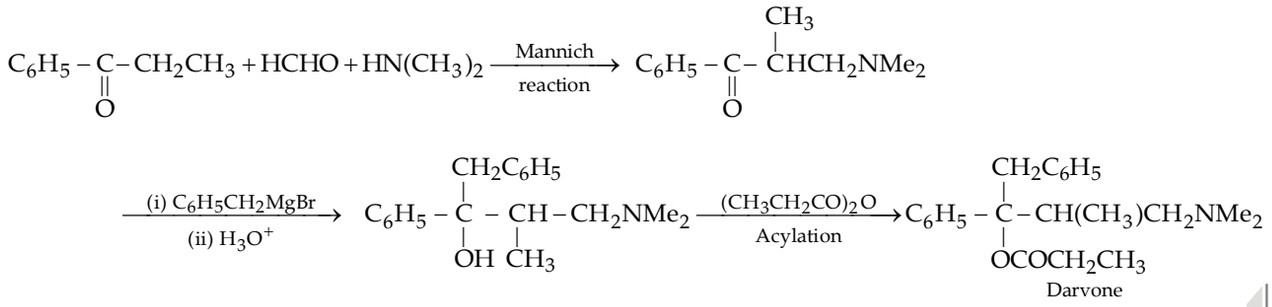
(darvone)

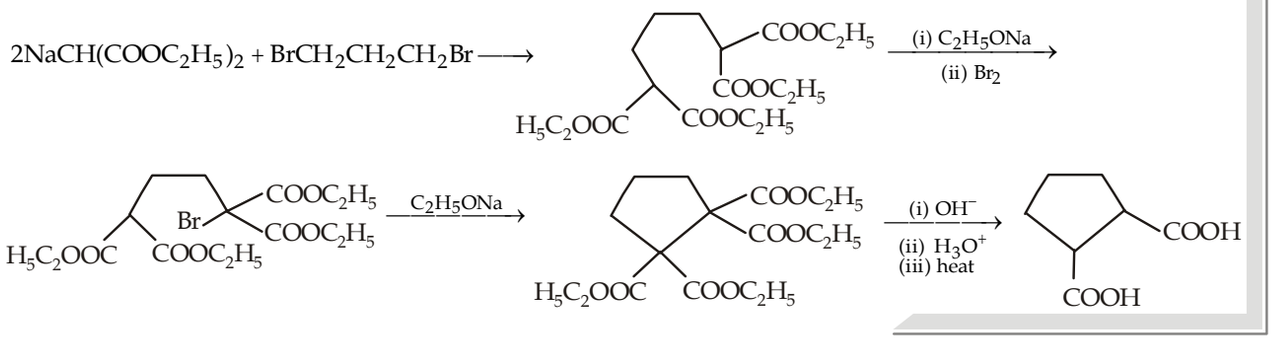
(d) $2NaCH(COOC_2H_5)_2 + BrCH_2CH_2CH_2Br \longrightarrow$ 

Solution :

(a) 

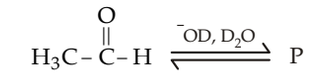
(b) 

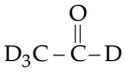
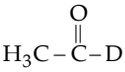
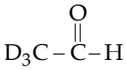
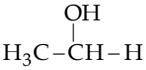
(c) 

(d) 

EXERCISE 15.1 (MCQ - ONE option correct)

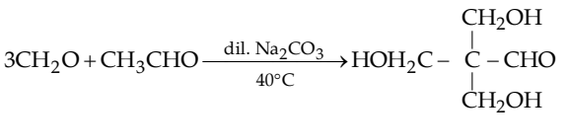
1. Predict the product P in the following reaction



(a) 
(b) 
(c) 
(d) 

2. Which of the following is true regarding conversion of a ketone into its enolic form by acids and bases?
(a) In both types, the first step is the protonation of the carbonyl group
(b) In both types, the first step is the removal of α-hydrogen
(c) The two steps i.e. protonation and removal of α-hydrogen are reversed in the base - and acid-catalyzed reactions
(d) None is true

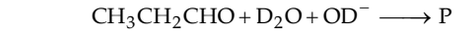
3. Which of the following reactions of optically active *sec*-butyl phenyl ketone undergoes fastest?
(a) Acid-catalyzed deuterium exchange
(b) Base-promoted bromination
(c) Acid-catalyzed racemization
(d) None of these

4. 

The above reaction involves
(a) one aldol condensation and one Cannizzaro reaction
(b) two aldol condensations
(c) two aldol condensation and one Cannizzaro reaction
(d) three aldol condensations

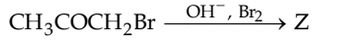
5. In case, there is a competition between intramolecular aldol condensation and intermolecular aldol condensation, which factor favours intramolecular aldol reaction over intermolecular?
(a) Using excess of base
(b) Using limited amount of base
(c) Using high dilution technique
(d) Using large excess of the compound

6. The compound P in the following reaction should be



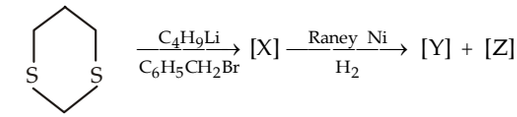
(a) CH_3CH_2CDO (b) CD_3CH_2CHO
(c) CH_3CD_2CHO (d) CD_3CD_2CHO

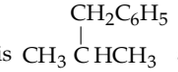
7. Predict the nature of Z in the following reaction



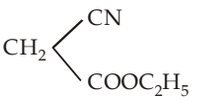
(a) $CH_2BrCOCH_2Br$ (b) $CH_3COCHBr_2$
(c) $CH_2BrCOCHBr_2$ (d) No reaction

8. Predict the nature of [Y] and [Z] in the following reaction



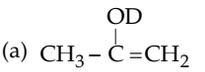
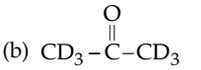
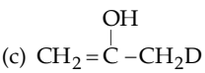
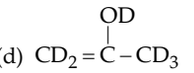
(a) Y is $C_6H_5CH_2CH_2CH_2CH_3$ and Z is CH_4
(b) Y is  and Z is CH_4
(c) Y is $C_6H_5CH_2CH_3 + CH_3CH_2CH_3$
(d) Y is $C_6H_5CH_2CH_2CH_3$ and Z is NiS

9. Which of the following order is correct regarding the percentage of enolic form of 2,4-pentanedione in three solvents : H_2O (A), CH_3CN (B) and C_6H_{14} (C)?
(a) A > B > C (b) B > A > C
(c) C > A > B (d) C > B > A

10. Which of the following compound does not form carbanion with sodium ethoxide?
(a) $CH_3COCH_2COOC_2H_5$ (b) $(CH_3)_3C.COOC_2H_5$
(c) $CH_2(COOC_2H_5)_2$ (d) 

11. Carbanion is
(a) an electrophile (b) a nucleophile
(c) a Zwitter ion (d) a free radical

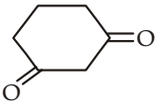
12. The enol form of acetone, after treatment with D_2O, gives.

(a) 
(b) 
(c) 
(d) 

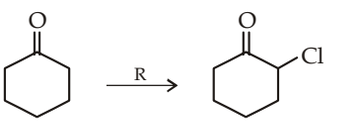
EXERCISE 15.2 (MCQ 1 or >1 option correct, Passage based, Matching, A/R)

DIRECTIONS for Q. 1 to Q. 7 : Multiple choice questions with one or more than one correct option(s).

1. Which of the following statement is false regarding enolization of



(a) It can form two enolic forms of equal stability
(b) It can form two enolic forms of different stability
(c) It can form more than two enolic forms of different stability
(d) It can form only one enolic form

2. 

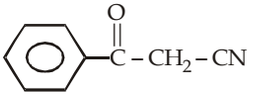
Here the reagent R is
(a) Cl_2 in presence of CH_3COOH
(b) Cl_2 in presence of NaOH
(c) Cl_2 in presence of water
(d) Cl_2 in presence of light

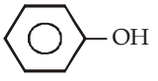
3. Which statement is true about acetoacetic ester?
   (a) Its keto form boils at a higher temp. than the enolic form
   (b) Its enolic form boils at a higher temp. than the keto form
   (c) Both boil at same temperature
   (d) It discharges the colour of bromine dissolved in CCl_4

4. $2C_6H_5CHO \xrightarrow[H_2O]{OH^-} C_6H_5CH_2OH + C_6H_5COO^-$

   Which statement is correct regarding the above reduction of benzaldehyde to benzyl alcohol?
   (a) One hydrogen is coming from H_2O as H^+ and another from C_6H_5CHO as H^-
   (b) One hydrogen is coming from H_2O as H^- and another from C_6H_5CHO as H^+
   (c) One hydrogen from H_2O and another from C_6H_5CHO, both in the form of H^-
   (d) The reduction is an example of disproportionation reaction

5. A primary carbanion is
   (a) more reactive than a secondary carbanion
   (b) more stable than a secondary carbanion
   (c) less stable than a secondary carbanion
   (d) more stable than a tertiary carbanion

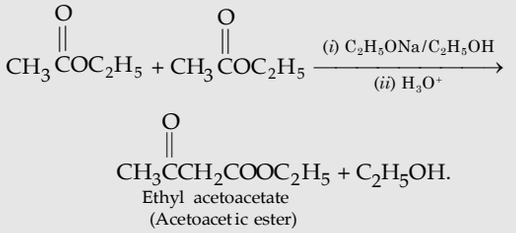
6. Which have active methylene group?
   (a) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$
   (b) $CH_3-CH_2-NO_2$
   (c) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CN$
   (d) 

7. Which have acidic H?
   (a) CH_3COOH (b) 
   (c) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CN$ (d) $NaNH_2$

INSTRUCTION for Q. 8 to 11 : Read the passages given below and answer the questions that follow.

PASSAGE 1

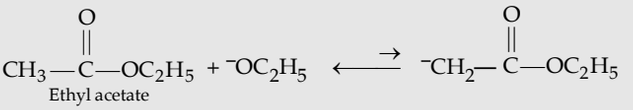
Due to acidic nature of α-hydrogens, esters when treated with a strong base (generally C_2H_5ONa) undergo condensation of form β-keto ester.



Ethyl acetoacetate
(Acetoacetic ester)

Mechanism

Step 1.

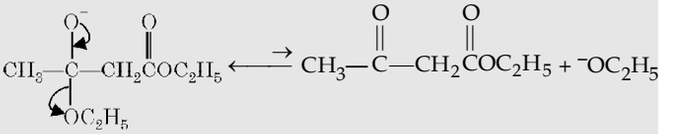


Ethyl acetate

Step 2.



Ethyl acetate (2nd mole)



Although the products at the end of the second step are acetoacetic ester and ethoxide ion, the reaction does not stop at this step ; had it so been, the yield of the β-keto ester would have been very little because the overall equilibrium upto this point is favourable to reactants and not to products.

8. The IUPAC name of ethylacetoacetate is
   (a) acetoacetic ester (b) ethyl 3-oxobutanoate
   (c) ethyl acetic ester (d) ethylacetoacetate

9. The net reaction in the step 2 of the reaction is
   (a) nucleophilic addition (b) nucleophilic substitution
   (c) both (a) and (b) (d) elimination

10. Which of the following statement is true ?
   (a) The reaction is still not complete because acetoacetic ester is a stronger acid than ethyl acetate
   (b) The reaction is still not complete because acetoacetic ester is a stronger acid than ethanol
   (c) Both (a) and (b)
   (d) The reaction stops at the given final step giving acetoacetic ester and ethoxide ion.

11. The above reaction, known as Claisen condensation involves the formation of new bond between
   (a) carbon and oxygen
   (b) the two carbonyl carbon atoms of the two components
   (c) α – carbon atoms of the two components
   (d) the α-carbon of one molecule and the carbonyl carbon of another molecule

Instructions for Q. 12 : Following questions are Multiple Matching type Questions :

12.

	Column - I (Reaction)		*Column - II* (Carbanion provided by)
(A)	Roformatsky reaction	(a)	$CH_3C\bar{O}CH_2$
(B)	Aldol condensation	(b)	$\bar{C}H_2COOC_2H_5$
(C)	Claisen condensation	(c)	$\bar{C}H_2CHO$
(D)	HVZ reaction	(d)	$R\bar{C}H-\overset{O}{\overset{\|}{C}}-Br$

EXERCISE 15.3 (Subjective Problems)

1. Give the important resonance forms for the enolate of
(a) acetone (d) ethyl acetoacetate
(b) cyclohexanone (e) ethyl cyanoacetate
(c) 2,4-pentanedione (f) nitroacetone

2. What happens when cyclohexanone is treated with (a) dil. NaOH, (b) dilute HCl

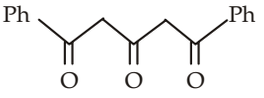
3. Give steps involved in the following conversions.

(a) $C_6H_5CHO \longrightarrow C_6H_5CHO^{18}$

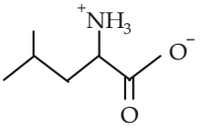
(b) $C_6H_5CHO \longrightarrow C_6H_5CH_2CHO$

(c) $C_6H_5CHO \longrightarrow C_6H_5CH = CH - CH = CHCHO$

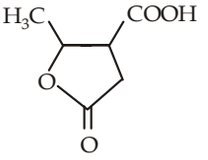
(d) $C_2H_5O\overset{\overset{O}{\|}}{C}OC_2H_5$ (ethyl carbonate) to



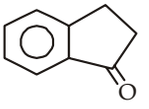
(e) $C_2H_5O-\overset{\overset{O}{\|}}{C}-OC_2H_5$ (ethyl oxalate) to



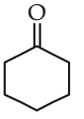
(f) CH_3CHO to



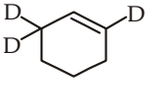
(g) C_6H_5CHO to



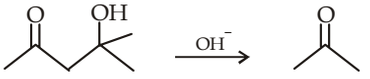
(h)



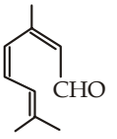
to



4. Is it possible to convert 4-hydroxy-4-methyl-2-pentanone to acetone?



5. Give steps involved in the conversion of acetone and ethanal to dehydrocitral,

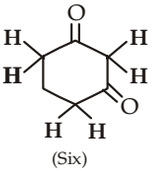


SOLUTIONS

TEST YOUR UNDERSTANDING - 15.1

1. (a) $CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{C}-CH_3$ (CH_3) (Three) (b) $C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3$ (Three) (c) $H_3C-\overset{\overset{CH_3}{|}}{C}-\overset{\overset{O}{\|}}{C}H$ (Zero)

(d)



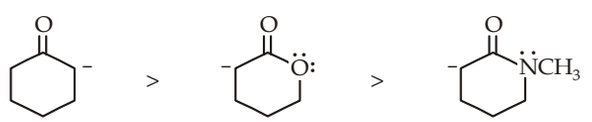
(Six)

2. Acidity of an acid follows the stability of the corresponding conjugate base. Conjugate bases of the corresponding acids are arranged in decreasing order.

(a) $CH_3-\overset{\overset{O}{\|}}{C}-O^- > CH_3-\overset{\overset{O}{\|}}{C}-\overset{-}{C}H_2 > \overset{-}{C}H_2-\overset{\overset{O}{\|}}{C}-\ddot{O}CH_3 > HC\equiv C^-$ ( )

Equivalent resonating structures; –ve charge is fully delocalized onto C=O; –ve charge is partly delocalized onto C=O; –ve charge not delocalized

(c)



I II III

I: –ve charge fully delocalized

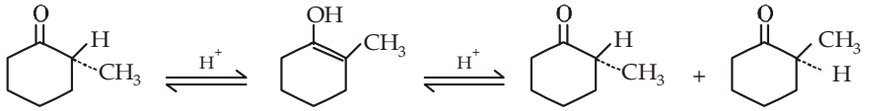
II > III: –ve charge partly delocalized, O is more electronegative than N hence II is more stable than III

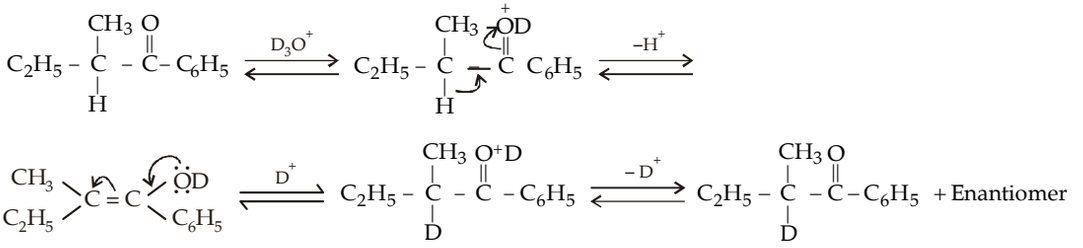
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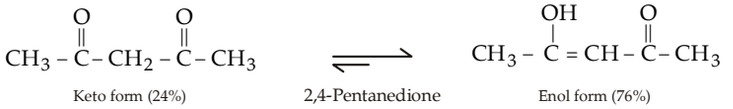
TEST YOUR UNDERSTANDING - 15.2

1. (a) The ketone does not have any hydrogen on its α-carbon (which is a stereocenter) and thus it will not undergo enolization.

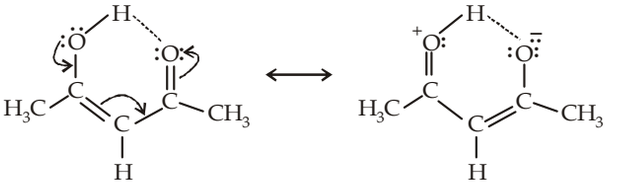
(b) The ketone has α-hydrogen on an achiral carbon, hence it will undergo enolization but *without racemization* because the stereocenter is a β-carbon which is not involved in enolization.

(c) 

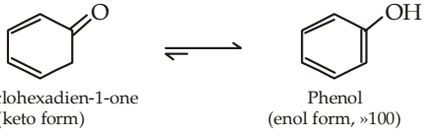
2. 

3. (a) 

The greater stability of the β-enol form is due to resonance stabilization of the conjugated double bonds and (in a cyclic form) through hydrogen bonding.

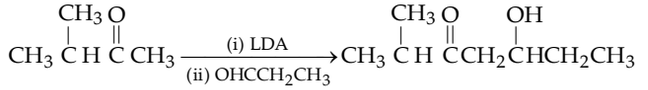


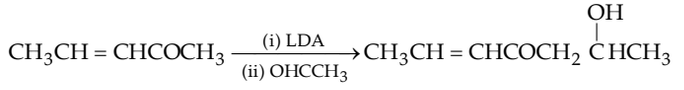
Resonance stabilization and H-bonding in the cyclic form of enol-2,4-pentanedione

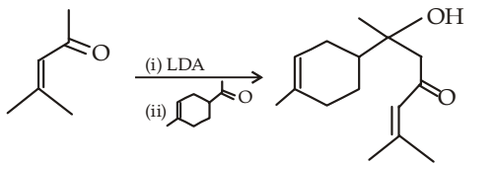
(b) 

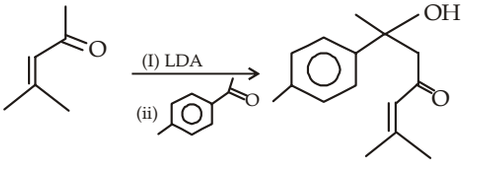
The stability of the enolic form is again due to high resonance energy of the benzene ring.

TEST YOUR UNDERSTANDING - 15.3

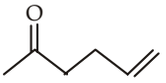
1. (a) 

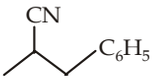
(b) 

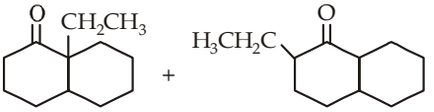
(c) 

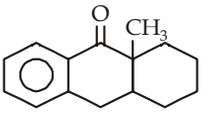
(d) 

TEST YOUR UNDERSTANDING - 15.4

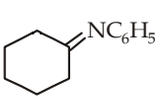
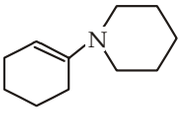
1. (a) 

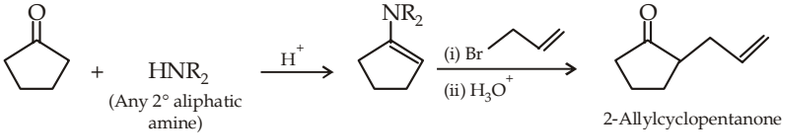
(b) 

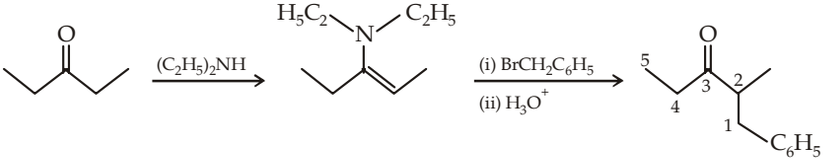
(c) 
(Minor) (Major)

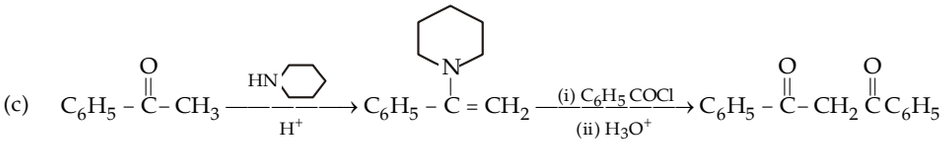
(d) 

TEST YOUR UNDERSTANDING - 15.5

1. (a) $C_6H_5-\underset{\displaystyle N(CH_3)_2}{\overset{|}{C}}=CH_2$ (b) $C_6H_5-\overset{\displaystyle NCH_3}{\overset{\|}{C}}-CH_3$ (c)  (d) 

2. (a) 
(Any 2° aliphatic amine)
2-Allylcyclopentanone

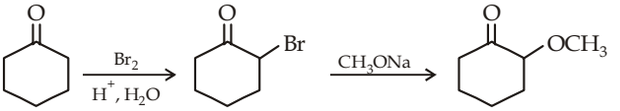
(b) 

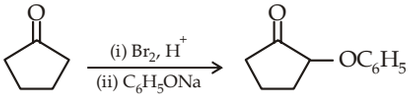
(c) 

TEST YOUR UNDERSTANDING - 15.6

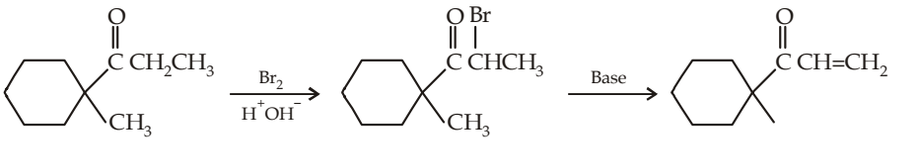
1. (a) $CH_3CH_2CHO + Br_2 \xrightarrow{H^+,\ H_2O} CH_3\underset{\displaystyle Br}{\overset{|}{C}}HCHO \xrightarrow{HNMe_2} CH_3\underset{\displaystyle NMe_2}{\overset{|}{C}}HCHO$

(b) $CH_3CH_2CHO + Br_2 \xrightarrow{H^+,\ H_2O} CH_3\underset{\displaystyle Br}{\overset{|}{C}}HCHO \xrightarrow{OH^-} CH_3\underset{\displaystyle OH}{\overset{|}{C}}HCHO$

(c) 

(d) 

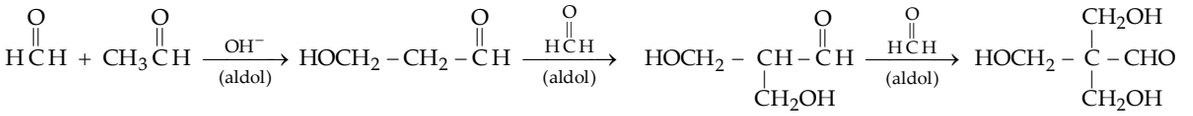
2. (a) $CH_3CH_2CH_2\overset{\displaystyle O}{\overset{\|}{C}}CH_2CH_2CH_3 \xrightarrow[H^+,\ OH^-]{Br_2} CH_3CH_2\underset{\displaystyle Br}{\overset{|}{C}}H\overset{\displaystyle O}{\overset{\|}{C}}CH_2CH_2CH_3 \xrightarrow{tert-BuO^-} CH_3CH=CH\overset{\displaystyle O}{\overset{\|}{C}}CH_2CH_2CH_3$

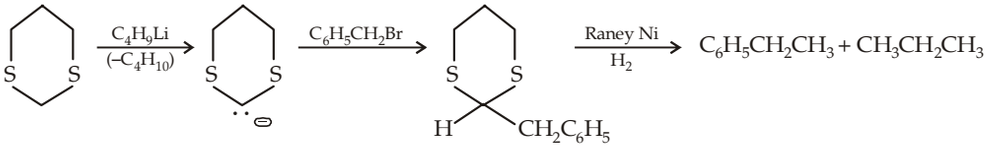
(b) 

EBD_7090

EXERCISE 15.1

1	(c)	**5**	(c)	**9**	(d)
2	(c)	**6**	(c)	**10**	(b)
3	(d)	**7**	(b)	**11**	(b)
4	(d)	**8**	(c)	**12**	(b)

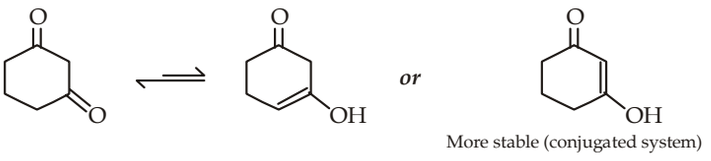
1. **Only acidic hydrogens** (α – to C = O) are replaced.
2. The steps in the base- and acid- catalyzed keto-enol interconversions are reversed. In the base-catalyzed reaction, the base removes the α-proton in the first step and the oxygen is protonated in the second step. In the acid-catalyzed reaction, the acid protonates the oxygen in the first step and the α-proton is removed in the second step.
3. All the three reactions proceed at about the same rate, because the rate determining step in each reaction is same (removal of a proton from the α-carbon atom).
4. 
5. For getting good yield in intramolecular aldol condensation leading to cyclization, very dilute solution must be used. When very dilute solutions are used (high dilution technique), probability for interacting one end of a molecule with the other end of the same molecule will be more than with the other molecule.
6. Only acidic hydrogens (α-hydrogen) of an aldehyde/ketone are easily exchanged.
7. Presence of Br in $CH_3-\overset{O}{\overset{\|}{C}}-CH_2Br$ makes the carbon, to which it is attached, more acidic hence hydrogen attached to it will be first and more readily replaced by Br.
8. Carbon-2 of 1,3-dithiane is more electropositive (acidic) due to the presence of electronegative sulphur on both sides. Hence it reacts with the nucleophile (C_4H_9Li) easily.

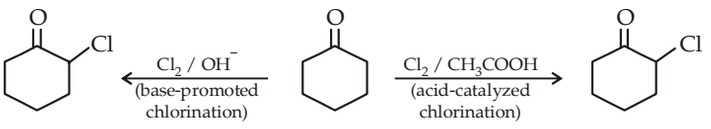


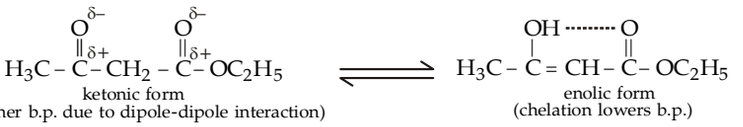
9. In a polar solvent, such as water, the keto form is stabilized by solvation, hence it is more stable. When the interaction between solvent becomes minimal, the enol form achieves stability by internal hydrogen bonding.

EXERCISE 15.2

>1 CORRECT OPTION	**1**	(a,c,d)	**2**	(a,b)	**3**	(a,d)
	4	(a,d)	**5**	(b, d)	**6**	(a, b, c, d)
	7	(a, b, c)				
PASSAGE 1	**8**	(b)			**9**	(b)
	10	(c)			**11**	(d)
MATCH THE FOLLOWING	**12**	(A) - b, (B) - a, c, (C) - b, (D) - d				

1. 

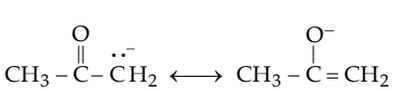
2. 

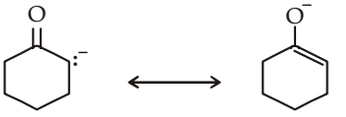
3. 

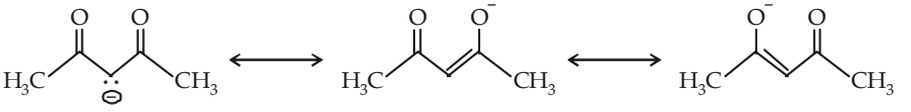
This form discharges colour of Br_2 in CCl_4.

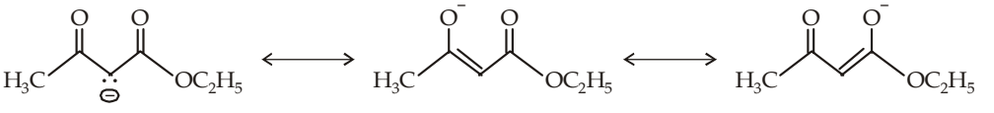
4. The hydrogen atom that is added to the carbonyl carbon of the aldehyde in the reduction is derived directly from the other aldehyde molecule as a hydride ion. The second hydrogen that is added to the negatively charged oxygen is coming from the solvent (consult mechanism of Cannizzaro reaction). Oxidation of one molecule of the compound at the expense of other molecule of the same compound is known as disproportionation.

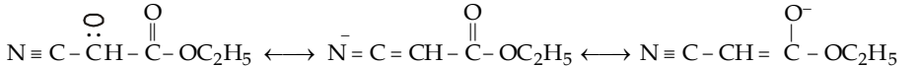
EXERCISE 15.3

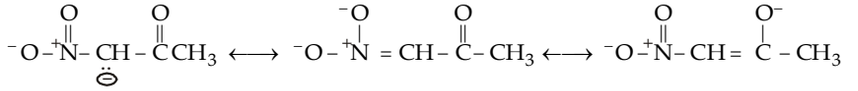
1. (a) 

(b) 

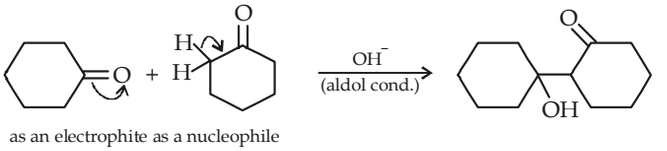
(c) 

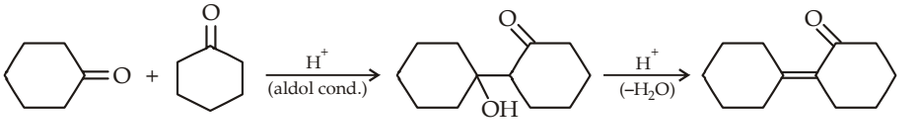
(d) 

(e) 

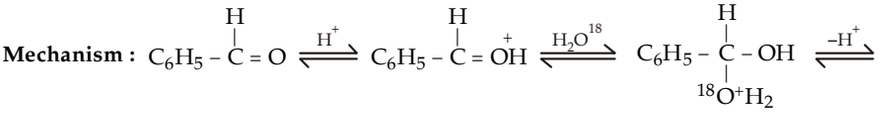
(f) 

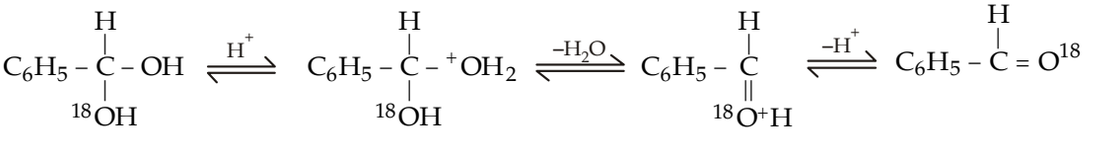
(Other resonance forms of the $-NO_2$ group are not shown)

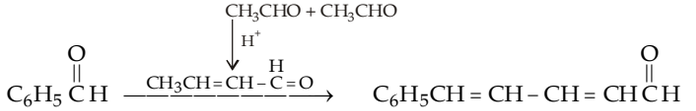
2. (a) 

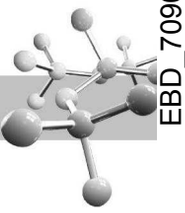
(b) 

3. (a) $C_6H_5CHO + H_2O^{18} \xrightarrow{H^+} C_6H_5CHO^{18} + H_2O$

Mechanism : 

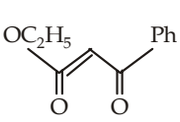
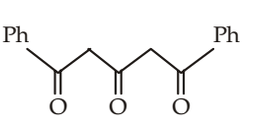


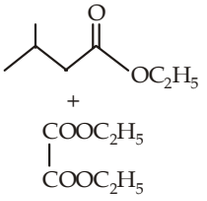
(b) 

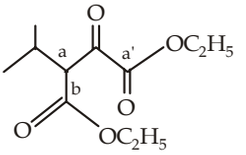


(c) $C_6H_5CH=O + Ph_3P=CH-OPh \xrightarrow[\text{reaction}]{\text{Wittig}} C_6H_5CH=CH-OPh \xrightarrow[\text{Cleavage of vinyl ether}]{H^+}$

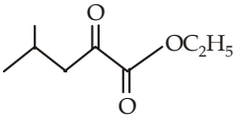
$C_6H_5CH=CH-OH \xrightarrow{\text{tantomerizes}} C_6H_5-CH_2-CH=O$

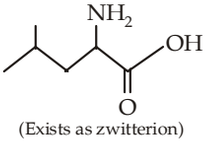
(d) $C_2H_5O-\overset{O}{\overset{\|}{C}}-OC_2H_5 + H_3C\overset{O}{\overset{\|}{C}}Ph \xrightarrow[\text{(Claisen cond.)}]{OC_2H_5^-}$  $\xrightarrow[-OC_2H_5\text{ (Claisen)}]{H_3C\overset{O}{\overset{\|}{C}}Ph}$ 

(e) 

$\xrightarrow[\text{(Crossed Claisen)}]{^-OC_2H_5}$ 

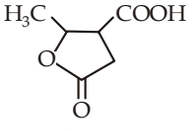
$\xrightarrow[\text{(ii) heat (}-CO_2\text{ from b-keto acids)}]{\text{(i) } H^+}$



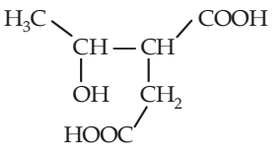
$\xrightarrow[\text{(Reductive amination)}]{NH_3,\ H_2/Pd}$ 

(Exists as zwitterion)

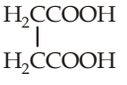
(f) Proceed backward, recall that a γ-lactone (a cyclic ester) can be easily obtained from a γ-hydroxy acid which in turn can be obtained from CH_3CHO and succinic acid by an aldol-*type* condensation.

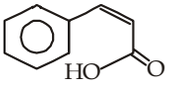
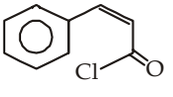
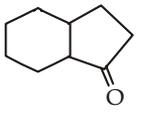


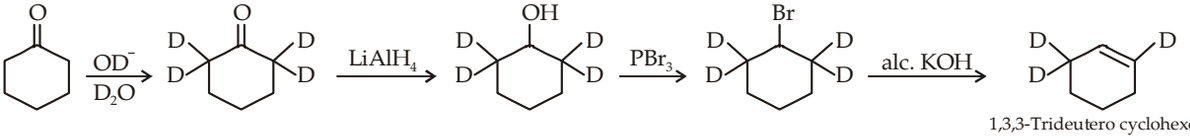
A r-lactone

$\longleftarrow$ 

A r-hydroxy acid

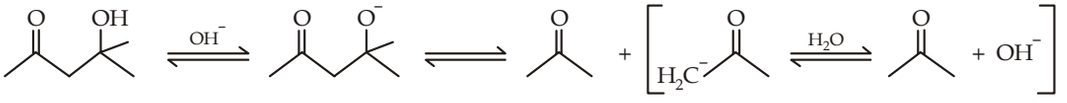
$\longleftarrow CH_3CHO +$ 

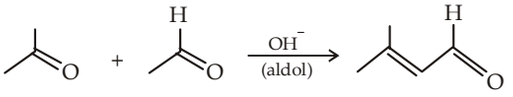
(g) $C_6H_5CHO \xrightarrow[CH_3COONa]{(CH_3CO)_2O}$  $\xrightarrow[\text{(ii) } SOCl_2]{\text{(i) } H_2/Ni}$  $\xrightarrow{HF}$ 

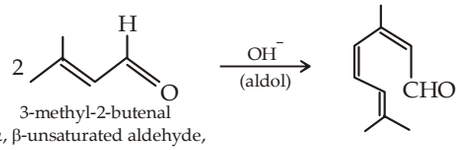
(h) 

1,3,3-Trideutero cyclohexene

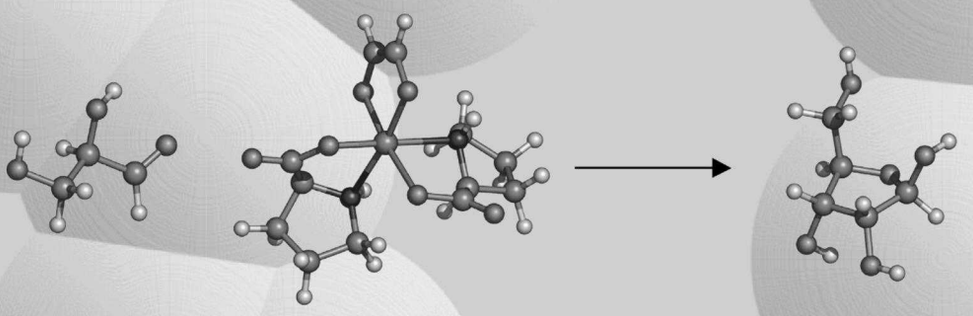
4. The reaction is an example of reverse of the aldol condensation commonly known as *retrograde aldol* or *retro aldol*. According to the *principle of microscopic reversibility* (a reaction and its reverse follow exactly the same path but in opposite directions), all steps in the aldol condensation take place in the reverse order.



5. 



3-methyl-2-butenal
(α, β-unsaturated aldehyde, α-H is acidic)



16

α,β-Unsaturated Carbonyl Compounds

CHAPTER HIGHLIGHTS

16.1 Preparation

16.2 Properties

16.3 Illustrative Examples

EXERCISES

SOLUTIONS

α, β-Unsaturated carbonyl compounds contain both a carbon-carbon double bond and a carbon-oxygen double bond separated by just one carbon-carbon single bond. Thus note that such compounds have a conjugated system $-\overset{|}{C}=C-\overset{|}{C}=O$.

16.1 Preparation

α, β - Unsaturated compounds are prepared by the following methods.

(i) Aldol condensation leads to α, β-unsaturated aldehydes and ketones.

(ii) Dehydrohalogenation of α-haloacids lead to α, β-unsaturated carboxylic acids.

(iii) Perkin reaction leads to α, β-unsaturated carboxylic acids.

(iv) Other methods specific for few compounds.

TEST YOUR UNDERSTANDING - 16.1

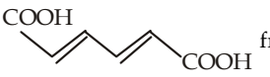
1. Give steps involved in the following preparation

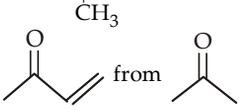
(a) $CH_3CH=CH\overset{O}{\overset{\|}{C}}OH$ from $CH\equiv CH$

(b) $CH_2=CH\overset{O}{\overset{\|}{C}}OCH_3$ from $CH_2=CH_2$

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(c) $CH_2=C(CH_3)COOCH_3$ from CH_3COCH_3

(d)  from adipic acid.

(e)  from

(f) Cinnamic acid from toluene

(g) Maleic acid from succinic acid

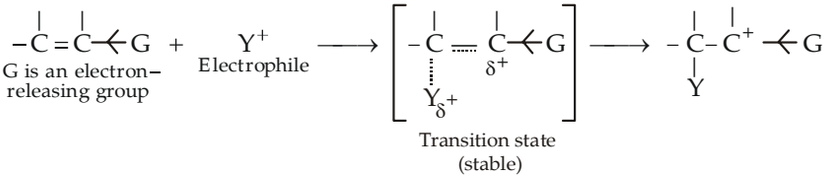
16.2 Properties

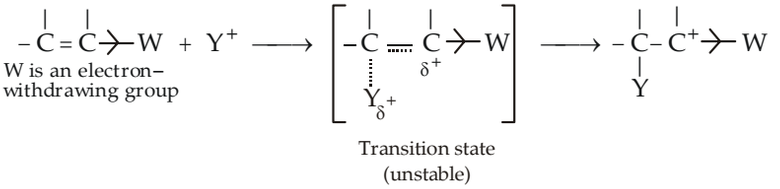
α, β-Unsaturated compounds possess not only the properties of the individual functional groups, i.e. C = C, and $-\overset{|}{C}=O$, but also certain other properties, characteristic of the conjugated system.

However, here stress is given only those properties which are due to the presence of α,β-unsaturated carbonyl moiety.

16.2.1 Electrophilic Addition

Usually, the carbon-carbon double bond is a rich source of electrons and hence undergoes electrophilic additions easily. Further, a carbon-carbon double bond is activated by an electron-releasing substituent toward electrophilic addition because an electron-releasing substituent stabilizes the transition state leading to carbocation by dispersing the developing positive charge, conversely an electron-withdrawing substituent (e.g. C = O, –COOH, –COOR, –CN, etc.) on a carbon-carbon double bond destabilizes the transition state hence it deactivates the C = C to electrophilic addition.





Thus α,β-unsaturated ketones, acids, esters and nitriles are in general less reactive than simple alkenes toward reagent like Br_2 and HX. However, the groups which deactivate a C=C bond toward electrophilic reagents activate the C=C bond toward nucleophiles. Hence, unlike ordinary alkenes, the C=C of an α,β-unsaturated ketones, acids, esters, or nitriles are susceptible to nucleophiles. This reactivity towards nucleophiles is due to inductive effect of the substituent as well as to its conjugation with the carbon-carbon double bond.

In the addition of an unsymmetrical reagent to the double bond of an α,β-unsaturated carbonyl compound, hydrogen (positive end of the reagent) is attached to the α-carbon and the negative end of the reagent is attached to the β-carbon.

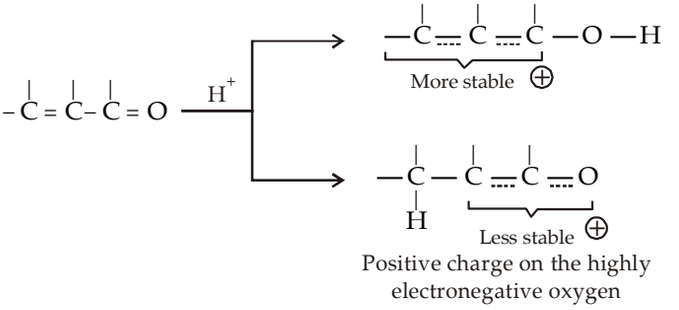
$$CH_2=CHCHO + HCl \longrightarrow \underset{Cl}{CH_2}-\underset{H}{CHCHO}$$

$$CH_2=CHCOOH + H_2O \longrightarrow \underset{OH}{CH_2}-\underset{H}{CHCHO}$$

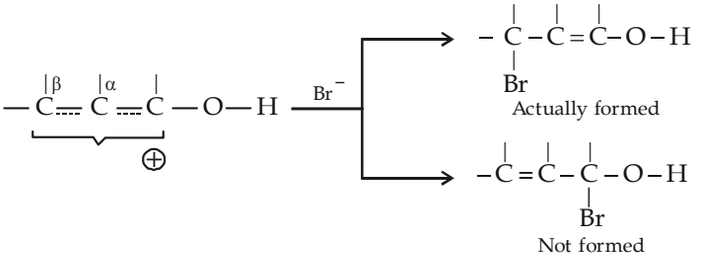
$$CH_3CH=CHCOOH + HBr \longrightarrow CH_3\underset{Br}{CH}\underset{H}{CH}-COOH$$

$$(CH_3)_2C=CHCOCH_3 + CH_3OH \xrightarrow{H_2SO_4} (CH_3)_2\underset{OCH_3}{C}-\underset{H}{CHCOCH_3}$$

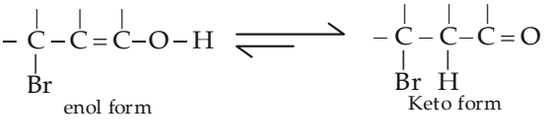
Such additions are again in consistent with the formation of the most stable carbocation.



The more stable carbocation, now adds the negative ion or basic molecule in either of the two ways.



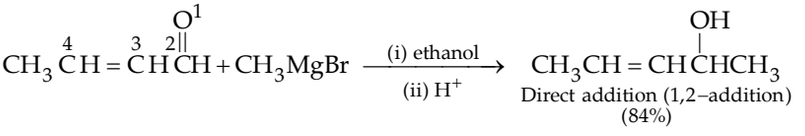
Of the above two possibilities, only addition to the β-carbon yields a stable product, the enol form of a saturated carbonyl compound.



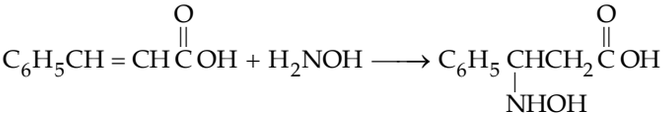
16.2.2 Nucleophilic Addition

α, β-Unsaturated carbonyl compounds contain two electrophilic sites, the carbonyl carbon and the carbon atom that is β to carbonyl group. Thus such compounds may react with nucleophiles in two different ways.

(a) **Direct or simple addition :** The nucleophile preferentially adds directly to the carbonyl group forming direct addition product, also known as 1,2-addition product (remember that the numbers 1 and 2 do not refer to IUPAC locants but are used in a manner analogous to that employed in additions on conjugated dienes). Strong but simple (not bulky) bases like organolithium and Grignard reagents and lithium aluminium hydride tend to react by simple addition.



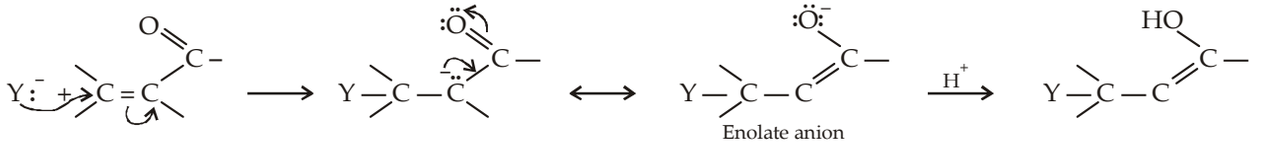
(b) **Conjugate or 1,4-addition :** When the nucleophiles are weak or bulky strong bases, they add preferentially to the β-carbon forming conjugated or 1,4-addition product.



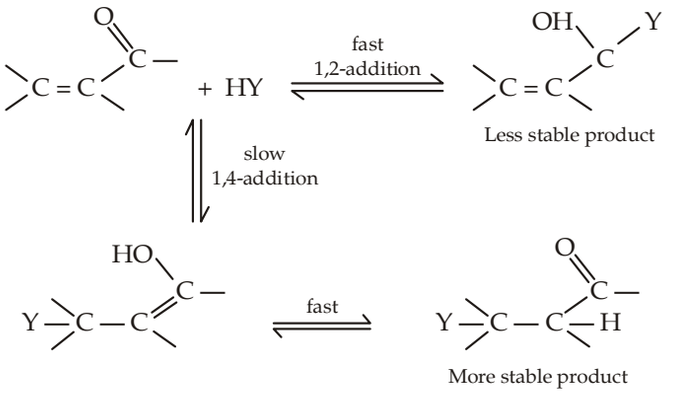
Note that in 1,4-addition, the nucleophile adds at the carbon-carbon double bond rather than at the carbon-oxygen double bond. Here the nucleophilic portion of the reagent is attached to the β carbon quite ignoring the fact that it has more or less number of hydrogen atoms.

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Remember that nucleophilic addition to the usual carbon-carbon double bond is very rare. However, it occurs easily with α,β-unsaturated carbonyl compounds because here the carbanion formed is an enolate i.e. the carbanion has a conjugated system, which is more stable and formed with a lower activation energy than a simple alkyl carbanion.



1,2- or 1,4-Nucleophilic addition to α,β-unsaturated carbonyl compounds may be governed by kinetic control or by thermodynamic control.



Direct addition (1,2-) occurs faster than conjugate addition (1,4-) but gives a less stable product. This kinetic control addition operates with strongly basic nucleophiles. The conjugate (1, 4-) addition gives the more stable product; recall that the carbon-oxygen double bond, in general, is a more stable structural unit than the carbon-carbon double bond. This thermodynamic control addition occurs in presence of a weakly basic nucleophile.

TEST YOUR UNDERSTANDING - 16.2

1. Write down the products in each of the following reactions :

(a) $C_6H_5CH=CHCOOC_2H_5 + OH^- \xrightarrow{\text{heat}}$ (b) $CH_3CH=CHCOCH_3 + I_2 + NaOH \longrightarrow$

(c) $CH_3CH=CHCOC_6H_5 + O_3 \longrightarrow [\quad] \xrightarrow[H_2O]{Zn}$ (d) Maleic acid + $Br_2(CCl_4) \longrightarrow$

(e) Fumaric acid + Cold alkaline $KMnO_4 \longrightarrow$ (f) $C_6H_5CH=CHCOOH + H_2 \xrightarrow[\text{pressure}]{\text{Ni, low temp.}}$

(g) $C_6H_5CH=CHCOOH + H_2 \xrightarrow[\text{pressure}]{\text{Ni, high temp.}}$

(h) $C_6H_5CH=CHCOOH + 9-BBN \longrightarrow [\quad] \xrightarrow{HOCH_2CH_2NH_2}$

(i) $CH_3CH=CHCOOC_2H_5 + (COOC_2H_5)_2 \xrightarrow{OC_2H_5^-}$

2. Compare the reaction of sodium azide in aqueous acetic acid with acrolein and propanal.

3. Give the product in each case.

(a) $CH_3CH=CHCHO + CH\equiv CMgBr \longrightarrow$ (b) $C_6H_5CH=CHCOC_6H_5 + HCN \longrightarrow$

4. Predict the nature of products in the following reactions.

(a) $CH_2=CHCN \xrightarrow{NH_3} X + Y$ (b) $CH_2=CHCOOCH_3 \xrightarrow{CH_3NH_2} [A] \xrightarrow{CH_2=CHCOOCH_3} [B]$

Michael reaction.

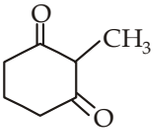
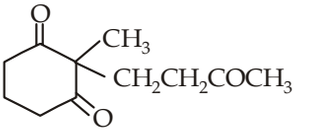
In the nucleophilic addition to α, β-unsaturated carbonyl compounds, when the nucleophile is a carbanion, the reaction is known as **Michael addition or Michael reaction**. The most common types of carbanions used are enolate ions derived from β-diketones, β-diketo esters, β-keto esters, and β-keto nitriles. Since these enolates are weak bases and quite bulky, addition occurs at the β-carbon to form 1,4-addition product.

(a) $CH_2=CHCH$ (α,β–unsaturated aldehyde) + $CH_3COCH_2COCH_3$ (A β–diketone) $\xrightarrow{OH^-}$ $CH_3C(CHCH_2CH_2CHO)COCH_3$

(b) $CH_3CH=CHCOCH_3$ (α,β–unsaturated ketone) + $C_2H_5OCOCH_2COOC_2H_5$ (A β–diketo ester) $\xrightarrow{C_2H_5O^-}$ $CH_3CH(CH_2COCH_3)CH(COOC_2H_5)_2$

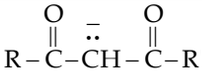
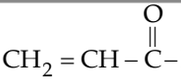
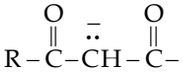
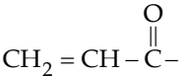
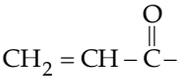
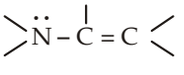
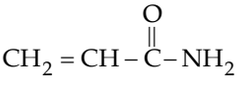
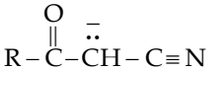
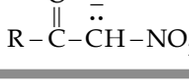
(c) $CH_3CH=CHCONH_2$ (α,β–unsaturated amide) + $C_2H_5COCH_2COOCH_3$ (a β–keto ester) $\xrightarrow{CH_3O^-}$ $CH_3CH(CH_2CONH_2)COCHCOOCH_3$

(d) $C_2H_5CH=CHCOOCH_3$ (α,β–unsaturated ester) + $CH_3COCH_2C\equiv N$ (a β–keto nitrile) $\xrightarrow{^-OCH_3}$ $C_2H_5CH(CH_2COOCH_3)COCHCN$

(e) $CH_2=CHCOCH_3$ (α,β-unsaturated ketone) +  (a β-diketone) $\xrightarrow{^-OCH_3}$ 

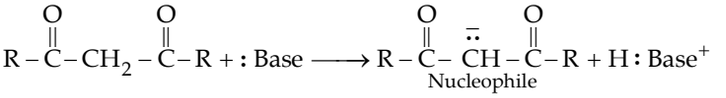
Thus, **Michael reaction** involves addition of a stabilized enolate ion to the double bond of an α,β-unsaturated carbonyl compound. The electrophile (the α,β-unsaturated carbonyl compounds) accepts a pair of electrons, and thus called the **Michael acceptor**; while the attacking nucleophile donates a pair of electrons, hence called the **Michael donor**. A wide variety of compounds can serve as Michael acceptors and donors (Table below). Common acceptors contain a double bond conjugated with a carbonyl group, a cyano group, or a nitro group. Common donors are enolates that are stabilized by two strong electron-withdrawing groups such as carbonyl groups, cyano groups, or nitro groups.

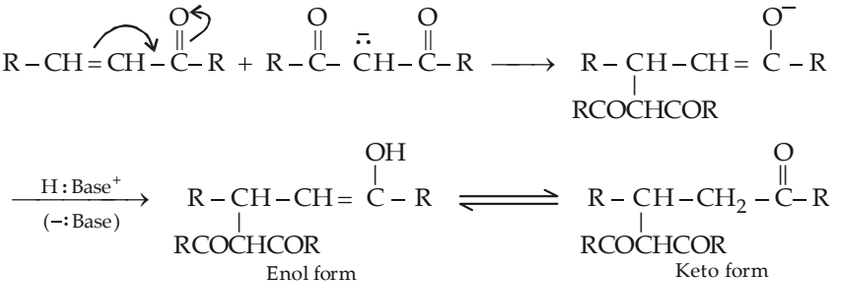
Table : Some common Michael donors and Michael acceptors

Michael donors	(Nucleophiles)	Michael acceptors	(Electrophile)
	β-Diketones		Conjugated aldehydes
	β-Keto esters		Conjugated ketones
$R_2Cu\ Li$	Dialkyl cuprates		Conjugated esters
	Enamines		Conjugated amides
	β-Keto nitriles	$CH_2=CH-C\equiv N$	Conjugated nitriles
	α-Nitro ketones	$CH_2=CH-NO_2$	Nitroethylene

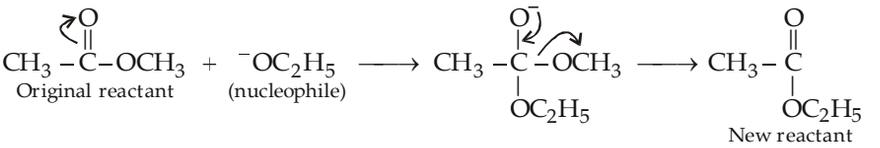
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Mechanism. The base removes a proton from α-carbon of the compound having active methylene group to form a carbanion which acts as a nucleophile. The nucleophile adds to the β-carbon of the conjugated system in the usual manner.

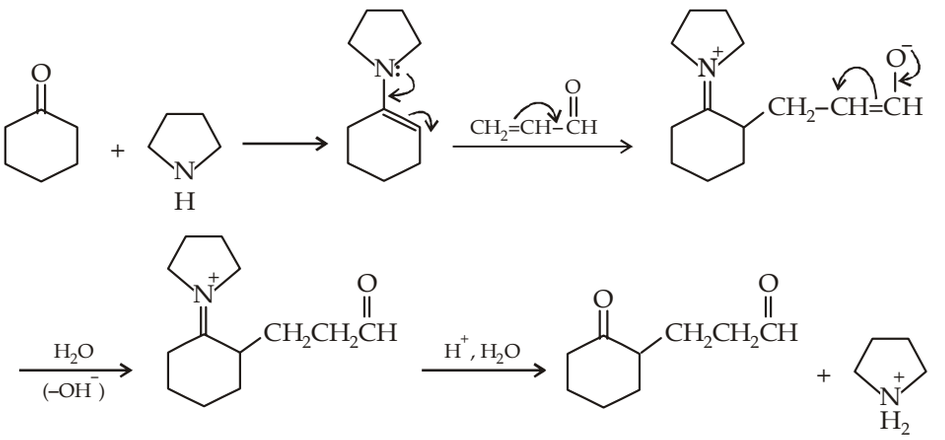




Note that if either of the reactant in a Michael reaction has an ester group, the base used to remove the α-proton must be the same as the leaving group of the ester. This is because the base can also act as a nucleophile and attack the carbonyl group of the ester. In case the nucleophile is different to the –OR group of the ester, the nucleophilic attack on the carbonyl group will change the reactant.



Ammonia, primary and secondary amines are especially powerful catalysts for the Michael addition. They function not merely as a base to regenerate a carbanion but also reacts with the carbonyl groups of the substrate to form an intermedciate imine or iminium ion which is highly reactive toward nucleophilic addition. When enamines (tautomer of imines) are used in place of enolates, the reaction is called **Stork enamine reaction**. Thus reaction between cyclohexanone and acrolein in presence of pyrrolidine takes place as below.



TEST YOUR UNDERSTANDING - 16.3

1. Write down the product obtained in the following reactions :

(a) Ethyl crotonate + Ethyl methylmalonate $\xrightarrow{^-OC_2H_5}$

(b) Ethyl α-methylacrylate + Ethyl cyanoacetate $\xrightarrow{^-OC_2H_5}$

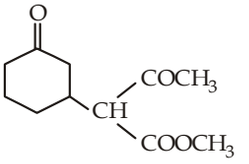
(c) Benzalacetophenone + Acetophenone $\xrightarrow{^-OC_2H_5}$

(d) Acrylonitrile + Allyl cyanide $\xrightarrow{^-OCH_3}$

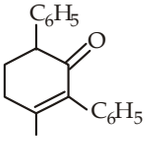
(e) $C_2H_5O_2CC \equiv CCO_2C_2H_5$ (1 mol.) + Acetoacetic ester (2 mol.) $\xrightarrow{^-OC_2H_5}$

(f) Ethyl crotonate + Malonic ester $\xrightarrow{^-OC_2H_5}$ [X] $\xrightarrow[(ii)\ H^+]{(i)\ OH^-}$ [Y] $\xrightarrow{heat}$ [Z]

2. What reagent would you use to prepare the following compounds?

(a) $CH_3COCH_2CH_2CH(COOCH_2CH_3)_2$ (b) 

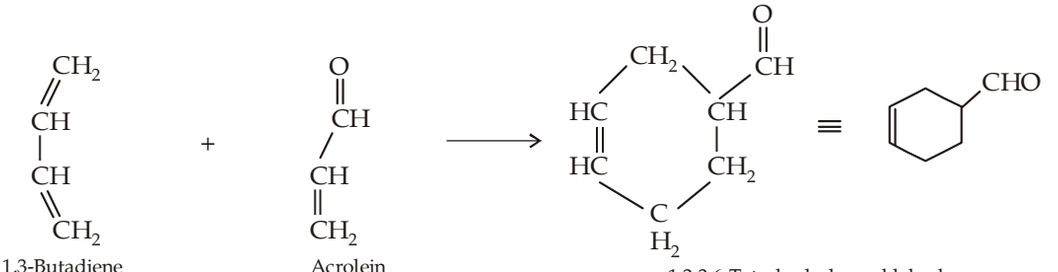
3. (a) Write structural formulas corresponding to the intermediates formed in the following reaction.

$$C_6H_5CH_2COCH_2C_6H_5 + CH_2=CHCOCH_3 \xrightarrow[CH_3OH]{CH_3ONa}$$ 

(b) Write down the structure of the resonance hybrid obtained by the attack of (i) an electrophile (H^+), (ii) a nucleophile on a typical α,β-unsaturated carbonyl compound, $-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=O$

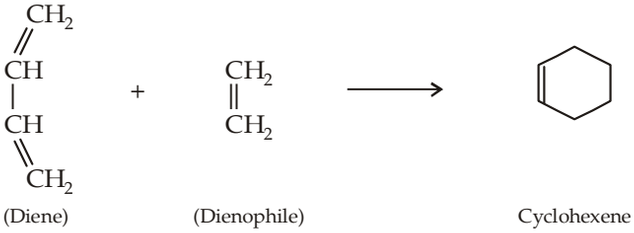
16.2.3 Diels-Alder Reaction

α,β-Unsaturated carbonyl compounds undergo addition reaction with conjugated dienes in which C-1 and C-4 of the conjugated diene is attached to the doubly bonded carbons of the α,β-unsaturated carbonyl compound to form a 6-membered ring. The reaction, known as Diels-Alder reaction, is the example of *cycloaddition*.



1,3-Butadiene (Diene) + Acrolein (Dienophile) (Greek : diene-loving) → 1,2,3,6-Tetrahydrobenzaldehyde

Diels-Alder reaction, is although favoured by the presence of electron-withdrawing group in dienophile as in the case of α,β-unsaturated carbonyl compounds, it also takes place when the dienophile is a simple alkene.



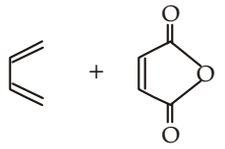
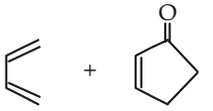
(Diene) + (Dienophile) → Cyclohexene

Since Diels-Alder reaction involves a system of four π electrons (the diene) and a system of two π electrons (the dienophile), it is also known as **[4+2] cycloaddition**.

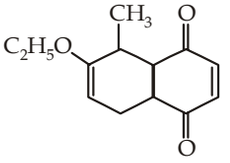
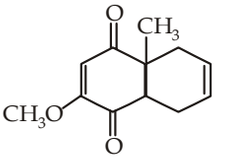
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TEST YOUR UNDERSTANDING - 16.4

1. Predict the product in each of the following reactions :

(a)  (b)  (c) 

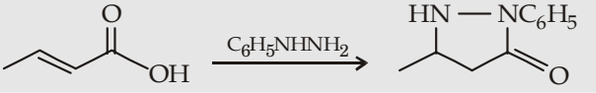
2. Write down the diene and dienophile from which following products can be obtained

(a)  (b) 

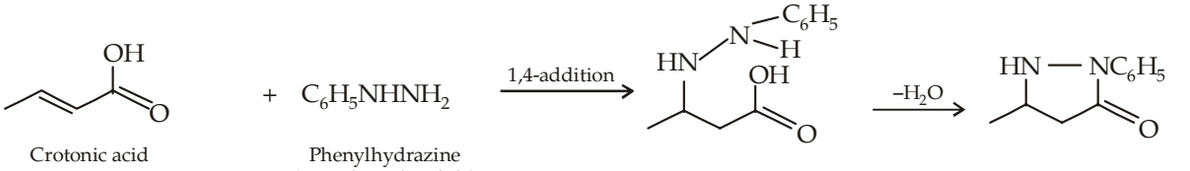
16.3 ILLUSTRATIVE EXAMPLES

Example 1 :

Give steps involved in the following conversion.



Solution :

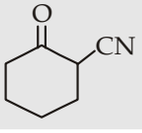
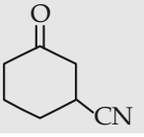


Crotonic acid (α,β-unsaturated carboxylic acid)

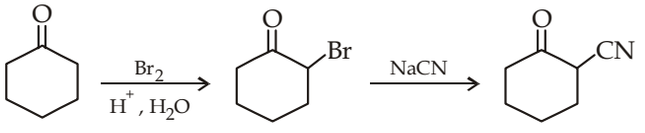
Phenylhydrazine (a weak nucleophile)

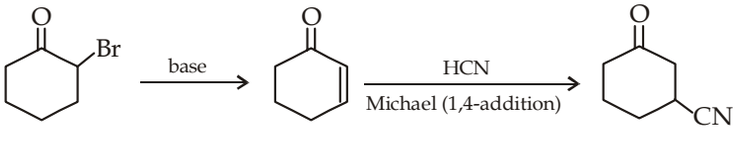
Example 2 :

Steps for converting cyclohexanone to each of the following

(a)  **(b)** 

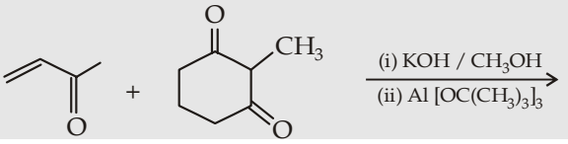
Solution :

(a) 

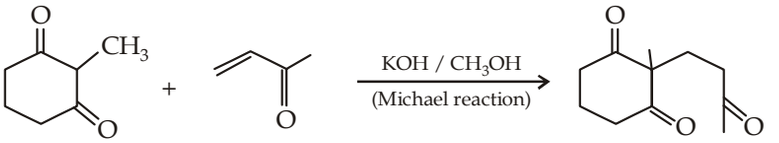
(b) 

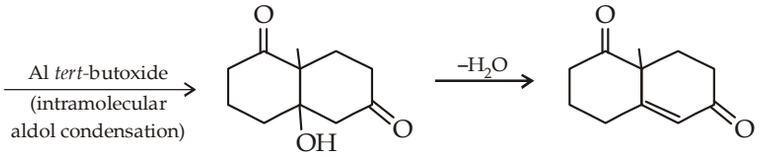
Example 3 :

Predict the final product in the following reaction and comment on the main concepts involved.



Solution :





First step of the reaction involves Michael reaction. The product of Michael addition has necessary functional groups to undergo intramolecular aldol condensation to form cyclic product which undergoes dehydration to form stable α,β-unsaturated ketone. The synthesis of cyclohexanone derivatives by Michael addition followed by intramolecular aldol condensation is called **Robinson annulation**. The term **annulation or annelation** means building of a ring onto some starting molecule.

Example 4 :

Give steps involved in the following conversion.

$$HCHO\ (1\ mol.) + CH_2(COOC_2H_5)_2\ (2\ mol.) \longrightarrow HOOC(CH_2)_3COOH$$

Solution :

The reaction involves aldol condensation followed by Michael additions.

$$\begin{matrix} H \\ | \\ HC=O \end{matrix} + H_2C(COOC_2H_5)_2 \xrightarrow[\text{(aldol conden.)}]{\text{base}} \begin{matrix} H_2C-CH(COOC_2H_5)_2 \\ | \\ OH \end{matrix}$$

$$\xrightarrow{-H_2O} H_2C=C(COOC_2H_5)_2 \xrightarrow[\text{Michael addition}]{CH_2(COOC_2H_5)_2} \begin{matrix} CH_2CH(COOC_2H_5)_2 \\ | \\ CH(COOC_2H_5)_2 \end{matrix}$$

$$\xrightarrow[\text{(ii) } H^+]{\text{(i) } OH^-} \xrightarrow[\text{(ii) } H^+]{\text{(i) } OH^-} \begin{matrix} CH_2CH(COOH)_2 \\ | \\ CH(COOH)_2 \end{matrix} \xrightarrow[(-2CO_2)]{\text{heat}} \begin{matrix} CH_2CH_2COOH \\ | \\ CH_2COOH \end{matrix}$$

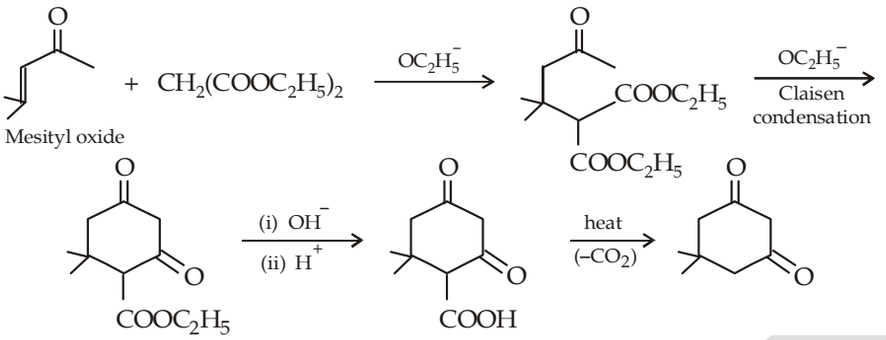
Glutaric acid

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Example 5 :

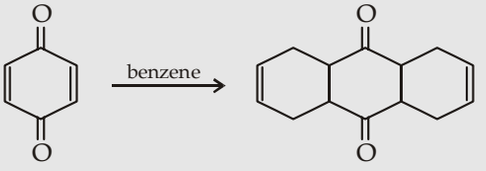
5,5-Dimethylcyclohexa-1,3-dione can be prepared from mesityl oxide, $(CH_3)_2C{=}CHCOCH_3$ and malonic ester using Michael reaction as the main rection. Give necessary steps involved in the conversion.

Solution :



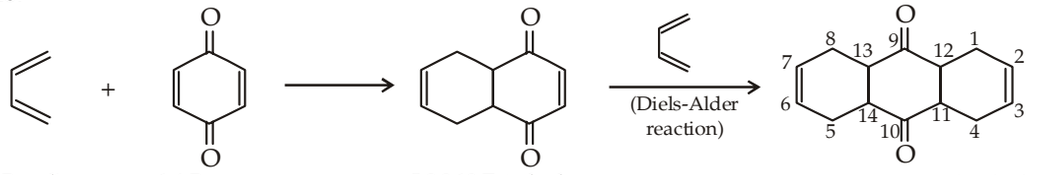
Example 6 :

Write steps involved in the following conversion using Diels-Alder reaction.



Solution :

The conversion involves the Diels-Alder reaction between one molecule of *p*-benzoquinone and two molecules of 1,3-butadiene.

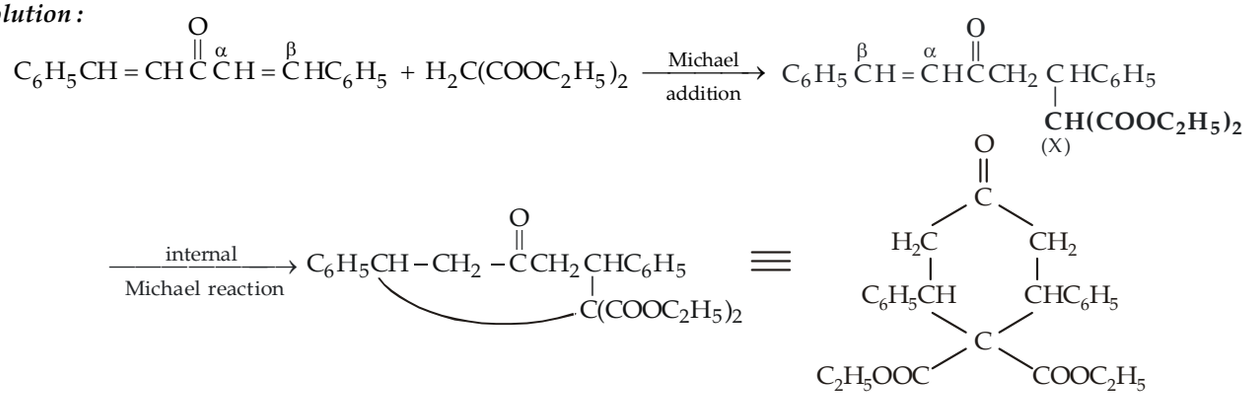


1,3-Butadiene — 1,4-Benzo-quinone — 5,8,9,10-Tetrahydro-1,4-naphthaquinone — 1,4,5,8,11,12,13,14-Octahydro-9,10-anthraquinone

Example 6 :

Dibenzalacetone, $C_6H_5CH{=}CHCOCH{=}CHC_6H_5$, and ethyl malonate are treated in equimolar amounts to give a product (X) which does not respond to olefinic reagent. Suggest the structure for (X) and explain its formation.

Solution :



Note that the compound (X) still has α,β-unsaturated carbonyl group and also a structural moiety capable of forming stable carbanion (marked by bold type), so it can undergo internal Michael reaction to form cyclic product having no carbon-carbon double bond.

EXERCISE 16.1 (MCQ - ONE option correct)

1. Which of the following is not an example of α,β-unsaturated carbonyl compound?

(a) Fumaric acid (b) *p*-Benzoquinone

(c) Mesityl oxide (d) None of these

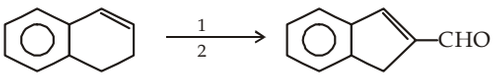
2. Which of the following is not formed during dehydration of glycerol to prop-2-enal?

$$CH_2(OH)-CH(OH)-CH_2(OH) \xrightarrow{KHSO_4} CH_2=CHCHO$$

(a) $CH_2(OH)-CH=CH(OH)$ (b) $CH_2=C(OH)-CH_2(OH)$

(c) CH_2CH_2CHO (OH) (d) None of these

3. The reactions 1 and 2 used in the preparation of the following unsaturated carbonyl compounds are



(a) Oxidation by conc. HNO_3 and intramolecular aldol condensation

(b) Oxidation by alkaline $KMnO_4$ and Michael reaction

(c) Ozonolysis and aldol condensation

(d) Ozonolysis and Michael addition

4. Which of the following carbocation is most likely to be formed during following reaction?

$$CH_2=CHCOOH + HBr \longrightarrow CH_2BrCH_2COOH$$

(a) $\overset{+}{C}H_2CH_2COOH$ (b) $CH_3\overset{+}{C}HCOOH$

(c) $CH_2=CH-\underset{+}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-OH$ (d) None of these

5. (i) $CH_2=CHCOCH_3 + HBr \longrightarrow P_1$

(ii) $CH_2=CH-CH_2CHO + HBr \longrightarrow P_2$

Here P_1 and P_2 respectively are

(a) $CH_3CH(Br)COCH_3$, $CH_3CH(Br)CH_2CHO$

(b) $CH_2(Br)CH_2COCH_3$, $CH_2BrCH_2CH_2CHO$

(c) $CH_2(Br)CH_2COCH_3$, $CH_3CH(Br)CH_2CHO$

(d) P_1 and P_2 are same

6. $CH_3CH=CHCOCH_3 + CH_3MgBr \xrightarrow[(ii)\ H_3O^+]{(i)\ (C_2H_5)_2O} P$. Here P may be

(a) $CH_3CH=CH\overset{OH}{\underset{|}{\overset{|}{C}}}(CH_3)_2$

(b) $CH_3\overset{CH_3}{\underset{|}{\overset{|}{C}}}H-CH_2COCH_3$

(c) Both

(d) None

7. $H_3CO-C_6H_4-\overset{CH_3}{\underset{|}{\overset{|}{C}}}=CHOCH_3 \xrightarrow{H_3O^+/H_2O} P$. Here P is

(a) $H_3CO-C_6H_4-\overset{CH_3}{\underset{|}{\overset{|}{C}}}=O$

(b) $H_3CO-C_6H_4-\overset{CH_3}{\underset{|}{\overset{|}{C}}}HCHO$

(c) $H_3CO-C_6H_4-\overset{CH_3}{\underset{OH}{\overset{|}{\underset{|}{\overset{|}{C}}}}}-CH_2OCH_3$

(d) None of these

8. Predict the nature of the product in the reaction

$$C_6H_5CH=CH\overset{O}{\overset{\|}{C}}C_6H_5 + NaCN(aq.) \longrightarrow$$

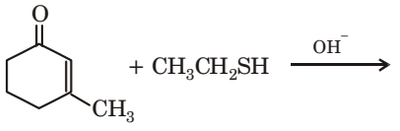
(a) $C_6H_5CH=CH\overset{OH}{\underset{CN}{\overset{|}{\underset{|}{\overset{|}{C}}}}}C_6H_5$

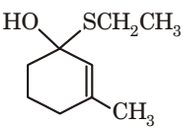
(b) $C_6H_5\underset{CN}{\underset{|}{CH}}CH_2\overset{O}{\overset{\|}{C}}C_6H_5$

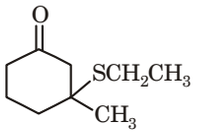
(c) $C_6H_5CH_2\underset{CN}{\underset{|}{CH}}\overset{O}{\overset{\|}{C}}C_6H_5$

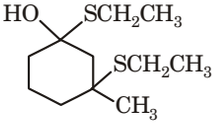
(d) None of these

9. Predict the major product in the following reaction



(a) 

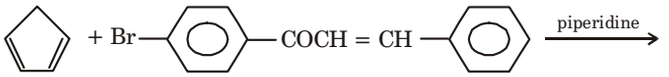
(b) 

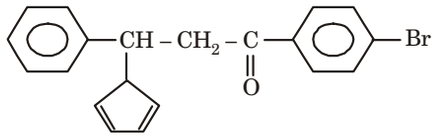
(c) 

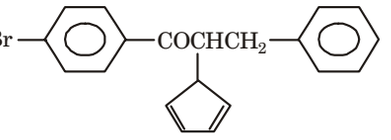
(d) None of these

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10. Predict the possible product in the following reaction :



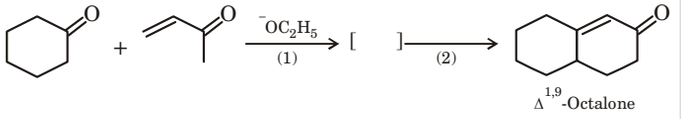
(a) 

(b) 

(c) Both (a) and (b)

(d) No reaction

11. $\Delta^{1,9}$ - Octalone is prepared according to the following series of reactions



$\Delta^{1,9}$-Octalone

The reactions involved at (1) and (2) steps are

(a) conjugate addition, 1,2-addition

(b) 1,2-addition, aldol condensation

(c) 1,4-addition, aldol condensation

(d) 1,2-addition and 1,4-addition

12. In the following Michael reaction

$$CH_2 = CHCHO + CH_3COCH_2COOC_3H_7 - n \xrightarrow{\text{base}}$$

$$CH_3COCHCOOC_3H_7 - n \text{ (with } CH_2CH_2CHO \text{ on the central C)}$$

the best yield is obtained, when the base is

(a) OCH_3^- (b) $OC_2H_5^-$

(c) $^-C_3H_7 - n$ (d) Equal

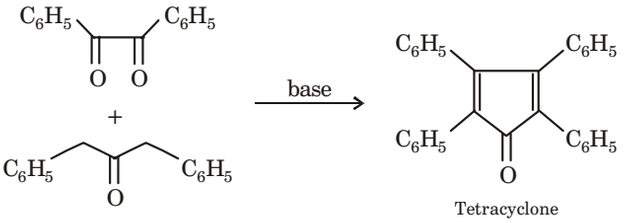
13. How many different products are possible by the Michael addition between following two compounds?

$$CH_3CH = CHCOCH = CHCH_3 + CH_2(COOC_2H_5)_2 \xrightarrow{OC_2H_5^-}$$

(a) One (b) Two

(c) Three (d) Four

14. Benzyl and dibenzyl ketone when treated in presence of a base leads to the formation of a cyclic compound, tetracyclone



Tetracyclone

The reaction involved in the conversion is

(a) Michael addition (b) Knoevenagel reaction

(c) aldol condensation (d) Both (a) and (c)

15. In Diels-Alder reaction, 1,3-butadiene can function as a

(a) diene (b) dienophile

(c) both (d) none

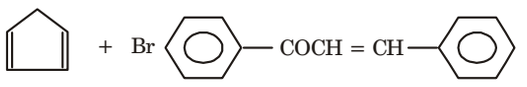
EXERCISE 16.2 (MCQ 1 or >1 option correct, Passage based, Matching, A/R)

DIRECTIONS for Q. 1 to 2 : Multiple choice questions with one or more than one correct option(s).

1. Which of the following does not undergo Michael addition?

(a) $C_6H_5CH = CHCOCH_3 + C_6H_5COCH_3$

(b) $C_6H_5CH = CHCH_2COC_6H_5 + CH_2(COOC_2H_5)_2$

(c) 

(d) $CH_2 = CHCOCH_3 + CH_3COCH_3$

2. In the absence of peroxide addition of HBr is by anti-Markownikoff rule :

(a) $CH_2 = CH - COOH$

(b) $CH_2 = CH - CHO$

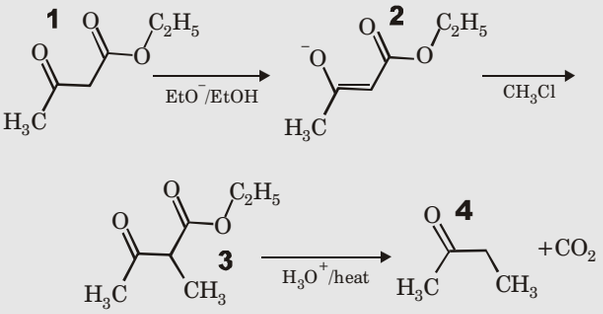
(c) $CH_2 = CH - CH_2OH$

(d) $CH_2 = CH - CN$

INSTRUCTION for Q. 3 to 11 : Read the passages given below and answer the questions that follow.

PASSAGE 1

The following questions relate to the reaction sequence outlined below



3. Compound 1 is a/an

(a) α-keto carboxylic acid

(b) β-keto carboxylic acid

(c) α-keto ester

(d) β-keto ester

4. The first step in the sequence could be enhanced by
(a) replacing the hydrogens at the alpha position by two alkyl groups
(b) replacing one of the hydrogens at the alpha position by a chlorine atom
(c) replacing one of the carbonyl groups with iodine atoms
(d) using ethanoate/ethanoic acid instead of ethoxide/ethanol

5. Although sodium methoxide is readily available, it was not used in the first step because
(a) it is not as strong base as ethoxide
(b) it would cause an undesired transesterification
(c) it would be more difficult to hydrolyze a methyl ester than an ethyl ester
(d) a hindered base is needed to protect the carbonyl group

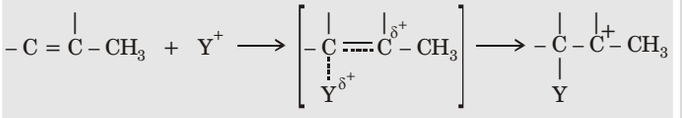
6. The second step is a type of reaction known as
(a) S_N1
(b) S_N2
(c) electrophilic addition.
(d) free radical substitution

7. The third step involves
I. protonation of O in the C=O of the ester group
II. S_N2 substitution of OC_2H_5 by OH
III. heat-induced decarboxylation
(a) I and II (b) I and III
(c) II and III (d) I, II, and III

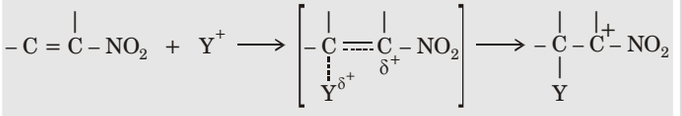
8. What type of reaction does not occur in the sequence?
(a) Hydrolysis (b) Acid-base
(c) Reduction (d) Decarboxylation

PASSAGE 2

A carbon-carbon double bond is a rich source of electrons and hence undergoes electrophilic additions easily. Further, a carbon-carbon double bond having an electropositive group undergoes such reactions very easily as compared to those having electronegative group.



I



II

9. Which of the following transition state is more stable?
(a) I (b) II
(c) I = II (d) It can't be predicted

10. $CH_2 = CHCHO + HCl \longrightarrow P$, here P should be

(a) $CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCHO$ (b) $ClCH_2CH_2CHO$
(c) both (d) other product

11. $CH_2 = CHCH_3 + HCl \longrightarrow P$, here P should be

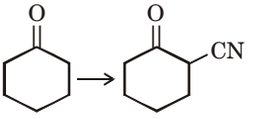
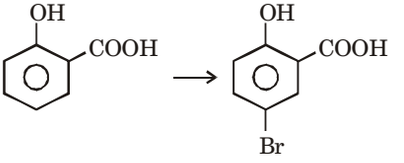
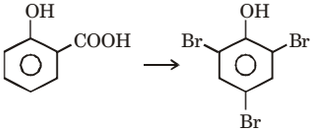
(a) $CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3$ (b) $ClCH_2CH_2CH_3$
(c) both (d) other product

Instructions for Q. 12 to 13 : Following questions are Multiple Matching type Questions :

12.

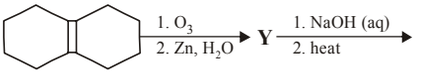
	Column - I **(Carbon Acid)**	*Column - II* **(pK_a)**
(A)	$CH_3COCH_2COOC_2H_5$	(a) 3.6
(B)	$CH_3COOC_2H_5$	(b) 10.7
(C)	$CH_3CON(CH_3)_2$	(c) 25
(D)	$O_2NCH_2NO_2$	(d) 30

13.

	Column - I **Minimum no. of steps required**	*Column - II* **Reaction**
(A)	One	(a) Aniline to *p*-bromoaniline
(B)	Two	(b) 
(C)	Three	(c) 
		(d) 

Instructions for Q. 14 : Following questions are Integer Type Questions :

14. In the scheme given below, the total number of intramolecular aldol condensation products formed from '**Y**' is



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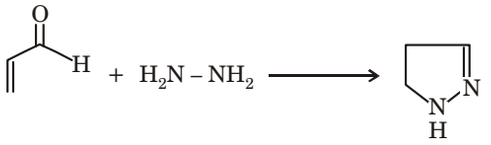
EXERCISE 16.3 (Subjective Problems)

1. Give the structures of the products obtained when benzalacetone, $C_6H_5CH{=}CHCOCH_3$ reacts with each of the following. Name the main reaction involved in each of the following

(a) HCl
(b) H_2O, H^+
(c) 1,3-butadiene
(d) Benzaldehyde in presence of a base
(e) NH_2OH
(f) Malonic ester

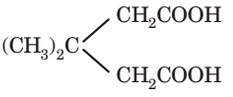
2. Give reactions involved in the conversion of ethyl 3-methylbut-2-enolate to 3,3-dimethylpentane-1,5-dioic acid using Michael addition.

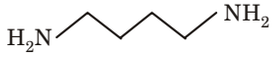
3. Suggest a mechanism for the reaction between acrolein and hydrazine to form dihydropyrazole

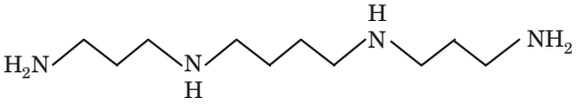


4. Write down the final stable product obtained by the reaction of HCl on *p*-benzoquinone.

5. Give steps involved in the following conversions

(a) $(CH_3)_2C=CHCOCH_3$ to 

(b)  to



6. (a) Which hydrogen of crotonaldehyde, $CH_3CH{=}CHCHO$, is acidic? Write the resonating structures of the corresponding carbanion; which resonating structure is more stable?

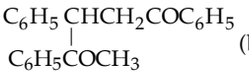
(b) Give mechanism for the following reaction

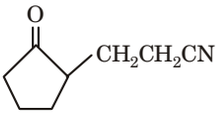
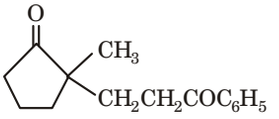
Crotonaldehyde + Cinnamaldehyde $\xrightarrow[C_2H_5OH]{\text{base}}$



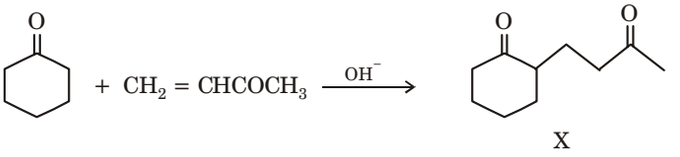
7. Propose a mechanism for the conjugate addition of a nucleophile to (a) acrylonitrile (CH_2 = CHCN) and to (b) nitroethylene (CH_2 = $CHNO_2$).

8. Give the suitable Michael donors and acceptors for synthesizing the following compounds by Michael reaction.

(a)  (b) $HOOCCH_2CH_2CH_2CN$

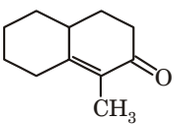
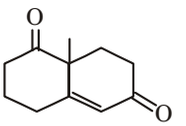
(c)  (d) 

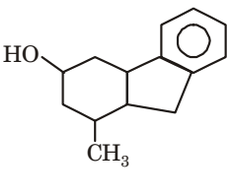
9. The ketone X can't be prepared in good yield by the following Michael addition between



Suggest a method for getting X in good yield from cyclohexanone and methyl vinyl ketone.

10. How the following can be prepared by using Robinson annulations?

(a)  (b) 

(c) 

SOLUTIONS

TEST YOUR UNDERSTANDING - 16.1

1. To achieve the best result and in a minimum time, carry out the conversion backwards.

(a) $\mathbf{CH_3CH=CHCOOH} \xleftarrow{Ag(NH_3)_2^+} CH_3CH=CHCHO \xleftarrow[(-H_2O)]{H^+} CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CHO$

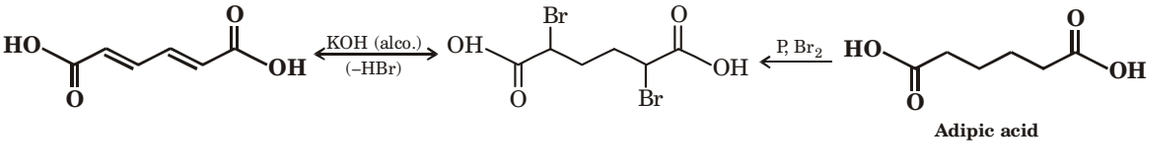
$\mathbf{CH\equiv CH} \xrightarrow{H^+,\ Hg^{2+}} CH_3CHO$; $CH_3CHO \xrightarrow[(\text{aldol cond.})]{OH^-} CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CHO$

(b) $\mathbf{CH_2=CHCOOCH_3} \xleftarrow[(-H_2O)]{H^+} \underset{\displaystyle OH}{\underset{|}{CH_2}}CH_2COOCH_3 \xleftarrow{CH_3OH} \underset{\displaystyle OH}{\underset{|}{CH_2}}CH_2COOH$

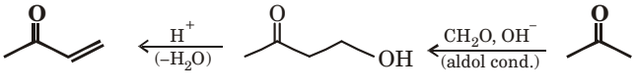
$\mathbf{CH_2=CH_2} \xrightarrow[(ii)\ CN^-]{(i)\ HOCl} \underset{\displaystyle OH}{\underset{|}{CH_2}}CH_2CN \xrightarrow{H^+} \underset{\displaystyle OH}{\underset{|}{CH_2}}CH_2COOH$

(c) $\mathbf{CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}COOCH_3} \xleftarrow[(-H_2O)]{H^+} CH_3-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-COOCH_3 \xleftarrow{CH_3OH} CH_3-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-COOH$

$\mathbf{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3} \longrightarrow CH_3-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CN \longrightarrow CH_3-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-COOH$

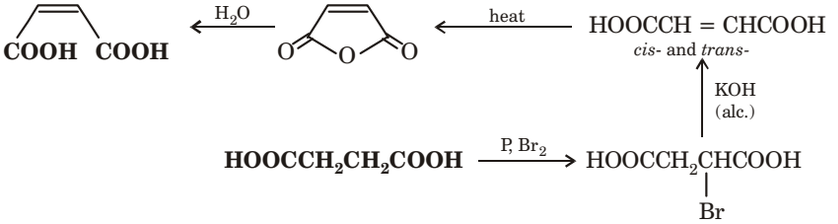
(d) 

Adipic acid

(e) 

(f) $\mathbf{C_6H_5CH=CHCOOH} \xleftarrow[CH_3COO^-]{(CH_3CO)_2O} C_6H_5CHO \xleftarrow[(ii)\ H_2O]{(i)\ CrO_3,\ Ac_2O} \mathbf{C_6H_5CH_3}$

(Perkin reaction)

(g) 

TEST YOUR UNDERSTANDING - 16.2

1. (a) $C_6H_5CH=CHCOO^-$
   (b) $CH_3CH=CHCOO^- + CHI_3$
   (c) $CH_3CHO + OHCCOC_6H_5$
   (d) *rac* – HOOCCH(Br)CH(Br)COOH
   (e) *rac* – HOOCCH(OH)CH(OH)COOH
   (f) $C_6H_5CH_2CH_2CHO$
   (g) $C_6H_5CH_2CH_2CH_2OH$
   (h) $C_6H_5CH=CHCH_2OH$

(i) The reaction is an example of crossed Claisen condensation. Here the carbanion is provided by γ-hydrogen due to conjugated system.

$$CH_3CH=CH\overset{\overset{O}{\|}}{C}-OC_2H_5 \xrightarrow{OC_2H_5^-} {}^-CH_2CH=CH-\overset{\overset{O}{\|}}{C}-OC_2H_5 \xrightarrow[OC_2H_5^-]{(COOC_2H_5)_2} \underset{\underset{COCOOC_2H_5}{|}}{CH_2CH=CHCOOC_2H_5}$$

2. Acrolein (CH_2=CHCHO) is an α,β-unsaturated aldehyde, hence it undergoes 1,4-addition reaction with sodium azide, a weak nucleophile.

$$CH_2=CHCHO \xrightarrow{NaN_3} N_3CH_2CH_2CHO$$

Propanal (CH_3CH_2CHO) does not contain any α,β-unsaturation, hence it does not undergo addition reaction with sodium azide.

3. (a) Acetylide ion is a strong base, hence it adds on α,β-unsaturated carbonyl compounds by 1,2-addition.

$$CH_3CH=CHCHO + CH\equiv CMgBr \longrightarrow CH_3CH=CH\underset{\underset{}{|}}{\overset{\overset{OMgBr}{|}}{C}}HC\equiv CH$$

(b) CN^- is a weak base, hence it gives conjugate (1,4-)addition product.

$$C_6H_5CH=CHCOC_6H_5 + HCN \longrightarrow C_6H_5\underset{\underset{CN}{|}}{C}HCH_2COC_6H_5$$

4. (a) $\underset{\alpha,\beta\text{–unsaturated nitrile}}{CH_2=CHC\equiv N} + NH_3 \xrightarrow[\text{addition}]{1,4-} \underset{\underset{NH_2}{|}}{CH_2CH_2CN} \xrightarrow[1,4\text{–addition}]{CH_2=CHCN} \underset{\underset{CH_2CH_2CN}{|}}{\underset{\underset{NH}{|}}{CH_2CH_2CN}}$

[X] (a weak nucleophile) [Y]

(b) $CH_2=CHCOOCH_3 \xrightarrow[\text{(conjugate addition)}]{CH_3NH_2} \underset{\underset{NHCH_3}{|}}{CH_2CH_2COOCH_3} \xrightarrow[\text{conjugate addition}]{CH_2=CHCOOCH_3} \underset{\underset{CH_2CH_2COOCH_3}{|}}{\underset{\underset{NCH_3}{|}}{CH_2CH_2COOCH_3}}$

[A], a weak nucleophile [B]

TEST YOUR UNDERSTANDING - 16.3

1. (a) $\underset{\text{Ethyl crotonate}}{CH_3CH=CHCOOC_2H_5} + \underset{\text{Ethyl methylmalonate}}{CH_3CH(COOC_2H_5)_2} \xrightarrow{{}^-OC_2H_5} \underset{\underset{CH_3C(COOC_2H_5)_2}{|}}{CH_3CHCH_2COOC_2H_5}$

(b) $\underset{\text{Ethyl α–methylacrylate}}{CH_2=\overset{\overset{CH_3}{|}}{C}COOC_2H_5} + \underset{\text{Ethyl cyanoacetate}}{CNCH_2COOC_2H_5} \xrightarrow{{}^-OC_2H_5} \underset{\underset{CNCHCOOC_2H_5}{|}}{\overset{\overset{CH_3}{|}}{C}H_2CHCOOC_2H_5}$

(c) $C_6H_5CH=CHCOC_6H_5 + \underset{\text{Acetophenone}}{C_6H_5COCH_3} \xrightarrow{{}^-OC_2H_5} C_6H_5\underset{\underset{CH_2COC_6H_5}{|}}{C}HCH_2COC_6H_5$

Acetophenone forms a stable carbanion ($C_6H_5COCH_2^-$) which, being a weak base, adds to form conjugate addition.

(d) $\underset{\text{Acrylonitrile}}{CH_2=CHCN} + \underset{\text{Allyl cyanide}}{CH_2=CHCH_2CN} \xrightarrow{{}^-OC_2H_5} \underset{\underset{CH_2=CHCHCN}{|}}{CH_2CH_2CN}$

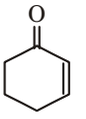
Allyl cyanide in presence of base forms a stable carbanion $\overset{-}{C}H_2=CHCHCN$ which undergoes Michael addition.

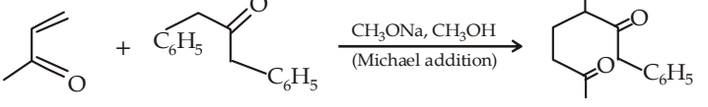
(e) $EtOOCC \equiv CCOOEt + CH_3COCH_2COOC_2H_5 \xrightarrow{^-OC_2H_5}$

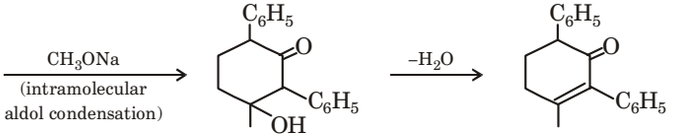
$$EtOOC\,C(CH_3COCHCOOC_2H_5)=CHCOOEt \xrightarrow{CH_3COCH_2COOC_2H_5} CH_3COCHCOOC_2H_5 \text{ with } EtOOCCCH_2COOEt \text{ and } CH_3COCHCOOC_2H_5$$

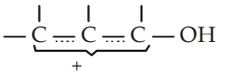
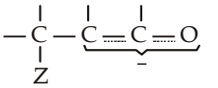
(f) $CH_3CH=CHCOOC_2H_5 + CH_2(COOC_2H_5)_2 \longrightarrow CH_3CH(CH(COOC_2H_5)_2)CH_2COOC_2H_5$ [X]

$$\xrightarrow[(ii)\ H^+]{(i)\ OH^-} CH_3CH(CH(COOH)_2)CH_2COOH \xrightarrow{heat} CH_3CH(CH_2COOH)CH_2COOH$$
[Y]

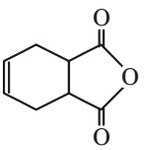
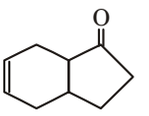
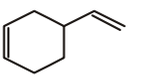
2. (a) $CH_2=CHC(=O)CH_3 + CH_3CH_2OC(=O)CH_2C(=O)OCH_2CH_3$ (b)  + $CH_3COCH_2C(=O)OCH_3$

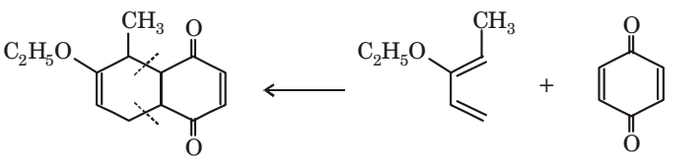
3. (a) 

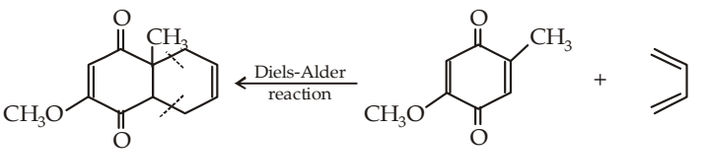


(b) (i)  (ii) 

TEST YOUR UNDERSTANDING - 16.4

1. (a)  (b)  (c) 

2. (a) 

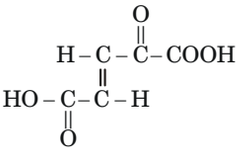
(b) 

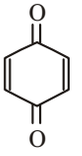
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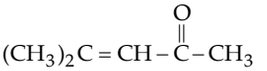
EXERCISE 16.1

1	(d)	**6**	(c)	**11**	(c)
2	(b)	**7**	(b)	**12**	(c)
3	(c)	**8**	(b)	**13**	(c)
4	(c)	**9**	(b)	**14**	(c)
5	(b)	**10**	(a)	**15**	(c)

1. All have unsaturation between α and β carbon atoms with respect to C=O linkage.

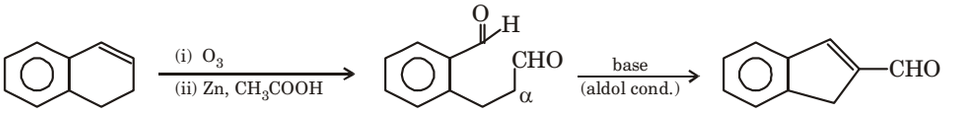
(a) 

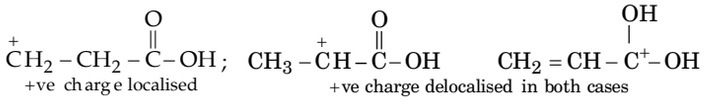
(b) 

(c) 

2. 2° Alcohol is more reactive than 1°, hence former is preferentially formed.

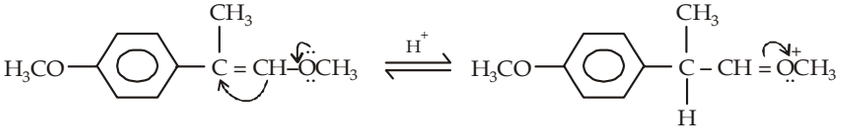


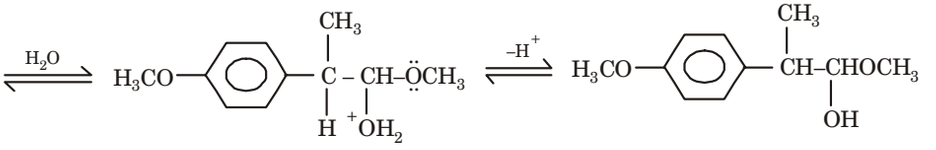
3. 

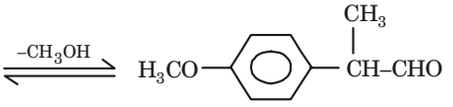
4. 

5. In reaction (i), HBr undergoes conjugate addition because the compound is α,β-unsaturated ketone. In reaction (ii), HBr adds according to Markownikov's way because α,β-unsaturation is not present.

6. Grignard reagent adds on α,β-unsaturated carbonyl compounds in a simple way as well as in conjugate way. However, simple addition product dominates because CH_3MgBr is a strong nucleophile.

7. 

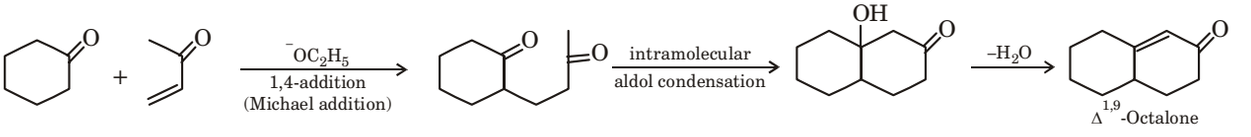




8. CN^-, being a weak nucleophile, adds on β-carbon w.r.t. the carbonyl group to form conjugate addition product (Michael reaction).

9. $CH_3CH_2S^-$ is a weak nucleophile, hence it adds in 1,4-addition way.

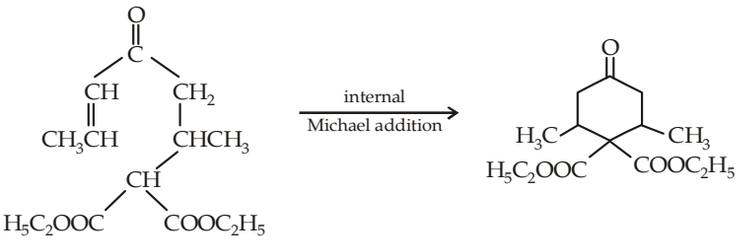
10. This is an example of Michael reaction in which nucleophile adds on β-carbon w.r.t. to carbonyl group.

11. 

12. The base used in Michael reaction may also act as a nucleophile, so it will add to the carbonyl carbon of the ester group and change the reactant leading to low yield of the desired product.

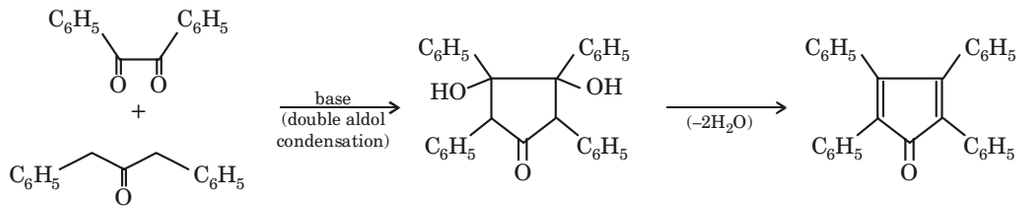
13. (i) $2H_2C(COOC_2H_5)_2 + CH_3\overset{\beta}{C}H=\overset{\alpha}{C}H\overset{O}{\overset{\|}{C}}\overset{\alpha}{C}H=\overset{\beta}{C}HCH_3 \xrightarrow[\text{at both C=C}]{\text{Michael addition}} CH_3-\underset{\underset{CH(COOC_2H_5)_2}{|}}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-\underset{\underset{CH(COOC_2H_5)_2}{|}}{CH}-CH_3$

(ii) $CH_3CH=CH-\overset{O}{\overset{\|}{C}}-CH=CHCH_3 + H_2C(COOC_2H_5)_2 \xrightarrow[\text{only at one C=C}]{\text{Michael addition}} CH_3-\underset{\underset{CH(COOC_2H_5)_2}{|}}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-CH=CHCH_3$ (A)

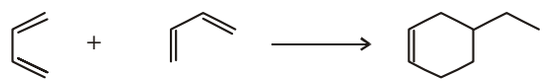
(iii) 

(A) from (ii)

14. The reaction involves *double* aldol condensation.



15. 1,3-Butadiene can function both as a diene as well as dienophile.



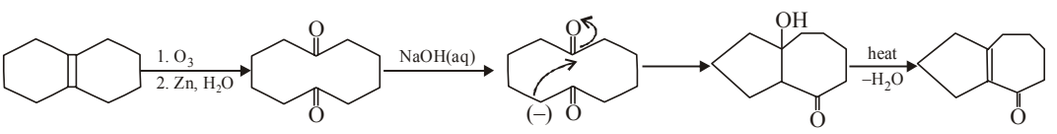
1,3-Butadiene (diene) 1,3-Butadiene (dienophile)

EXERCISE 16.2

>1 CORRECT OPTION	**1**	(b,d)	**2**	(a, d)		
PASSAGE 1	**3**	(d)	**4**	(b)	**5**	(b)
	6	(b)	**7**	(b)	**8**	(c)
PASSAGE 2	**9**	(a)	**10**	(b)	**11**	(a)
MATCH THE FOLLOWING	**12**	(A) - b, (B) - c, (C) - d, (D) - a				
	13	(A) – c,d; (B) – b; (C) – a				
INTEGER	**14**	**1**				

1. (b) does not have α,β-unsaturated carbonyl group, while (d) can't form stable carbanion (from acetone). Remember that cyclopentadiene is quite acidic in nature, because its carbanion is stable due to presence of conjugated system; hence it functions as the nucleophile required in Michael reaction.

14. 1



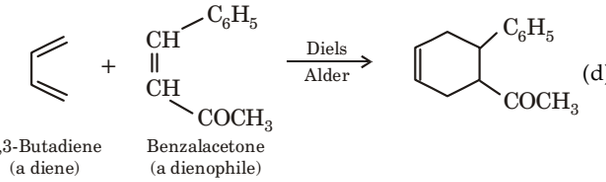
The number of intra molecular aldol condensation products (α, β –unsaturated carbonyl compound formed from **Y** is 1.

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EXERCISE 16.3

1. (a) $C_6H_5\underset{\displaystyle Cl}{\underset{|}{C}}HCH_2COCH_3$
Obtained by 1,4-electrophilic addition

(b) $C_6H_5\underset{\displaystyle OH}{\underset{|}{C}}HCH_2COCH_3$

(c) 
1,3-Butadiene (a diene) + Benzalacetone (a dienophile) $\xrightarrow[\text{Alder}]{\text{Diels}}$

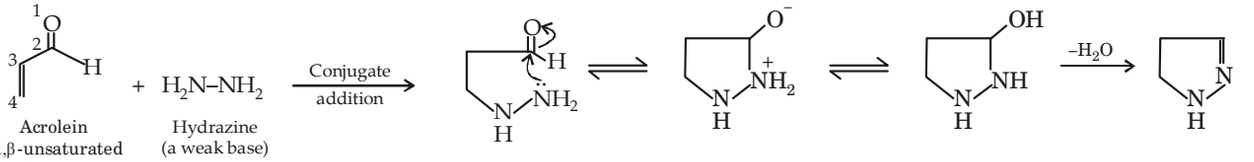
(d) $C_6H_5CH = CHCOCH = CHC_6H_5$
formed by crossed aldol condensation

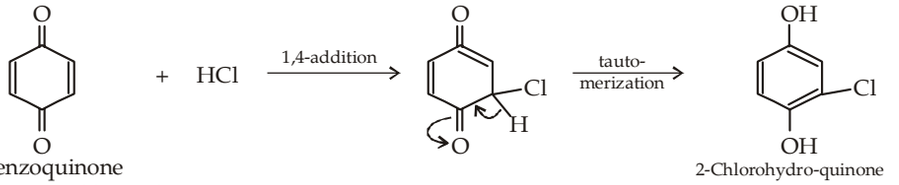
(e) $C_6H_5\underset{\displaystyle NHOH}{\underset{|}{C}}HCH_2COCH_3$
formed by 1,4–nucleophilic addition

(f) $C_6H_5\underset{\displaystyle CH(COOC_2H_5)_2}{\underset{|}{C}}HCH_2COCH_3$
formed by 1,4–nucleophilic addition

2. $CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-\overset{\displaystyle O}{\overset{\|}{C}}-OC_2H_5 + CH_2(COOC_2H_5)_2 \xrightarrow[\text{(Michael addition)}]{^-OC_2H_5} CH_3-\underset{\displaystyle CH(COOC_2H_5)_2}{\underset{|}{\underset{|}{C}}}-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-OC_2H_5$
Ethyl 3–methylbut–2–enoate; Ethyl malonate

$\xrightarrow[(ii)\ H^+]{(i)\ OH^-} CH_3-\underset{\displaystyle CH(COOH)_2}{\underset{|}{\underset{|}{C}}}-CH_2COOH \xrightarrow[(-CO_2)]{\text{heat}} CH_3-\underset{\displaystyle CH_2COOH}{\underset{|}{\underset{|}{C}}}-CH_2COOH \equiv HOOCCH_2\underset{\displaystyle CH_3}{\underset{|}{\underset{|}{C}}}CH_2COOH$
3,3–Dimethylpentane–1,5–dioic acid

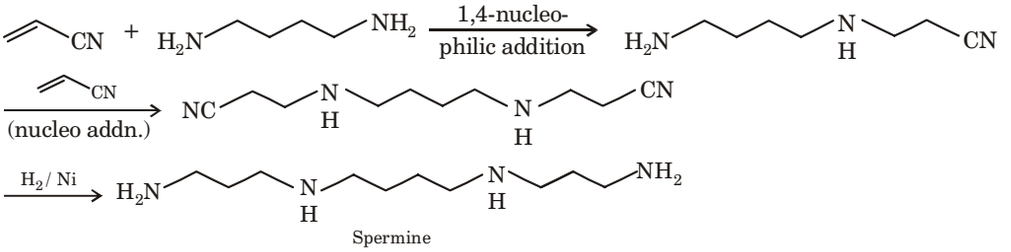
3. 
Acrolein (α,β-unsaturated ketone) + Hydrazine (a weak base) $\xrightarrow{\text{Conjugate addition}}$

4. 
p-Benzoquinone (α,β-unsaturated ketone) + HCl $\xrightarrow{\text{1,4-addition}}$ $\xrightarrow[\text{merization}]{\text{tauto-}}$ 2-Chlorohydro-quinone

5. (a) $(CH_3)_2C = CHCOCH_3 \xrightarrow[\text{(Michael addition)}]{H_2C(COO\ Et)_2} (CH_3)_2\underset{\displaystyle CH(COOEt)_2}{\underset{|}{C}}CH_2COCH_3 \xrightarrow[(ii)\ OH^-]{(i)\ NaOI}$

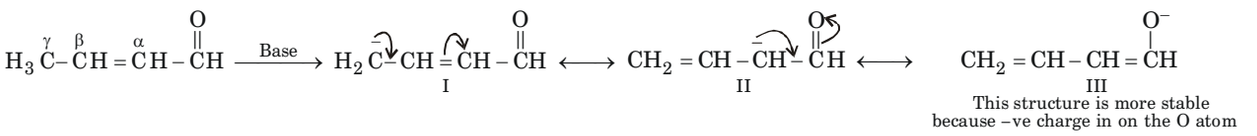
$(CH_3)_2\underset{\displaystyle CH(COO^-)_2}{\underset{|}{C}}CH_2COO^- \xrightarrow[(ii)\ heat]{(i)\ H^+} (CH_3)_2\underset{\displaystyle CH_2COOH}{\underset{|}{C}}CH_2COOH$

(b) The required compound, *spermine* (a compound found in seminal fluid) can be prepared by the double nucleophilic addition of 1,4-diaminobutane (*putrescine*) on acrylonitrile.

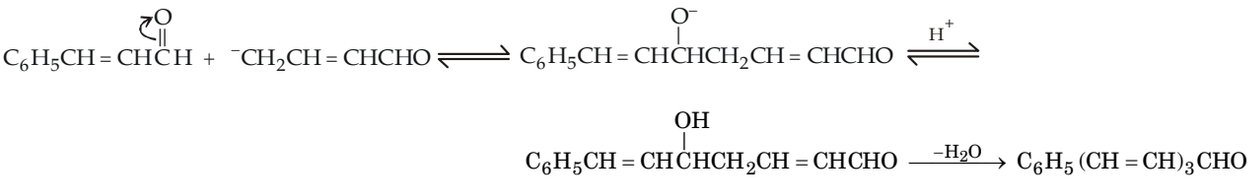


Spermine

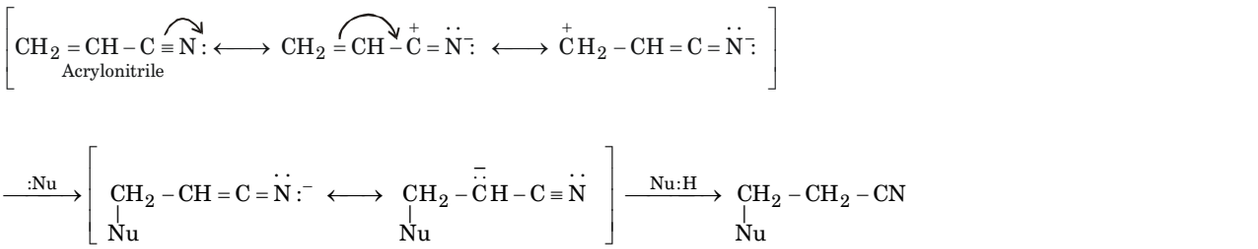
6. (a) **Crotonaldehyde is an** α,β-unsaturated aldehyde so here γ-hydrogens are acidic.



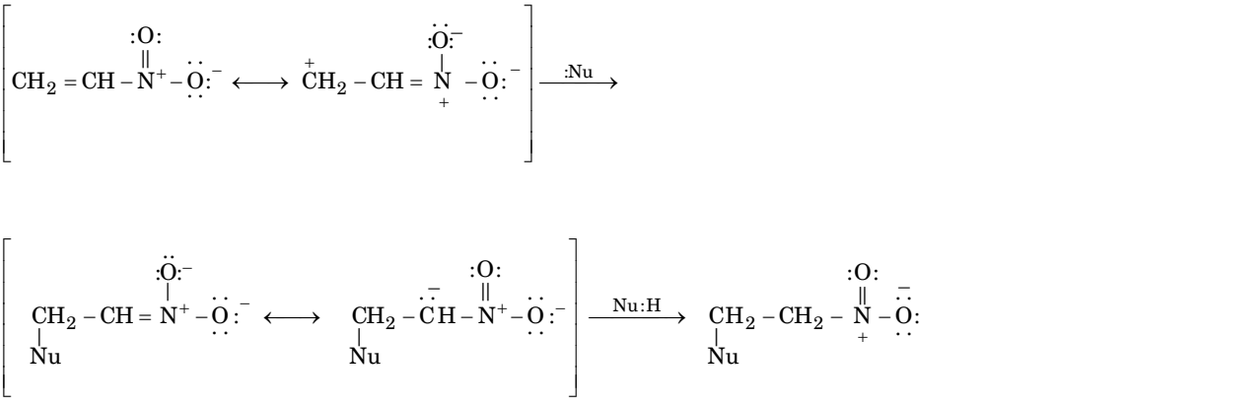
(b)



7. (a)

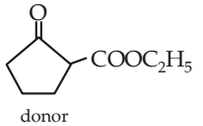


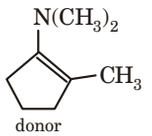
(b)



8. (a) $C_6H_5CH=\underset{\text{acceptor}}{CH}\overset{O}{\overset{\|}{C}}-C_6H_5$, $C_6H_5\overset{-}{\underset{\text{donor}}{C}}H-\overset{O}{\overset{\|}{C}}-CH_3$ supplied as $C_6H_5-\underset{COOC_2H_5}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-CH_3$

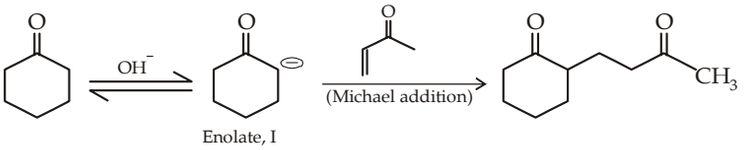
(b) $\underset{\text{acceptor}}{CH_2=CH-C\equiv N}$, $\overset{-}{\underset{|}{C}}HCOOH$ supplied as $\underset{COOC_2H_5}{\underset{|}{CH_2COOC_2H_5}}$

(c) $\underset{\text{acceptor}}{CH_2=CH-C\equiv N}$;  donor

(d) $\underset{\text{acceptor}}{CH_2=CH-\overset{O}{\overset{\|}{C}}C_6H_5}$;  donor

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9. Although theoretically following reaction should take place



Enolate, I

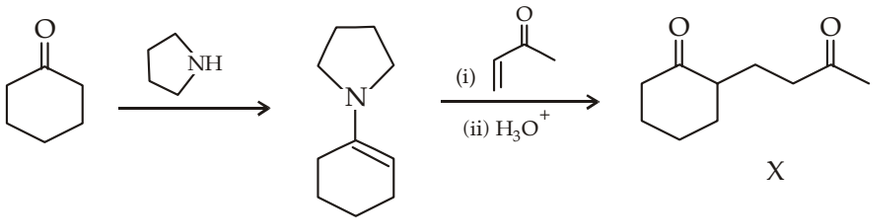
However, in such reaction, yield of the final product is very low due to following competitive reactions.

(i) The ketone enolate I can undergo self aldol condensation.

(ii) The ketone enolate I can condense with methyl vinyl ketone in aldol condensation manner.

(iii) The ketone enolate I can deprotonate the methyl vinyl ketone to form a new nucleophile.

Thus the ketone cyclohexanone must be converted into other resonance stabilized enolate, *enamine* which does not undergo any side reaction and also undergoes Michael addition smoothly.



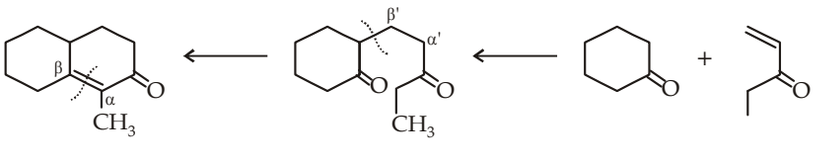
X

10. Always remember that the Robinson annulation consists of a Michael addition followed by aldol cyclizaton with dehydration. In the retrosynthetic direction, perform following two disconnections.

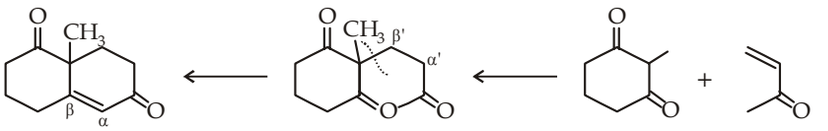
(i) Disconnect the alkene formed in the aldol/dehydration. Since aldol condensation with dehydration forms α,β-unsaturated double bond, disconnect this double bond.

(ii) Disconnect the Michael addition to get the reactants. Since Michael addition forms a bond to the β' carbon atom, disconnect this particular β' bond.

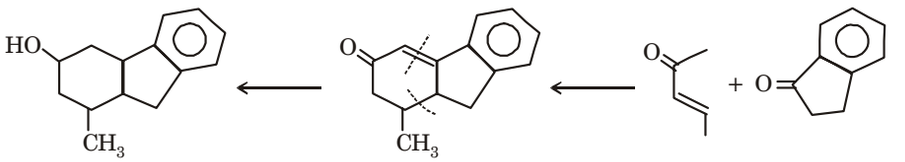
(a)

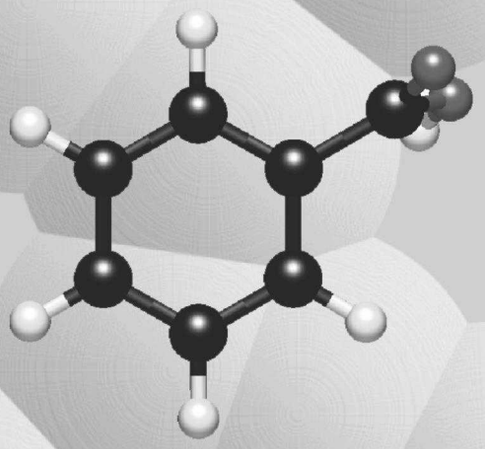


(b)



(c)





17

Carboxylic Acids

CHAPTER HIGHLIGHTS

17.1 Nomenclature
17.2 Preparation of Carboxylic Acids
17.3 Physical Properties
17.4 Chemical Properties
17.5 Special Properties of Formic Acid
17.6 Dicarboxylic Acids
17.7 Distinction Between α-, β-, and γ-Substituted Carboxylic Acids
17.8 Additional Chemistry of Aromatic Carboxylic Acids
17.9 Analysis of Carboxylic Acids
17.10 Illustrative Examples
EXERCISES
SOLUTIONS

17.1 Nomenclature

Carboxylic acids are the organic compounds having the carboxyl group, $-\overset{\overset{O}{\|}}{C}-OH$ (abbreviated as $-COOH$ or $-CO_2H$). Many of the carboxylic acids are better known by **common names** than by their systematic names. For example, formic acid (Latin : *formica,* ant), acetic acid (Latin : *acetum, vinegar*), butyric acid (Latin : *butyrum,* butter), and caproic, caprylic and capric acids (Latin : *caper,* goat) are named on their natural sources. The positions of the substituent groups are shown by Greek letters α, β, γ, δ, etc. Names of some acids are derived from acetic acid, *e.g.*

$(CH_3)_3CCOOH$ Trimethylacetic acid

$C_6H_5CH_2COOH$ Phenylacetic acid

Occasionally, they are named as carboxylic acids, *e.g.* cyclohexane carboxylic acid.

In IUPAC system, names of carboxylic acids are obtained by replacing the *-e* of the corresponding alkane with **-oic acid**. The carboxyl carbon atom is always assigned number 1.

$HCOOH$ Methanoic acid (Formic acid)

$CH_3CH_2CH_2CH_2COOH$ Pentanoic acid (Valeric acid)

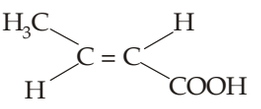
$CH_3CH=CHCOOH$ 2-Butenoic acid

$CH_3(CH_2)_4COOH$ Hexanoic acid (Caproic acid)

$CH_3(CH_2)_6COOH$ Octanoic acid (Caprylic acid)

$CH_3(CH_2)_8COOH$ Decanoic acid (Capric acid)

$CH_2=\overset{CH_3}{\overset{|}{C}}COOH$ 2-Methyl-2-propenoic acid or 2-Methylpropenoic acid (Methacrylic acid)



trans-2-Butenoic acid (Crotonic acid)

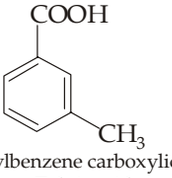
Common name, if any, is given in bracket.

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When a carboxyl group is attached to a ring, the parent ring is named (retaining the final *-e*) and the suffix *-carboxylic acid* is added. For example,

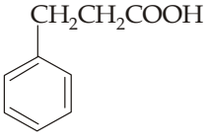


Benzene carboxylic acid
Benzoic acid

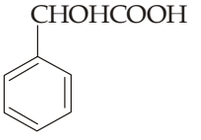


m-Methylbenzene carboxylic acid
m-Toluic acid

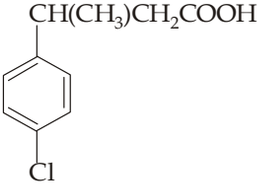
In case, carboxylic is present on the side chain, compound is named as a derivative of the corresponding alkane.



3-Phenylpropanoic acid



2-Hydroxy-2-phenylethanoic acid
(Mandelic acid)

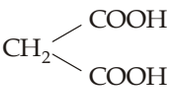


3-(*p*-Chlorophenyl)butanoic acid

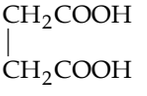
Compounds with two carboxyl groups are designated by the suffix *-dioic acid* or *dicarboxylic acid*. The final *-e* in the base name of the alkane is retained.



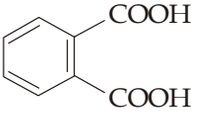
Ethanedioic acid
(Oxalic acid)



Propanedioic acid
(Malonic acid)



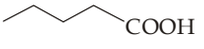
Butanedioic acid
(Succinic acid)

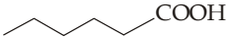


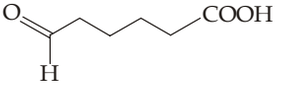
1, 2-Benzene dicarboxylic
(Phthalic acid)

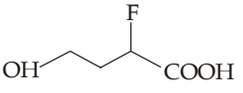
TEST YOUR UNDERSTANDING - 17.1

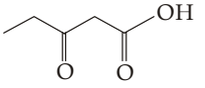
1. Give IUPAC name of the following compunds.

(*a*) 

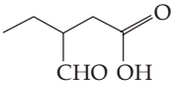
(*b*) 

(*c*) 

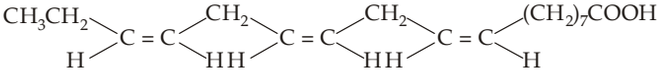
(*d*) 

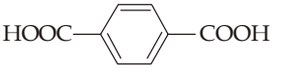
(*e*) 

(*f*) $CH_2 = CHCOOH$

(*g*) 

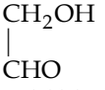
(*h*) $CH_3(CH_2)_7CH = CH(CH_2)_7COOH$

(*i*) 

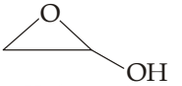
(*j*) 

Carboxylic acids exhibit chain, position and functional isomerism. Its functional isomers are esters, hydroxyaldehydes, hydroxyketones and hydroxyoxirane. Thus functional isomers of ethanoic acid are

$HCOOCH_3$
Methyl formate

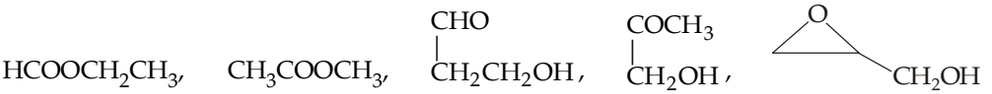


Glycolaldehyde



Hydroxyoxirane

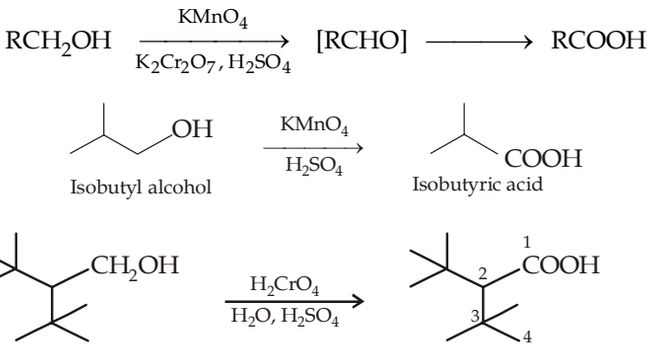
Similarly, functional isomers of propanoic acid (CH_3CH_2COOH) are



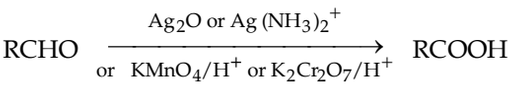
17.2 Preparation of Carboxylic Acids

Many carboxylic acids were first isolated from natural sources, viz. formic acid was obtained by distilling ants, lactic acid from sour milk, etc. However, such methods are now only of historical importance.

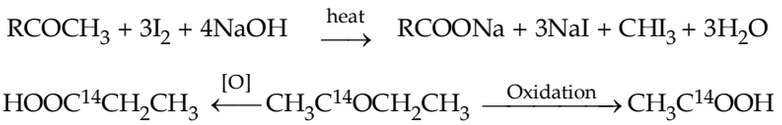
1. **By oxidation of 1° alcohols and aldehydes.** Potassium permanganate (acidic or alkaline) and chromic acid convert primary alcohols to carboxylic acids through the formation of corresponding aldehydes.



Aldehydes are very sensitive to oxidation and oxidised easily even with mild oxidising agents like Tollen's reagent, $[Ag(NH_3)_2]^+$.

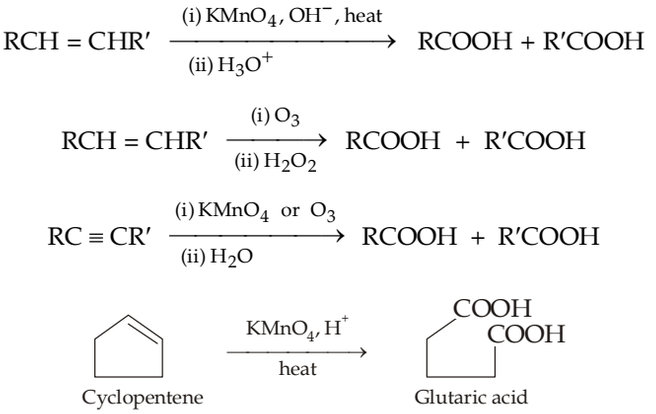


Ketones, although are also oxidised by strong oxidising reagents to carboxylic acids having lesser number of carbon atoms, these give poor yields. However, methyl ketones are good sources for carboxylic acids as these are quantitatively oxidised to carboxylic acids by hypohalites (haloform reaction).



However, remember that in mixed ketones, major oxidation product is that in which carbonyl carbon (C^{14}) remains with smaller alkyl group.

2. **By oxidation of alkenes, alkynes and cycloalkenes.** These compounds can be oxidised to carboxylic acids by hot alkaline $KMnO_4$ or by ozonolysis followed by reaction with H_2O_2.



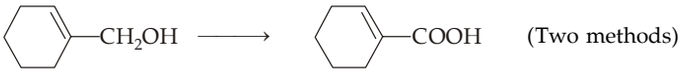
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TEST YOUR UNDERSTANDING - 17.2

1. From the knowledge of the chemistry so far studied, try to give steps for converting.

(*a*) $CH_3CH = CH_2$ to CH_3CH_2COOH

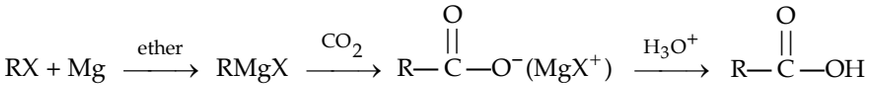
(*b*) $Me_3CCH = CH_2$ to Me_3CCOOH by four different methods.

(*c*)  (Two methods)

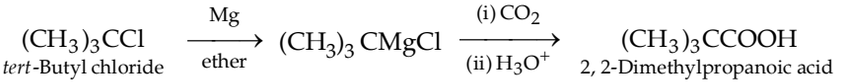
2. (*a*) Formulate the compounds from which $Me_2CHCOOH$ can be prepared by oxidation in good yield.

(*b*) Give the structure of a compound that gives an equimolar amount of succinic acid on oxidative cleavage.

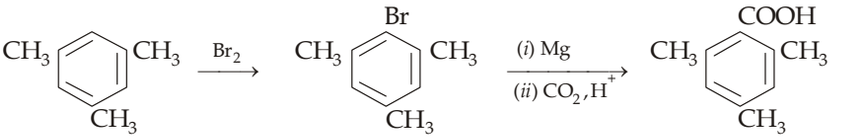
3. **By the carbonation of Grignard reagents.** (For details, consult chapter on "Organometallic Compounds'').



This synthesis of carboxylic acids is applicable to 1°, 2°, 3°, allyl, benzyl and aryl halides, provided they have no groups incompatible with a Grignard reaction, such as OH, SH, NH or C = O.

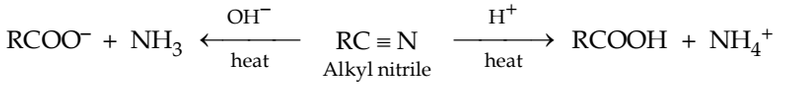




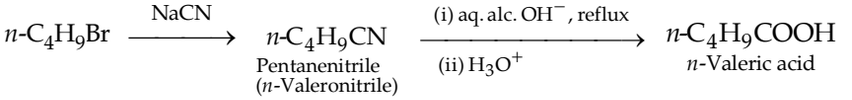


Mesitylene — 2, 4, 6-Trimethylbenzoic acid (Mesitoic acid)

4. **By hydrolysis of nitriles.** Aliphatic nitriles, obtained by the reaction of an alkyl halide with sodium cyanide in dimethyl sulphoxide (DMSO) as solvent, are easily hydrolysed by boiling aqueous alkali or acid to corresponding carboxylic acids.



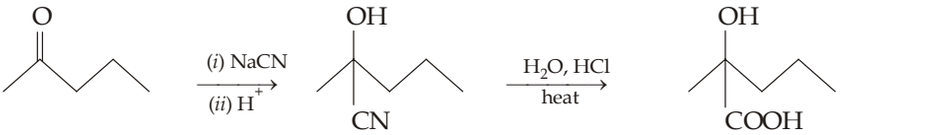
The fact that HCN is a very weak acid tells us that CN^- ion is a strong base and hence can cause elimination as well as substitution. Indeed, with *tert*-halides elimination is the principal reaction ; even secondary halides undergo elimination reaction to some extent. Hence this synthetic method of carboxylic acids from alkyl halides is limited to the use of primary alkyl halides. Aryl halides (except for those with *o*- and *p*-nitro groups) do not react with sodium cyanide ; hence aryl nitriles are obtained from diazonium salts.







Nitrile groups in cyanohydrins (aldehyde or ketone + CN^- → cyanohydrin) are hydrolyzed to corresponding α-hydroxy carboxylic acids.



2-Pentanone — 2-Pentanonecyanohydrin — 2-Hydroxy-2-methylpentanoic acid

Grignard synthesis and the **nitrile synthesis** for carboxylic acids have the advantage of increasing the length of a carbon chain by one carbon atom. Moreover, in both methods parent compounds are halides which in turn are usually prepared from alcohols, so the net result involves the conversion of an alcohol to a carboxylic acid with one more carbon atom.

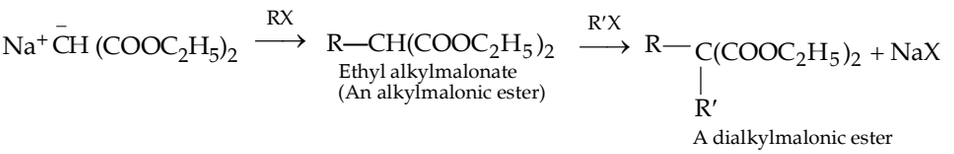
5. Malonic ester synthesis. This is one of the most valuable methods for preparing carboxylic acids. The synthesis is based upon following two important properties of ethyl malonate (*malonic ester*), $CH_2(COOC_2H_5)_2$.

(*i*) High acidity of the α-hydrogens of malonic ester.

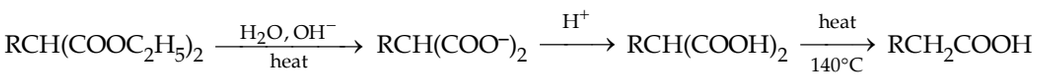
(*ii*) Extreme ease of decarboxylabion of malonic acid and substituted malonic acids.

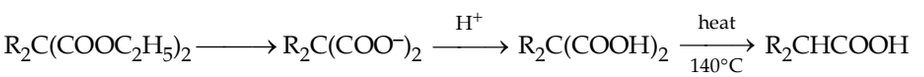


Malonic ester (stronger acid) — Sodiomalonic ester — Weaker acid



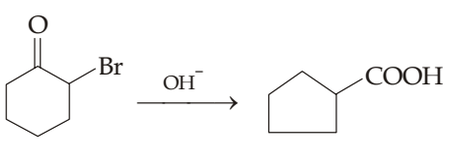
The monoalkylmalonic and dialkylmalonic esters, so prepared are readily converted into monocarboxylic acids by hydrolysis, acidification, and heat



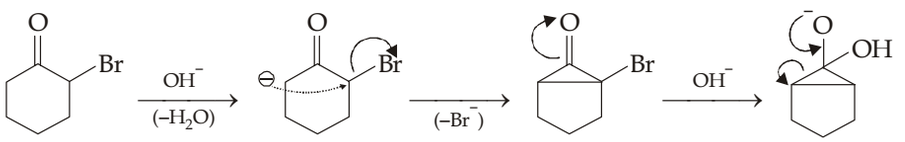


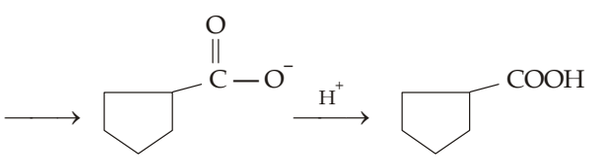
Thus malonic ester provides an important method for synthesising RCH_2COOH, $R_2CHCOOH$ and $RR'CHCOOH$.

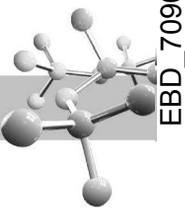
6. Favorskii rearrangement. α-Haloketones, when treated with base, are converted into carboxylic acids.



Mechanism.







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Industrial sources. Acetic acid is considered to be the most important carboxylic acid. Industrially, it is prepared

(*a*) By catalytic air oxidation of acetaldehyde or of various hydrocarbons.

$$CH_3CHO \xrightarrow[\text{Catalyst}]{O_2} CH_3COOH \longleftarrow \text{Hydrocarbons}$$

(*b*) From the reaction of methanol with carbon monoxide in the presence of iodine-rhodium catalyst (**Modern method)**.

$$CH_3OH + CO \xrightarrow{Rh/I_2} CH_3COOH$$

(*c*) Dilute aqueous solution of acetic acid, known as *vinegar*, is prepared by air oxidation of ethyl alcohol in the presence of bacterial enzymes (*acetobacter*).

Formic acid is prepared by the reaction of carbon monoxide with sodium hydroxide followed by acidification with sulphuric acid.

$$CO + NaOH \longrightarrow HCOO^-Na^+ \xrightarrow{H_2SO_4} HCOOH$$

The important source of aliphatic carboxylic acids are the animal and vegetable fats from which straight chain carboxylic acids of even number of carbon atoms ranging from 6 to 18 are obtained in purity of over 90%. It is important to note that naturally occurring fatty acids (acids obtained from fats) always contains even number of carbon atoms because plants and animals biosynthesize fatty acids by building up CH_3COOH (a C_2 compound) units.

TEST YOUR UNDERSTANDING - 17.3

1. Which of the two methods : Grignard synthesis and nitrile synthesis ; is suitable for converting each of the halide to the corresponding carboxylic acid. Also write down the steps involved during the reaction.

(*a*) 2-Chloroethanol to 3-hydroxypropanoic acid. (*b*) 2-Chloro-2-methylpropane to 2, 2-dimethylpropanoic acid.

(*c*) Chlorobenzene to benzoic acid. (*d*) 1, 2-Dibromoethane to succinic acid

(*e*) Vinyl bromide to propenoic acid.

2. (*a*) Show how you would prepare each of the following carboxylic acid through a Grignard synthesis ?

(*i*) 2, 2-Dimethylpentanoic acid (*ii*) 3-Butenoic acid (*iii*) 4-Methylbenzoic acid.

(*b*) Which of the above carboxylic acids can be prepared by a nitrile synthesis as well ?

3. Give the structure and name of the acids formed by a step-up reaction of the following halides.

(*a*) C_6H_5Cl (*b*) $CH_3CHClCH_2CH_2CH_3$ (*c*) $C_6H_{11}CMe_2Cl$ (*d*) *Z*-MeCH = CHBr.

4. Synthesize succinic acid from $CH_2 = CH_2$.

5. Use malonic ester to prepare

(*a*) 2-ethylbutanoic acid (*b*) 3-methylbutanoic acid

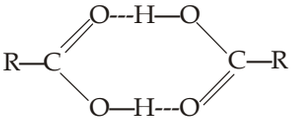
(*c*) 2-methylbutanoic acid (*d*) trimethylacetic acid.

6. A sulphuric acid solution of each of the following compounds, when treated with carbon monoxide, gives the same acid, 2, 2-dimethylbutanoic acid. Explain.

2-Methyl-2-butene, Neopentyl alcohol, *tert*-Pentyl alcohol

17.3 Physical Properties

(*i*) Carboxylic acids are rolar substances. Like alcohol molecules, their molecules can form hydrogen bonds with each other and also with water. As a result, low molecular weight carboxylic acids (the first four members) are miscible with water in all proportions ; water solubility decreases with increase in the length of the carbon chain.



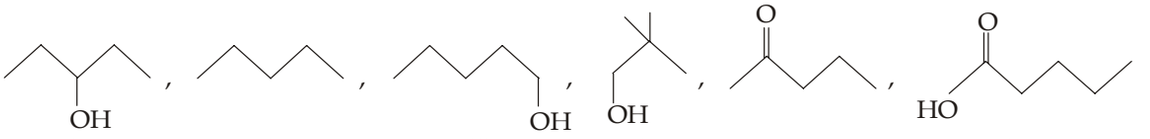
(*ii*) Carboxylic acids have higher boiling points than the corresponding alcohols. This is due to a unique hydrogen bonding arrangement in carboxylic acids ; carboxylic groups of two molecules are held together not by one but by two hydrogen bonds. This hydrogen bonding is so efficient that some carboxylic acids exist as hydrogen-bonded dimers even in the gas phase. In the pure liquid state, a mixture of hydrogen-bonded dimers and higher aggregates is present.

(*iii*) First two carboxylic acids have a sharp and acrid odour, while the acids with four to eight carbon atoms have unpleasant odours. These acids, formed by bacterial action, are present in trace amounts in the skin secretions of most mammals. Since metabolic processes of different persons are not exactly identical, these acids are present in different compositions on the skin of different persons which give a characteristic smell different from person to person ; this is the reason why dogs (having highly developed sense of smell) are able to differentiate one person from another.

TEST YOUR UNDERSTANDING - 17.4

1. Arrange the following compounds in order of decreasing boiling points :

(*a*)



(*i*) (*ii*) (*iii*) (*iv*) (*v*) (*vi*)

(*b*) C_3H_8 (A), $CH_3CH_2CH_2OH$ (B), $CH_3CHOHCH_2OH$ (C), $CH_3OCH_2CH_3$ (D), CH_3CH_2COOH (E).

2. The true value of molecular weight of acetic acid is found to be 60, however, just above its boiling point, it is found to be 120. Explain.

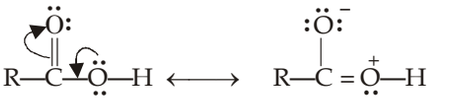
3. What is glacial acetic acid and why it is so called ? What is vinegar and how is it made ?

17.4 Chemical Properties

17.4.1 Acidity of Carboxylic Acids

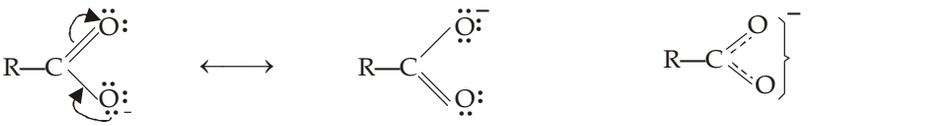
Carboxylic acids are the most acidic compounds that contain C, H and O. Ionization constants (K_a) of the caboxylic acid, is of the order of 10^{-5} ($pK_a \sim 5$), they are much stronger acids than water and alcohols.

The acidic character of carboxylic acids is due to resonance* in the acidic group which imparts electron deficiency (positive charge) on the oxygen atom of the hydroxyl group.



Non-equivalent structures (Resonance less important)

The positive charge (electron deficiency) on oxygen atom causes a displacement of electron pair of the O—H bond towards the oxygen atom with the result the hydrogen atom of the O—H group is eliminated as proton and a carboxylate ion is formed. Once the carboxylate ion is formed, it is stabilised by means of resonance.



Resonating forms of carboxylate ion (Equivalent structures), hence resonance more important.

Resonance hybrid of carboxylate ion

Due to equivalent resonating structures, resonance in carboxylate anion is more important than in the parent carboxylic acid. Hence carboxylate anion is more stabilised than the acid itself and hence the equilibrium of the ionisation of acids shifts to the right hand side.

$$RCOOH \rightleftharpoons RCOO^- + H^+$$

The existence of resonance in carboxylate ion is supported by bond lengths. For example, in formic acid, there is one C = O double bond (121 pm) and one C—O single bond. (136 pm), while in sodium formate both of the carbon-oxygen bond lengths are identical (125 pm) which is nearly intermediate between C = O and C—O bond length values. This proves resonance in carboxylate anion.



Formic acid Sodium formate

* Note that in resonance of carboxylic acids, —CO part of the acidic group enters into resonance with the lone pair of the —OH group and hence —COOH does not give reactions of the carbonyl group.

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It is important to note that although carboxylic acids and alcohols both contain —OH group, the latter are not acidic in nature. It is due to the absence of resonance (factor responsible for acidic character of —COOH) in both the alcohols as well as in their corresponding ions (alkoxide ions).

$$\underset{\text{Alcohol (No resonance)}}{R—O—H} \rightleftharpoons \underset{\text{Alkoxide ion (No resonance)}}{R—O^-} + H^+$$

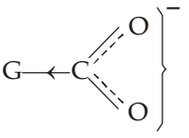
Alkoxide ions are stabilized by solvation forces, while carboxylate ions are stabilized by solvation as well as resonance and inductive effect of the carbonyl group.

Role of inductive effect of the carbonyl group. The carbonyl group is electron-withdrawing, and by attracting electrons away from the negatively charged oxygen, carboxylate anion is stabilized.

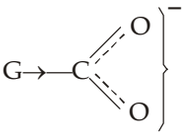
Relative acidic character of carboxylic acids with common species not having —COOH group.

$$RCOOH > HOH > ROH > HC \equiv CH > NH_3 > RH$$

Effect of substituents on acidity. We know that the carboxylic acids are acidic in nature because of stabilisation (*i.e.*, dispersal of negative charge) of carboxylate ion. So any factor which can enhance the dispersal of negative charge of the carboxylate ion will increase the acidity and *vice versa.* Thus electron-withdrawing substituents (like halogens, $—NO_2$, $—C_6H_5$ etc.) would disperse the negative charge and hence stabilise the carboxylate ion and thus increase acidity of the parent acid. On the other hand, electron-releasing substituents would intensify the negative charge, destabilise the carboxylate ion and thus decrease acidity of the parent acid.



The substituent G withdraws electrons, stabilises anion and hence increases acidity



The substituent G releases electrons, destabilises anion and hence decreases acidity

Now since alkyl groups are electron-releasing, their presence in the molecule will decrease the acidity. In general, greater the length of the alkyl chain, lower shall be the acidity of the acid. Thus formic acid (HCOOH), having no alkyl group, is about 10 times stronger than acetic acid (CH_3COOH) which in turn is stronger than propanoic acid (CH_3CH_2COOH) and so on. Similarly, following order is observed in chloro acids.

$$\underset{\text{Trichloroacetic acid}}{Cl_3CCOOH} > \underset{\text{Dichloroacetic acid}}{Cl_2CHCOOH} > \underset{\text{Monochloroacetic acid}}{ClCH_2COOH} > \underset{\text{Acetic acid}}{CH_3COOH}$$

Trichloroacetic acid is more than 10,000 times more stronger than acetic acid, actually it is almost as strong acid as a mineral acid. For further details of the relative acidities of the carboxylic acids, consult inductive effect in Chapter on "General Organic Chemistry".

Decreasing order of aliphatic acids

(*i*) $O_2NCH_2COOH > FCH_2COOH > ClCH_2COOH > BrCH_2COOH$

(*ii*) $HCOOH > CH_3COOH > (CH_3)_2CHCOOH > (CH_3)_3CCOOH$

(*iii*) $CH_3CH_2CCl_2COOH > CH_3CHCl.CHCl.COOH > ClCH_2CHClCH_2COOH$

(*iv*) $F_3CCOOH > Cl_3CCOOH > Br_3CCOOH$

Benzoic acid is somewhat stronger than simple aliphatic acids. Here the carboxylate group is attached to a more electronegative carbon (sp^2 hybridised) than in aliphatic acids (sp^3 hybridised). Remember that carbon becomes more electron-withdrawing as its *s* character increases.

Acidity of dicarboxylic acids

Here two ionization constants (K_1 and K_2) characterise the two successive ionization steps of a dicaboxylic acid.

$$HO—\overset{\overset{O}{\|}}{C}—\overset{\overset{O}{\|}}{C}—OH \overset{K_1}{\rightleftharpoons} HO—\overset{\overset{O}{\|}}{C}—\overset{\overset{O}{\|}}{C}—O^- \quad , \quad K_1 = 6.5 \times 10^{-2} \; ; \; pK_1 = 1.2$$

Hydrogen oxalate (monoanion)

$$HO—\overset{\overset{O}{\|}}{C}—\overset{\overset{O}{\|}}{C}—O^- \overset{K_2}{\rightleftharpoons} {}^-O—\overset{\overset{O}{\|}}{C}—\overset{\overset{O}{\|}}{C}—O^- \quad , \quad K_2 = 5.3 \times 10^{-5} \; ; \; pK_2 = 4.3$$

Oxalate (dianion)

The first ionization constant of dicarboxylic acids is larger than K_a for monocarboxylic analogs. There are two reasons for this.

(*a*) Presence of two potential sites for ionization rather than one.

(*b*) One carboxyl group acts as an electron-withdrawing group to facilitate dissociation of the other. This factor is significant when two carboxyl groups are separated by only a few bonds. Thus oxalic and malonic acids are highly acidic than the corresponding monocarboxylic acids while heptanedioic acid is only slightly stronger than acetic acid.

	$HOOCCOOH$ Oxalic acid	$HOOCCH_2COOH$ Malonic acid	$HOOC(CH_2)_5COOH$ Heptanedioic acid
K_1	6.5×10^{-2}	1.4×10^{-3}	3.1×10^{-5}
pK_1	1.2	2.8	4.3

TEST YOUR UNDERSTANDING - 17.5

1. (*a*) Compare the carbon-oxygen bond length in sodium formate and sodium carbonate.

(*b*) Compare the carbon-oxygen single bond in carboxylic acids with that in alcohols.

2. Which is the stronger acid in each of the following pairs.

(*i*) Me_3CCH_2COOH or $Me_3\overset{+}{N}CH_2COOH$

(*ii*) CH_3CH_2COOH or $CH_3CHOHCOOH$

(*iii*) $CH_3COCOOH$ or $CH_2=CHCOOH$

(*iv*) $CH_3CH_2CH_2COOH$ or $CH_3SO_2CH_2COOH$

(*v*) Me_3CCH_2COOH or Me_3SiCH_2COOH

(*vi*) 3-Butenoic acid or 3-Butynoic acid

3. Arrange the following in decreasing order of acidity.

(*i*) C_2H_5OH, $HCOOH$, CH_3COOH, C_6H_5OH

(*ii*) $HCOOH$, C_2H_5COOH, CH_3COOH, $CH_2ClCOOH$, C_6H_5COOH

(*iii*) $CH_3CH_2CH_2COOH$, $CH_3CHClCH_2COOH$, $CH_3CH_2CHClCOOH$, $ClCH_2CH_2CH_2COOH$

(*iv*) CH_3COOH, $CH_2ClCOOH$, $CHCl_2COOH$, CCl_3COOH

(*v*) $CH_2BrCOOH$, $CH_2ClCOOH$, CH_2ICOOH, CH_2FCOOH

(*vi*) $ClCH_2COOH$, CH_3CH_2COOH, $ClCH_2CH_2COOH$, $Me_2CHCOOH$,CH_3COOH

(*vii*) $HCOOH$, C_6H_5COOH, C_6H_5OH, HCl

(*viii*) Acetic acid, acetylene, ammonia, ethane, ethanol, sulphuric acid, water.

(*ix*) Acetic acid, malonic acid, succinic acid.

(*x*) α-Chlorophenylacetic acid, *p*-chlorophenylacetic acid, phenylacetic acid, α-phenylpropanoic acid.

4. Explain the following :

(*a*) Peroxy acids are much weaker acids than carboxylic acids.

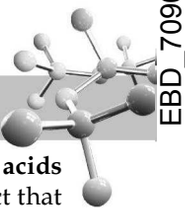
(*b*) Highly branched acids are less acidic than unbranched acids.

(*c*) The K_2 for fumaric acid (*trans*-butenedioic acid) is greater than for maleic acid, the *cis* isomer.

Although much weaker than the strong mineral acids (H_2SO_4, HCl, HNO_3), carboxylic acids are most acidic among organic compounds containing C, H and O. They are neutralized rapidly and quantitatively in presence of strong bases like sodium hydroxide. Aqueous mineral acids readily convert the salts back into the carboxylic acids.

$$\underset{\text{Carboxylic acid (stronger acid)}}{RCOOH} + \underset{\text{Hydroxide ion (stronger base)}}{OH^-} \underset{H^+}{\rightleftharpoons} \underset{\text{Carboxylate ion (weaker base)}}{RCOO^-} + \underset{\text{Water (weaker acid)}}{H_2O}$$

Salts of carboxylic acids are crystalline, non-volatile solids. The strong electrostatic forces holding the ions in the crystal lattice can be overcome only by heating to a high temperature, or by a very strong polar solvent. The mp of the salts are so high that before it can reach, carbon-carbon bonds break and the molecule decomposes (300° – 400°C). The alkali metal salts of carboxylic acids (sodium, potassium, ammonium) are soluble in water but insoluble in non-polar solvents ; however most of the heavy metal salts (iron, silver, copper etc.) are insoluble in water.



Except for the first four carboxylic acids, which are soluble both in water and organic solvents, **carboxylic acids and their alkali metal salts show exactly opposite solubility behaviour**. This solubility difference along with the fact that acids and their salts are readily interconvertible has been used for identifying and separation of carboxylic acids from compounds having other functional group.

(*i*) In case an organic compound is insoluble in water but soluble in cold dilute aqueous sodium hydroxide or aq. $NaHCO_3$, it must be an organic compound which is more acidic than water, *i.e.*, generally a carboxylic acid.

$$\underset{\text{Stronger acid (insoluble in } H_2O)}{RCOOH} + NaOH \longrightarrow \underset{\text{Weaker base (soluble in } H_2O)}{RCOONa} + \underset{\text{Weaker acid}}{H_2O}$$

$$\underset{\text{Insoluble in water}}{RCOOH} + NaHCO_3 \longrightarrow \underset{\text{Soluble in } H_2O}{RCOONa} + H_2O + CO_2\uparrow$$

(*ii*) A carboxylic acid can be saparated from non-acidic compounds by taking advantage of its solubility in aqueous base. The acid can be easily regenerated by acidifying the aqueous solution containing salt.

Scheme for separation of carboxylic acid from non-acidic compounds.

For solids : Mixture + *aq*. base $\xrightarrow{\text{filter}}$ **Insoluble**

Soluble $\xrightarrow{H^+}$ RCOOH

For liquids : Mixture + *aq*. base (In a separatory funnel)

Ether layer (Non acidic component)

Aq. layer (—COONa component) $\xrightarrow{H^+}$ RCOOH

For complete separation, generally a water-insoluble solvent like ether is added to the acidified mixture. Since carboxylic acids are soluble in ether, ether layer containing carboxylic acid is separated, ether evaporated leaving carboxylic acids.

(*iii*) Salts of higher fatty acids such as palmitic acid, $C_{15}H_{31}COOH$, stearic acid, $C_{17}H_{35}COOH$, oleic acid [$C_{17}H_{33}COOH$] are known as **soaps** ; potassium salts are soft soaps while sodium salts are hard sops.

TEST YOUR UNDERSTANDING - 17.6

1. Write an ionic equation for the reaction of acetic acid with each of the following, and specify whether the equilibrium favours starting materials or products.

(*a*) Sodium ethoxide (*b*) Potassium *tert*-butoxide (*c*) Sodium bromide

(*d*) Sodium acetylide (*e*) Potassium nitrate (*f*) Lithium amide.

17.4.2 Reactions in which —OH of —COOH Group is Replaced (*Conversion into functional derivatives*)

$$R-\overset{\overset{O}{\|}}{C}-OH \longrightarrow R-\overset{\overset{O}{\|}}{C}-Z \quad (\text{Where, } Z = -Cl, -OR', -NH_2)$$

1. **Conversion into acid chlorides.** Three reagents are commonly used for this purpose, namely thionyl chloride, phosphorus trichloride and phosphorus pentachloride.

$$RCOOH + SOCl_2 \longrightarrow RCOCl + HCl\uparrow + SO_2\uparrow$$

$$3RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$$

$$RCOOH + PCl_5 \longrightarrow RCOCl + HCl\uparrow + POCl_3$$

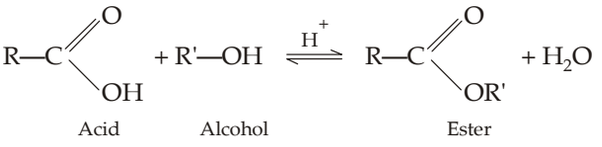
However, thionyl chloride is particularly convenient since the two gaseous products (SO_2 and HCl) are readily removed from RCOCl, any excess of the low-boiling thionyl choride (79°C) is easily removed by distillation.

2. Conversion into esters. A carboxylic acid may be converted into esters in two ways ; (*i*) direct esterification with an alcohol, (*ii*) esterification through acid chlorides

$$\underset{\text{Acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH} \overset{H^+}{\rightleftharpoons} \underset{\text{Ester}}{RCOOR'} + H_2O$$

$$RCOOH \xrightarrow{SOCl_2} RCOCl \xrightarrow{R'OH} RCOOR'$$

(*i*) **Direct esterification.** A carboxyl group is converted directly into an ester when heated with an alcohol in the presence of a little mineral acid, usually conc. H_2SO_4 or dry hydrogen chloride.



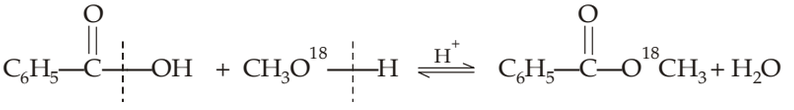
This reaction is reversible and generally reaches equilibrium when appreciable quantities of both reactants and products are present. Although reversibility is a disadvantage in the direct esterification, the process has the advantage of being a single-step process and can often be made useful by application of our knowledge of equilibria. Since the position of equilibrium controls the amount of the ester formed, the use of an excess of either the carboxylic acid or the alcohol increases the yield. Just which component is used in excess depends on its availability and cost ; *e.g.*

$$\underset{\substack{\gamma\text{-Phenylbutyric acid}\\ \text{valuable, 1 mole}}}{C_6H_5CH_2CH_2CH_2COOH} + \underset{\substack{\text{Ethanol}\\ \text{cheap, 8 mole}}}{C_2H_5OH} \xrightleftharpoons{H_2SO_4,\ \text{reflux}} \underset{\text{Ethyl-}\gamma\text{-phenylbutyrate}}{C_6H_5CH_2CH_2CH_2COOC_2H_5} + H_2O$$

The yield of esterification can also be increased by removing water (one of the products) from the reaction mixture as soon as it is formed. For example, in the preparatioon of ethyl adipate, water is removed as lowest boiling point component (75°C) of the mixture in the form of azeotrope of water, ethyl alcohol, and toluene. Hence the reaction should be carried out in presence of excess of ethanol and in presence of toluene.

$$\underset{\text{Adipic acid (non-volatile)}}{HOOC(CH_2)_4COOH} + \underset{\text{(b.p.78°C)}}{2C_2H_5OH} \xrightarrow[H_2SO_4]{\text{toluene,}} \underset{\text{Ethyl adipate (boiling point 245°C)}}{C_2H_5OOC(CH_2)_4COOC_2H_5} + \underset{\substack{\text{Removed as}\\ \text{azeotrope,}\\ \text{boiling point 75°C}}}{2H_2O}$$

Note that it is the C—OH bond of the carboxylic acid that breaks up during esterification.



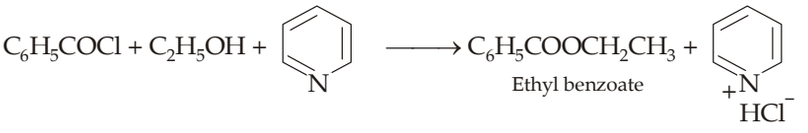
Mechanism of esterification is necessarily the exact reverse of the mechanism of acidic ester hydrolysis that will be discussed in the chemisty of esters.

(*ii*) The presence of bulky groups near the site of reaction, whether in alcohol or in the acid, slows down esterification (as well as its reverse, hydrolysis).

Reactivity in	CH_3OH	>	1°	>	2°	(>3°)
esterification	HCOOH	>	CH_3COOH	>	RCH_2COOH	> $R_2CHCOOH$

In some cases steric hindrance is so marked that special methods are required to prepare esters of tertiary alcohols or esters of acids like 2, 4, 6-trimethylbenzoic acid (mesitoic acid).

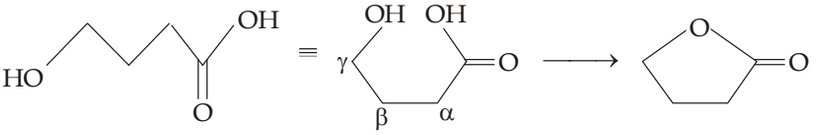
(*iii*) **Esterification through acid chlorides.** Since acyl chlorides are much more reactive toward nucleophilic addition-elimination than carboxylic acids, reaction of an acyl chloride and an alcohol occurs rapidly and does not require an acid catalyst. Pyridine is generally added to remove the HCl formed during reaction. Moreover, pyridine may also react with the acyl chloride to form an acylpyridinium ion, an intermediate that is even more reactive toward the nucleophile than the acyl chloride itself.



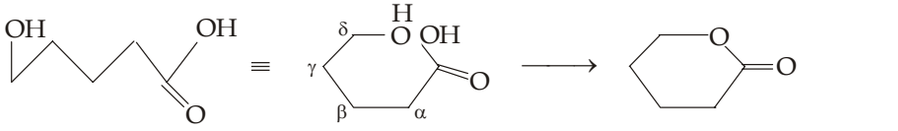
Esterification through acid chloride gives better results when *tert*-alcohols are used as one of the components because in the direct esterification, the acid used may cause dehydration by elimination reaction.

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Intramolecular esterification. Hydroxy acids (compounds containing a hydroxyl and a carboxyl group in the same molecule) have the capacity to form cyclic esters called lactones. This intramolecular esterification takes place spontaneously and is especially favourable when the ring formed is either 5-membered or 6-membered. Lactones having a five membered ring are known as **γ-lactones** since they are formed from γ-hydroxy acids. The six-membered analogs are known as **δ-lactones**.



4-Hydroxybutanoic acid 4-Butanolide (γ-Butyrolactone)



δ-Hydroxypentanoic acid 5-Pentanolide (δ-Valerolactone)

Like other esters, lactones are hydrolyzed by aqueous base.

3. **Conversion into amides.** Acids are converted into amides by treating acid chlorides with ammonia, primary amines, and secondary amines.

$$RCOOH \xrightarrow{SOCl_2} RCOCl \xrightarrow{NH_3} RCONH_2$$

$$\underset{\text{Phenylacetic acid}}{C_6H_5CH_2COOH} \longrightarrow \underset{\substack{\text{Phenylacetyl chloride}\\(\text{Phenacyl chloride})}}{C_6H_5CH_2COCl} \xrightarrow{NH_3} \underset{\text{Phenylacetamide}}{C_6H_5CH_2CONH_2}$$

TEST YOUR UNDERSTANDING - 17.7

1. (*a*) Which bond of carboxylic acid is broken in the formation of acid chloride, *i.e.* whether C—OH or CO—H ?
   (*b*) When benzoic acid is allowed to stand in water enriched in O^{18} in presence of acids, heavier oxygen becomes incorporated into the benzoic acid. Explain.
   (*c*) When reactive alcohols like $CH_2 = CHCH_2O^{18}H$ are esterified in acid, some H_2O^{18} is found in the product.
2. Discuss in three lines, how will you prepare ethyl acetate (an important commercial solvent) from ethanol.

4. **Formation of anhydrides.** Only one monocarboxylic acid anhydride (acetic anhydride) is important. It is prepared by the reaction of acetic acid with ketene ($CH_2 = C = O$), which in turn is prepared by high temperature dehydration of acetic acid.

$$CH_3COOH \xrightarrow[-H_2O]{AlPO_4,\ 700°C} CH_2 = C = O \xrightarrow{CH_3COOH} (CH_3CO)_2O$$

Acid anhydrides, in general, can be prepared by treating acyl chloride with —COOH in the presence of pyridine or by treating sodium salts of carboxylic acids with acyl chlorides.

$$RCOCl + R'COOH \text{ (or } R'COONa) \longrightarrow RCO.O.COR' + HCl \text{ (or } NaCl)$$

17.4.3 Reduction of >C = O of –COOH to $–CH_2OH$

For details, consult preparation of alcohols.

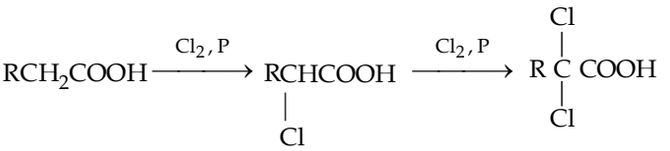
$$RCOOH \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4,\ ether} RCH_2OH$$

An alternate way of reducing carboxylic acid is *via* esters.

$$RCOOH \longrightarrow RCOOR' \xrightarrow[150°C\ pressure]{H_2,\ Copper\ chromite} RCH_2OH + R'OH$$

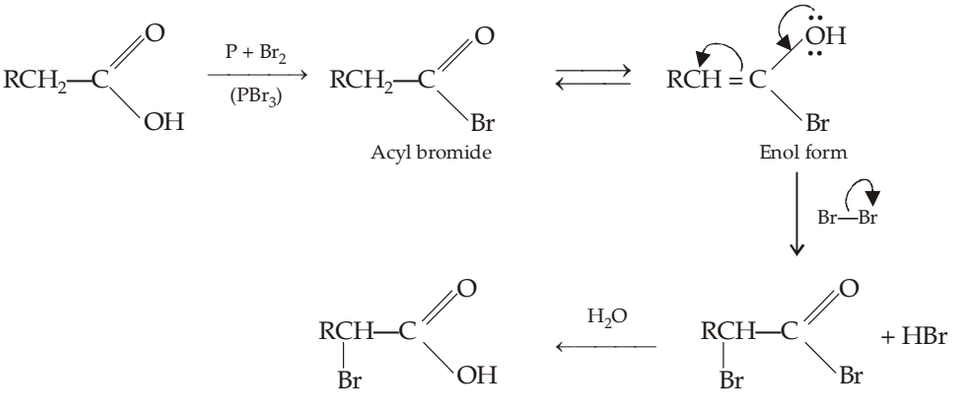
17.4.4 Halogenation of α-Hydrogens

Aliphatic carboxylic acids react with bromine or chlorine in the persence of phosphorus (or a phosphorus halide) to give α-halo acids, the reaction as known as **Hell-Volhard-Zelinski (or HVZ) reaction.**

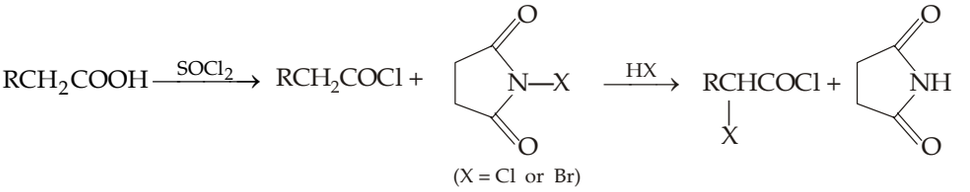


Halogenation occurs specifically at the α-carbon ; because of this regioselectivity and the ease with which it takes place, HVZ reaction is of considerable importance in synthesis.

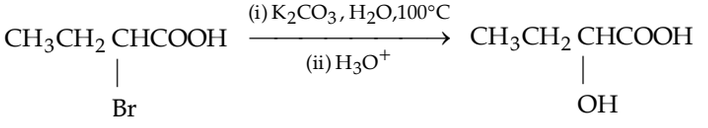
The function of phosphorus is to convert a little of the acid into **acid halide which is the actual molecule on which halogenation takes place** and not on acid itself. Specific halogenation at α-position is due to formation of enols which are readily formed by acyl halides than from carboxylic acids itself.



Harpp reaction is the modification of HVZ reaction. This reaction involves α-halogenation of carboxylic acid with N-halosuccinimide in presence of HCl or HBr and $SOCl_2$.



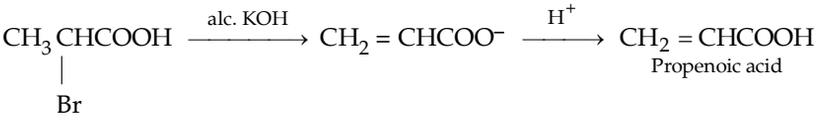
Like alkyl halides, the halogen of these halogenated acids undergoes *nucleophilic displacement* and *elimination*, hence α-halo acids are important synthetic intermediates.

(*i*) 

2-Bromobutanoic acid 2-Hydroxybutanoic acid

(*ii*) 

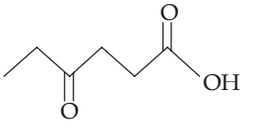
Aminoacetic acid (glycine)

(*iii*) 

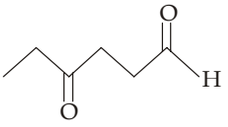
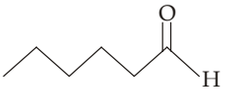
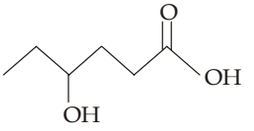
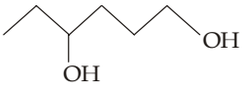
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TEST YOUR UNDERSTANDING - 17.8

1. Give the reagent(s) required to convert the keto acid,



into each of the following compunds. In case two steps are required, give the proper order.

(*a*)  (*b*)  (*c*)  (*d*) 

2. α-Iodo acids are not normally prepared by direct HVZ reaction. Show how you could convert octadecanoic acid to its 2-iodo derivative by efficient sequence of reactions.

3. Predict the product of each of the following reactions :

(*a*) $C_6H_5CH(OH)CH_2COOH \xrightarrow[(-H_2O)]{H^+,\ heat}$ (*b*) *o*-$HOOCC_6H_4CH_2OH \xrightarrow[(-H_2O)]{H^+,\ heat}$

(*c*)  (*d*) 

4. (*a*) Convert ethanoic acid into propanedioic acid.

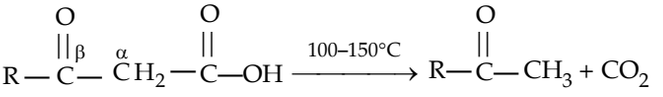
(*b*) One of the steps in the above sequence involves conversion of chloroacetic acid to cyanoacetic acid ; for this step chloroacetic acid is first converted into its salt before treatment with cyanide ion. Explain.

17.4.5 Decarboxylation of Carboxylic Acids

The loss of a molecule of carbon dioxide from a carboxylic acid is known as **decarboxylation.**

$$RCOOH \longrightarrow RH + CO_2$$

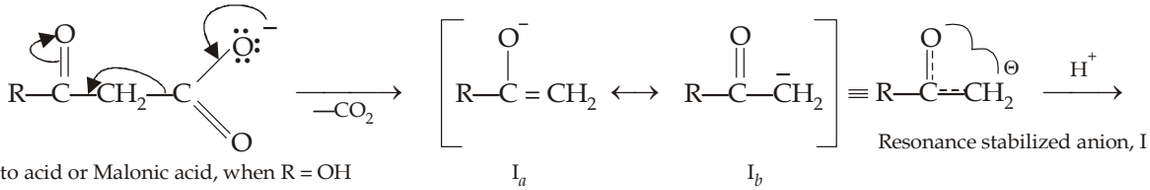
Decarboxylation of simple carboxylic acids takes place with great difficulty and is rarely encountered. However, there are certain groups which if present in β-position of a carboxylic acid, decarboxylation takes place readily. Thus β-keto and β, γ-unsaturated carboxylic acids decarboxylate readily when they are heated to 100–150°C (some β-keto acids decarboxylate although slowly even at room temperature).



$$\overset{\gamma}{C}H_2=\overset{\beta}{C}H\overset{\alpha}{C}H_2COOH \xrightarrow{heat} CH_2=CHCH_3+CO_2$$

Decarboxylation of β-keto acids takes place in the form of free acid or in the form of carboxylate ion.

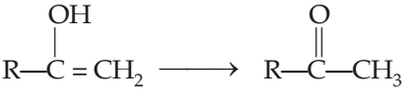
(*a*) When the carboxylate anion decarboxylates, it forms a resonance stabilized enolate anion ; I.



β-Keto acid or Malonic acid, when R = OH

I_a I_b

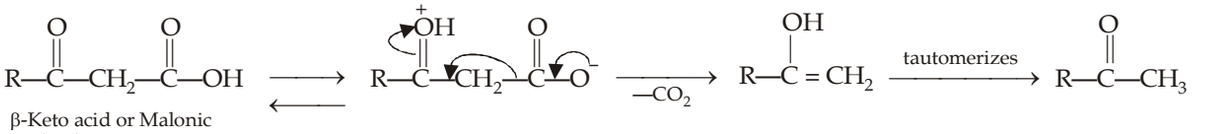
Resonance stabilized anion, I



This carbanion is formed faster than the simple carbanion ($R:^-$) from a simple carboxylate ion ($RCOO^-$) because it is more stable. Recall that of the two contributing structures (I_a and I_b), I_a is more stable because here the negative charge is accommodated by oxygen (every atom has eight electrons, except hydrogen).

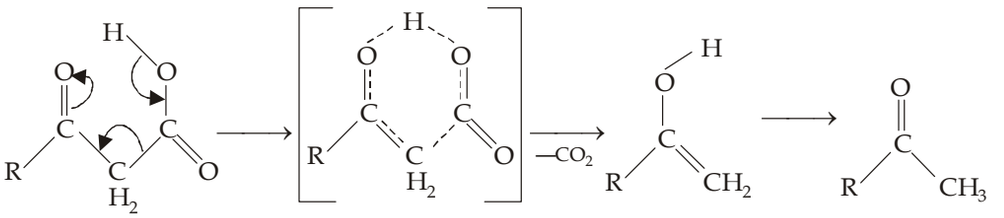
(*b*) Decarboxylation of the acid itself involves transfer of the carboxylic acidic hydrogen to the keto group, either prior to loss of carbon dioxide, or simultaneously with loss of carbon dioxide.

(*i*)



β-Keto acid or Malonic acid, when R = OH

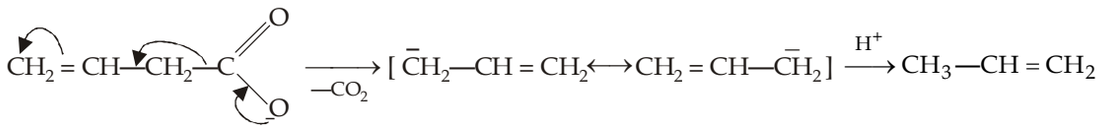
(*ii*)



β-Keto acid or (Malonic acid, when R = OH) | Transition state | Enol | Keto

Malonic acid and its monoanion undergo decarboxylation exactly in the same ways. Replace R— by —OH.

β, γ-Unsaturated carboxylic acids also undergo decarboxylation in the same ways.



TEST YOUR UNDERSTANDING - 17.9

1. (*a*) It is difficult to decarboxylate $C_6H_5CH_2CH_2COOH$, while the corresponding phenylpropiolic acid, $C_6H_5C \equiv CCOOH$ undergoes decarboxylation in alkaline solution. Explain.

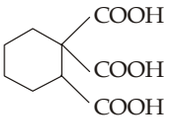
(*b*) It is difficult to decarboxylate benzoic acid and phenylacetic acid, while 2, 4, 6-trinitrobenzoic acid can be decarboxylated easily by heating.

2. Give the product isolated after thermal decarboxylation of each of the following :

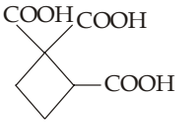
(*a*) 1, 1-Cyclobutane dicarboxylic acid. (*b*) 2-Cyclopentenylmalonic acid. (*c*) Phenylmethylmalonic acid.

3. Give the products obtained on heating each of the following compounds.

(*a*)



(*b*)



17.4.6 Reactions of Salts of Carboxylic Acids

(*i*) Heating of sodium salts with soda lime (NaOH + CaO) to *form alkanes.*

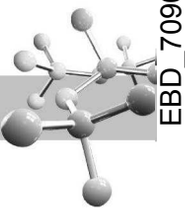
$$\underset{\text{Sod. acetate}}{CH_3COONa} + NaOH \xrightarrow{\text{heat}} \underset{\text{Methane}}{CH_4} \uparrow + Na_2CO_3$$

However, sodium formate on decarboxylation with soda lime gives hydrogen.

$$HCOONa \xrightarrow{NaOH} H_2 + Na_2CO_3$$

(*ii*) Sodium formate on heating gives sodium oxalate and hydrogen.

$$2HCOONa \xrightarrow{300°C} \begin{matrix} COONa \\ | \\ COONa \end{matrix} + H_2$$



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(*iii*) Heating of sod. formate with conc. H_2SO_4.

$$2HCOONa + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O + 2CO$$

(*iv*) **Electrolysis of conc. aq. solution of sod. or pot. salts gives alkanes** (*reaction is not given by sod. or pot. formate*).

$$\underset{\text{Sod. acetate}}{2CH_3COONa} + 2H_2O \xrightarrow{\text{electrolysis}} \underbrace{CH_3 - CH_3 + 2CO_2}_{\text{at anode}} + \underbrace{2NaOH + H_2}_{\text{at cathode}}$$

(*v*) **Heating of ammonium salts** (*Formation of amides*).

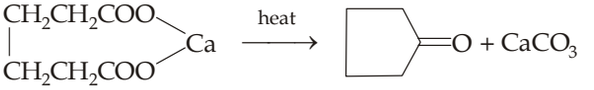
$$\underset{\text{Ammo. acetate}}{CH_3COONH_4} \xrightarrow{\text{heat}} \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O$$

(*vi*) **Dry distillation of calcium salts** (*Formation of aldehydes and ketones*).

(*a*) $\underset{\text{Cal. formate}}{(HCOO)_2Ca} \xrightarrow{\text{heat}} \underset{\text{Formaldehyde}}{HCHO} + CaCO_3$

(*b*) $\underset{\text{Cal. acetate}}{(CH_3COO)_2Ca} \xrightarrow{\text{heat}} \underset{\text{Acetone}}{CH_3COCH_3} + CaCO_3$

(*c*) $\underset{\text{Cal . accetate}}{(CH_3COO)_2Ca} + \underset{\text{Cal . formate}}{(HCOO)_2Ca} \xrightarrow{\text{heat}} \underset{\text{Acetaldehyde}}{2CH_3CHO} + 2CaCO_3$

(*d*) 

Calcium adipate — Cyclopentanone

(*vii*) **Silver salt of a carboxylic acid on heating** with bromine gives alkyl halide (**Hunsdiecker reaction**).

$$RCOOAg + Br_2 \xrightarrow{CCl_4,\ \text{heat}} R\text{–}Br + CO_2 + AgBr$$

17.5 Special Properties of Formic Acid

In addition to properties discussed earlier, formic acid gives the following reactions.

1. **Action of conc. H_2SO_4** (*Dehydration*). $HCOOH \xrightarrow{H_2SO_4,\ \text{heat}} H_2O + CO$

2. **Action of heat.** $HCOOH \xrightarrow{160°C} H_2 + CO_2$

3. **Reducing agent.** *(Reactions due to —CHO group).* Like aldehydes, but unlike other acids, **formic acid reduces Tollen's reagent, Fehling solution, mercuric chloride and potassium permanganate.**

(*i*) $HCOOH + \underset{\text{Tollen's reagent}}{Ag_2O} \longrightarrow CO_2 + H_2O + \underset{\text{Silver mirror}}{2Ag\downarrow}$

(*ii*) $HCOOH + \underset{\text{Fehling solution}}{2CuO} \longrightarrow CO_2 + H_2O + \underset{\substack{\text{Cuprous oxide}\\ \text{(reddish brown)}}}{Cu_2O\downarrow}$

(*iii*) $HCOOH + 2HgCl_2 \longrightarrow CO_2 + 2HCl + \underset{\text{Mercurous chloride (white)}}{Hg_2Cl_2\downarrow}$

$HCOOH + Hg_2Cl_2 \longrightarrow CO_2 + 2HCl + \underset{\text{Mercury (black)}}{2Hg\downarrow}$

or $2HCOOH + 2HgCl_2 \longrightarrow 2CO_2 + 4HCl + 2Hg\downarrow$

(*iv*) $2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4\ 3H_2O + 5O$

$5HCOOH + 5O \longrightarrow 5CO_2 + 5H_2O$

$2KMnO_4 + 3H_2SO_4 + 5HCOOH \longrightarrow K_2SO_4 + 2MnSO_4 + 5CO_2 + 8H_2O$

However, remember that formic acid does not react with NH_2OH, semicarbazide, phenylhydrazine, etc.

17.6 Dicarboxylic Acids

Important dicarboxylic acids along with their IUPAC and common names are given below.

HOOC.COOH Ethanedioic acid (Oxalic acid)	$HOOCCH_2COOH$ Propanedioic acid (Malonic acid)	$HOOCCH_2CH_2COOH$ 1, 4-Butanedioic acid (Succinic acid)
$CH_2(CH_2COOH)_2$ 1, 5-Pentanedioic acid (Glutaric acid)	CH_2CH_2COOH $\vert$ CH_2CH_2COOH 1, 6-Hexanedioic acid (Adipic acid)	$CH_2(CH_2CH_2COOH)_2$ 1, 7-Heptanedioic acid (Pimelic acid)

Dicarboxylic acids exhibit position isomerism among themselves, *e.g.*

CH_2COOH $\vert$ CH_2COOH Succinic acid	$CH_3CH(COOH)_2$ Methylmalonic acid

Methods of preparation and chemical properties are similar to that of monocarboxylic acids. Two properties deserve special attention.

1. **Acidity.** Like inorganic acids containing two or more ionizable hydrogen (H_2SO_4, H_2CO_3, H_3PO_4 etc.), ionization of the second carboxyl group occurs less readily than ionization of the first, *i.e.* $K_1 > K_2$. This is because, more energy is required to separate a positive hydrogen ion from the charged anion than from the uncharged species. Dicarboxylic acids are stronger than monocarboxylic acids because one —COOH group (electron-withdrawing group) enhances the acidity of the other. This also explains that the K_1 value of dicarboxylic acids decreases with the increase in number of intervening CH_2 group(s). Thus the acidic order is

$$\underset{\text{Oxalic acid}}{HOOCCOOH} > \underset{\text{Malonic acid}}{HOOCCH_2COOH} > \underset{\text{Succinic acid}}{HOOCCH_2CH_2COOH}$$

2. **Effect of heating.** Different dicarboxylic acids on heating give different products depending upon the relative position of the two carboxyl groups.

(*i*) Dicarboxylic acids having two carboxyl groups on the same carbon atom eliminate a molecule of carbon dioxide (decarboxylation) on heating to form monocarboxylic acids.

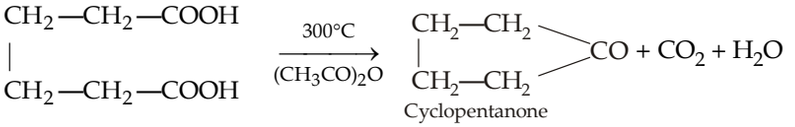
$$\underset{\text{Oxalic acid}}{COOH\text{—}COOH} \xrightarrow{\text{heat}} \underset{\text{Formic acid}}{HCOOH} + CO_2\ ;\ \underset{\text{Malonic acid}}{HOOCCH_2COOH} \xrightarrow{\text{heat}} \underset{\text{Acetic acid}}{CH_3COOH} + CO_2$$

(*ii*) Dicarboxylic acids in which the two carboxylic groups are separated by two or three carbon atoms, *i.e.*, 1, 4- and 1, 5-dicarboxylic acids lose a molecule of water on heating or on distillation with acetic anhydride to form cyclic anhydrides. The reaction is known as **cyclodehydration.** For example,

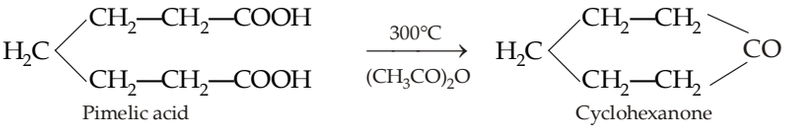
$$\underset{\text{Succinic acid}}{CH_2COOH\text{—}CH_2COOH} \xrightarrow[(-H_2O)]{\text{heat}} \underset{\text{Succinic anhydride}}{CH_2(CO)_2O}\ ;\ \underset{\text{Glutaric acid}}{CH_2(CH_2COOH)_2} \xrightarrow[(-H_2O)]{\text{heat}} \underset{\text{Glutaric anhydride}}{CH_2(CH_2CO)_2O}$$

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(*iii*) Dicarboxylic acids in which the two carboxyl groups are separated by four or more carbon atoms (*i.e.* 1, 6- and 1, 7-dicarboxylic acids) when distilled with acetic anhydride form cyclic ketones. For example,



Cyclopentanone

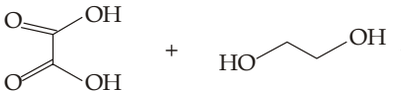


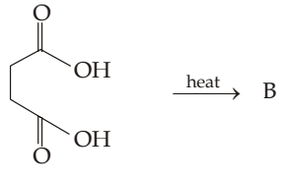
Pimelic acid Cyclohexanone

The effect of heating on various dicarboxylic acids can be summarised in the form of **Blanc rule** according to which *dicarboxylic acids having two carboxylic groups on the same carbon atom when heated form monocarboxylic acids ; 1, 4- and 1, 5-dicarboxylic acids, on heating or on distillation with acetic anhydride form cyclic anhydrides while 1, 6- and 1, 7-dicarboxylic acids on distillation with acetic anhydride form cyclic ketones.*

TEST YOUR UNDERSTANDING - 17.10

1. Give the structure of the compound formed in each of the following reaction :

(*a*) 

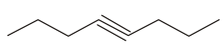
(*b*) 

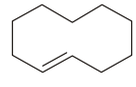
2. (*a*) Give the products obtained on heating the following with conc. H_2SO_4.

(*i*) CH_3COOH (*ii*) HCOOH (*iii*) Ph_3CCOOH (*iv*) $C_6H_5COCOOH$

(*b*) Compare the reactivities of CH_3COOH and Cl_3CCOOH on heating with a base like soda lime, a mixture of NaOH and CaO.

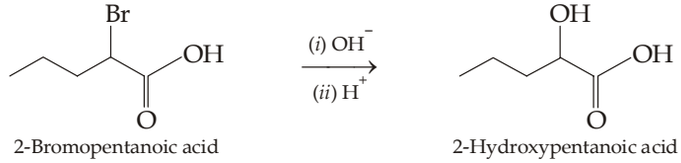
(*c*) Give the product obtained by the oxidative cleavage of the following compounds with conc. $KMnO_4$.

(*i*) 

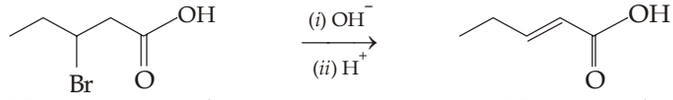
(*ii*) 

17.7 Distinction Between α-, β-, and γ-Substituted Carboxylic Acids

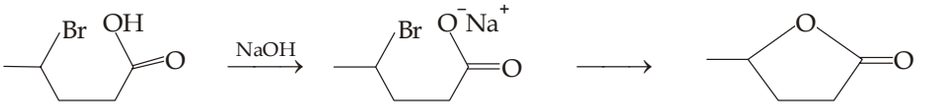
1. The three halogen substituted acids (α-, β- and γ-) give different compounds with aqueous base (NaOH).



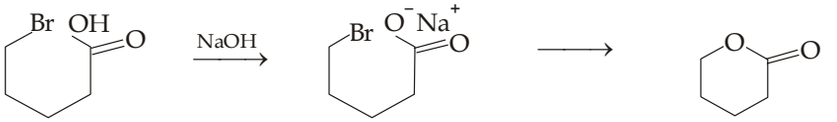
2-Bromopentanoic acid 2-Hydroxypentanoic acid



3-Bromopentanoic acid 2-Pentenoic acid (conjugated system)



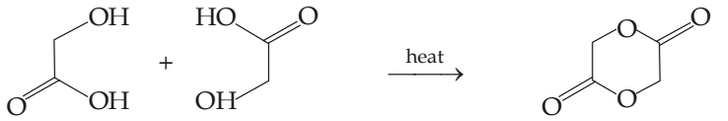
4-Bromopentanoic acid — 3-Methyl-γ- butyrolactone



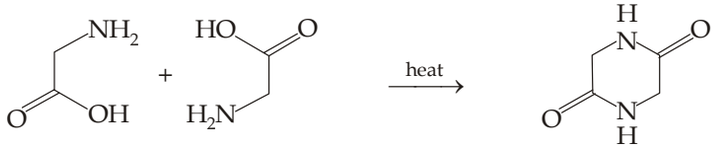
5-Bromopentanoic acid — δ-Valerolactone

2. The three (α-, β-, and γ-) hydroxy and amino acids behave differently, on heating. Hydroxy and amino acids behave in similar ways.

(*a*)

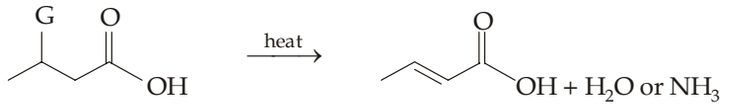


(Two molecules of α-hydroxy acids) — Glycollide



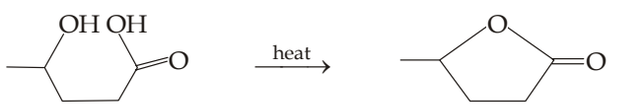
(Two molecules of α-amino acids) — Diketopiperazine

(*b*)

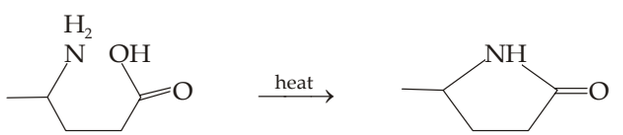


Two molecules of β-hydroxy acids or β-amino acids (G = OH or NH_2)

(*c*)

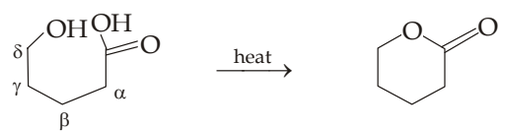


γ-Hydroxy acid — A γ-lactone

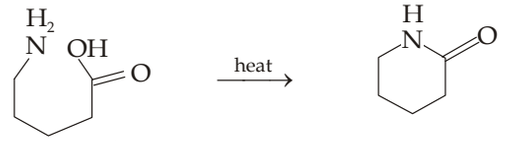


γ-Amino acid — A γ-lactam

(*d*)



δ-Hydroxy acid — A δ-lactone



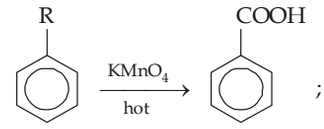
δ-Amino acid — A δ-lactam

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17.8 Additional Chemistry of Aromatic Carboxylic Acids

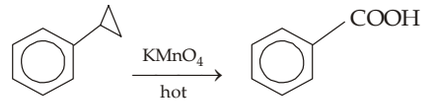
Preparation. Although the methods used for aliphatic carboxylic acis can be applied for preparing aromatic carboxylic acids, the most important one is due to oxidation of side chain.

Oxidation of the side chain. Generally, benzene ring is very resistant to oxidation and hence benzene homologues are oxidised in the side chain to form a carboxylic acid, the side chain is always oxidised to —COOH group, ignoring its length.

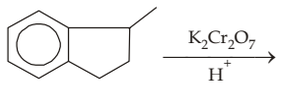


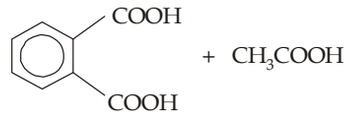
(R = —CH_3, —CH_2CH_3, -*n*-C_3H_7)

;

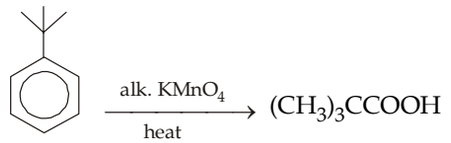


Cyclopropylbenzene

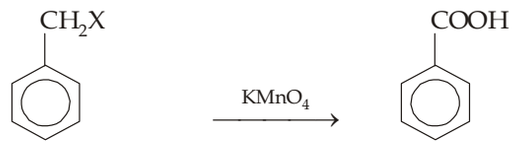




(*i*) If the side chain is a *tert*-alkyl group, oxidation is difficult, but on vigorous oxidaton benzene ring in oxidised.

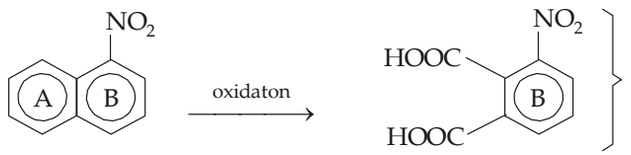


(*ii*) Side chain, like —CH_2Cl, —CH_2OH, and —CH_2NH_2, attached to benzene ring is also oxidised to —COOH group.

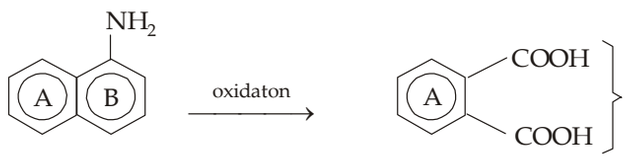


(X = —Cl, —OH, —NH_2)

(*iii*) Presence of electron withdrawing group like —NO_2 makes the ring resistant to oxidation, while presence of electron-repelling group lik —NH_2 makes the benzene ring susceptible to oxidation.

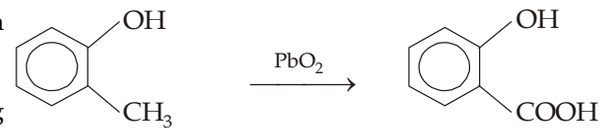


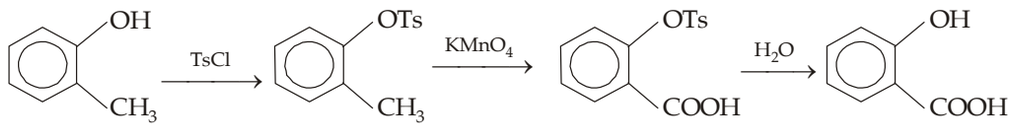
Ring B containing —NO_2 group is retained



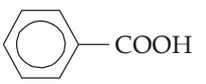
Ring B containing —NH_2 group is oxidised

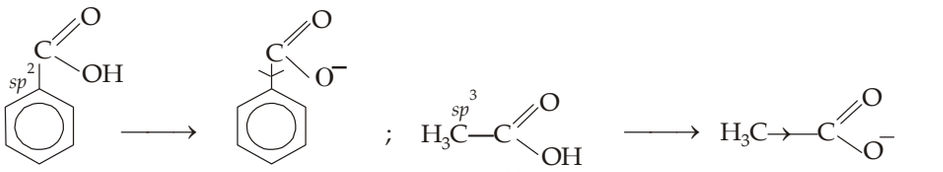
However, oxidation of alkyl group to —COOH group in compounds containing alkyl group as well as electron-repelling group can be achieved either by carrying oxidation with a mild oxidising agent (like PbO_2) or by protecting the electron-releasing group first with tosyl chloride followed by oxidation.





Acidity of aromatic acids. Benzoic acid itself is somewhat stronger acid than acetic acid. Its carboxyl group is attached to an sp^2 hybridized carbon and ionizes to a greater extent than one that is attached to an sp^3 hybridized carbon (recall that carbon becomes more electron-withdrawing as its *s* character increases).

	CH_3COOH	$CH_2 = CHCOOH$	
	Acetic acid	Acrylic acid	Benzoic acid
K_a	1.8×10^{-5}	5.5×10^{-5}	6.3×10^{-5}
pK_a	4.8	4.3	4.2



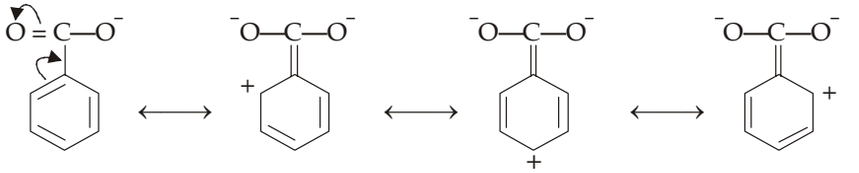
—COOH group attached on sp^2 C, hence more electronegative

–ve charge on O dispersed (hence more stable)

—COOH group on sp^3 C, hence less electronegative

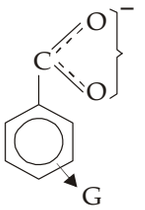
–ve charge on O intensified (hence less stable)

Moreover, benzoate anion is more stable, due to presence of benzene ring, than acetate ion.

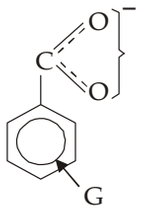


Resonance in benzoate anion due to benzene ring

Like aliphatic acids, acidity of aromatic acids is affected by substituents : electron-releasing groups like —CH_3, —OH and —NH_2 make benzoic acid weaker, while electron-withdrawing groups like —Cl, —NO_2, —CN, etc. make benzoic acid stronger.



G (—NO_2, —Cl, —CN) withdraws electrons, disperses –ve charge on O, stabilises the anion, hence strengthens acidity



G (—CH_3, —OH, —NH_2, —OCH_3) releases electrons, intensifies –ve charge on O, destabilises the anion, hence weakens acidity

Following table lists the ionization constants (acidity) of some substituted benzoic acids,

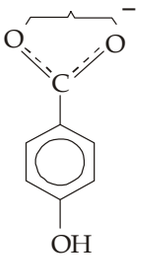
Acidity of some substituted benzoic acids, XC_6H_4COOH

$K_a(pK_a)$ for different positions of the substituent X

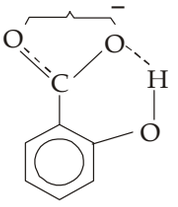
Value of X	*ortho*	*meta*	*para*
H	6.3×10^{-5} (4.2)	6.3×10^{-5} (4.2)	6.3×10^{-5} (4.2)
CH_3	1.2×10^{-4} (3.9)	5.3×10^{-5} (4.3)	4.2×10^{-5} (4.4)
F	5.4×10^{-4} (3.3)	1.4×10^{-4} (3.9)	7.2×10^{-5} (4.1)
Cl	1.2×10^{-3} (2.9)	1.5×10^{-4} (3.8)	1.0×10^{-4} (4.0)
Br	1.4×10^{-3} (2.8)	1.5×10^{-4} (3.8)	1.1×10^{-4} (4.0)
I	1.4×10^{-3} (2.9)	1.4×10^{-4} (3.9)	9.2×10^{-5} (4.0)
CH_3O	8.1×10^{-5} (4.1)	8.2×10^{-5} (4.1)	3.4×10^{-5} (4.5)
O_2N	6.7×10^{-3} (2.2)	3.2×10^{-4} (3.5)	3.8×10^{-4} (3.4)

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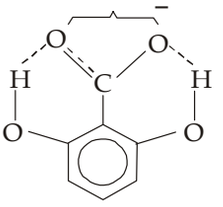
(*a*) Nearly all *ortho* substituents, whether electron-withdrawing or electron-releasing, exert an acid-strengthening effect, and the effect is unsually large. This *ortho* effect is partly due to closeness of the groups involved. Sometimes H—bonding also plays a role, *e.g.*, *o*-hydroxybenzoic acid (salicylic acid) is far stronger than the corresponding *m*- and *p*- isomers. The carboxylate ion of the *o*-isomer is stabilised by intramolecular H-bonding.



p-Hydroxybenzoate ion, I



o-Hydroxybenzoate ion, II (more stable than I)



2, 6-Dihydroxybenzoate ion, III (more stable than II)

(*b*) The —OH and —OCH_3 groups display both kinds of effect. When present in *meta* position, these groups produce electron-withdrawing acid-strengthening effect. When present in *para* position, these groups produce electron-releasing acid-weakneing resonance effect.

TEST YOUR UNDERSTANDING - 17.11

1. Discuss the resonance of the *p*-NO_2 group in *p*-$NO_2C_6H_4COO^-$.

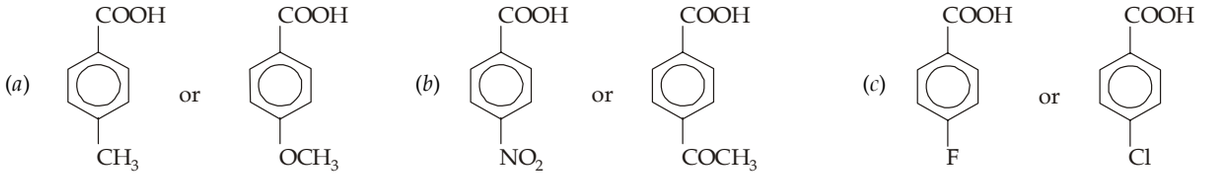
2. Account for the following

(*a*) *p*-Nitrobenzoic acid is more acidic than its *meta* isomer, while *p*-chlorobenzoic acid is less acidic than its *meta* isomer

(*b*) *p*-Toluic acid is weaker than *m*-toluic acid.

(*c*) *p*-Hydroxybenzoic acid is weaker than benzoic acid while the corresponding *m* —OH acid is stronger than benzoic acid.

3. Which of the two carboxylic acids is more stronger ?



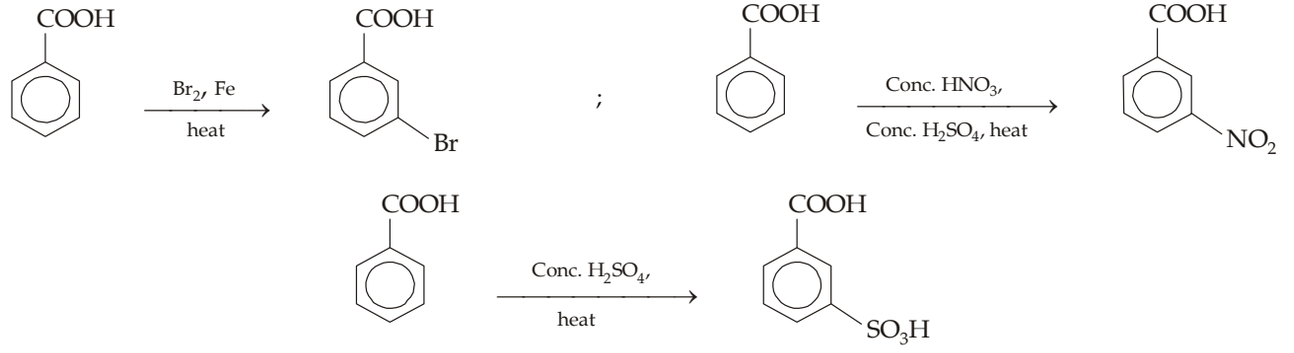
4. Arrange the following carboxylic acids in decreasing order of acidity.

(*a*) Benzoic acid, *p*-chlorobenzoic acid, 2, 4-dichlorobenzoic acid

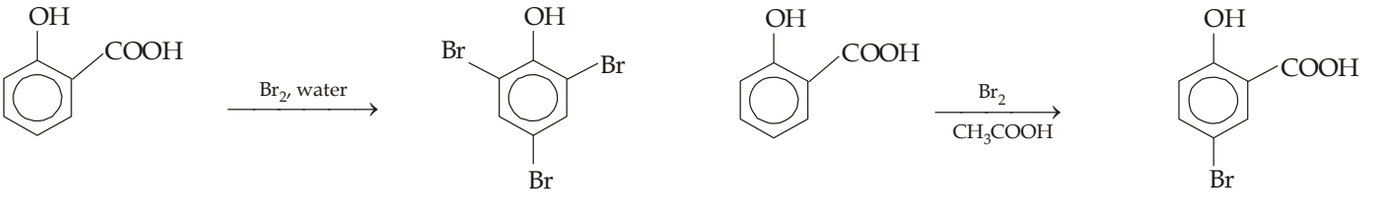
(*b*) Benzoic acid, *p*-toluic acid, *p*-nitrobenzoic acid

(*c*) *p*-Nitrobenzoic acid, *p*-nitrophenylacetic acid, β–(*p*-nitrophenyl)propanoic acid

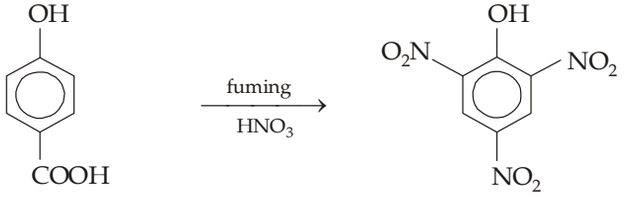
Substitution in benzene nucleus. As described earlier, —COOH group is *m*-directing and deactivating group, so substitution takes palce in *meta*- position and require stronger conditions.



When some activating group *e.g.*, —OH is present along with —COOH, substitution occurs w.r.t. —OH and —COOH group is replaced by the new group. For example,

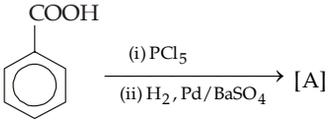


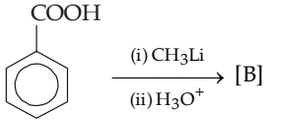
In the second example, brominating agent is mild, hence only monobromo product will be formed. Further, bromination will be favoured at *para* position because of steric factors.

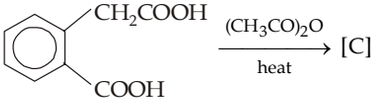


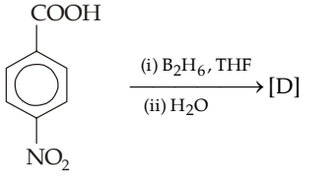
TEST YOUR UNDERSTANDING - 17.12

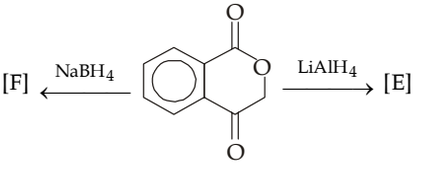
1. Identify the bracketed compounds in the following reactions.

(*a*) 

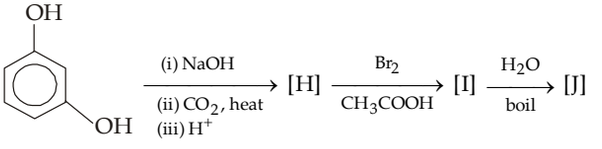
(*b*) 

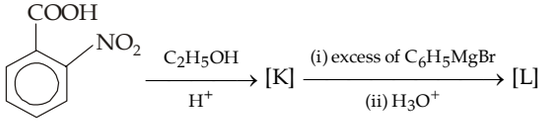
(*c*) 

(*d*) 

(*e*) 

(*f*) 

(*g*) 

(*h*) 

17.9 Analysis of Carboxylic Acids

(*i*) Carboxylic acids are recognized through their acidity. They dissolve in aqueous NaOH and in aqueous $NaHCO_3$; in the latter case bubbles (effervescences) of CO_2 are evolved.

NOTE.

(*a*) Phenols, with certain exceptions, are considerably weaker than carboxylic acids. Thus although they dissolve in aq. NaOH (a strong base), but not in aq. sodium bicarbonate (a weak base).

(*b*) Sulphonic acids are even more acidic than carboxylic acids, but they can be differentiated by presence of sulphur.

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(*ii*) Determination of **neutralization equivalent (NE)**, *the equivalent weight of the acid as determined by titration with standard base*, is one of the characteristics of a carboxylic acid. For this, a known weight of the acid is dissolved in water or aqueous alcohol. The volume of a standard base required to neutralize the solution is measured by titration using phenolphthalein as an indicator. Suppose *x* g of an unknown acid requires V mL. of 1M NaOH for neutralisation. It means

Since 1000 mL of the base contains 1 equivalent of the base

V mL of the base contains $\frac{1\,M}{1000} \times V$ equivalent of base.

Since No. of eq. of base required = No. of eq. of acid present = $\frac{1\,M \times V}{1000}$

$\frac{1\,M \times V}{1000}$ eq. of acid = *x g* (Wt. of acid present)

$\therefore$ 1 eq. of acid = $\frac{x \times 1000}{1\,M \times V}$ g of acid

Thus by knowing the wt. of acid, and volume of standard base (known molarity), neturalization equivalent of the acid can be ascertained.

Detection of a metal salt of a carboxylic acid

(*i*) On strongly heating, it leaves a residue;

(*ii*) it decomposes at a high temperature instead of melting, and

(*iii*) it is converted into a carboxylic acid upon acidification.

TEST YOUR UNDERSTANDING - 17.13

1. (*a*) What is the relation between NE and the number of acidic hydrogens per molecule of acid?

(*b*) What is the neutralization equivalent of terephthalic acid, *p*-$HOOCC_6H_4COOH$, and melittic acid, $C_6(COOH)_6$? How many moles of a base (NaOH) are needed to neutralize one mole of each of the two acids ?

2. Differentiate among 2-chloropropanoic acid ($CH_3CHClCOOH$), pyruvic acid ($CH_3COCOOH$), acrylic acid ($CH_2 = CHCOOH$) and propanoic acid (CH_3CH_2COOH).

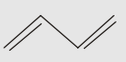
3. Give a chemical reaction with the help of which we can distinguish among following three carboxylic acids.

n-Pentanoic acid, 2-methylbutanoic acid, and 2, 2-dimethylpropanoic acid.

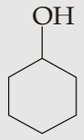
17.10 ILLUSTRATIVE EXAMPLES

Example 1 :

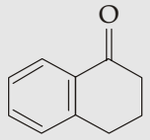
Identify the bracketed compounds in each of the following reactions.

(i)  $\xrightarrow{1\text{ mole HBr}}$ [A] $\xrightarrow[(ii)\ CO_2,\ H_3O^+]{(i)\ Mg}$ [B] $\xrightarrow{heat}$ [C]

(ii) $CH_2BrCOOC_2H_5 \xrightarrow{Zn}$ [A] $\xrightarrow[(ii)\ H_2O]{(i)\ acetone}$ [B] $\xrightarrow[(ii)\ heat]{(i)\ H_3O^+}$ [C]

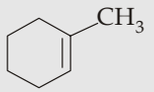
(iii)  $\xrightarrow[H^+]{K_2Cr_2O_7}$ [A] $\xrightarrow{C_6H_5MgBr}$ [B] $\xrightarrow[heat]{CrO_3, CH_3COOH}$ [C]

(iv) Cyclopentanol $\xrightarrow{HNO_3}$ [A] $\xrightarrow{HCN/CN^-}$ [B] $\xrightarrow[H_2SO_4]{conc.}$ [C] $\xrightarrow{H_3O^+}$ [D] $\xrightarrow{LiAlH_4}$ [E]

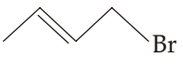
(v)  $\xrightarrow[(ii)\ H^+]{(i)\ C_6H_5MgBr}$ [A] $\xrightarrow{S,\ heat}$ [B]

(vi) [E] $\xleftarrow[(ii)\ H^+]{(i)\ NaOH}$ [D] $\xleftarrow[excess]{P, Br_2}$ CH_3COOH $\xrightarrow{SOCl_2}$ [A] $\xrightarrow{[B]}$ CH_3CHO $\xrightarrow[\Delta]{dil.\ NaOH}$ [C]

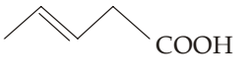
(vii) Benzyl alchol $\xrightarrow[H_2SO_4]{conc.}$ A $\xrightarrow{NBS}$ B $\xrightarrow{KCN}$ C $\xrightarrow{H_3O^+}$ D

(viii)  $\xrightarrow{O_3/H_2O}$ A $\xrightarrow[(ii)\ H^+]{(i)\ HCN}$ B $\xrightarrow{heat}$ C

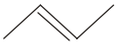
Solution :

(*i*) 

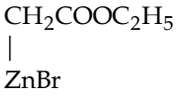
[A] obtained by 1, 4- addition



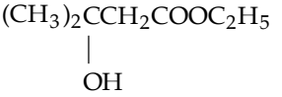
[B]



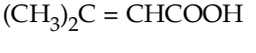
[C]

(*ii*) 

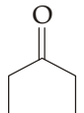
[A]



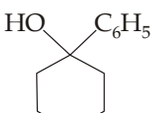
[B]



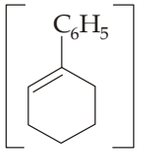
[C]

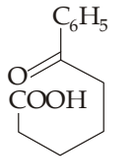
(*iii*) 

[A]



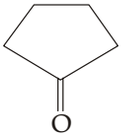
A cyclanol [B]





6-Oxo-6-phenylhexanoic acid [C]

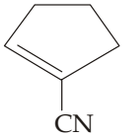
Cyclanols undergo acid catalyzed oxidative cleavage, probably *via* the alkene.

(*iv*) 

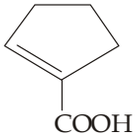
[A]



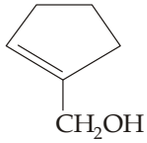
[B]



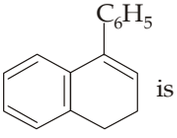
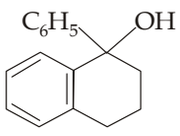
[C]



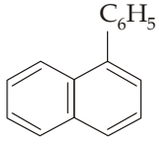
[D]



[E]

(*v*)  is formed via 

[A]



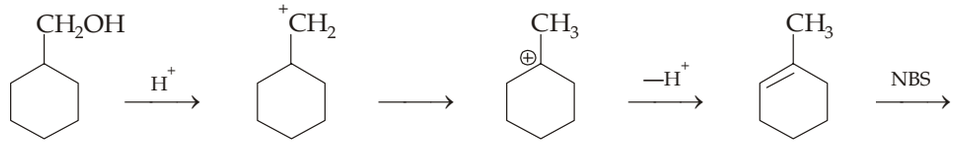
[B]

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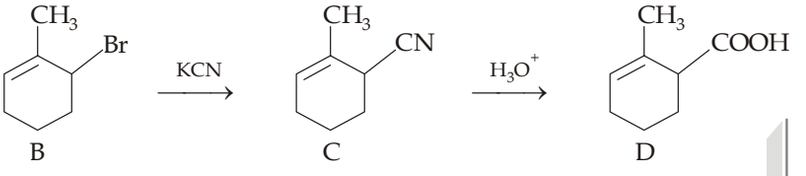
(*vi*) CH_3COCl, $H_2/Pd/BaSO_4$, $CH_3CH = CHCHO$, Br_3CCOOH, HOOC.COOH

A B C D E

(*vii*)

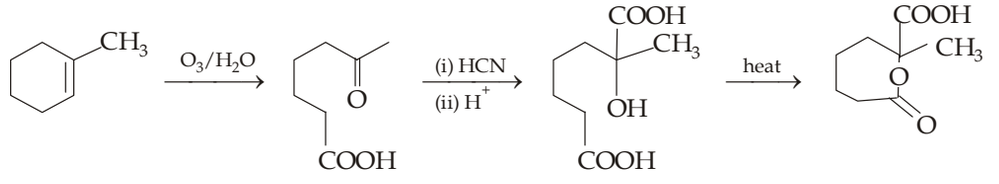


1° Carbocation 3°Carbocation A



B C D

(*viii*)



(A) (B) (C)

Example 2 :

Establish the structure of [X] on the basis of following reactions/facts.

$$[X] \xrightarrow{HBr} C_9H_9O_2Br \xrightarrow{KOH\ alc.} [Y] \xrightarrow{H_2/Ni} [Z]$$

(i) Compound X gives a positive test with CrO_3 in acid.

(ii) Compound Z can be obtained by the carbonation reaction of $C_6H_5CH(CH_3)$ MgBr. Is there any isomer of X ?

Solution :

Structure of Z can be ascertained by its synthesis from carbonation reaction.

$$C_6H_5CH(CH_3)\,MgBr \xrightarrow[(ii)\ H_3O^+]{(i)\ CO_2} \underset{[Z]}{C_6H_5CH(CH_3)COOH}$$

Thus going backward from Z, structure of X can be ascertained

$$\underset{Z}{C_6H_5\overset{CH_3}{\overset{|}{C}}HCOOH} \xleftarrow{H_2/Ni} \underset{Y}{C_6H_5\overset{CH_2}{\overset{||}{C}}COOH} \xleftarrow{alc.KOH} \underset{(C_9H_9O_2Br)}{C_6H_5\overset{CH_2Br}{\overset{|}{C}}HCOOH} \xleftarrow{HBr} \underset{X}{C_6H_5\overset{CH_2OH}{\overset{|}{C}}HCOOH}$$

Structure of X is confirmed by positive response with CrO_3 in acid.

Isomer of X is $C_6H_5\overset{OH}{\overset{|}{C}}(CH_3)COOH$; but it, being a 3°alcohol, is inert to CrO_3.

Example 3 :

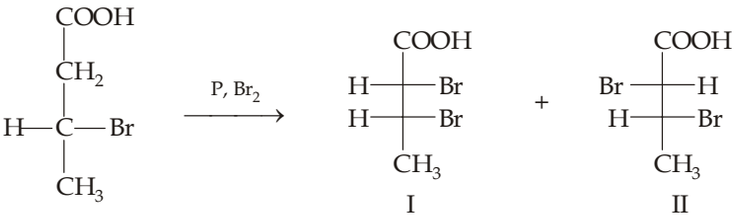
Give stereochemical formulas of compounds A to G.

(a) *rac*-β-Bromobutyric acid $\xrightarrow{\text{1 mole P, } Br_2}$ A + B

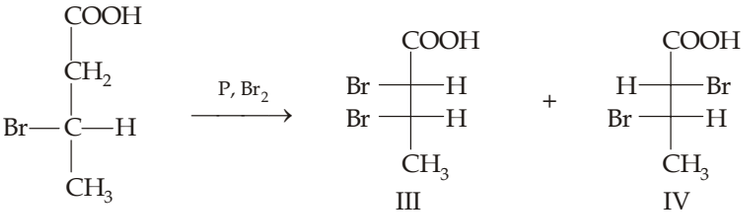
(b) Maleic acid + Performic acid $\longrightarrow$ C + D

(c)  $\xrightarrow[tert\text{–BuOK}]{CHBr_3}$ E $\xrightarrow{KMnO_4}$ F $\xrightarrow{H_2/Ni}$ G.

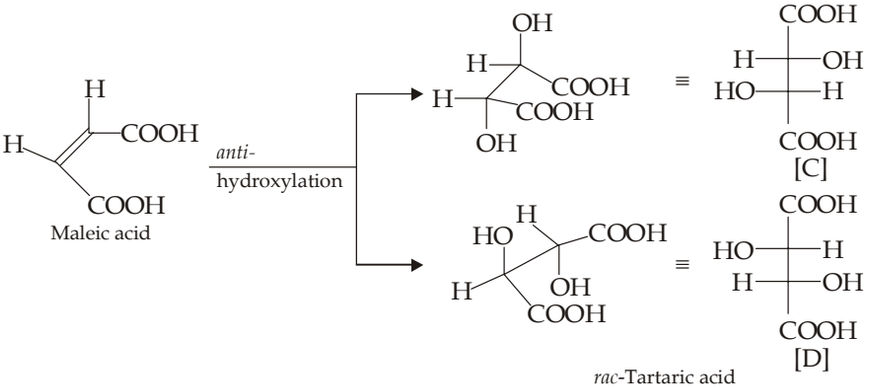
Solution :

(*a*) 

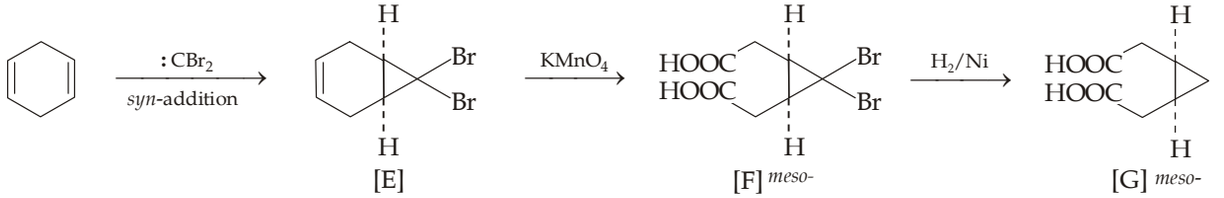
Or



Note that I and III are enantiomers, hence they represent one racemic mixture ; similarly II and IV are enantiomers; and respresent a different racemic mixture. The two racemic mixtures are thus A and B.

(*b*) 

(*c*) $CHBr_3 \xrightarrow{tert\text{-BuOK}} :CBr_2 + HBr$



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Example 4 :

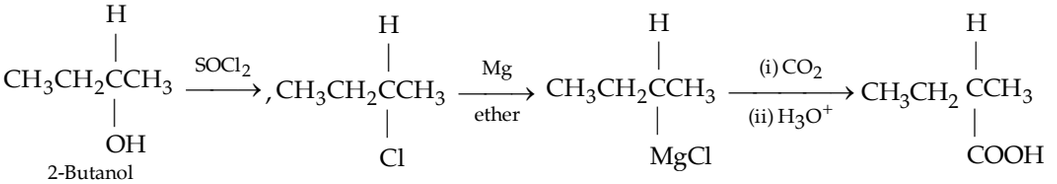
Give essential steps involved in the following conversions :

(i) Ethanol to glycine
(ii) 2-Butanol to 2-methylbutanoic acid.
(iii) 2-Chlorobutanoic acid to 3-chlorobutanoic acid.
(iv) 2-Propanol, $(CH_3)_2CHOH$ to 3-hydroxybutyric acid.
(v) Benzene to adipic acid, $HOOC.(CH_2)_4 . COOH$.
(vi) Toluene to 2-methyl-5-chlorobenzoic acid.
(vii) Tetrahydrofuran to adipic acid.
(viii) Tetrahydrofuran to succinic acid.
(ix) Cyclopentanol to 2-oxocyclopentanecarboxylic acid.
(x) Benzene to 6-oxo-6-phenylhexanoic acid.

Solution :

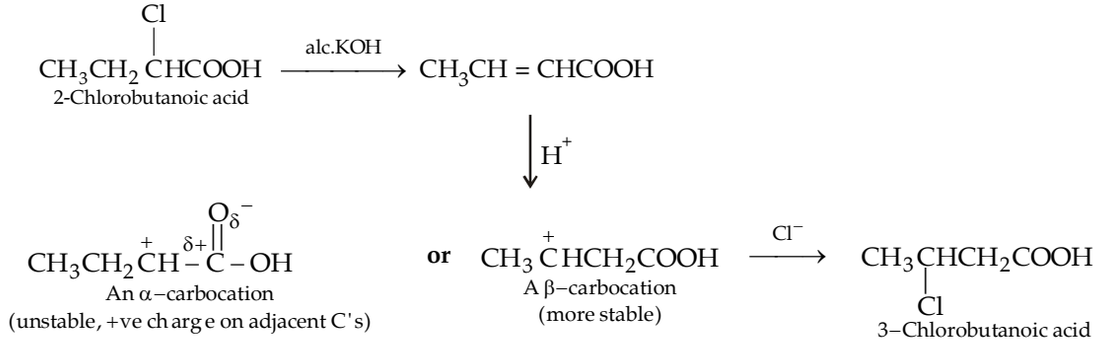
(*i*) $CH_3CH_2OH \xrightarrow{MnO_4^-, H^+} CH_3COOH \xrightarrow{Cl_2/P} ClCH_2COOH \xrightarrow{NH_3} H_2NCH_2COOH$

(*ii*) The conversion involves the conversion of —OH to —COOH, which can be easily accomplished through Grignard reagent.

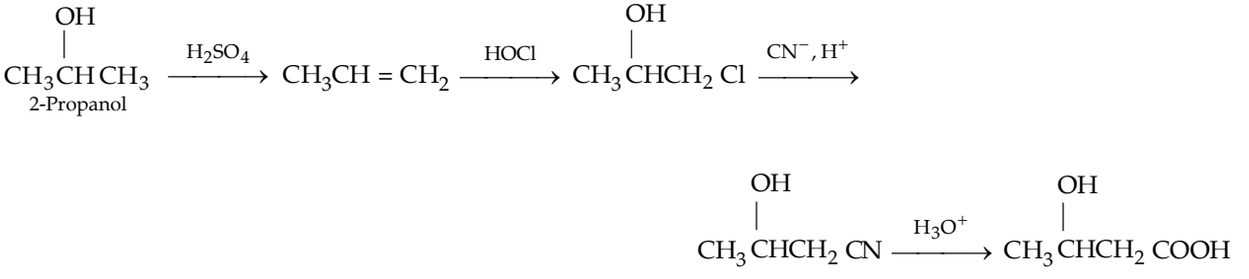


Nitrile route should not be used because a 2° halide may undergo extensive dehydrohalogenation.

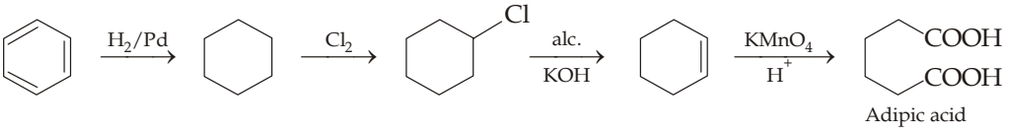
(*iii*)

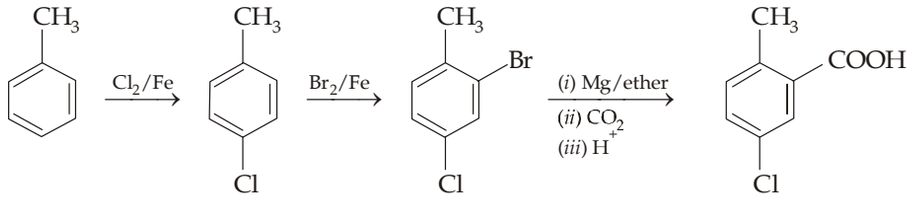


(*iv*)

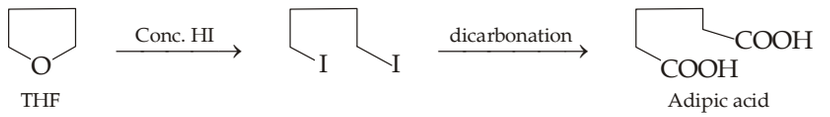


(*v*)

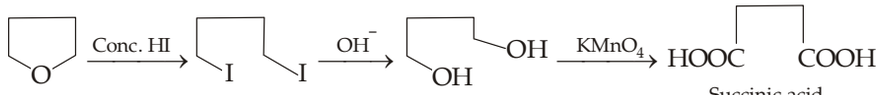


(*vi*) 

Here it is advisable to introduce —COOH grop through carbonation route, because route involving the oxidation of the alkyl group gives poor yields, until a strong electron-withdrawing group like —NO_2 is present.

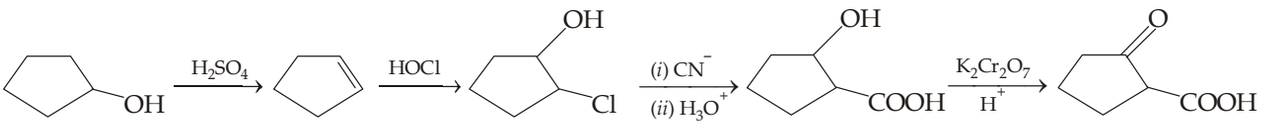
(*vii*) 

THF Adipic acid

(*viii*) 

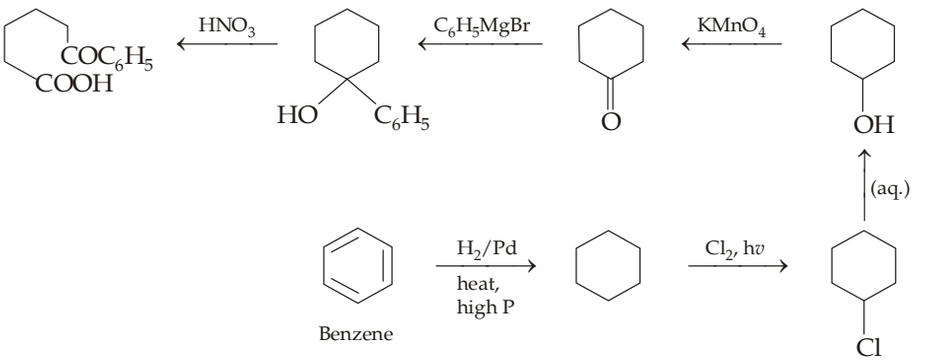
THF Succinic acid

(*ix*) The required product has a keto and a carboxylic group for which CHOH and CN should be the respective precursor.



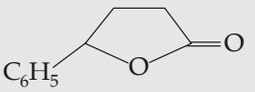
2-Oxocyclopentane carboxylic acid

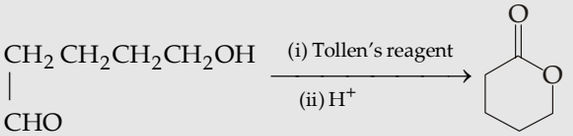
(*x*) First write down the structure of the product and then think of its precursor, *i.e.* proceed backward. It will be very easy to write reactions.

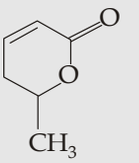


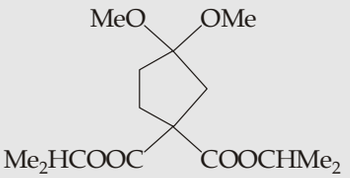
Example 5 :

Give necessary steps (reagents) to explain the following reactions :

(a) $C_6H_5CH = CHCH_2COOH \xrightarrow{H^+}$ 

(b) 

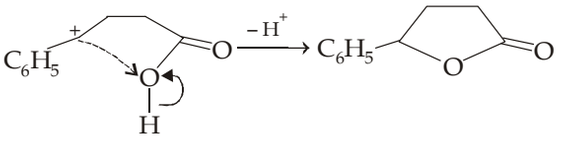
(c) $CH_3CH(OH)CH_2C \equiv CCOOH \longrightarrow$ 

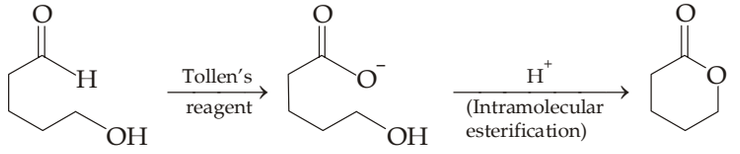
(d) 

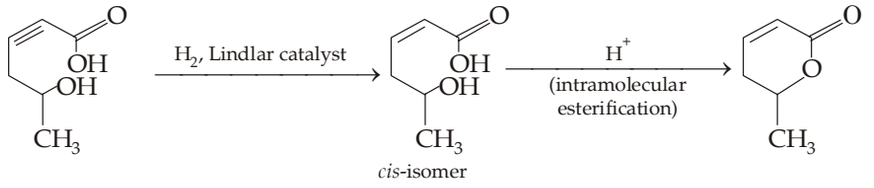
refluxed with HCl → A keto acid

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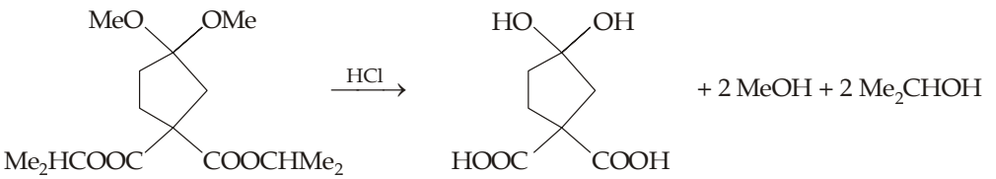
Solution :

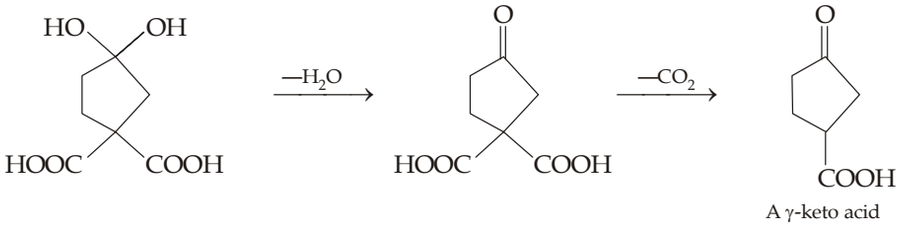
(*a*) $C_6H_5CH{=}CHCH_2COOH \xrightarrow{H^+} C_6H_5\overset{+}{C}HCH_2CH_2COOH \equiv$ (Benzyl carbocation)  $\xrightarrow{-H^+} C_6H_5$

(*b*) 

(*c*) 

(*d*) The given compound has two types of functional groups (acetal and ester) both of which are hydrolysed by HCl.



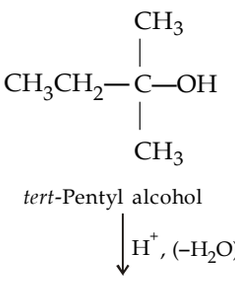


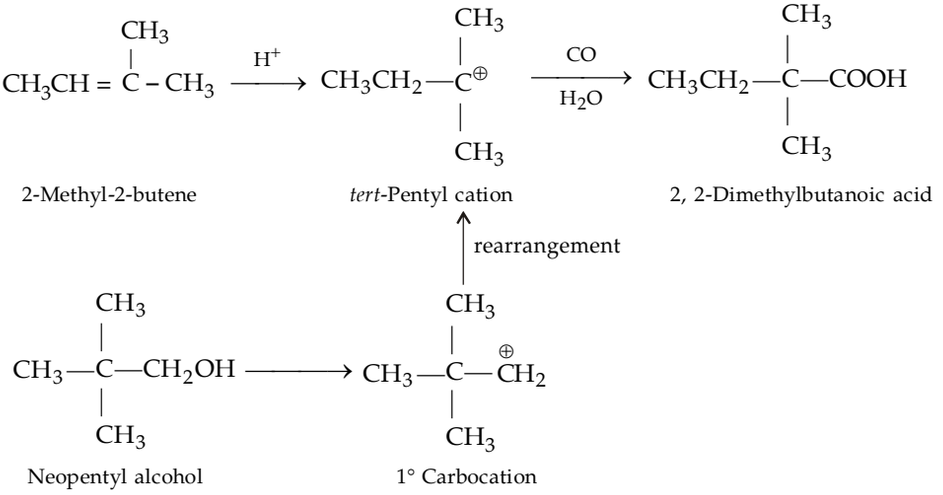
Example 6 :

A sulphuric acid solution of each of the compounds namely tert -pentyl alcohol, neopentyl alcohol and 2-methyl-2-butene when treated with carbon monoxide gives 2, 2-dimethylbutanoic acid. Explain with mechanism.

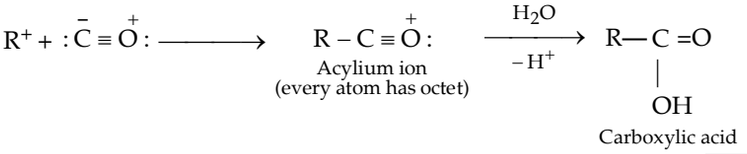
Solution :

Each of the three compound gives *tert*-pentyl cation in presence of sulphuric acid.





Mechanism of conversion of R^+ to RCOOH by means of CO



Example 7 :

Outline a typical method for resolving *rac*-(R,S)—RCOOH.

Solution :

Racemic mixture of carboxylic acids are best separated by using optically active (R)- or (S)- naturally occurring base like quinine.

$$\text{(R, S)-RCOOH + (R)-base} \longrightarrow \underset{\text{Insoluble}}{\text{[(R)-RCOO}^-\text{ (R)-base H}^+\text{]}} + \underset{\text{Diastereomeric salts}}{\text{[(S)-RCOO}^-\text{(R)-base H}^+\text{]}}$$

Due to difference in solubilities, [A] and [B] are separated by fractional crystallization and then hydrolysed to give back the corresponding acid and the (R)-base.

$$\text{A} \xrightarrow{HX} \text{(R)-RCOOH + (R)-base H}^+\text{X}^- \qquad \text{B} \xrightarrow{HX} \text{(S)-RCOOH + (R)-base H}^+\text{X}^-$$

Example 8 :

Write down the structures of the various isomers of the formula $C_4H_4O_4$, corresponding to following reaction.

(a) A dibasic acid which on heating gives propenoic acid.

(b) An unsaturated dibasic acid which gives a meso compound on reaction with alkaline $KMnO_4$.

(c) An unsaturated dibasic acid which gives a racemic mixture on reaction with alkaline $KMnO_4$.

(d) A cyclic ester that on hydrolysis gives glycol and oxalic acid.

Solution :

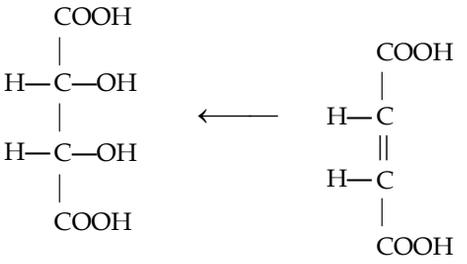
Write down the structure of the product and proceed backward keeping in mind the type of reaction that can give the desired product.

(*a*) $CH_2 = CHCOOH \xleftarrow{-CO_2} CH_2 = C(COOH)_2$

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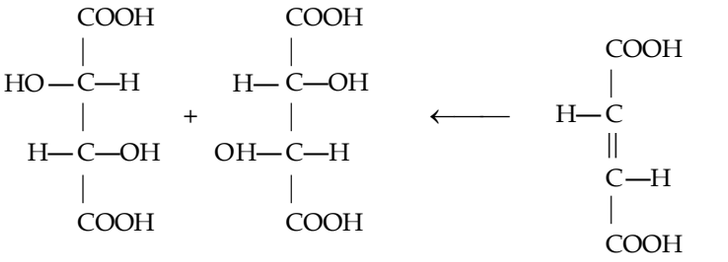
(*b*) Recall that alk. $KMnO_4$ is a hydroxylating reagent and causes hydroxylation in *syn*- manner. Thus *meso* product is obtained from *cis*-isomer, while *rac*-from *trans*-.

(*b*)



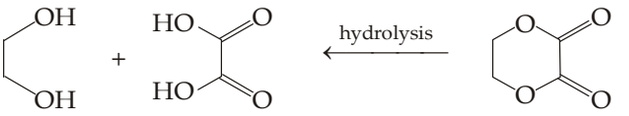
meso- Maleic acid *(cis)*

(*c*)



rac- Fumaric acid *(trans)*

(*d*)



Glycol Oxalic acid Glycol oxalate

Example 9 :

There are four isomeric hydrocarbons corresponding to molecular formula C_8H_{14}. On ozonolysis, different isomers give different products, assign the structure to each.

(a) Isomer A gives isobutyric acid.

(b) Isomer B gives α, α′- dimethyladipic acid.

(c) Isomer C gives β, β- dimethyladipic acid.

(d) Isomer D gives diketone giving iodoform test at both ends of the molecule.

Assign structure to A, B, C and D.

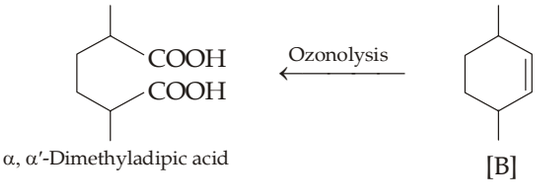
Solution :

Molecular formula C_8H_{14} suggests that the compounds have 2° of unsaturation ; which means they may contain (*i*) a triple bond, or (*ii*) two double bonds, or (*iii*) a double bond and a ring. Nature of unsaturation and structure of various isomers can be ascertained by their ozonolysis products :

(*a*) $(CH_3)_2CHCOOH \xleftarrow{\text{Ozonolysis}} (CH_3)_2CHC \equiv CCH(CH_3)_2$

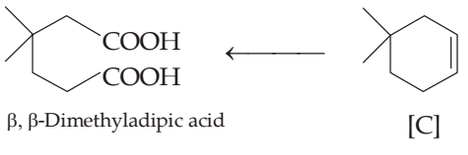
Isobutyric acid [A]

(*b*)



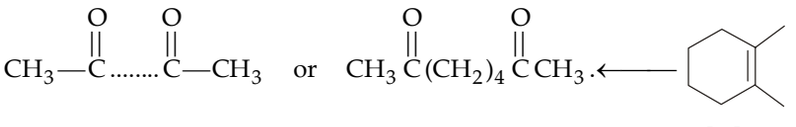
α, α′-Dimethyladipic acid [B]

(*c*)



β, β-Dimethyladipic acid [C]

(*d*)



[D]

Example 10 :

Assign structure to each isomer of the formula $C_4H_8O_2$ corresponding to the following reaction.

(a) The isomer (A) that can be hydrolysed to form ethanoic acid and alcohol.

(b) The isomer (B) that can reduce Tollen's reagent due to —CHO group and also responds haloform test.

(c) The isomer (C) that can reduce Tollen's reagent but does not respond haloform best.

(d) The isomer (D) that gives haloform test due to —$COCH_3$ group and also reduces Tollen's reagent

(e) The isomer (E) that gives haloform test due to —$COCH_3$ group and also gives turbidity with Lucas reagent.

Solution :

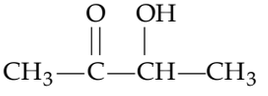
(*a*) $CH_3COOH + C_2H_5OH \xleftarrow{\text{hydrolysis}} CH_3COOC_2H_5$ (A)

(*b*) Molecular formula $C_4H_8O_2$ indicates that all isomers, including (B) has 1° of unsaturation which is present in the form of —CHO group. Hence the positive haloform reaction must be due to CH_3CHOH– grouping (presence of CH_3CO— grouping is discarded due to fact that the compound has only 1° of unsaturation which is in the form of —CHO group). Thus the isomer B should be $CH_3CH(OH)CH_2CHO$.

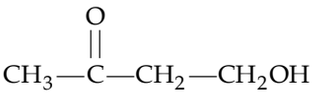
(*c*) $HOCH_2CH_2CH_2CHO$ (C)

(*d*) Since the compound D has —$COCH_3$, it can't have —CHO group (note that 1° of unsaturation is present in $C_4H_8O_2$). Hence the positive reaction with Tollen's reagent is due to α-hydroxy ketone. Thus D should be as shown below.

(*e*) Since the compound gives turbidity with Lucas reagent, it must have 1° aloholic group.



(D)



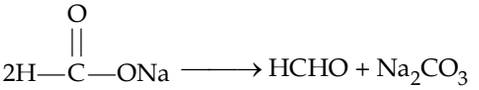
(E)

Example 11 :

Sodium salt of a carboxylic acid on ignition gives a white residue. The residue is soluble in water, reacts with hydrochloric acid with the evolution of bubbles, and turns moist litmus blue. Give the probable chemical structure of the residue and explain its formation.

Solution :

The residue should be Na_2CO_3



Example 12 :

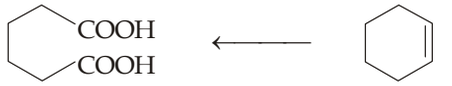
A hydrocarbon of the molecular formula C_6H_{10} has two isomers ; X and Y. On oxidation X gives butanoic acid and ethanoic acid, while Y gives 1, 6-hexanedioic acid Assign structure to X and Y.

Solution :

Molecular formula C_6H_{10} indicates that it has two degree of unsaturation which may be in the form of a triple bond or one double bond and one ring. Proceed backward from the oxidation product(s) in each case.

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$$n\text{-}C_3H_7COOH + CH_3COOH \xleftarrow{\text{oxidation}} \underset{[X]}{n\text{-}C_3H_7C \equiv CCH_3}$$



1, 6-Hexanedioic acid — Cyclohexene [Y]

Example 13 :

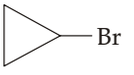
(i) An alkyl halide A of the formula C_3H_5Br reacts with Mg in presence of ether of form Grignard reagent which, on reaction with dry ice followed by acidification, is converted into a carboxylic acid B.

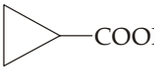
(ii) Two molecules of B are also formed by the ozonolysis of a compound C, C_8H_{10}.

Assign structures to A, B and C. Is there any isomer of A, if yes give its structure and ozonolysis.

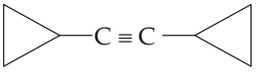
Solution :

Alkyl halide has one degree of unsaturation ; which may be in the form of ring or a double bond. So three possible structures for A are

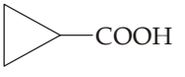
$CH_2 = CHCH_2Br$, $\underset{[\text{Not possible}]}{CH_3CH = CHBr}$ 

However, $CH_3CH = CHBr$, being vinylic halide does not form Grignard reagent under given conditions. So the two possible carboxylic acids (B) from the remaining alkyl halides will be $CH_2 = CHCH_2COOH$ and  .

Two molecules of B are formed from C (C_8H_{10}) by ozonolysis, so corresponding C should be either

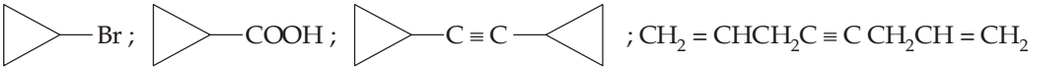
$CH_2 = CHCH_2—C \equiv C—CH_2CH = CH_2$ or 

↓ ozonolysis ↓ ozonolysis

$2CH_2O + 2OHCCH_2COOH$ 2 

It is not [B] [B]

So, compounds A, B, C and isomer of A are



[A] [B] [C] Isomer of [A]

Example 14 :

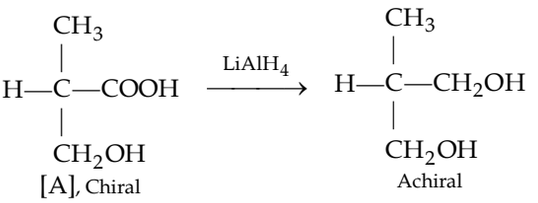
Give structures of the four optically acitve structural isomers A to D for $C_4H_8O_3$ that evolve CO_2 with aqueous $NaHCO_3$.

One of the isomers (say A) reacts with $LiAlH_4$ to give an achiral product. Assign the structure to A, B, C and D. Give chemical reactions to distinguish among B, C and D.

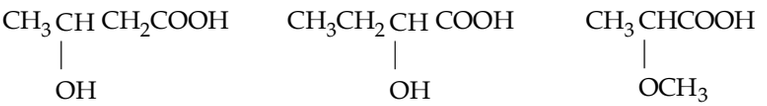
Solution :

(*i*) The molecular formula $C_4H_8O_3$ suggests that the isomers have 1° of unsaturation that must be due to —COOH, indicated by their reaction with aq. $NaHCO_3$. Hence the third oxygen may be present either as —OH or —OR.

(*ii*) Since A on reduction with $LiAlH_4$ (—COOH ⟶ —CH_2OH) gives an achiral product, a —CH_2OH group should already be is present in A . Hence the structure of A is



Thus the three other isomers may be written as below.



[B] [C] [D]

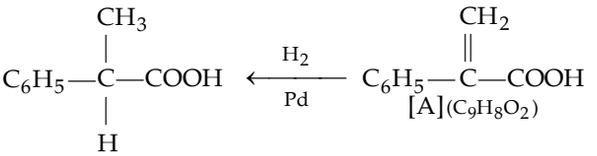
Differentiation between B, C and D. B and C are oxidisable by $KMnO_4$ or CrO_3, while D (an ether) is inert. Further, B gives a positive haloform test, while C does not respond to it.

Example 15 :

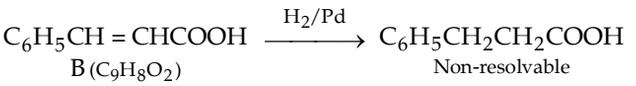
Two isomeric carboxylic acids (A and B) of the formula $C_9H_8O_2$, on oxidation, give benzoic acid. Acid A takes up one mole of hydrogen to form resolvable carboxylic acid, while acid B on similar treatment gives non-resolvable carboxylic acid. Assign structures to A and B and their corresponding hydrogenated products.

Solution :

The given statements indicate tht A and B have a C = C linkage and a phenyl group. Since the hydrogenated product from A is resolvable, it must have four different groups to the central carbon atom, two of which are —COOH and —C_6H_5. The remaining fragment (CH_4) can be present only as H and CH_3. Hence the complete structure of the resolvable product and its precursor, A can be drawn as below.



Thus the isomeric carboxylic acid B and its hydrogenated product (non-resolvable) should have following structure.



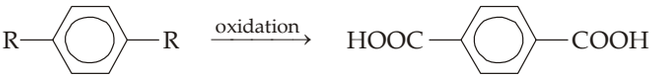
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Example 16 :

Write the structural formula for a chiral hydrocarbon, $C_{11}H_{16}$, which on oxidaton affords terephthalic acid.

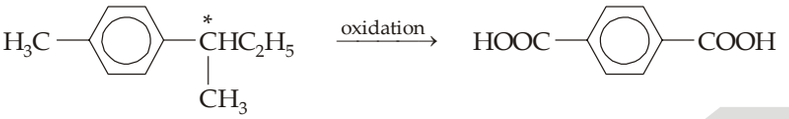
Solution :

Oxidaton of the hydrocarbon ($C_{11}H_{16}$) to terephthalic acid indicates that the hydrocarbon is 1, 4-dialkylsubstituted benzene.



tere-Phthalic acid

Thus the two alkyl groups of the hydrocarbon should have five carbon atoms. The smallest alkyl group with a chiral carbon is *sec*-butyl, hence the other alkyl group should be methyl.



Example 17 :

Assign structure to the compound A, C_8H_9Br which responds following series of reactions.

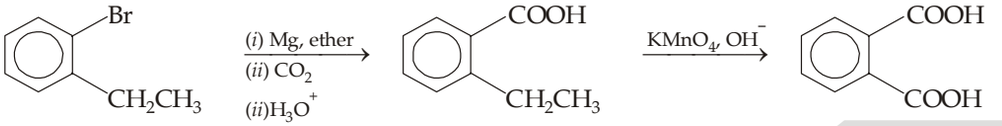
$$[A] \xrightarrow[(ii)\,CO_2,\,(iii)\,H_3O^+]{(i)\,Mg,\ ether} [B] \xrightarrow{KMnO_4,\,OH^-} \text{Phthalic acid}$$

Solution :

Reaction of compound A with Mg in ether followed by CO_2 points out the conversion of Br to MgBr which reacts with CO_2 to form —COOH.

$$C_8H_9—Br \xrightarrow{Mg,\ ether} —MgBr \xrightarrow[(ii)\,H_3O^+]{(i)\,CO_2} —COOH$$

Since the final product has two —COOH groups, the second must have been introduced through the oxidation of the side chain, which should be $—CH_2CH_3$. Hence A is *o*-bromoethylbenzene.



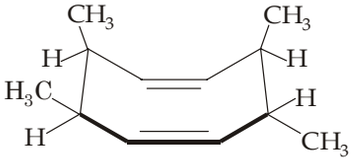
Example 18 :

Give structure of a hydrocarbon ($C_{12}H_{20}$) which gives two diastereomeric aliphatic dicarboxylic acids on oxidation.

Solution :

(*i*) Molecular formula of the hydrocarbon indicates that it has 3° of unsaturation ; two of which must be present in the form of double bonds (indicated by the formation of two dicarboxylic acids) ; the third degree of unsaturation should be present in the form of ring.

(*ii*) The two diastereomeric dicarboxylic acids must be meso and recemic which is possible for the following cyclo-octadiene derivative.



One half of the molecule with the *cis* Me's gives the *meso* diacid and the other half with the *trans* Me's gives the racemic diacid.

EXERCISE 17.1 (MCQ - ONE option correct)

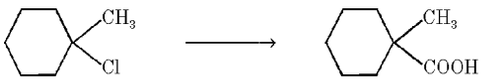
1. The systematic name of $CH_2 = C(CH_3)\,COOH$ is

(*a*) 2-methyl-2-propenoic acid

(*b*) 2-methylpropenoic acid

(*c*) both (*a*) and (*b*)

(*d*) Methacrylic acid.

2. 

Above reaction can be achieved satisfactorily by which set of reagents ?

(*a*) NaCN, H^+, heat (*b*) Mg + ether, CO_2, H_3O^+

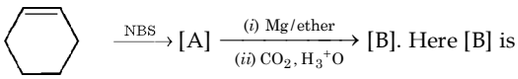
(*c*) Both (*a*) and (*b*) (*d*) Oxidation.

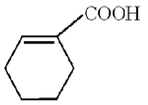
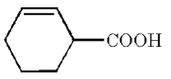
3. Which method is expected to give good result for following reaction ?

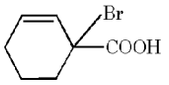
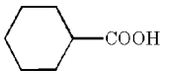
$HOCH_2CH_2CMe_2Cl \longrightarrow HOCH_2CH_2C(Me_2)COOH$

(*a*) Grignard synthesis (*b*) Nitrile synthesis

(*c*) Either of the two (*d*) None of the two.

4.  [B]. Here [B] is

(*a*)  (*b*) 

(*c*)  (*d*) 

5. $CH_3CH_2CH_2CH_2OH \xrightarrow{CO,\,H_2SO_4}$ A ; $CH_3CH_2CH(OH)\,CH_3 \xrightarrow[H_2SO_4]{CO}$ B. Predict the nature of A and B.

(*a*) A is $CH_3CH_2CH_2CH_2COOH$ and B is $CH_3CH_2CH(CH_3)COOH$

(*b*) A and B both are $CH_3CH_2CH(CH_3)COOH$

(*c*) A is $CH_3CH_2CH = CH_2$ and B is $CH_3CH = CHCH_3$

(*d*) Reaction is not possible.

6. Sodium malonate having one labelled oxygen is decarboxylated to form monocarboxylic acid. Predict the final products.

$$HOOC{-}CH_2{-}COO^{18}H \xrightarrow{1.NaOH} HOOC{-}CH_2{-}\overset{18}{C}OO^-Na^+ \xrightarrow{heat}$$

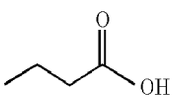
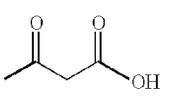
(*a*) $CH_3COOH + O = C = O^{18}$

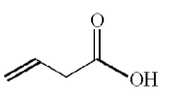
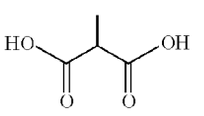
(*b*) $CH_3COOH + O^{18} = C = O^{18}$

(*c*) $CH_3COO^{18}H + O = C = O^{18}$

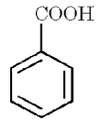
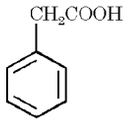
(*d*) $CH_3COO^{18}H + O = C = O$

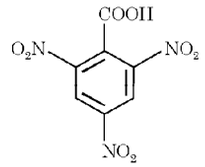
7. Which of the following is most difficult to decarboxylate ?

(*a*)  (*b*) 

(*c*)  (*d*) 

8. Which of the following carboxylic acids is decarboxylated easily?

(*a*)  (*b*) 

(*c*)  (*d*) *n*-C_4H_9COOH.

9. 0.187 g of an acid required 18.7 mL of 0.0972 M NaOH for neutralisation. The acid should be

(*a*) methoxyacetic acid

(*b*) ethoxyacetic acid

(*c*) caproic acid, $C_5H_{11}COOH$

(*d*) datas are insufficient.

10. Which type of halogen containing compound could react with OH^- to give a carboxylic acid ?

(*a*) RCH_2X (*b*) $RCHX_2$

(*c*) RCX_3 (*d*) None.

11. Identify the nature of reducing agent in the following reaction.

$$BrCH_2CH_2COOH \xrightarrow{?} Br\,CH_2CH_2CH_2OH$$

(*a*) $LiAlH_4$ (*b*) BH_3/THF followed by H_3O^+

(*c*) Both (*d*) None.

12. Identify the respective final products in the following two reactions.

(*i*) $CH_3CH_2COOH \xrightarrow{Br_2/PCl_3}$ [A] $\xrightarrow{Br_2}$ [B] $\xrightarrow{H_2O}$ [C]

(*ii*) $CH_3CH_2COOH \xrightarrow{Cl_2/PBr_3}$ [D] $\xrightarrow{Cl_2}$ [E] $\xrightarrow{H_2O}$ [F]

(*a*) $CH_3CHOHCOOH$ and $CH_3CHOHCOOH$

(*b*) $CH_3CHOHCOCl$ and $CH_3CHOHCOBr$

(*c*) $CH_3CHBrCOOH$ and $CH_3CHClCOOH$

(*d*) $CH_3CHClCOOH$ and $CH_3CHBrCOOH$.

13. Both propanoic acid, CH_3CH_2COOH as well as 2-chloropropanoic acid give precipitate with aq. $AgNO_3$. How you distinguish the precepitates in the two ?

(*a*) By aq. NH_4OH (*b*) By aq. HNO_3

(*c*) By either of the two (*d*) By none of the two.

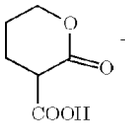
14. Identify the product A

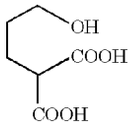
$$HC \equiv CH \xrightarrow[(ii)\,2CO_2]{(i)\,2Na} [Intermediate] \xrightarrow{Na/C_2H_5OH} [A]$$

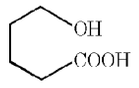
(*a*) Maleic acid (*b*) Fumaric acid

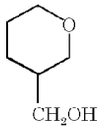
(*c*) Both (*a*) and (*b*) (*d*) Succinic acid.

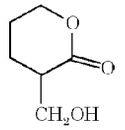
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15.  $\xrightarrow[(ii)\ H_2O]{(i)\ BH_3/THF}$ P. Here product P is

(*a*) 

(*b*) 

(*c*) 

(*d*) 

16. Predict the nature of P

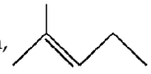
$$CH_3CH_2CH_2CH_2OH + CO \xrightarrow{H_2SO_4} P$$

(*a*) $CH_3CH_2CH = CH_2$

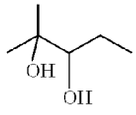
(*b*) $CH_3CH = CHCH_3$

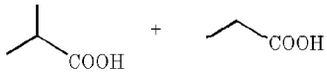
(*c*) $CH_3CH_2CH_2CH_2COOH$

(*d*) $CH_3CH_2CH(CH_3)COOH$.

17. On vigorous oxidation by permanganate solution, 

gives

(*a*) 

(*b*) 

(*c*) 

(*d*) 

18. Identify the correct order of boiling points of the following compounds.

$CH_3CH_2CH_2CH_2OH$ **(1)** ; $CH_3CH_2CH_2CHO$ **(2)** ; $CH_3CH_2CH_2COOH$ **(3)**

(*a*) 1 > 2 > 3 (*b*) 3 > 1 > 2

(*c*) 1 > 3 > 2 (*d*) 3 > 2 > 1.

19. Which of the following acids has smallest dissociation constant?

(*a*) $CH_3CHFCOOH$ (*b*) FCH_2CH_2COOH

(*c*) $BrCH_2CH_2COOH$ (*d*) $CH_3CHBrCOOH$.

20. Dimerisation of carboxylic acids is due to

(*a*) ionic bond

(*b*) covalent bond

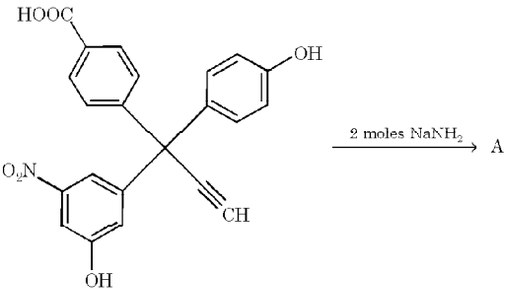
(*c*) coordinate bond

(*d*) intermolecular hydrogen bond.

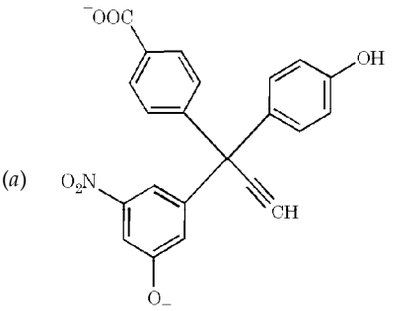
21. When propionic acid is treated with aqueous sodium bicarbonate, CO_2 is liberated. The carbon of CO_2 comes from

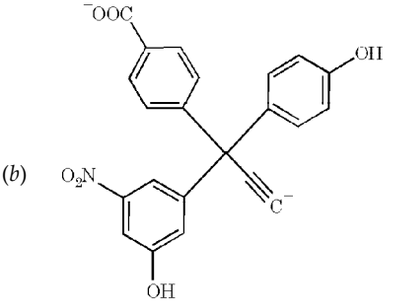
(*a*) methyl group (*b*) carboxyl group

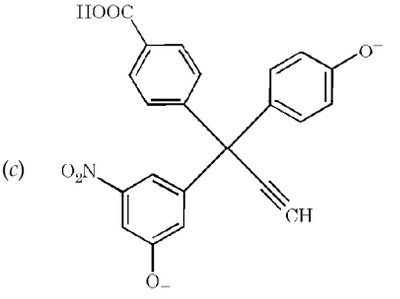
(*c*) methylene group (*d*) bicarbonate.

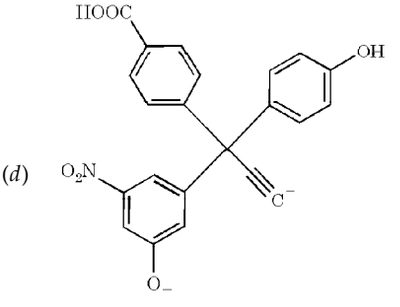
22. 

The product A will be

(*a*) 

(*b*) 

(*c*) 

(*d*) 

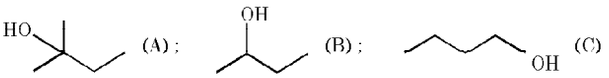
23. Two moles of acetic acid are heated with P_2O_5. The product formed is
(*a*) 2 moles of ethyl alcohol
(*b*) formic anhydride
(*c*) ethanoic anhydride
(*d*) 2 moles of methyl cyanide.

24. $CH_3CH_2COOH \xrightarrow{Cl_2, red\ P} A \xrightarrow{alc.\ KOH} B$; B is
(*a*) CH_3CH_2COCl (*b*) CH_3CH_2CHO
(*c*) $CH_2 = CHCOOH$ (*d*) $ClCH_2CH_2COOH$.

25. Lactic acid, $CH_3CHOHCOOH$, on oxidation by alkaline $KMnO_4$ gives.
(*a*) tartaric acid (*b*) pyruvic acid
(*c*) cinnamic acid (*d*) propionic acid.

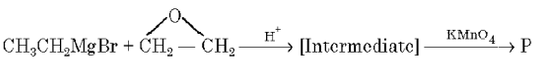
26. An enantiomerically pure acid is treated with racemic mixture of an alcohol having one chiral carbon. The ester formed will be
(*a*) optically active mixture
(*b*) pure enantiomer
(*c*) meso compound
(*d*) racemic mixture.

27. Arrange the following alcohols in increasing order of acid-catalyzed esterification by ethanol.



(*a*) A < B < C (*b*) C < B < A
(*c*) B < C < A (*d*) C < A < B.

28. Identify the final porduct, P.



(*a*) CH_3CH_2CHO (*b*) $CH_3CH_2CH_2CHO$
(*c*) CH_3CH_2COOH (*d*) $CH_3CH_2CH_2COOH$.

29. $HC \equiv CH \xrightarrow[(ii)\ CH_3I]{(i)\ 2NaNH_2} [X] \xrightarrow{H_2SO_4/Hg^{2+}} [Y] \xrightarrow{OH^-/Br_2} [Z]$

Here Z is
(*a*) CH_3CH_2COOH (*b*) $CH_3CHBrCOOH$
(*c*) CH_3COOH (*d*) $CH_2BrCOOH$.

30. Which of the following reactions yields acetic acid as the final product ?

(*i*) $CH_3CCl_3 \xrightarrow{OH^-}$

(*ii*) $CH_3COOC_2H_5 \xrightarrow{OH^-}$

(*iii*) $CH_3CHO \xrightarrow[(ii)\ H^+]{(i)\ Tollen's\ regent}$

(*a*) Only (*i*) (*b*) Only (*ii*)
(*c*) Only (*iii*) (*d*) All the three.

31. Identify the main product in the following reaction.

$$CH_2(COOH)_2 \xrightarrow{P_2O_5,\ heat} X$$

(*a*) CH_3COOH (*b*) $CO_2 + H_2O$
(*c*) C_3O_2 (*d*) COOH.COOH.

32. Identify the product Z in the following series of reactions.

$$\begin{matrix} CH_2COOH \\ | \\ CH_2COOH \end{matrix} \xrightarrow{P/Br_2} X \xrightarrow{alc.\ KOH} Y \xrightarrow{CF_3COOH} Z$$

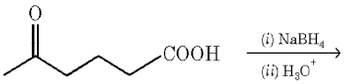
(*a*) Maleic anhydride (*b*) Maleic acid
(*c*) *meso*-Tartaric acid (*d*) *rac*-Tartaric acid.

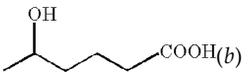
33. Which of the following acids has the least pK_a value ?
(*a*) CH_3COOH (*b*) C_6H_5COOH
(*c*) $CH_2 = CHOOH$ (*d*) All have same pK_a

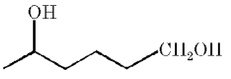
34. Arrange the following in increasing order of their pK_a values.
CH_3COOH (**1**) ; Me_3CCH_2COOH (**2**) ; $Me_3N^+CH_2COOH$ (**3**)
(*a*) 1 < 2 < 3 (*b*) 2 < 1 < 3
(*c*) 3 < 2 < 1 (*d*) 3 < 1 < 2.

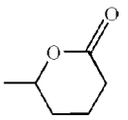
35. Acetic acid reacts with ketene to form
(*a*) ethyl acetate (*b*) propanoic acid
(*c*) acetic anhydride (*d*) methyl acetate

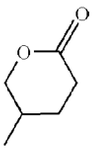
36. Predict the structure of the product in the following reaction.

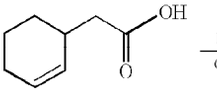


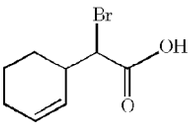
(*a*) 

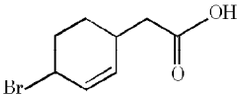
(*b*) 

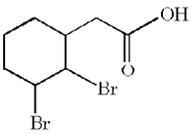
(*c*) 

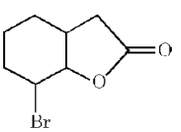
(*d*) 

37. Identify Z in the reaction 

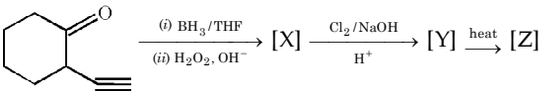
(*a*) 

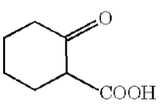
(*b*) 

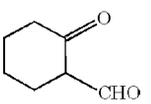
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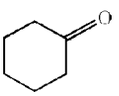
(*d*) 

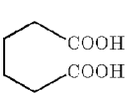
38. The possible structure for Z in the following reaction is



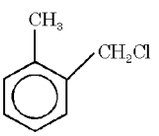
(*a*) 

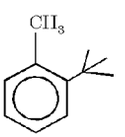
(*b*) 

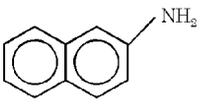
(*c*) 

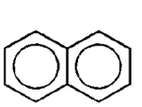
(*d*) 

39. Which of the following set of reactants does not form phthalic acid on oxidation ?

(*a*) 

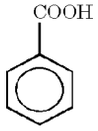
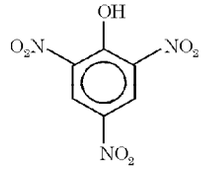
(*b*) 

(*c*) 

(*d*) 

40. Which of the following has minimum pK_a value ?

(*a*) FCH_2COOH (*b*) Cl_3CCOOH

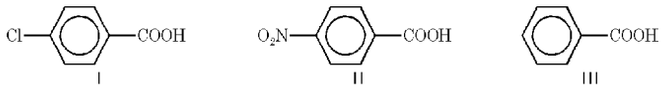
(*c*)  (*d*) 

41. The correct decreasing order of pK_a values of the *o*-, *m*-, and *p*-nitrobenzoic acids is

(*a*) *o* > *m* > *p* (*b*) *m* > *p* > *o*

(*c*) *p* > *m* > *o* (*d*) *o* > *p* > *m*

42. The correct order of decreasing acidity of the three acids is



(*a*) III > II > I (*b*) II > I > III

(*c*) II > III > I (*d*) I > II > III

43. Which of the following carboxylic acids undergoes decarboxylation easily ?

(*a*) $C_6H_5CHOHCOOH$ (*b*) $C_6H_5COCOOH$

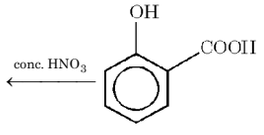
(*c*) $C_6H_5COCH_2COOH$ (*d*) $C_6H_5COCH_2CH_2COOH$

44. Predict the nature of P in the following reaction.

$$C_6H_5COCH(CH_3)COOH \xrightarrow{heat} P$$

(*a*) $C_6H_5COCH_3$ (*b*) $C_6H_5COCH_2CH_3$

(*c*) C_6H_5COOH (*d*) No action

45. B  A

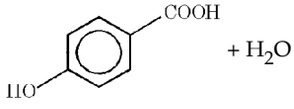
Here A and B are ... and ... respectively

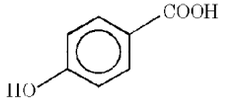
(*a*) *o*-bromophenol, *o*-nitrophenol

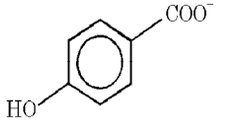
(*b*) 3-bromosalicylic acid, 3-nitrosalicylic acid

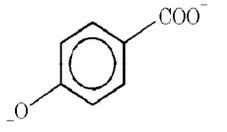
(*c*) 2, 4, 6-tribromophenol, picric acid

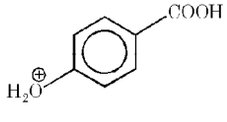
(*d*) 4-bromosalicylic acid, 4-nitrosalicylic acid

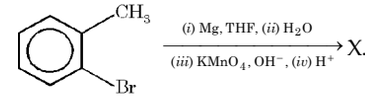
46.  A. Here A should be

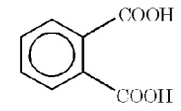
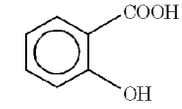
(*a*) 

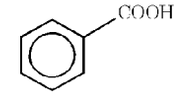
(*b*) 

(*c*) 

(*d*) 

47.  X. Here X is

(*a*)  (*b*) 

(*c*)  (*d*) 

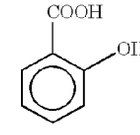
48. Predict the nature of the final product Z in the following series of reactions.

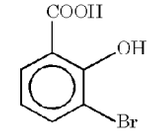
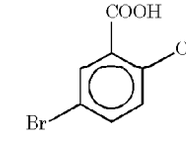
$$C_6H_5COOH \xrightarrow{PCl_5} [X] \xrightarrow[AlCl_3]{C_6H_6} [Y] \xrightarrow{C_6H_5CO_3H} [Z]$$

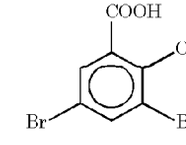
(*a*) $C_6H_5COOC_2H_5$ (*b*) C_6H_5COOH

(*c*) $C_6H_5COOC_6H_5$ (*d*) C_6H_5OH

49. Pick up the major product in the following reaction.

 + Br_2 (in CH_3COOH) ⟶

(*a*)  (*b*) 

(*c*) both (*a*) and (*b*) (*d*) 

50. The organic product(s) formed in the reaction

$$C_6H_5COOH \xrightarrow[II\ H_2O^+]{I\ LiAlH_4}$$

(a) $C_6H_5CH_2OH$ (b) C_6H_5COOH

(c) $C_6H_5CH_3$ (d) CH_4

51. Which of the following gives effervescences of CO_2 with $NaHCO_3$ solution ?

(a) HCOOH (b) 2, 4, 6-Trinitrophenol

(c) Both (d) None

52. H. V. Z reaction involves the use of P and Cl_2

$$CH_3CH_2COOH \xrightarrow{P, Cl_2} CH_3CHClCOOH$$

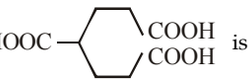
The function of phosphorus is

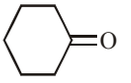
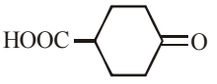
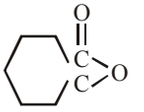
(a) as a catalyst.

(b) in the formation of PCl_3 which carries out halogenation at the α-carbon atom.

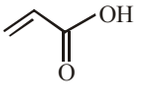
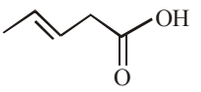
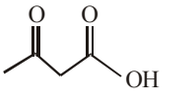
(c) in the formation of PCl_3 which converts –COOH into –COCl.

(d) none of the three.

53. What is the main product when  is heated ?

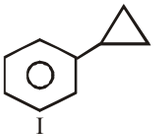
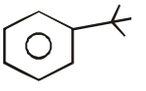
(a) 
(b) 
(c) 
(d) 

54. The correct order of decarboxylation of the three acids is


I

II

III

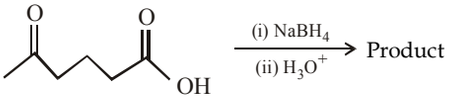
(a) III > II > I (b) III = II > I
(c) III > II = I (d) III = II = I

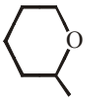
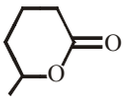
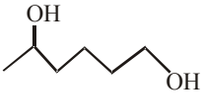
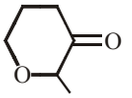
55. Which statement is true regarding oxidation of the following two compounds


I

II

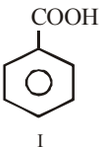
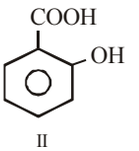
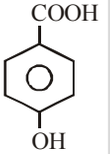
(a) Both are oxidisable to benzoic acid under similar conditions
(b) It is very difficult to oxidise either of the two
(c) Compound I is oxidisable to benzoic acid easily while compound II is oxidisable only under vigorous conditions to benzoic acid
(d) Compound I is oxidisable to benzoic acid, while II is oxidisable only under vigorous conditions to 2, 2-dimethylpropanoic acid.

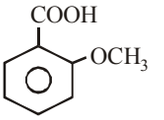
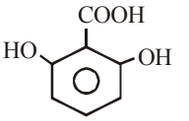
56. Predict the nature of end product in the following reaction.



(a) 
(b) 
(c) 
(d) 

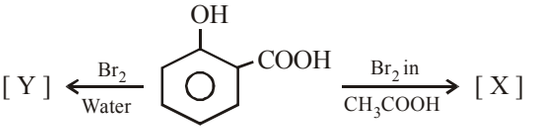
57. The correct order for the acidic character of the following carboxylic acids is


I

II

III

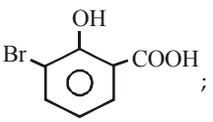
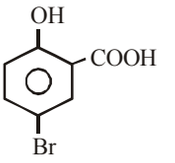

IV

V

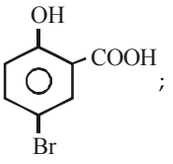
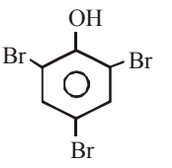
(a) IV > I > II > III > V (b) V > II > III > I > IV
(c) V > II > IV > III > I (d) V > II > IV > I > III

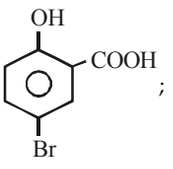
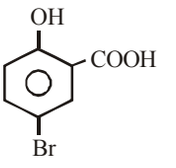
58. Salicylic acid is treated with bromine under two different conditions.

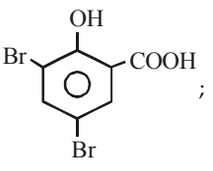
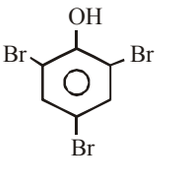


Predict the nature of [X] and [Y] in the above reactions

(a)  ; 
[X] [Y]

(b)  ; 
[X] [Y]

(c)  ; 
[X] [Y]

(d)  ; 
[X] [Y]

59. Choose the correct statement regarding acidic character of acetic acid, CH_3COOH and peroxyacetic acid, CH_3COOOH.

(a) Peroxyacetic acid is stronger acid than acetic acid since the former has one extra oxygen, an electronegative element
(b) Peroxyacetic acid is stronger than acetic acid because its conjugate base is a weaker base than acetate
(c) Peroxyacetic acid is weaker than acetic acid because its conjugate base is less stable than that of acetate ion.
(d) Both are equally strong

EBD_7090

60. β-Keto acids on heating easily undergo decarboxylation because

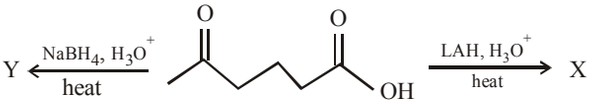
(a) it is a very storng acid

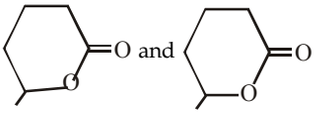
(b) it is a very weak acid

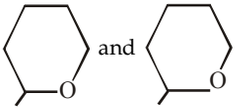
(c) its carboxylate ion is highly stable.

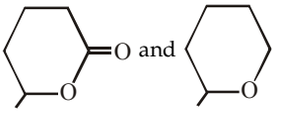
(d) it involves the formation of a cyclic six-membered transition state.

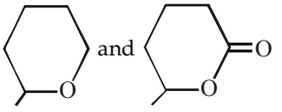
61. The products X and Y are respectively

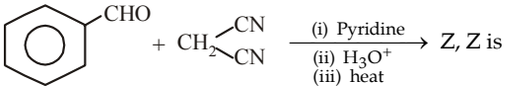


(a) 

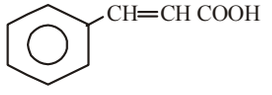
(b) 

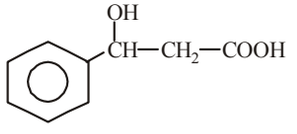
(c) 

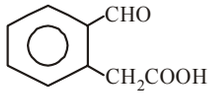
(d) 

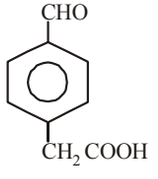
62. 

Z, Z is

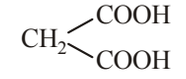
(a) 

(b) 

(c) 

(d) 

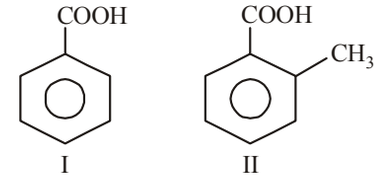
63. Which of the following is least acidic in nature ?

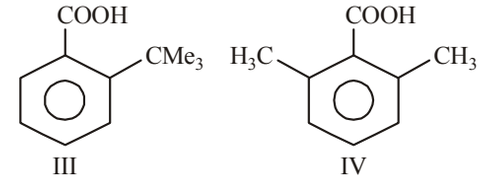
(a) CH_3COOH (b) 

(c) CH_3CH_2COOH

(d) $Me_3N^+CH_2CH_2CH_2COOH$

64. Arrange the following four acids in their decreasing order of acidity

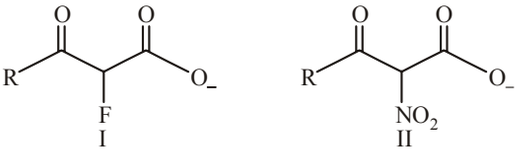


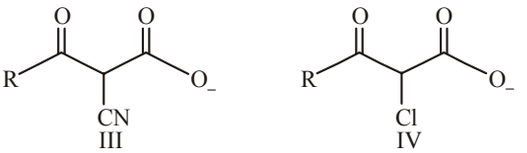


(a) I > II > III > IV (b) IV > III > II > I

(c) II > IV > III > I (d) III > IV > II > I

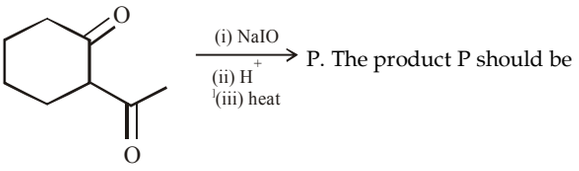
65. Which of the following is the correct order of decarboxylation of β-keto carboxylate anion ?



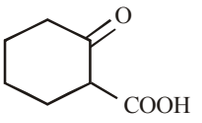


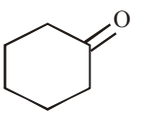
(a) I > II > III > IV (b) II > I > III > IV

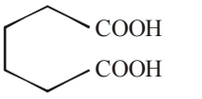
(c) II > III > IV > I (d) I > IV > II > III

66. 

P. The product P should be

(a) 

(b) 

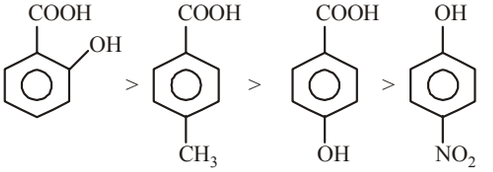
(c) 

(d) A mixture of (a), (b) and (c)

67. Among the following compounds, the most acidic is

(a) p-nitrophenol (b) p-hydroxybenzoic acid

(c) o-hydroxybenzoic acid (d) p-toluic acid



EXERCISE 17.2 (MCQ 1 or >1 option correct, Passage based, Matching, A/R)

DIRECTIONS for Q. 1 to Q. 22 : Multiple choice questions with one or more than one correct option(s).

1. $C_6H_5-\overset{O}{\overset{\|}{C}}-OH + H_2O^{18} \xrightarrow{H^+}$ Product

Here the product may be

(*a*) $C_6H_5CO^{18}OH$ (*b*) $C_6H_5COO^{18}H$

(*c*) $C_6H_5COOO^{18}H$ (*d*) $C_6H_5C^{18}OOOH$.

2. RCOOH can be reduced to RCH_2OH by

(*a*) $NaBH_4$ (*b*) $LiAlH_4$

(*c*) Na/C_2H_5OH (*d*) H_2/Catalyst

3. Which of the following statement is true for the following reaction ?

$$RCOOH + LiAlH_4 \longrightarrow RCH_2OH$$

(*a*) The first step of the reaction is the formation of AlH_3 and H_2.

(*b*) A hydride ion is transferred from AlH_3 to the carboxylate carbon.

(*c*) An aldehyde is formed as an intermediate.

(*d*) Aldehyde is not the intermediate in this reaction

4. Which of the following statement is not true ?

(*a*) Maleic acid and fumaric acid are similar in their acidic strength, same is true for their corresponding monoanions.

(*b*) Maleic acid is a stronger acid than fumaric acid, similarly maleate monoanion is a stronger acid than fumarate monoanion.

(*c*) Maleic acid is a stronger acid than fumaric acid, but maleate monoanion is a weaker acid than fumarate monoanion.

(*d*) Maleic acid is a stronger acid than fumaric acid, but the corresponding monoanions have similar acidic strength.

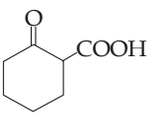
5. Which of the following compound can be methylated by diazomethane ?

(a) C_2H_5COOH (b) $C_2H_5NH_2$

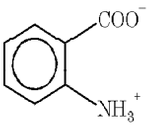
(c) C_6H_5OH (d) $CH_3COCH_2COOC_2H_5$

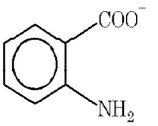
6. Which of the following compound is decarboxylated on heating ?

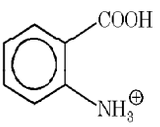
(a) $\begin{matrix}CH_2COOH\\|\\CH_2COOH\end{matrix}$ (b) $C_2H_5CH(COOH)_2$

(c) CH_3COCH_2COOH (d) 

7. Anthranilic acid can exist in the form of following structures?


I


II


III

Which of the following statement is not correct regarding anthranilic acid structure ?

(*a*) Structure I exists in neutral solution (pH = 7), structure II in acidic solution (pH < 7) and structure III exists in alkaline solution (pH > 7).

(*b*) Structure II exists when pH > 7 and structure III exists when pH < 7.

(*c*) Structures I and II exist when pH > 7 and structures I and III exist when pH < 7.

(*d*) All the thre structures exist in all the three mediums.

8. Which of the following exhibit hydrogen bonding?

(a) Chloroform (b) Ethyl alcohol

(c) Acetic acid (d) Dimethyl ether

9. Which of the following statements are correct?

(a) Carboxylic acids have higher boiling points than those of alcohols of similar molecular weight

(b) Carboxylic acids have lower boiling points than those of alcohols of similar molecular weight

(c) Carboxylic acids (C_1 to C_4) are soluble in water

(d) The melting points of carboxylic acids increase or decrease in irregular manner

10. Which of the following statements are correct?

(a) The two carbon-oxygen bond lengths in formic acid are different

(b) The two carbon-oxygen bond lengths in sodium formate are equal

(c) The carbon-oxygen bond length in formic acid is less than that in sodium formate

(d) The carbon-oxygen bond length in formic acid is greater than that in sodium formate

11. Tollen's reagent reacts with

(a) formaldehyde (b) acetaldehyde

(c) acetone (d) formic acid

12. Pyroligneous acid, obtained by destructive distillation of wood, can be used for the manufacture of

(a) methyl alcohol (b) acetaldehyde

(c) acetic acid (d) propanol

13. Which are correct statements?

(a) Methyl malonic acid is converted into propanoic acid on heating

(b) Succinic acid forms succinic anhydride on heating

(c) 3-Hydroxy propanoic acid forms acrylic acid on heating

(d) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2COOH$ forms acetone on heating

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14. Which can be used as fire-extinguisher?

(a) $CH_3COOH + NaHCO_3$

(b) Pyrene

(c) Formalin

(d) Dry ice

15. CH_3COOH can be obtained by

(a) $CH_3Br \xrightarrow{Mg/ether} \xrightarrow{CO_2/H_3O^+}$

(b) $CH_3Br \xrightarrow{AgCN} \xrightarrow{H_3O^+}$

(c) $CH_3CH = CHCH_3 \xrightarrow{KMnO_4}$

(d) $CH_3CCl_3 \xrightarrow{aq.\ KOH}, \xrightarrow{H_3O^+}$

16. Decarboxylation will take place on heating :

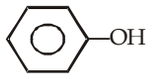
(a) methyl malonic acid

(b) succinic acid

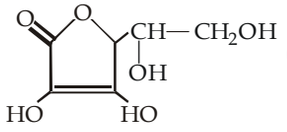
(c) 2, 2-dimethyl acetoacetic acid

(d) Glutaric acid

17. Which of the following will liberate CO_2 on reaction with $NaHCO_3$:

(a) 

(b) CH_3COOH

(c) 

(d) 

18. Which of the following compounds can be used as an acylating agent ?

(*a*) CH_3COCl (*b*) $(CH_3CO)_2O$

(*c*) CH_3COOH (*d*) CH_3CH_2COCl.

19. Which of the following statement is true for the following reaction ?

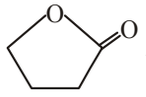
$$RCOOH + LiAlH_4 \longrightarrow RCH_2OH$$

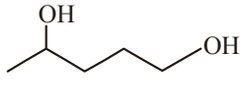
(a) The first step of the reaction is the formation of AlH_3 and H_2.

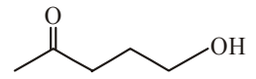
(b) A hydride ion is transferred from AlH_3 to the carboxylate carbon.

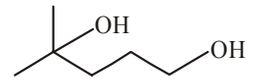
(c) An aldehyde is formed as an intermediate.

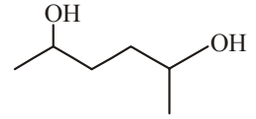
(d) Aldehyde is not the intermediate in this reaction

20.  $\xrightarrow[(ii)\ H_3O^+]{(i)\ CH_3MgBr}$ Z, Z may be

(a) 

(b) 

(c) 

(d) 

21. Formic acid and acetic acid can be distinguished by the action of

(a) conc. H_2SO_4

(b) Tollen's reagent

(c) Fehling solution

(d) heating of sodium salt

22. $C_6H_5-\overset{\overset{O}{\|}}{C}-OH + H_2O^{18} \xrightarrow{H^+}$ Product

Here the product may be

(a) $C_6H_5CO^{18}OH$ (b) $C_6H_5COO^{18}H$

(c) $C_6H_5COOO^{18}H$ (d) $C_6H_5CO^{18}OOH$

INSTRUCTION for Q. 23 to 34 : Read the passages given below and answer the questions that follow.

PASSAGE 1

Alkyl halides can be converted easily into carboxylic acids through two routes,

(i) through Grignard reagent formation, and

(ii) through hydrolysis of nitriles.

(i) $CH_3Br + Mg \longrightarrow CH_3MgBr \xrightarrow[(ii)\ H_3O^+]{(i)\ CO_2} CH_3COOH$

(ii) $CH_3CH_2Br \xrightarrow{NaCN} CH_3CH_2CN \xrightarrow{(i)\ H^+} CH_3COOH + NH_4^+$

Other methods, generally opted in laboratory are oxidation of alcohols, 1° alcohols give carboxylic acids with same number of carbon, while 2° alcohols give acids with lesser number of C atoms.

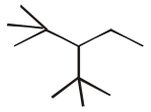
23. Dimethyl propanoic acid can be prepared easily from 2-chloro-2-methylpropane through

(a) Grignard reagent route

(b) nitrile route

(c) both routes

(d) none of the two

24.  $\xrightarrow{\text{chromic acid}}$ Carboxylic acid

The carboxylic acid formed in the above reaction is

(a) 2-tert-butyl-3, 3-dimethylbutanoic acid

(b) 2-(1, 1'-dimethylethyl)-3, 3-dimethylbutanoic acid

(c) Methanoic acid

(d) Tricarballylic acid

25. During oxidation of $CH_3\overset{*}{C}OCH_2CH_2CH_3$, labelled carbon is mainly found in

(a) $CH_3\overset{*}{C}OOH$ (b) $CH_3CH_2CH_2\overset{*}{C}OOH$

(c) $H\overset{*}{C}OOH$ (d) $CH_3CH_2\overset{*}{C}OOH$

PASSAGE 2

Although the carboxyl group consists of C=O and – OH, it is the – OH that undergoes change, either loss of H^+ or replacement by another group takes place. However, the carbonyl group markedly influences the reactions of carboxylic acids. The presence of the C = O part is also responsible for nucleophilic substitution reactions in acid derivatives.

Presence of an electron withdrawing group increases the acidity of aliphatic as well as aromatic acids. On the other hand, electron releasing groups imparts opposite effect.

26. The marked acidity of RCOOH over ROH is due to the presence of

(a) – OH (b) C = O

(c) Both (d) None

27. Chloroacetic acid is more acidic than acetic acid because

(a) electron withdrawing group destabilizes the acid

(b) electron donating group stabilizes the acid

(c) electron withdrawing group stabilizes the carboxylate ion

(d) all the three

28. Which statement is correct when an acid weakening group is present in benzoic acid?

(a) Acid weakening groups activate the ring towards electrophilic substitution

(b) Acid weakening groups deactivate the ring towards electrophilic substitution

(c) Acid weakening groups activate the ring toward nucleophilic substitution

(d) None of the above

29. The C = O part in carboxylic acids and their derivatives make acyl compounds more reactive than alkyl compounds toward nucleophilic attack because

(a) The carbonyl group is electron donating

(b) The alkyl group is electron donating

(c) Attack of a nucleophile on a flat acyl compound is less sterically hindered

(d) Tetrahedral carbon atoms cannot have pentavalent transition states

30. Aldehydes and ketones react with nucleophiles to give addition product rather substituion because

(a) They are more acidic

(b) They are less acidic

(c) They are sterically hindered

(d) The C – H & C – C bonds do not break easily

PASSAGE 3

Hell-Volhard-Zelinsky (HVZ) reaction involves the reaction of aliphatic carboxylic acid with bromine in the presence a trace of PBr_3 to form α-bromocarboxylic acid.

$$CH_3CH_2COOH \xrightarrow{Br_2/PBr_3} CH_3CH_2COBr$$

$$\longrightarrow CH_3CHBrCOBr \xrightarrow{H_2O} CH_3CHBrCOOH$$

31. When two equivalents of the reagent are used, the product formed in the above reaction will be

(a) $CH_3CHBrCOBr$ (b) $CH_2BrCHBrCOOH$

(c) CH_3CBr_2COOH (d) both (b) and (c)

32. What will be the product when three equivalent of Br_2 is treated with 2,2-dimethylbutanoic acid?

(a) $CH_2Br-\underset{\displaystyle CH_2Br}{\overset{\displaystyle CH_2Br}{\underset{|}{\overset{|}{C}}}}-COOH$ (b) $Br_2CH-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2Br}{\underset{|}{\overset{|}{C}}}}-COOH$

(c) $Br_3C-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-COOH$ (d) No reaction

33. What product will be formed when PBr_3 in the given set of reactions is replaced by PCl_3?

(a) $CH_3-\underset{|}{\overset{\displaystyle Cl}{CH}}COOH$ (b) $CH_3-\underset{|}{\overset{\displaystyle Br}{CH}}-COOH$

(c) Both (d) Reaction not possible

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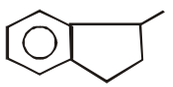
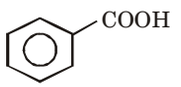
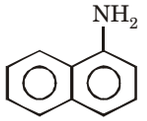
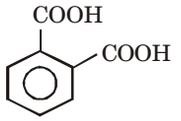
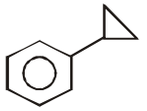
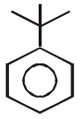
34. When Br_2 in the above given set of reactions is replaced by Cl_2, the product formed will be

(a) $CH_3-\underset{Cl}{\underset{|}{CH}}-COOH$ (b) $CH_3-\underset{Br}{\underset{|}{CH}}-COOH$

(c) $CH_3-\underset{Cl}{\underset{|}{CH}}-COCl$ (d) $CH_3-\underset{Cl}{\underset{|}{CH}}-COBr$

Instructions for Q. 35 : Following questions are Multiple Matching type Questions :

35.

	Column - I **(Compound)**		*Column - II* **(Oxidation product)**
(A)		(a)	
(B)		(b)	
(C)		(c)	Oxidation difficult
(D)		(d)	$(CH_3)_3CCOOH$

Instructions for Q. 36 to 43 : Following questions are Assertion and Reasoning Type Questions :

Note : Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 5 choices (a), (b), (c), (d) and (e) out of which ONLY ONE is correct.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.

(c) Statement -1 is True, Statement-2 is False.

(d) Statement -1 is False, Statement-2 is True.

(e) Statement -1 is False, Statement-2 is False.

36. **Statement 1 :** The pK_a of acetic acid is lower than that of phenol.

Statement 2 : Phenoxide ion is more resonance stabilised.

37. **Statement 1 :** During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as fast as it is formed.

Statement 2 : The reaction between an acid and an alcohol in the presence of an acid catalyst is a reversible reaction.

38. **Statement 1 :** A carboxylic acid is a stronger acid than phenol

Statement 2 : The conjugate base of carboxylic acid, a carboxylate ion, is stabilised by two equivalent resonance structures in which the negative charge is at the more electronegative oxygen atom.

39. **Statement 1 :** C_6H_5COOH is stronger than CH_3COOH.

Statement 2 : C_6H_5COOH is weaker than HCOOH.

40. **Statement 1 :** Dichloro and trichloro acids are stronger than monochloroacetic acid.

Statement 2 : An increase in the number of electronegative groups on the alkyl chain increases the strength of the acid.

41. **Statement-1** : The pK_a value of acetic acid is lower than that of phenol.

Statement-2 : Phenoxide ion is more resonance stabilized

42. **Statement-1** : Nitration of benzoic acid gives *m*-nitrobenzoic acid.

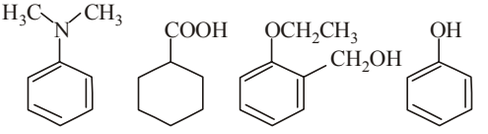
Statement-2 : Carboxyl group increases the electron-density at *meta*-position.

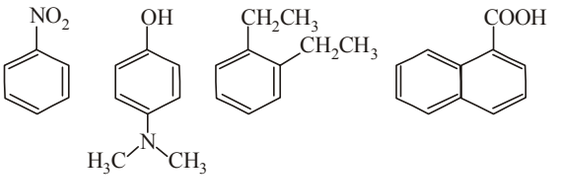
43. **Statement-1** : RCOCl, $(RCO)_2O$ and RCOOR′ all react with Grignard reagents to form 3° alcohols.

Statement-2 : RCOCl reacts with R_2Cd to form ketones but $(RCO)_2O$ and RCOOR' do not react at all.

Instructions for Q. 44 : Following questions are Integer Type Questions :

44. Amongst the following, the total number of compounds soluble in aqueous NaOH is





EXERCISE 17.3 (Subjective Problems)

1. (*a*) Give the common and IUPAC names for the straight chain saturated carboxylic acids containing 5, 6, 8, 10 and 12 carbon atoms.

(*b*) Give the structural formula and IUPAC name for each of the following :

(*i*) Isovaleric acid

(*ii*) Trimethylacetic acid

(*iii*) α, β-Dimethylcaproic acid

(*iv*) α-Methyl-γ-ethyloctanoic acid.

2. Write equations to obtain *n*-butanoic acid from (*a*) *n*-propanol (two different methods), and (*b*) 2-pentanone.

3. Write the products obtained from the reaction of *n*-valeric acid with

(*a*) Al (*b*) CaO

(*c*) NH_3(aq) (*d*) H_2, Ni, 20°C, 1 atm

(*e*) $LiAlH_4$ (*f*) hot $KMnO_4$

(*g*) Br_2/P (*h*) Br_2/Fe

(*i*) fuming H_2SO_4 (*j*) HNO_3/H_2SO_4

(*k*) *n*-Valeryl alcohol.

4. Give balanced equations for the reaction of each of the following reagents with phenylacetic acid.

(*i*) $SOCl_2$ (*ii*) PCl_3

(*iii*) PCl_5 (*iv*) $(CH_3CO)_2O$

(*v*) CH_3OH/H_2SO_4 (*vi*) NH_3 followed by heat.

5. Write the equations for converting isobutyric acid into each of the following.

(*a*) Isobutyramide (*b*) Isobutyl alcohol

(*c*) Butane (*d*) Magnesium isobutyrate.

6. Give steps involved in the following conversions :

(*a*) $^{14}CO_2 \longrightarrow CH_3CH_2CH_2{}^{14}COOH$

(*b*) $^{14}CO_2 \longrightarrow CH_3CH_2{}^{14}CH_2COOH$

(*c*) $^{14}CO_2 \longrightarrow CH_3{}^{14}CH_2CH_2COOH$

(*d*) $^{14}CH_3OH \longrightarrow {}^{14}CH_3CH_2CH_2CH_2COOH$

7. Give steps involved in the following transformations :

(*a*) Toluene to α-bromophenylacetic acid

(*b*) Benzene to α-methylphenylacetic acid.

(*c*) *n*-Butanol to 2-pentenoic acid.

8. (*a*) Arrange the following in order of decreasing acidic character.

(*i*) $CH_3COOH, CH \equiv CH, NH_3, C_2H_6, C_2H_5OH, H_2SO_4, H_2O$

(*ii*) Acetic acid, malonic acid, succinic acid

(*b*) Arrange the monosodium salts of the acids given in (*a*) (*i*) in order of decreasing basicity.

9. Complete the following reactions :

(*a*) $CH \equiv CH \xrightarrow{CH_3MgBr} A \xrightarrow[(ii)\ H^+]{(i)\ CO_2}$

$B \xrightarrow{H_2SO_4/HgSO_4} C \xrightarrow{KMnO_4} CH_2(COOH)_2$

(*b*) $CH_3COOH \xrightarrow{LiAlH_4} A \xrightarrow{HBr} B \xrightarrow[(ii)\ CO_2]{(i)\ Mg}$

$C \xrightarrow{Ag_2O} D \xrightarrow{Br_2} E$

10. Compare the reaction of CH_3CH_2COOH with excess of (*i*) CH_3MgBr and (*ii*) CH_3Li.

11. (*a*) Use simple chemical tests to differentiate among the following dry compounds. *n*-Butanol, *n*-butanoic acid, butane, butanal and ethyl methyl ether.

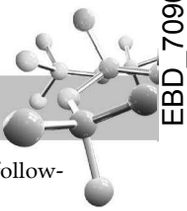
(*b*) Differentiate between (*i*) CH_3COOH and HCOOH, (*ii*) oxalic acid and malonic acid ; and (*iii*) CH_3CH_2COCl and CH_3CH_2COOH.

(*c*) Name the reagent or test that can be used for distinguishing between the members of each of the following pairs.

(*i*) Acrylic acid, CH_2=CHCOOH and propionic acid, CH_3CH_2COOH.

(*ii*) Mandelic acid, $C_6H_5CHOHCOOH$ and benzoic acid, C_6H_5COOH.

(*iii*) Mesotartaric acid and *o*-chlorobenzoic acid.



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12. (*a*) Define the term neutralization equivalent of an acid. How many equivalents of NaOH would be neutralized by one mole of a polycarboxylic acid whose MW is 210 g/mol and NE is 70 g/eq. ?

(*b*) Can you predict the NE of melittic acid, $C_6(COOH)_6$?

13. Compare acetic acid and sodium acetate with respect to following properties.

(*a*) m.p. (*b*) b.p.

(*c*) Solubility in water and ether

(*d*) acidity and basicity.

14. Give schematic pathways for separation for each of the following mixtures.

(*a*) Caproic acid and ethyl carproate (*both liquids*).

(*b*) *n*-Butanoic acid and 1-hexanol (*both liquids*).

(*c*) Sodium benzoate and triphenylmethanol (*both solids*).

15. Benzoic acid and *o*-chlorobenzoic acid, both are water insoluble solids, and are separated by treatment with an aqueous solution of sodium formate. Explain.

SOLUTIONS

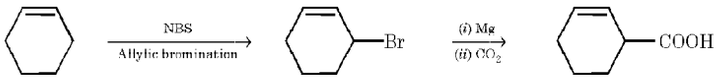
EXERCISE 17.1

1	(c)	**6**	(a)	**11**	(b)	**16**	(d)	**21**	(d)	**26**	(a)	**31**	(c)	**36**	(c)	**41**	(b)	**46**	(b)	**51**	(c)	**56**	(b)	**61**	(d)	**66**	(b)
2	(b)	**7**	(a)	**12**	(c)	**17**	(d)	**22**	(b)	**27**	(a)	**32**	(d)	**37**	(d)	**42**	(b)	**47**	(c)	**52**	(c)	**57**	(d)	**62**	(b)	**67**	(c)
3	(d)	**8**	(c)	**13**	(b)	**18**	(b)	**23**	(c)	**28**	(d)	**33**	(b)	**38**	(c)	**43**	(c)	**48**	(c)	**53**	(c)	**58**	(b)	**63**	(b)		
4	(b)	**9**	(b)	**14**	(b)	**19**	(c)	**24**	(c)	**29**	(a)	**34**	(d)	**39**	(b)	**44**	(b)	**49**	(b).	**54**	(b).	**59**	(c)	**64**	(b)		
5	(b)	**10**	(c)	**15**	(d)	**20**	(d)	**25**	(b)	**30**	(c)	**35**	(c)	**40**	(d)	**45**	(c)	**50**	(a)	**55**	(d)	**60**	(d)	**65**	(c)		

1. Here it is not essential to indicate the position (2) of the double bond, because no other position for the double bond is possible.

2. Since chloride is 3°, it will undergo elimination reaction with CN^- ion, hence route (*a*) can't be applied. Route (*b*) is a successful Grignard synthsis.

3. Neither method can be used because the halide is 3° and undergoes elimination reaction rather than substitution. Further, the presence of —OH group in the compound prevents the preparation of organometallic compound. A successful synthesis can be achieved by first protecting the OH group and then carrying carbonation.

4. 

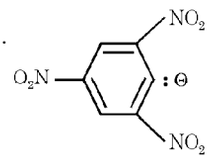
5. $CH_3CH_2CH_2CH_2OH$ or $CH_3CH_2CH(CH_3)OH \xrightarrow{H^+} \underset{\text{sec-Butyl cation}}{CH_3CH_2\overset{\overset{CH_3}{|}}{\overset{\ominus}{C}}H} \xrightarrow[H_2O]{CO} \underset{\text{2–Methylbutanoic acid}}{CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCOOH}$

6. The charged end loses CO_2 (for details, see mechanism in text).

7. Carbanion formed from simple carboxylate anions can't be stabilized, while other carbanions are quite stable.

$$CH_3CH_2CH_2COOH \rightleftharpoons CH_3CH_2CH_2COO^- \xrightarrow[-CO_2]{} \underset{\text{Not stable, hence not formed}}{CH_3CH_2CH_2^-}$$

8. Higher the stability of the carbanion formed after loss of CO_2, more will be the ease of decarboxylation. Carbanion from 2, 4, 6-trinitrobenzoic acid is stabilised by the dispersal of charge due to strong–I effect of the three —NO_2 groups



9. $\text{N.E. of acid} = \dfrac{\text{Wt. of acid} \times 1000}{\text{Molarity of NaOH} \times \text{Vol. of NaOH}} = \dfrac{0.187 \times 1000}{0.972 \times 18.7} = 103 \text{ g}$

Thus the equivalent wt. of the acid is 103 which coincides with the molecular/wt. (and eq. wt.) of ethoxyacetic acid, $C_2H_5OCH_2COOH$ (Mol. wt. and eq. wt. = 104).

10. $RCX_3 \xrightarrow{OH^-} RC(OH)_3 \xrightarrow[-H_2O]{} RCOOH$

11. $LiAlH_4$ reduces halides to alkanes.

12. (*i*) $CH_3CH_2COOH \xrightarrow[PCl_3]{Br_2} CH_3CH_2COCl \xrightarrow{Br_2} CH_3CH(Br)COCl \xrightarrow{H_2O} CH_3CH(Br)COOH.$

(*ii*) $CH_3CH_2COOH \xrightarrow[PBr_3]{Cl_2} CH_3CH_2COBr \xrightarrow{Cl_2} CH_2CHClCOBr \xrightarrow{H_2O} CH_3CH(Cl)COOH.$

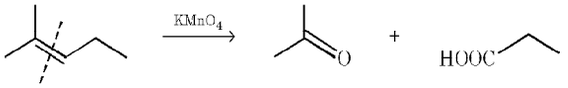
13. Precipitates in two cases is due to different compounds.

$\underset{\text{From propanoic acid}}{CH_3CH_2CH_2COO^-Ag^+}$ (Soluble in HNO_3) $\quad \underset{\text{From chloropropanoic acid}}{AgCl}$ (Insoluble in HNO_3)

14. Reduction of alkynes by Na-C_2H_5OH occurs in *trans*-manner.

15. B_2H_6 selectively reduces a carboxylic group in presence of an ester.

16. $CH_3CH_2CH_2CH_2OH \xrightarrow[-H_2O]{H^+} \underset{\text{1° Carbocation}}{CH_3CH_2CH_2\overset{+}{C}H_2} \xrightarrow{\text{rearranges}} \underset{\text{2° Carbocation}}{CH_3CH_2\overset{\overset{CH_3}{|}}{\overset{\oplus}{C}}H} \xrightarrow{CO} CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCOOH.$

17. 

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18. Hydrogen bonding is maximum in acids, and minimum in aldehydes.

19. In (*c*), weaker electron-withdrawing group (Br) is present maximum away from —COOH group.

20. Theoretical.

21. $CH_3CH_2\overset{O}{\overset{\|}{C}}—OH + NaH\overset{14}{C}O_3 \longrightarrow CH_3CH_2\overset{O}{\overset{\|}{C}}—O^-Na^+ + H_2O + {}^{14}CO_2$.

22. —COOH and —C ≡ CH are more acidic than enolic group = C(OH).

23. $CH_3COOH + HOOCCH_3 \xrightarrow{P_2O_5} CH_3COOCOCH_3 + H_2O$

24. $CH_3CH_2COOH \xrightarrow{\text{red } P/Cl_2} CH_3CHClCOOH \xrightarrow{\text{alc. KOH}} CH_2 = CHCOOH.$

25. $CH_3CHOH\,COOH \xrightarrow{KMnO_4/OH^-} CH_3COCOOH.$

26. An optically active reagent reacts with different rate with the two enantiomers, with the result the products formed will be unequal in amounts and hence mixture (product) will be optically active.

27. Steric factor is responsible for relative esterification.

28. $\underset{\text{Intermediate}}{CH_3CH_2CH_2CH_2OH} \xrightarrow{KMnO_4} \underset{P}{CH_3CH_2CH_2COOH}$

29. $\underset{[X]}{CH_3C \equiv CCH_3}$; $\underset{[Y]}{CH_3CH_2COCH_3}$; $\underset{[Z]}{CH_3CH_2COOH}$

30. Option (*i*) and (*ii*) will form CH_3COO^- ions, not free CH_3COOH.

31. $CH_2(COOH)_2 + P_2O_5 \xrightarrow{heat} \underset{\text{Carbon suboxide}}{O = C = C = C = O} + H_3PO_4$

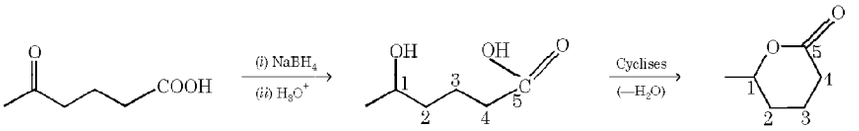
32. $\begin{matrix}CH_2COOH\\|\\CH_2COOH\end{matrix} \xrightarrow[\text{HVZ reaction}]{P/Br_2} \begin{matrix}CH_2COOH\\|\\BrCHCOOH\end{matrix} \xrightarrow{\text{alc. KOH}} \underset{\text{Maleic acid}}{\begin{matrix}CHCOOH\\\|\\CHCOOH\end{matrix}} \xrightarrow[\textit{anti}-\text{hydroxylation}]{CF_3CO_3H}$ *rac*-Tartaric acid.

33. Lesser the pK_a value, stronger is the acid. Benzoic acid is strongest because benzoate ion is highly stabilized by resonance.

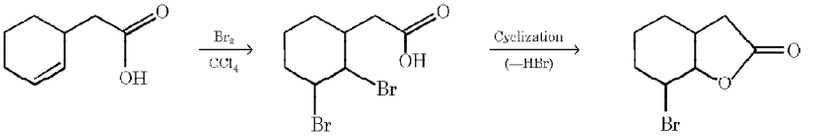
34. $Me_3\overset{+}{N}CH_2COOH$ is strongest acid, because of powerful – I effect of the $Me_3\overset{+}{N}—$ group , while Me_3CCH_2COOH is the least acidic because of powerful + I effect of the Me_3C — group.

35. $CH_3COOH + O = C = CH_2 \longrightarrow CH_3COOCOCH_3$.

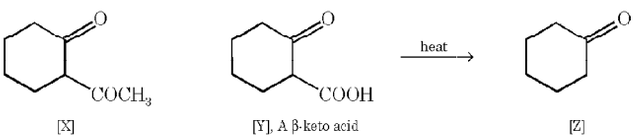
36. $NaBH_4$ reduces only C = O group and not —COOH group. The product formed undergoes cyclization to form γ-lactone (six-membered rings are formed easily).



37.



38.

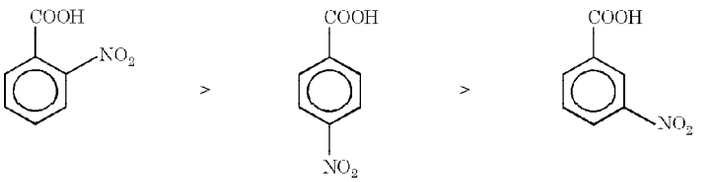


[X] [Y], A β-keto acid [Z]

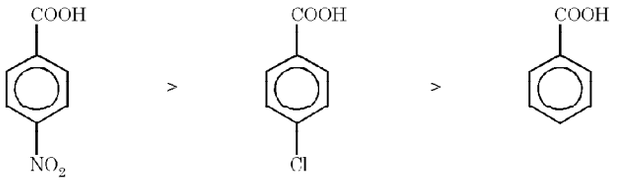
39. *tert*-Alkyl groups are resistant to oxidation.

40. The three —NO_2 (electron-withdrawing) groups in *o*- and *p*-positions make phenolic —OH group highly acidic. Moreover, the corresponding phenoxide is highly stable.

41. Lower the pK_a value higher is the acidity. The acidity of the three isomeric nitrobenzoic acids follows the order :



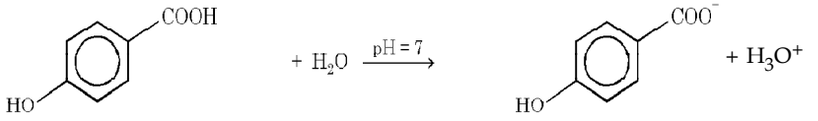
Due to ortho effect, –M effect., –I effect. Due to –M effect., –I effect. Only due to –I effect.

42. 

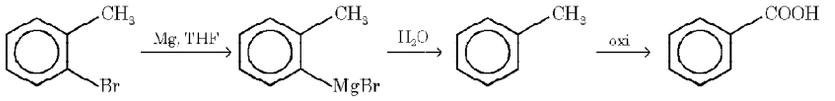
43. β-Keto carboxylic acids undergo decarboxylation very easily.

44. $C_6H_5CO\underset{\beta\text{-keto acid}}{\underset{|}{\overset{CH_3}{CH}}COOH} \xrightarrow{heat} C_6H_5CO\overset{CH_3}{\underset{|}{CH_2}}$

45. —COOH group when present along with activating group like —OH is easily eliminated as CO_2.

46. 

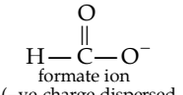
(—COOH is more acidic than phenolic group)

47. 

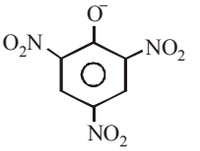
48. $C_6H_5COOH \xrightarrow{PCl_5} C_6H_5COCl \xrightarrow[AlCl_3]{C_6H_6} C_6H_5COC_6H_5 \xrightarrow[\text{Baeyer-Villiger oxidation}]{C_6H_5CO_3H} C_6H_5OCOC_6H_5$

49. —OH group is activating, hence electrophilic substitution will be taking place w.r.t. —OH. Future, bromine in CH_3COOH is a mild brominating agent, hence only monobromo product will be the main product. *p*-Substituted is major product due to steric factor.

51. **(c)** Conjugate bases of both of the compounds, formic acid and 2, 4, 6-trinitrophenol, are highly stable.



formate ion
(–ve charge dispersed due to resonance)



(–ve charge dispersed due to three electron-withdrawing $-NO_2$ groups)

52. **(c)** Phosphorus converts a little of the acid into acid chloride which is more reactive than the parent carboxylic acid. Thus it is the acid chloride, not the acid itself, that undergoes chlorination on the α-carbon.

$$CH_3CH_2COOH \xrightarrow{PCl_3 \text{ from } P+Cl_2} CH_3CH_2COCl \xrightarrow{Cl_2}$$

$$CH_3\overset{Cl}{\underset{|}{C}}HCOCl \xrightarrow{H_2O} CH_3\overset{Cl}{\underset{|}{C}}HCOOH$$

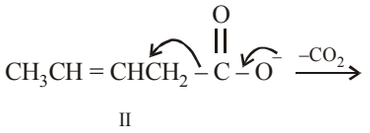
53. **(c)** 1, 6- and 1, 7-dicarboxylic acids on heating form cyclic ketones (Blanc rule)

54. **(b)** β-Keto carboxylic acids and β, γ-unsaturated carboxylic acids undergo decarboxylation easily because the corresponding carbanion is quite stable due to resonance.

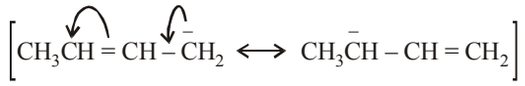
$$\underset{\text{III}}{CH_3-\overset{O}{\overset{||}{C}}-CH_2-COOH} \xrightarrow{-H^+} CH_3-\overset{O}{\overset{||}{C}}-CH_2-\overset{O}{\overset{||}{C}}-O^- \xrightarrow{-CO_2}$$

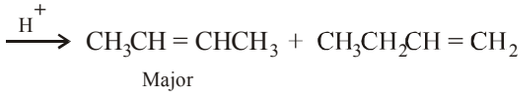
$$\left[CH_3-\overset{O}{\overset{||}{C}}-\overset{-}{C}H_2 \longleftrightarrow CH_3-\overset{O^-}{\overset{|}{C}}=CH_2\right] \xrightarrow{H^+}$$

$$CH_3-\overset{OH}{\overset{|}{C}}=CH_2 \rightleftharpoons CH_3-\overset{O}{\overset{||}{C}}-CH_3$$

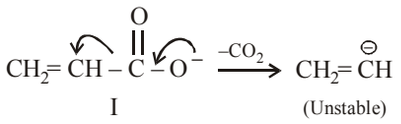


II



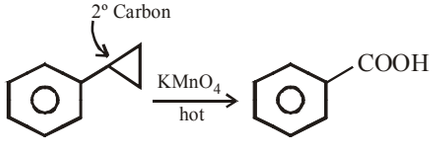


Major

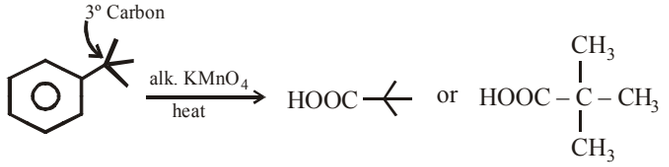


I (Unstable)

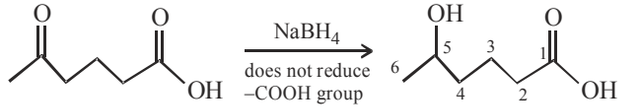
55. (d) If the key atom of the side chain of a benzene ring is 1° or 2°, it is oxidised to –COOH irrespective of its nature.



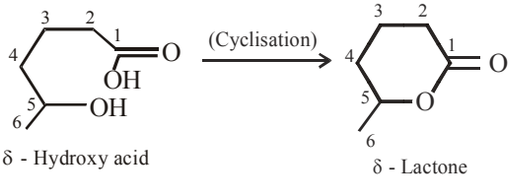
In case the key atom of the side chain is 3°, i.e. when it is not having any H, oxidation is very difficult. However, on vigorous oxidation, benzene ring is oxidised instead of side chain.



56. (b)



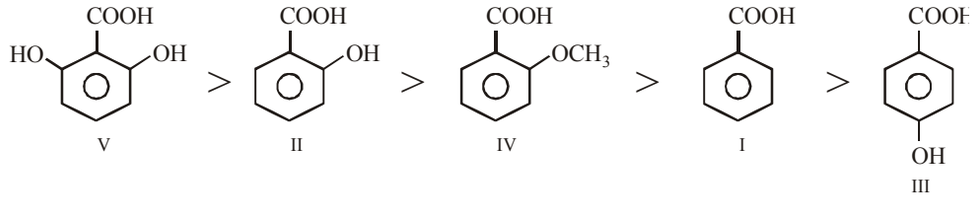
or



δ - Hydroxy acid

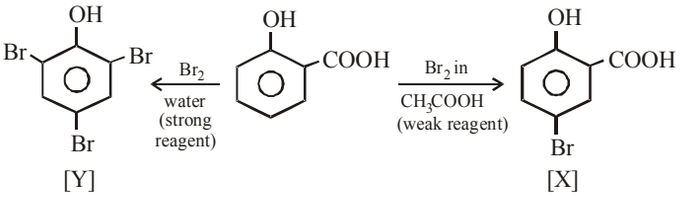
δ - Lactone

57. (d) V is most stable because its anion is stabilized to a greater extent through H – bonding with H atom of OH present on both *ortho*-positions ; followed by II in which one OH group is present. Compound IV comes next to II because here $-OCH_3$ group is present in *ortho* position which although is not capable of forming H–bonding yet more acidic than *p*-HOC_6H_4COOH (III) due to ortho effect. Compound III is less acidic than benzoic acid because of electron-releasing group in the para position. Thus



V II IV I III

58. **(b)** Note that when some activating group, e.g. –OH is present along with –COOH in ortho or para position substitution occurs with respect to –OH preferably at para position due to steric factors. In case the reagent used is strong, electrophile enters at all possible positions even with the replacement of –COOH group.

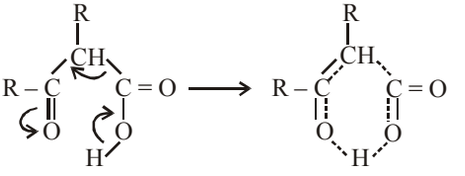


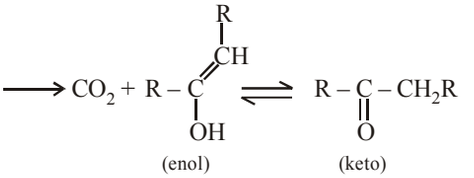
59. **(c)** $CH_3-\overset{\overset{O}{\|}}{C}-O-H \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-O^- + H^+$; $CH_3-\overset{\overset{O}{\|}}{C}-O-O-H \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-O-O^-$

Acetic acid → Conjugate base (Resonance possible, hence stable and weak base)

Peroxyacetic acid → Conjugate base (Resonance not possible, hence unstable and strong base)

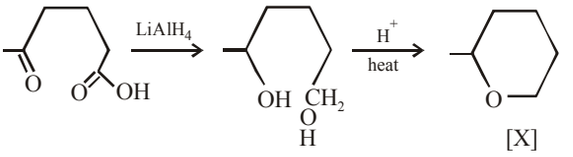
60. **(d)** Decarboxylation of β-keto acids involves transfer of the acidic hydrogen to the group followed by loss of CO_2 via a cylic six-membered transition state.

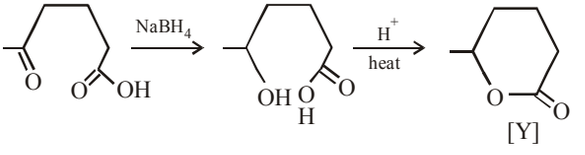




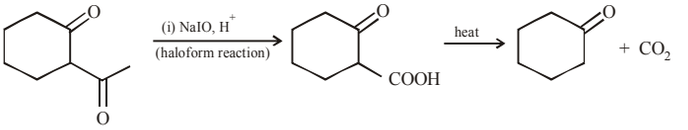
(enol) (keto)

61. **(d)** Remember that $LiAlH_4$ reduces both >C = O as well as –COOH to alcohols, while $NaBH_4$ reduces only $\rangle C = O$ without affecting –COOH.





66. **(b)**



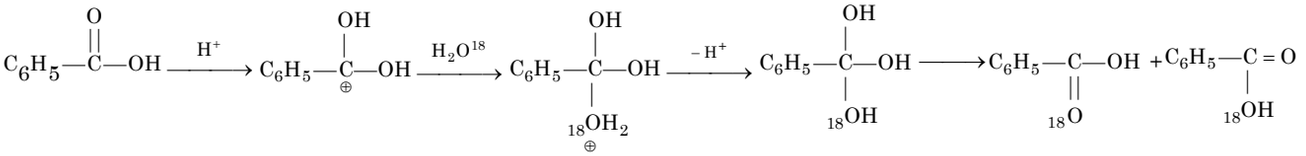
β-keto acid

67. (c) *o* - hydroxybenzoic acid is strongest acid and the decreasing order of acidity is

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EXERCISE 17.2

>1 CORRECT OPTION	1	(a,b)	2	(b, d)	3	(a,b,c)	4	(a,b,d)	5	(a,c,d)
	6	(b,c,d)	7	(a,c,d)	8	(b, c)	9	(a, c, d)	10	(a, b, d)
	11	(a, b, d)	12	(a, c)	13	(a, b, c, d)	14	(a, b, d)	15	(a, c, d)
	16	(a, c)	17	(b, c)	18	(a, b, d)	19	(a, b, c)	20	(b, c)
	21	(a, b, c, d)	22	(a, b)						
PASSAGE 1	23	(a)	24	(b)	25	(a)				
PASSAGE 2	26	(b)	27	(d)	28	(a)	29	(c)	30	(d)
PASSAGE 3	31	(c)	32	(d)	33	(b, a)	34	(b, a)		
MATCH THE FOLLOWING	35	(A) - b, (B) - b, (C) - a, (D) - c, d								
A/R	36	(b)	37	(a)	38	(a)	39	(b)	40	(a)
	41	(b)	42	(c)	43	(b)				
INTEGER	44	4								

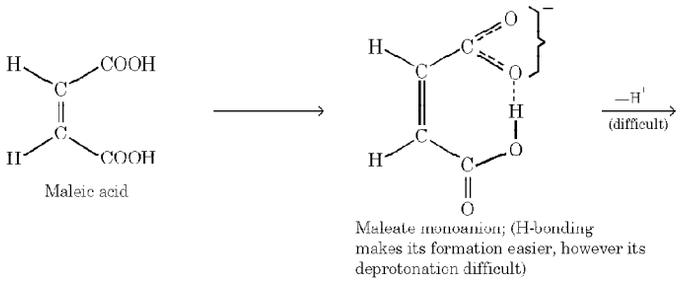
1. 

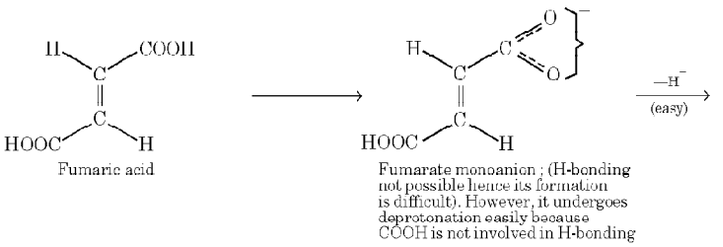
Remember that C—O^{18} bond is difficult to break than the C—O bond.

2. Theoretical.

3. Consult mechanism of the reaction in text.

4. Maleic acid is stronger because its monoanion is stabilized due to H-bonding between the *cis* COOH and COO^- ; while there is no such stabilization factor in fumarate monoanion (*trans* isomer), hence its formaton, *i.e.* dissociation of fumaric acid is less than that of maleic acid.

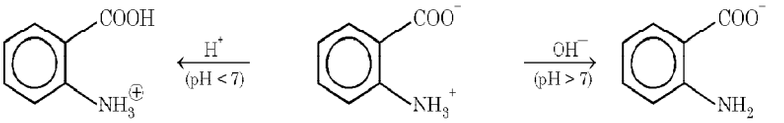




5. Diazomethane is used for methylating acidic groups ; compound (c) has enolic —OH group, hence it can also be methylated by CH_2N_2.

6. Dicarboxylic acids having two —COOH groups on the same carbon atom ; and β-keto acids are easily decarboxylated on heating.

7. When pH is greater than seven, medium is alkaline hence the Zwitterion of anthranilic acid is converted to an anion.



Cation, III Zwitterion, I (when pH = 7) Anion, II

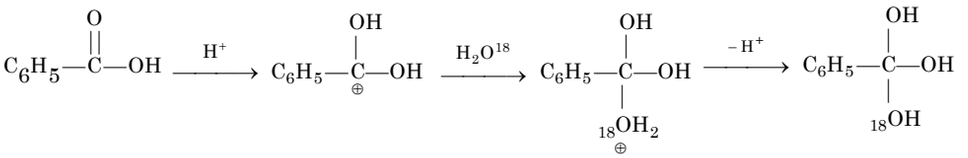
18. **(a,b,d)** Stronger the basic nature of the leaving group, weaker will be its leavability. In CH_3COOH, OH^- is a strong base so it can't be removed easily to form $CH_3\overset{+}{C}O$ required for acetylation (acylation).

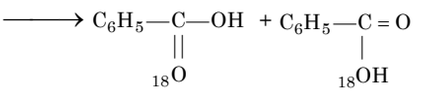
19. **(a,b,c)** Consult mechanism of the reaction in text.

20. (b,c)

21. **(a,b,c,d)**

22. **(a,b)**





Remember that C—O^{18} bond is difficult to break than the C—O bond.

31. **(c)** The HVZ reaction brings about halogenation only at the α-carbon of the fatty acid. In case the acid has two α-H's, α-dihalo product will be formed when 2 equivalents of halogen are used.

32. **(d)** The acid does not have an α–H, necessary for the reaction.

33–34.(b, a)

The α-halogen comes from halogen (Cl_2 or Br_2) whatever might the nature of PX_3 which is used for converting acid to acid halide.

41. (b)

42. **(c)** **The correct reason :** Carboxyl group only marginally decreases the electron density at *m*-position relative to *o*- and *p*-positions.

43. **(b)** **The correct explanation :** RCOCl, $(RCO)_2O$ and RCOOR' all add two molecules of Grignard reagents to give 3° alcohols.

44. **4.**

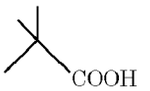
All carboxylic acids and phenols are soluble in aqueous NaOH. Four compounds are soluble in aqueous NaOH.

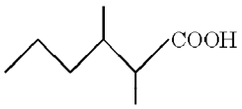
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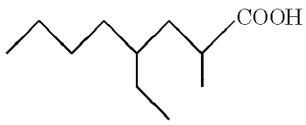
EXERCISE 17.3

1. (a) C-5 : n-Valeric, pentanoic C-6 : n-Caproic, hexanoic C-8 : n-Caprylic, octanoic
C-10 : *n*-Capric, decanoic C-12 : Lauric, dodecanoic.

(*b*) (*i*)  3-Methylbutanoic acid

(*ii*)  2, 2-Dimethylpropanoic acid

(*iii*)  2, 3-Dimethylhexanoic acid

(*iv*)  2-Methyl-4-ethyloctanoic acid

2. (*a*) $n\text{-}C_3H_7OH \xrightarrow{PBr_3} n\text{-}C_3H_7Br \xrightarrow[(ii)\ H^+]{(i)\ CN^-} n\text{-}C_3H_7COOH$

or $\xrightarrow{(i)\ Mg/ether,\ (ii)\ CO_2}$

(*b*) $CH_3COCH_2CH_2CH_3 \xrightarrow[\text{(haloform raction)}]{(i)\ NaOI^-, (ii)\ H^+} CHI_3 + CH_3CH_2COOH$

3. (*a*) $(n\text{-}C_4H_9COO)_3Al$ (*b*) $(n\text{-}C_4H_9COO)_2Ca$
(*c*) $n\text{-}C_4H_9COONH_4$ (*d*), (*f*), (*h*), (*i*) and (*j*) no reaction.
(*e*) $n\text{-}C_4H_9CH_2OH$ (*g*) $n\text{-}C_3H_7CHBrCOOH$
(*k*) $n\text{-}C_4H_9COOCH_2C_4H_9\text{-}n$.

4. (*i*) $C_6H_5CH_2COOH + SOCl_2 \longrightarrow C_6H_5CH_2COCl + SO_2\uparrow + HCl\uparrow$
(*ii*) $3C_6H_5CH_2COOH + PCl_3 \longrightarrow 3C_6H_5CH_2COCl + H_3PO_3$
(*iii*) $C_6H_5CH_2COOH + PCl_5 \longrightarrow C_6H_5CH_2COCl + POCl_3 + HCl$
(*iv*) $2C_6H_5CH_2COOH + (CH_3CO)_2O \longrightarrow C_6H_5CH_2COOCOCH_2C_6H_5 + 2CH_3COOH$
(*v*) $C_6H_5CH_2COOH + CH_3OH \xrightarrow{H_2SO_4} C_6H_5CH_2COOCH_3 + H_2O$
(*vi*) $C_6H_5CH_2COOH + NH_3 \longrightarrow C_6H_5CH_2COONH_4 \xrightarrow{\Delta} C_6H_5CH_2CONH_2 + H_2O.$

5. (*a*) $Me_2CHCOOH \xrightarrow{SOCl_2} Me_2CHCOCl \xrightarrow{NH_3} Me_2CHCONH_2$
(*b*) $Me_2CHCOOH \xrightarrow{LiAlH_4} Me_2CHCH_2OH$
(*c*) $Me_2CHCOOH + n\text{-}C_4H_9MgBr \longrightarrow n\text{-}C_4H_{10}$
(*d*) $Me_2CHCOOH \xrightarrow{Mg} (Me_2CHCOO)_2Mg.$

6. (*a*) $^{14}CO_2 + CH_3CH_2CH_2MgBr \longrightarrow CH_3CH_2CH_2{}^{14}COOH$

(*b*) $^{14}CO_2 + C_2H_5MgBr \longrightarrow C_2H_5{}^{14}COOH \xrightarrow{LiAlH_4} C_2H_5{}^{14}CH_2OH \xrightarrow{SOCl_2} C_2H_5{}^{14}CH_2Cl \xrightarrow[(i)\ H^+]{(i)\ CN^-} C_2H_5{}^{14}CH_2COOH$

(*c*) $^{14}CO_2 + CH_3MgBr \rightarrow CH_3{}^{14}COOH \xrightarrow{LiAlH_4} CH_3{}^{14}CH_2OH \xrightarrow[(ii)\ Mg]{(i)\ PBr_3} CH_3{}^{14}CH_2MgBr \xrightarrow[\text{oxide}]{\text{ethylene}} CH_3{}^{14}CH_2CH_2CH_2OH \xrightarrow{KMnO_4} CH_3{}^{14}CH_2CH_2COOH$

(*d*) $^{14}CH_3OH \xrightarrow[(ii)\ Mg]{(i)\ PBr_3} {}^{14}CH_3MgBr \xrightarrow{HCHO} {}^{14}CH_3CH_2OH \xrightarrow[(ii)\ Mg]{(i)\ PBr_3} {}^{14}CH_3CH_2MgBr \xrightarrow[\text{oxide}]{\text{ethylene}} {}^{14}CH_3CH_2CH_2CH_2OH \xrightarrow{KMnO_4} {}^{14}CH_3CH_2CH_2COOH$

7. It is advisable to proceed backward.

(*a*) $C_6H_5\underset{\displaystyle Br}{\underset{|}{CH}}COOH \xleftarrow{P,Br_2} C_6H_5CH_2COOH \xleftarrow[(ii)\ H_3O^+]{(i)\ CN^-} C_6H_5CH_2Cl \xleftarrow{Cl_2,\ heat} C_6H_5CH_3$

(*b*) $C_6H_5\underset{\displaystyle CH_3}{\underset{|}{C}}HCOOH \xleftarrow{CO_2} C_6H_5\underset{\displaystyle CH_3}{\underset{|}{C}}HMgCl \xleftarrow{Mg} C_6H_5\underset{\displaystyle CH_3}{\underset{|}{C}}HCl \xleftarrow{HCl} C_6H_5\underset{\displaystyle CH_3}{\underset{|}{C}}HOH$

$C_6H_6 \xrightarrow[FeCl_3]{Br_2} C_6H_5Br \xrightarrow{Mg} C_6H_5MgBr \xrightarrow{CH_3CHO}$ (product as above)

(*c*) $CH_3CH_2CH=CHCOOH \xleftarrow{\text{alc. KOH}} CH_3CH_2CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCOOH \xleftarrow{P,\ Br_2} CH_3CH_2CH_2CH_2COOH$

$CH_3CH_2CH_2CH_2OH \xrightarrow[(ii)\ Mg]{(i)\ PBr_3} CH_3CH_2CH_2CH_2MgBr \xrightarrow{CO_2}$ (product as above)

8. (*a*) (*i*) $H_2SO_4 > CH_3COOH > H_2O > C_2H_5OH > CH\equiv CH > NH_3 > C_2H_6$

(*ii*) $HOOCCH_2COOH > HOOCCH_2CH_2COOH > CH_3COOH$

(*b*) The weaker the acid , the more basic will be its anion.

$NaC_2H_5 > NaNH_2 > NaC\equiv CH > NaOC_2H_5 > NaOH > NaOOCCH_3 > NaHSO_4$

9. (*a*) $CH\equiv CH \xrightarrow{CH_3MgBr} \underset{A}{HC\equiv CMgBr} \xrightarrow[(ii)\ H^+]{(i)\ CO_2} \underset{B}{HC\equiv CCOOH} \xrightarrow{H_2SO_4/HgSO_4}$

$\underset{OH}{HC=CHCOOH} \xrightarrow{\text{tautomerises}} \underset{O}{HC(=O)-CH_2-COOH} \xrightarrow{KMnO_4} \underset{C}{CH_2(COOH)_2}$

Note that compound B on hydration may also give ketone but it will not be oxidised to malonic acid, C.

$HC\equiv CCOOH \xrightarrow{H_2SO_4/HgSO_4} H_2C=\underset{OH}{CCOOH} \xrightarrow{\text{tautomerises}} H_3C-\underset{O}{C(=O)}-COOH \xrightarrow{KMnO_4} CH_3COOH$

(*b*) $CH_3COOH \xrightarrow{LiAlH_4} \underset{A}{CH_3CH_2OH} \xrightarrow{HBr} \underset{B}{CH_3CH_2Br} \xrightarrow[(ii)\ CO_2]{(i)\ Mg} \underset{C}{CH_3CH_2COOH} \longrightarrow \underset{D}{CH_3CH_2COOAg} \xrightarrow{Br_2} \underset{E}{CH_3CH_2Br}$

10. Excess or limited amount of CH_3MgBr forms CH_4, while excess of CH_3Li forms ketone.

(*i*) $CH_3CH_2COOH + CH_3MgBr \longrightarrow CH_4\uparrow + CH_3CH_2COO^-(MgBr)^+$

(*ii*) $CH_3CH_2COOH + CH_3Li \longrightarrow CH_4\uparrow + CH_3CH_2COO^-Li^+$

Since Li is more electropositive than Mg, R from R—Li will bear a more negative charge than R from R—MgX, hence RLi is a stronger nucleophile and capable of adding to the C = O of —COO^-.

$CH_3CH_2\overset{O}{\overset{\|}{C}}-O^-Li^+ \xrightarrow{CH_3Li} CH_3CH_2\underset{CH_3}{\underset{|}{C}}(\overset{\bar{O}Li^+}{\overset{|}{}})-O^-Li^+ \xrightarrow{H_2O} CH_3CH_2\underset{CH_3}{\underset{|}{C}}(OH)-OH \xrightarrow{-H_2O} CH_3CH_2\underset{CH_3}{\underset{|}{C}}=O$

11. (*a*) (*i*) *n*-Butanoic acid gives effervescences of CO_2 with aq. $NaHCO_3$ solution.

(*ii*) Butanal gives a silver mirror on addition of Tollen's reagent, $[Ag(NH_3)_2]^{2+}$ (a solution of $AgNO_3$ in aq. NH_3).

(*iii*) *n*-Butanol evolves H_2 with metallic sodium.

(*iv*) Ether (methyl ethyl ether) dissolves in conc. H_2SO_4 with the evolution of heat.

(*v*) Alkane (butane) remains inert to all tests.

(*b*) (*i*) Formic acid (HCOOH) has an aldehydic type of hydrogen, hence it is readily oxidized by acidified $KMnO_4$ (indicated by decolourization of purple colour), and Tollen's reagent (indicated by formation of silver mirror).

(*ii*) Oxalic acid (HOOCCOOH) is oxidized by acidic $KMnO_4$, again indicated by decolourization of purple colour. Malonic acid loses CO_2 (*g*), on heating.

(*iii*) Here aq. $NaHCO_3$ solution will give CO_2 with both (acid chlorides are readily hydrolysed in alkaline as well as acidic medium), hence $AgNO_3$ solution in presence of HNO_3 should be used which will give white precipitate of AgCl with CH_3CH_2COCl insoluble in HNO_3.

(*c*) (*i*) $KMnO_4$ or Br_2/CCl_4 (*ii*) CrO_3/H_2SO_4 (positive for mandelic acid)

(*iii*) Hot $KMnO_4$ (positive for mesotartaric acid) ; elemental analysis for chlorine (positive for *o*-chlorobenzoic acid).

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12. (*a*) Neutralization equivalent (NE) is the equivalent weight (g/eq.) of an acid as determined by titration with standard NaOH solution.

No. of eq of NaOH = No. of ionizable H's (No. of eq of acid)

$$= \frac{MW}{NE} \quad (\because \text{ NE = ME/No. of ionizable H's})$$

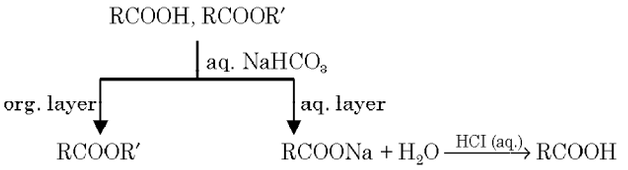
$$= \frac{210 \text{ g / mol}}{70 \text{ g / eq}} = \textbf{3 eq / mol}$$

(*b*) $$NE = \frac{MW}{\text{No. of ionizable H'S}} = \frac{342 \text{ g / mol}}{6 \text{ eq / mol}} = \textbf{57 g/eq}$$

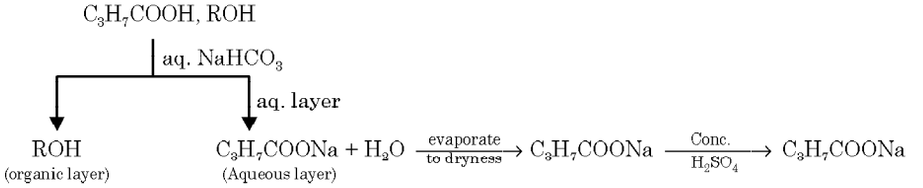
13. **Acetic acid.** Low m.p. ; low b.p. , soluble in water as well as in ether, stronger acid and weaker base.

Sodium acetate. High m.p. (decomposes), high b. p. (*d*), soluble in water, insoluble in ether, weaker acid and stonger base.

14. (*a*)

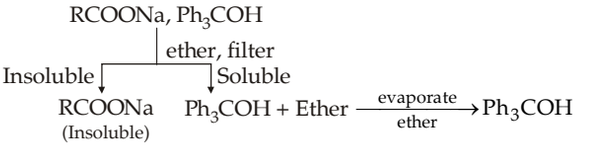


(*b*)



Butyric acid is very much soluble in water, hence water should be evaporated from the aqueous solution.

(*c*)

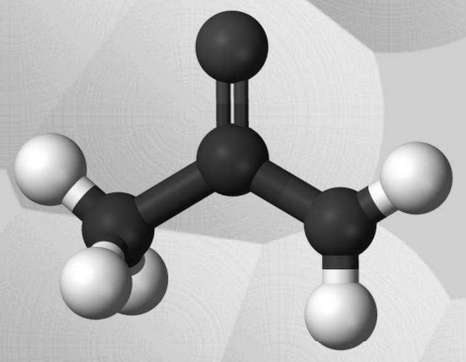


15. Separation by sodium formate is similar like that by sodium bicarbonate ; sodium formate is so selected because formic acid is stronger than benzoic acid and weaker than *o*-chlorobenzoic acid.

$$\underset{\text{Weaker acid}}{C_6H_5COOH} + \underset{\text{Weaker base}}{HCOO^-} \rightleftharpoons \underset{\text{Stronger base}}{C_6H_5COO^-} + \underset{\text{Stronger acid}}{HCOOH}$$

$$o\text{-}ClC_6H_4COOH + HCOO^- \rightleftharpoons o\text{-}ClC_6H_4COO^- + HCOOH$$

Stronger acid Stronger base Weaker base Weaker acid



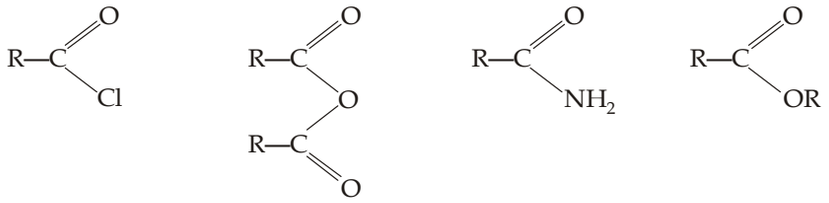
18

Functional Derivatives of Carboxylic Acids

CHAPTER HIGHLIGHTS

18.1 Structure of Carboxylic Acid Derivatives
18.2 Nucleophilic Acyl Substitution
18.3 Preparation of Acid Derivatives
18.4 Properties of Acid Derivatives
18.5 Cyclic Esters or Lactones
18.6 Analysis of Carboxylic Acid Derivatives
18.7 Illustrative Examples
EXERCISE
SOLUTIONS

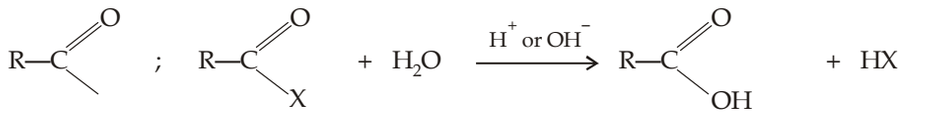
Four closely related functional derivatives of carboxylic acids are obtained by replacing —OH of the carboxylic group by —Cl, —OCOR, —NH_2, or —OR.



Acid chloride | Acid anhydride | Amide | Ester

They all contain the **acyl group** $\left[R-\overset{\overset{O}{\|}}{C}-\right]$, and may be hydrolyzed to the parent acid using dilute OH^- or H_3O^+

.



Acyl group | Carboxylic acid derivative | Water | Carboxylic acid | Conjugate acid of leaving group

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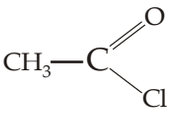
Acid derivatives are named from either the common name or the IUPAC name of the corresponding carboxylic acid. For example, four derivatives of acetic acid, CH_3COOH (IUPAC name : ethanoic acid) are named as below.

(*a*) **Acid chlorides.** Change *–ic acid* to *–yl chloride.*

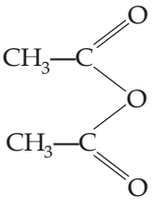
(*b*) **Acid anhydrides.** Change *acid* to *anhydride.*

(*c*) **Acid amides.** Change *–ic acid* of common name (or *–oic acid* of IUPCA name) to *–amide.*

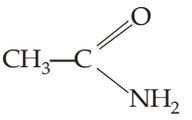
(*d*) **Esters.** Change *–ic acid* to *–ate*, preceded by name of alcohol or phenol group.

(*a*) 

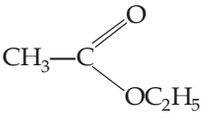
Acetyl chloride
(Ethanoyl chloride)

(*b*) 

Acetic anhydride
(Ethanoic anhydride)

(*c*) 

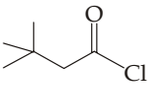
Acetamide
Ethanamide

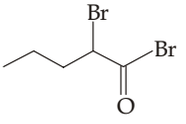
(*d*) 

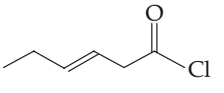
Ethyl acetate
Ethyl ethanoate

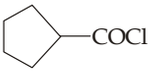
TEST YOUR UNDERSTANDING - 18.1

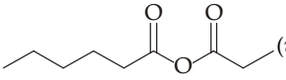
1. Write IUPAC names of the following :

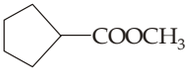
(*i*) 

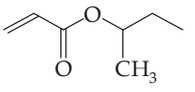
(*ii*) 

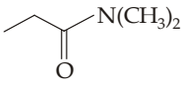
(*iii*) 

(*iv*) 

(*v*) 

(*vi*) 

(*vii*) 

(*viii*) 

(*ix*) $CH_3NHCONHCH_3$ (*x*) $(CH_3)_2NCONH_2$

2. Write structural formula for each of the two following compounds.

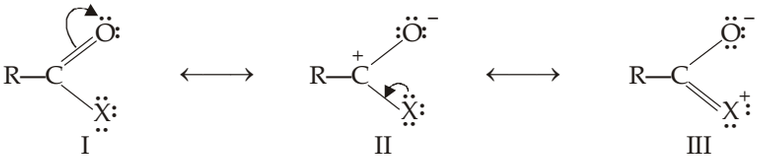
(*i*) 2-Phenylbutanoyl chloride (*ii*) 2-Phenylbutanamide (*iii*) 2-Phenylbutanoic anhydride

(*iv*) N-Ethyl-2-phenylbutanamide (*v*) Butyl-2-phenylbutanoate (*vi*) 2-Phenylbutyl butanoate.

3. Why nitriles are often classified as acid derivatives ?

18.1 Structure of Carboxylic Acid Derivatives

Like other carbonyl containing compounds (aldehydes, ketones and carboxylic acids), derivatives of carboxylic acids have a planar arrangement of bonds to their carbonyl group. An important structural feature of these derivatives is that the atom attached to the acyl carbon bears an unshared pair of electrons that is capable of interacting with the carbonyl π system.



I II III

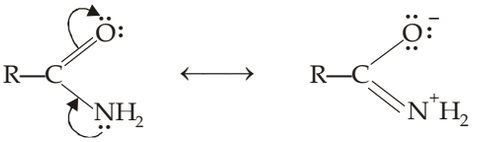
This interaction of the unshared electron pair (structures II and III) stabilizes the carbonyl group and decreases its electrophilic character. The extent of this electron delocalization due to X dependes upon the nature of the substituent X. More is the electronegativity of X, lesser is the electron donation to the carbonyl group and thus lesser will be the stabilizing effect ; consequently more will be electrophilic character of the carbonyl group and hence higher will be the reactivity of the derivative toward nucleophiles.

The atom X in acid chlorides, acid anhydrides, esters and amides is Cl, O, O and N respectively. Since electronegativity of these atoms follows the order Cl > O > N, we can say that carbonyl group of acid chlorides are weakly stabilized, while that of acid amides are greatly stabilized due to resonance.



Acid chloride

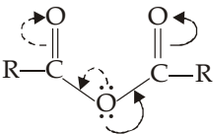
Weak resonance stabilization due to —I effect of chlorine as well as poor overlaping of 3*p* orbital of Cl with the *p* orbital of the carbonyl carbon.



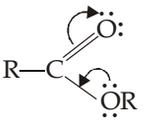
Acid amide

Very effective resonance stabilization due to least —I effect of N as well as better overlaping of 2*p* orbital of N with *p* orbital of carbonyl carbon

As far as acid anhydrides and esters are concerned, carbonyl group of an ester is stabilized more than that of an acid anhydride because in acid anhydride there is a competition between two acyl groups for the oxygen lone pair, with the result each carbonyl group is stabilized less than the single carbonyl group of an ester.



Acid anhydride
(Each carbonyl group is less stabilized than that of an ester)



Ester
(Carbonyl group is more stable)

Thus the relative stability of the carbonyl group of the four acid derivatives follows the order.

Acid chloride < Acid anhydride < Ester < Amide

Hence electrophilic character of the carbonyl group of these derivatives will be

Acid chloride > Acid anhydride > Ester > Amide

(Decreasing electrophilic character (and hence reactivity toward nucleophiles of the carbonyl group)

Carbonyl group of carboxylate anion is extremely stabilized because the negatively charged oxygen (substituent X) is a powerful electron donor to the carbonyl group, hence carboxylates do not react with nucleophiles.



Relative stability and reactivity of carboxylic acid derivatives.

Derivative	*Formula*	*Stabilization*	*Relative Rate of hydrolysis*
Acid chloride	RCOCl	Very Small	10^{11}
Anhydride	$(RCO)_2O$	Small	10^{7}
Ester	RCOOR	Moderate	1.0
Amide	$RCONH_2$	Large	$< 10^{-2}$
Carboxylate anion	$RCOO^-$	Very large	

Rates are relative to ester as standard substrate at pH 7.

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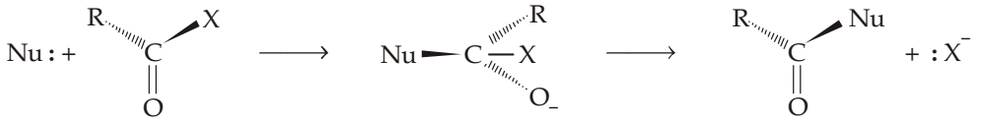
18.2 Nucleophilic Acyl Substitution

As in aldehydes and ketones, the carbonyl group in carboxylic acids and their derivatives performs two functions.

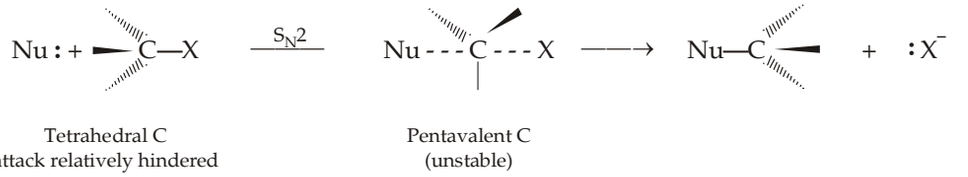
(*i*) It provides a site for nucleophilic attack.

(*ii*) It increases the acidity of α-hydrogens. This aspect is partly discussed in carboxylic acids and will be further discussed at a later stage.

Acyl compounds (carboxylic acids and their derivatives) typically undergo nucleophilic substitution in which —OH, —Cl, —OCOR, —OR, or —NH_2 is replaced by some other basic group, of course stronger than the group to be removed. Substitution at acyl carbon takes place much more readily than at a saturated carbon atom, *i.e.* at alkyl carbon in alkyl halides, R—X. Greater reactivity of carbonyl group toward nucleophiles is due to both electronic and steric factors : (*a*) the capability of oxygen to acquire electrons, and (*b*) the relatively unhindered transition state leading to tetrahedral intermediate from the trigonal reactant.

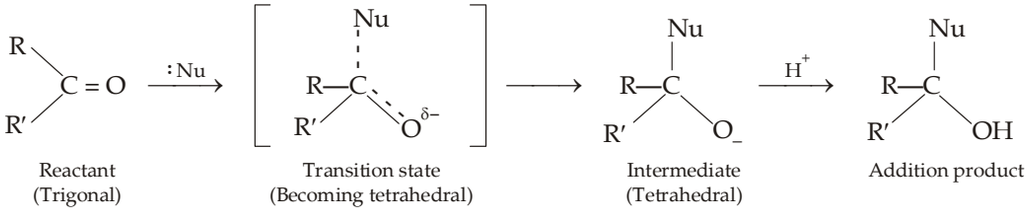


Acyl nucleophilic substitution

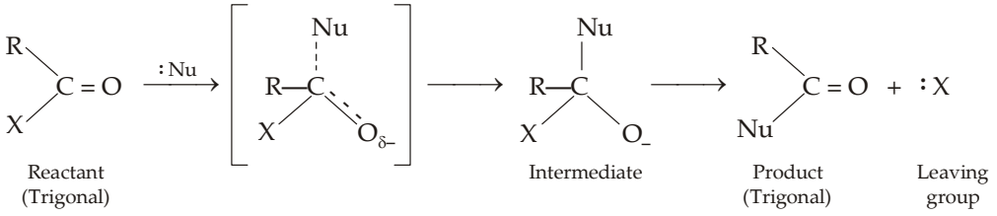


Alkyl nucleophilic substitution.

Thus toward nucleophiles, acid chlorides are more reactive than alkyl chlorides, amides are more reactive than amines, and esters are more reactive than ethers. Nucleophilic substitution at acyl carbon (nucleophilic addition-elimination) is similar to some extent (first step or initial step) to the nucleophilic addition to aldehydes and ketones. The two reactions differ in the second step. The tetrahedral intermediate from an aldehyde or ketone accepts a proton to form a stable **addition product**. In contrast, the tetrahedral intermediate from an acyl compound eliminates a leaving group leading to regeneration of the carbon oxygen double bond (a trigonal compound) and thus the net result is a **substitution product**. Therefore, the overall process in the case of acyl substitution occurs by a **nucleophilic addition-elimination** mechanism.



Nucleophilic addition on aldehydes and ketones



Nucleophilic addition-elimination on acyl compounds.

Now the question arises why the two classes of compounds differ in their reaction toward nucleophiles. The difference lies in the nature of the substituent present on acyl carbon ; in aldehydes and ketones, this substituent (R′) is either H or an alkyl group while in acyl compounds, it (X) is OH (in carboxylic acids), Cl (in acid chlorides), OCOR, COR, or NH_2. The ease with which, **:**X is lost depends upons its basicity ; *the weaker the base, the better the leaving group.* For acid chloride, acid anhydrides, esters, and amides, **:**X is respectively

$$\underset{\text{very weak base}}{Cl^-}\ ,\ \underset{\text{moderately weak base}}{{}^-OOCR}\ ,\ \underset{\text{strong base}}{{}^-OR}\ \text{and}\ \underset{\text{stronger base}}{{}^-NH_2}$$

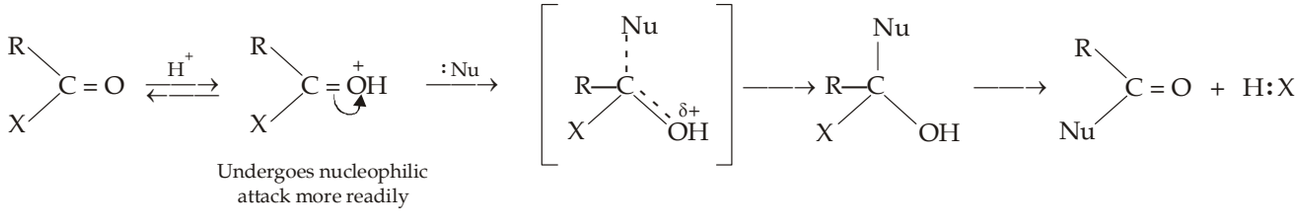
Hence Cl^- is lost with maximum ease and hence acid chlorides are the most reactive, while NH_2^- is lost with the most difficulty hence acid amides are the least reactive toward nucleophilic substitution. In general, the overall order of reactivity is

$$\underset{\text{Acid chloride}}{RCOCl} > \underset{\text{Acid anhydride}}{RCOOCOR} > \underset{\text{Ester}}{RCOOR'} > \underset{\text{Amide}}{RCONH_2}$$

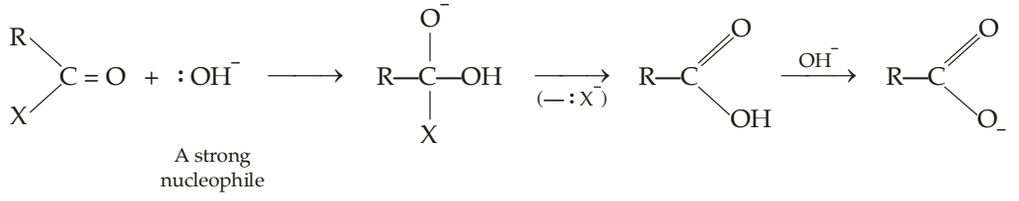
For an aldehyde or ketone to react by nucleophilic addition-eliminiation way, their intermediate would have to eliminate a hydride ion ($H:^-$) or an alkanide ion ($R:^-$), both of which are the strongest bases of all and hence very poor leaving groups. Thus the intermediates of aldehydes and ketones undergo addition reaction. Remember that alkanide ion from the haloform reaction behaves as a good leaving group, this is because here the leaving group is a weakly basic trihalomethyl anion, $X_3C:^-$.

Thus nucleophilic acyl substitution proceeds by two steps. Generally, the overall rate is affected by the rate of both steps, but the first step (formation of tetrahedral intermediate) is more important. As in nucleophilic additions on aldehydes and ketones, here also the first step is (*a*) favoured by electron withdrawal, which stabilizes the developing negative charge in the transition state, and (*b*) hindered by the presence of bulky groups, which become crowded together in the transition state. The second step depends on the basicity of the leaving group, **:**X (weaker a base, more readily it will be lost).

Acyl nucleophilic substitution takes place readily and even by weaker nucleophiles in presence of acid because protonation of carbonyl oxygen makes carbonyl carbon more electrophilic and hence more reactive toward nucleophile. Futher, here oxygen can now acquire π electrons without having a negative charge.



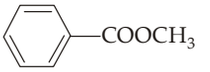
Thus we can explain why acid derivatives are hydrolyzed more readily in acidic solution (here **:** Nu is H_2O**:**) than in neutral medium. Acid derivatives are also more readily hydrolyzed in alkaline medium than in neutral medium. Here the reason being the fact that the alkaline solutions provide a strong nucleophile (OH^-).



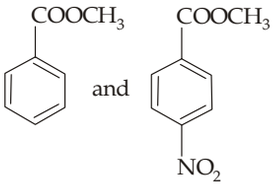
TEST YOUR UNDERSTANDING - 18.2

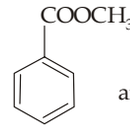
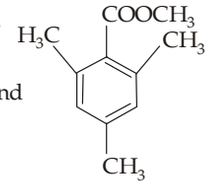
1. Which of the compound of each pair undergoes hydrolysis rapidly ?

(*i*) Cl_3CCOCl and F_3CCOCl.

(*ii*) CH_3COOCH_3 and 

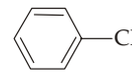
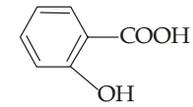
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(*iii*)  and

(*iv*)  and 

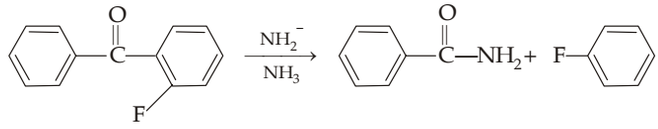
(*v*) CH_3COOCH_3 and $CH_3CONHCH_3$.

2. Give the structure of the product obtained when each of the following compound is treated with ammonia.

(*i*) $CH_3CHClCOOH$ (*ii*) $ClCH_2COCl$ (*iii*)  (*iv*) 

3. Although ketones do not undergo nucleophilic substitution, following reactions occur. Explain.

(*i*) $RCOCCl_3 \xrightarrow{OH^-} RCOOH + CHCl_3$

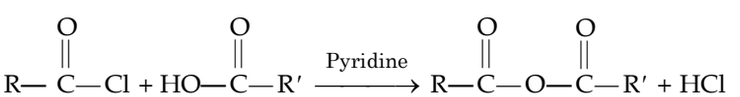
(*ii*) 

18.3 Preparation of Acid Derivatives

We will come across many instances where one acid derivative is converted into other. The order of reactivity (or the stabilization order) of acid derivatives given earlier gives us a clue as to which syntheses are practical and which are not. In general, **a more stable (less reactive) acyl compound can be synthesised from less stable (more reactive), but the reverse is usually difficult** *and, when possible, requires special reagents*. For example, an ester can be made from the corresponding acid chloride or anhydride, but not from amide. In general, for synthesis of acid derivatives by acyl transfer the reactant must have a better leaving group at the acyl carbon than the product.

(*a*) **Preparation of acid chlorides**. Since acyl chlorides are the most reactive of the acid derivatives, we must use special reagents to prepare them. We use acid chlorides of inorganic acids, *viz* PCl_5 (an acid chloride of phosphoric acid), PCl_3 (an acid chloride of phosphorous acid), and thionyl chloride (an acid chloride of sulphurous acid). Reactions have already been given in properties of carboxylic acids. All of these reactions are examples of acyl nucleophilic substitution reactions.

(*b*) **Preparation of acid anhydrides.** Of the four carboxylic acid derivatives, acid anhydrides are less reactive (*i.e.* more stable) only from acid chlorides ; hence acid anhydrides can be prepared only from acid chlorides.



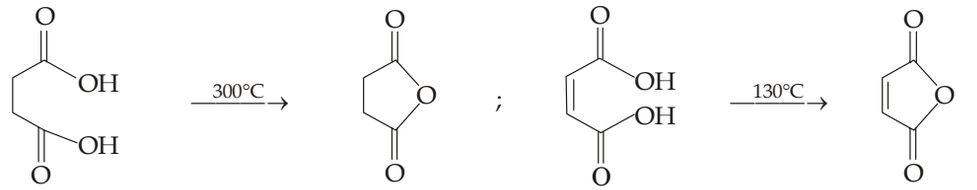
This method is applicable to the preparation of both symmetrical (R and R′ are same) and mixed anhydrides.

Sodium salts of carboxylic acids also react with acyl chlorides to give anhydrides.

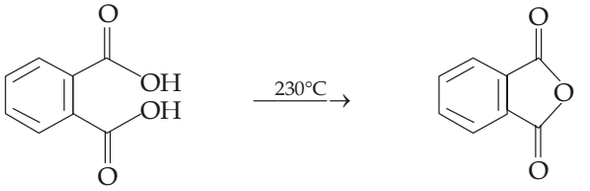


In this reaction a carboxylate anion acts as a nucleophile and brings about nucleophilic substitution at the acyl carbon of the chloride.

Cyclic anhydrides can sometimes be prepared by simply heating the appropriate dicarboxylic acid. However, this method succeeds, only when anhydride formation leads to a five- or six -membered ring.



Succinic acid — Succinic anhydride — Maleic acid — Maleic anhydride



Phthalic acid — Phthalic anhydride

TEST YOUR UNDERSTANDING - 18.3

1. Explain the following.

(*a*) Adipic acid (1, 6-hexanedioic) does not form a cyclic anhydride on heating, but forms a cyclic ketone ; while suberic acid (1, 8-octanedioic acid) does not form a cyclic ketone.

(*b*) Benzoic anhydride is formed in excellent yield by adding one molar equivalent of water to two molar equivalents of benzoyl chloride.

The most important member of acid anhydrides, **acetic anhydride**, is prepared by the reaction of acetic acid with **ketene**, $CH_2 = C = O$, which itself is prepared by high temperature dehydration of acetic acid.

$$CH_3COOH \xrightarrow[(-H_2O)]{AlPO_4,\,700°C} CH_2 = C = O \xrightarrow{CH_3COOH} \underset{\text{Acetic anhydride}}{(CH_3CO)_2O}$$

(*c*) Preparation of esters. Esters are usually prepared by the reaction of alcohols (or phenols) with acids or acid chlorides.

1. **From carboxylic acids** (*esterification*). Carboxylic acids react with alcohols to form esters through a condensation reaction known as **esterification**, or **Fischer esterification**.

$$R{-}\overset{\overset{O}{\|}}{C}{-}OH + R'{-}OH \underset{}{\overset{HA}{\rightleftharpoons}} R{-}\overset{\overset{O}{\|}}{C}{-}OR' + H_2O$$

Esterifications are acid catalyzed (conc. H_2SO_4 or HCl), and proceed very slowly in the absence of strong acids. Since the reaction is reversible, the yield of ester can be increased in two manners. (For details, consult chapter on "Carboxylic Acids").

(*a*) By using excess of either the carboxylic acid or the alcohol depending on the availability and cost.

(*b*) By removing water from the reaction mixture as soon as it is formed .

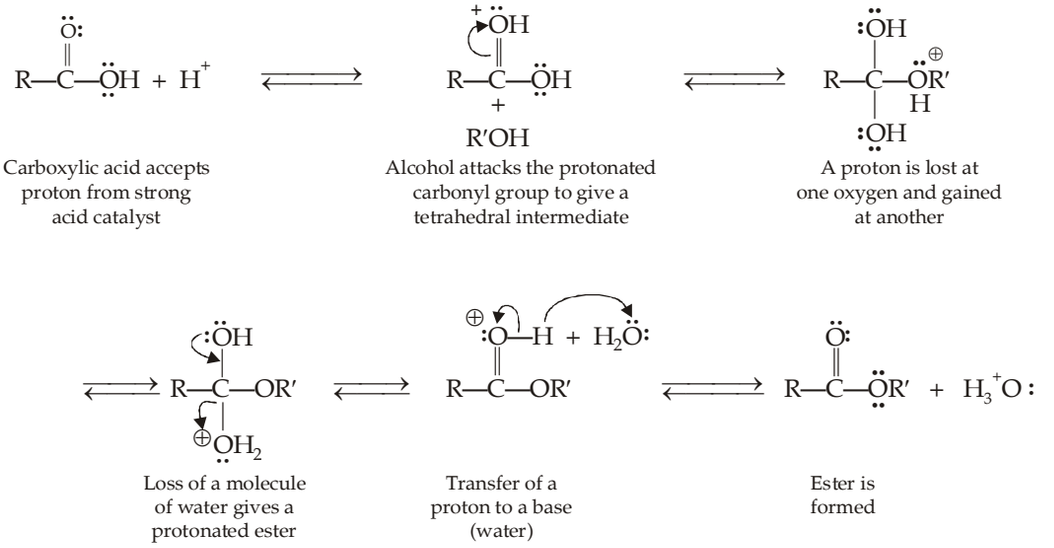
Mechanism of esterification. This is a typical mechanism of acid-catalyzed nucleophilic addition-elimination at acyl carbon atom.

An important question about the mechanism of acid-catalyzed esterification is the origin of alkoxy oxygen of the ester, *i.e.* whether it is coming from carboxylic acid or alcohol. In other words whether it is the C—O bond of the alcohol or of the carboxylic acid that is broken during esterification. It has been proved by isotopically labelled experiment that the C—O bond of the carboxylic acid is broken .

$$C_6H_5{-}\overset{\overset{O}{\|}}{C}{-}OH + CH_3{-}\overset{18}{O}{-}H \underset{}{\overset{HA}{\rightleftharpoons}} C_6H_5{-}\overset{\overset{O}{\|}}{C}{-}\overset{18}{O}{-}CH_3 + H_2O$$

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The essential steps of the mechanisum are summarised below



Salient features of acid-catalyed esterification

(*i*) All steps of the reaction are reversible, so steps leading to forward reaction constitute mechanism of *acid-catalyzed esterification of an acid*. However, the reverse steps of the reaction constitute the *mechanism of acid catalyzed hydrolysis of an ester.*

(*ii*) The reaction can be forced to proceed in a particular direction by changing the conditions. The reaction can be forced to esterification by taking excess of alcohol and removing water (product) as soon as it is formed. On the other hand, for carrying out the reverse reaction (*i.e.* for acidic hydrolysis of an ester), large excess of water should be used, *i.e.* the ester is refluxed with dilute aqueous HCl or dil. aqueous H_2SO_4.

(*iii*) Both reactions *i.e.* acid-catalyzed esterification of an acid as well as acid-catalyzed hydrolysis of an ester are affected by steric factors.

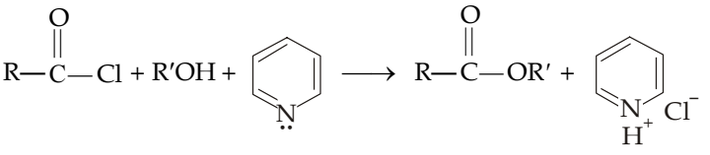
(*iv*) Mineral acid speeds up both processes by protonating carbonyl oxygen and thus rendering carbonyl carbon more susceptible to nucleophilic attack. In esterification, the nucleophile is an alcohol molecule and the leaving group is a water molecule ; in acidic hydrolysis, the roles are exactly reversed.

(*v*) Both processes involve similar type of C—O cleavage (*acyl-oxygen cleavage*).

Esterification. $C_6H_5—C(=O)—O—H + CH_3—O(^{18})—H \underset{}{\overset{H^+}{\rightleftharpoons}} C_6H_5—C(=O^{18})—OCH_3 + H_2O$

Hydrolysis. $C_6H_5—C(=O)—OCH_3 + H—O(^{18})—H \overset{H^+}{\rightleftharpoons} C_6H_5—C(=O^{18})—OH + CH_3OH$

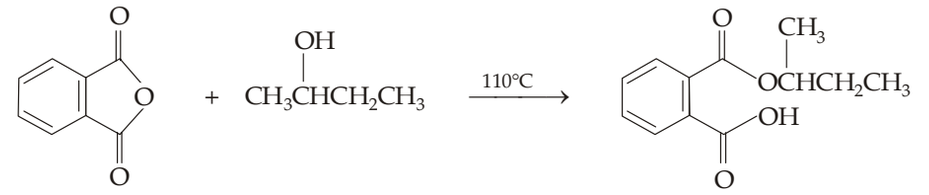
2. **Esters from acid chlorides and acid anhydrides.** Since acid chlorides and acid anhydrides are more reactive toward nucleophilic substitution than carboxylic acids, the reaction of an acyl chloride with an alcohol occurs rapidly in an irreversible manner and in absence of an acid catalyst. However, pyridine is often added to the reaction mixture to remove HCl (pyridine may also react with the acyl chloride to form an acylpyridinium ion which is more reactive toward the nucleophile even than the acyl chloride).



Aromatic acid chlorides (ArCOCl) are considerably less reactive than the aliphatic acid chlorides.

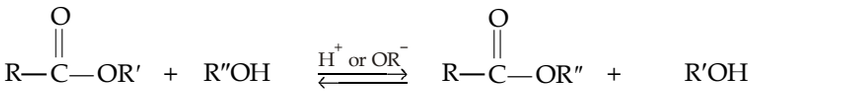
$$(RCO)_2O + R'OH \longrightarrow RCOOR' + RCOOH$$

Cyclic anhydrides react with one molar equivalent of an alcohol to form compounds that are both esters and acids.



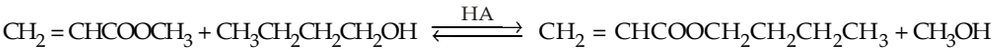
Phthalic anhydride *sec*-Butyl hydrogen phthalate

3. Transesterification. When an ester is treated with an alcohol in presence of acid (H_2SO_4 or dry HCl) or base (usually alkoxide ion), alcoholysis (cleavage by an alcohol) of an ester takes place to form new ester.



High boiling High boiling Higher boiling Lower boiling alcohol

Since the reaction is reversible, to carry out the reaction toward completion, it is necessary either to use a large excess of the alcohol or to remove one of the products from the reaction mixture (when the alcohol formed has low boiling point).



Methyl acrylate Butyl alcohol Butyl acrylate

(*d*) Preparation of amides. Among the four acid derivatives, amides are the least reactive, hence these can be prepared by treating acyl chlorides, anhydrides, or esters with ammonia or amines (acylation of amines or ammonia). As expected, acid chlorides are the most reactive and carboxylate ions are the least.

$$\underbrace{RCOCl + 2NH_3}_{1:2\text{ molar ratio}} \longrightarrow RCONH_2 + NH_4Cl$$

$$\underbrace{(RCO)_2O + 2R'NH_2}_{1:2\text{ molar ratio}} \longrightarrow RCONHR' + RCOO^{-}H_3\overset{+}{N}R'$$

$$\underbrace{RCOOR' + R''_2NH}_{1:1\text{ molar ratio}} \longrightarrow RCONR_2'' + R'OH$$

Note that two molar equivalents of amine are required in the reaction with acyl chlorides and acid anhydrides ; one molecule of amine acts as a nucleophile while the other as a Bronsted base to remove the acid formed during these reactions. In case the amine used is costly or available only in small quantities, the reaction is carried out successfully using one molar equivalent of amine in presence of some other base like NaOH to react with the acid (HCl or RCOOH) formed. In case acid chloride (or acid anhydride) and ammonia are taken in 1 : 1 molar ratio, whole of the reactant will not be converted into product as is evident by following example.

$$RCOCl + NH_3 \longrightarrow \frac{1}{2}RCONH_2 + \frac{1}{2}NH_4Cl + \frac{1}{2}RCOCl$$

In industry, amides are more often made by heating ammonium salts of carboxylic acids.

$$RCOOH \xrightarrow{NH_3} RCOO^{-}NH_4 \xrightarrow{\text{evaporate to dryness}} RCONH_2 + H_2O$$

Since carboxylate ion has low reactivity toward nucleophilic addition-elimination, further reaction does not take place in aqueous solution. However, if the dry ammonium salt is heated, dehydration takes place forming amide.

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TEST YOUR UNDERSTANDING - 18.4

1. (*a*) Predict which of the reaction takes place easily.

(*i*) $CH_3COCl + H_2O \longrightarrow CH_3COOH + HCl$ (*ii*) $CH_3COOH + NH_3 \longrightarrow CH_3CONH_2 + H_2O$

(*iii*) $(CH_3CO)_2O + NaOH \longrightarrow CH_3COOH + CH_3COONa$ (*iv*) $CH_3COBr + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + HBr$

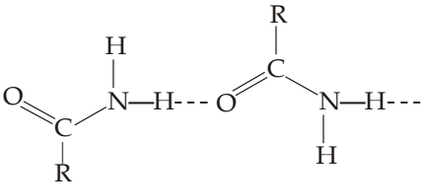
(*v*) $CH_3CONH_2 + NaOH \longrightarrow CH_3COONa + NH_3$ (*vi*) $CH_3COOCH_3 + Br^- \longrightarrow CH_3COBr + OCH_3^-$

(*b*) Give chemical reaction used for preparing *ter*-butyl acetate from acetic acid.

(*c*) RCOCl cannot be perpared by the reaction of HCl with RCOOH. Explain.

18.4 Properties of Acid Derivatives

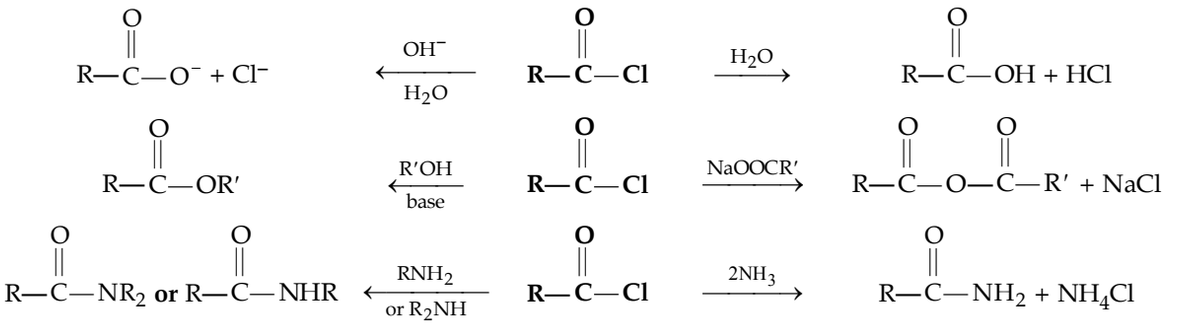
1. The presence of the C = O group in acid derivatives makes them polar and thus these compounds have definite dipole moments. Dipole-dipole interactions contribute to the intermolecular attractive forces and hence these compounds have higher boiling points than hydrocarbons of similar shape and molecular weight. Further, they lack a hydrogen attached to electronegative oxygen (except amides in which H is attached to N), their molecules cannot form strong hydrogen bonds to each other ; hence their boiling points are lower than those of acids and alcohols of comparable molecular weight. The boiling points of these derivatives (except amides) are about the same as those of comparable aldehydes and ketones. However, amides have quite high boiling points because they are capable of forming strong intermolecular hydrogen bonding. Since N, N-disubstituted amides cannot form hydrogen bonds to each other, they have lower melting and boiling points.



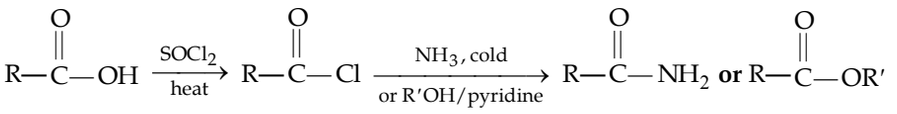
2. Lower esters and amides are soluble in water as these are capable of forming hydrogen bonding with water.
3. Acid chlorides have sharp, irritating odors, at least partly due to their ready hydrolysis to HCl and carboxylic acids. Low molecular weight esters are fairly volatile and have pleasant odors ; hence these are often used in the preparation of perfumes and artificial flavourings.

(*A*) Reactions of Acyl Chlorides

(*i*) Since acyl chlorides are the most reactive of the acyl derivatives, they are easily converted to less reactive ones, *viz.* anhydrides, esters, and amides and also acids very easily (Reactions discussed earlier).

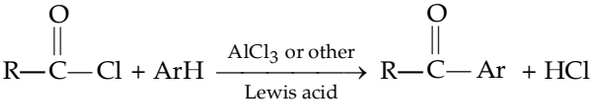


In the laboratory, amides and esters are usually prepared from the acid chloride rather than from the acid itself since both the steps (preparation of acid chloride and its reactions with ammonia or an alcohol) are rapid and irreversible.



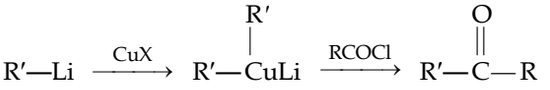
Acetyl chloride is frequently used in **acetylation (acylation, in general)** ; a reaction in which hydrogen of alcoholic, phenolic, amino, or imino group is replaced by acetyl (CH_3CO –) group.

(*ii*) **Friedel-Carft acylation.**

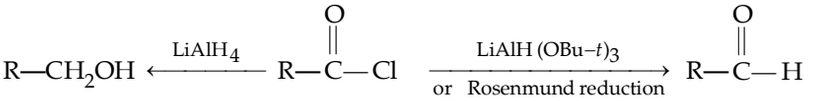


A ketone

(*iii*) **Reaction of organometallic compounds.** Recall that ketones are formed with Grignard reagents, organolithium compounds, and organocopper compounds ; however the latter are preferred because organocopper reagents do not react with many of the functional groups with which Grignard reagents and organolithiums do react, *viz.*, —NO_2, —CN, —CO—, —COOR, etc.



(*iv*) **Reduction**



TEST YOUR UNDERSTANDING - 18.5

1. Write the structure of the tetrahedral intermediate formed in the reaction of benzoyl choride with each of the following :

(*a*) CH_3COOH (*b*) C_2H_5OH (*c*) $(CH_3)_2NH$ (*d*) H_2O.

2. The values of K_a for hydrazoic acid (HN_3) and acetic acid (CH_3COOH) are 2.6×10^{-5} and 1.8×10^{-5} respectively. Place the acyl azides ($RCON_3$) at proper place regarding reactivity of acyl derivatives.

3. List the reagent for converting benzoyl chloride to

(*a*) benzaldehyde (*b*) benzamide (*c*) benzyl alcohol (*d*) benzyl benzoate

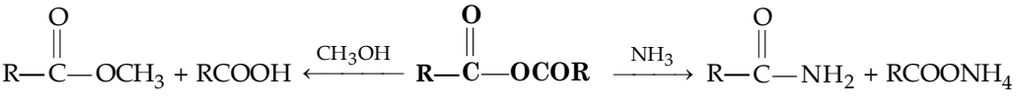
(*e*) benzoic anhydride (*f*) N-benzylbenzamide (*g*) benzoyl azide, $C_6H_5CON_3$.

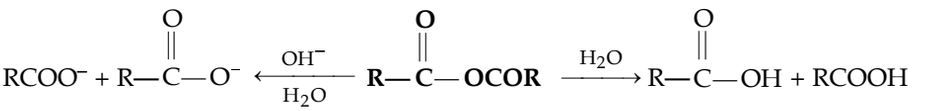
4. Give the products of reaction of Me_2CuLi followed by hydrolysis with each of the following

(*a*) NC $(CH_2)_4COCl$ (*b*) CH_3CO—  —COCl (*c*) $H_5C_2O_2C(CH_2)_4COCl$.

(*B*) Reactions of Acid Anhydrides.

(*i*) Acid anhydrides undergo the same reactions as acid chlorides, but a little more slowly. Compounds containing acetyl group are often prepared from acetic anhydride because it is cheap, readily available, less volatile and more easily handled than acetyl chloride and it does not form corrosive hydrogen chloride.



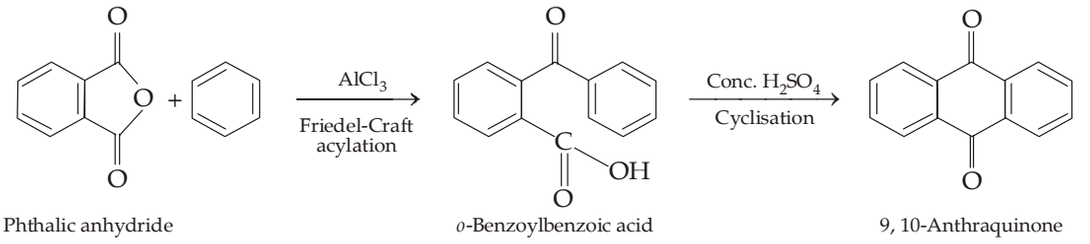


Like acetyl chloride, acetic anhydride is used in acetylation (acylation) of alcohols, phenols, amines and imines.

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(*ii*) **Friedel-Craft acylation.**

$$(RCO)_2O + ArH \xrightarrow{AlCl_3} Ar{-}\overset{\overset{O}{\|}}{C}{-}R + RCOOH$$



Phthalic anhydride — *o*-Benzoylbenzoic acid — 9, 10-Anthraquinone

TEST YOUR UNDERSTANDING - 18.6

1. Write down the structures of the major organic product of each of the following reactions.

(*a*) Acetic anhydride + $CH_3OH \xrightarrow{H^+}$ (*b*) Acetic anhydride + $2CH_3OH \xrightarrow{H^+}$

(*c*) Acetic anhydride + NH_3 (1 mol) $\longrightarrow$ (*d*) Succinic anhydride + $(CH_3)_2NH$ (2 mol) $\longrightarrow$

(*e*) Succinic anhydride + NaOH (2 mol) $\longrightarrow$ (*f*) Acetic anhydride + $2CH_3MgBr \xrightarrow{H_3O^+}$

(*g*) Succinic anhydride + Benzene $\xrightarrow{AlCl_3}$

2. (*a*) Give the possible ways for preparing following anhydrides :

(*i*) $CH_3\overset{\overset{O}{\|}}{C}{-}O{-}\overset{\overset{O}{\|}}{C}CH_2CH_3$ (*ii*) $H{-}\overset{\overset{O}{\|}}{C}{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH_3$

(*b*) Can formic anhydride be prepared by heating formic acid ?

3. Predict the products of the following reactions :

$$\text{Toluene + Phthalic anhydride} \xrightarrow{AlCl_3} [A] \xrightarrow[\text{heat}]{\text{Conc. } H_2SO_4} [B]$$

(*C*) Reactions of Esters.

Esters are less reactive than acyl chlorides and acid anhydrides toward nucleophilic substitution. The three important reactions are conversion to amides, other esters (*transesterification or alcoholysis*) and hydrolysis.

(*i*) $CH_3COOC_2H_5 + NH_3 \longrightarrow CH_3CONH_2 + C_2H_5OH$

(*ii*) $CH_3COOC_2H_5 + CH_3OH \longrightarrow CH_3COOCH_3 + C_2H_5OH$

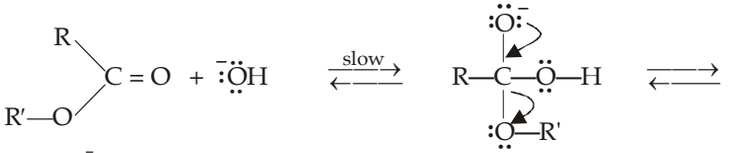
(*iii*) $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+ \text{ or } OH^-} CH_3COOH \text{ (or } CH_3COO^-) + C_2H_5OH$

Since acid catalyzed esterification and acid hydrolysis of esters are reversible, if we reverse the mechanism of esterification (discussed earlier), we get the mechanism of acid catalyzed ester hydrolysis.

Mechanism of base promoted ester hydrolysis. Unlike acid catalyzed, base promoted hydrolysis of ester, also known as **saponification**, forms an alcohol and sodium salt of the acid.

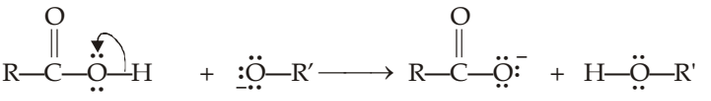
$$R{-}\overset{\overset{O}{\|}}{C}{-}OR' + OH^- \longrightarrow R{-}\overset{\overset{O}{\|}}{C}{-}O^- + R'OH$$

The carboxylate ion is very unreactive toward nucleophilic substitution because it is quite stable and negatively charged, hence base-catalyzed hydrolysis of ester is an irreversible reaction. Since base is consumed in the reaction, we generally speak *base-promoted rather than base-catalyzed.* The base-promoted hydrolysis of an ester is also an example of nucleophilic addition-elimination at the acyl carbon



OH^- attacks the carbonyl carbon

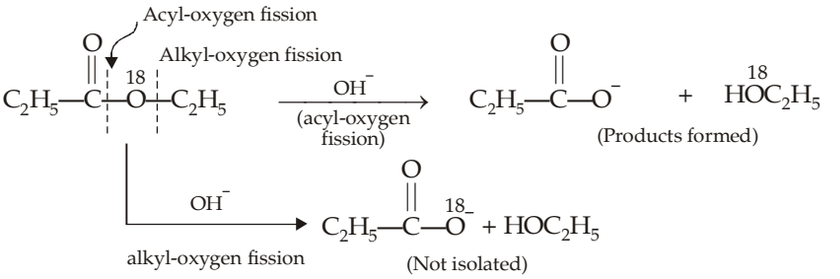
The tetrahedral intermediate expels an alkoxide ion (acyl-oxygen fission)



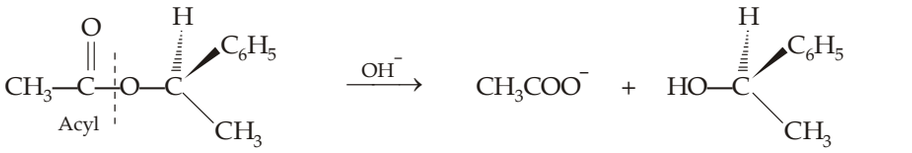
Transfer of a proton leads to more stable carboxylate ion

Evidence for the above acyl-oxygen fission.

(*a*) **Istotopically labelled experiment.** When ethyl propanoate labelled with ^{18}O in the ether type oxygen of the ester is subjected to hydrolysis with aqueous base, all of the ^{18}O is found to be present in ethanol, and none in the propanoate ion. This indicates that the bond between acyl group and oxygen is cleaved during hydrolysis.



(*b*) **Stereochemical evidence.** Saponification of esters of optically active alcohols proceeds with **retention of configuration.**

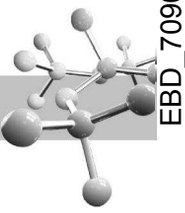


(R)-(+)-1-Phenylethyl acetate

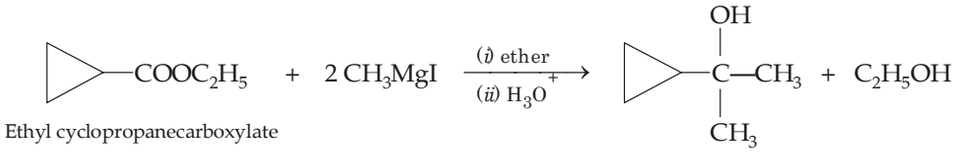
(R)-(+)-Phenylethyl alcohol (same optical purity as ester)

Retention in configuration in the chiral alcohol indicates that none of the bonds to the stereogenic center are broken which is possible when acyl-oxygen fission takes place. Had alkyl-oxygen fission occurred, it would have been accompanied by inversion of configuration since bond to the stereogenic carbon is cleaved to form carbocation, and the product would have been (S)-(–)-1-phenylethyl alcohol.

(*iv*) **Reaction with Grignard reagents.** Esters react with two equivalents of a Grignard reagent to produce tertiary alcohols. Since two of the three alkyl groups of the tertiary alcohol come from the Grignard reagent, hence these must be identical.



$$R{-}\overset{\overset{O}{\|}}{C}{-}OR' + 2R''MgX \xrightarrow[(ii)\ H_3O^+]{(i)\ \text{diethyl ether}} R{-}\overset{\overset{OH}{|}}{\underset{\underset{R''}{|}}{C}}{-}R'' + R'OH$$



Ethyl cyclopropanecarboxylate

(*v*) **Reduction.** $RCOOR' \xrightarrow[H_2\text{, Copper chromite, high pressure, 150°C}]{Na/C_2H_5OH,\ \text{or}\ LiAlH_4,\ \text{or}} RCH_2OH + R'OH$

Hydrogenolysis (cleavage by hydrogen) of esters may also be carried out by heating ester with H_2 in presence of Pd/C.

$$C_6H_5COOCH_2C_6H_5 + H_2 \xrightarrow{Pd/C} C_6H_5COOH + CH_3C_6H_5$$

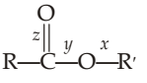
Note that here acidic part of the ester is not reduced, hence this type of hydrogenolysis is used for regenerating the protected acidic group.

$$-COOH \xrightarrow{SOCl_2} -COCl \xrightarrow{C_6H_5CH_2OH} -COOCH_2C_6H_5 \xrightarrow{H_2\ ;\ Pd/C} -COOH + CH_3C_6H_5$$

TEST YOUR UNDERSTANDING - 18.7

1. (*a*) An ester has two oxygen atoms, carbonyl oxygen and carboxyl oxygen, which of the two is more basic?

(*b*) An ester group has three carbon-oxygen bonds, can you think about their relative bond lengths ?



2. How we can explain the lower rate of esterification and hydrolysis of esters when the alcohol, the acid, or both are highly branched?

3. (*a*) Predict the relative rate of alkaline hydrolysis of following esters.

Ethyl acetate, isopropyl acetate, methyl acetate, *ter*-butyl acetate

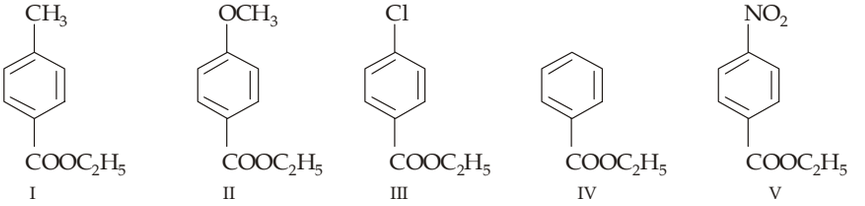
I II III IV

What two factors are responsible for their relative rate of hydrolysis ?

(*b*) Predict the order of reactivity toward alkaline hydrolysis of methyl acetate (I), methyl formate (II), methyl isobutyrate (III), methyl propionate (IV), and methyl trimethylacetate (V).

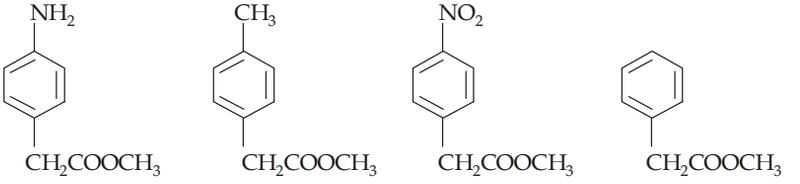
4. Arrange the following esters in decreasing ease of alkaline hydroysis.

(*a*)



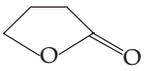
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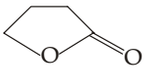
(*b*)



I II III IV

5. (*a*) Give the structural formula for the products in each of the following reaction.

(*i*) $CH_3CH_2COOCH_3 + 2C_6H_5MgBr$ (*ii*)  $+ \ 2CH_3MgBr$

(*iii*)  $+ \ CH_3NH_2$ (*iv*) $CH_3COOC_2H_5 + H_2NNH_2$

(*v*) $C_6H_5COOC_2H_5 + NH_2OH$.

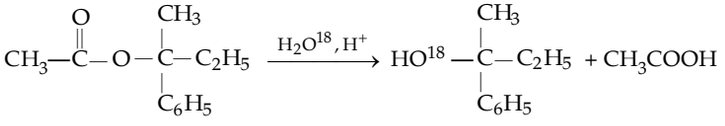
(*b*) Write down structure of the products formed in the following reaction.

$$CH_3CH = CHCH_2COOCH_2CH_2Br + NaOH \xrightarrow[(ii)\,H^+]{(i)\,heat}$$

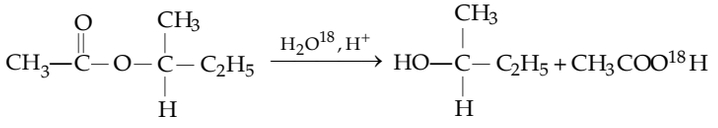
(*c*) Give the structure of the product obtained by hydrogenolysis of *n*-butyl oleate over copper chromite.

6. Esters of which acid would give secondary alcohols on reaction with Grignard reagents ? Give chemical reaction involved in the preparation of 4-heptanol by the reaction of an ester with a Grignard reagent.

7. Explain the following anamoly in the acid-catalyzed hydrolysis of the following two esters.

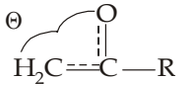
(*a*) 

(+) – (±) –

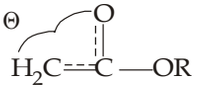
(*b*) 

(+) – (+) –

(*vi*) Claisen condensation. An α-hydrogen in an ester is weakly acidic (similarity to aldehydes and ketones) and again like aldehydes and ketones the negative charge of the carbanion of esters is dispersed to the carbonyl group through resonance.

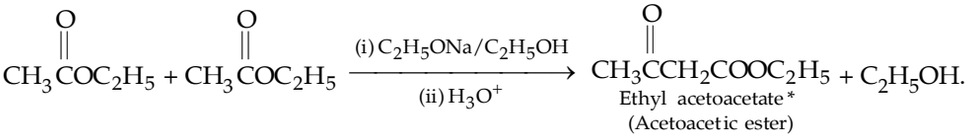


Carbanion of aldehyde / ketone



Carbanion of an ester

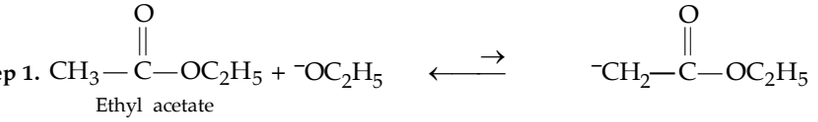
Due to acidic nature of α-hydrogens, esters when treated with a strong base (generally C_2H_5ONa) undergo condensation to form β-keto ester.



Ethyl acetoacetate*
(Acetoacetic ester)

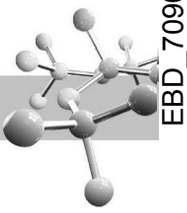
The reaction, known as **Claisen condensation**, is related to aldol condensation given by aldehydes and ketones : *both reactions involve the attack of a carbanion (a nucleophile) on an electron deficient carbonyl carbon.* However, the two reactions differ in the next step : in the *aldol condensation, nucleophilic attack leads to addition,* the typical reaction of aldehydes and ketones, *while in the Claisen condensation, nucleophilic attack leads to substitution,* the typical reaction of acyl compounds.

Mechanism.

Step 1. 

Ethyl acetate

* The systematic name of ethylacetoacetate is *ethyl 3-oxobutanoate.*



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Step 2. $CH_3—\overset{\overset{O}{\|}}{C}—OC_2H_5$ + $^-CH_2—\overset{\overset{O}{\|}}{C}OC_2H_5$ $\longleftrightarrow$ $CH_3—\overset{\overset{O^-}{|}}{\underset{\underset{OC_2H_5}{|}}{C}}—CH_2\overset{\overset{O}{\|}}{C}OC_2H_5$

Ethyl acetate (2nd mole)

$\longleftrightarrow$ $CH_3—\overset{\overset{O}{\|}}{C}—CH_2\overset{\overset{O}{\|}}{C}OC_2H_5 + {}^-OC_2H_5$

Although the products at the end of the second step are acetoacetic ester and ethoxide ion, the reaction does not stop at this step ; had it so been, the yield of the β-keto ester would have been very little because the overall equilibrium upto this point is favourable to reactants and not to products.

In β-keto esters (*e.g.* acetoacetic ester), α-hydrogens are surrounded at both ends by carbonyl groups, hence such compounds are much stronger acids than ordinary esters because the negative charge can be delocalised into two carbonyl groups instead of one in ordinary esters. Due to stronger acidic nature than ethyl alcohol, the β-keto ester formed at step 2 reacts with ethoxide ion to form ethyl alcohol and an anion.

Step 3. $CH_3—\overset{\overset{O}{\|}}{C}—CH_2—\overset{\overset{O}{\|}}{C}OC_2H_5 + {}^-OC_2H_5 \rightleftharpoons CH_3—\overset{\overset{O}{\|}}{C}—\overset{-}{C}H—\overset{\overset{O}{\|}}{C}OC_2H_5 + C_2H_5OH$

Stronger acid ($pK_a = 11$) — Anion of acetoacetic ester — Weaker acid ($pK_a = 16$)

Note that the position of equilibrium for this step is favourable, and can be made more favourable by distilling ethanol from the reaction mixture. Although, the reaction is complete at step 3, an acid is added to the reaction mixture to obtain the product in its neutral form.

$CH_3—\overset{\overset{O}{\|}}{C}—\overset{-}{C}H—\overset{\overset{O}{\|}}{C}OC_2H_5 \xrightarrow{H_3O^+} CH_3—\overset{\overset{O}{\|}}{C}—CH_2—\overset{\overset{O}{\|}}{C}OC_2H_5 + H_2O$

Acetoacetic ester

Like aldol condensation, Claisen condensation always involves bond formation between the α-carbon atom of one molecule and the carbonyl carbon of another.

$2CH_3\overset{\alpha}{C}H_2\overset{\overset{O}{\|}}{C}O\overset{\beta}{C}H_2CH_3 \xrightarrow[(ii)\ H_3O^+]{(i)\ C_2H_5ONa} CH_3CH_2\underset{\underset{CH_3}{|}}{\overset{\overset{O}{\|}}{C}—CH}\overset{\overset{O}{\|}}{C}OC_2H_5 + CH_3CH_2OH$

Ethyl propanoate — Ethyl 2-methyl-3-oxopentanoate

Unlike aldol condensation, Claisen condensation is possible only for esters having **two α hydrogen atoms;** *i.e.* for the type RCH_2COOR', but neither for $R_2CHCOOR'$ nor for R_3CCOOR'.

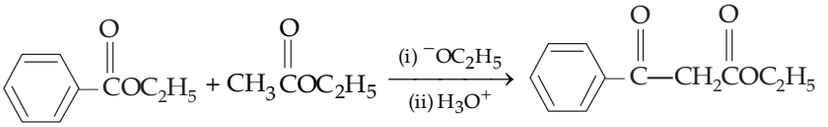
Intramolecular Claisen condensation (Dieckmann reaction). Esters of dicarboxylic acids undergo intramolecular Claisen condensation, provided a five or six-membered ring can be formed

$C_2H_5O\overset{\overset{O}{\|}}{C}(CH_2)_4\overset{\overset{O}{\|}}{C}OC_2H_5$ or $\overset{\overset{O}{\|}}{C}—OC_2H_5$ (cyclic: H_2C, CO, OC_2H_5) $\xrightarrow[(ii)\ H_3O^+]{(i)\ C_2H_5ONa}$ (cyclic: O, $\overset{\overset{O}{\|}}{C}OC_2H_5$)

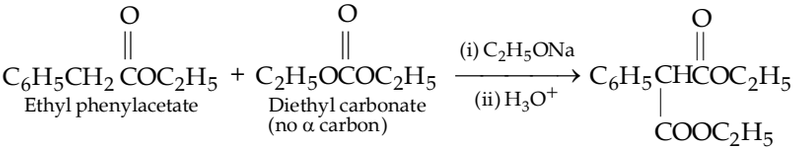
Diethyl hexanedioate (Diethyl adipate) — Ethyl 2-oxocyclopentanecarboxylate

Note that the α hydrogen atom and the ester group for the condensation are coming from the same molecule.

Crossed Claisen condensation. Like a crossed aldol condensation, a crossed Claisen condensation is possible **when one of the reactants has no α-hydrogen** and thus is incapable of undergoing self-condensation ; this component acts as an *acylating agent*.



Ethyl benzoate (no α hydrogen) Ethyl acetate Ethyl benzoylacetate



Ethyl phenylacetate; Diethyl carbonate (no α carbon); Diethyl phenylmalonate (Phenylmalonic ester)

In such cases, an ester without an α-hydrogen is mixed with the base, and then ester carrying α-hydrogen is added.

TEST YOUR UNDERSTANDING - 18.8

1. (*a*) Write structural formulas for the Claisen condensation products of each of the following.

(*i*) $CH_3CH_2CH_2CH_2COOCH_2CH_3$ (*ii*) $C_6H_5COOCH_2CH_3$ (*iii*) $C_6H_5CH_2COOCH_2CH_3$

(*b*) Give the structure of the product obtained when ethyl phenylacetate ($C_6H_5CH_2COOCH_2CH_3$) is treated with each of the following esters in presence of sodium ethoxide.

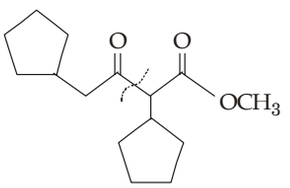
(*i*) ethyl formate (*ii*) diethyl oxalate (*iii*) ethyl phenylacetate (*iv*) ethyl benzoate.

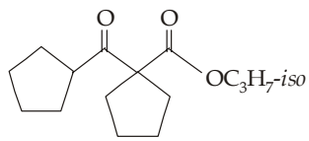
2. Can we replace C_2H_5ONa by other base like CH_3ONa or NaOH in the following reaction?

$$2CH_3COOC_2H_5 \xrightarrow{C_2H_5ONa} CH_3COCH_2COOC_2H_5$$

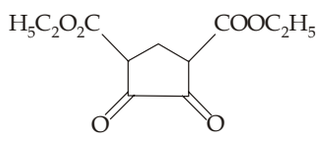
3. Although ethyl propanoate gives good yield in the Claisen condensation, ethyl-2-methylpropanoate gives poor yield. Explain.

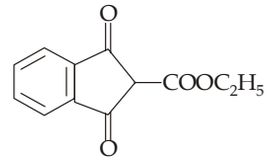
4. Name the starting material used for getting following product by Claisen condensation.

(i) 

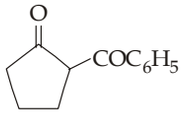
(ii) 

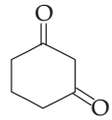
5. Following β-keto esters are formed by crossed Claisen condensation, write down the structure of the two components in each of the following.

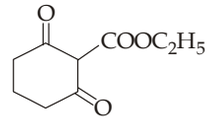
(*i*) $C_6H_5COCH\ (C_6H_5)\ COOC_2H_5$ (*ii*) 

(*iii*) 

6. Give the different possible reactant(s) from which each of the following can be prepared using Claisen condensation.

(a) 

(b) 

(c) 

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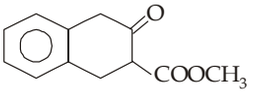
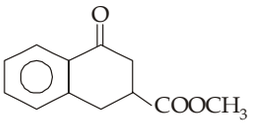
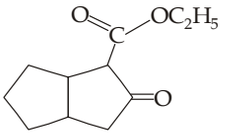
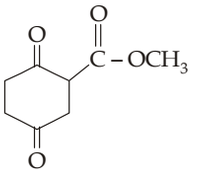
7. (*a*) Write the structure of the Dieckmann cyclization product formed on treatment of each of the following diesters with sodium ethoxide followed by acidification.

(*i*) $CH_3CH_2OOC(CH_2)_5COOC_2H_5$ (*ii*) $C_2H_5O_2CCH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2COOC_2H_5$

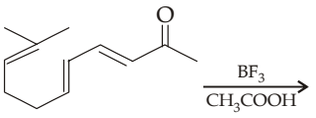
(*iii*) $C_2H_5O_2C\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2CH_2COOC_2H_5$

(*b*) Do you expect Dieckmann condensation when ethyl succinate or ethyl glutarate is treated with sodium ethoxide ?

8. Draw the structures of the starting diesters from which the following keto esters can be prepared using Dieckmann condensation.

(a)  (b)  (c)  (d) 

9. Give the product(s) in the following reaction.



(*D*) Reactions of amides

1. Amides are slowly hydrolyzed when heated under either acidic or basic conditions.

$$RCOO^- + NH_3 \xleftarrow[\text{heat}]{OH^-} RCONH_2 + H_2O \xrightarrow[\text{heat}]{H^+} RCOOH + NH_4^+$$

The mechanism for acid hydrolysis of an amide is similar to that for acid hydrolysis of an ester. Water acts as a nucleophile and attacks the protonated amide ; the leaving group is ammonia (or an amine). In **basic hydrolysis** of amides, hydroxide ion acts as nucleophile as well as base.

2. Unsubstituted amides are converted to RCOOH with HNO_2, and are dehydrated to RCN with P_2O_5, $SOCl_2$, $POCl_3$ or PCl_5.

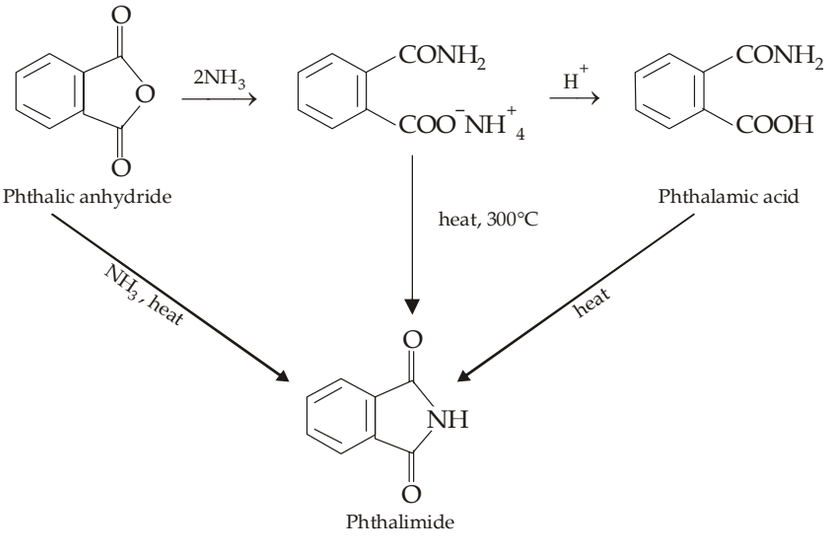
$$RCONH_2 + HONO \longrightarrow RCOOH + N_2 + H_2O$$

$$RCONH_2 \xrightarrow[\text{Heat}]{P_2O_5} RCN + H_2O$$

3. **Hofmann degradation of amides.** On treatment with bromine in basic solution, unsubstituted amides are degraded to amines with one carbon atom less. This is a useful method for the preparation of 1° amines, and discussed in detail in amines.

$$RCONH_2 + Br_2 + 4OH^- \longrightarrow RNH_2 + 2Br^- + CO_3^{2-} + 2H_2O$$

4. **Conversion to imides.** Compounds containing acidic as well as amide group in the same molecule at the two ends when heated, lose a molecule of water and produce a cyclic compound in which two acyl groups have become attached to nitrogen ; such compounds are called **imides.**



Phthalimide

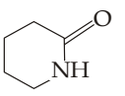
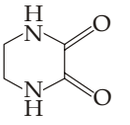
TEST YOUR UNDERSTANDING - 18.9

1. (*a*) Outline all steps in the synthesis of succinimide from succinic acid.

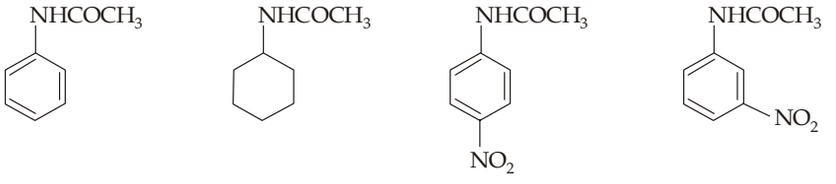
(*b*) Outline an efficient synthesis of 1-propanamine from butanoic acid.

2. Arrange the following in decreasing order of acidity : Benzamide, phthalimide and ammonia.

3. Give structure of the product obtained by acidic hydrolysis of each of the following amides.

(*a*) N, N-Dimethylacetamide (*b*) $HOOC.\underset{\displaystyle CH_3}{\underset{|}{C}}HNHCO\underset{\displaystyle C_2H_5}{\underset{|}{C}}HNH_2$ (*c*)  (*d*) 

4. Arrange the following amides in increasing ease of base-promoted hydrolysis.

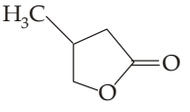
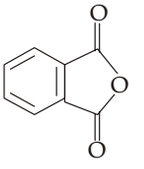


I II III IV

5. How do amides (1°, 2° and 3°) react (*a*) with organometallic reagents ; and (*b*) with nitrous acid.

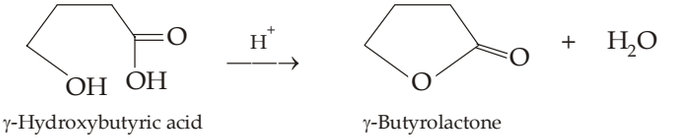
6. Give the products of reactions of $LiAlH_4$ with

(*i*) $C_6H_5CH_2COOCH_3$ (*ii*) $(CH_3CO)_2O$ (*iii*) C_6H_5COCl (*iv*) $CH_3CH = CHCH_2CONHC_6H_5$

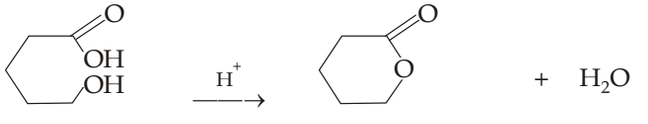
(*v*)  (*vi*)  (*vii*) 

18.5 Cyclic Esters or Lactones

Certain hydroxy acids have the capacity to form cyclic esters, also known as **lactones**. This intramolecular esterification takes place spontaneously and is especially favourable when the ring formed is 5- or 6-membered. Lactones containing 5- and 6-membered cyclic esters are referred to as γ-lactones and δ-lactones respectively, because these are derived from the corresponding (γ- or δ-) hydroxy carboxylic acids.



γ-Hydroxybutyric acid γ-Butyrolactone



δ-Hydroxyvaleric acid γ-Valerolactone

A lactone is named by replacing the *-oic acid* ending of the parent carboxylic acid by *-olide* and identifying its oxygenated carbon by number. Thus γ-butyrolactone and δ-valerolactone may be named as 4-butanolide and 5-pentanolide, respectively.

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Reactions that are expected to produce hydroxy acids often yield the derived lactones provided a 5- or 6-membered ring can be formed, *e.g.*

(*a*) $CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2CH_2COOH \xrightarrow[(ii)\ H_3O^+]{(i)\ NaBH_4} [CH_3\overset{\overset{OH}{|}}{C}HCH_2CH_2CH_2COOH] \longrightarrow$ A 5-hexanolide

5-Oxohexanoic acid

5-Hydroxyhexanoic acid
(δ-Hydroxy carboxylic acid)

(*b*) $CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2COOH \xrightarrow[200°C]{Ni/H_2} [CH_3\overset{\overset{OH}{|}}{C}HCH_2CH_2COOH] \longrightarrow$

A γ-hydroxy carboxylic acid

(*c*) $CH_3\overset{\overset{OH}{|}}{C}HCH_2C \equiv CCOOH \xrightarrow[catalyst]{H_2/Lindlar} [CH_3\overset{\overset{OH}{|}}{C}HCH_2 \quad CH=CH \quad COOH] \xrightarrow{H_3O^+}$

cis-Alkene

A δ-hydroxy carboxylic acid

(*d*) $CH_3\overset{\overset{O}{\|}}{C}CH_2\ CH_2COOCH_3 \xrightarrow[(ii)\ H_3O^+]{(i)\ 1\ CH_3MgBr} \left[CH_3\overset{\overset{CH_3}{|}}{C}CH_2CH_2COOH\right] \xrightarrow[-CH_3OH]{}$

A γ–hydroxy acid

Remember that a ketonic group is more reactive than an ester toward Grignard reagent.

Lactones whose rings are 3- or 4-membered (α-lactones and β-lactones) are very reactive, making their isolation difficult. However, if attempt is made to prepare a β-lactone from a β-hydroxy acid, β-elimination usually occurs forming α, β-unsaturated acid.

$$RCH\overset{\overset{OH}{|}}{C}HCH_2COOH \xrightarrow{H^+ \text{ or heat}} RCH = CHCOOH + H_2O$$

Similarly, when α-hydroxy acids are heated, they form *cyclic diesters* called **lactides**.

$$2RCH\overset{\overset{OH}{|}}{C}HCOOH \xrightarrow{heat}$$

α-Hydroxy acid

A lactide (cyclic diester)

Lactones react nearly in the same way as ester, *e.g.*

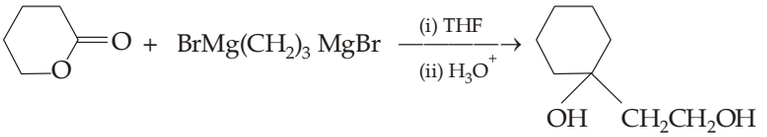
(*i*) δ-Valerolactone $\underset{H^+}{\overset{OH^-}{\rightleftharpoons}}$ δ-Hydroxypentanoate

(*ii*) δ-Valerolactone $\xrightarrow{NH_3}$ $HOCH_2CH_2CH_2CH_2CONH_2$

(*iii*) δ-Valerolactone $\xrightarrow{CH_3OH/H_2SO_4}$ $HOCH_2CH_2CH_2CH_2COOCH_3$

(*iv*) δ-Valerolactone $\xrightarrow[(ii)\,H_2O]{(i)\,LiAlH_4}$ $HOCH_2CH_2CH_2CH_2CH_2OH$

Like esters, lactones (cyclic esters) are inert to $NaBH_4$

(*v*) 

Ester group reacts with both parts of Grignard reagent forming a diol.

18.6 Analysis of Carboxylic Acid Derivatives

1. Carboxylic acid derivatives are recognized by their hydrolysis products. We know that the ease of hydrolysis of the four products follows the following order.

Acid chlorides	>	Acid anhydrides	>	Esters	>	Amides
(hydrolyzed by water)		(hydrolyzed when heated briefly with NaOH)				(hydrolyzed when refluxed with NaOH)

2. **Saponification equivalent of ester.** An ester is hydrolyzed with excess, but known amount of base, and the amount of base used is measured and used to give the **saponification equivalent** ; the equivalent weight of the ester, which is similar to the neutralization equivalent of an acid.

$$\underset{\text{One equivalent}}{RCOOR'} + \underset{\text{One equivalent}}{OH^-} \longrightarrow RCOO^- + R'OH$$

However, unlike neutralization equivalent, saponification equivalent of esters is less useful in identification of esters because of great number of possible combinations of the two alkyl groups present in an ester, RCOOR'.

TEST YOUR UNDERSTANDING - 18.10

1. Identify each type of acid derivative which responds following test :

(*a*) gives white precipitate insoluble in nitric acid, on treatment with alcoholic silver nitrate.

(*b*) gives ethyl alcohol when heated with acid or base.

(*c*) gives only propanoic acid on hydrolysis.

(*d*) reacts immediately with cold NaOH to liberate a gas that turns moist litmus paper blue.

(*e*) reacts with boiling NaOH and produce a gas that turns moist red litmus paper blue.

2. What is the saponification equivalent of *n*-propyl acetate ? Is this equivalent possible for any other ester or carboxylic acid ? Give their structures.

3. (*a*) What is the saponification equivalent of methyl phthalate ?

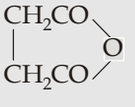
(*b*) What is the relation between saponification equivalent and the number of ester groups per molecule ?

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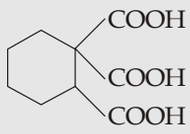
18.7 Illustrative Examples

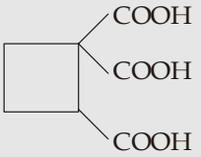
Example 1 :

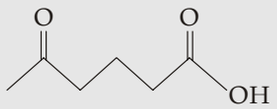
Identify the braketed compound(s) in the following reactions :

(i)  +  $\xrightarrow{AlCl_3}$ **[A]** $\xrightarrow[HCl]{Zn(Hg)}$ **[B]** $\xrightarrow{SOCl_2}$ **[C]** $\xrightarrow{AlCl_3}$ **[D]**

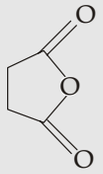
$\xrightarrow{H_2/Pt}$ **[E]** $\xrightarrow{H_2SO_4, heat}$ **[F]** $\xrightarrow{Pt, heat}$ **[G] + H_2**

(ii)  $\xrightarrow{heat}$ **[A] + [B]**

(iii)  $\xrightarrow{heat}$ **[A] + [B]**

(iv)  $\xrightarrow{NaBH_4}$ **[A]** $\xrightarrow[heat]{H_2SO_4}$ **[B]**

(v) Calcium adipate $\xrightarrow{heat}$ **[A]** $\xrightarrow{C_6H_5CO_3H}$ **[B]**

(vi)  $\xrightarrow{CH_3OH}$ **[A]** $\xrightarrow{PCl_5}$ **[B]** $\xrightarrow{CH_3NH_2}$ **[C]**

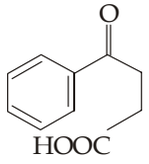
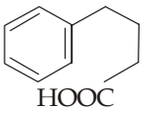
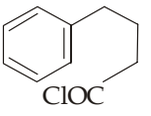
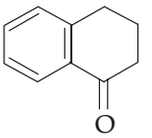
(vii) Phthalic acid $\xrightarrow{NH_3}$ **[A]** $\xrightarrow[300°C]{heat}$ **[B]**

(viii) CH ≡ CH $\xrightarrow{2CH_3COOH}$ **[A]** $\xrightarrow{heat}$ **[B]**

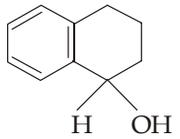
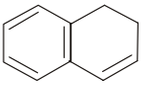
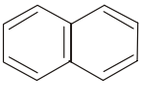
(ix) [A] $\xrightarrow[(ii)\ H_3O^+]{(i)\ excess\ of\ CH_3MgBr}$ **2, 3-Dimethyl-2-butanol**

(x) CH ≡ CH $\xrightarrow{Hg^{2+}/H_2SO_4}$ **[A]** $\xrightarrow{Al(OC_2H_5)_3}$ **[B]** $\xrightarrow{C_2H_5ONa}$ **[C]**

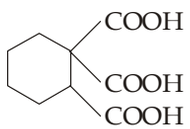
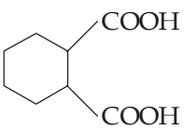
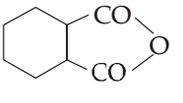
Solution :

(*i*)  ;  ;  ; 

[A] [B] [C] [D]

 ;  ; 

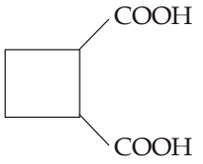
[E] [F] [G]

(*ii*)  $\xrightarrow[(-CO_2)]{heat}$  $\xrightarrow[(-H_2O)]{heat}$ 

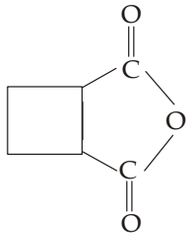
cis- and *trans*-Cyclohexane-1, 2-dicarboxylic acid

cis- and *trans*-Anhydride [A] and [B]

(*iii*)



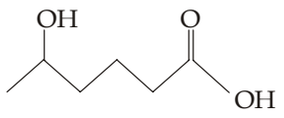
trans-1, 2-Cyclobutane-dicarboxylic acid
[A]



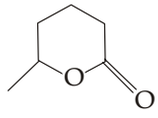
cis-Anhydride
[B]

Remember that unlike above reaction, *trans*-dicarboxylic acid cannot form the anhydride because a 5- and 4-membered ring cannot be fused *trans*.

(*iv*)

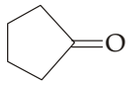


[A]

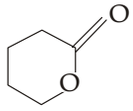


[B]

(*v*)



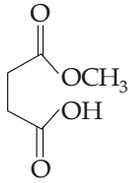
[A]



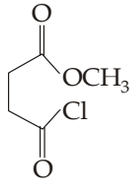
[B]

(through Baeyer-Villeger reaction)

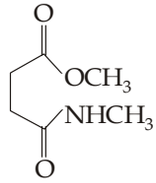
(*vi*)



[A]

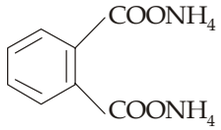


[B]

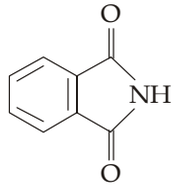


[C]

(*vii*)



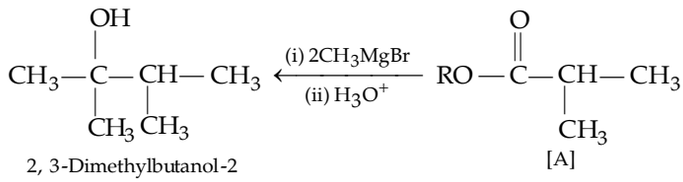
[A]



[B]

(*viii*) $CH_3CH(OCOCH_3)_2$ CH_3CHO
[A] [B]

(*ix*) Recall that *tert*-alcohols (2, 3-dimethyl-2-butanol) are formed by the action of excess of Grignard reagents on esters. Hence the compound A should be an ester. Now further recall that in the *tert*-alcohol, two identical alkyl groups are introduced by the alkyl group of the RMgX, so the third alkyl group (which may be different or identical) is coming from the acidic moiety to the ester. So here first examine the structure of the *tert*-alcohol and then write down the structure of the ester.



2, 3-Dimethylbutanol-2 [A]

(*x*) $CH_3CHO \xrightarrow[\text{reaction}]{\text{Tischenko}} CH_3COOC_2H_5 \xrightarrow[\text{condensation}]{\text{Claisen}} CH_3COCH_2COOC_2H_5$.
[A] [B] [C]

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Example 2 :

Give steps involved in the following reactions :

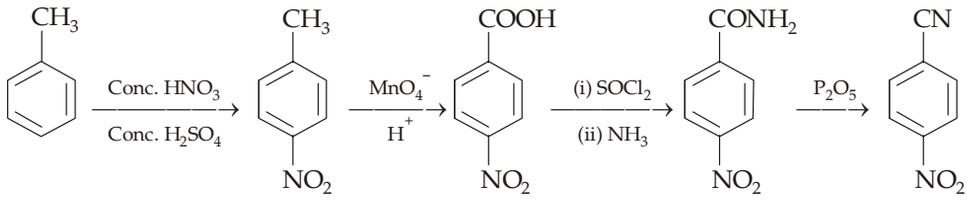
(i) C_2H_5OH **to** CH_3CN **(ii)** $C_6H_5CH_3$ **to p-**$NO_2C_6H_4CN$

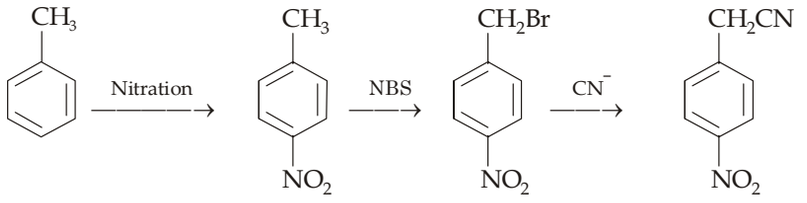
(iii) $C_6H_5CH_3$ **to** *p*-$NO_2.C_6H_4.CH_2CN$ **(iv)** $C_6H_5CH_3$ **to** $C_6H_5CH_2CN$

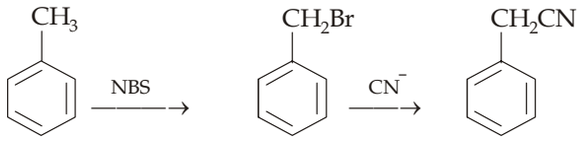
(v) $C_6H_5CH_2CH_2COOH$ **to 1-Phenylpropane.**

Solution :

(*i*) $C_2H_5OH \xrightarrow{Cr_2O_7^{2-}/H^+} CH_3COOH \xrightarrow{PCl_5} CH_3COCl \xrightarrow[(ii)\ P_2O_5]{(i)\ NH_3} CH_3CN$

(*ii*) 

(*iii*) 

(*iv*) 

(*v*) $C_6H_5CH_2CH_2COOH \xrightarrow{LiAlH_4} C_6H_5CH_2CH_2CH_2OH \xrightarrow[(-H_2O)]{H_2SO_4} C_6H_5CH_2CH=CH_2 \xrightarrow{H_2/Pt} \underset{\text{1-Phenylpropane}}{C_6H_5CH_2CH_2CH_3}$

Example 3 :

Prepare 2-methylbutanoic acid from ethanol as the only organic compound, of course you can use inorganic reagents; you require.

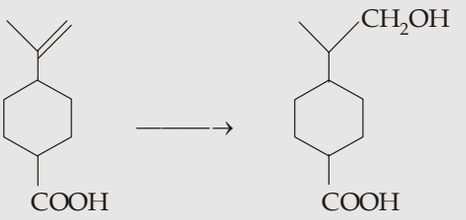
Solution :

$$C_2H_5OH \xrightarrow{PBr_3} C_2H_5Br \xrightarrow[ether]{Mg\ in} C_2H_5MgBr \xrightarrow[(ii)\ H_3O^+]{(i)\ CH_3CHO} C_2H_5CHCH_3 \quad (CH_3CH_2OH \xrightarrow{Oxidation} CH_3CHO)$$

$$\xrightarrow{PCl_3} C_2H_5\underset{Cl}{CHCH_3} \xrightarrow{Mg} C_2H_5\underset{MgCl}{CHCH_3} \xrightarrow[(ii)\ H_3O^+]{(i)\ CO_2} C_2H_5\underset{COOH}{CHCH_3}$$

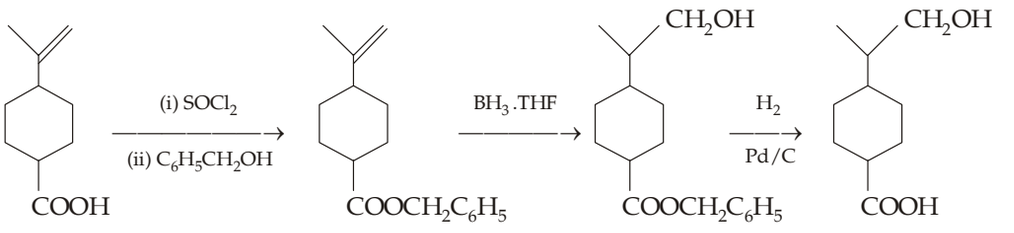
Example 4 :

Give all steps involved in the following conversions.



Solution :

The conversion involves simply addition of water molecule in anti-Markovnikov way which can best be achieved by the use of BH_3. THF. However, this reagent also reacts with —COOH group so the latter must first be protected which is done by converting it into —$COOCH_2C_6H_5$.



Note that *tert*-butyl group can't be used as a protective group in place of —$CH_2C_6H_5$ group because its removal as isobutene requires H^+ which would dehydrate the —CH_2OH group giving back the starting material.

Example 5 :

Give reaction(s) involved in the conversion of $(CH_3)_3CCHOHCH_3$ to $(CH_3)_3$ CCH = CH_2.

Solution :

Although the reaction seems to be achieved simply by dehydration, but in such case a 2° carbocation would be formed as an intermediate which will rearrange to 3° carbocation and thus the major product would be $(CH_3)_2$ C = C$(CH_3)_2$. To avoid this, pyrolyze the acetate ester of the given alcohol.

$$(CH_3)_3CCHOHCH_3 \xrightarrow{CH_3COCl} (CH_3)_3C\underset{\displaystyle OCOCH_3}{\underset{|}{C}}HCH_3 \xrightarrow[(-CH_3COOH)]{heat} (CH_3)_3CCH = CH_2$$

Example 6 :

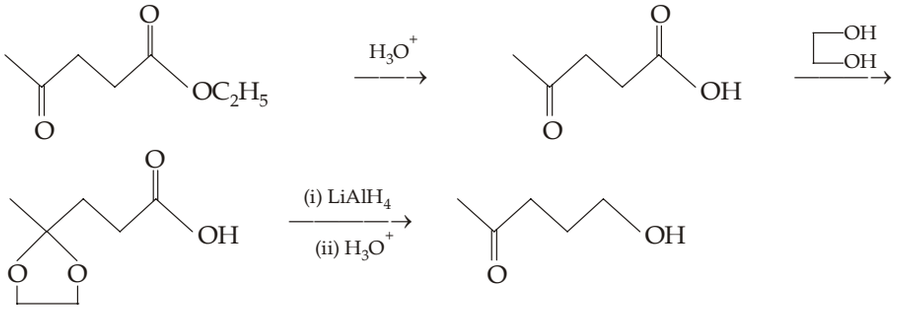
Give steps involved in the following conversion :



Solution :

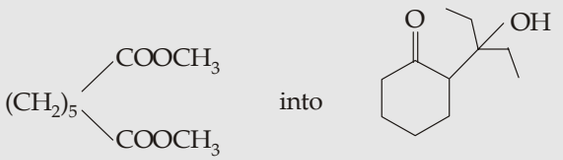
The reaction involves simply conversion of —$COOC_2H_5$ to —CH_2OH, which can be easily accompanied by reducing either —$COOC_2H_5$ or —COOH to —CH_2OH by means of $LiAlH_4$. However, since $LiAlH_4$ also reduces ketonic group so it should first be protected. Hence the various steps are as follows.

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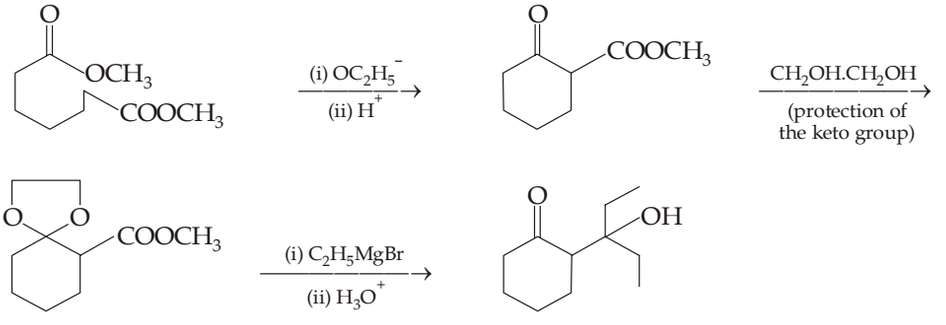
Example 7 :

Give steps involved in the following conversion :



Solution :

Note that the product is a *tert*-alcohol which is prepared by the interaction of an ester with excess of RMgX which here must be CH_3CH_2MgX because the *tert*-alcohol has two CH_3CH_2— groups ; the third alkyl group here is substituted cyclohexyl. Further, recall that esters of dicarboxylic acids can be converted into cyclic β-keto esters by means of Dieckmann reaction (*intramolecular Claisen condensation*). Thus the various steps can be written as below.



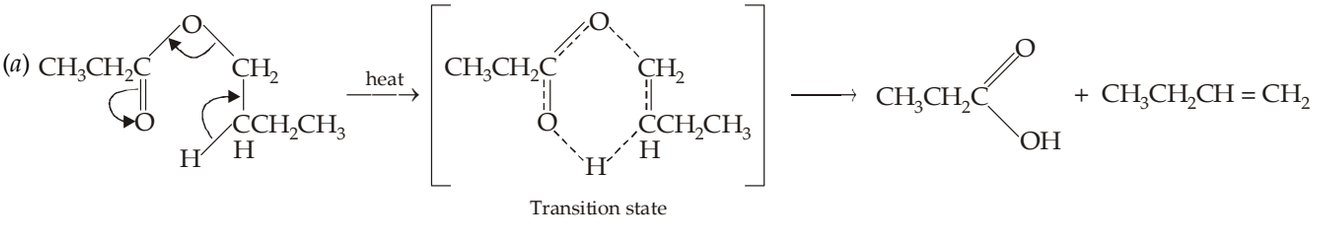
Example 8 :

Explain the products formed by the pyrolysis of

(a) $CH_3CH_2COOCH_2CH_2CH_2CH_3$ **(b) $CH_3COOCH(CH_3)CH_2CH_3$**

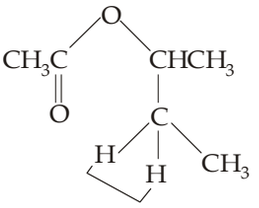
Solution :

The reaction is believed to proceed through a cyclic six-centre transition state, and involves simultaneous *syn*-elimination of a β hydrogen of the alcohol and the acetoxy group.



Transition state

(*b*)

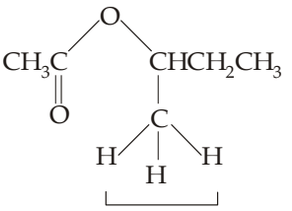


Two β-H's are present

$$\xrightarrow{\text{heat}} CH_3C(=O)OH + CH_3CH=CHCH_3$$

2-Butene

(OR)



Three β-H's are present

$$\xrightarrow{\text{heat}} CH_3C(=O)OH + CH_3CH_2CH=CH_2$$

1-Butene

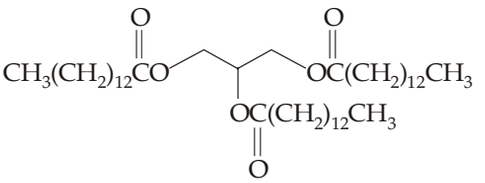
Since there are two β-hydrogens that may be eliminated to give 2-butene and there are three β-hydrogens which may lead to 1-butene, hence 2-butene and 1-butene are formed in 2 : 3 ratio.

Example 9 :

Trimyristin ($C_{45}H_{86}O_6$), obtained from coconut oil, when heated with aqueous sodium hydroxide followed by acidification, gives glycerol and tetradecanoic acid as the only products. Can you assign a structure to trimyristin?

Solution :

Molecular formula and hydrolysis products of trimyristin indicate that it is a triester of glycerol with tetradecanoic acid, $CH_3(CH_2)_{12}COOH$.



Example 10 :

Alar ($C_6H_{12}O_3N_2$), a growth regulator for apples, itself is harmless but on hydrolysis it gives a dicarboxylic acid [X] of molecular formula $C_4H_6O_4$ and a carcinogenic compound, unsymmeterical dimethylhydrazine (UDMH). Compound X on heating yields an anhydride. Assign structure to alar.

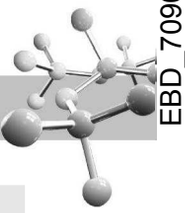
Solution :

$$\underset{C_6H_{12}O_3N_2}{\text{Alar}} \xrightarrow{H_2O} \underset{X}{C_4H_6O_4} + \underset{UDMH}{H_2NN(CH_3)_2}$$

(*i*) Since alar, on hydrolysis, gives a carboxylic acid and a substituted amine, it must be an amide.

(*ii*) The dicarboxylic acid (X), $C_4H_6O_4$ on heating gives an anhydride, the two —COOH groups must be present on different carbon atoms, so X should be succinic acid. Hence alar should be an amide of succinic acid and UDMH.

$$\underset{\text{Succinic acid, X}}{HOOCCH_2CH_2COOH} + \underset{UDMH}{H_2NN(CH_3)_2} \xleftarrow{H_2O} \underset{\text{Alar}}{HOOCCH_2CH_2CONHN(CH_3)_2}$$



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Example 11 :

An organic compound (A) of the formula $C_5H_{10}O$ is treated with perbenzoic acid to form compound (B) of the formula $C_5H_{10}O_2$. Compound (B) on acidic hydrolysis gives acetic acid and an alcohol (C) which responds haloform tert. Identify compounds (A) to (C).

Solution :

$$\underset{[A]}{C_5H_{10}O} \xrightarrow{C_6H_5CO_3H} \underset{[B]}{C_5H_{10}O_2} \xrightarrow{H^+} CH_3COOH + RCHOHCH_3$$

Given reactions indicate that compound [B] is an ester of acetic acid and the alcohol $RCHOHCH_3$, so B ($C_5H_{10}O_2$) should be an ester of the formula $CH_3COOCHCH_3$ (with R) or $CH_3COOCHCH_3$ (with CH_3); hence [A] should be a ketone. Recall that ketones when treated with per acids give esters (Baeyer-Villeger oxidation).

$$\underset{[A],\ C_5H_{10}O}{CH_3COCH(CH_3)_2} \xrightarrow{RCO_3H} \underset{[B],\ C_5H_{10}O_2}{CH_3COOCH(CH_3)_2} \longrightarrow \underset{\substack{[C],\ \text{responds}\\ \text{haloform test}}}{CH_3COOH + HOCH(CH_3)_2}$$

Example 12 :

An organic ester (A) of the formula $C_8H_{16}O_2$ reacts with phosphorus pentachloride and gives two compounds (B) and (C) . When (B) is treated with palladised-hydrogen supported over barium sulphate, it gives another compound (D) which on reduction with $LiAlH_4$ forms a primary alcohol (E) of the formula $C_4H_{10}O$; E can also be produced from (C), which has a branched alkyl group, by reaction with aqueous sodium hydroxide. Identify compounds (A) to (E) and explain the reactions involved.

Solution :

Let us summarise the given facts

$$\underset{\text{Ester, } C_8H_{16}O_2}{(A)} \xrightarrow{PCl_5} (B) + (C)$$

(B) $\xrightarrow[BaSO_4]{H_2/Pd}$ (D) $\xrightarrow{LiAlH_4}$ (E)

(C) $\xrightarrow{\text{aq. NaOH}}$ (E)

(*i*) Since the given compound (A) is an ester, with PCl_5 it will form an acid chloride and alkyl halides which are (B) and (C).

$$\underset{A}{R-\overset{O}{\overset{\|}{C}}-O-R'} + PCl_5 \longrightarrow \underset{B \text{ and } C}{R-\overset{O}{\overset{\|}{C}}-Cl} + R'-Cl + POCl_3$$

(*ii*) The given statement indicates that the compound (B) is reduced by Rosenmund reduction (specific reduction for acid chloride), so (B) should be acid chloride and (C) should be alkyl chloride. Now let us write down the given reactions of (B).

$$\underset{(B)}{R-\overset{O}{\overset{\|}{C}}-Cl} \xrightarrow[BaSO_4]{H_2/Pd} \underset{(D)}{R-\overset{O}{\overset{\|}{C}}-H} \xrightarrow{LiAlH_4} \underset{(E),\ C_4H_{10}O}{RCH_2OH}$$

So (E) can now be written as $C_3H_7CH_2OH$.

(*iii*) Nature of (C) as an alkyl halide is confirmed by its conversion to (E), a primary alcohol by reaction with aq. NaOH.

$$(C) \xrightarrow{\text{aq. NaOH}} \underset{(E),\ C_4H_{10}O}{RCH_2OH}$$

Hence the structure of (C) can be expanded as RCH_2Cl or $C_3H_7CH_2Cl$. Since (C) has a branched alkyl group, it should be $(CH_3)_2CHCH_2Cl$ and thus (E) as $(CH_3)_2CHCH_2OH$.

(*iv*) Now going backward, we can write the structure of (D), (B) and hence (A).

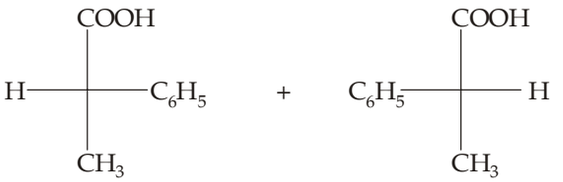
$$\underset{(E)}{(CH_3)_2CHCH_2OH} \xleftarrow{LiAlH_4} \underset{(D)}{(CH_3)_2CH.CHO} \xleftarrow[BaSO_4]{H_2/Pd} \underset{(B)}{(CH_3)_2CHCOCl}$$

$$\underset{(B)}{2(CH_3)_2CHCOCl} + \underset{(C)}{ClCH_2CH(CH_3)_2} \xleftarrow{PCl_5} \underset{A,\ C_8H_{16}O_2}{(CH_3)_2CH\overset{\overset{O}{\|}}{C}OCH_2CH(CH_3)_2}$$

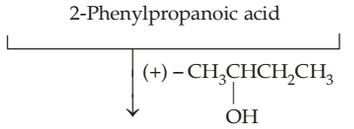
Example 13 :

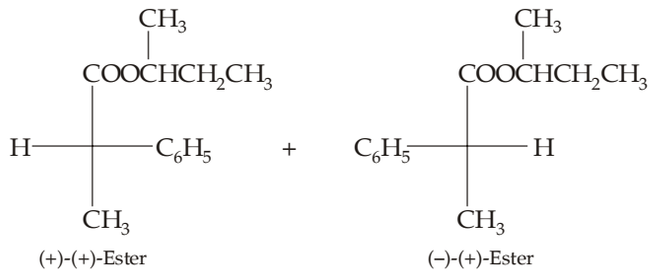
A reaction mixture of (±)-2-phenylpropanoic acid on esterification with (+) -2-butanol gives two esters. Mention the stereochemistry of the two esters produced.

Solution :



Enantiomers





(+)-(+)-Ester (–)-(+)-Ester

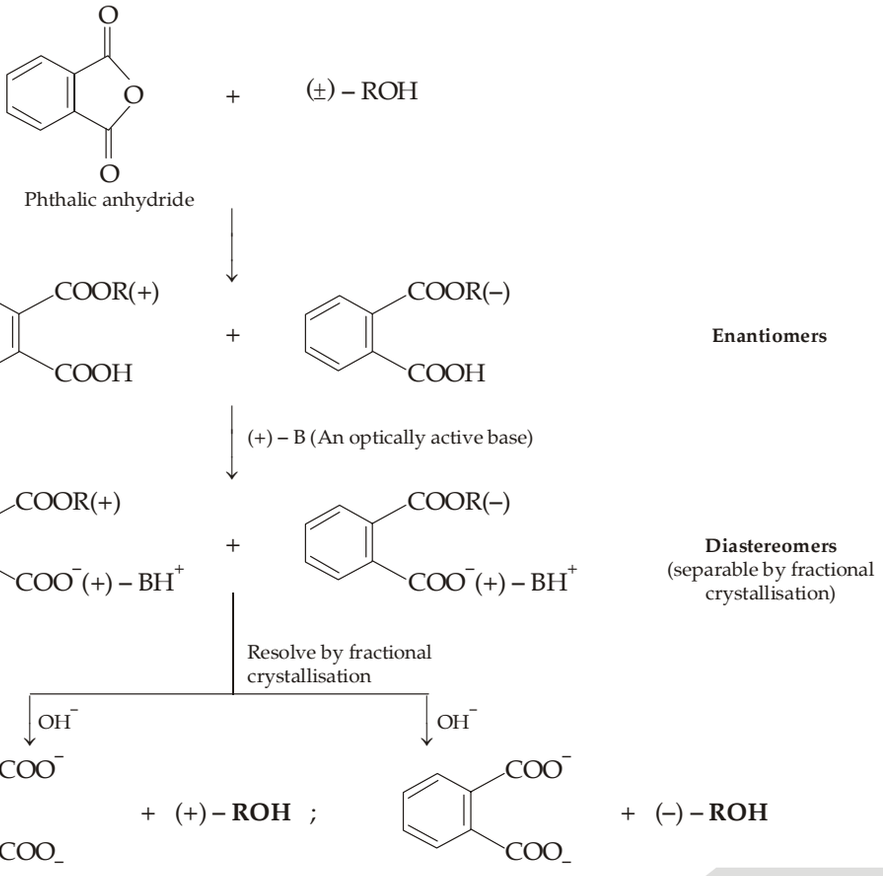
Diastereomers

Example 14 :

Although alcohols are neither acidic enough nor basic enough to form stable salts, these are frequently resolved. Outline the steps used for resolving racemic mixture of sec-butyl alcohol using (+)-base as a resolving agent.

Solution :

Although alcohols, themselves, are not strong acids or bases, these are converted into acidic compounds (alkyl hydrogen phthalate) on reaction with phthalic anhydride. The enantiomers of the racemic modification of alkyl hydrogen phthalate, being acidic, react with an optically active base to form diastereomeric salts which can be separated by fractional crystallisation (remember that enantiomers have similar solubility while diastereomers have different solubilities). The two separated diastereomers are then hydrolyzed to give optically active alcohols. Since hydrolysis of a carboxylic ester does not usually involve cleavage of the alkyl-oxygen bond, there is no loss of optical activity in the hydrolysis step.



Example 15 :

When benzoic acid is esterified by methanol in presence of a little sulphuric acid, the final reaction mixture contains five substances : benzoic acid, methanol, water, methyl benzoate and sulphuric acid. Outline a procedure used for the separation of the pure ester (methyl benzoate).

Solution :

$$C_6H_5COOH + CH_3OH \xrightarrow{H_2SO_4} C_6H_5COOCH_3 + H_2O$$

(*i*) The mixture containing five substances, *viz.* $C_6H_5COOCH_3$, H_2O (formed as products), C_6H_5COOH, CH_3OH and H_2SO_4 (left as residual amounts) is shaken with benzene which dissolves only methyl benzoate and benzoic acid ; while the other three substance (CH_3OH, H_2O and H_2SO_4) remain in water layer.

(*ii*) Benzene extract is now treated with aq. Na_2CO_3 which converts benzoic acid to water soluble sodium benzoate which is thus removed as water layer.

(*iii*) Benzene layer containing methyl benzoate and some residual water is distilled when benzene and water distils over first, followed by distillation of methyl benzoate at high temperature (200°C).

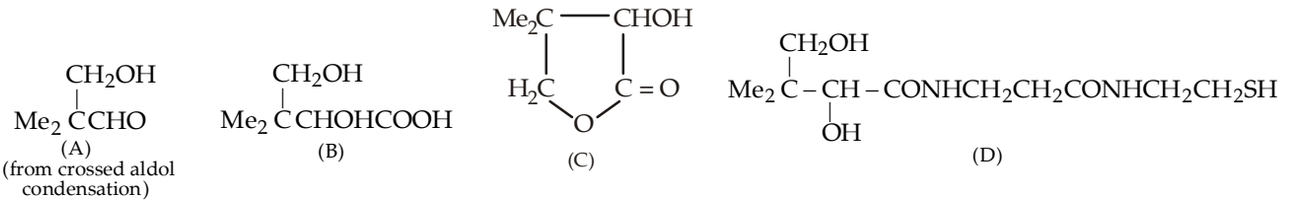
Example 16 :

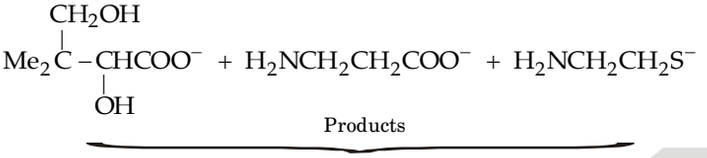
Identify the bracketed compounds from [A] to [D] in the following sereies of reactions.

$$Me_2CHCHO + HCHO \xrightarrow{K_2CO_3\ aq.} [A] \xrightarrow[(ii)\ H_3O^+]{(i)\ HCN} [B] \xrightarrow{-H_2O} [C]$$

$$\xrightarrow{H_2NCH_2CH_2CONHCH_2CH_2SH} [D] \xrightarrow[heat]{aq.\ NaOH} \text{Products}$$

Solution :





Example 17 :

Write stereochemical formulas for the compounds A to G.

(a) ***cis*-3-Methylcyclopentanol +** $C_6H_5COCl \longrightarrow [A] \xrightarrow[\text{reflux}]{OH^-} [B]$

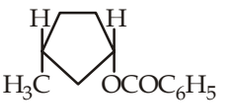
(b) ***cis*-3-Methylcyclopentanol +** $C_6H_5SO_2Cl \longrightarrow [C] \xrightarrow[\text{heat}]{OH^-} [D]$

(c) **(*R*)-2-Bromoheptane +** $OH^- \xrightarrow{\text{acetone}} [E]$

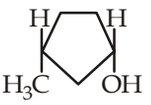
(d) **(*R*)-2-Bromoheptane +** $CH_3COONa \longrightarrow [F] \xrightarrow[\text{reflux}]{OH^-,\ H_2O} [G]$

Solution :

(a)

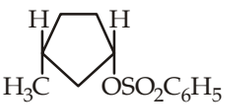


cis-(A)

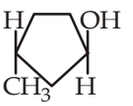


cis-(B)

(b)

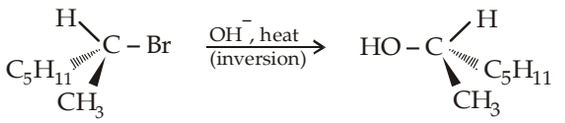


cis-(C)



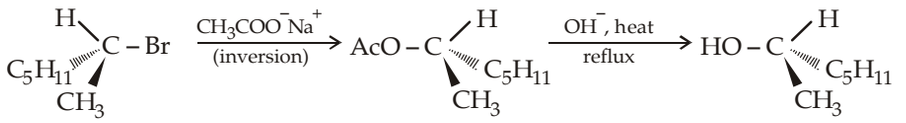
trans-(D)

(c)



(E)

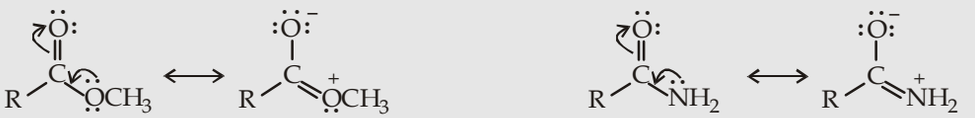
(d)



(F) (G)

Example 18 :

Esters (or carboxylic acids), and amides have two major resonance contributors, one of which involves charged structures.



Account for the fact that the charged structure in amides has a significant contribution than in esters or in carboxylic acids.

Solution :

In amides, positive charge resides on a lesser electronegative element (N) than that in esters or carboxylic acids where positive charge is present on a more electronegative element (oxygen).

EBD_7090

Example 19 :

Arrange the following compounds in order of their decreasing boiling points.

Carboxylic acids, alcohols, esters, amides, nitriles

Solution :

For knowing the relative boiling point of different compounds of comparable molecular weights, consider following factors, dipole-dipole interaction, hydrogen bonding, van der Waal forces, etc. Here no specific compounds are given, so it is assumed that the vander waal forces are nearly similar in each case, hence other two factors are responsible for their following relative boiling points.

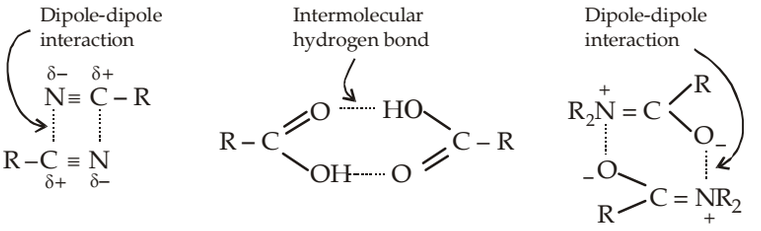
Amides > carboxylic acids > alcohols ≈ nitriles >>> esters.

(i) Boiling points of esters are lower than the boiling points of alcohols because their molecules can't form hydrogen bonds with each other. However, boiling points of esters (also for acyl chlorides, aldehydes, and ketones) are higher than those of ethers because of polar carbonyl group. Further, due to resonance polarity is less than in nitriles.

(ii) Boiling point of nitriles are similar to that of alcohols becasue the former have a strong dipole-dipole interactions, while alcohols have strong hydrogen bonds.

(iii) Carboxylic acids have relatively high boiling points than alcohols because they can form hydrogen-bonded dimers, giving them larger effective molecular weight.

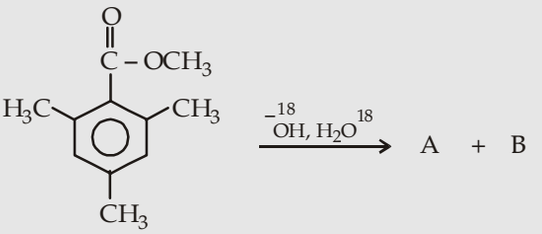
(iv) Amides have the highest boiling points, because here the dipole-dipole interactions are strong than in nitriles because here dipole-dipole interaction involves separated complete charges (recall that in an amide resonating structure having separated charges contribute *significantly* to the hybrid).



Further if an amide has a hydrogen, bonded to nitrogen as in $RCONH_2$ or RCONHR, the molecules also form intermolecular hydrogen bonds.

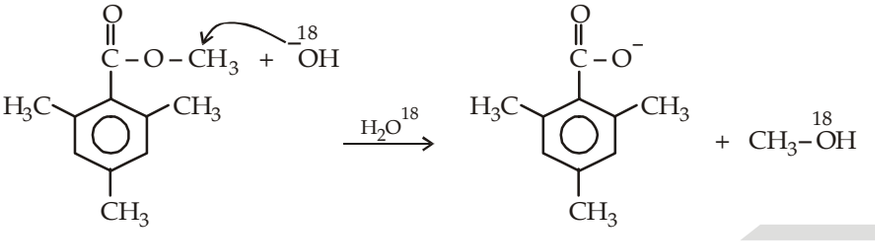
Example 20 :

Predict the products in the following reaction with proper explanation.



Solution :

Although base promoted hydrolysis of an ester involves the attack of ^-OH on the carbonyl carbon to form a tetrahedral intermediate which is then converted to carboxylic acid and alcohol. Here it is not so, steric hindrance due to two *ortho*-methyl groups prevents formation of the tetrahedral intermediate; and thus the nucleophile attacks on the alkyl carbon of the alcoholic portion instead of the acyl carbon of the acidic portion leading to alcohol having –OH provided by nucleophile.



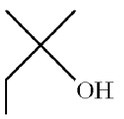
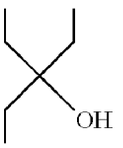
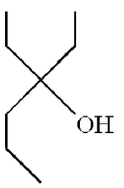
EXERCISE 18.1 (MCQ - ONE option correct)

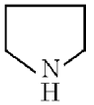
1. Bouvealt-Blanc reduction of an ester ($CH_3COOC_2H_5 \xrightarrow{Na/C_2H_5OH} C_2H_5OH$) involves
(*a*) reduction by H_2
(*b*) reduction by nascent H
(*c*) electron transfer from Na to C = O
(*d*) none of the three.

2. Benzoic anhydride is formed according to following reaction
$C_6H_5COCl + C_6H_5COONa \longrightarrow C_6H_5COOCOC_6H_5 + NaCl$
Here the nucleophile is provided by
(*a*) C_6H_5COCl
(*b*) C_6H_5COONa
(*c*) either of the two
(*d*) It is not an example of nucleophilic substitution.

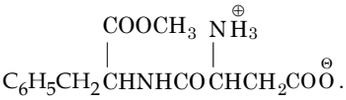
3. Which of the following is different regarding nucleophilic substitution ?
(*a*) $CH_3COCl + CH_3COONa \longrightarrow CH_3COOCOCH_3$
(*b*) $CH_3COONa + CH_3CH_2Br \longrightarrow CH_3COOCH_2CH_3$
(*c*) $CH_3COOC_2H_5 \xrightarrow{H^+} CH_3COOH + C_2H_5OH$
(*d*) $CH_3COOCOCH_3 + CH_3OH \longrightarrow CH_3COOCH_3 + CH_3COOH$

4. Which of the following ester can be used as acylating agent in mixed Claisen condensation ?
(*a*) $H-\overset{\overset{O}{\|}}{C}-OCH_3$
(*b*) $C_6H_5-\overset{\overset{O}{\|}}{C}-OCH_3$
(*c*) $C_2H_5O-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OC_2H_5$
(*d*) All

5. The product P in the following reaction will be
Ethyl ester $\xrightarrow{CH_3MgBr\ (excess)}$ P
(*a*) 
(*b*) 
(*c*) 
(*d*) 

6. Predict the nature of B.
$H_2NCH_2CH_2CH_2COOH \xrightarrow{heat} A \xrightarrow{LiAlH_4} B$
(*a*) $H_2NCH_2CH_2CH_2CH_2OH$
(*b*) $CH_2 = CHCH_2CH_2OH$
(*c*) $CH_3CH_2CH_2CH_2OH$
(*d*) 

7. Predict the nature of the product P in the following reaction:
$(+)\text{-}C_6H_5\underset{\underset{OCOC_2H_5}{|}}{CHCH} = CHCH_3 \xrightarrow{dil.\ NaOH} P$
(*a*) $(+) - C_6H_5\underset{\underset{OH}{|}}{CHCH} = CHCH_3$
(*b*) $(\pm) - C_6H_5\underset{\underset{OH}{|}}{CHCH} = CHCH_3$
(*c*) $(+) - C_6H_5CH{=}CH\underset{\underset{OH}{|}}{C}HCH_3$
(*d*) $(\pm) - C_6H_5CH = CH\underset{\underset{OH}{|}}{C}HCH_3$.

8. Aspartame, an artificial sweetening agent, has following structure

On hydrolysis with dil. HCl, it will give
(*a*) three neutral molecules.
(*b*) one neutral molecule and two molecules as cations
(*c*) two neutral molecules and one molecule as cation.
(*d*) three molecules, all in the form of cations.

9. Unlabelled 4-butanolide is allowed to stand in an acidic solution in which water has been labelled with O^{18}. When the lactone is extracted from the solution after 4 days, what will you expect ?
(*a*) Both oxygen of 4-butanolide should have O^{18}
(*b*) Only carbonyl oxygen should have O^{18}
(*c*) Oxygen other than carbonyl group should be O^{18}
(*d*) Both oxygen should have O^{16}.

10. An ester molecule reacts with two eq. of a Grignard reagent and forms
(*a*) a 3° alcohol having at least two identical alkyl groups.
(*b*) a 3° alcohol having all the three identical alkyl groups.
(*c*) a 2° alcohol having both identical alkyl groups.
(*d*) both (*a*) and (*c*).

11. Hydrolysis of an ester may be achived under acidic as well as basic conditions. Pick up the correct statement regarding this
(*a*) Acidic hydrolysis is faster than alkaline hydrolysis.
(*b*) Alkaline hydrolysis is faster than acidic hydrolysis.
(*c*) Both occur at the same rate.
(*d*) In both, the first step is protonation of the —OH part of the —COOH group.

12. In an ester molecule there are three C—O bonds, $R-\overset{\gamma}{\underset{\overset{\|}{O}}{C}}-\overset{\beta}{O}-\overset{\alpha}{}R'$. What do you expect regarding their relative bond lengths ?
(*a*) $\alpha > \beta > \gamma$ (*b*) $\beta = \gamma > \alpha$
(*c*) $\gamma > \beta > \alpha$ (*d*) $\alpha = \beta = \gamma$.

13. $C_2H_5COOCH_3 + {}^{18}OH^- \longrightarrow A + B$

In the above reaction, products A and B respectively are

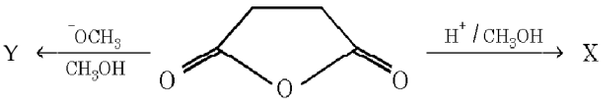
(*a*) $C_2H_5\overset{\overset{O}{\|}}{C}-O^- + CH_3\overset{18}{O}H$

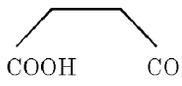
(*b*) $C_2H_5-\overset{\overset{O^{18}}{\|}}{C}-\overset{18}{O}^- + CH_3OH$

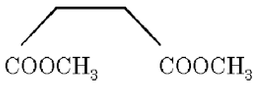
(*c*) $C_2H_5-\overset{\overset{O}{\|}}{C}-\overset{18}{O}^- + CH_3OH$

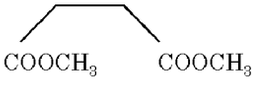
(*d*) $C_2H_5-\overset{\overset{O^{18}}{\|}}{C}-O^- + CH_3OH$

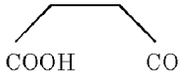
14. In the following reactions, X and Y are

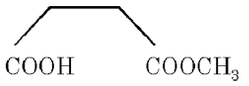


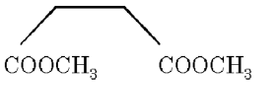
(*a*) X is  and

Y is 

(*b*) X is  and

Y is 

(*c*) Both are 

(*d*) Both are 

15. Acetic acid is dissolved in water having oxygen as O^{18}, What do you expect about the resulting acetic acid ? It should be

(*a*) $CH_3\overset{\overset{O}{\|}}{C}-OH$ (*b*) $CH_3-\overset{\overset{O}{\|}}{C}-O^{18}H$

(*c*) $CH_3-\overset{\overset{O^{18}}{\|}}{C}-OH$ (*d*) $CH_3-\overset{\overset{O^{18}}{\|}}{C}-O^{18}H$.

16. When butyramide is boiled with aqueous NaOH and then acidified, the resulting product contains

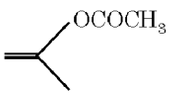
(*a*) $CH_3CH_2CH_2COO^- + NH_3$

(*b*) $CH_3CH_2CH_2COO^- + NH_4^+ + Cl^-$

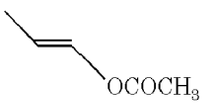
(*c*) $CH_3CH_2CH_2COONa + NH_3$

(*d*) $CH_3CH_2CH_2COOH + Na^+ + Cl^-$.

17. The product of acid hydrolysis of P and Q can be distinguished by



(P)



(Q)

(*a*) Lucas reagent (*b*) 2, 4-DNP

(*c*) Fehling solution (*d*) $NaHSO_3$.

18. An enantiomerically pure acid is treated with racemic mixture of an alcohol having one chiral carbon. The ester formed will be

(*a*) optically active mixture

(*b*) pure enantiomer

(*c*) meso compound

(*d*) racemic mixture.

19. Reactivity order of different nucleophiles (OH^-, $\bar{O}COCH_3$ and NH_2^-) toward $RCOCl + :Z \longrightarrow RCOZ + Cl^-$ is

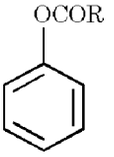
(*a*) $OH^- > {}^-OCOCH_3 > NH_2^-$

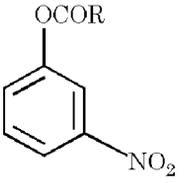
(*b*) ${}^-OCOCH_3 > OH^- > NH_2^-$

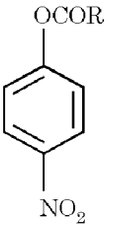
(*c*) $NH_2^- > OH^- > {}^-OCOCH_3$

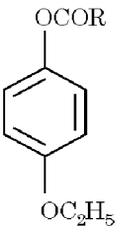
(*d*) $OH^- > NH_2^- > {}^-OCOCH_3$.

20. Acidic hydrolysis is minimum in

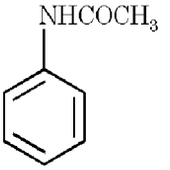
(*a*) 

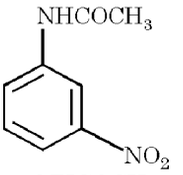
(*b*) 

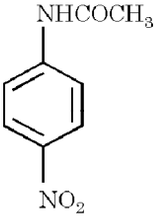
(*c*) 

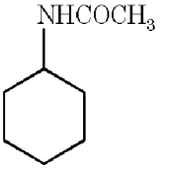
(*d*) 

21. Which of the following amide undergoes alkaline hydrolysis most easily ?

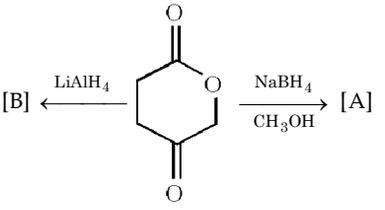
(*a*) 

(*b*) 

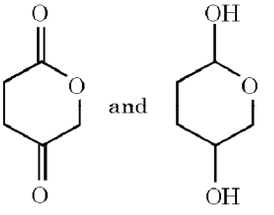
(*c*) 

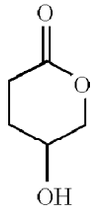
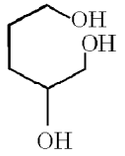
(*d*) 

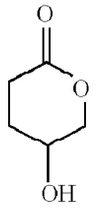
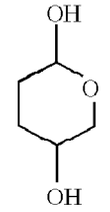
22. A keto lactone is reduced by different reagents to give A and B

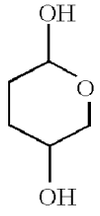


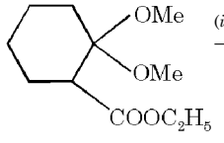
Here [A] and [B] respectively are

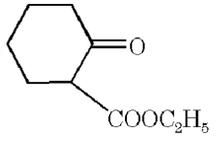
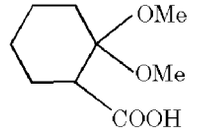
(*a*) 

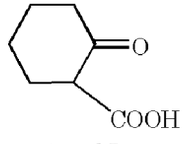
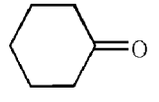
(*b*)  and 

(*c*)  and 

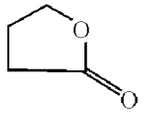
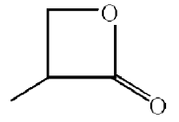
(*d*)  in both cases

23.  Z. Here Z is

(*a*)  (*b*) 

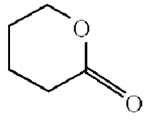
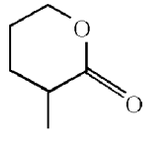
(*c*)  (*d*) 

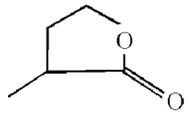
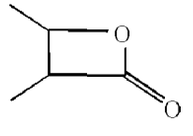
24. Lactones A and B are respectively named as

(A)  (B) 

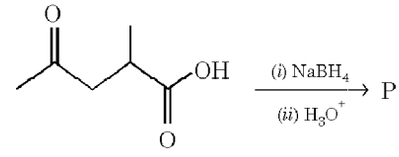
(*a*) γ-Pentanolactone, 2-methylbutyrolactone
(*b*) γ-Butyrolactone, 2-methyl-γ-butyrolactone
(*c*) γ-Butyrolactone, β-Butyrolactone
(*d*) α-Pentanolactone, 2-methyl α-butyrolactone.

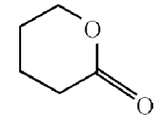
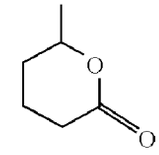
25. Which of the following represents the structure of γ-pentanolactone ?

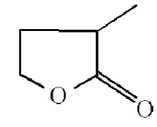
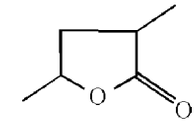
(*a*)  (*b*) 

(*c*)  (*d*) 

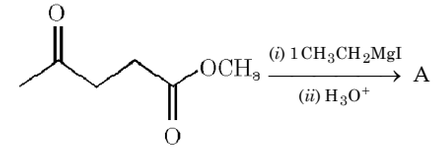
26. Predict the nature of the product P in the following reaction.

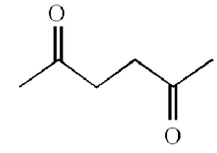


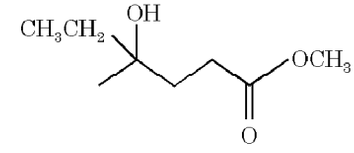
(*a*)  (*b*) 

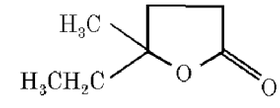
(*c*)  (*d*) 

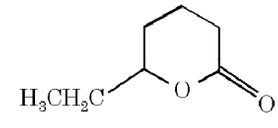
27. Give the structure of the compound A formed in the following reaction.

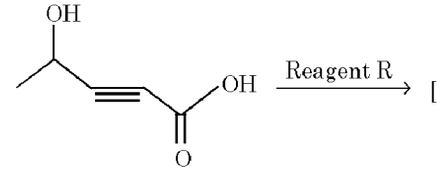


(*a*) 

(*b*) 

(*c*) 

(*d*) 

28. 

Here R and R′ respectively are

(*a*) Pt/ H_2, H_3O^+ (*b*) H_2/Pd, H_3O^+
(*c*) Li/NH_3, H_3O^+ (*d*) Ni/H_2.

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29. Predict the respective compounds A and B in the following reaction :

$$CH_3CH_2COCH_3 \xrightarrow{C_6H_5CO_3H} [\quad] \xrightarrow{H_3O^+} A + B$$

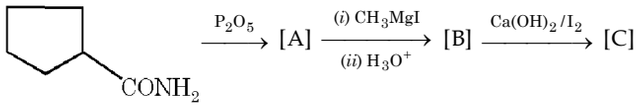
(*a*) CH_3CH_2COOH, CH_3OH

(*b*) CH_3CH_2COOH, CH_3COOH

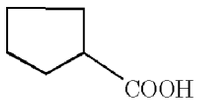
(*c*) CH_3CH_2OH, CH_3COOH

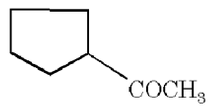
(*d*) $CH_3CH_2COCH_3, C_6H_5COOH.$]

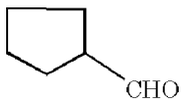
30. In the given series of reactions, the final product D is

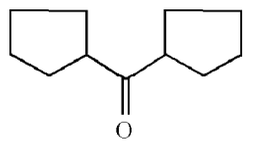


$\xrightarrow{heat}$ [D]

(*a*) 

(*b*) 

(*c*) 

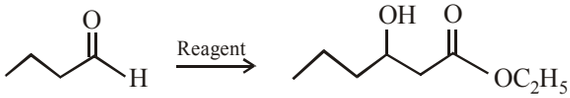
(*d*) 

31. $C_2H_5O-\overset{\overset{O}{\|}}{C}-OC_2H_5 + 2CH_3MgBr \longrightarrow A$; A is

(a) $(CH_3)_2\overset{\overset{OH}{|}}{C}-C_2H_5$ (b) $C_2H_5-\overset{\overset{OH}{|}}{\underset{\underset{C_2H_5}{|}}{C}}-CH_3$

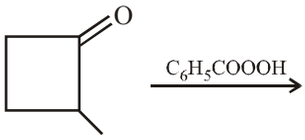
(c) CH_3COOH (d) CH_3COCH_3

32. Which of the following reagent can be used for carrying out the reaction outlined below?

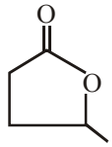


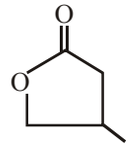
(a) $BrMgCH_2COOC_2H_5$ (b) $BrZnCH_2COOC_2H_5$

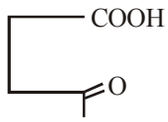
(c) $LiCH_2COOC_2H_5$ (d) Any of the three

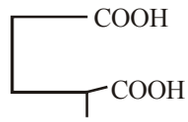
33. 

Here the product is

(a) 

(b) 

(c) 

(d) 

34. Acetyl chloride does not react with

(a) Water

(b) Sodium acetate

(c) 2-methylpropene

(d) It reacts with all the three

35. Which of the following reaction is possible ?

(i) $CH_3COCl + H_2O \rightarrow CH_3COOH + HCl$

(ii) $CH_3COOCH_3 + HBr \rightarrow CH_3COBr + CH_3OH$

(iii) $CH_3CONH_2 + HBr \rightarrow CH_3COBr + NH_3$

(iv) $CH_3COOCOCH_3 + H_2O \rightarrow 2CH_3COOH$

(a) (i) and (iv) (b) (i), (iii) and (iv)

(c) (i), (ii) and (iv) (d) All the four

36. Acid amides do not undergo the usual properties of carbonyl, C = O group because

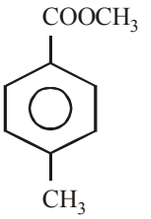
(a) it is a weak base

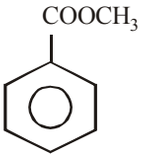
(b) it is a weak acid

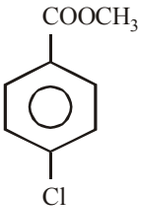
(c) it is amphoteric

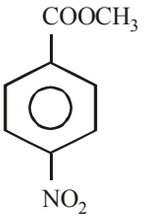
(d) its carbonyl carbon is not electron deficient

37. Which of the following will undergo alkaline hydrolysis most rapidly ?

(a) 

(b) 

(c) 

(d) 

38. Hydrolysis of esters in presence of an acid is a reversible reaction, what is true about ester hydrolysis in presence of a base?

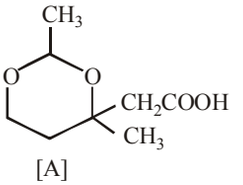
(a) It is irreversible because salts of carboxylic acids are insoluble.

(b) It is irreversible because salts of carboxylic acids have high melting points.

(c) It is irreversible because carboxylate ion is resonance stabilized.

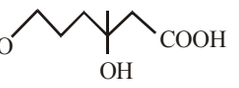
(d) It is reversible reaction.

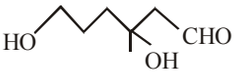
39. Compound A is formed by the interaction of

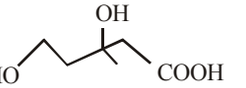


[A]

(a) CH_3COOH and 

(b) CH_3CHO and 

(c) CH_3COCH_2COOH and 

(d) CH_3CHO and 

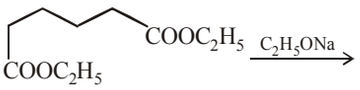
40. The yield of ester in esterification can be increased by

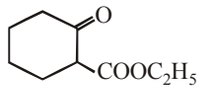
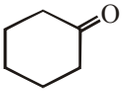
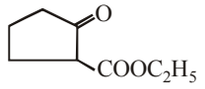
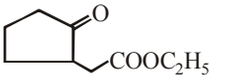
$CH_3CH_2OH + CH_3COOH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$

(a) removing water
(b) taking ethanol in excess
(c) taking acetic acid in excess
(d) all the above factors

41. The yield of acid amide in the reaction, $RCOCl + NH_3 \rightarrow RCONH_2$, is maximum when

(a) acid chloride and ammonia are treated in equimolar ratio
(b) acid chloride and ammonia are treated in 1 : 2 molar ratio
(c) acid chloride and ammonia are treated in 2 : 1 molar ratio
(d) All the three gives nearly similar result

42.  Z. Here Z is

(a) 
(b) 
(c) 
(d) 

43. Both aldol and Claisen condensations are given by compounds having α-hydrogen atom to a C = O group. Pick up the compound which responds aldol condensation but not Claisen condensation.

$CH_3CH_2COOC_2H_5$ (I)

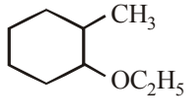
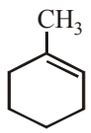
$(CH_3)_2CHCOOC_2H_5$ (II)

$(CH_3)_3CCOOC_2H_5$ (III)

(a) II (b) III
(c) II and III (d) None of the three

44. 

$+ CH_3COOC_2H_5 \rightarrow [\ ] \xrightarrow{H_3O^+} A$. Compound A is

(a) 
(b) 
(c) 
(d) 

45. Which of the following can be used for introducing a ketonic group in the compound ?

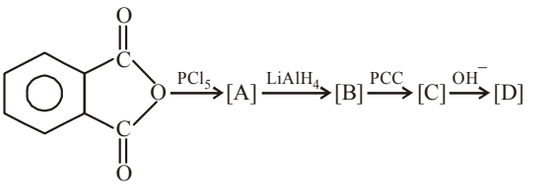
(a) Claisen rearrangement (b) Claisen reaction
(c) Pinacol rerarrangement (d) All the three

46. Which statement is true regarding reaction of an acid chloride (RCOCl) and ammonia when taken in 1 : 1 molar ratio?

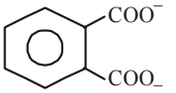
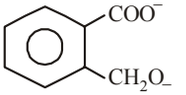
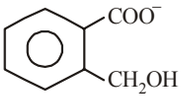
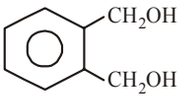
(a) Whole of acid chloride is converted into $RCONH_2$
(b) One-half of acid chloride is converted into $RCONH_2$ and the other half into $RCOONH_4$
(c) One-half of acid chloride is converted into $RCONH_2$ and the remaining half remains unreacted
(d) None of the three is correct

47. Esterification of acid chloride with ethanol is usually carried out in the presence of pyridine. The function of pyridine is

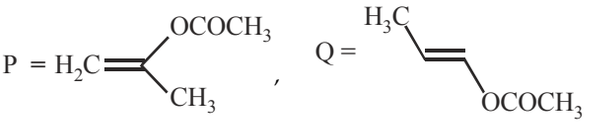
(a) to remove HCl formed in the reaction
(b) to react with acid chloride to form an acylpyridinium ion
(c) both (a) and (b)
(d) as a catalyst

48. 

Compound D is

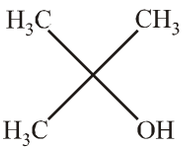
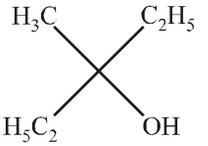
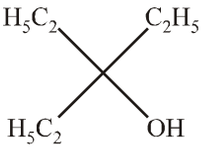
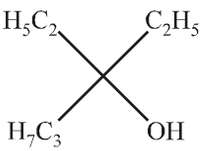
(a) 
(b) 
(c) 
(d) 

49. The product of acid hydrolysis of P and Q can be distinguished by



(a) Lucas Reagent (b) 2,4–DNP
(c) Fehling's Solution (d) $NaHSO_3$

50. Ethyl ester $\xrightarrow[\text{excess}]{CH_3MgBr}$ P. The product P will be

(a) 
(b) 
(c) 
(d) 

EBD_7090

51. An enantiomerically pure acid is treated with a racemic mixture of an alcohol having one chiral carbon. The ester formed will be
(a) Optically active mixture (b) Pure enantiomer
(c) Meso compound (d) Racemic mixture

52. Which of the following statement is not upto the mark?

(a) $R-\overset{O}{\overset{\|}{C}}-OR' \xrightarrow{OH^-} R-\overset{O}{\overset{\|}{C}}-O^- + R'OH$
(A base-catalysed reaction)

(b) $CH_3COOC_2H_5 \xrightarrow{OH^-} CH_3COOH + C_2H_5OH$
(reaction involves acyl-oxygen fission)

(c) $C_6H_5COOH + CH_3OH \xrightarrow{H^+} C_6H_5COOCH_3 + H_2O$
(reaction involves acyl-oxygen fision)

(d) $CH_3COOCH(CH_3)C_2H_5 \xrightarrow{OH^-} CH_3COO^- + HOCH(CH_3)C_2H_5$
(configuration of the reactant is retained)

53. The products in the following reaction are

$$C_6H_5COOCH_2C_6H_5 \xrightarrow{H_2-Pd/C}$$

(a) $C_6H_5CH_2OH + C_6H_5CH_2OH$

(b) $C_6H_5CH_3 + C_6H_5CH_3$

(c) $C_6H_5CH_2OH + C_6H_5CH_3$

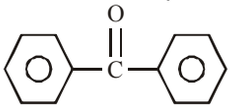
(d) $C_6H_5COOH + C_6H_5CH_3$

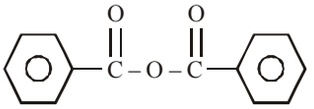
54. Pyrolysis of $CH_3COO\overset{CH_3}{\overset{|}{C}}HCH_2CH_3$ gives
(a) 1-butene and 2-butene in equimolar ratio
(b) 1-butene and 2-butene in 1 : 2 molar ratio
(c) 1-butene and 2-butene in 3 : 2 molar ratio
(d) 1-butene and 2-butene in 2 : 3 molar ratio

55. The relative stability of the four acid derivatives towards nucleophiles is
(a) Amide > Ester > Acid anhydride > Acid chloride
(b) Amide > Acid anhydride > Ester > Acid chloride
(c) Acid Chloride > Acid anhydride > Ester > Amide
(d) Acid Chloride > Ester > Acid anhydride > Amide

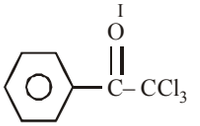
56. Which of the following statement is true about the hydrolysis of acetic anhydride ?
(i) It is more easily hydrolysed in acidic medium than in neutral
(ii) It is more easily hydrolysed in alkaline medium than in neutral
(iii) It is equally hydrolysed in all the three medium
(iv) It is more easily hydrolysed in neutral than in acidic medium
(v) It is more easily hydrolysed in neutral than in alkaline medium
(a) (i) and (ii) (b) (iii)
(c) (iv) and (v) (d) (i) and (v)

57. Which of the following compounds can undergo nucleophilic substitution easily ?

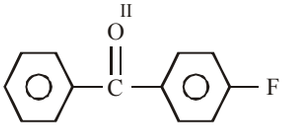




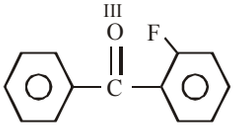
I



II



III



IV

V

(a) Only II (b) I, II, III and IV
(c) II, III and V (d) II, III and IV

58. The reason for greater reactivity of acetyl chloride for nucleophilic substitution than methyl chloride is due to
(i) capability of oxygen to acquire electrons
(ii) difference in the nature of carbon of the intermediate: a tetrahedral in case of acetyl chloride and a pentavalent in case of methyl chloride
(iii) difference in attack of nucleophile on the compound
(iv) better leavability of –COCl than –Cl
(a) (i) and (ii) (b) (i) and (iii)
(c) (i), (ii) and (iii) (d) (iv)

59. The driving force for the completion of Claisen condensation between ethyl acetate and sodium ethoxide to ethyl acetoacetate is
(a) the presence of reactive methylene group in ethyl acetoacetate
(b) the phenomenon of keto enol tautomerism
(c) the presence of at least α-hydrogen atom in ester
(d) all the three factors

60. Which of the following compound undergoes Claisen condensation in presence of C_2H_5ONa ?

(i) $CH_3CH_2COOC_2H_5$

(ii) $(CH_3)_2CHCOOC_2H_5$ (iii) $ClCH_2COOC_2H_5$

(a) only (i) (b) (i) and (ii)
(c) (i) and (iii) (d) all of the three

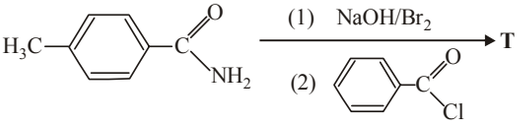
61. Ester + CH_3MgBr (excess) $\xrightarrow{H_3O^+} C_4H_{10}O$ (Alcohol)
The alcohol formed gives white ppt. with $ZnCl_2/HCl$ immediately, the ester may be

$HCOOC_3H_7$ (I) $CH_3COOC_5H_{11}$ (II)

CH_3COOCH_3 (III) $C_2H_5COOCH_3$ (IV)

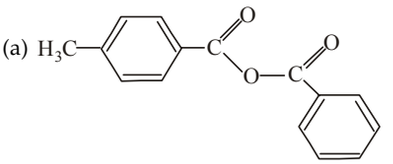
(a) II (b) II and III
(c) II and IV (d) I

62. In the reaction

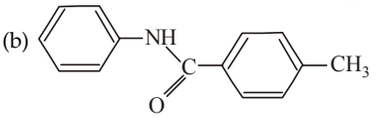


the structure of the product **T** is :

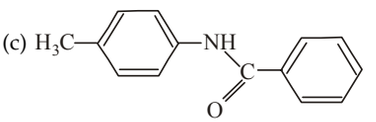
(a)



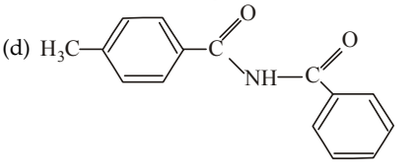
(b)

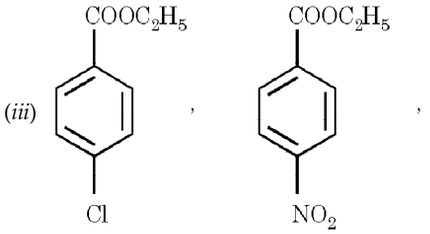


(c)

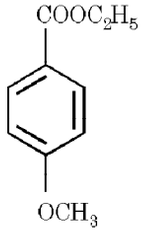


(d)

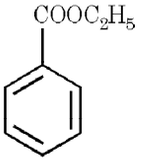


(*iii*)  ,

 ,



and



(*iv*) $CH_3COOC_2H_5$, CH_3COCl, $(CH_3CO)_2O$ and CH_3CONH_2.

(*c*) Compare the reactivity of benzoyl chloride with cyclohexanecarboxyl chloride.

8. Predict the product of the reaction of γ-butyrolactone with

(*a*) ammonia (*b*) $LiAlH_4$ (*c*) $C_2H_5OH + H_2SO_4$.

9. Describe simple chemical tests that would serve to distinguish between

(*a*) Acetyl chloride and acetic anhydride.

(*b*) *n*-Butyryl chloride and *n*-butyl chloride.

(*c*) Benzoyl bromide and *p*-bromobenzoic acid.

(*d*) Propanoic acid and ethyl acetate.

(*e*) Acetic anhydride and *n*-butyl alcohol.

(*f*) Ammonium benzoate and benzamide.

(*g*) Glyceryl monopalmitate and glyceryl tripalmitate.

10. (*a*) Write an equation for the reaction of $CH_3COOC_2H_5$ with CH_3MgI.

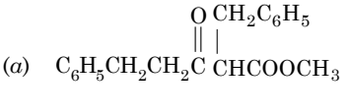
(*b*) Why a ketone is not isolated from the reaction of an ester with one equivalent of CH_3MgI ?

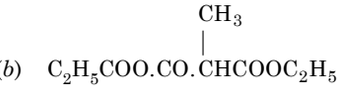
(*c*) Can you prepare a 2° alcohol from an ester and an organometallic reagent ?

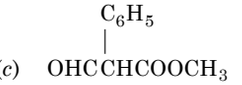
11. (*a*) What is an ortho ester, give its general formula ? Give the product obtained by the mild hydrolysis of ethyl orthoformate.

(*b*) Write down the steps involved in the preparation of ethyl orthoformate by the reaction of chloroform with sodium ethoxide.

12. Give the ester or combination of esters required to prepare the following products by a Claisen condensation.

(*a*) 

(*b*) 

(*c*) 

13. Compare the reactants, conditions, and products of the Hofmann, Lossen, Curtius and Schmidt reactions.

14. Compare the acidity of the N—H in

(*a*) an acid amide (*e.g.*, CH_3CONH_2) and a sulphonamide (*e.g.*, $CH_3SO_2NH_2$).

(*b*) benzamide ($C_6H_5CONH_2$),a phthalimide and ammonia.

15. Explain the following :

(*a*) Dimethyl sulphate is a good methylating agent.

(*b*) An acyl chloride undergoes nucleophilic attack more rapidly than does an alkyl chloride.

(*c*) Trialkyl phosphates are readily hydrolyzed with OH^- to dialkyl phosphate salts, while the hydrolysis of dialkyl hydrogen phosphates and alkyl dihydrogen phosphates with OH^- becomes increasingly more difficult.

(*d*) Hydrolysis of the ester (A) with 5 M NaOH gives optically active alcohol, C_6H_5 while hydrolysis with dil. NaOH gives optically inactive alcohol.

(*e*) The reaction '$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$' is slow in the beginning, but fast subsequently.

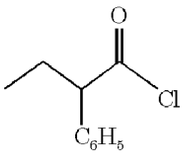
16. An ester (A) of the formula $C_5H_8O_2$ on acidic hydrolysis gives an acid (B) which reduces Tollen's regent and an alcohol (C) which gives iodoform test. Ester (A) can also be converted into alcohol (B) by reaction with excess of Grignard reagent (D). Identify (A) to (D).

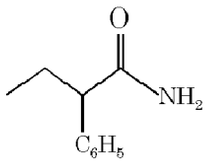
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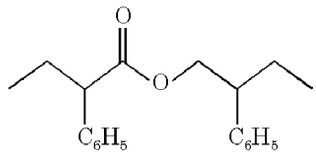
SOLUTIONS

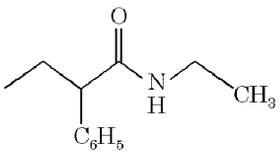
TEST YOUR UNDERSTANDING - 18.1

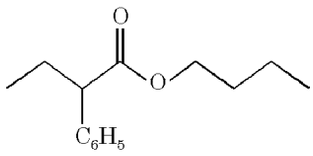
1. (*i*) 3, 3-Dimethylbutanoyl chloride (*ii*) 2-Bromopentanoyl bromide (*iii*) 3-Hexenoyl chloride
(*iv*) Cyclopentyl methanoyl chloride (*v*) Propanoic hexanoic anhydride (*vi*) Methyl cyclopentanecarboxylate
(*vii*) 1-Methylpropyl propenoate (*viii*) N, N-Dimethylpropanamide (*ix*) N, N′-Dimethylurea
(*x*) N, N-Dimethylurea.

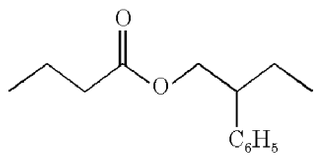
2. (*i*) 

(*ii*) 

(*iii*) 

(*iv*) 

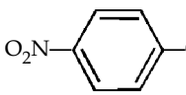
(*v*) 

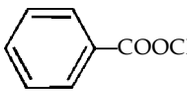
(*vi*) 

3. Nitriles are hydrolyzed by H^+ or OH^- to acids.

TEST YOUR UNDERSTANDING - 18.2

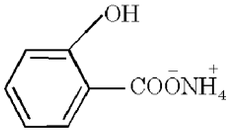
1. Recall that the first step in nucleophilic substitution at acyl carbon is the addition of a nucleophile at acyl carbon which is facilitated by (*a*) any factor that increases the electrophilic character of the acyl carbon ; and (*b*) less steric hindrance at carbonyl carbon. Thus
(*i*) F_3CCOCl is more reactive due to strong electron-withdrawing nature of F.
(*ii*) CH_3COOCH_3 is more reactive because the other compound has benzene ring which decreases the electrophilic character of carbonyl carbon by supplying electrons due to resonance,

(*iii*)  is more reactive due to electron-withdrawing nature of the —NO_2 group.

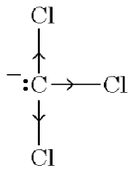
(*iv*)  is more reactive due to less steric hindrance.

(*v*) An ester is more reactive (less stable) than an amide.

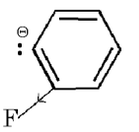
2. (*i*) $CH_3CH(Cl)\ COO^-NH_4^+$. Here addition of nucleophile takes place on —COOH. Recall that alkyl halides (CH_3CHCl —) react very slowly with nucleophiles than acyl compounds.
(*ii*) $ClCH_2CONH_2$ (Acyl nucleophilic substitution is very fast than alkyl nucleophilic substitution).
(*iii*) C_6H_5Cl does not react with NH_3 at room temperature.

(*iv*) 

3. Aldehydes and ketones do not undergo nucleophilic substitution (nucleophilic addition-elimination) because generally the eliminated anions ($H:^-$ or $R:^-$) are strongly basic and hence poor leaving groups. In the two given cases, the leaving anions are stabilized by powerful electron withdrawing groups ; hence these are weak bases and behave as good leaving groups.



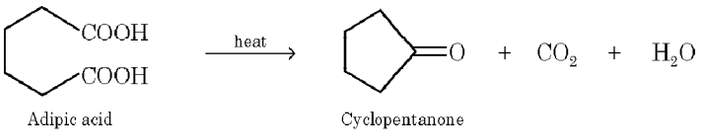
Stabilized by three electron-withdrawing groups



Stabilized by powerful electron withdrawing *ortho* F

TEST YOUR UNDERSTANDING - 18.3

1. (*a*) Formation of anhydride from adipic acid would produce a seven-membered ring which is too difficult to be formed. Instead, it loses a molecule of CO_2 and converted into a cyclic ketone with five-membered ring.



Adipic acid Cyclopentanone

Suberic acid (1, 8-octanedioic acid) does not form cyclic ketone because again here seven-membered ring would be formed which is too difficult to be formed.

(*b*) $C_6H_5—\overset{\overset{O}{\|}}{C}—Cl + H_2O \longrightarrow C_6H_5—\overset{\overset{O}{\|}}{C}—OH + HCl$

$C_6H_5—\overset{\overset{O}{\|}}{C}—Cl + HO—\overset{\overset{O}{\|}}{C}—C_6H_5 \longrightarrow C_6H_5—\overset{\overset{O}{\|}}{C}—O—\overset{\overset{O}{\|}}{C}—C_6H_5 + HCl$

TEST YOUR UNDERSTANDING - 18.4

1. (*a*) Nucleophilic substitution of acyl compounds takes place readily (*i*) if the final product is more resonance stabilized than the reactant or (*ii*) if the incoming group (nucleophile) is a stronger base than the leaving group.

(*i*) Yes. CH_3COOH is more resonance stabilized than CH_3COCl ; also OH^- is a stronger base than Cl^- .

(*ii*) No. CH_3CONH_2 is lesser resonance stabilized than CH_3COOH. NH_3 reacts with RCOOH to form $RCOO^-NH_4^+$ which does not react. Amides are prepared from RCOOH by strongly heating dry $RCOO^- NH_4^+$ because now reaction is catalysed by acid (NH_4^+).

(*iii*) Yes. CH_3COO^- is more stabilized than $(CH_3CO)_2O$; also the leaving group $RCOO^-$ is a weaker base than OH^-.

(*iv*) Yes. $CH_3COOC_2H_5$ is more stabilized than CH_3COBr, and also Br^- is a much weaker base than HOC_2H_5.

(*v*) Yes. CH_3COO^- is highly stable than CH_3CONH_2 ; although NH_2^- (the leaving group) is a stronger base than OH^- (the nucleophile).

(*vi*) No. CH_3COBr is less stable than CH_3COOCH_3 (ester) ; also Br^- is a weaker base than OCH_3^-.

(*b*) $CH_3COOH \xrightarrow{NaOH} CH_3COO^-Na^+ \xrightarrow{(CH_3)_3CBr}$ Elimination reaction.

Hence $CH_3COO^- Na^+ + (CH_3)_2 C = CH_2 \xrightarrow{\text{Conc. } H_2SO_4} CH_3COOC(CH_3)_3$

(*c*) Since acyl chloride is more reactive than the carboxylic acid, it will react with water rapidly to give the starting material

$RCOOH + HCl \rightleftharpoons RCOCl + H_2O$

Water (one of the products) cannot be removed as it is formed because here HCl (being gas) would escape.

TEST YOUR UNDERSTANDING - 18.5

1. (*a*) $C_6H_5—\overset{\overset{OH}{|}}{\underset{\underset{Cl}{|}}{C}}—OCOCH_3$ (*b*) $C_6H_5—\overset{\overset{OH}{|}}{\underset{\underset{Cl}{|}}{C}}—OC_2H_5$ (*c*) $C_6H_5—\overset{\overset{OH}{|}}{\underset{\underset{Cl}{|}}{C}}—N(CH_3)_2$ (*d*) $C_6H_5—\overset{\overset{OH}{|}}{\underset{\underset{Cl}{|}}{C}}—OH$

2. Since hydrazoic acid (HN_3) is slightly more acidic than acetic acid (CH_3COOH), the azide ion (N_3^-) is slightly less basic than the acetate ion (CH_3COO^-). Thus azide ion will be slightly better leaving group than the acetate ion ; hence acyl azide ($RCON_3$) will be a little more reactive than the anhydride (RCOOCR). Thus the position of acyl azide in the order of reactivity of various acyl derivatives will be between acyl chlorides and acid anhydrides.

$$RCOCl > RCON_3 > (RCO)_2O$$

3. (*a*) Pd/C, poisoned with quinolione and S or LBAH (*b*) NH_3 (*c*) $LiAlH_4$ (*d*) $C_6H_5CH_2OH + H^+$
(*e*) $C_6H_5COO^-Na^+$ or heat with $(CH_3CO)_2O$ (*f*) $C_6H_5CH_2NH_2$ (*g*) NaN_3 (sodium azide).

4. In each case, the less reactive organometallic Me_2CuLi reacts with the more reactive —COCl group to form methyl ketone.

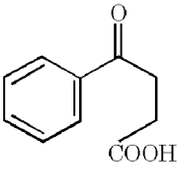
(*a*) $NC(CH_2)_4COCH_3$ (*b*) $2CH_3CO$—C$_6$H$_4$—$COCH_3$ (*c*) $H_5C_2OOC(CH_2)_4COCH_3$.

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TEST YOUR UNDERSTANDING - 18.6

1. (*a*) $CH_3COOCH_3 + CH_3COOH$ (*b*) $2CH_3COOCH_3$

(*c*) $\frac{1}{2}\,CH_3CONH_2 + \frac{1}{2}\,CH_3COO^-NH_4^+ + \frac{1}{2}\,(CH_3CO)_2O$ (*d*) $\begin{matrix} CH_2CON(CH_3)_2 \\ | \\ CH_2COO^-\ H_2N^+(CH_3)_2 \end{matrix}$ (*e*) $\begin{matrix} CH_2COO^-Na^+ \\ | \\ CH_2COO^-Na^+ \end{matrix}$

(*f*) $(CH_3)_3COH$ (*g*) 

2. (*a*) Mixed anhydrides are prepared by reacting the acid chloride of one of the acids with the carboxylic salt of the other. Thus

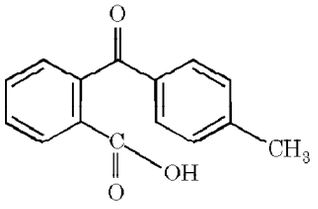
(*i*) $CH_3-\overset{O}{\overset{\|}{C}}-Cl + Na^+\,{}^-O-\overset{O}{\overset{\|}{C}}-CH_2CH_3$ or $CH_3CH_2-\overset{O}{\overset{\|}{C}}-Cl + Na^+\,{}^-O-\overset{O}{\overset{\|}{C}}-CH_3$ $\longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_2CH_3$

(*ii*) $CH_3-\overset{O}{\overset{\|}{C}}-Cl + Na^+\,{}^-O-\overset{O}{\overset{\|}{C}}-H \longrightarrow \underset{\text{Acetic formic anhydride}}{CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-H}$

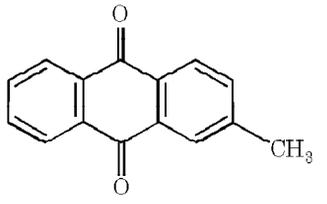
Since HCOCl is not stable, HCOCl + $CH_3\ COO^-Na^-$ does not constitute the alternate pair for preparing acetic formic anhydride.

(*b*) No. On heating, formic acid undergoes dehydration intramolecularly rather than intermolecularly.

$$HCOOH \longrightarrow CO + H_2O$$

3. 

o-(*p*-Tolyl)benzoic acid
[A]



2-Methyl-9, 10-anthraquinone
[B]

TEST YOUR UNDERSTANDING - 18.7

1. (*a*) $R-\overset{\ddot{O}:}{\overset{\|}{C}}-\ddot{O}-R'$. The π electrons of the C = O bond are more easily displaced than the σ electrons of the C—O bond with the result the carbonyl oxygen acquires negative charge, hence acyl oxygen (or carbonyl oxygen) is more basic.

(*b*) The three C—O bonds have different bond lengths, because of relative displacement of electrons along their bonds ;

$$R-\overset{O}{\overset{z\|}{C}}-\overset{y}{O}-\overset{x}{O}-R'$$

The relative value of bond lengths is $x > y > z$.

2. The carbonyl carbon of RCOOH and RCOOR′ is trigonal sp^2 hybridised, while that of the intermediate is tetrahedral sp^3 hybridised. If alkyl group in alcohol or in acid is extensively branched, transition state will be crowded leading to slow reaction and with difficulty too.

3. (*a*) $\underset{III}{CH_3COOCH_3} > \underset{I}{CH_3COOC_2H_5} > \underset{II}{CH_3COOCHMe_2} > \underset{IV}{CH_3COOCMe_3}$

Steric effect, and relative basic character of the leaving groups. Basic character of the leaving groups is

$$Me_3CO^- > Me_2CHO^- > C_2H_5O^- > CH_3O^-$$

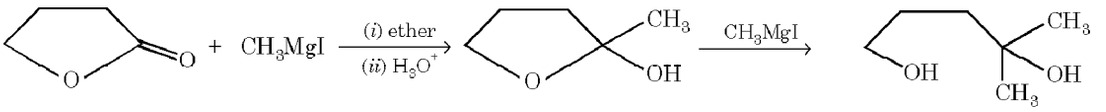
(*b*) $\underset{II}{HCOOCH_3} > \underset{I}{CH_3COOCH_3} > \underset{IV}{CH_3CH_2COOCH_3} > \underset{III}{Me_2CHCOOCH_3} > \underset{V}{Me_3CCOOCH_3}$

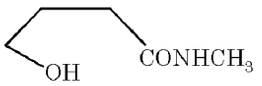
Remember that an alkyl group releases electrons, and thus destabilizes the transition state by intensifying the negative charge developing on oxygen. Thus lesser is electron releasing character of an alkyl group, more will be the stability of the transition state.

4. Presence of electron-withdrawing group speeds up the reaction since it helps to disperse the negative charge developing on oxygen.

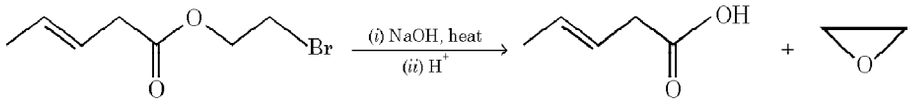
(*a*) V > III > IV > I > II (*b*) III > IV > II > I.

5. (*a*) (*i*) $CH_3CH_2C(C_6H_5)_2OH$

(*ii*) 

(*iii*) 

(*iv*) $CH_3CONHNH_2$ Acetyl hydrazide (*v*) $C_6H_5CONHOH$ Benzoylhydroxamic acid

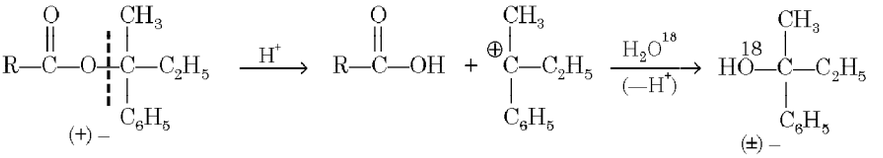
(*b*) 

(*c*) $CH_3(CH_2)_7CH=CH(CH_2)_7COOC_4H_9\text{-}n \longrightarrow \underset{\text{1–Octadecanol}}{CH_3(CH_2)_{16}CH_2OH} + n\text{-}C_4H_9OH$

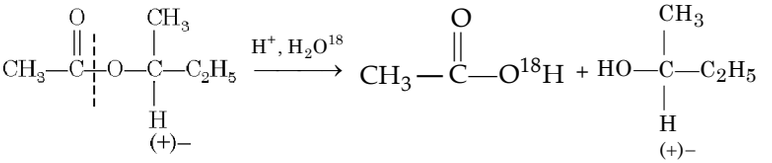
6. Esters of formic acid, when treated with excess of Grignard reagents, give secondary alcohols having similar alkyl groups.

$$H{-}C(=O){-}OC_2H_5 + 2\,n\text{-}C_3H_7MgBr \longrightarrow \underset{\text{4–Heptanol}}{n\text{-}C_3H_7{-}CH(OH){-}C_3H_7\text{-}n}$$

7. (a) However, with 3° alcohols, ester hydrolysis occurs by alkyl-oxygen cleavage leading to a 3° carbocation which being planar gives racemic product.



(b) Hydrolysis of esters having 2° or 1° alcohol occur by acyl-oxygen cleavage. Since no bond to chiral carbon is broken, configuration is retained and O^{18} from water appears in acidic part.



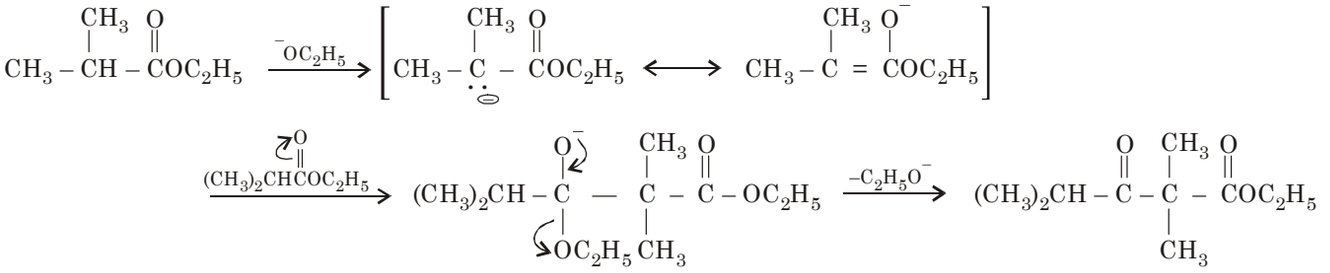
TEST YOUR UNDERSTANDING - 18.8

1. (*a*) (*i*) $CH_3CH_2CH_2CH_2C(=O)CH(CH_2CH_2CH_3)COOCH_2CH_3$ (*ii*) Not possible (*iii*) $C_6H_5CH_2C(=O)CH(C_6H_5)COOCH_2CH_3$

(*b*) (*i*) $C_6H_5CH(CHO)COOC_2H_5$ (*ii*) $C_6H_5CH(COCOOC_2H_5)COOC_2H_5$ (*iii*) $C_6H_5CH(COCH_2C_6H_5)COOC_2H_5$ (*iv*) $C_6H_5CH(COC_6H_5)COOC_2H_5$.

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2. The side reaction with sodium methoxide is transesterification. The starting material, and therefore the product, would be a mixture of methyl and ethyl esters. Sodium hydroxide would irreversibly saponify the ester, completely stopping the claisen condensation as the carbonyl no longer has a leaving group attached to it.

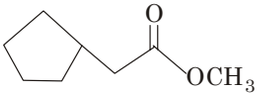
3. 

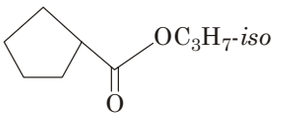
The two reasons for the poor yield in this reaction are

(i) The nucleophilic carbon in the enolate is 3° and attack is hindered.

(ii) More important, the final product has no hydrogen on the α-carbon, so the deprotonation by base which is the driving force in Claisen condensation can't occur. Thus, the product will be an equilibrium mixture of product (minor) and starting materials (major).

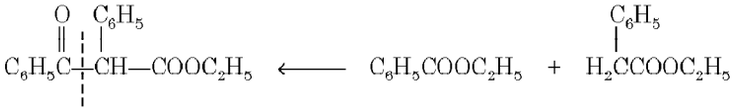
4. Dissect the α,β-bond of the β-keto ester. Add the appropriate alcohol (ROH) to the two carbon atoms (RO^- to the carbonyl carbon and H^+ to other carbon).

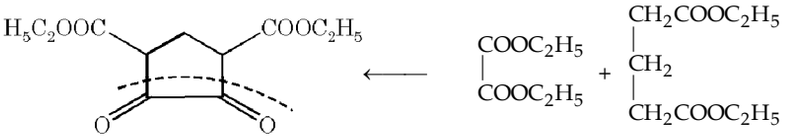
(i) 

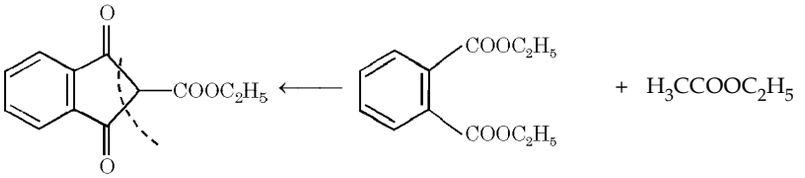
(ii) 

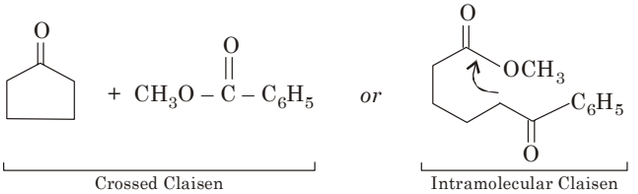
Note that in (b) the product of Claisen condensation would be formed in low yield because it does not have acidic hydrogen between two C = O groups to be removed to form the stable carbanion (driving force for the reaction).

5. Remove the acyl group of the product in the form of an ester.

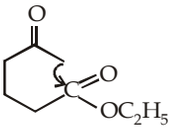
(*i*) 

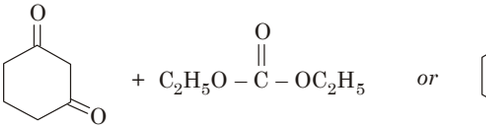
(*ii*) 

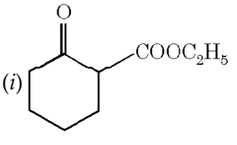
(*iii*) 

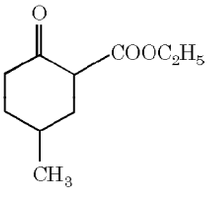
6. (a) 

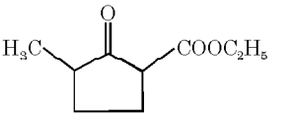
Crossed Claisen | Intramolecular Claisen

(b) 

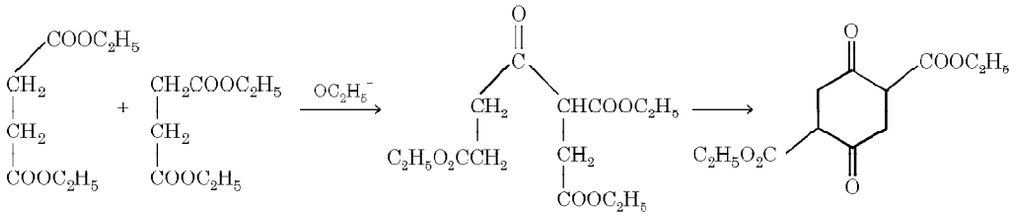
(c) 

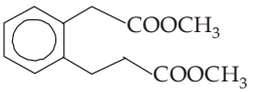
7. (*a*) (*i*) 

(*ii*) 

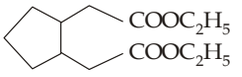
(*iii*) 

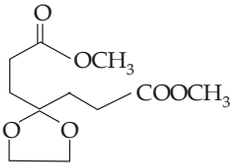
(*b*) Since three and four membered rings are difficult to form, ethyl succinate and ethyl glutarate do not undergo Dieckmann reaction. However, ethyl succinate on prolonged treatment with sodium ethoxide undergoes double Claisen condensation to form six-membered cyclic compound.



8. (a) 

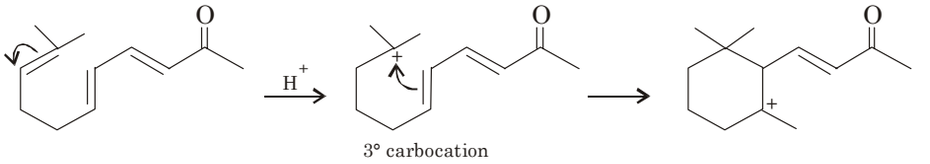
(b) It is a γ-keto ester, hence can't be prepared by Dieckmann condensation.

(c) 

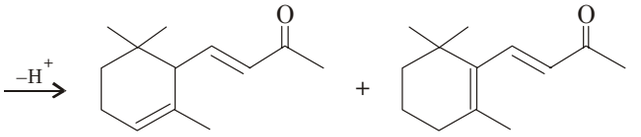
(d) 

Ketonic group is protected to avoid aldol condensation.

9. $CH_3COOH + BF_3 \rightleftharpoons CH_3COOBF_3^- + H^+$

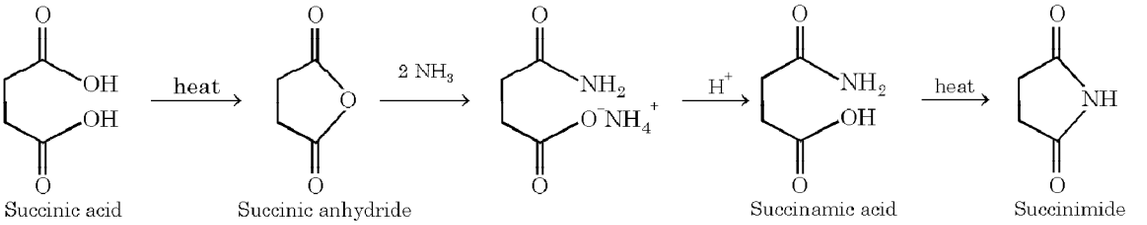


3° carbocation



(major)

TEST YOUR UNDERSTANDING - 18.9

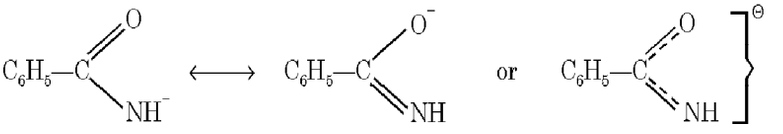
1. (*a*) 

Succinic acid — Succinic anhydride — Succinamic acid — Succinimide

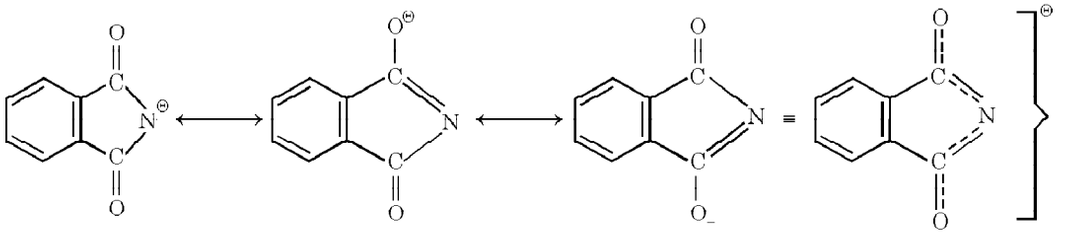
(*b*) $CH_3CH_2CH_2COOH \xrightarrow{SOCl_2} CH_3CH_2CH_2COCl \xrightarrow{NH_3} CH_3CH_2CH_2CONH_2 \xrightarrow{Br_2/NaOH} CH_3CH_2CH_2NH_2$

Butanoic acid — 1-Propanamine

2. Let us draw the structure of the conjugate base and study their relative basicity.



Resonance in conjugate base of benzamide.

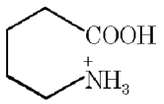
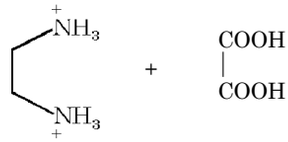


In conjugate base of NH_3, *i.e.* NH_2^-, the negative charge is localised. Thus the order of basic character of the three conjugate bases is

$$NH_2^- > C_6H_5CONH^- > \text{Conjugate base of phthalimide}$$

Acidity order is Phthalimide > Benzamide > NH_3

3. (*a*) $CH_3COOH + Me_2\overset{+}{N}H_2$ (*b*) $COOH.\underset{CH_3}{\underset{|}{C}}HNH_3^+ + COOH\underset{C_2H_5}{\underset{|}{C}}HNH_3^+$

(*c*)  (*d*) 

4. Hydrolysis of amides is an example of nucleophilic addition-elimination reaction which is enhanced in presence of electron-withdrawing group. Thus II < I < IV < III

5. (*a*) $\underset{1^\circ \text{ amide}}{RCONH_2} + R'Li \longrightarrow \underset{\text{metal salt}}{RCONH^-Li^+} + R'H$

$\underset{2^\circ \text{ amide}}{RCONHR'} + R''Li \longrightarrow RCON^-R'Li^+ \downarrow + R''H$

$\underset{3^\circ \text{ amide}}{RCONR_2'} + R''Li \longrightarrow RCOR'' + R_2'NLi$

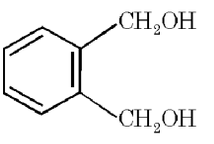
(*b*) $\underset{1^\circ \text{ amide}}{RCONH_2} + HONO \longrightarrow RCOOH + N_2 + H_2O$

$RCONHR' + HONO \longrightarrow \underset{\text{N-Nitrosoamide}}{RCO\underset{R'}{\underset{|}{N}} - N = O}$

$RCONR_2'$ (3° amide) does not react with nitrous acid.

6. (*i*) $C_6H_5CH_2CH_2OH + CH_3OH$ (*ii*) $2CH_3CH_2OH$

(*iii*) $C_6H_5CH_2OH$ (*iv*) $CH_3CH = CHCH_2CH_2NHC_6H_5$

(*v*) $HOCH_2\underset{CH_3}{\underset{|}{C}}HCH_2CH_2OH$ (*vi*)  (*vii*) 

TEST YOUR UNDERSTANDING - 18.10

1. (*a*) RCOCl (*b*) $RCOOC_2H_5$ (c) $(CH_3CH_2CO)_2O$

(*d*) $RCOO^-NH_4^+$ (*e*) $RCOO^-NH_4^+$, $RCONH_2$, or RCN.

2. $\underset{n\text{-Propyl acetate}}{CH_3COOC_3H_7\text{–}n} + OH^- \longrightarrow CH_3COO^- + n\text{-}C_3H_7OH$

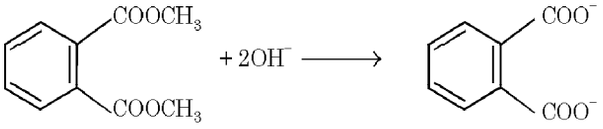
One mole of the ester requires one mole of OH^- for hydrolysis (saponification), thus Saponification equivalent (SE) = M.W. of ester = 102 ($C_5H_{10}O_2$).

Number of esters (RCOOR') having $C_5H_{10}O_2$ as the molecular formula can be ascertained by taking different possibilities for R and R' (total number of C in R and R' should be 4). Since R' is coming from alcohol part, it can CH_3, C_2H_5, *n*-C_3H_7, *iso*-C_3H_7, *n*-C_4H_9, *iso*-C_4H_9, *sec*-C_4H_9, or *tert*-C_4H_9 ; while R (coming from acidic part) can be *n*-C_3H_7, *iso*-C_3H_7, C_2H_5, CH_3, or H. Thus nine different esters are possible, including *n*-propyl acetate.

(*i*) $HCOOC_4H_9$-*n* (*ii*) $HCOOC_4H_9$-*iso* (*iii*) $HCOOC_4H_9$-*sec* (*iv*) $HCOOC_4H_9$-*tert*
(*v*) $CH_3COOC_3H_7$-*n* (*vi*) $CH_3COOC_3H_7$-*iso* (*vii*) $C_2H_5COOC_2H_5$ (*viii*) *n*-$C_3H_7COOCH_3$
(*ix*) *iso*-$C_3H_7COOCH_3$.

Number of carboxylic acids (RCOOH) having $C_5H_{10}O_2$ as molecular formula. Since here one carbon atom is present as —COOH, so the remaining four carbon atoms must be present as butyl group, *i.e.*

$CH_3CH_2CH_2CH_2COOH$ — Butanoic acid
$(CH_3)_2CHCH_2COOH$ — Isobutanoic acid
$C_2H_5\underset{\displaystyle CH_3}{\underset{|}{C}}HCOOH$ — sec. Butanoic acid
$(CH_3)_3C.COOH$ — *tert*-Butanoic acid

3. (*a*) 

Methyl phthalate (M.W. = 194) — Phthalate anion

Since 1 mole of phthalate used 2 moles of OH^- ; S. E. = M.W./2 = 194/2 = 97

(*b*) S.E. = M.W./No. of ester groups per molecule.

EXERCISE 18.1

1	(c)	**6**	(d)	**11**	(b)	**16**	(d)	**21**	(c)	**26**	(d)
2	(b)	**7**	(d)	**12**	(a)	**17**	(c)	**22**	(b)	**27**	(c)
3	(b)	**8**	(b)	**13**	(c)	**18**	(a)	**23**	(d)	**28**	(b)
4	(d)	**9**	(b)	**14**	(a)	**19**	(c)	**24**	(c)	**29**	(c)
5	(a)	**10**	(d)	**15**	(d)	**20**	(d)	**25**	(c)	**30**	(d)

1. In Bouvealt-Blanc reduction, reduction involves the transfer of electron from metal (Na or Li).

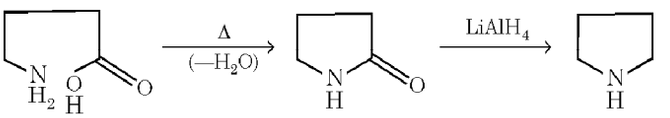
2. $C_6H_5-\overset{\displaystyle O}{\overset{\|}{C}}-O^-$ is a nucleophile, while $C_6H_5-\overset{\displaystyle \delta+}{\overset{}{C}}(=O^{\delta-})-Cl$ acts as an electrophile.

3. Only reaction (*b*) is S_{N^2} while the others are acyl bimolecular nucleophilic substitution.

4. In mixed condensation, an ester not having any α-hydrogen atom acts as acylating agent because it does not form enolate ion.

5. Esters (other than formates) react with excess of RMgX forming 3° alcohols having two alkyl groups corresponding to alkyl part of the RMgX. Since here RMgX is CH_3MgBr, so the 3° alcohol formed should have at least two methyl groups which is only option (*a*).

6. Like γ- and δ-hydroxy acids, γ- and δ- amino carboxylic acids form corresponding lactam.



[A] [B]

7. In presence of dil. NaOH, esters are hydrolysed *via* S_N1 mechanism which involves the formation of carbocation, hence the product (alcohol) will be optically inactive, provided chiral carbon is present in the parent ester. Further, carbocation is formed as an intermediate which rearranges to the more stable carbocation, thus the rearranged product is formed as the final product.

$$C_6H_5\underset{\displaystyle OCOC_2H_5}{\underset{|}{C}}HCH=CHCH_3 \xrightarrow{\text{dil. NaOH}} C_6H_5\overset{+}{C}HCH=CHCH_3 \longleftrightarrow \underset{\text{More Stable}}{C_6H_5CH=\overset{+}{C}HCH_3} \xrightarrow{OH^-} \underset{(\pm)-\text{Alcohol}}{C_6H_5CH=\underset{\displaystyle OH}{\underset{|}{C}}HCH_3}$$

8. $C_6H_5CH_2\underset{\displaystyle COOCH_3}{\underset{|}{C}}H-NH-\overset{\displaystyle O}{\overset{\|}{C}}-\underset{\displaystyle NH_3^{\oplus}}{\underset{|}{C}}HCH_2COO^{\ominus} \xrightarrow{H_3O^{\oplus}} C_6H_5CH_2\underset{\displaystyle CO\,OH}{\underset{|}{C}}H\overset{\oplus}{N}H_3 + HOOC.\underset{\displaystyle \overset{\oplus}{N}H_3}{\underset{|}{C}}HCH_2COOH + CH_3OH$

9. Consult mechanism of lactone (or ester) hydrolysis by acids.

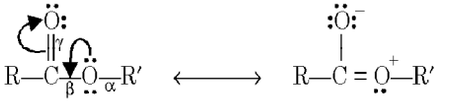
10. $HCOOR + R'MgX \text{ (excess)} \longrightarrow H-\underset{\displaystyle R'}{\underset{|}{C}}(OH)-R'$; $RCOOR'' + R'MgX \text{ (excess)} \longrightarrow R-\underset{\displaystyle R'}{\underset{|}{C}}(OH)-R''$

A 2° alcohol — (A 3° alcohol)

EBD_7090

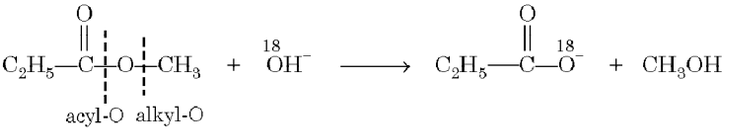
11. Alkaline hydrolysis is irreversible because here $RCOO^-$ is isolated ; moreover the product $RCOO^-$ stabilizes itself due to resonance.

12. The γ-carbon-oxygen bond is shortest because it has double bond character. The β-C—O bond is shorter because it also has some double bond character due to resonance. The α-C—O bond is longest because it is always a single bond.



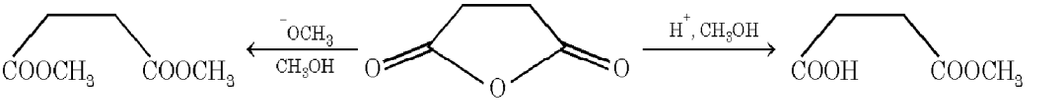
I (More important) II (Less important)

13. Esters undergo acyl-oxygen cleavage during hydrolysis.

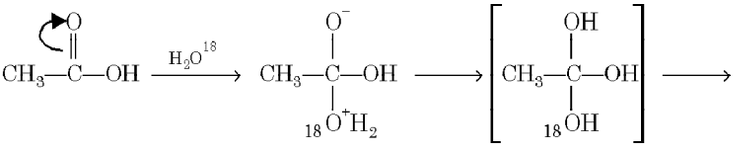


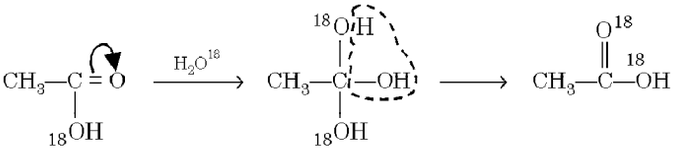
acyl-O alkyl-O

14.



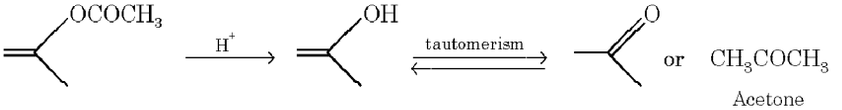
15.



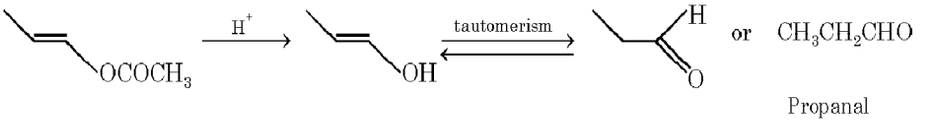


16. $CH_3CH_2CH_2CONH_2 \xrightarrow[(-NH_3)]{OH^-} CH_3CH_2CH_2COO^-\,Na^+ \xrightarrow{HCl} CH_3CH_2CH_2COOH + Na^+ + Cl^-$

17.



Acetone



Propanal

Acetone and propanal can be distinguished by Fehling solution.

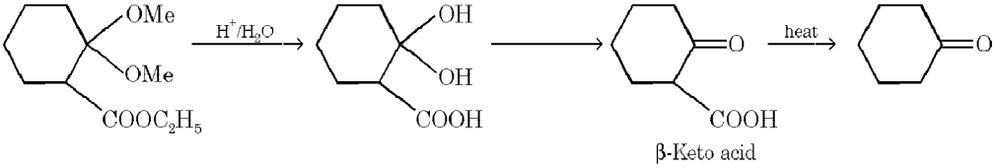
18. Remember that the two enantiomers react differently *i.e.* at different rate with an optically active reagent leading to the formation of two isomers (diastereomers) in different amounts, hence the resulting mixture will be optically active.

19. Stronger a nucleophile, more will be its reactivity toward nucleophilic substitution.

20,21. Recall that presence of electron-withdrawing group in *p*- or *o*-position increases nucleophilic substitution, while electron-releasing group decreases the reactivity.

22. Only ketonic group is reduced by $NaBH_4$, while $LiAlH_4$ reduces both ketonic as well as lactone group to the —OH groups.

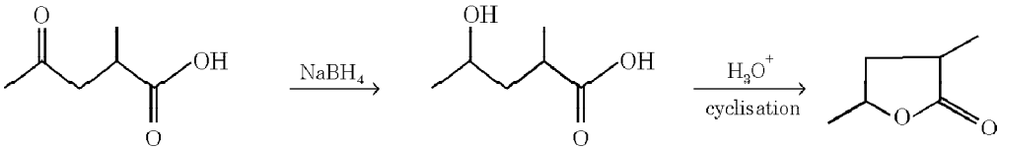
23.



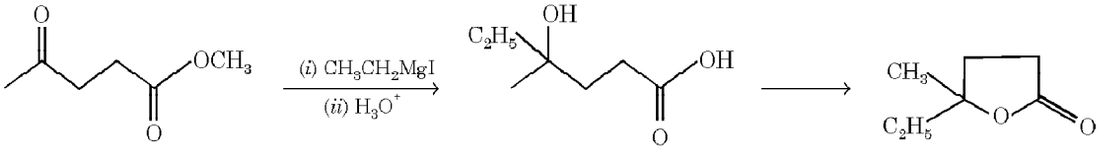
β-Keto acid

Remember that β-keto acids undergo decarboxylation on heating.

24,25. In lactones, the root word is derived from the name of the parent carboxylic acid prefix α, β or γ- is inserted on the basis of relative positions of the —OH and —COOH groups in the parent hydroxy acid.

26. 

A γ-hydroxy acid

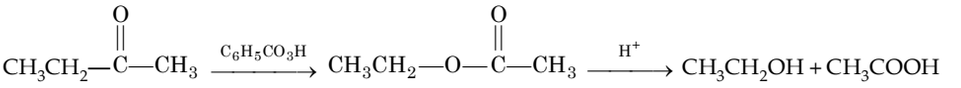
27. 

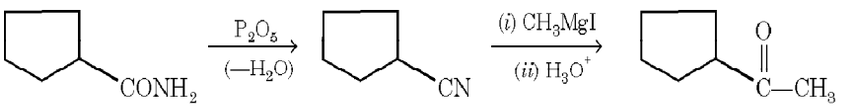
A keto ester (ketonic gp. is more reactive toward RMgX)

A γ-hydroxy acid

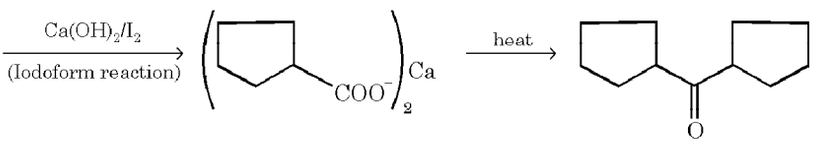
28. (*i*) Since the product has a C = C bond, so C ≡ C should be partially reduced to C = C.
(*ii*) Since the final prouct is a cyclic, the intermediate should be *cis*- or *syn*- alkene, because *anti*-alkene will not be able to undergo cyclisation. Hence the reagent R should be H_2/Pd (Lindlar catalyst) which gives *syn*-alkene. The second reagent R′ is H_3O^+.

29. In Baeyer Villeger oxidation (conversion of ketones to esters by per acids), oxygen is introduced between the larger alkyl group and the C = O carbon.



30. 

[A] [B]



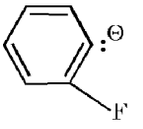
[C] [D]

EXERCISE 18.2

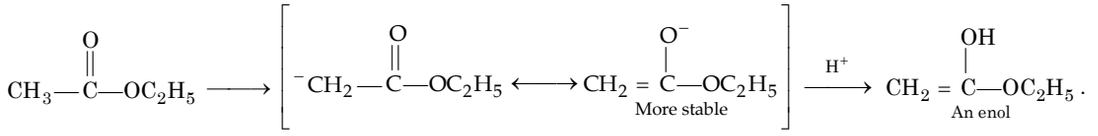
MCQ > 1 CORRECT OPTION	**1**	(a,b,c)	**2**	(a,b,c)	**3**	(a,c,d)	**4**	(c,d)
	5	(a,b,d)	**6**	(a, b, c, d)	**7**	(a, b, c, d)	**8**	(a, b, c)
	9	(a, c)	**10**	(a, b, c, d)	**11**	(a, d)		
PASSAGE 1	**12**	(c)	**13**	(c)	**14**	(b)		
Match the following	**15**	(A) - (b, c), (B) - (d), (C) - (a), (D) - (a)						
	16	(A) – b; (B) – d; (C) – c; (D) – a						
	17	(A) - a, b; (B) - a, b; (C) - c; (D) - d						
A/R	**18**	(c)	**19**	(a)	**20**	(c)	**21**	(c)

1. Alkyl isonitriles are not hydrolysed to acids, all others give carboxylic acids on hydrolysis.

2. The first three are examples of nucleophilic addition elimination reaction, option (*c*) is although ketone, it undergoes acyl type of nucleophilic substitution, *i.e.* nucleophilic addition elimination because the leaving group here is an aryl anion having electron withdrawing F in the *o*-position making the carbanion stable.



Thus it is a weaker base and better leaving group than the ordinary Ar^-. In (d) –OH is a poor leaving group.

3. 

4. Nature of the final products indicate that Q is an ester, and hydrolysed by alkali. Thus P must be $(CH_3)_2CHCHO$ which undergoes Tischenko reaction.

5. Stronger the basic nature of the leaving group, weaker will be its leavability. In CH_3COOH, OH^- is a strong base so it can't be removed easily to form $CH_3\overset{+}{C}O$ required for acetylation (acylation).

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EXERCISE 18.3

1. (*a*) $C_6H_5COCH_2CH_3$ Propiophenone (Ethyl phenyl ketone) (*b*) $CH_3CH_2CONHOH$ Propanehydroxamic acid (*c*) $CH_3CH_2CONHCH_3$ N-Methylpropanamide (*d*) $CH_3CH_2COC_3H_7$-*n* 3-Hexonone

(*e*) CH_3CH_2CHO Propanal (*f*) $CH_3CH_2\overset{O}{\overset{\|}{C}}—O—O—\overset{O}{\overset{\|}{C}}CH_2CH_3$ Propionyl peroxide

2. (*a*) $CH_3(CH_2)_3NH_2$ (*b*) $CH_3(CH_2)_3NH_2$ (*c*) No reaction (*d*) $CH_3(CH_2)_2COOC_2H_5$

3. (*a*) The hydrolysis involves *O*-acyl cleavage and hence configuration of the alcohol is retained. The products formed are

$$CH_3COO^-Na^+ + (R) - HO\overset{CH_3}{\overset{|}{C}}HCH_2CH_3$$

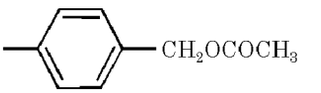
(*b*) Here also *O*-acyl cleavage occurs. $CH_3COOH + (R) - HO\overset{CH_3}{\overset{|}{C}}HCH_2CH_3$

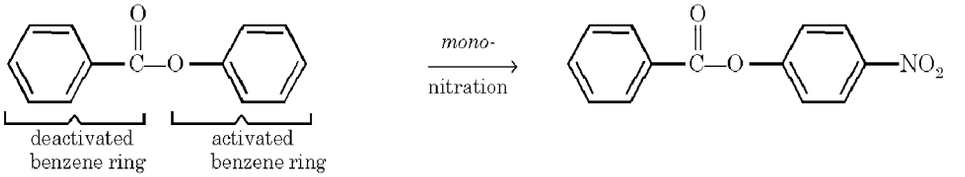
(*c*) In presence of a high concentration of nucleophile (5 M NaOH), the ester undergoes bimolecular nucleophilic acyl substitution, with the *O*-acyl cleavage. Further since the bond to the chiral carbon is not broken, configuration of the alcohol is retained.

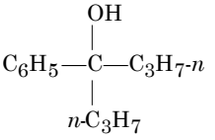
$$(R)—C_6H_5\overset{O\overset{\cdot\cdot}{+}COR}{\overset{|}{C}}HCH = CHCH_3 \xrightarrow{5M\,NaOH} (R)—C_6H_5\overset{OH}{\overset{|}{C}}HCH = CHCH_3 + RCOOH$$

(*d*) In presence of a low concentration of nucleophile (dil. NaOH), ester undergoes S_{N^1} reaction involving alkyl-oxygen fission. Further note that carbocation is formed as an intermediate, so it stabilizes to the more stable benzylic- allylic cation having double bond in conjugation with the ring. Since carbocation is planar, the product formed will be racemic mixture.

$$(R)—C_6H_5\overset{OCOR}{\overset{|}{C}}HCH = CHCH_3 \xrightarrow{dil.\ NaOH} C_6H_5—\overset{+}{C}H—CH = CHCH_3 \longleftrightarrow \underset{\text{More stable}}{C_6H_5CH = CH—\overset{\oplus}{C}HCH_3} \xrightarrow{OH^-} \underset{\text{racemic mixture}}{C_6H_5CH = CH—\overset{OH}{\overset{|}{C}}HCH_3}$$

(*e*) $C_6H_5CH_2OH + C_2H_5OH$ (*f*) $C_6H_5\overset{O}{\overset{\|}{C}}—O—O^-Na^+ + C_6H_5COOCH_3$ Sod. peroxybenzoate (*g*) 

(*h*) 

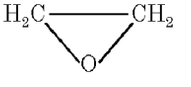
4. (*a*) 
4-Phenyl-4-heptanol

(*b*) $C_6H_5COOCH_2CH(CH_3)_2$ Isobutyl benzoate

(*c*) $HCONH_2 + HOCH_2(CH_2)_3CH_3$ Formamide 1-Pentanol

(*d*) $CH_3CH_2CH_2—\overset{O}{\overset{\|}{C}}—O—\overset{O}{\overset{\|}{C}}—CH_2CH_3$. Butyric propionic anhydride

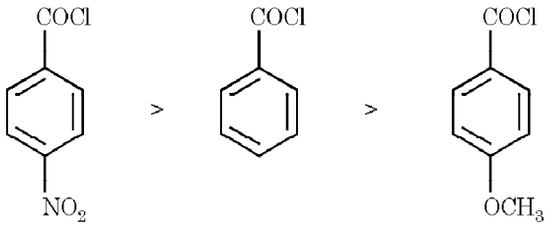
5. (*a*) $CH_3CH_2CH_2COOH + C_6H_5CH_2OH$ (*b*) *m*-$ClC_6H_4COOH + CH_3OH$

(*c*) $HOCH_2CH_2CH(CH_3)COOH$ (*d*) $CH_3CH = CHCH_2COOH +$ 

6. (*a*) $(CH_3)_2CHCH_2CuLi$, $C_6H_5COCH_2CH(CH_3)_2$ [A] [B] (*b*) $C_6H_5CH_2C(OH)(n\text{-}C_4H_9)_2$ [C]

(*c*) $CH_2 = CHCH_2COC_6H_5$ [D]

(*d*) $Br\ CH_2\ COOH$ [E] $Br\ Zn\ CH_2COOC_2H_5$ [F] $(CH_3)_2C(OH)CH_2COOC_2H_5$ [G] $(CH_3)_2C = CHCOOH$ [H] $(CH_3)_2C = CHCH_2OH$ [I]

7. (*a*)  Greater the partial +ve charge on carbonyl carbon, higher is the reactivity of carbonyl group towards nucleophilic substitution.

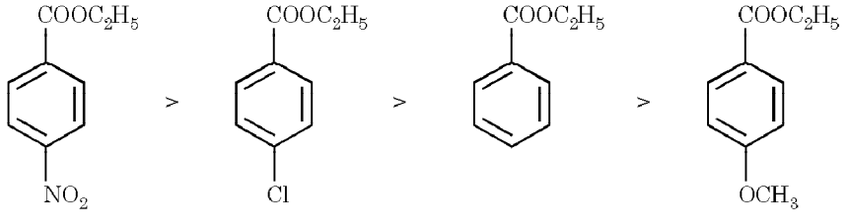
(*b*) (*i*) $CH_3COO\mathbf{CH_3}$ > $CH_3COO\mathbf{CH_2CH_3}$ > $CH_3COO\mathbf{CH(CH_3)_2}$ > $CH_3COOC\mathbf{(CH_3)_3}$

Size of the alkyl group of the alcoholic part increases from left to right, steric hindrance increases, and hence rate of hydrolysis decreases.

(*ii*) $\mathbf{H}COOCH_3$ > $\mathbf{CH_3}COOCH_3$ > $\mathbf{(CH_3)_2CH}COOCH_3$ > $\mathbf{(CH_3)_3C}COOCH_3$

Size of the alkyl group of the acidic part increases from left to right.

(*iii*) – I group disperses negative charge in transition state and thus increases reactivity of ester for hydrolysis. Thus the relative order of ester hydrolysis is



(*iv*) Lesser the basic character of the leaving group (Cl^- < $\bar{O}COCH_3$ < $^-OC_2H_5$ < NH_2^-), more easily it is removed.

$$CH_3COCl > (CH_3CO)_2O > CH_3COOC_2H_5 > CH_3CONH_2$$

(*c*) Cyclohexanecarboxyl chloride reacts faster than benzoyl chloride.

8. (*a*) $HOCH_2CH_2CH_2CONH_2$ (*b*) $HOCH_2CH_2CH_2CH_2OH$ (*c*) $HOCH_2CH_2CH_2COOC_2H_5$.

9. (*a*) On reaction with water, acetyl chloride reacts with water and liberates HCl which is detected by giving a white precipitate of AgCl on adding $AgNO_3$. Acetic anhydride on reaction with water liberates only acetic acid and no HCl.

(*b*) *n*-Butyryl chloride (n-C_3H_7COCl) gives pleasant smelling ester with ethyl alcohol.

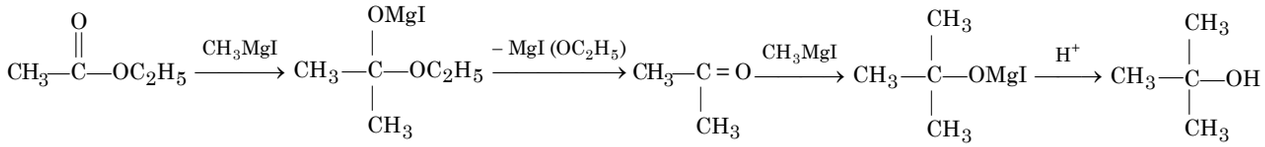
(*c*) Only benzoyl bromide (C_6H_5COBr) gives yellow precipitate of AgBr with alcoholic $AgNO_3$.

(*d*) Only propanoic acid gives CO_2 with aqueous $NaHCO_3$ solution.

(*e*) Only acetic anhydride reacts with aq. $NaHCO_3$ solution and evolve CO_2.

(*f*) Ammonium benzoate evolves ammonia immediately on treatment with *cold* aq. NaOH.

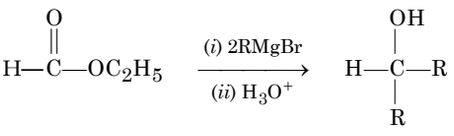
(*g*) Glyceryl monopalmitate has two free alcoholic groups ; hence it is oxidised by CrO_3 / H_2SO_4.

10. (*a*) 

Acetone (as intermediate) *tert*-Butanol

(*b*) Ketones are more reactive than esters towards RMgX.

(*c*) A formate ester when treated with 2 eq. of Grignard reagent gives 2° alcohol with identical alkyl groups.



A 2° alcohol

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11. (*a*) An *ortho ester* has three alkoxy groups (– OR) attached to the same carbon atom ; thus the general formula for ortho esters is $RC(OR')_3$; where R = H or an alkyl group, while R′ = an alkyl group.

$$\underset{\text{Ethyl orthoformate}}{HC(OC_2H_5)_3} \xrightarrow{\text{mild hydrolysis}} \underset{\text{Ethyl formate}}{HCOOC_2H_5} + 2C_2H_5OH$$

(*b*) $$CHCl_3 + 3C_2H_5ONa \xrightarrow{C_2H_5O^-} HC(OC_2H_5)_3 + 3NaCl$$

Mechanism. Dichlorocarbene, formed from chloroform, inserts between H and O of C_2H_5OH to form α, α-dichloromethyl ethyl ether which solvolyses rapidly *via* S_N1 in ethyl alcohol.

$$HCCl_3 \xrightarrow{C_2H_5O^-} :CCl_2 \xrightarrow{C_2H_5O—H} C_2H_5O—CHCl_2 \xrightarrow{-Cl^-}$$

$$\left[C_2H_5\ddot{O}\text{—}\overset{+}{C}HCl \longleftrightarrow C_2H_5\overset{+}{O} = CHCl \right] \xrightarrow{C_2H_5OH} C_2H_5O\text{—}\underset{OC_2H_5}{\underset{|}{CH}}Cl \xrightarrow[(-HCl)]{C_2H_5OH} HC(OC_2H_5)_3$$

12. In the Claisen condensation, the bond formed is between the carbonyl carbon of one ester and the carbon which is α to the —COOR group of the ester molecule. Thus work backward by breaking this C—C bond and adding OR to the carbonyl carbon and H to the other carbon. Mixed Claisen condensations are practical, when one ester has α H.

(*a*) $$\underset{\substack{C_2H_5O \quad H}}{C_6H_5CH_2CH_2\overset{O}{\overset{\|}{C}}\text{—}\overset{CH_2C_6H_5}{\overset{|}{C}}HCOOCH_3} \xleftarrow[(ii)\ -C_2H_5OH]{(i)\ C_2H_5ONa} C_6H_5CH_2CH_2\overset{O}{\overset{\|}{C}}\text{—}OC_2H_5 + \underset{CH_2COOCH_3}{\overset{CH_2C_6H_5}{\overset{|}{C}}H}$$

(*b*) $$C_2H_5OOC\text{—}\overset{O}{\overset{\|}{C}}\text{—}\overset{CH_3}{\overset{|}{C}}HCOOC_2H_5 \xleftarrow[(ii)\ -C_2H_5OH]{(i)\ C_2H_5ONa} C_2H_5OOC\text{—}\overset{O}{\overset{\|}{C}}\text{—}OC_2H_5 + \underset{CH_2COOC_2H_5}{\overset{CH_3}{\overset{|}{C}}H}$$

(*c*) $$H\text{—}\overset{O}{\overset{\|}{C}}\text{—}\overset{C_6H_5}{\overset{|}{C}}HCOOCH_3 \xleftarrow[(ii)\ -C_2H_5OH]{(i)\ C_2H_5ONa} H\text{—}\overset{O}{\overset{\|}{C}}\text{—}OC_2H_5 + \underset{CH_2COOCH_3}{\overset{C_6H_5}{\overset{|}{C}}H}$$

13.

Reaction	*Reactant*	*Reagents/Conditions*	*Product*
Hofmann	$RCONH_2$ (Amides)	Br_2, OH^-	RNH_2
Lossen	RCONHOH Hydroxyamic acids	OH^-	$RNCO \xrightarrow{H_2O} RNH_2$
Curtius	$RCON_3$ Acid azides	(*i*) heat in benzene (*ii*) heat in H_2O or R′OH	(*i*) RNCO (*ii*) RNH_2 or RNHCOOR′
Schmidt	RCOOH Carboxylic acids	HN_3, H_2SO_4, OH^-	RNH_2

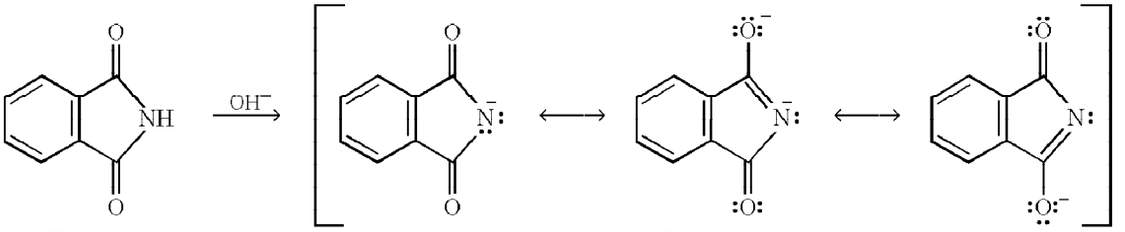
14. More stable a conjugate base of an acid, higher will be its acidic character.

(*a*) Since the conjugate base of the sulphonamide is stabilized by delocalization of the negative charge to two oxygens, the parent compound sulphonamide will be more acidic than the acid amide, CH_3CONH_2, where delocalization is possible to only one oxygen.

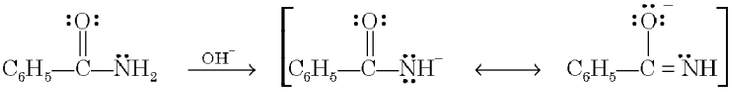
$$R\text{—}\overset{:O:}{\overset{\|}{\underset{\|}{S}}}\text{—}\ddot{N}H_2 \xrightarrow{B^-} \left[R\text{—}\overset{:O:}{\overset{\|}{\underset{\|}{S}}}\text{—}\ddot{N}H^- \longleftrightarrow R\text{—}\overset{:\ddot{O}:^-}{\overset{|}{\underset{\|}{S}}} = \ddot{N}H \longleftrightarrow R\text{—}\overset{:O:}{\overset{\|}{\underset{|}{S}}} = \ddot{N}H \right]$$

$$R\text{—}\overset{:O:}{\overset{\|}{C}}\text{—}\ddot{N}H_2 \xrightarrow{B^-} \left[R\text{—}\overset{:O:}{\overset{\|}{C}}\text{—}\ddot{N}H^- \longleftrightarrow R\text{—}C = \ddot{N}H \right]$$

(*b*) Amides are much more acidic than NH_3 because the negative charge on $:NH_2^-$ from ammonia is localised, while in amides it is delocalized to the oxygen of C = O. Since phthalimide has two C = O's, while benzamide has only one, the imide anion from phthalimide is more stabilized than the amide anion from benzamide.



Phthalimide Phthalimide anion

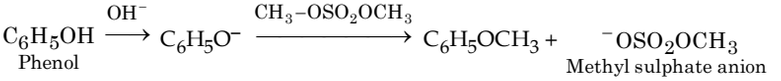


Benzamide

Thus the acidic character of the three compounds follows the order :

Phthalimide > Benzamide >>> NH_3.

15. (*a*) Dialkyl sulphates, in general, are good alkylating agents, because the alkyl sulphate anion, *e.g.* $CH_3OSO_3^-$ is the conjugate base of a strong acid , methyl sulphuric acid, CH_3OSO_3H. Thus due to very weak basic nature of the methyl sulphate anion, it is a good leaving group.



Phenol Methyl sulphate anion

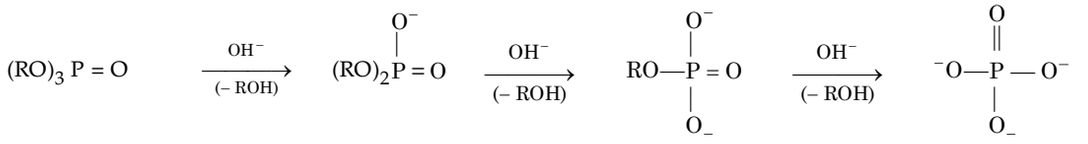
(*b*) Acyl chlorides are more reactive than alkyl chlorides due to following factors.

(*i*) Presence of C = O in acid chlorides makes the acyl carbon more electrophilic by attracting electrons.

(*ii*) The transition state of the acyl chloride leading to tetrahedral intermediate is less sterically hindered than the transition state with the petavalent carbon in the S_N2 reaction of RX.

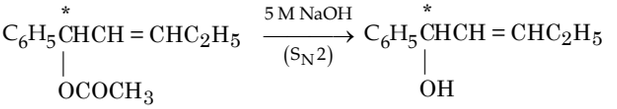
(*iii*) In the formation of an alkyl transition state, a stronger σ-bond must be partially broken , while a weaker π-bond is broken in the acyl case.

(*c*) In the hydrolysis of trialkyl phosphates, OH^- attacks on the neutral molecule (having no charge), while in the dialkyl and monoalkyl phosphates the substrates have –1 and –2 charges which make the attack of OH^- progressively more difficult.



Trialkyl phosphate (neutral) Dialkyl phosphate (carries –1 charge) Monoalkyl phosphate (carries –2 charge) Phosphate ion

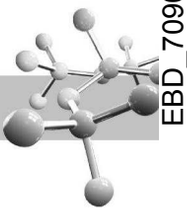
(*d*) Recall that concentration of the reagent affects the kinetics of the S_N reaction. In presence of high concentration of nucleophile, reaction opts S_N2 mechanism, while in low concentration (dil. NaOH) S_N1 mechnism is followed. Since in S_N2 reaction configuration is retained, so the optically active ester will be hydrolysed to optically active alcohol.



Optically active Optically acitve

However, in S_N1 reaction since carbocations are formed as intermediate which may rearrange, if possible, to the more stable carbocation. Thus rearranged product may be formed. Further, carbocation being planar, may be attacked on either side of the face forming racemic mixture.

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$$C_6H_5\underset{\underset{OCOCH_3}{|}}{CH}—CH = CHC_2H_5 \xrightarrow[S_{N^1}]{\text{dil. NaOH}} \left[C_6H_5\overset{+}{C}H — CH = CHC_2H_5 \longleftrightarrow \underset{\text{More stable}}{C_6H_5CH = CH—\overset{+}{C}HC_2H_5} \right]$$

$$\xrightarrow{OH^-} C_6H_5CH = CH—\underset{\underset{OH}{|}}{CHCH_3}$$

Rearranged (optically inactive) alcohol

(*e*) Acetic acid formed in the reaction, catalyses the hydrolysis of ester by providing H^+.

16. $H—\overset{\overset{O}{\|}}{C}—OCH(CH_3)_2$ [A] $H—\overset{\overset{O}{\|}}{C}—OH$ [B] $HOCH(CH_3)_2$ [C] CH_3MgI [D]



CARBONYL COMPOUNDS

PAST YEAR QUESTIONS JEE ADVANCED/IIT-JEE (2013 - 2017)

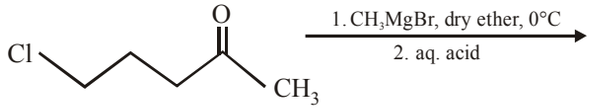
MCQs with One Correct Answer

1. The compound that does **NOT** liberate CO_2, on treatment with aqueous sodium bicarbonate solution, is

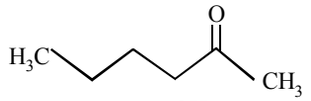
[JEE Adv. 2013]

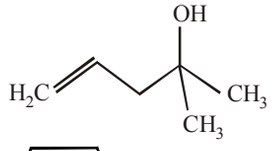
(a) Benzoic acid (b) Benzenesulphonic acid
(c) Salicylic acid (d) Carbolic acid (Phenol)

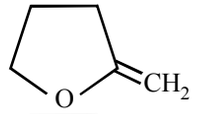
2. The major product in the following reaction is

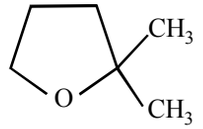


[JEE Adv. 2014]

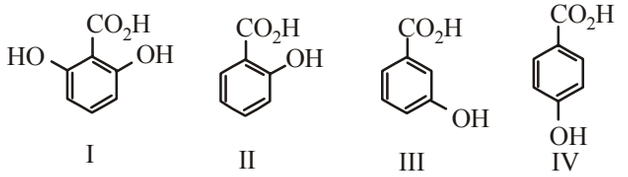
(a) 

(b) 

(c) 

(d) 

3. The correct order of acidity for the following compounds is

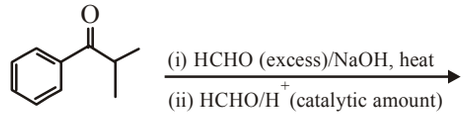


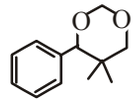
[JEE Adv. 2016]

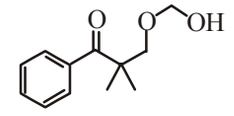
(a) I > II > III > IV (b) III > I > II > IV
(c) III > IV > II > I (d) I > III > IV > II

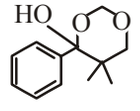
4. The major product of the following reaction sequence is

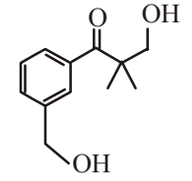
[JEE Adv. 2016]



(a) 

(b) 

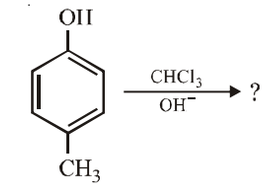
(c) 

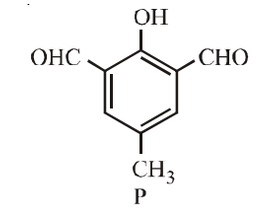
(d) 

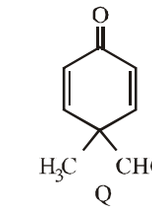
MCQs with One or More Than One Correct

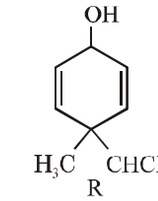
1. In the following reaction, the product(s) formed is(are)

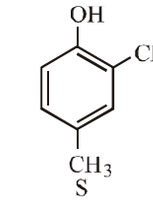
[JEE Adv. 2013]







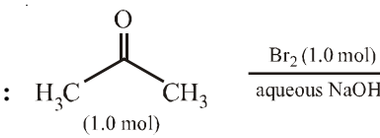


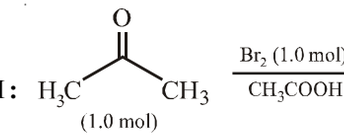


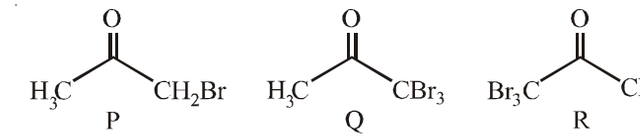
(a) P (major) (b) Q (minor)
(c) R (minor) (d) S (major)

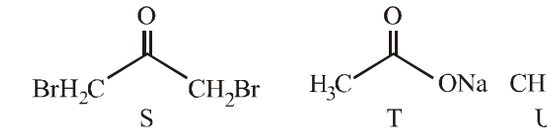
2. After completion of the reactions (I and II), the organic compound(s) in the reaction mixtures is(are)

[JEE Adv. 2013]

Reaction I : 

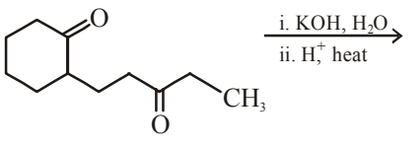
Reaction II : 

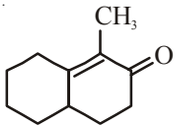


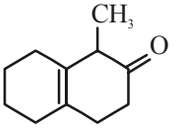


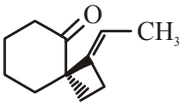
(a) Reaction I : P and Reaction II : P
(b) Reaction I : U, acetone and Reaction II : Q, acetone
(c) Reaction I : T, U, acetone and Reaction II : P
(d) Reaction I : R, acetone and Reaction II : S, acetone

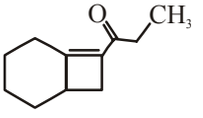
3. The major product of the following reaction is **[JEE Adv. 2015]**



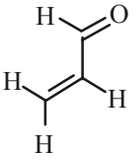
(a) 

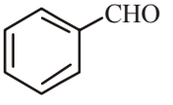
(b) 

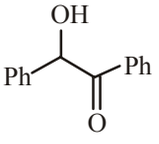
(c) 

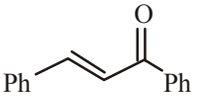
(d) 

4. Positive Tollen's test is observed for **[JEE Adv. 2016]**

(a) 

(b) 

(c) 

(d) 

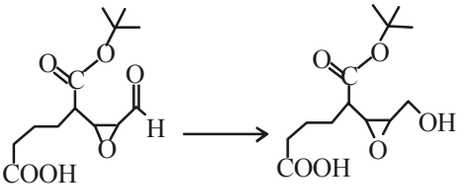
5. The correct statement(s) about the following reaction sequence is(are) **[JEE Adv. 2016]**

$$\text{Cumene}(C_9H_{12}) \xrightarrow[(ii)H_3O^+]{(i)O_2} \mathbf{P} \xrightarrow{CHCl_3/NaOH} \mathbf{Q}\ (\text{major}) + \mathbf{R}\ (\text{minor})$$

$$\mathbf{Q} \xrightarrow[PhCH_2Br]{NaOH} \mathbf{S}$$

(a) **R** is steam Volatile
(b) **Q** gives dark violet coloration with 1% aqueous $FeCl_3$ solution
(c) **S** gives yellow precipitate with 2, 4–dinitro-phenylhydrazine
(d) **S** gives dark violet coloration with 1% aqueous $FeCl_3$ solution

6. Reagent(s) which can be used to bring about the following transformation is (are) **[JEE Adv. 2016]**



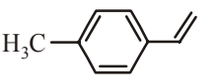
(a) $LiAlH_4$ in $(C_2H_5)_2O$ (b) BH_3 in THF
(c) $NaBH_4$ in C_2H_5OH (d) Raney Ni/H_2 in THF

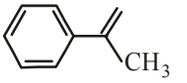
7. Compounds P and R upon ozonolysis produce Q and S, respectively. The molecular formula of Q and S is C_8H_8O. Q undergoes Cannizzaro reaction but not haloform reaction, whereas S undergoes haloform reaction but not Cannizzaro reaction **[JEE Adv. 2017]**

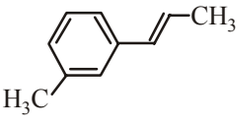
(i) $\mathrm{P} \xrightarrow[ii)Zn/H_2O]{i)O_3/CH_2Cl_2} \underset{(C_8H_8O)}{\mathrm{Q}}$

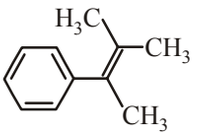
(ii) $\mathrm{R} \xrightarrow[ii)Zn/H_2O]{i)O_3/CH_2Cl_2} \underset{(C_8H_8O)}{\mathrm{S}}$

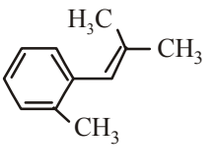
The option(s) with suitable combination of P and R, respectively, is(are)

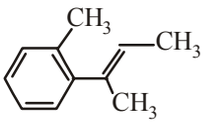
(a) 

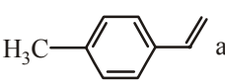
and 

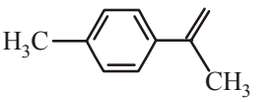
(b) 

and 

(c) 

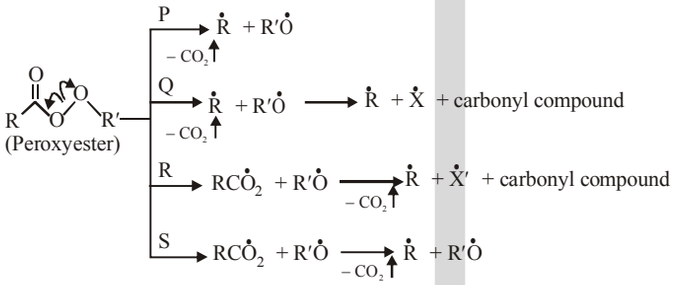
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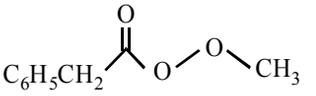
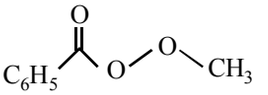
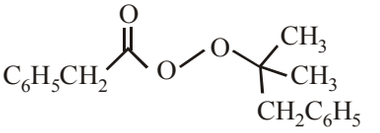
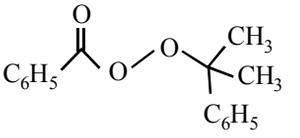
(d) 

and 

Match the Following

1. Different possible **thermal** decomposition pathways for peroxyesters are shown below. Match each pathway from **List-I** with an appropriate structure from **List-II** and select the correct answer using the code given below the lists. **[JEE Adv. 2014]**



List-I	List-II
P. Pathway P	**1.** 
Q. Pathway Q	**2.** 
R. Pathway R	**3.** 
S. Pathway S	**4.** 

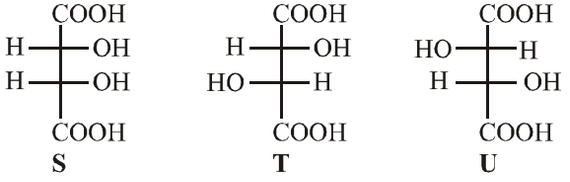
Code :

	P	Q	R	S
(a)	1	3	4	2
(b)	2	4	3	1
(c)	4	1	2	3
(d)	3	2	1	4

Comprehension Based Questions

PASSAGE-1

P and Q are isomers of dicarboxylic acid $C_4H_4O_4$. Both decolorize Br_2/H_2O. On heating, P forms the cyclic anhydride. Upon treatment with dilute alkaline $KMnO_4$, P as well as Q could produce one or more than one from S, T and U.



S **T** **U**

[JEE Adv. 2013]

1. Compounds formed from P and Q are, respectively

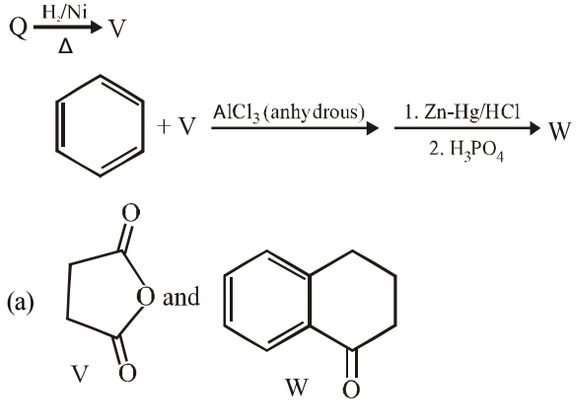
(a) Optically active S and optically active pair (T, U)

(b) Optically inactive S and optically inactive pair (T, U)

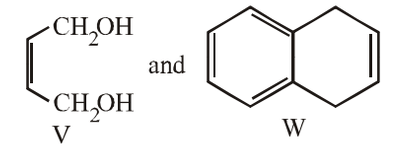
(c) Optically active pair (T, U) and optically active S

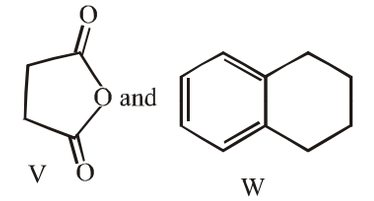
(d) Optically inactive pair (T, U)) and optically inactive S

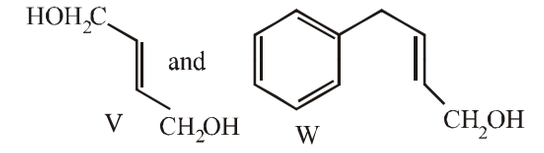
2. In the following reaction sequences V and W are respectively



(a)

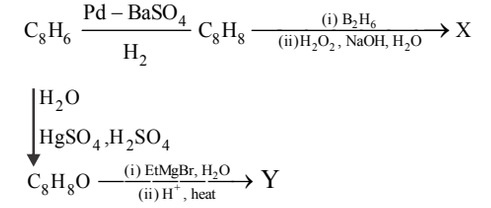
(b) 

(c) 

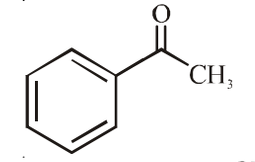
(d) 

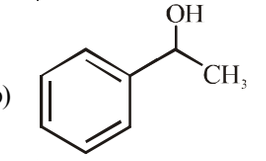
PASSAGE-2

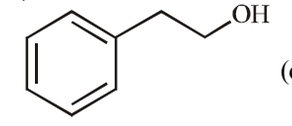
In the following reactions

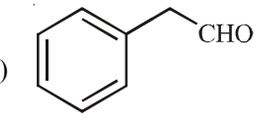


3. Compound X is **[JEE Adv. 2015]**

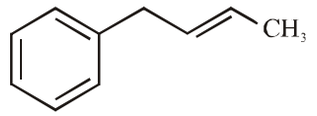
(a) 

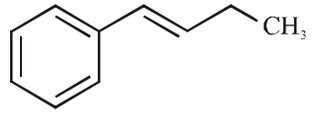
(b) 

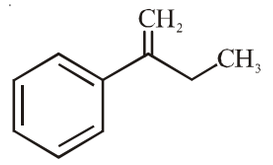
(c) 

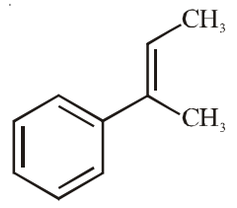
(d) 

4. The major compound Y is **[JEE Adv. 2015]**

(a) 

(b) 

(c) 

(d) 

PASSAGE-3

By appropriately matching the information given in the three columns of the following table. **[JEE Adv. 2017]**

Columns 1, 2 and 3 contain starting materials, reaction conditions, and type of reactions, respectively.

	Column 1		Column 2		Column 3
(I)	Toluene	(i)	$NaOH/Br_2$	(P)	Condensation
(II)	Acetophenone	(ii)	Br_2/hv	(Q)	Carboxylation
(III)	Benzaldehyde	(iii)	$(CH_3CO)_2O/CH_3COOK$	(R)	Substitution
(IV)	Phenol	(iv)	$NaOH/CO_2$	(S)	Haloform

5. For the synthesis of benzoic acid, the only CORRECT combination is

(a) (II) (i) (S) (b) (IV) (ii) (P)

(c) (I) (iv) (Q) (d) (III) (iv) (R)

6. The only CORRECT combination that gives two different carboxylic acids is

(a) (II) (iv) (R) (b) (IV) (iii) (Q)

(c) (III) (iii) (P) (d) (I) (i) (S)

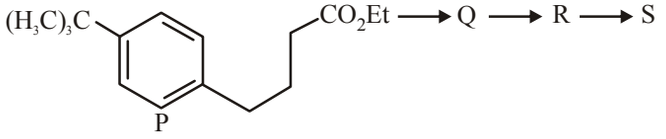
7. The only CORRECT combination in which the reaction proceeds through radical mechanism is

(a) (III) (ii) (P) (b) (IV) (i) (Q)

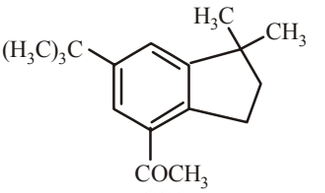
(c) (II) (iii) (R) (d) (I) (ii) (R)

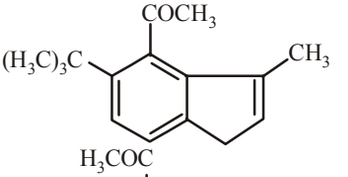
PASSAGE-4

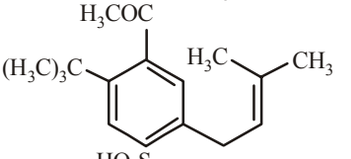
The reaction of compound P with CH_3MgBr (excess) in $(C_2H_5)_2O$ followed by addition of H_2O gives Q. The compound Q on treatment with H_2SO_4 at 0°C gives R. The reaction of R with CH_3COCl in the presence of anhydrous $AlCl_3$ in CH_2Cl_2 followed by treatment with H_2O produces compound S. [Et in compound P is ethyl group]

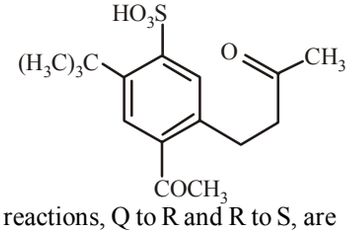


8. The product S is **[JEE Adv. 2017]**

(a) 

(b) 

(c) 

(d) 

9. The reactions, Q to R and R to S, are **[JEE Adv. 2017]**

(a) Dehydration and Friedel–Crafts acylation

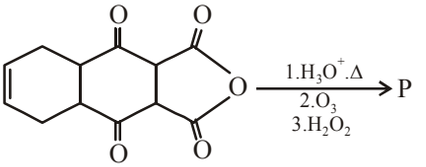
(b) Aromatic sulfonation and Friedel–Crafts acylation

(c) Friedel–Crafts alkylation, dehydration and Friedel–Crafts acylation

(d) Friedel–Crafts alkylation and Friedel–Crafts acylation

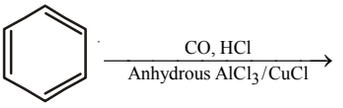
Integer Value Correct Type

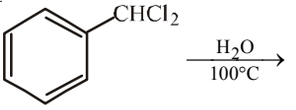
1. The total number of carboxylic acid groups in the product P is **[JEE Adv. 2013]**

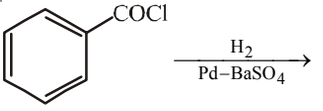


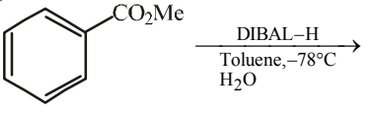
2. Consider all possible isomeric ketones, including stereoisomers of MW = 100. All these isomers are independently reacted with $NaBH_4$ (**NOTE:** stereoisomers are also reacted separately). The total number of ketones that give a racemic product(s) is/are **[JEE Adv. 2014]**

3. Among the following, the number of reaction(s) that produce(s) benzaldehyde is **[JEE Adv. 2015]**

I. 

II. 

III. 

IV. 

PAST YEAR QUESTIONS JEE MAIN/AIEEE (2013 - 2017)

1. The most suitable reagent for the conversion of $R-CH_2-OH \rightarrow R-CHO$ is: **[JEE M 2014]**

(a) $KMnO_4$
(b) $K_2Cr_2O_7$
(c) CrO_3
(d) PCC (Pyridinium Chlorochromate)

2. In the reaction,

$$CH_3COOH \xrightarrow{LiAH_4} A \xrightarrow{PCl_5} B \xrightarrow{Alc.KOH} C,$$

the product C is: **[JEE M 2014]**

(a) Acetaldehyde (b) Acetylene
(c) Ethylene (d) Acetyl chloride

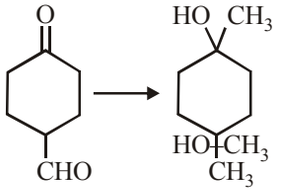
3. In the following sequence of reactions : **[JEE M 2015]**

$$\text{Toluene} \xrightarrow{KMnO_4} A \xrightarrow{SOCl_2} B \xrightarrow[BaSO_4]{H_2/Pd} C$$

the product C is :

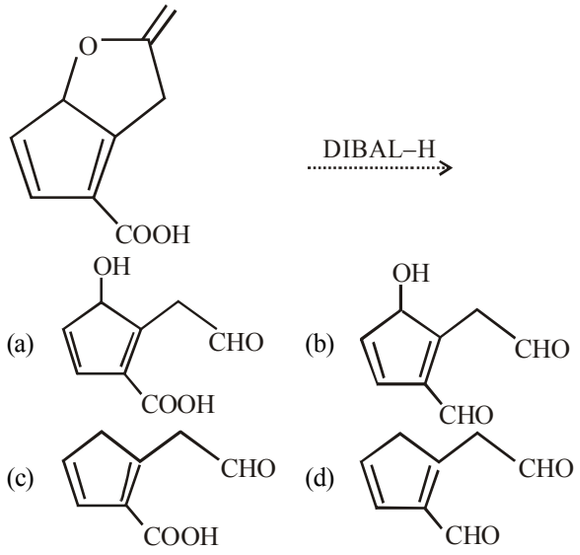
(a) $C_6H_5CH_2OH$ (b) C_6H_5CHO
(c) C_6H_5COOH (d) $C_6H_5CH_3$

4. The correct sequence of reagents for the following conversion will be : **[JEE M 2017]**



(a) $[Ag(NH_3)_2]^+ OH^-$, H^+/CH_3OH, CH_3MgBr
(b) CH_3MgBr, H^+/CH_3OH, $[Ag(NH_3)_2]^+ OH^-$
(c) CH_3MgBr, $[Ag(NH_3)_2]^+ OH^-$, H^+/CH_3OH
(d) $[Ag(NH_3)_2]^+ OH^-$, CH_3MgBr, H^+/CH_3OH

5. The major product obtained in the following reaction is : **[JEE M 2017]**



6. Sodium salt of an organic acid 'X' produces effervescence with conc. H_2SO_4. 'X' reacts with the acidified aqueous $CaCl_2$ solution to give a white precipitate which decolourises acidic solution of $KMnO_4$. 'X' is : **[JEE M 2017]**

(a) C_6H_5COONa (b) HCOONa
(c) CH_3COONa (d) $Na_2C_2O_4$

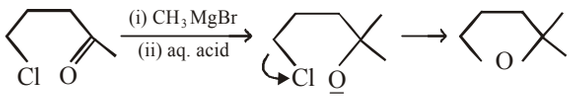
SOLUTIONS

PAST YEAR QUESTIONS JEE ADVANCED/IIT-JEE (2013 - 2017)

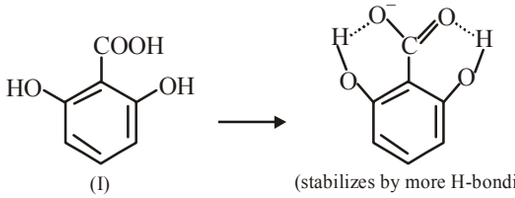
MCQs with One Correct Answer

1. (d) Carbolic acid (Phenol) is weaker acid than carbonic acid and hence does not liberate CO_2 on treatment with aq. $NaHCO_3$ solution.

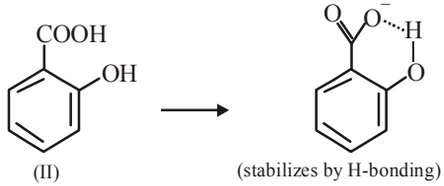
2. (d)



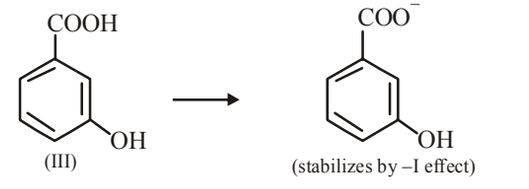
3. (a)



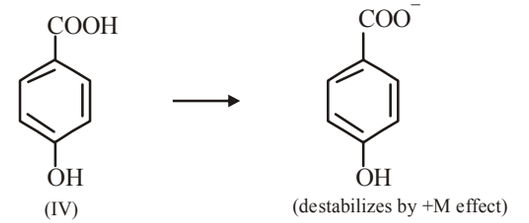
(I) (stabilizes by more H-bonding)



(II) (stabilizes by H-bonding)



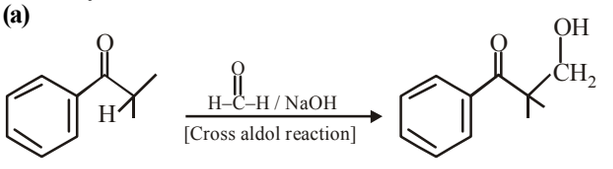
(III) (stabilizes by –I effect)

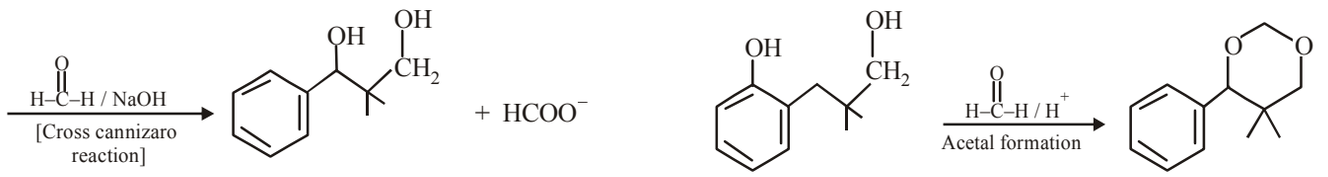


(IV) (destabilizes by +M effect)

$\therefore$ acidity order is I > II > III > IV

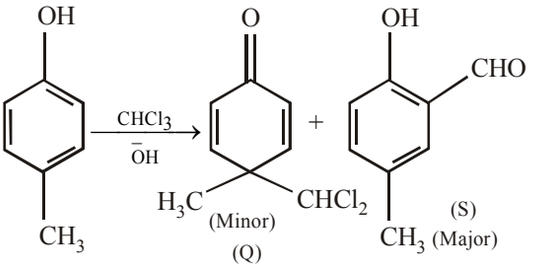
4. (a)



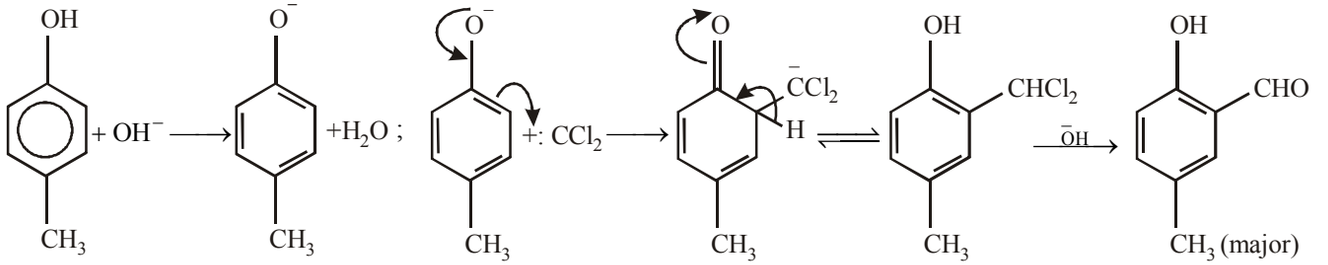


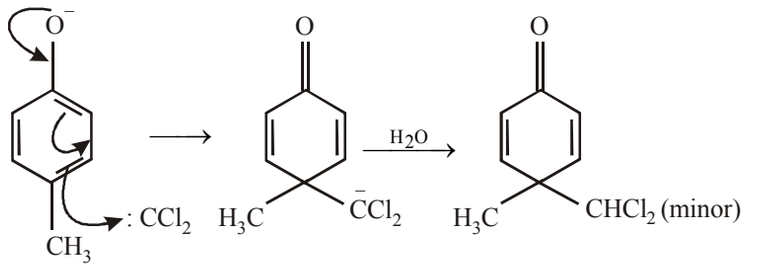
MCQs with One or More Than One Correct

1. **(b, d)**

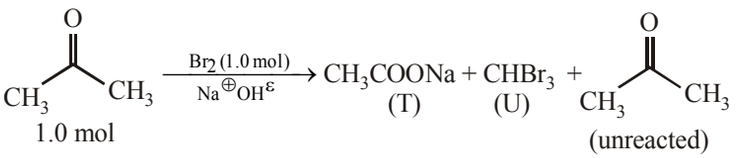


$$CHCl_3 + \bar{O}H \longrightarrow :CCl_2 + H_2O + Cl^-$$

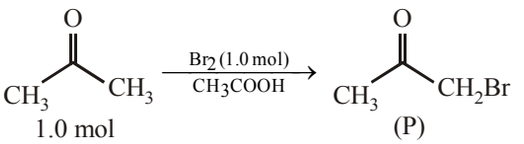




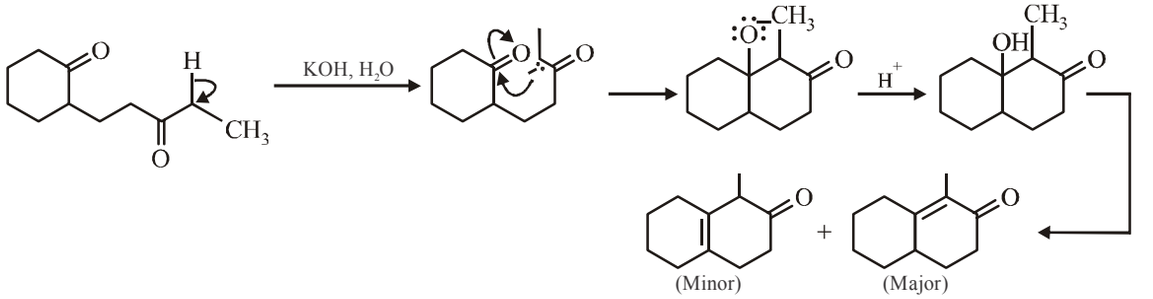
2. **(c)** Reaction I :



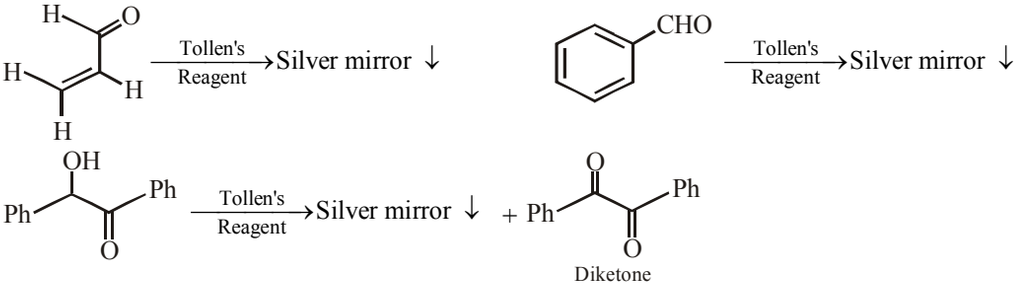
Reaction II :



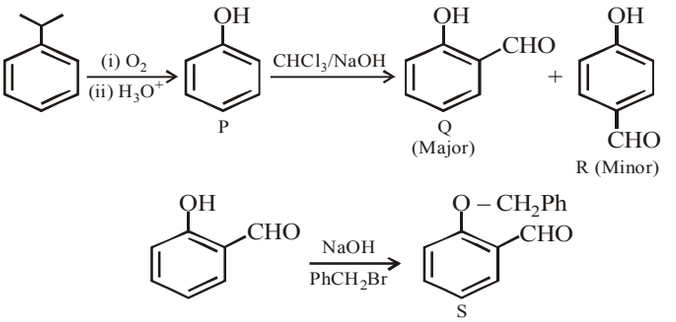
3. **(a)**



4. **(a, b, c)** Aldehydes and α-Hydroxyketones show positive Tollen's test.



5. **(b, c)**



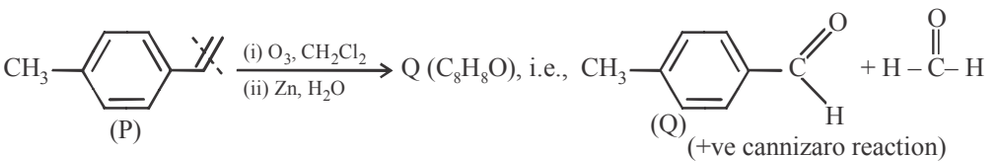
Q is steam volatile not R.
Q and R show positive test with 1% aqueous $FeCl_3$ solution.
Q, R, S give yellow precipitate with 2, 4-dinitrophenyl hydrazine.

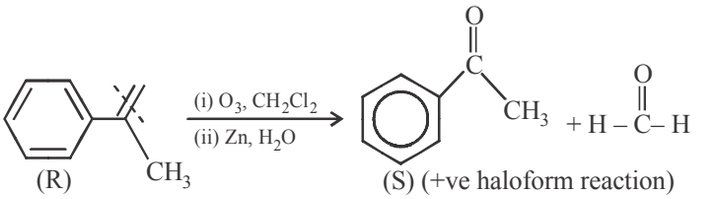
6. **(c, d)**

$LiAlH_4/(C_2H_5)_2O$: Reduces to esters, carboxylic acid, epoxides and aldehydes and ketones.
BH_3 in T.H.F : Reduces to –COOH and aldehydes into alcohols but do not reduce to esters and epoxides.
$NaBH_4$ in C_2H_5OH : Reduces only aldehydes and ketones into alcohols but not to others.
Raney Ni in T.H.F. : Do not reduce to –COOH, –COOR and epoxide but it can reduce aldehyde into alcohols.

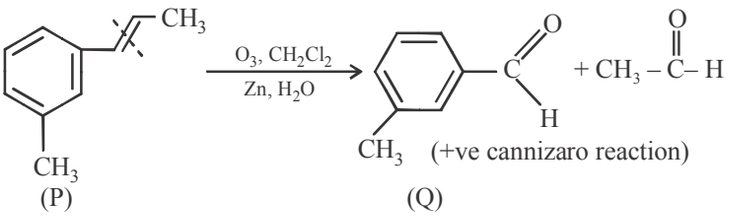
7. **(a, b)**

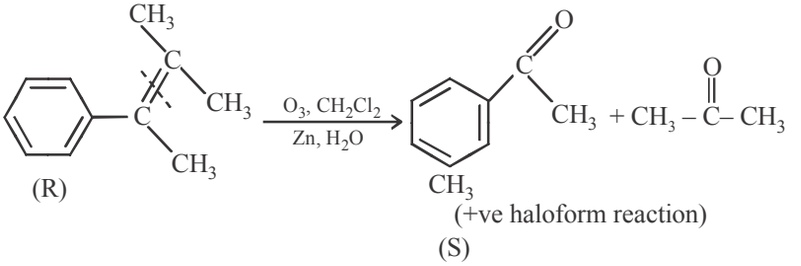
(c)





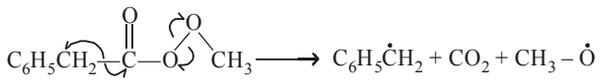
(d)

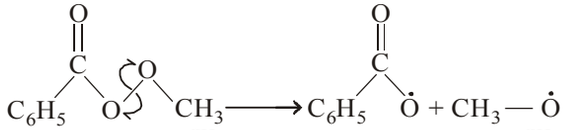


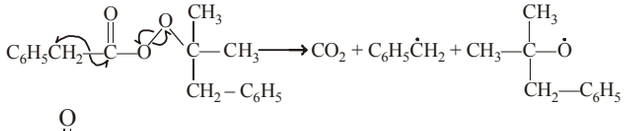


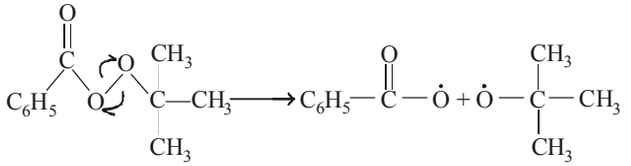
Match the Following

1. (a)

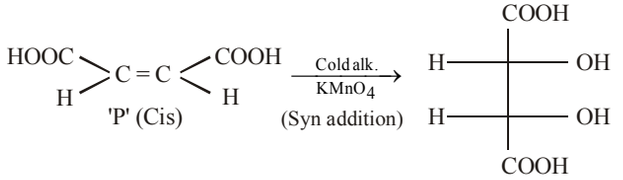
(1) 

(2) 

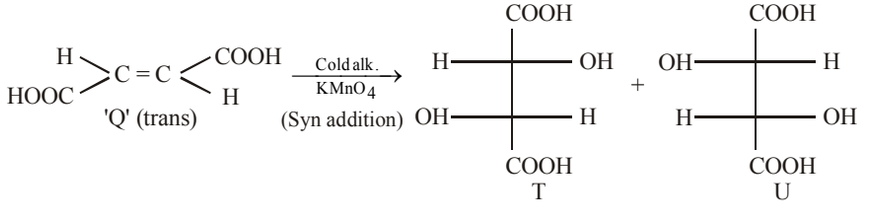
(3) 

(4) 

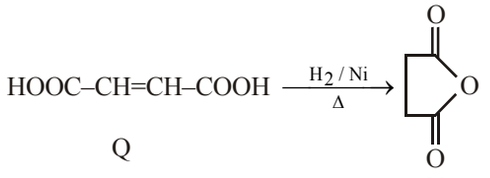
Comprehension Based Questions

1. (b) 

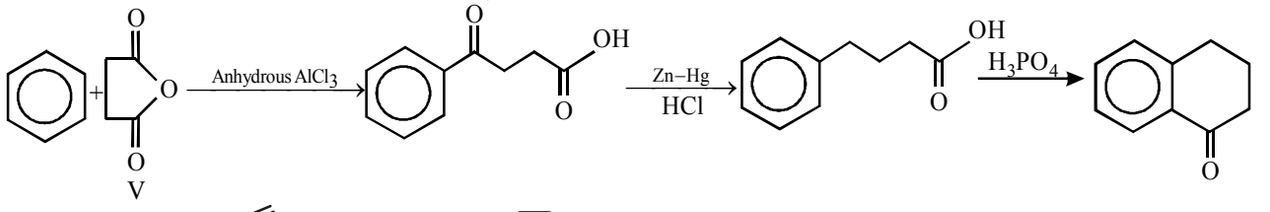
Meso (S), optically inactive

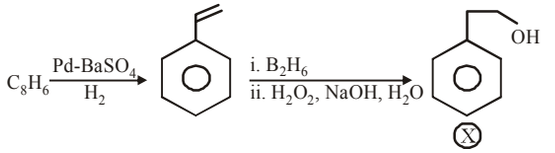


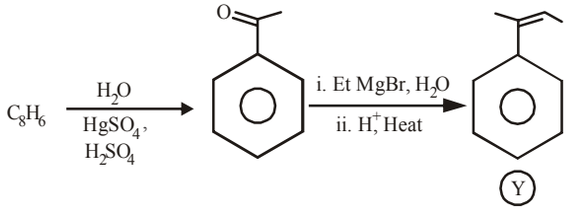
(Racemic Mixture), optically inactive

2. (a) 

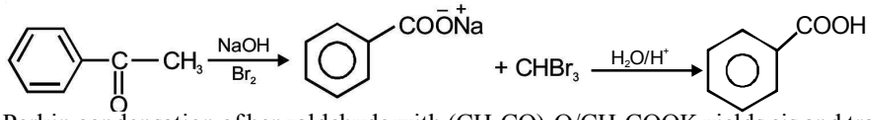
Q V



3. (c) 

4. (d) 

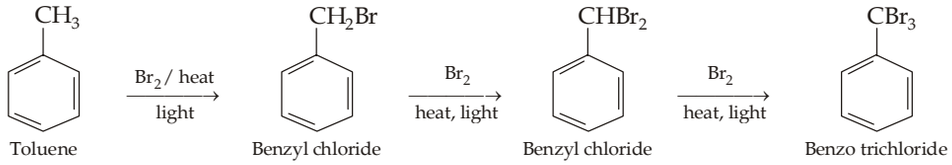
5. (c)



6. (d) Perkin condensation of benzaldehyde with $(CH_3CO)_2O/CH_3COOK$ yields cis and trans form of cinnamic acid.

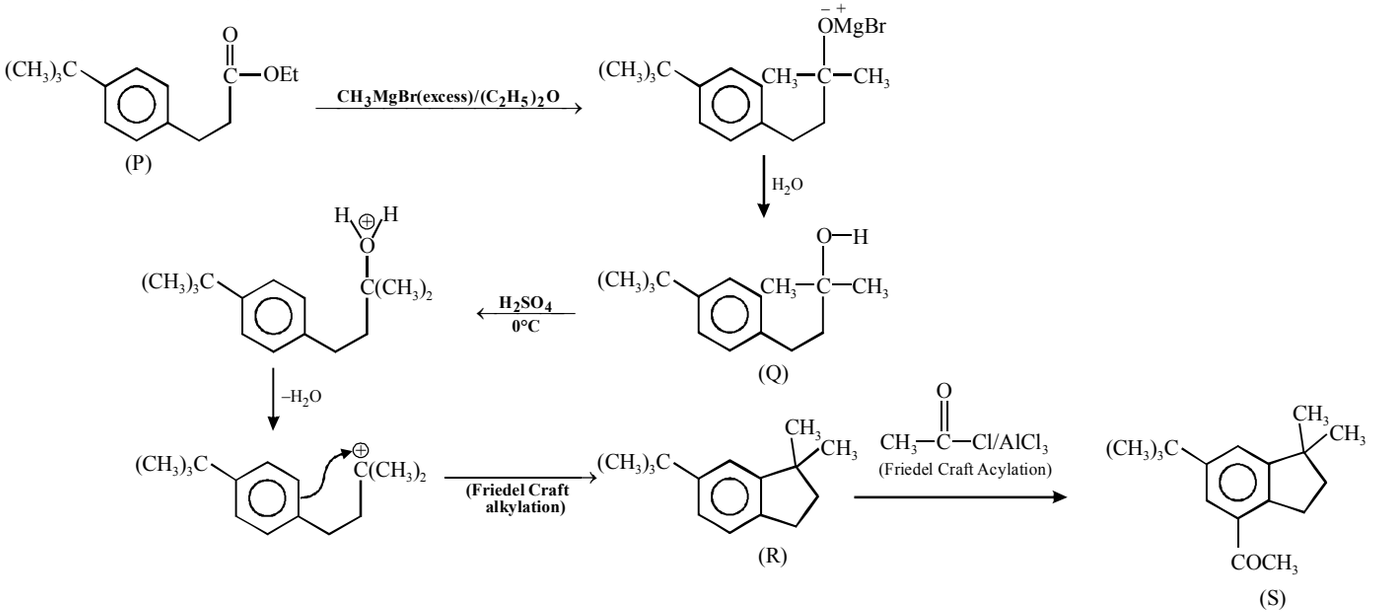
$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} \xrightarrow[(ii)\ H^+]{(i)\ CH_3COONa} \underset{\substack{\text{Cinnamic acid}\\ \text{cis and trans}}}{C_6H_5CH=CHCOOH}$$

7. (a) Alkylbenzenes when treated with Br_2 at high temperature, in the presence of sunlight and absence of halogen carrier undergo **halogenation in the side chain.** Thus



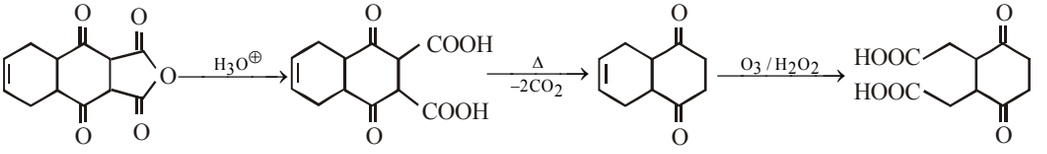
Toluene — Benzyl chloride — Benzyl chloride — Benzo trichloride

8. (a) & 9. (d)



Integer Value Correct Type

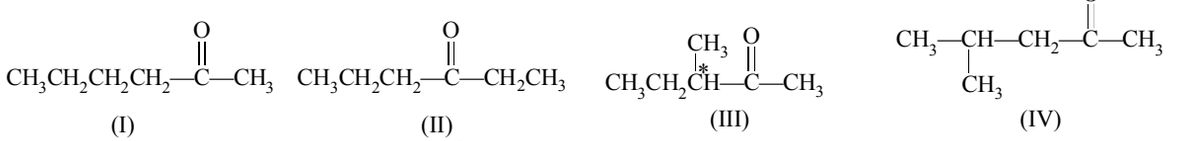
1. (2)

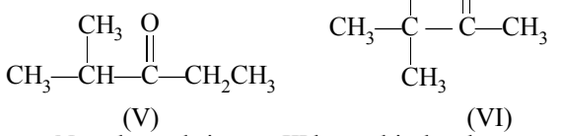


No. of –COOH group is '2'

2. (5) General molecular formula for ketones is $C_nH_{2n}O$ $\quad\therefore\ C_nH_{2n}O = 100$ or $12n + 2n + 16 = 100$, $n = 6$

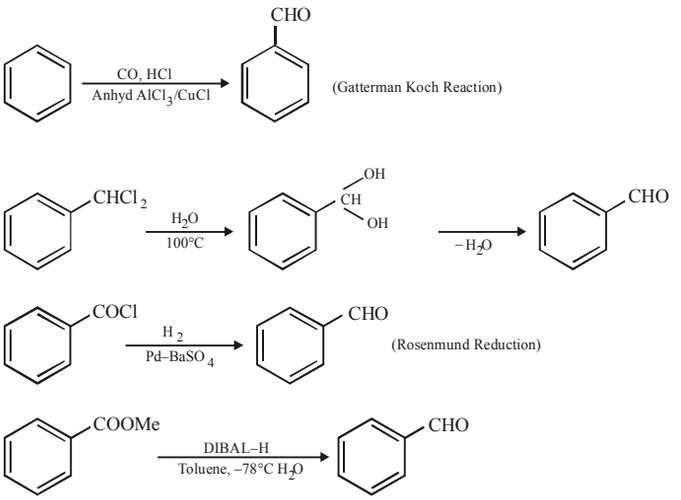
Possible isomeric ketones with 6 carbon atoms are





Note that only isomer III has a chiral carbon so on reduction with $NaBH_4$ it will give diastereomeric alcohols, while all other five isomers will give racemic mixture.

3. (4)



PAST YEAR QUESTIONS JEE MAIN/AIEEE (2013 - 2017)

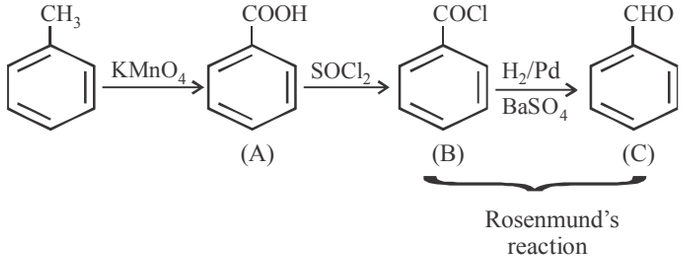
1. (d) An excellent reagent for oxidation of 1° alcohols to aldehydes is PCC.

$$R-CH_2-OH \xrightarrow{PCC} R-CHO$$

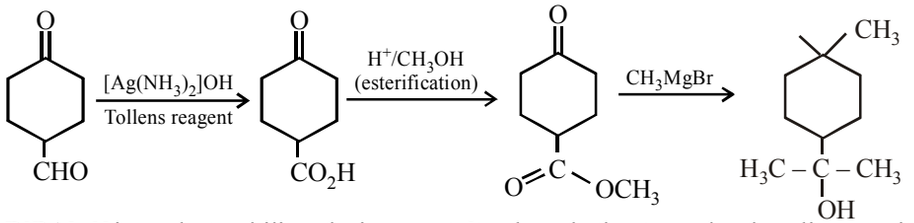
2. (c) $CH_3COOH \xrightarrow{LiA1H_4} \underset{(A)}{CH_3CH_2OH} \xrightarrow{PCl_5} \underset{(B)}{CH_3CH_2Cl} \xrightarrow{\text{Alc. KOH}} \underset{(C)}{CH_2=CH_2}$

Hence the product (C) is ethylene.

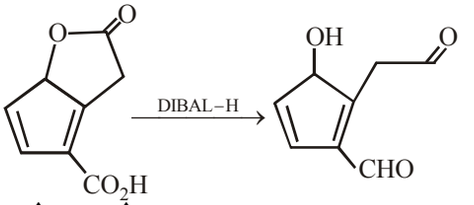
3. (b)



4. (a)



5. (b) DIBAL-H is an electrophilic reducing agent. It reduces both ester and carboxylic group into an aldehyde at low temperature.



6. (d) $\underset{\text{'x'}}{Na_2C_2O_4} + \underset{\text{(conc.)}}{H_2SO_4} \rightarrow Na_2SO_4 + CO\uparrow + CO_2\uparrow + H_2O$

$\underset{\text{x'}}{Na_2C_2O_4} + CaCl_2 \rightarrow \underset{\text{(white ppt.)}}{CaC_2O_4\downarrow} + 2NaCl$

$\underset{\text{(purple)}}{5CaC_2O_4\downarrow} + 2KMnO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 5CaSO_4 + \underset{\text{(colourless)}}{2MnSO_4} + 10CO_2 + 8H_2O$

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PREFACE

REVISED EDITION

It gives us immense pleasure and satisfaction to bring out the thoroughly revised and updated edition of the book **"Disha's Amines and Biomolecules"** The book has been designed to give a better look & feel and to make the text more lucid. The new pattern of JEE Main & Advanced has been kept in mind throughout.

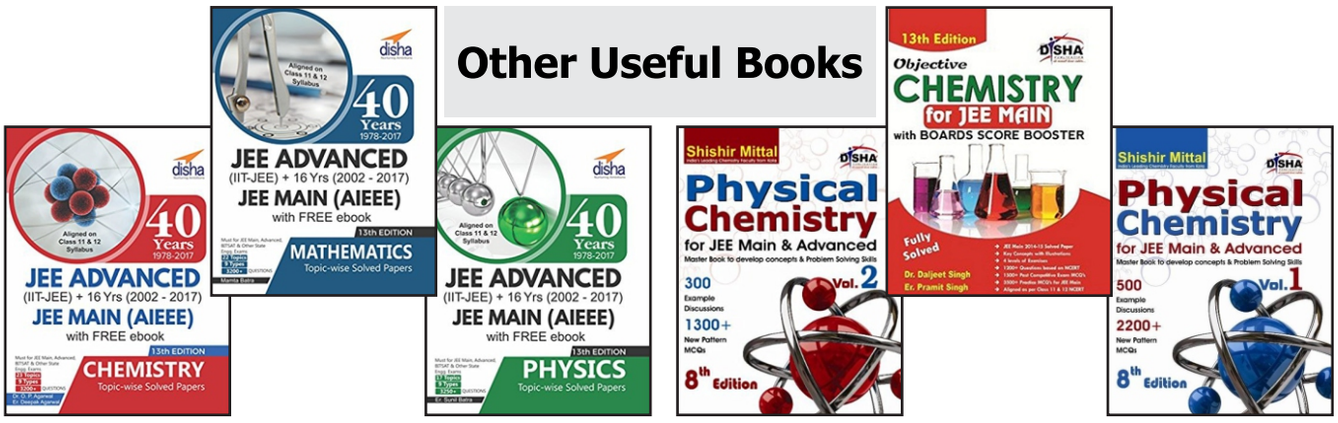
The exercises at the end of each chapter have been designed in the flavour of the new pattern of JEE Main & Advanced. The question from the previous JEE papers have been incorporated in the different exercises. A separate section having past JEE questions is also provided at the end.

1. **Exercise 1 - MCQ with One correct option :** This exercise contains a collection of question, which has been very carefully selected and it is ensured that there is no repetition. The exercise contains a collection of questions, which has been very carefully selected and it is ensured that there is no repetition. The exercise has been designed so as to cover all the concepts involved in the chapter.
2. **Exercise 2 :** This exercise contains all the four new variety of questions which have been asked in the last 3-4 JEE examinations. These variety of questions are-
   - **(i) MCQ's with one or more than one correct answers :** Around 20-30 well selected problems introduced in each chapter.
   - **(ii) Comprehension based questions :** More than 50 passages which tests the student's comprehension and analytical ability have been added. All these are newly framed problems.
   - **(iii) Matching type question :** Match the following type of question with multiple matching have been introduced in each chapter. These are unique and newly framed problems which will definitely pose a big challenge to the student. I feel that this type of problem is the best way to check a student's concepts.
   - **(iv) Assertion & Reason type questions :** Assertion and Reason type of questions have been incorporated in each and every chapter.
3. **Exercise 3 - Subjective Problems :** This exercise contains a unique collection of subjective problems which will not only give practice to the students but will also help in revising the complete chapter.

In the end, We would like to request all readers to highlight the printing errors and come forward with suggestions for further improvement of the book.

DR. O.P. AGARWAL

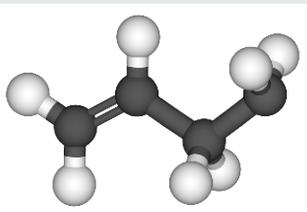
Other Useful Books

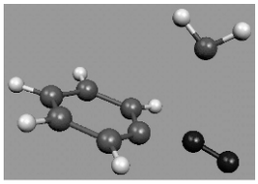


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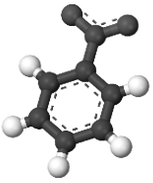


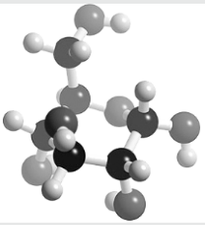
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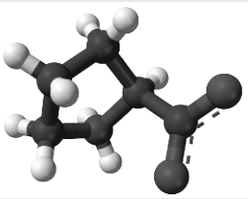


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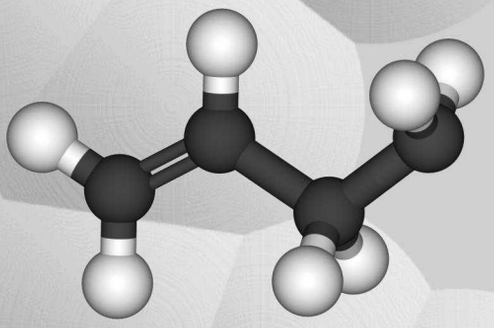




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19

Aliphatic Amines

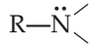
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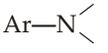
Nitrogen-containing compounds are essential to life and are ultimately derived from atmospheric nitrogen. Atmospheric nitrogen is reduced to ammonia, then converted into organic nitrogen compounds, the complete process is named as **nitrogen fixation**. The most important organic nitrogen compounds are **amines**.

19.1 Nomenclature

Amines are alkyl or aryl derivatives of ammonia in which one or more hydrogen atoms are replaced by alkyl or aryl groups. In **alkylamines**, nitrogen is attached to sp^3 hybridized carbon, while in **arylamines** nitrogen is attached to sp^2 hybridized carbon of a benzene or benzene-like ring.

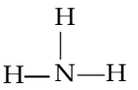


Alkylamine

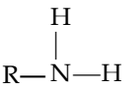


Arylamine

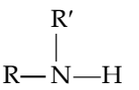
Amines are **classified** as primary, secondary, or tertiary, according to the number of groups attached to the nitrogen atom.



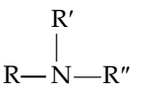
Ammonia



Primary amine



Secondary amine



Tertiary amine

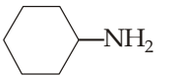
Amines are named in two ways, either as *alkylamines* or as *alkanamines* (**chemical abstract names**). The latest vesion of the IUPAC rules accepts both.

EBD_7091

1° Amines

CH_3NH_2
Methylamine
(Methanamine)

$CH_3CH(CH_3)CH_2NH_2$
Isobutylamine
(2-Methylpropylamine)
(2-Methyl-1-propanamine)


Cyclohexylamine
(Cyclohexanamine)

2° Amines

$CH_3NHCH_2CH_3$
Ethylmethylamine
(N-Methylethanamine)

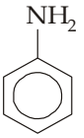
$(CH_3CH_2)_2NH$
Diethylamine
(N-Ethylethanamine)

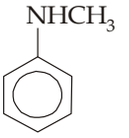
3° Amines

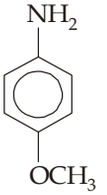
$(CH_3CH_2)_3N$
Triethylamine
(N, N-Diethylethanamine)

$CH_3N(CH_2CH_3)CH_2CH_2CH_3$
Ethylmethylpropylamine
(N-Ethyl-N-methyl-1-propanamine)

Arylamines


Aniline
(Benzenamine)


N-Methylaniline
(N-Methylbenzenamine)


p-Ansidine
(4-Methoxybenzenamine)

As replacement of 1, 2 or 3 hydrogen atoms of NH_3 gives amines, replacement of 1, 2, 3 or 4 hydrogen atoms of NH_4^+ give corresponding amine salts ; when all the four hydrogen atoms of NH_4^+ are replaced by alkyl groups it is known as **quaternary ammonium salt**. These are named by replacing —*amine* by —*ammonium* (or —*aniline* by —*anilinium*) and adding the name of the anion (chloride, nitrate, sulphate, etc.) For example,

$CH_3NH_3^+Cl^-$
Methylammonium chloride

$(C_2H_5NH_3^+)_2SO_4^{2-}$
Ethylammonium sulphate

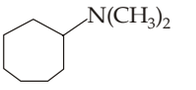
$C_6H_5NH_3^+Cl^-$
Anilinium chloride

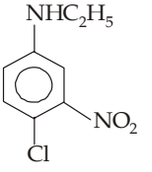
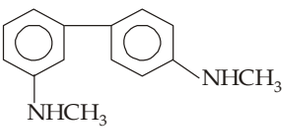
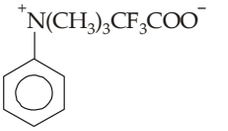
$(CH_3)_3NH^+NO_3^-$
Trimethylammonium nitrate

$C_6H_5CH_2N^+(CH_3)_3I^-$
Benzyltrimethylammonium iodide
(a quaternary ammonium salt)

TEST YOUR UNDERSTANDING - 19.1

1. Give IUPAC names for the following compounds :

(*a*) $C_6H_5CH_2CH_2NH_2$ (*b*) $CH_2 = CHCH_2NH_2$ (*c*)  (*d*) 

(*e*)  (*f*)  (*g*)  (*h*) 

2. Write structure for the following compounds.

(*a*) N-Methyl-1-butanamine
(*b*) N, N-bis (1-chloroethyl)ethanamine
(*c*) 1, 5-Pentanediamine
(*d*) 1, 1, 1″-tri (chloroethyl)amine
(*e*) N, N-Dicyclopropylcyclopropylamine
(*f*) β-(3, 4-dihydroxyphenyl)ethylamine.

19.2 Preparation of Amines

19.2.1 Preparation of Amines from Alkyl Halides

(*i*) **By alkylation of ammonia** (*Ammonolysis of alkyl halides*). Alkyl halides react with ammonia by nucleophilic substitution to form the amine salt, from which free amine can be liberated by treatment with base, which may be NH_3 itself or OH^- added from outside.

$$H_3N: + R{-}X \xrightarrow{S_N2} H_3N^{\delta+} \text{--- } R \text{ --- } X^{\delta-} \longrightarrow \underset{\text{1° Amine salt}}{H_3N^+ - R \;\; X^-}$$

$$H_2O + \underset{\text{1° Amine}}{R{-}NH_2} \xleftarrow{OH^-} R{-}N^+H_3 \xrightarrow{NH_3} \underset{\text{1° Amine}}{R{-}NH_2} + NH_4^+$$

However, this method is of very limited synthetic application because multiple alkylations occur. The free primary amine can compete with ammonia and react with alkyl halide to form salt of a secondary amine.

$$\underset{\text{1° Amine}}{RNH_2} + RX \longrightarrow R_2NH_2^+X^- \xrightarrow{NH_3} \underset{\text{2° Amine}}{R_2NH} + NH_4^+X^-$$

Similarly, secondary amine may react with alkyl halide to give *tert*-amine. Even the *tert*-amine competes with ammonia to form a quaternary ammonium salt.

$$\underset{\text{2° Amine}}{R_2NH} + RX \longrightarrow R_3N^+HX^- \xrightarrow{NH_3} \underset{\text{3° Amine}}{R_3N} \xrightarrow{RX} \underset{\text{Quaternary ammonium salt}}{R_4N^+X^-}$$

Conversion of ammonia or 1° amine to quaternary ammonium salt is known as **exhaustive methylation**.

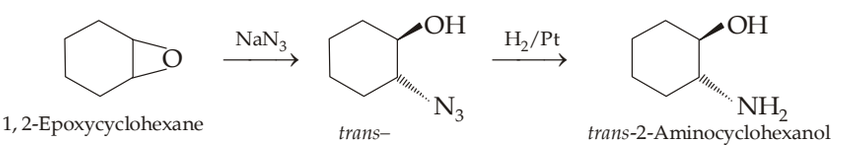
$$NH_3 \xrightarrow{RX} \underset{\text{1° Amine}}{RNH_2} \xrightarrow{RX} \underset{\text{2° Amine}}{R_2NH} \xrightarrow{RX} \underset{\text{3° Amine}}{R_3N} \xrightarrow{RX} \underset{\text{4° Ammonium salt}}{R_4N^+X^-}$$

Multiple alkylations, *i.e.* preparation of 2°, and 3° amines and quaternary ammonium salt, can be minimized by using a large excess of ammonia. In presence of large excess of ammonia, a molecule of RX is more likely to be attacked by one of the numerous ammonia molecules rather than one of the relatively few RNH_2 molecules. Further except the special case of methylamine, the primary amine can be separated from other products by distillation.

Because of their low reactivity, aryl halides do not normally react with ammonia under ordinary conditions. Aryl halides can be converted into amines, by ammonia, only (*a*) if the ring carries strongly electron-withdrawing group (*e.g.* $-NO_2$) at *o*- and *p*- positions to the halogen, or (*b*) if a high temperature or a strongly basic reagent is used.

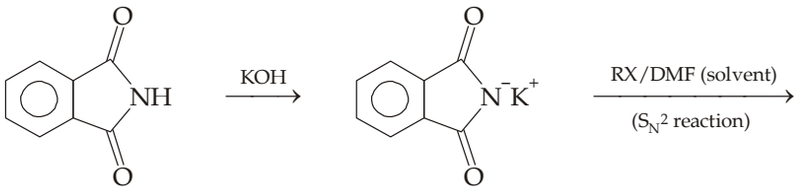
(*ii*) **Alkylation of azide ion followed by reduction**. A much better method for preparing primary amine from an alkyl halide is *via* alkyl azide route. Azide is a very good nucleophile and reacts with primary and secondary alkyl halides to give alkyl azides which can be reduced to primary amine with sodium and alcohol or with $LiAlH_4$ or with H_2 in presence of Pt or Raney Ni.

$$R{-}X + \underset{\text{Azide ion}}{{}^-:\ddot{N}=N=\ddot{N}:^-} \xrightarrow{S_N2} \underset{\text{Alkyl azide}}{R{-}\ddot{N}=N^+=\ddot{N}:^-} \xrightarrow[\text{or } LiAlH_4]{\text{Na / alcohol}} R{-}\ddot{N}H_2$$

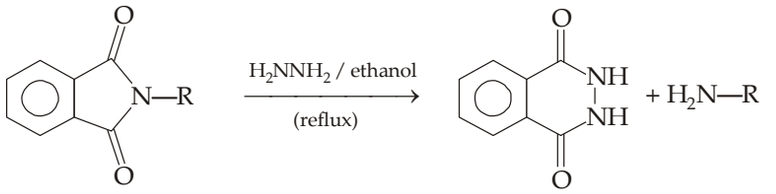


1, 2-Epoxycyclohexane — *trans*– — *trans*-2-Aminocyclohexanol

(*iii*) **The Gabriel synthesis.** Another method used for preparing primary amines from alkyl halides, an easily available starting material, without the formation of secondary and tertiary amines is the Gabriel synthesis. The key reagent of Gabriel synthesis, potassium phthalimide, is prepared by reacting phthalimide with KOH. Potassium phthalimide acts as a nucleophile and react with alkyl halides by S_N2 process to form an N-alkylphthalimide. Imides are diacyl derivatives of amines and can be hydrolysed by aqueous acid or base to liberate primary amine. However, more effective method for cleaving the imide to primary amine is reaction with hydrazine



Phthalimide N-Potassium phthalimide (a nucleophile)



N-Alkylphthalimide Phthalylhydrazide

(*i*) Aryl halides can't be converted into arylamines because they do not undergo nucleophilic substitution with N-potassiophthalimide.

(*ii*) Since phthalimide can undergo only a single alkylation, the formation of secondary and tertiary amines does not occur, and thus the Gabriel synthesis is a valuable method for the laboratory preparation of primary amines.

Further, like above two methods, Gabriel synthesis restricted the use of methyl, 1° and 2° alkyl halides because the 3° alkyl halides lead almost exclusively to elimination products.

TEST YOUR UNDERSTANDING - 19.2

1. Which of the following amines can be prepared by the Gabriel synthesis ; give equations for it.

(*a*) Isobutylamine (*b*) Benzylamine (*c*) Aniline (*d*) 2-Phenylethylamine

(*e*) *tert*-Butylamine (*f*) N-Methylbenzylamine.

19.2.2 Preparation of Amines by Reduction

Almost any nitrogen-containing organic compound can be reduced to amine. However, availability of a suitable precursor and the choice of an appropriate reducing agent determine whether a reaction can be used for preparing the amine or not.

Reduction of azides (described above), nitro, nitriles, oximes and amides. Reduction of an azide, a nitro, a nitrile or an oxime gives a primary amine ; while reduction of an amide can yield a primary, secondary, or tertiary amine.

(*a*) Nitro group can be reduced to primary amines in two general ways : (*i*) by catalytic hydrogenation over Pt, Pd, or Ni, or (*ii*) by reduction with acid and relatively inexpensive metal like Fe, Sn, Zn or a metal salt like $SnCl_2$. This method is more important in preparing 1° aromatic amines, although it is equally suitable for the preparation of 1° aliphatic amines.

$$CH_3NO_2 \xrightarrow{Sn,\ HCl} CH_3NH_2 \ ; \ C_6H_5NO_2 \xrightarrow{Sn—HCl} C_6H_5NH_2$$

(*b*)

$$\underset{\text{Nitrile}}{R—C \equiv N} \xrightarrow{LiAlH_4 \text{ or } H_2,\ \text{catalyst}} \underset{1° \text{ Amine}}{RCH_2NH_2}$$

Since nitriles can be prepared from alkyl halides by a nucleophilic substitution reaction with cyanide ion, the overall process $RX \rightarrow RC \equiv N \rightarrow RCH_2NH_2$, leads to primary amines that have one carbon atom more than the starting alkyl halide. Cyano groups in cyanohydrins are reduced under the same reaction conditions.

(*c*)

$$\underset{\text{Oxime}}{RCH=NOH} \xrightarrow[\text{or Na in } C_2H_5OH]{LiAlH_4 \text{, or } H_2\text{, catalyst}} \underset{1^\circ \text{ Amine}}{RCH_2NH_2}$$

Oximes, in turn, can be prepared from aldehydes and ketones.

(*d*)

$$\underset{\text{Amide}}{R-\overset{\overset{O}{\|}}{C}-NR_2'} \xrightarrow{LiAlH_4} \underset{3^\circ \text{ Amine}}{R-CH_2-NR_2'}$$

Here, if R′ = H, the product is a 1° amine, if one R′ = H and other R′ = an alkyl group the product is 2° amine. Amides, in turn, can be prepared from acid chlorides, acid anhydrides, and esters.

19.2.3 Preparation of Amines through Reductive Amination (*Reduction of imines*)

Imines are the products formed by the reaction of aldehydes and ketones with ammonia, 1° amine, or 2° amine. Imines can be reduced to amines by catalytic hydrogenation or $LiAlH_4$.

$$\underset{\text{Aldehyde or ketone}}{R-\overset{R'}{\overset{|}{C}}=O} + NH_3 \longrightarrow \underset{\text{Imine}}{R-\overset{R'}{\overset{|}{C}}=NH} \xrightarrow{H_2\text{ / catalyst}} \underset{\text{Amine}}{R-\overset{R'}{\overset{|}{C}}H-NH_2}$$

The reaction can be carried out in a single operation by catalytic hydrogenation of a solution containing both ammonia and the carbonyl compound.

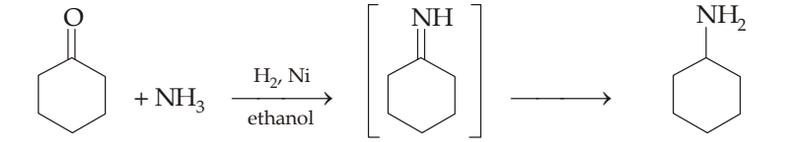
$$R-\overset{R'}{\overset{|}{C}}=O \xrightarrow[[H]]{NH_3} R-\overset{R'}{\overset{|}{C}}H-NH_2 \quad 1^\circ \text{ Amine}$$

$$R-\overset{R'}{\overset{|}{C}}=O \xrightarrow[[H]]{R''NH_2} R-\overset{R'}{\overset{|}{C}}H-NHR'' \quad 2^\circ \text{ Amine}$$

$$R-\overset{R'}{\overset{|}{C}}=O \xrightarrow[[H]]{R''R'''NH} R-\overset{R'}{\overset{|}{C}}H-NR''R''' \quad 3^\circ \text{ Amine}$$

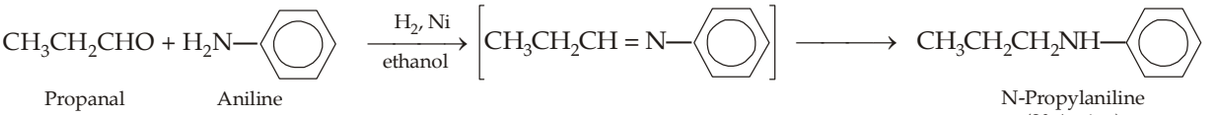
Reductive amination has been used successfully with a wide variety of aldehydes and ketones, both aliphatic and aromatic. For example,

(*i*)



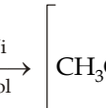
Cyclohexanone — Not isolated — Cyclohexylamine (1° Amine)

(*ii*)



Propanal — Aniline — N-Propylaniline (2° Amine)

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(*iii*) $CH_3CH_2CH_2CHO$ +  $\xrightarrow[\text{ethanol}]{H_2, Ni}$ $CH_3CH_2CH_2CH(OH)$—  $\rightleftharpoons$ $CH_3CH_2CH_2CH=\overset{+}{N}$  OH^-

Butanal Piperidine Carbinolamine Iminium ion

$\longrightarrow$ $CH_3CH_2CH_2CH_2$—

N-Butylpiperidine (3° amine)

Especially effective reducing agents for reductive aminations are sodium or lithium cyanoborohydride ($NaBH_3CN$ or $LiBH_3CN$). All that is required is to add sodium cyanoborohydride to an alcoholic solution of the carbonyl compound and an amine.

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow[NaBH_3CN]{CH_3CH_2NH_2} \underset{\text{N-Benzylethylamine}}{C_6H_5CH_2NHCH_2CH_3}$$

Sodium cyanoborohydride (more toxic and less effective) has now-a-days been replaced by sodium triacetoxyborohydride, $Na(AcO)_3BH$ which is non-toxic and more effective. The $NaBH_3CN$ and $Na(AcO)_3BH$ are especially recommended while preparing 3° amines by reductive amination.

TEST YOUR UNDERSTANDING - 19.3

1. Give reactions involved in the preparation of each of the following amine by reductive amination.

(*a*) Dibenzylamine (*b*) N, N-Dimethylbenzylamine

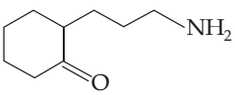
(*c*) N-Benzylpiperidine (*d*) α-Phenylethylamine (*e*) β-Phenylethylamine.

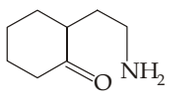
2. Reductive amination of a ketone is always a better method for the preparation of amines of the type R_2CHNH_2 than treatment of an alkyl halide with ammonia. Explain.

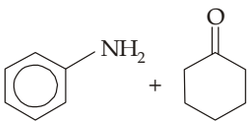
3. Why sodium cyanoborohydride ($NaBH_3CN$) is considered to be a better reducing agent in reductive amination.

4. (*a*) Give steps involved in the conversion of acetyl chloride to ethyl amine.

(*b*) Give the product obtained in the following reactions :

(*i*)  $\xrightarrow{H_2/Ni}$ [A]

(*ii*)  $\xrightarrow{H_2/Ni}$ [B]

(*iii*)  $\xrightarrow{H_2/Ni}$ [C] .

19.2.4 Hofmann Degradation of Amides

Amides, *with no substituent on the nitrogen*, react with solutions of bromine or chlorine in sodium hydroxide to yield amines. This reaction is called the *Hofmann rearrangement* or *Hofmann degradation*.

$$R{-}\overset{\overset{O}{\|}}{C}{-}NH_2 + Br_2 + 4NaOH \longrightarrow RNH_2 + 2NaBr + Na_2CO_3 + 2H_2O$$

From the above reaction, it is evident that the carbonyl carbon atom of the amide is lost (as CO_3^{2-}) and the R group of the amide is attached to the nitrogen atom of the amide group, thus a primary amine having one carbon atom less than the amide is the final product.

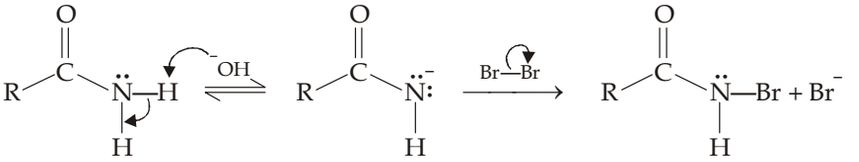
Mechanism. The mechanism of the Hofmann rearrangement involves three stages :

(*i*) formation of N-bromoamide intermediate (steps 1 and 2),

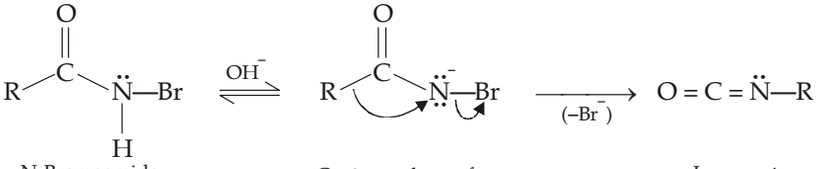
(*ii*) rearrangement of the N-bromoamide to an isocyanate (steps 3 and 4), and

(*iii*) hydrolysis of the isocyanate (steps 5 and 6).

Steps 1 and 2. Amides of the type $RCONH_2$ are appreciably acidic in nature because their conjugate bases are stabilized by electron delocalization. Conjugate base of the amide reacts with bromine to form N-bromoamide.

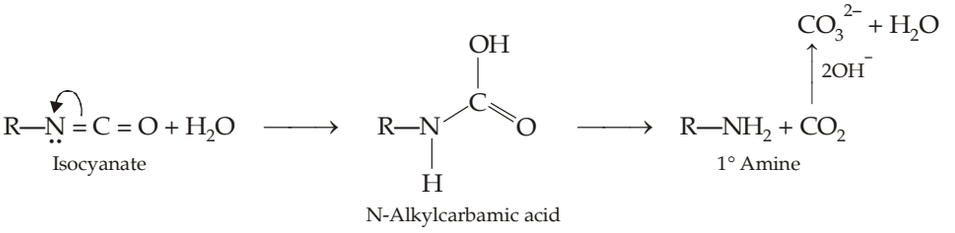


Steps 3 and 4. Because of the presence of electron-withdrawing bromine, N-bromoamide is even more acidic than the starting amide, hence it easily undergoes deprotonation to form corresponding conjugate base. Due to the presence of electron-withdrawing Br as substituent, the nitrogen atom of the conjugate base of N-bromoamide becomes electron-deficient which causes the alkyl group to shift along with its bonding pair of electrons from acyl carbon to electron-deficient nitrogen. Actually, attachment of R to nitrogen helps in pushing out bromide ion. Migration of R— and elimination of bromide ion both take place simultaneously to form isocyanate.



Note that the C—C bond cleavage and C—N bond formation take place simultaneously, and the migrating alkyl group does not become free. Hence if the R— group has chiral carbon, its configuration will be retained in the product (isocyanate and hence amine).

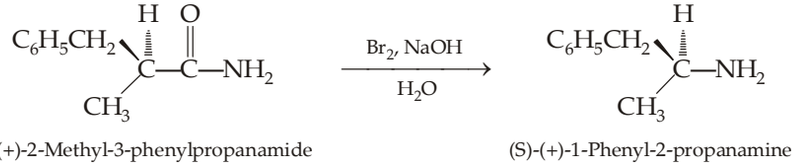
Steps 5 and 6. The isocyanate is quickly hydrolysed by base-catalyzed addition of water to form N-alkylcarbamic acid, which, being unstable, dissociates to an amine and carbon dioxide; CO_2 is then converted into CO_3^{2-} ion by base.

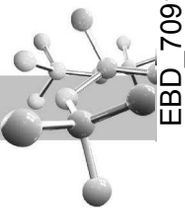


Salient features of the Hofmann rearrangement.

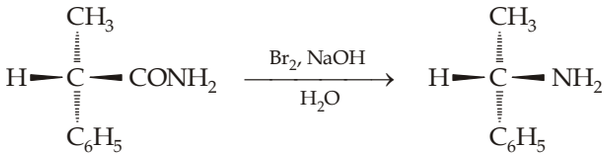
(*i*) The method is equally suitable for the preparation of primary amines with 1°, 2°, or 3° alkyl groups, or aryl amines.

(*ii*) Only amides of the type $RCONH_2$ undergo Hofmann rearrangement. In other words, the amide nitrogen must have two protons attached to it ; of which one is replaced by bromine to give the N-bromo amide, while abstraction of the second by base is necessary to trigger the rearrangement. Thus amides of the type RCONH(R') although can form N-bromoamides, RCONBr(R'), under the reaction conditions, but these do not rearrange.





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(+)-α-Phenylpropionamide (–)-α-Phenylethylamine

Retention of configuration

(*iii*) Rearrangement proceeds with *retention of configuration* at the migrating group.

(*iv*) Isocyanates are formed as important intermediates. This can be proved if the reaction of an amide with bromine is carried out in methanol containing sodium methoxide instead of aqueous base. In such case, the product isolated is carbamate (ester of carbamic acid, H_2N COOH). Since **carbamates**, also known as **urethans**, are stable, these can be isolated.

$$CH_3(CH_2)_{14}CONH_2 \xrightarrow[CH_3OH]{Br_2,\ CH_3ONa} CH_3(CH_2)_{14}NHCOOCH_3$$

Hexadecanamide Methyl N-pentadecylcarbamate

In such case, the isocyanate reacts with CH_3OH to form methyl carbamate.

$$\underset{\text{Isocyanate}}{RN = C = O} + CH_3OH \longrightarrow \underset{\text{Methyl N-alkylcarbamate}}{RNHCOOCH_3}$$

(*v*) In the product R—NH_2, both hydrogen atoms are coming from OH^-, *i.e.* the two original H atoms of the —$CONH_2$ group are removed. Thus,

$$CH_3—\overset{\overset{O}{\|}}{C}—NH_2 \xrightarrow{OD^-/Br_2} CH_3—ND_2$$

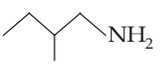
$$CH_3—\overset{\overset{O}{\|}}{C}—ND_2 \xrightarrow{OH^-/Br_2} CH_3—NH_2$$

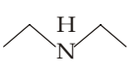
(*vi*) Presence of electron-releasing substituent in the migrating alkyl group speeds up the migration of the alkyl group and hence the Hofmann rearrangement. Thus when the migrating group is aryl, the rate of degradation is increased by the presence of electron-releasing substituents in the ring, thus substituted amides show the following order of reactivity.

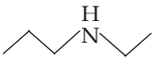
$$—OCH_3 > —CH_3 > —H > —Cl > —NO_2.$$

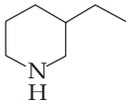
TEST YOUR UNDERSTANDING - 19.4

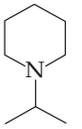
1. Following amines are prepared by the reduction of an amide with $LiAlH_4$; provide the structure(s) of the parent amide(s) :

(*a*) 

(*b*) 

(*c*) 

(*d*) 

(*e*) 

2. (*a*) Give the starting compound to prepare *n*-propylamine by reduction of following type of compound with $LiAlH_4$:

(*i*) A nitro compound (*ii*) An amide (*iii*) A nitrile (*iv*) An oxime (*v*) An azide.

(*b*) Which of these compounds are commonly reduced with

(*i*) Na and ethanol, and (*ii*) H_2/Pt.

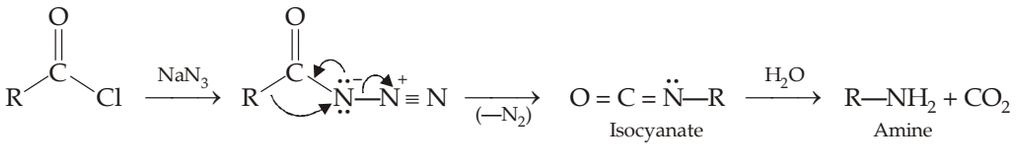
3. Give reactions involved in the preparation of *n*-pentylamine from the alcohol having 5– or 6– carbon atoms by following methods.

(*i*) Ammonolysis of alcohols (*ii*) Gabriel synthesis (*iii*) Reduction of nitrile (*iv*) Reductive amination

(*v*) Hofmann degradation (*vi*) Amide reduction.

19.2.5 Preparation of Amines by Cutius and Schmidt Reactions

The Curtius rearrangement involves rearrangement of acyl azides to alkyl isocyanates. It resembles Hofmann rearrangement in the sense that the R— group migrates from the acyl carbon to the nitrogen atom as the leaving group departs, which is N_2 here (remember that N_2 is the best of all leaving groups since it is highly stable, nonbasic and escapes from the medium as it is a gas).

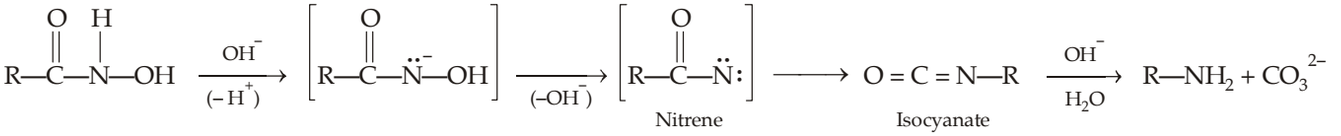


Schmidt reaction involves the reaction of a carboxylic acid, hydrazoic acid and conc. H_2SO_4 to form amine *via* azide as intermedite

$$R—COOH + HN_3 \xrightarrow[\text{heat}]{\text{conc. } H_2SO_4} R—NH_2 + N_2 + CO_2$$

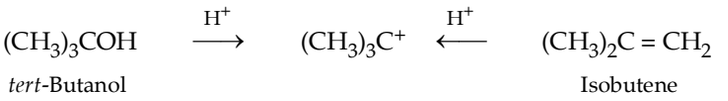
19.2.6 Preparation of Primary Amines by Lossen Rearrangement

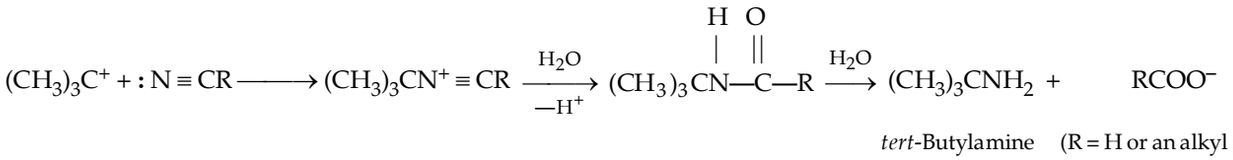
Lossen rearrangement involves the conversion of a hydroxamic acid to primary amine by means of a base. Here also an isocyanate is formed as an intermediate



19.2.7 Preparation of Primary Amine Containing a 3° Alkyl Group (Ritter Reaction)

Reaction of Me_3COH or $Me_2C = CH_2$ with HCN or RCN in conc. H_2SO_4 followed by hydrolysis gives primary amines.



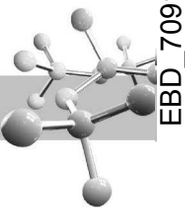


This method is especially useful for preparing 1° amines in which —NH_2 group is present on 3° carbon atom. Since such amines can't be prepared by reductive amination, nitrile reduction, oxime reduction, and Gabriel synthesis. However, Hofmann bromamide degradation can be used for preparing such amines.

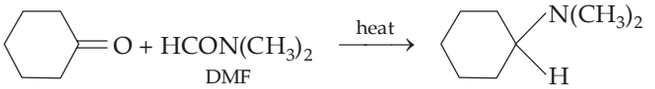
19.2.8 By Leuckart Reaction

A ketone is heated with ammonium formate or dimethyl formamide (DMF) to form 1° and 3° amine respectively.

$$C_6H_5COCH_3 + HCOONH_4 \xrightarrow{\text{heat}} C_6H_5\underset{\displaystyle NH_2}{\underset{|}{C}}HCH_3 + H_2O + CO_2$$



$$(C_2H_5)_2CO + HCON(CH_3)_2 \xrightarrow[\text{DMF}]{\text{heat}} C_2H_5—\underset{\displaystyle N(CH_3)_2}{\overset{|}{C}}H—C_2H_5$$



Note that the reaction is similar to reductive amination.

19.2.9 By Grignard Reagents

$$\underset{\text{Chloramine}}{RMgCl} + ClNH_2 \longrightarrow \underset{\text{A 1° amine}}{RNH_2} + MgCl_2$$

$$\underset{\text{N-Alkylchloramine}}{RMgCl} + ClNHR' \longrightarrow \underset{\text{A 2° amine}}{RNHR'} + MgCl_2$$

19.2.10 By the hydrolysis of Isocyanides and Isocyanates

$$\underset{\text{Alkyl isonitrile}}{RNC} + 2H_2O \xrightarrow{HCl} RNH_2 + HCOOH$$

$$\underset{\text{Alkyl isocyanate}}{RNCO} + 2KOH \xrightarrow{\text{heat}} RNH_2 + K_2CO_3$$

19.2.11 Special Methods for Preparing Secondary and Tertiary Amines

1. **By the reduction of isocyanides.** In this method one alkyl group is always methyl.

$$RNC + 4H \longrightarrow RNHCH_3 \quad \text{or} \quad RNC \xrightarrow{Na/C_2H_5OH} RNHCH_3$$

2. **Eschweiler-Clarke synthesis for tertiary amines.** This method is used for preparing a dimethyl 3° amine ($RNMe_2$). Primary or secondary amines are treated with formaldehyde and formic acid.

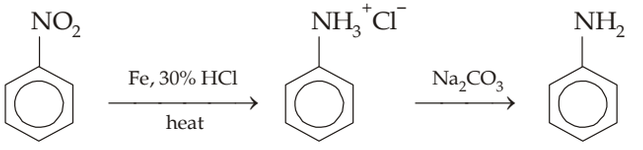
$$C_6H_5CH_2NH_2 + 2CH_2O + 2HCOOH \longrightarrow C_6H_5CH_2N(CH_3)_2 + 2H_2O + 2CO_2$$

$$(C_2H_5)_2NH + CH_2O + HCOOH \longrightarrow (C_2H_5)_2NCH_3 + H_2O + CO_2$$

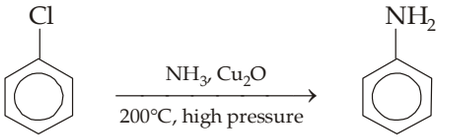
Formic acid acts as a reducing agent by transferring its hydride ion to the electron-deficient carbon of formaldehyde and is oxidised to CO_2.

3. **Industrial methods.** Aniline, the most important of all amines, is prepared by following three methods :

(*a*) By the reduction of nitrobenzene by cheap reagents like Fe and dil. HCl or by catalytic hydrogenation.



(*b*) By treating chlorobenzene with ammonia at high temperature and high pressure in the presence of a catalyst



Methylamine, dimethylamine, and trimethylamine are synthesized from methanol and ammonia.

$$NH_3 \xrightarrow[Al_2O_3,\,450°C]{CH_3OH} \underset{\text{Methylamine}}{CH_3NH_2} \xrightarrow[Al_2O_3,\,450°C]{CH_3OH} \underset{\text{Dimethylamine}}{(CH_3)_2NH} \xrightarrow[Al_2O_3,\,450°C]{CH_3OH} \underset{\text{Trimethylamine}}{(CH_3)_3N}$$

Function of Al_2O_3. Al_2O_3 is a Lewis acid and thus makes complexes with the O of ROH, making OH a better leaving group as H_2O.

TEST YOUR UNDERSTANDING - 19.5

1. How will you prepare $C_6H_5N(CH_3)_2$ from $C_6H_5NH_2$ in quantitative yield ?

19.3 Properties of Amines

1. Amines are moderately polar substances ; these are more polar than alkanes but less than alcohols. Thus amines have higher boiling points than alkanes and lower than alcohols of comparable molecular weight.
2. Molecules of primary and secondary amines can form strong hydrogen bonds to each other and to water or other hydroxylic solvents. However, tertiary amines although can form hydrogen bonds to water, their molecules do not form hydrogen bonds to each other. Hence
   (*a*) tertiary amines generally boil at lower temperatures than primary and secondary amines of comparable molecular weight. Among isomeric amines, primary amines have the highest boiling point, and tertiary amines the lowest.
   (*b*) lower amines (1°, 2° as well as 3°) are quite soluble in water.
3. Aniline, the simplest arylamine, is a liquid at room temperature. It is only slightly soluble in water and boils at 184°C. Other arylamines are less water-soluble and have higher boiling points than aniline.

TEST YOUR UNDERSTANDING - 19.6

1. Arrange the following isomeric amines in order of decreasing boiling points :

$CH_3CH_2CH_2CH_2NH_2$, $CH_3CH_2NHCH_2CH_3$ and $(CH_3)_2NC_2H_5$.

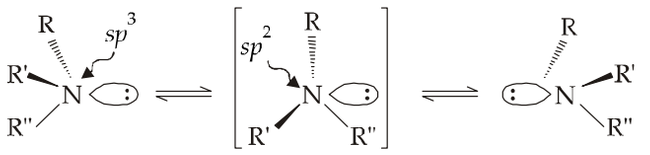
2. Compare the dipole moments of the following compounds :

$CH_3CH_2CH_2CH_2NH_2$, $CH_3CH_2CH_2CH_2OH$ and $CH_3(CH_2)_3CH_3$.

3. Ethanolamine ($HOCH_2CH_2NH_2$) can form two different types of intramolecular H-bonding. Give their structures and discuss their relative importance.

4. *Optical isomerism in amines*. Like ammonia, nitrogen atom of most amines is sp^3 hybridised. The three substituents (alkyl groups or hydrogen atoms) occupy three corners of a tetrahedron, the fourth corner is occupied by an sp^3 orbital containing the unshared electron pair. Due to the presence of a free electron pair, the regular tetrahedral geometry (having bond angles of 109.5°) is somewhat distorted to trigonal pyramidal, having a bond angle less than 109.5°, *e.g.* 108° in trimethylamine.

If the three alkyl groups of a tertiary amine are different, the amine molecule will be chiral as hence should exist in two enantiomeric forms which should be resolvable. However, in practice, resolution is usually impossible because the two enantiomers interconvert rapidly.



Interconversion of amine enantiomers

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This interconversion, due to unshared pair of electrons, occurs through a **pyramidal** or **nitrogen inversion**. For most simple amines, the barrier to this interconversion is about 25 kJ mol^{-1} which is quite low to occur readily at room temperature. In other words, the two enantiomers of most of simple amines are interconverted readily at room temperature, and hence such amines can't be resolved, although they may have chiral nitrogen.

Ammonium salts do not have an unshared pair, hence they can't undergo inversion. Thus, quaternary ammonium salts having four different groups can be resolved into separate (relatively stable) enantiomers.



Enantiomers of quaternary ammonium salts (Resolvable)

TEST YOUR UNDERSTANDING - 19.7

1. Which of the following compounds are (*i*) chiral, (*ii*) resolvable ?

(*a*) $n\text{-}C_3H_7N(CH_3)C_2H_5$ (*b*) $C_6H_5—\overset{\displaystyle CH_3}{\underset{\displaystyle C_2H_5}{\overset{|}{\underset{|}{N^+}}}}—O^-$ (*c*) $C_3H_7N^+(CH_3)_2C_2H_5\ Br^-$

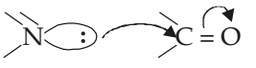
(*d*) $CH_3CH_2\overset{\displaystyle CH_3}{\overset{|}{C}}HN(CH_3)C_2H_5$ (*e*) $Me_2C\!\!-\!\!\!-\!\!\overset{\displaystyle \cdot\cdot}{N}CH_3$ (with CH_2 bridge)

19.4 Reactions of Amines

Like ammonia, the three classes of amines contain nitrogen that bears an unshared pair of electrons. The tendency of nitrogen to share this pair of electrons is the sole reason for the entire chemical behaviour of amines, *i.e.* their basicity, their action as nucleophiles (in both aliphatic and acyl substitution) and the unusual high reactivity of aromatic rings bearing amino or substituted amino groups.



Amine acting as a base



Amine acting as a nucleophile

19.4.1 Basic and Nucleophilic Character of Amines

1. Basicity of amines. Like ammonia, amines are converted into their salts by aqueous mineral acids and are liberated from their salts by aqueous hydroxides. Thus, like ammonia, amines are more basic than water and less basic than hydroxide ions.

$$\underset{\text{Stronger base}}{RNH_2} + H_3O^+ \longrightarrow \underset{\text{Weaker base}}{RNH_3^+} + H_2O$$

$$\underset{\text{Stronger base}}{RNH_3^+} + OH^- \longrightarrow \underset{\text{Weaker base}}{RNH_2} + H_2O$$

There are two conventions to measure the basicity of amines.

(*a*) **Basicity constant, K_b concept.** Basicities of amines are compared by measuring the extent to which they accept proton from water

$$RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^-$$

$$K_b = \frac{[RNH_3^+][OH^-]}{[RNH_2]} \; ; pK_b = -\log K_b$$

Here the basicity is expressed in terms of **basicity constant**, K_b. Each amine has its characteristic K_b, **the larger the K_b, the stronger is the base**.

(*b*) **Acidity constant of the conjugate acid, K_a concept.** This is a convenient way for comparing the basic character of amines. The expression for this acidity constant is as follows.

$$RNH_3^+ + H_2O \rightleftharpoons RNH_2 + H_3O^+$$

$$K_a = \frac{[RNH_2][H_3O^+]}{[RNH_3^+]} \; ; pK_a = -\log K_a$$

If the amine is strongly basic, the aminium (or ammonium) ion will hold the proton tightly and consequently, will not be very acidic (indicated by its large pK_a value). On the other hand, if the amine in weakly basic, the aminium ion will not hold the proton tightly and will be much more acidic (indicated by its small pK_a value). In short, **the more basic the amine, the weaker is its conjugate acid and vice versa**.

TEST YOUR UNDERSTANDING - 19.8

1. The K_b value for a base is 1×10^{-6} ; determine its pK_b value. Also calculate the K_a and pK_a values for its conjugate acid.

Structure and basicity. Relation between structure and basicity of amines can well be understood by comparing the stabilities of amines with the stabilities of their ions ; **the more stable the ion relative to the parent amine, the more basic is the amine**.

1. Since nitrogen is less electronegative than oxygen, and thus can better accommodate the positive charge of the ion, amines are more basic than alcohols, ethers, esters, etc.
2. **Basicity of aliphatic amines.** An aliphatic amine is more basic than ammonia. This can be explained in two ways.

   (*a*) The alkyl group pushes electrons towards nitrogen (due to +I effect), and thus makes the lone pair of electrons more available for sharing with an acid.

$$R \rightarrow \ddot{N}H_2 + H^+ \rightleftharpoons R \rightarrow N^+H_3$$

R pushes electrons, makes unshared pair more available — R pushes electrons, stabilizes ion by neutralising charge

   (*b*) The alkyl group releases electrons and thus tends to disperse the positive charge of the alkylammonium ion and therefore stabilizes it. Since NH_4^+ (from NH_3) has no such alkyl group, it is not stabilised to such an extent as alkylammonium ion.

The above explanation is supported by the following relative basicities of the amines in the *gas phase*.

$$(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3 \quad \textbf{(Basicity in gas phase)}$$

However, in *aqueous solution*, the order of basicity of these amines (as shown below) is somewhat different.

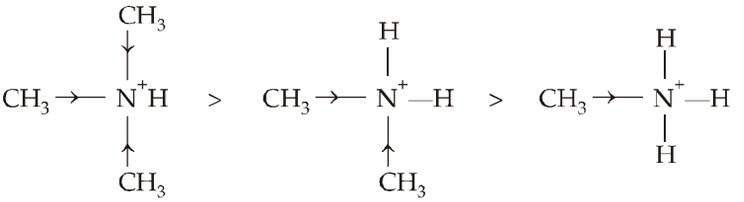
$$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3 \quad \textbf{(Basicity in aq. solution)}$$

The altered order of amine basicities in solution, as compared to those in the gas phase, is due to **solvation effects**.

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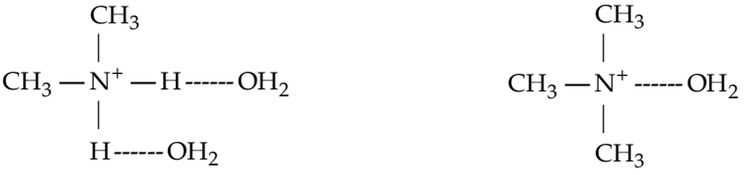
Stability of the alkylammonium ions (conjugate acids of alkylamines) can be explained in the following two ways :

(*i*) Dispersal of the positive charge by alkyl group(s). More the number of alkyl groups, more should be the stability of the alkylammonium ion and hence more is the basic character of the parent amine



From $(CH_3)_3\ddot{N}$ From $(CH_3)_2\ddot{N}H$ From $(CH_3)\ddot{N}H_2$

(*ii*) Formation of H-bond between H of the ammonium ion and O of H_2O, a solvent (*solvation effect*). Greater the number of H atoms on the N atom of the ammonium ion, more will be H-bonding and hence more will be the stability of the ammonium ion. Thus ammonium ion from *tert*-, *sec*.-, and primary amines have 1, 2 and 3 such H atoms, respectively ; hence the ammonium ion from *tert*-amines will be least stable. Actually poorer solvation of the ammonium ion formed from a tertiary amine more than compensates the electron-releasing effect of the three alkyl groups and makes the ammonium ion less stable and hence the parent *tert*-amine less basic than primary and secondary amines in aqueous solution.

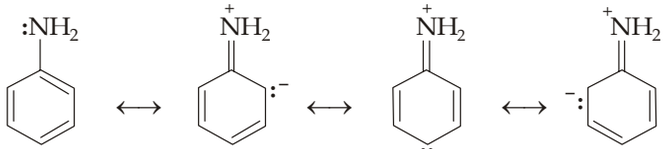


Dimethylammonium ion
(two protons on N available for H-bonding).
More stable from $(CH_3)_2NH$

Trimethylammonium ion
(only one proton on nitrogen available for H-bonding)
Less stable from $(CH_3)_3N$

Secondary amines are more basic than either primary or tertiary amines because their conjugate acids possess the best combination of alkyl and hydrogen substituents to permit stabilization both by electron release from alkyl group and by solvation due to hydrogen bonding. Higher basic character of *tert*-amine than ammonia is due to electron-releasing effect of the three alkyl groups.

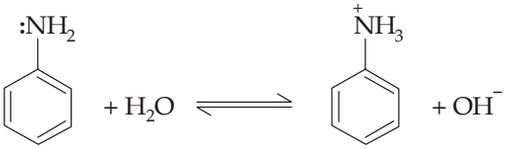
Basicity of arylamines. Arylamines, *e.g.* aniline and *p*-toluidine, are less basic than even ammonia what to speak of alkylamines. We can account for this effect, in part, on the basis of resonance. In arylamines, the lone pair of electrons on N is partly shared with the ring and is thus less available for sharing with a proton.



I II III IV

Delocalization of the electron pair to the ring also stabilizes the parent compound, aniline.

When aniline accepts a proton, it becomes anilinium ion.



Aniline Anilinium ion

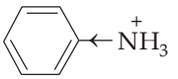
Since N atom of anilinium ion does not have lone pair of electrons, structures corresponding to II, III and IV are not possible for the anilinium ion, and thus anilinium ion is considerably less stable than aniline. This greater stabilization of the reactant (aniline) as compared to product (anilinium ion) means that ΔH^0 for the reaction between aniline and water will be a larger positive quantity than that for the reaction between NH_3 and H_2O

$$\text{Aniline} + H_2O \longrightarrow \text{Anilinium ion} + OH^-$$

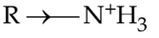
$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$$

Hence, aniline will be the weaker base than ammonia. When the proton donor is a strong acid, arylamines (weak bases) can be completely protonated.

Another important effect in explaining the lower basicity of aromatic amines is the **electron-withdrawing effect of a phenyl group** because its carbon atoms are sp^2 hybridised which are more electronegative than the sp^3 hybridised carbon atoms of alkyl groups. Further, anilinium ion is less stable than the alkylammonium ion, again because of electron-withdrawing nature of the phenyl group which destabilizes the anilinium ion by intensifying the positive charge on N.

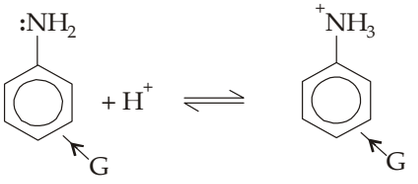


Positive charge on N intensified



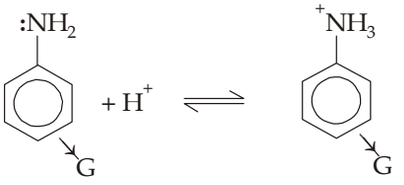
Positive charge on N dispersed

Effect of substituents on basicity of aromatic amines. In general, electron-donating substituents on the aromatic ring increase the basicity of arylamines ; while electron-withdrawing groups decrease the basicity. Electron-releasing group tends to disperse the positive charge of the anilinium ion, and thus stabilizes the ion relative to the amine. On the other hand, electron-withdrawing group tends to intensity the positive charge of the anilinium ion, and thus destabilizes the ion relative to the amine.



Here G = —NH_2, —OCH_3, —CH_3

G releases electrons, stabilizes cation, increases basicity of the parent amine



Here G = —NH_3^+, —NO_2, —SO_3^-, —COOH, —X

G withdraws electrons, destabilizes cation, decreases basicity of the parent amine

Ortho effect. It is important to note that a group present in the *ortho* position to the —NH_2 group always weakens the basicity whether it is electron-releasing or electron-withdrawing. An electron-withdrawing substituent in the *ortho* position decreases the basicity to a much greater extent than the same group when present in *meta*- or *para*-position.

Since amines act as bases, they react with aqueous acids forming compounds called **aminium salts** ;in an aminium salt, the positively charged nitrogen atom is attached to at least one hydrogen atom.

$$CH_3CH_2NH_2 + HCl \xrightarrow{H_2O} CH_3CH_2NH_3^+Cl^-$$

Ethylaminium chloride

$$(CH_3CH_2)_3N + HI \xrightarrow{H_2O} (CH_3CH_2)_3NH^+I^-$$

Triethylaminium iodide

When the central nitrogen atom of a compound is positively charged but not attached to a hydrogen atom, the compound is called a **quaternary ammonium salt**. Since quaternary ammonium halides do not have an unshared electron pair on the nitrogen atom, these can not act as bases, *i.e.* they do not react with acids. However, quaternary ammonium

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hydroxides are as strong bases as NaOH or KOH because they consist entirely of quaternary ammonium cations (R_4N^+) and hydroxide ions in the solid or in solution.

$$(CH_3)_4N^+ OH^- + HCl \longrightarrow (CH_3)_4N^+Cl^- + H_2O$$

Almost all alkylaminium and quaternary ammonium halides, nitrates, and sulphates are soluble in water (properties of salts). Thus although amines are water-insoluble, they dissolve in dilute aqueous HCl, HBr, HI or H_2SO_4 due to the formation of corresponding salts which are soluble in water. Parent amines can be regenerated from the soluble salt by making the salt solution alkaline. This difference in solubility behaviour between amines and their salts can be used both to detect amines and to separate them from non-basic compounds which do not react with aqueous acids.

$$\underbrace{\underset{1^\circ \text{ amine}}{RNH_2}, \quad \underset{2^\circ \text{ amine}}{R_2NH}, \quad \text{or} \quad \underset{3^\circ \text{ amine}}{R_3N}}_{\text{Insoluble in water}} \quad \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} \quad \underbrace{RNH_3^+, \quad R_2NH_2^+, \quad \text{or} \quad R_3NH^+}_{\text{Soluble in water}}$$

Corresponding aminium ion (salt)

TEST YOUR UNDERSTANDING - 19.9

1. 3-Aminopropanol, $H_2\ddot{N}CH_2CH_2CH_2\ddot{O}H$, can form conjugate acid, or conjugate base, or both ; write the possible structure for the same.

2. (*a*) What kind of reagents are used to form the conjugate base of an amine ?

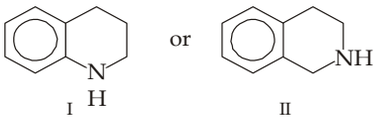
(*b*) Give the generic name for the conjugate base of an amine.

3. Write equations for the reaction of following hydrazines with an aqueous acid :

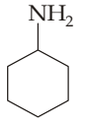
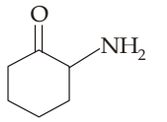
(*a*) CH_3NHNH_2 (*b*) $C_6H_5NHNH_2$.

4. Name the factors that affect relative basicities.

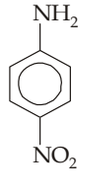
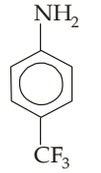
5. Which one is more basic ?

(*a*)  or

I II

(*b*)  or 

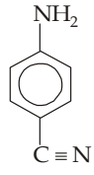
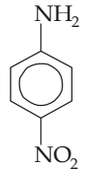
(*c*) $F_3CCH_2NH_2$ or $F_2CHCH_2NH_2$

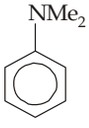
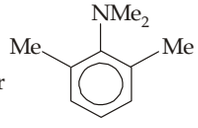
(*d*)  or 

(*e*) Aq. $(CH_3)_2NH$ or Aq. $(CH_3)_3N$

(*f*) $(CH_3)_2NH$ or $(CH_3)_3N$ in gas phase

(*g*) $Me_3CCH_2CH_2NH_2$ or $Me_3N^+CH_2CH_2NH_2$

(*h*)  or 

(*i*)  or 

6. Arrange the following in their decreasing basicity :

(*a*) $CH_3NH^-Na^+$, $C_2H_5NH_2$, CH_3CONH_2 and $[(CH_3)_2CH]_3N$ (*b*) $C_6H_5NH_2$, CH_3NH_2, $(C_6H_5)_2NH$, NH_3 and $(C_6H_5)_3N$

(*c*) $CH_3CH_2NH_2$, $HOCH_2CH_2NH_2$, and $HOCH_2CH_2CH_2NH_2$ (*d*) $CH_3CH = NH$, $CH_3CH_2NH_2$ and CH_3CN

(*e*) $CH_3CH_2CH_2NH_2$, $CH_2 = CHCH_2NH_2$ and $CH \equiv CCH_2NH_2$

(*f*) $C_6H_5CH_2NH_2$, $C_6H_{11}CH_2NH_2$ and p-$NO_2C_6H_4CH_2NH_2$ (*g*) $CH_3CH_2NH_2$, CH_3CONH_2 and $C_6H_5CONH_2$.

7. Arrange the following in decreasing basic strength :

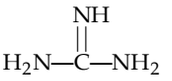
(*a*) $C_6H_5NH_2$, *p*-$NO_2C_6H_4NH_2$, *m*-$NO_2C_6H_4NH_2$, and *p*-$H_3COC_6H_4NH_2$

(*b*) $C_6H_5NH_2$, *o*-$NO_2C_6H_4NH_2$, *m*-$NO_2C_6H_4NH_2$, and *p*-$NO_2C_6H_4NH_2$

(*c*) $C_6H_5NH_2$, *o*-$CH_3OC_6H_4NH_2$, *m*-$CH_3OC_6H_4NH_2$, and *p*-$CH_3OC_6H_4NH_2$

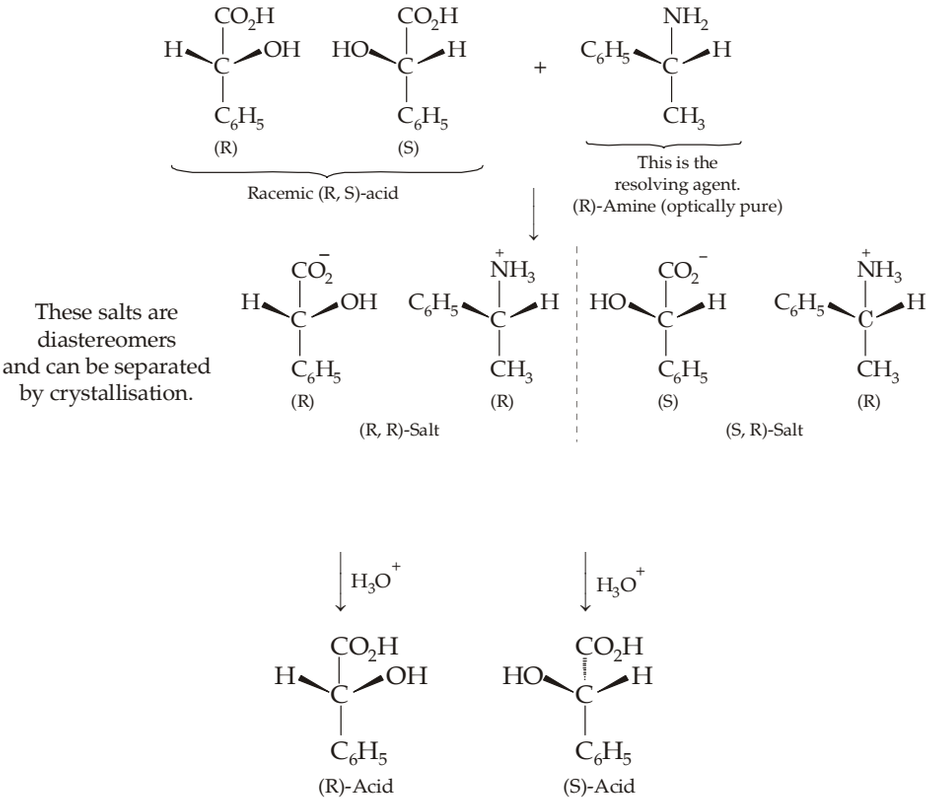
(*d*) $C_6H_5NH_2$, *o*-$CH_3C_6H_4NH_2$, *m*-$CH_3C_6H_4NH_2$, and *p*-$CH_3C_6H_4NH_2$.

8. In terms of *s* character, amino N of guanidine should be more basic, but actually imino N is found to be more basic. Explain.



9. Give the schematic representation involved in separating a mixture of the three water-insoluble liquids : aniline (b.p. 184°C), *n*-butylbenzene (b.p. 183°C), and *n*-valeric acid (b.p. 187°C).

Amines as resolving agents : Basic properties of amines has been applied in resolving (separating) the racemic forms of acidic compounds. Let us illustrate it by showing the resolution of a racemic form of an organic acid with the help of a single enantiomer of an amine, a resolving agent. The two enantiomeric components of the acid are converted into two salts. The two salts are not enantiomers, but diastereomers (the stereocenters of the acid portion of the two salts are enantiomerically related to each other, but the stereocenters of the amine portion are not). The diastereomers have different solubilities and thus can be separated by careful crystallization. The separated salts are then acidified with hydrochloric acid and the enantiomeric acids are obtained from the separate solutions. The amine remains in solution as its hydrochloride salt.



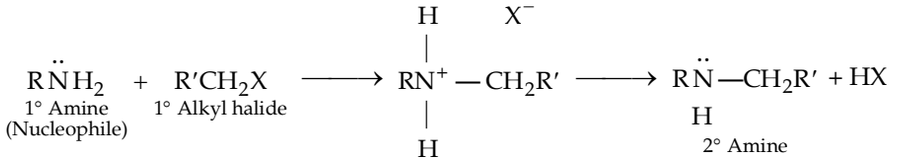
Resolution of the racemic form of an organic acid by the use of an optically active amine. Acidification of the separated diastereomeric salts causes the enantiomeric acids to precipitate (assuming they are insoluble in water) and leaves the resolving agent in solution as its conjugate acid.

EBD_7091

TEST YOUR UNDERSTANDING - 19.10

1. Give the schematic representation involved in the resolution of (±)-2-phenylpropanoic acid using (+)-*sec*-butylamine as the resolving agent.

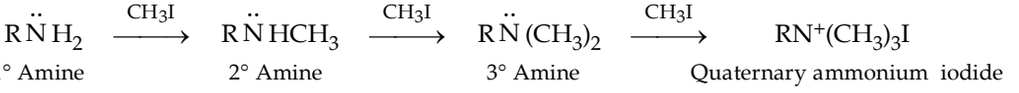
2. **Reaction with alkyl halides (*Alkylation of amines*) :** Like ammonia, an amine (1°, 2° or 3°) can react with an alkyl halide to form next higher class of amine. Here, again it is the presence of electron pair on nitrogen which makes amines to behave as nucleophile and alkyl halides thus undergo nucleophilic substitutions.



1° Amine (Nucleophile) + 1° Alkyl halide → 2° Amine

A second alkylation may follow, converting the secondary amine to a tertiary amine which may be alkylated to give a quaternary ammonium salt.

Because of its high reactivity towards nucleophilic substitution, methyl iodide is the most frequently used alkyl halide to proceed to the quaternary ammonium stage.

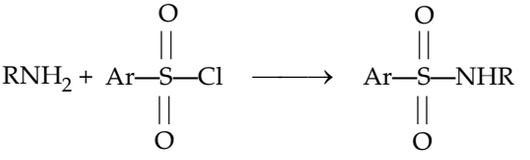


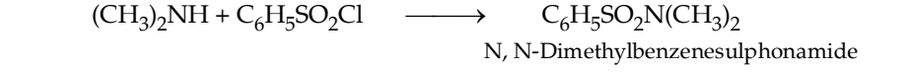
1° Amine → 2° Amine → 3° Amine → Quaternary ammonium iodide

Quaternary ammonium salts are useful in synthetic organic chemistry as phase-transfer catalysts* and in the preparation of alkenes.

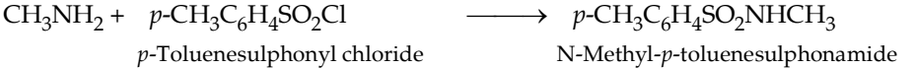
3. **Reaction with acid chlorides :** Like ammonia, amines (1° and 2°) react with acid chlorides of carboxylic acid or of sulphonic acids to form N-substituted amides.





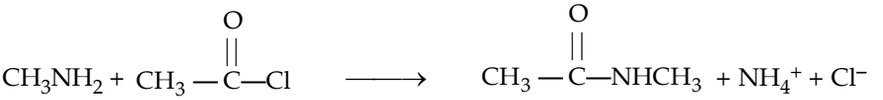


N, N-Dimethylbenzenesulphonamide



p-Toluenesulphonyl chloride (Tosyl chloride) → N-Methyl-*p*-toluenesulphonamide

In these reactions ammonia, 1° amine, or 2° amine serves as a nucleophile and attacks the carbonyl carbon or sulphur and displace chloride ion. Simultaneously, nitrogen loses a proton to a second molecule of ammonia or another base.



* A small amount of a quaternary ammonium salt promotes the transfer of an anion from aqueous solution, where it is highly solvated, to an organic solvent, where it is much less solvated and much more reactive.

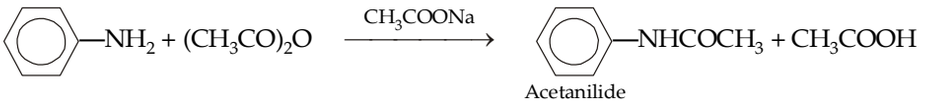
Tertiary amines, although basic and hence nucleophile, do not react with acid chlorides because they cannot lose a proton (to stabilize the product) after attaching themselves to carbon or sulphur. Hence for a reaction of amines with acid chlorides, there are two essential conditions : (*a*) amine should be nucleophilic to attack on the electron-deficient carbonyl C, (*b*) amine should possess a hydrogen atom on the nitrogen atom which is lost as proton to form the stable product (amide).

$$CH_3NH_2 + C_6H_5SO_2Cl \longrightarrow C_6H_5SO_2NHCH_3$$

$$(CH_3)_2NH + CH_3COCl \longrightarrow CH_3CON(CH_3)_2$$

$$(CH_3)_3N + CH_3COCl \text{ or } C_6H_5SO_2Cl \longrightarrow \text{No reaction}$$

Acetylation is generally carried out using acetic anhydride rather than acetyl chloride. For example,



Acetanilide

Schotten-Baumann reaction. Reaction of acid chloride or sulphonyl chloride of aromatic carboxylic acids or aromatic sulphonic acid with an amine (1° or 2° ; alphatic or aromatic) in presence of aqueous sodium hydroxide or pyridine to form substituted amides is known as Schotten-Baumann reaction.

$$C_6H_5NH_2 + C_6H_5COCl \xrightarrow{\text{pyridine}} C_6H_5CONHC_6H_5$$

Benzanilide

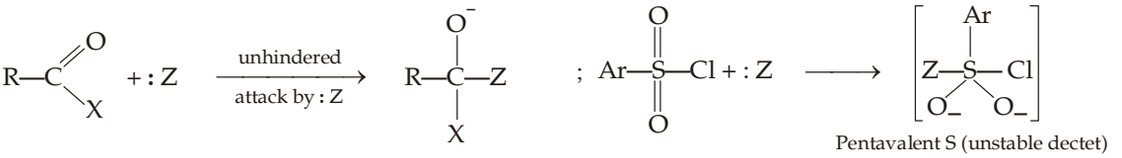
$$(n\text{-}C_3H_7)_2NH + C_6H_5SO_2Cl \xrightarrow{\text{NaOH}} C_6H_5SO_2N(C_3H_7\text{-}n)_2$$

N, N-Di-*n*-Propylbenzenesulphonamide

$$C_2H_5NHCH_3 + p\text{-}CH_3C_6H_4SO_2Cl \xrightarrow{\text{aq. NaOH}} p\text{-}CH_3.C_6H_4SO_2N(CH_3)C_2H_5$$

p-Toluene sulphonylchloride

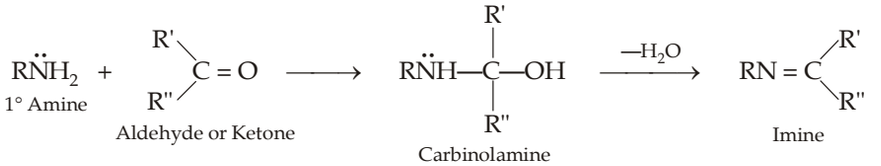
Carboxamides as well as sulphonamides are easily hydrolysed to parent acid and amine. However, sulphonamides are hydrolysed more slowly than carboxamides (amides of carboxylic acids). Nucleophilic attack on a trigonal acyl carbon is relatively unhindered while that on a tetrahedral sulphonyl sulphur is relatively hindered. Moreover, the intermediate in the former is tetrahedral C, having octet of electrons, while that in the latter intermediate is a pentavalent sulphur, having dectet of electrons (a less stable system).



Tetrahedral C (stable octet)

Pentavalent S (unstable dectet)

4. **Reaction with aldehydes and ketones :** Primary amines add (as nucleophiles) to the carbonyl group of an aldehyde or a ketone to form *carbinolamines*, which then dehydrate to form imines (also known as **Schiff's bases**) as the final product.



1° Amine — Aldehyde or Ketone — Carbinolamine — Imine

$$CH_3NH_2 + C_6H_5CHO \longrightarrow CH_3N = CHC_6H_5$$

N-Benzylidenemethylamine

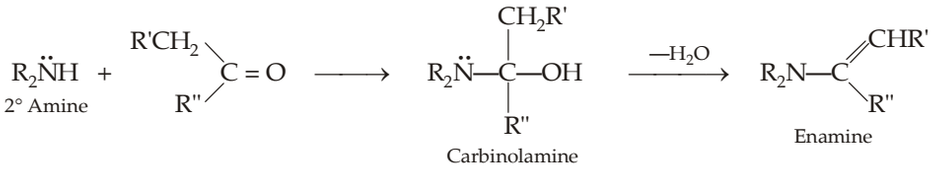
$$(CH_3)_2CHCH_2NH_2 + \text{C}_6\text{H}_{10}\text{O} \longrightarrow \text{C}_6\text{H}_{10}\text{=NCH}_2\text{CH(CH}_3\text{)}_2$$

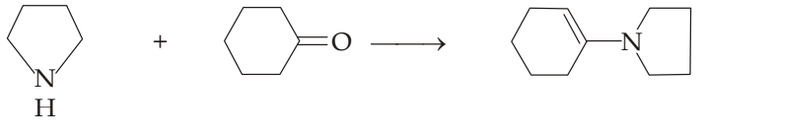
N-Cyclohexylideneisobutylamine

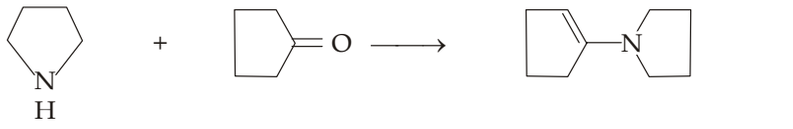
Both the addition and elimination phase of the reaction are accelerated by acid catalysis.

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Secondary amines add to aldehydes and ketones to form carbinolamines which can dehydrate to a stable product leading to a carbon-carbon double bond (difference from 1° amines which form product having carbon-nitrogen double bond).

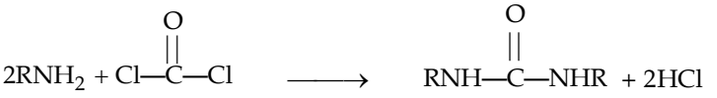






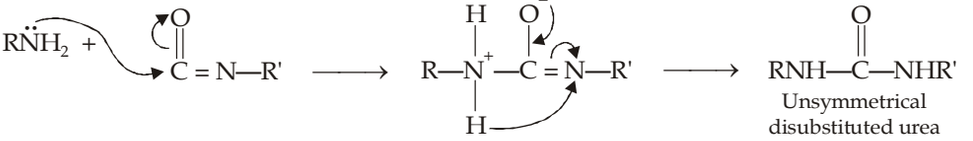
This reaction is not given by *tert*-amines.

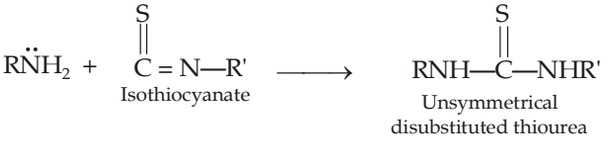
5. **Reaction with carbonyl chloride** to form *sym*-disubstituted urea.



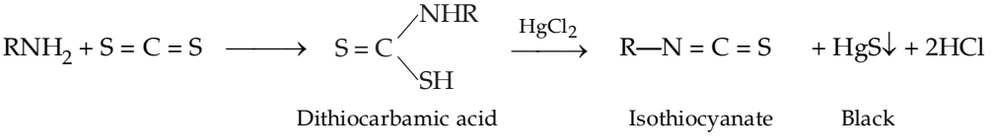
This reaction is given only by 1°, and **not by 2° and 3° amines**.

6. **Reaction with isocyanates and isothiocyanates** to form disubstituted urea and thiourea respectively.

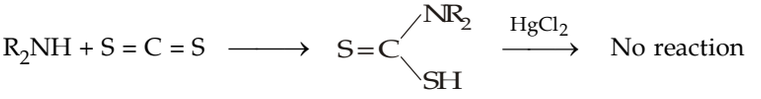




7. **Reaction with carbon disulphide.** Primary amines when warmed with carbon disulphide form a **dithiocarbamic acid** which is decomposed by mercuric chloride to give alkyl isothiocyanates, having mustard oil smell, along with black precipitate of mercuric sulphide. This reaction, known as **Hofmann mustard oil reaction**, is used as a test for 1° amines.



Secondary amines also react with CS_2 to form dithiocarbamic acids, but the latter do not react with mercuric chloride (difference from 1° amines).



Tertiary amines do not react with carbon disulphide.

8. Carbylamine reaction of 1° amines.

$$RNH_2 + CHCl_3 + 3KOH \longrightarrow \underset{\text{An isocyanide (foul smelling)}}{R{-}N^+ \equiv C^- :} + 3\,KCl + 3H_2O$$

Recall that here the nucleophile RNH_2 attacks the electrophilic intermediate (dichlorocarbene, $:CCl_2$) formed by the action of a base on $CHCl_3$.

$$HCCl_3 \xrightarrow{OH^-} :CCl_3^- \xrightarrow{-Cl^-} \underset{\text{Dichlorocarbene}}{:CCl_2}$$

Since carbylamines have unpleasant smell which can be easily detected, the reaction is used to **identify primary amines**.

TEST YOUR UNDERSTANDING - 19.11

1. Give the structures for the products of the reaction of the following :

(*a*) $(CH_3)_2NH + C_6H_5COCl$

(*b*) $C_2H_5NH_2$ + Succinic anhydride

(*c*) $C_6H_5NHCH_3 + C_6H_5COOC_2H_5$

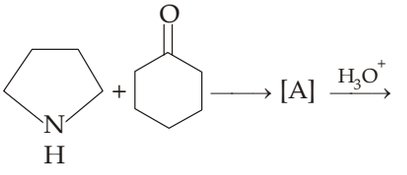
(*d*) $(CH_3)_2NH + C_6H_5SO_2Cl$

(*e*) $C_6H_5CH_2NH_2 + HCOOH \xrightarrow{\text{heat}}$

(*f*) $C_6H_5NH_2 + C_6H_5CHO$.

2. Complete the following :

(*a*) $CH_3COCH_2CH_3 + (CH_3)_2NH$

(*b*) 

9. Reaction with nitrous acid. Nitrous acid (HONO) is a weak, unstable acid. It is always prepared *in situ*, usually by treating sodium nitrite with an aqueous solution of a strong acid.

$$NaNO_2(aq) + HCl(aq) \longrightarrow NaCl(aq) + HONO(aq)$$

$$2NaNO_2(aq) + H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + 2HONO(aq)$$

Nitrous acid reacts with all classes of amines, although different product is obtained from different class of amines.

Reaction of nitrous acid with all amines (1°, 2°, or 3°, aliphatic, or aromatic) involves electrophilic attack by nitrosyl cation, NO^+ followed by displacement of H^+. This attack occurs at position of highest electron density which is N atom in 1° and 2° amines, and *para*- or *ortho*-carbon atom of the highly reactive ring in case of aromatic 3° amines.

Formation of nitrosyl cation by the reaction of $NaNO_2$ with HCl

$$\underset{\text{Nitrite ion (from } NaNO_2)}{{}^-O{-}N = O} \xrightarrow{H^+} \underset{\text{Nitrous acid}}{HO{-}N = O} \xrightarrow{H^+} \underset{\text{Protonated nitrous acid}}{HO^+(H){-}N = O} \longrightarrow {}^+N = O + H_2O$$

$$\downarrow Cl^-$$

$$H_2O + Cl{-}N = O \longrightarrow {}^+N = O + Cl^-$$

(better leaving group) — Nitrosyl chloride

Primary aromatic amines react with nitrous acid to form diazonium salts. This is one of the most important reactions in organic chemistry because the arenediazonium salts, although unstable, are far more stable than aliphatic diazonium salts. They do not decompose at an appreciable rate in solution at temperature below 5°C.

$$\underset{\text{1° Aromatic amine}}{Ar{-}NH_2} + NaNO_2 + 2HX \longrightarrow \underset{\text{Arenediazonium salt (stable below 5°C)}}{Ar{-}N^+ \equiv N : X^-} + NaX + 2H_2O$$

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Details of preparation and synthetic importance of aromatic diazonium salts will be discussed in the next chapter.

Primary aliphatic amines also react with nitrous acid to yield aliphatic diazonium salts. However, aliphatic diazonium salts are quite unstable and decompose spontaneously, even at low temperatures, by losing nitrogen to form carbocations (hence the reaction is commonly known as **deamination**). The carbocations, in turn, produce a mixture of alkenes, alcohols, and alkyl halides.

$$CH_3CH_2CH_2NH_2 \xrightarrow[HCl]{HONO} [CH_3CH_2CH_2N_2^+Cl^-] \longrightarrow CH_3CH_2CH_2^+ + \mathbf{N_2} + Cl^-$$

$$CH_3CH=CH_2 \xleftarrow{-H^+} \mathbf{CH_3CH_2CH_2^+} \longrightarrow CH_3^+CHCH_3 \xrightarrow{-H^+} CH_3CH=CH_2$$

Propene

$\mathbf{CH_3CH_2CH_2^+} \xrightarrow{H_2O,\ or\ Cl^-}$ $CH_3CH_2CH_2OH$ (1-Propanol) or $CH_3CH_2CH_2Cl$ (1-Chloropropane)

$CH_3^+CHCH_3 \xrightarrow{H_2O,\ or\ Cl^-}$ $CH_3CHOHCH_3$ (2-Propanol) or $CH_3CHClCH_3$ (2-Chloropropane)

Since the reaction yields a complex mixture of products, it is of little synthetic importance. However, since the evolution of nitrogen is quantitative, diazotisation of 1° aliphatic amines is used in detecting the presence of —NH_2 group, especially in amino acids and proteins.

Secondary amines, both aliphatic and aromatic, react with nitrous acid to yield N-nitrosoamines which useually separate from the reaction mixture as oily yellow liquids.

$$(CH_3)_2NH + HONO \longrightarrow (CH_3)_2N—N=O$$

Dimethylamine — N-Nitrosodimethylamine

$$C_6H_5NHCH_3 + HONO \longrightarrow C_6H_5N(CH_3)N=O$$

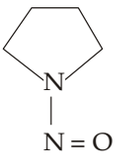
N-Methylaniline — N-Nitroso-N-methylaniline

Nitrosamines are easily hydrolysed by dil. HCl back to form 2° amines. An important property of nitrosamines is their reaction with phenol and conc. H_2SO_4 to form green coloured solution which changes to deep blue on adding aq. NaOH (**Libermann's nitroso reaction**, used as a test for 2° amines).

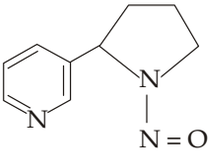
N-Nitrosoamines are cancer-causing agents (**carcenogens**). We encounter several nitrosamines in the environment, *e.g.*

$(CH_3)_2NN=O$

N-Nitrosodimethylamine
(formed during tanning of leather; also found in beer and herbicides)



N-Nitrosopyrrolidine
(formed when bacon, cured with $NaNO_2$, is fried)

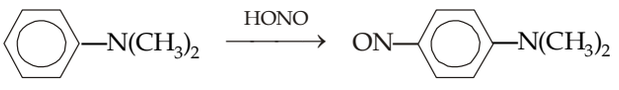


N-Nitrosonornicotine
(present in tobacco smoke)

Nirosamines are probably also synthesized within our body. Enzyme-catalyzed reduction of NO_3^- gives NO_2^- which combines with amines present in the body to form N-nitrosamines. In the human body, HONO is also formed by the action of gastric HCl on nitrites ingested in foods ; HONO then can react with 2° amino group to form N- nitrosamine.

Aliphatic tertiary amines form R_3N^+—N = O type of compounds which do not have any amino H, hence stable at low temperature. These compounds are of little importance.

Tertiary aromatic amines undergo ring substitution almost exclusively at the para position (electrophilic aromatic substitution).



p-Nitroso-N, N-dimethylaniline

Since nitrosonium ion, NO^+ (produced *via* H_2O^+—NO or NOCl) is very weak electrophile, nitrosation ordinarily occurs only in very strongly activated aromatic rings, *viz.* rings bearing dialkylamino (—NR_2) or hydroxy (—OH) group.

TEST YOUR UNDERSTANDING - 19.12

1. Give the various possible products obtained by the reaction of nitrous acid on :

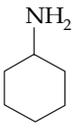
(*a*) 2, 2-dimethylpropylamine, (*b*) 1, 1-dimethylpropylamine, and (*c*) benzylamine.

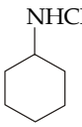
2. Write down the structures of the alcohols produced by the reaction of nitrous acid on *sec*-butylamine.

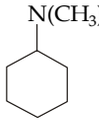
3. N-Nitrosamines are stabilized by electron delocalization. Write the two most stable resonance forms of N-nitrosodimethylamine, $(CH_3)_2NO$

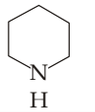
4. N-Methylaniline and N, N-dimethylaniline give different products with nitrous acid. Comment.

5. Give the structure of the products obtained by the reaction of nitrous acid on the following.

(*a*) 

(*b*) 

(*c*) 

(*d*) 

10. Oxidation of amines. Amines are usually oxidized at N, rather than at C in RCH_2OH. Primary and secondary aliphatic amines are although oxidisable, in most cases useful products are not obtained. Complicated side reactions often occur, causing the formation of complex mixtures.

(*a*) $CH_3CH_2NH_2 \xrightarrow{KMnO_4} \underset{\text{Aldimine}}{CH_3CH = NH} \xrightarrow{H^+} CH_3CHO$

$(CH_3)_2CHNH_2 \xrightarrow[\text{Caro's acid}]{H_2SO_5} \underset{\text{Ketoxime}}{(CH_3)_2C = NOH}$

$(CH_3)_3CNH_2 \xrightarrow{H_2SO_5} (CH_3)_3CN = O$

(*b*) $\underset{\text{Dimethylamine}}{(CH_3)_2NH} \xrightarrow{H_2SO_5} \underset{\text{Dimethylhydroxylamine}}{(CH_3)_2NOH}$

$2(CH_3)_2NH \xrightarrow{KMnO_4} \underset{\text{Tetramethylhydrazine}}{(CH_3)_2N{-}N(CH_3)_2}$

Tertiary amines can be oxidized quantitatively by H_2O_2 or a peroxy acid to tetiary amine oxides, $R_3N^+{-}O^-$, a dipolar ion or Zwitterion.

$$R_3N: \xrightarrow{H_2O_2 \text{ or } RCOOOH} R_3N^+{-}\ddot{O}:^-$$

Tertiary amine oxides containing a β-hydrogen atom, on heating, undergo a useful elimination reaction to form alkenes (**Cope reaction**).

Cope elimination. Tertiary amine oxides, prepared by treating tertiary amines with hydrogen peroxide, containing β-hydrogen atom, when heated undergo the elimination of a dialkylhydroxylamine and form alkene.

$$RCH_2CH_2N(CH_3)_2 \xrightarrow{H_2O_2} RCH_2CH_2\overset{\displaystyle :\ddot{O}:^-}{\overset{|}{\underset{\displaystyle CH_3}{\overset{|}{N^+}}}}{-}CH_3 \xrightarrow{150^\circ C} RCH = CH_2 + \underset{\text{N, N-Dimethylhydroxylamine}}{\overset{\displaystyle OH}{\overset{|}{N(CH_3)_2}}}$$

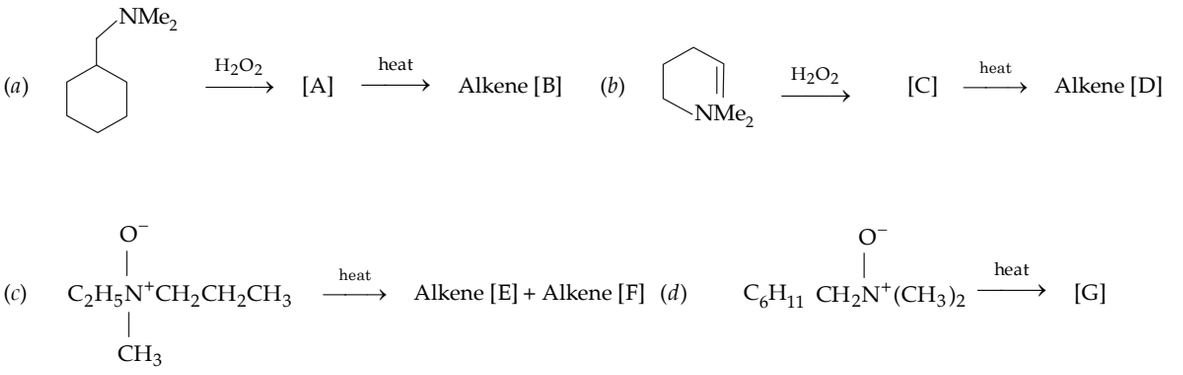
The cope elimination is a *syn* elimination and proceeds through a cyclic transition state.

$$R{-}\overset{\displaystyle H}{\overset{|}{C}}{-}CH_2{-}\overset{\displaystyle O^-}{\overset{|}{\underset{\displaystyle CH_3}{\overset{|}{N^+}}}}{-}CH_3 \xrightarrow{\text{heat}} R{-}\overset{\displaystyle H\text{- - - - - -}O^-}{\overset{|}{\underset{\displaystyle H}{C}}}{-}CH_2{-}\overset{\displaystyle |}{\underset{\displaystyle CH_3}{N^+}}{-}CH_3 \longrightarrow R{-}CH = CH_2 + HON(CH_3)_2$$

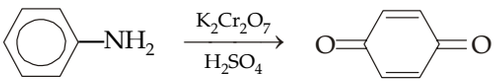
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TEST YOUR UNDERSTANDING - 19.13

1. Identify the compounds [A] to [G] in the following reactions :



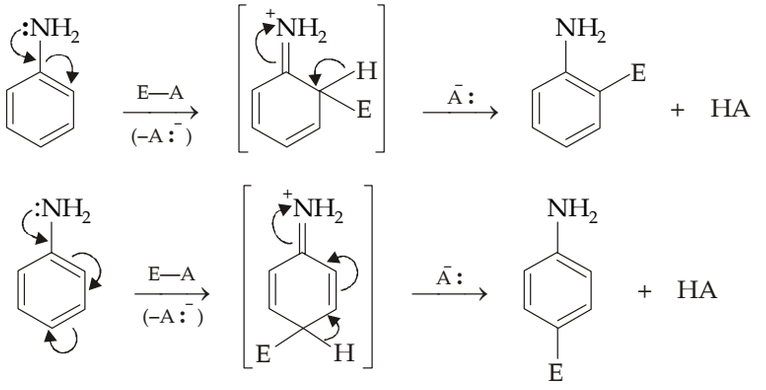
Arylamines are very easily oxidized by a variety of reagents, including the oxygen in air. Further, here oxidation is not confined to the amino group but also occurs in the ring (the electron-releasing ability of the —NH_2 group makes the ring electron rich, and hence especially susceptible to oxidation). The oxidation of other oxidizable functional group on an aromatic ring cannot be usually accomplished when an amino group is present on the ring, because ring is oxidized first.



Aniline *p*-Benzoquinone

19.4.2 Ring Substitution in Aromatic Compounds

In the preceding reactions No. 1 to 10, the amine acts as a nucleophile by donating its electron pair to an electrophilic reagent. However, in ring substitution, electron pair on nitrogen makes *ortho* and *para* carbon atoms of the ring nucleophilic.



Due to presence of electron pair on nitrogen, the —NH_2, —NHR or —NR_2 group acts as an activating group and an *o*- and *p*-director in electrophilic aromatic ring substitution. The important examples of electrophilic substitution in aromatic ring will be discussed in aniline.

19.4.3 Reactions of Quaternary Ammonium Salts

(*i*) *Formation of quaternary (4°) ammonium hydroxides*. When an aqueous solution of a 4° ammonium halide is treated with silver oxide, silver halide precipitates out, and a solution of quaternary ammonium hydroxide is formed.

$$\underset{\text{4° Ammonium halide}}{2R_4N^+X^-} + Ag_2O + H_2O \longrightarrow \underset{\substack{\text{4° Ammonium hydroxide}\\ \text{(a very strong base, like NaOH)}}}{2R_4N^+OH^-} + 2AgX\downarrow$$

(*ii*) *Hofmann elimination*. When a quaternary hydroxide is heated strongly (to 125°C or higher), it decomposes to form an alkene and a tertiary amine.

$$CH_3CHCH_2CH_3 \xrightarrow{\text{heat}} \underset{\text{1-Butene(95\%)}}{CH_2=CHCH_2CH_3} + (CH_3)_3N + H_2O$$
$$\quad\quad\quad

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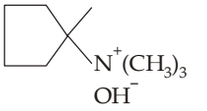
TEST YOUR UNDERSTANDING - 19.14

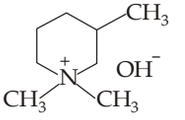
1. Write down the structure of the various alkenes obtained :

(*a*) during dehydrohalogenation of *n*-$C_3H_7CHBrCH_3$, and

(*b*) Hofmann elimination of *n*-$C_3H_7CH(CH_3)N^+Me_3OH^-$.

2. Give the structure of the major alkene formed during heating following salts :

(*a*) $(CH_3)_3CCH_2\underset{\displaystyle N^+(CH_3)_3\,OH^-}{\underset{|}{C}}(CH_3)_2$ (*b*) $CH_3CH_2\,\underset{OH^-}{N^+}\,(CH_3)_2CH_2CH_2CH_3$ (*c*) 

(*d*) $CH_3CH_2\underset{\displaystyle S^+(CH_3)_2}{\underset{|}{C}}HCH_3\;OC_2H_5^-$ (*e*)  (*f*) $C_6H_{11}N^+Me_2(CH_2CH_2CH_3)OH^-$.

3. Write down the structures of the alkenes formed on E2 elimination from

(*a*) 1-ethyl-2-methylpropyltrimethylammonium ion. (*b*) diethyldi-*n*-propylammonium ion

(*c*) dimethylethyl-2-chloroethylammonium ion (*d*) dimethylethyl-*n*-propylammonium ion.

Mention the major product, if any, in each case.

4. Predict the structures of the main products (A) and (B) in the following reactions :

(*a*) $CH_3CH_2-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-S^+(CH_3)_2\;OC_2H_5^- \xrightarrow[\text{ethanol}]{\text{heat in}} A$

Dimethyl-*tert*-pentylsulphonium ethoxide

(*b*) $CH_3CH_2-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-S^+(CH_3)_2I^- \xrightarrow[\text{ethanol}]{\text{heat in}} B$

5. Predict and account for the product of Hofmann elimination of

(*a*) $PhCH_2CH_2\underset{\displaystyle CH_2CH_3}{\underset{|}{N^+}}(CH_3)_2OH^-$ (*b*) $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{N^+}}}}-C(CH_3)_3OH^-$.

19.5 Analysis of Amines

Amines are characterized by their basicity. A water-insoluble compound that dissolves in cold dil. HCl, or a water-soluble compound (not a salt) whose aqueous solution turns red litmus blue must be an amine. The nature of amine (primary, secondary, or tertiary) can best be distinguished from each other by the **Hinsberg test** which is based upon the formation of sulphonamide.

1. **The Hinsberg test.** The amine is shaken with benzenesulphonyl chloride (also known as **Hinsberg reagent**) in the presence of aqueous potassium hydroxide. Each type of amine gives a different set of visible results.

(*i*) A clear solution is obtained in case of primary amines.

(*ii*) A precipitate is obtained in case of secondary amines.

(*iii*) No apparent change is observed in case of water-insoluble tertiary amine.

When the above mixture (amine + $C_6H_5SO_2Cl$ + aq. KOH) is acidified with HCl, again different set of results is observed in the three types of amines.

(*a*) A precipitate is obtained in case of primary amine.

(*b*) No change is observed in case of secondary amine.

(*c*) A clear solution is obtained in case of tertiary amine.

In short,

$$1° \text{ Amine} + C_6H_5SO_2Cl \xrightarrow{\text{aq. KOH}} \text{Clear solution} \xrightarrow{\text{HCl}} \text{Precipitate}$$

$$2° \text{ Amine} + C_6H_5SO_2Cl \xrightarrow{\text{aq. KOH}} \text{Precipitate} \xrightarrow{\text{HCl}} \text{No change}$$

$$\underset{\text{(water insoluble)}}{3° \text{ Amine}} + C_6H_5SO_2Cl \xrightarrow{\text{aq. KOH}} \underset{\text{(water insoluble)}}{3° \text{ Amine}} \xrightarrow{\text{HCl}} \text{Water soluble clear salt sol.}$$

Chemistry of the Hinsberg test.

$$\underset{1° \textbf{ Amine}}{RNH_2} + C_6H_5SO_2Cl \xrightarrow{OH^-} \underset{\substack{\text{N-Substituted sulphonamide}\\ \text{(acidic H on N)}}}{[C_6H_5SO_2NHR]} \xrightarrow{KOH} \underset{\text{Clear solution}}{C_6H_5SO_2N^-RK^+} \xrightarrow{H^+} \underset{\text{Precipitate}}{C_6H_5SO_2NHR}$$

$$\underset{2° \textbf{ Amine}}{R_2NH} + C_6H_5SO_2Cl \longrightarrow \underset{\substack{\text{N, N-Disubstituted}\\ \text{sulphonamide}\\ \text{(no acidic H)}}}{C_6H_5SO_2NR_2} \downarrow \xrightarrow{KOH} \text{No reaction} \xrightarrow[\text{room temp.}]{H^+} \text{No reaction}$$

Remember that N, N-disubstituted sulphonamides are hydrolysed to give parent amine when heated with an acid.

$$C_6H_5SO_2NR_2 \xrightarrow[(ii)\ OH^-]{(i)\ H_3O^+,\ \text{heat}} C_6H_5SO_2O^- + R_2NH$$

$$\underset{3° \textbf{ Amine}}{R_3N} + \underset{\text{Insoluble}}{C_6H_5SO_2Cl} \xrightarrow{OH^-} R_3N \xrightarrow{HCl} \underset{\text{Clear solution}}{R_3N^+Cl^-}$$

2. Primary amines can also be detected by the following tests.

(*a*) **Carbylamine test.** Unpleasant smelling carbylamine is formed when a 1° amine (aliphatic or aromatic) is treated with alkaline chloroform solution.

(*b*) **Mustard oil reaction.** Primary amines (aliphatic or aromatic) form isothiocyanates having mustard oil like smell.

(*c*) **Reaction with nitrous acid :**

(*i*) *Aliphatic primary amines* evolve quantitative amount of N_2 and form alcohols, when treated with nitrous acid.

(*ii*) *Primary aromatic amines*, when treated with nitrous acid at low temperatures (0–5°C), are converted into **diazonium salts** which yield highly coloured azo compounds upon treatment with β-naphthol (a phenol) in presence of sodium hydroxide.

19.6 Separation of Mixture of Amines

As described earlier, Hofmann ammonolysis of alkyl halide and alcohol, gives a mixture of 1°, 2° and 3° amines along with quaternary ammonium salt. The four can be separated easily. First of all, the mixture is distilled over KOH when all the three types of amines distil over leaving behind quaternary ammonium salt as residue.

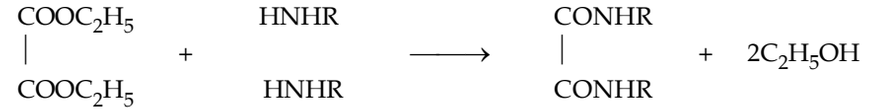
$$RNH_2 + R_2NH + R_3N + R_4N^+I^- \xrightarrow[\text{distil}]{\text{KOH}} \begin{cases} \longrightarrow RNH_2 + R_2NH + R_3N \text{ (Distillate)} \\ \longrightarrow R_3N^+OH^- \text{ (Residue)} \end{cases}$$

The mixture of the three types of amines collected as distillate can be separated into the individual type by the following methods.

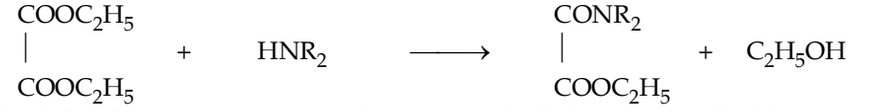
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1. **Fractional distillation.** The three types of amines have sufficiently different boiling points (3° > 2° > 1°), these can separated by fractional distillation when 1° amine distils over first, followed by 2° and then 3° in the last. This method is widely used for industrial purposes.

2. **Hofmann method.** The mixture is treated with diethyl oxalate, also known as **Hofmann reagent**, when 1° amine forms oxamide (solid), 2° amine forms oxamic ester (liquid), while the 3° amine does not react.



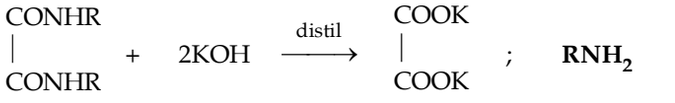
Diethyl oxalate 1° Amine (2 moles) N, N′-Dialkyloxamide (**solid**)



Diethyl oxalate 2° Amine (1 mole) Dialkyloxamic ester (**liquid**)

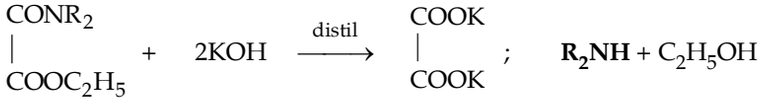
The mixture containing dialkyloxamide (solid), dialkyloxamic ester, and unreacted 3° amine is filtered.

Recovery of 1° amine. The solid oxamide is distilled over potassium hydroxide, when primary amine distils over leaving potassium oxalate (a salt) as residue.



(Residue) (Distillate)

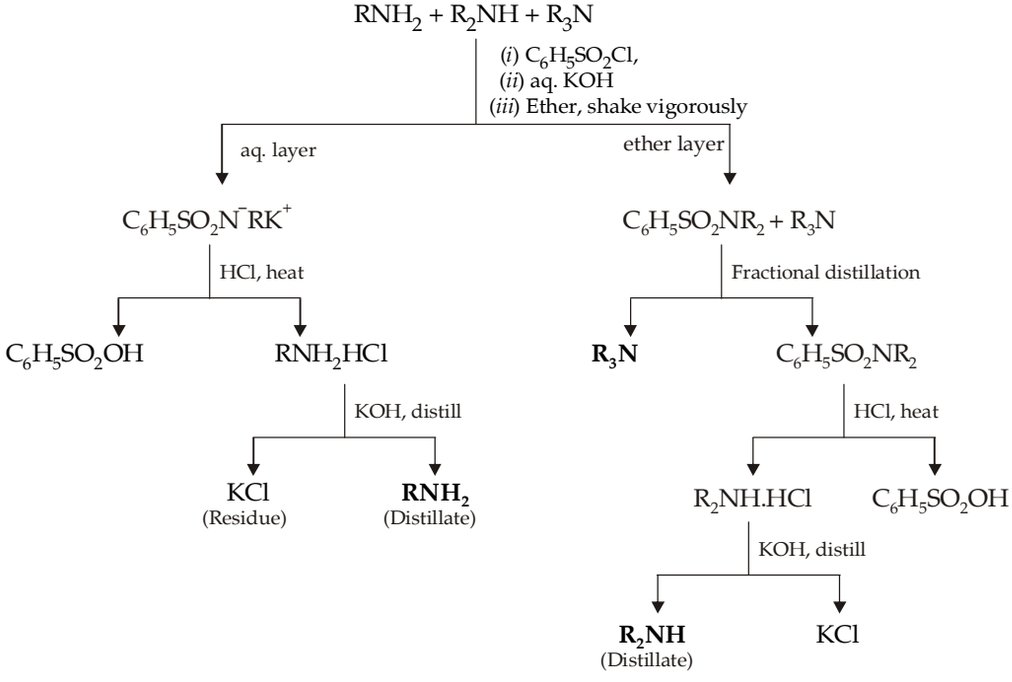
Recovery of 2° and 3° amine. The filtrate containing oxamic ester and 3° amine is fractionally distilled when **tertiary amine** having low boiling point distils first. Secondary amine is then recovered from the oxamic ester by distilling over potassium hydroxide.



Residue Distillate

3. **Hinsberg method.** This method is based upon the difference in solubility of benzensulphonamides, formed by the reaction of 1° and 2° amines with benzenesulphonyl chloride, also known as **Hinsberg reagent**, in aqueous KOH and ether (recall that 3° amines do not react with the reagent).

Details of chemistry of the 1° and 2° amines with the reagent has already been discussed in Hinsberg's test. Hence, here only an outline involved in the separation of the three amines is given.



TEST YOUR UNDERSTANDING - 19.15

1. What are limitations of Hinsberg test ?

2. Distinguish among RNH_2, R_2NH and R_3N using succinic anhydride as the reagent.

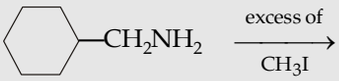
19.7 Illustrative Examples

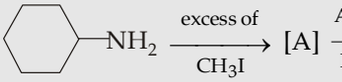
Example 1 :

Identify the bracketed compounds in the following reactions :

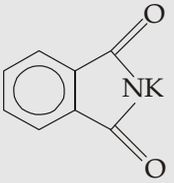
(i) $n\text{-}C_3H_7COOH \xrightarrow{LiAlH_4} [A] \xrightarrow{PBr_3} [B] \xrightarrow[(ii)\ CuI]{(i)\ Li} [C] \xrightarrow{n\text{–}C_3H_7COCl} [D] \xrightarrow[H_2/Ni]{NH_3} [E]$

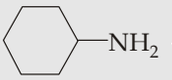
(ii) $C_6H_5SO_2Cl \xrightarrow{CH_3NH_2} [A] \xrightarrow{NaOH} [B] \xrightarrow{CH_3Br} [C] \xrightarrow{H_3O^+} [D] + [E]$

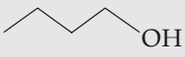
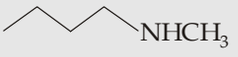
(iii)  $\xrightarrow[CH_3I]{\text{excess of}}$ [A] $\xrightarrow[H_2O]{Ag_2O}$ [B]

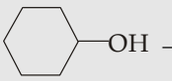
(iv)  $\xrightarrow[CH_3I]{\text{excess of}}$ [A] $\xrightarrow[H_2O]{Ag_2O}$ [B] $\xrightarrow{\text{heat}}$ [C] + $(CH_3)_3N$ $\xrightarrow{\text{heat}}$ [C] + [D]

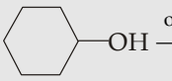
(v) $C_6H_5NH_2 \xrightarrow{2CH_3I} [A] \xrightarrow{HNO_2} [B] \xrightarrow{NaOH} [C] + [D]$

(vi)  $\xrightarrow{Br(CH_2)_2COO^-}$ [A] $\xrightarrow[(ii)\ H^+]{(i)\ OH^-}$ [B]

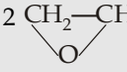
(vii)  $\xrightarrow[HCl]{NaNO_2}$ [A] + [B] + [C]

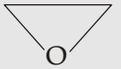
(viii)  $\xrightarrow{[A]}$ [B] $\xrightarrow{CH_3NH_2}$ [C] $\xrightarrow{NaBH_3CN}$ 

(ix)  $\xrightarrow{PBr_3}$ [A] $\xrightarrow{NH_3}$ [B] $\xrightarrow{oxid.}$ [C] $\xrightarrow{NH_3}$ [D] $\xrightarrow{H_2/Ni}$ [E]

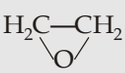
(x)  $\xrightarrow{\text{oxidation}}$ [A] $\xrightarrow{NH_3}$ [B] $\xrightarrow{H_2/Ni}$ [C]

(xi) $HOCH_2CH_2CH_2OH \xrightarrow{1\,eq.\,SOCl_2} [A] \xrightarrow{KCN} [B] \xrightarrow{SOCl_2} [C] \xrightarrow{H_2/Ni} [D] \xrightarrow{NaOH} [E]$

(xii) 2  $\xrightarrow{NH_3}$ [A] $\xrightarrow{P_2O_5}$ [B]

(xiii)  + $(CH_3)_3N \longrightarrow$ [A] $\xrightarrow{H_2O}$ [B] $\xrightarrow[\text{(a strong base)}]{CH_3COCl}$ [C]

(xiv) $(CH_3)_2CHCHO \xrightarrow[\text{base}]{CH_2O}$ [A] $\xrightarrow[H^+]{CN^-}$ [B] $\xrightarrow[H^+]{H_2O}$ [C] $\longrightarrow$ [D] $\xrightarrow{H_2NCH_2CH_2COOH}$ [E]

(xv)  $\xrightarrow{(C_2H_5)_2NH}$ [A] $\xrightarrow{p\text{-}O_2NC_6H_4COCl}$ [B] $\xrightarrow{H_2,\,Ni}$ [C]

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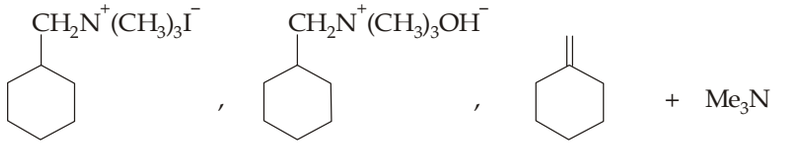
Solution :

(*i*) $n\text{-}C_3H_7CH_2OH$, $n\text{-}C_3H_7CH_2Br$, $(n\text{-}C_3H_7CH_2)_2CuLi$, $n\text{-}C_3H_7CH_2COC_3H_7\text{-}n$, $n\text{-}C_3H_7CH_2\underset{\displaystyle NH_2}{\underset{|}{C}}HC_3H_7\text{-}n$

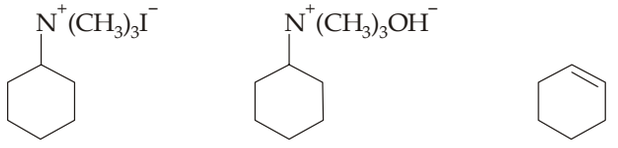
[A] [B] [C] [D] [E]

(*ii*) $C_6H_5SO_2NHCH_3$, $C_6H_5SO_2N^-CH_3$, $C_6H_5SO_2N(CH_3)_2$, $C_6H_5SO_2OH + (CH_3)_2NH_2^+$

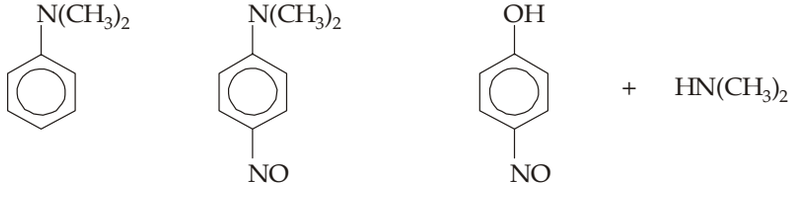
[A] [B] [C] [D] [E]

(*iii*) 

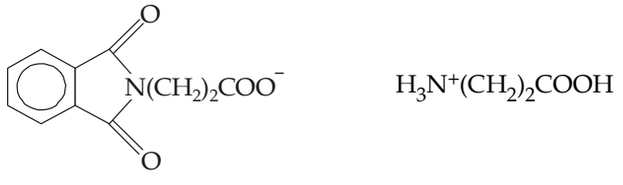
[A] [B] [C] [D]

(*iv*) 

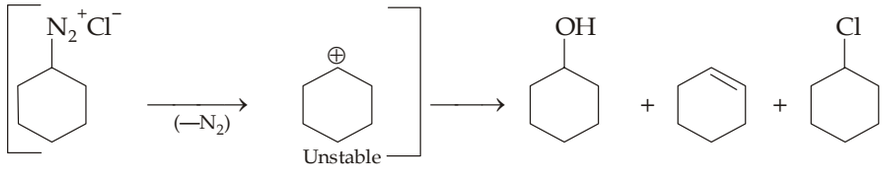
[A] [B] [C]

(*v*) 

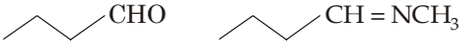
[A] [B] [C] [D]

(*vi*) 

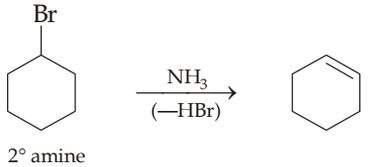
[A] [B]

(*vii*) 

[A] [B] [C]

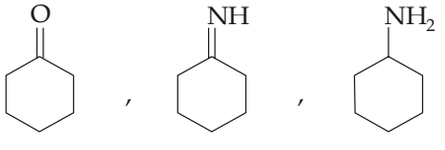
(*viii*) PCC (Pyridinium chlorochromate) 

[A] [B] [C]

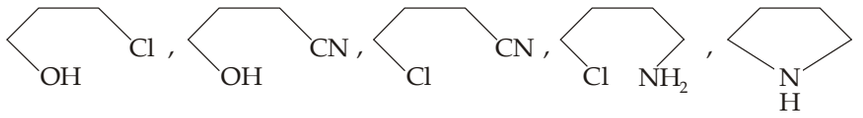
(*ix*) 

2° amine

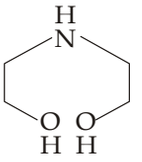
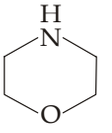
A B

(*x*) 

A B C

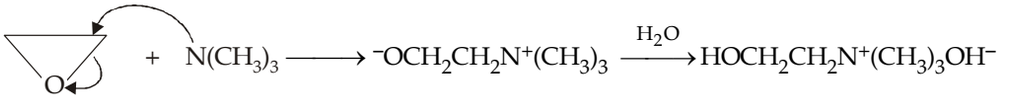
(*xi*) 

[A] [B] [C] [D] [E]

(*xii*) $HOCH_2CH_2NHCH_2CH_2OH$ or  ; 

Morpholine

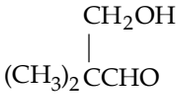
[A] [B]

(*xiii*) 

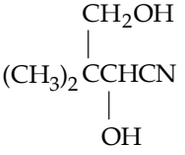
[A] [B]



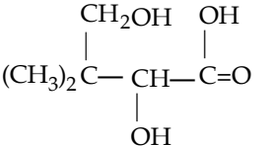
[C]

(*xiv*) 

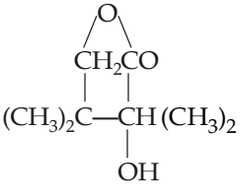
[A]



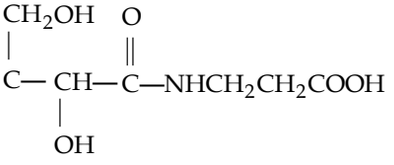
[B]



γ-Hydroxy acid [C]

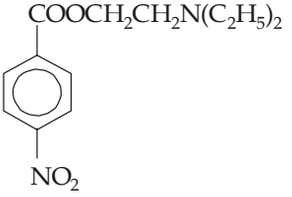


γ-Lactone [D]

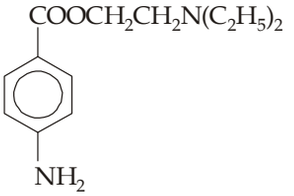


[E]

(*xv*) $HOCH_2CH_2N(C_2H_5)_2$



[B]



[A] [C]

Example 2 :

Write down the structure of the amine in the following two cases :

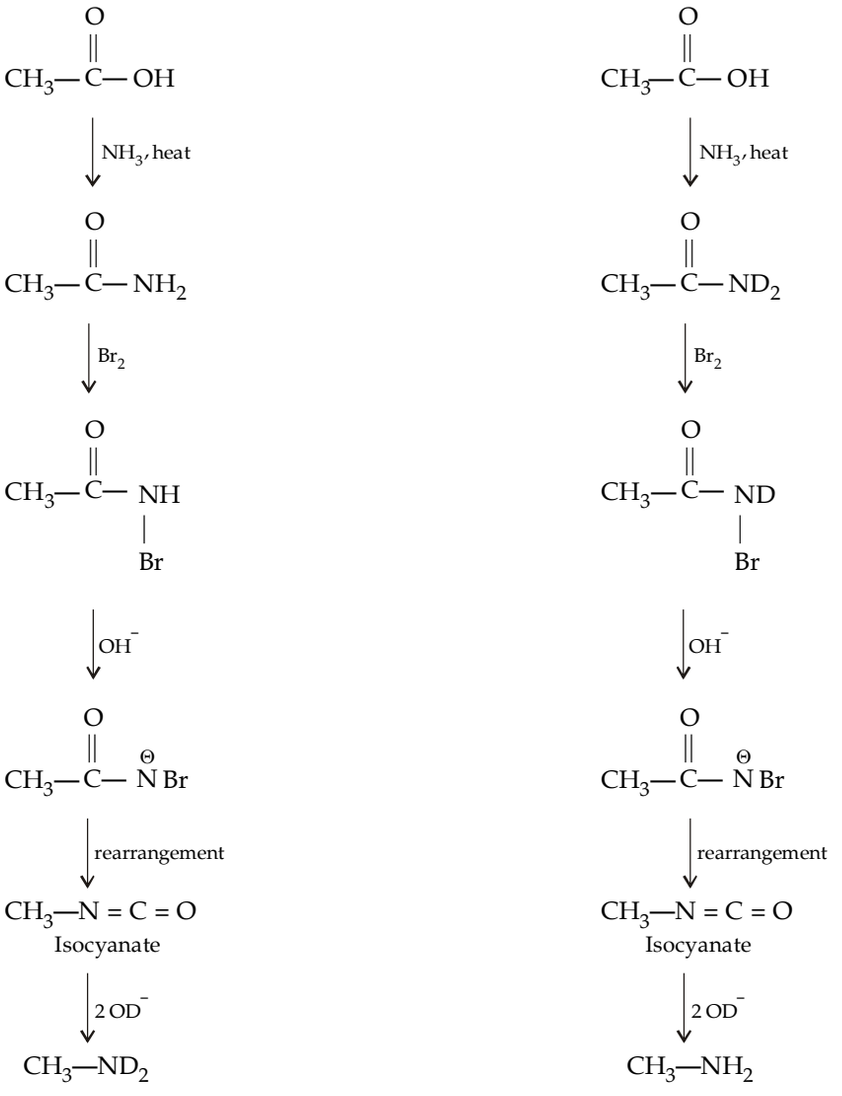
(a) $CH_3COOH \xrightarrow[\text{(ii) KOD, } Br_2]{\text{(i) } NH_3\text{, heat}} A$

(b) $CH_3COOH \xrightarrow[\text{(ii) KOH/}Br_2]{\text{(i) } ND_3\text{, heat}} B$

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Solution :

The two reactions will give methyl amine, but having different isotopes of hydrogen in the amino group. It can be easily understood by the mechanism of Hofmann degradation.



Example 3 :

Give steps involved in the following conversions.

(i) Propene into allylamine.

(ii) Succinic anhydride to β-alanine (β-aminopropionic acid)

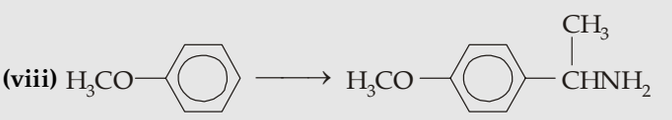
(iii) 1, 3-Butadiene to hexamethylenediamine, one of the raw materials for the manufacture of nylon-6, 6.

(iv) Ethylamine to (a) methylethylamine, and (b) dimethylethylamine

(v) *n*-Butanol to *n*-hexylamine

(vi) Ethyl cyanide to ethylamine

(vii) 

(viii) 

(ix) 

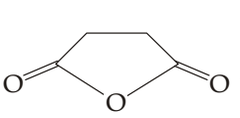
(x) 

(xi) 

(xii) 

Solution :

(*i*) $CH_2 = CHCH_3 \xrightarrow{Cl_2,\ 400°C} CH_2 = CHCH_2Cl \xrightarrow{NH_3} CH_2 = CHCH_2NH_2$

(*ii*) 
Succinic anhydride

$\xrightarrow{NH_3}$ $H_2N\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}OH \xrightarrow[(ii)\ H^+]{(i)\ NaOBr}$ $H_2NCH_2CH_2\overset{O}{\overset{\|}{C}}OH$
β–Alanine

(*iii*) $\underset{\text{1, 3–Butadiene}}{CH_2 = CHCH = CH_2} \xrightarrow[(1,\ 4\text{–addition})]{Cl_2} ClCH_2CH = CHCH_2Cl \xrightarrow{H_2,\ Ni} Cl(CH_2)_4Cl$

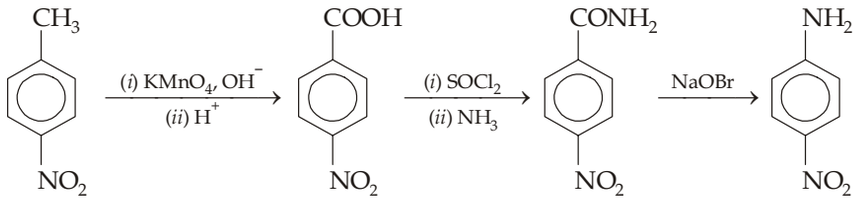
$\xrightarrow{2\ KCN} NC(CH_2)_4CN \xrightarrow{H_2,\ Ni} H_2NCH_2(CH_2)_4CH_2NH_2$
Hexamethylenediamine

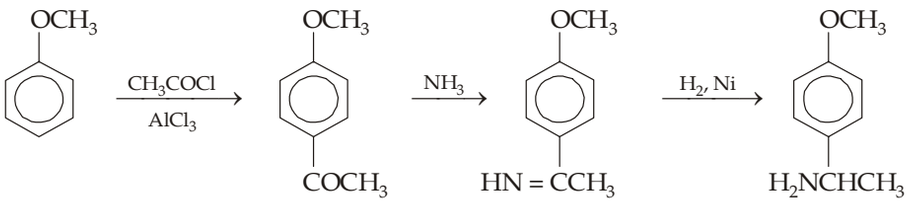
(*iv*) (*a*) $CH_3CH_2NH_2 \xrightarrow[KOH]{CHCl_3} CH_3CH_2NC \xrightarrow{H_2/Pt} CH_3CH_2NHCH_3$
Ethylamine — Methylethylamine

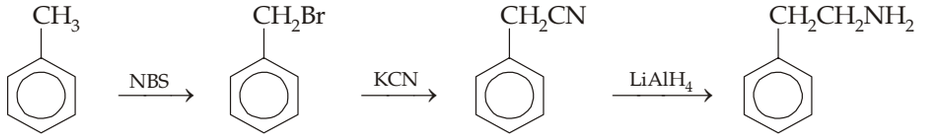
(*b*) $CH_3CH_2NH_2 \xrightarrow[HCOOH]{H_2C = O} CH_3CH_2N(CH_3)_2$
Ethylamine — Dimethylethylamine

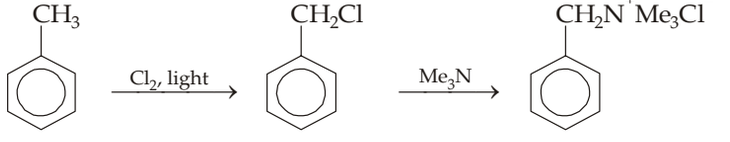
(*v*) $n\text{-}C_3H_7CH_2OH \xrightarrow[(ii)\ Mg,\ ether]{(i)\ PBr_3} n\text{-}C_3H_7CH_2MgBr \xrightarrow[oxide]{ethylene} n\text{-}C_3H_7CH_2CH_2CH_2OH \xrightarrow{NH_3} n\text{-}C_3H_7CH_2CH_2CH_2NH_2$
n-Butanol — *n*-Hexylamine

(*vi*) $\underset{\text{Ethyl cyanide}}{CH_3CH_2CN} \xrightarrow{H_3O^+} CH_3CH_2COOH \xrightarrow{NH_3,\ heat} CH_3CH_2CONH_2 \xrightarrow{NaBrO} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$

(*vii*) 

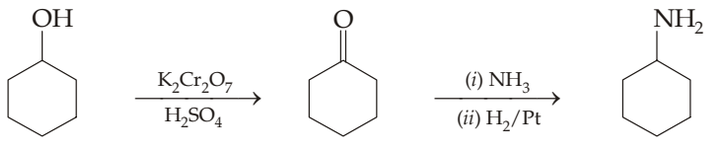
(*viii*) 

(*ix*) 

(*x*) 

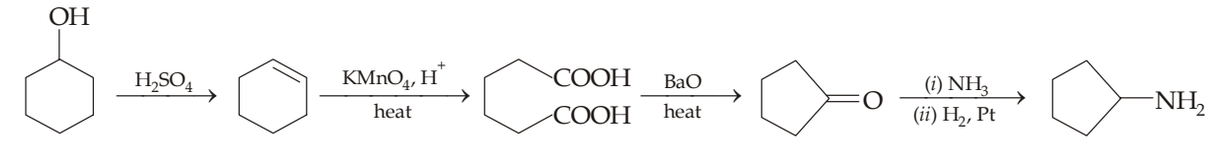
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(*xi*)



Cyclohexanol Cyclohexylamine

(*xii*)



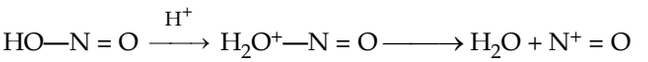
Cyclohexanol Cyclopentylamine

Example 4 :

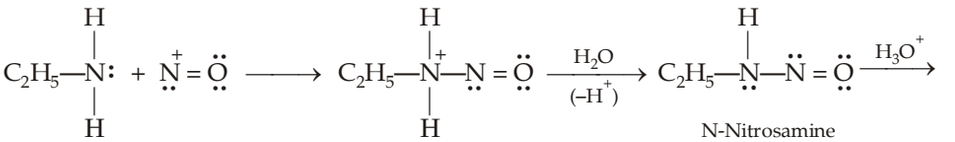
Give all steps involved in the reaction of nitrous acid with ethylamine.

Solution :

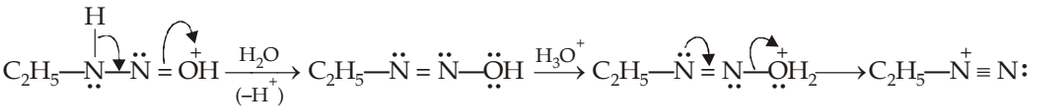
Nitrous acid gives nitrosonium ion (an electrophile).



Nucleophilic attack of the electron pair of the amine on the nitrosonium ion produces N-nitrosomine which undergoes a series of proton transfer to form a diazocation as the final product.



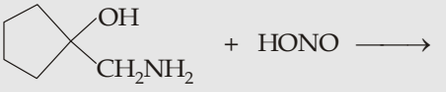
N-Nitrosamine



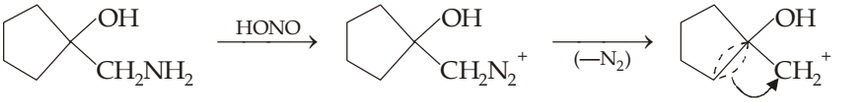
Ethyl diazoic acid Ethyl diazonium cation

Example 5 :

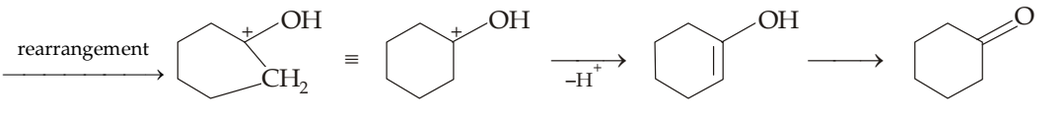
Write down the final product in the following reaction, giving steps involved.



Solution :



1° Carbocation



3° Carbocation

Example 6 :

How will you distinguish between each of the following pairs by simple chemical tests.

(a) Aniline and cyclohexylamine **(b) $(CH_3)_4N^+Cl^-$ and $(CH_3)_3NH^+Cl^-$**

(c) $(CH_3)_4N^+OH^-$ and $(CH_3)_2NCH_2OH$ **(d) $(C_6H_5NH_3)_2\,SO_4$ and p-$N^+H_3C_6H_4SO_3^-$.**

Solution :

(*a*) At low temperature, aniline ($C_6H_5NH_2$), on treatment with HONO, undergoes diazotisation to form diazonium salt which form highly coloured azo dyes on addition of β-naphthol. Cyclohexylamine ($C_6H_{11}NH_2$) also forms diazonium salt with nitrous acid but the salt, cyclohexyl-N_2^+ is unstable, even at low temperatures and evolves N_2 detected by its bubbles.

(*b*) Add conc. NaOH and heat the mixture, when only $(CH_3)_3NH^+Cl^-$ is changed into the volatile free base, $(CH_3)_3$ N, detected by its typical ammonia-like odour.

$$(CH_3)_3N^+HCl^- \xrightarrow{\text{Conc. NaOH, heat}} (CH_3)_3N + NaCl + H_2O$$

$$(CH_3)_4N^+Cl^- \xrightarrow{\text{Conc. NaOH, heat}} \text{No reaction}$$

However, remember that $Me_4N^+OH^-$ gives Me_3N, on thermal decomposition.

(*c*) $(CH_3)_4N^+OH^-$ is a strong base and its solution turns red litmus blue. It also gives a white precipitate of $Ba(OH)_2$ when $BaCl_2$ is added. The other compound, Me_2NCH_2OH is a covalent alcohol.

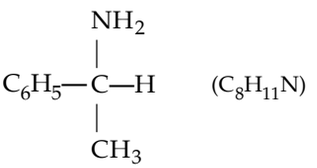
(*d*) Only $(C_6H_5NH_3)_2^{2+}\,SO_4^{2-}$ gives white precipitate of $BaSO_4$, on adding $BaCl_2$. The other compound is a sulphonate which does not give precipitate with Ba^{2+}.

Example 7 :

Suggest a structural formula for an optically active amine, $C_8H_{11}N$, which evolves nitrogen on treatment with nitrous acid.

Solution :

Molecular formula, $C_8H_{11}N$, of the compound indicates that it has four degree of unstauration (a saturated compound with 8 carbons would have the formula $C_8H_{19}N$) which points out the presence of a benzene ring. Further, since the amine evolves N_2 with HONO, it should be 1°. Further, since the amine is optically active, it will have chiral carbon, hence its two other substituents should be H and CH_3.



($C_8H_{11}N$)

Example 8 :

Deduce the structures of the following amines from the products obtained from exhaustive methylation and Hofmann elimination.

(a) Amine of the molecular formula $C_5H_{13}N$ reacts with 1 mole of methyl iodide and finally gives propene.

(b) Amine of the formula $C_5H_{13}N$ reacts with 2 moles of methyl iodide and gives ethene and a 3° amine which in turn reacts with 1 mole of CH_3I and give propene.

Solution :

(*a*) The amine is a 3° amine because it reacts with only 1 mole of CH_3I. Formation of propene indicates that one of the alkyl groups is C_3H_7 – (*n*- or *iso*-). Hence amine ($C_5H_{13}N$) should be $C_3H_7N(CH_3)_2$.

(*b*) Given reactions indicate that amine is a 2° amine. Separate formation of ethene and propene shows that the two alkyl groups are C_2H_5 and C_3H_7. Hence amine is $C_3H_7NHC_2H_5$.

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Example 9 :

A resolvable amine (A) when subjected to exhaustive methylation, it takes up 3 equivalents of methyl iodide and the product when heated gives an alkene (B). Alkene (B) on ozonolysis yields an equimolar mixture of methanal and butanal. Suggest the structure of the amine (A).

Solution :

$$\underset{\text{(amine)}}{A} \xrightarrow[\text{(ii) heat}]{\text{(i) } 3CH_3I} \underset{\text{(alkene)}}{B} \xrightarrow{O_3} \underset{\text{Methanal}}{H_2C=O} + \underset{\text{Butanal}}{O=CHCH_2CH_2CH_3}$$

(*i*) Nature of alkene (B) can be evaluated from its ozonolysis products.

$$\underset{\text{Methanal}}{H_2C=O} + \underset{\text{Butanal}}{O=CHCH_2CH_2CH_3} \xleftarrow{O_3} \underset{\text{Alkene, B}}{H_2C=CHCH_2CH_2CH_3}$$

(*ii*) Since the amine takes up 3° equivalents of CH_3I, to form 4° ammonium ion, it must be 1° amine which can be either I or II.

$$\underset{\text{I (Achiral)}}{H_2NCH_2CH_2CH_2CH_2CH_3} \qquad \underset{\text{II (Chiral)}}{H_3C\underset{\displaystyle NH_2}{\underset{|}{C}}HCH_2\,CH_2CH_3}$$

However, resolvable nature of the amine indicates that it is II, and not I which is optically inactive.

Example 10 :

A carboxylic acid A ($C_5H_{10}O_2$) when heated with hydrazoic acid in presence of conc. H_2SO_4 gives a compound B which on treatment with alkaline chloroform forms another compound C. Compound C gives following reactions.

(i) On hydrolysis in presence of acid, it gives compound B and methanoic acid.

(ii) On reduction it gives tert-butylmethylamine.

Identify compound A and give all reactions.

Solution :

Let us summarise the give reactions.

$$\underset{\text{(–COOH group)}}{A,\ C_5H_{10}O_2} \xrightarrow[\text{conc. } H_2SO_4]{N_3H} B \xrightarrow[KOH]{CHCl_3} C \xrightarrow{\text{reduction}} (CH_3)_3CNHCH_3$$

$$C \xrightarrow{H_3O^+} HCOOH + B$$

Reactions of the compound C indicate that it should be an isonitrile, Me_3CNC. Hence B should be corresponding amine and A corresponding carboxylic acid.

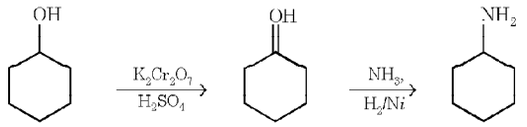
$$\underset{\text{tert-Butylmethyl amine}}{(CH_3)_3CNHCH_3} \xleftarrow{\text{reduction}} \underset{\text{C (Isonitrile)}}{(CH_3)_3CNC} \xleftarrow[KOH]{CHCl_3} \underset{\text{B (1°amine)}}{(CH_3)_2CNH_2} \longleftarrow \underset{\text{A}}{(CH_3)_3CCOOH}$$

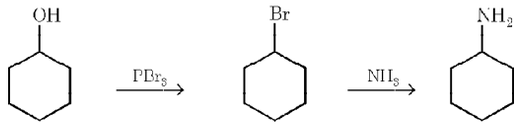
EXERCISE 19.1 (MCQ - ONE option correct)

1. Pick up the incorrect name, if any
(*a*) N-methylaniline (*b*) N-methylbenzenamine
(*c*) methylaniline (*d*) All are correct.

2. Which of the following is more correct ?
(*a*) $RX + NH_3$ (excess) $\rightleftharpoons RNH_3^+ + X^-$
(*b*) $RX + NH_3$ (excess) $\rightleftharpoons RNH_2 + NH_4^+$
(*c*) Both are equal important
(*d*) $RX + NH_3$ (excess) $\rightleftharpoons R_4N^+ + X^-$.

3. Cyclohexanol can be converted into cyclohexylamine by following two routes. Which of the following methods is expected to give good yield of cyclohexylamine ?

(*a*) 

(*b*) 

(*c*) Both are equally suitable
(*d*) Neither of the two.

4. Best method for preparing 1° amines from alkyl halides is by
(*a*) Hofmann bromamide reaction
(*b*) Gabriel phthalimide reaction
(*c*) Both are equally good
(*d*) Reaction with NH_3.

5. Which is the best method for preparing N, N-dimethylaniline from aniline ?
(*a*) $C_6H_5NH_2 + CH_3I \longrightarrow$
(*b*) $C_6H_5NH_2 + CH_3OH \xrightarrow{H^+}$
(*c*) $C_6H_5NH_2 + CH_2O \xrightarrow{HCOOH}$
(*d*) Both (*a*) and (*b*) are equally good.

6. Ethyl cyanide can be converted to ethylamine by
(*a*) reduction with Sn and HCl
(*b*) Reduction with $LiAlH_4$
(*c*) Acidic hydrolysis followed by heating with ammonia and then alkaline bromine
(*d*) None.

7. Predict the nature of the product P

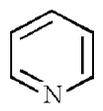
$$C_6H_5CONH_2 \xrightarrow{Br_2/OD^-} P$$

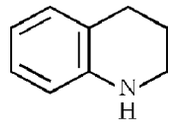
(*a*) $C_6H_5NH_2$ (*b*) C_6H_5NHD
(*c*) $C_6H_5ND_2$ (*d*) All the three.

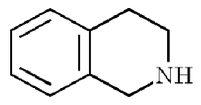
8. The tertiary amine, $CH_3\overset{C_2H_5}{\overset{|}{C}}HN(CH_3)(C_2H_5)$, is
(*a*) resolvable due to the presence of chiral N atom
(*b*) resolvable due to the presence of chiral C atom
(*c*) both (*a*) and (*b*)
(*d*) non-resolvable.

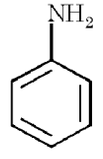
9. Which of the following species is basic in nature ?
(*a*) $(CH_3CH_2)_4N^+Br^-$ (*b*) $(CH_3CH_2)_4N^+OH^-$
(*c*) Both (*d*) None.

10. Which of the following is most basic ?

(*a*) 

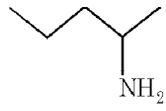
(*b*) 

(*c*) 

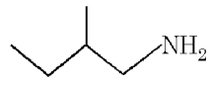
(*d*) 

11. Which of the following is most basic in gas phase ?
(*a*) NH_3 (*b*) $CH_3CH_2NH_2$
(*c*) $(CH_3CH_2)_2NH$ (*d*) $(CH_3CH_2)_3N$.

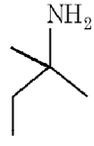
12. The correct order of decreasing basic character of the four amines (I to IV) is



I



II



III



IV

(*a*) I > II > III > IV
(*b*) IV > II > III > I
(*c*) III > II > I > IV
(*d*) All are equal since all are 1° amines.

13. Which of the following is most volatile ?
(*a*) n-$C_3H_7NH_2$ (*b*) $CH_3NHC_2H_5$
(*c*) $(CH_3)_3N$ (*d*) CH_3OH.

14. The correct arrangement of decreasing dipole moment of the following three compounds is
CH_3CH_2OH (I) ; $CH_3CH_2NH_2$ (II), $CH_3CH_2CH_3$ (III)
(*a*) I > II > III (*b*) III > II > I
(*c*) II > III > I (*d*) II > I > III.

15. Which of the following in least basic ?
(*a*) $FCH_2CH_2NH_2$ (*b*) $CH_3CH_2NH_2$
(*c*) $ClCH_2CH_2NH_2$ (*d*) All are equally basic.

16. Which of the following can form salt with aqueous acids ?
(*a*) $CH_3\ddot{N}H_2$ (*b*) $CH_3CO\ddot{N}H_2$
(*c*) Both (*d*) None

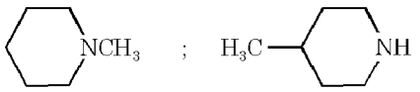
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17. Phenylhydrazine hydrochloride, $C_6H_5NHNH_3^+Cl^-$, an important carbonyl reagent is formed by treating phenylhydrazine, $C_6H_5NHNH_2$ with aq. hydrochloric acid. What product you expect when methylhydrazine, CH_3NHNH_2 is treated with aq. hydrochloric acid ?

(*a*) $CH_3NHNH_3^+Cl^-$ (*b*) $CH_3N^+H_2NH_2Cl^-$

(*c*) Both (*d*) No reaction.

18. Predict about the relative boiling point of the following two amines.



I II

(*a*) Boiling point of I > II

(*b*) Boiling point of II > I

(*c*) Both should have equal boiling points

(*d*) It can't be predicted.

19. A nitro group in the *para* or *ortho* to the amino group decreases the basicity of the —NH_2 group by

(*a*) destabilizing the corresponding anilinium ion

(*b*) stabilizing the parent amine

(*c*) both of the above factors

(*d*) None of the above statement is correct.

20. Which one of the following is better nitrosating agent ?

(*a*) HONO (*b*) NOCl

(*c*) Both are equal (*d*) None.

21. N, N-Dimethylaniline is converted to *p*-nitroso-N, N-dimethylaniline easily by

(*a*) H_2O^+—NO (*b*) HO—NO

(*c*) Both are equal (*d*) None.

22. Which of the following amine is more reactive ?

(*a*) $CH_3CH_2NH_2$ (*b*) $HOCH_2CH_2NH_2$

(*c*) Both are equal reactive (*d*) It can't be predicted.

23. Which of the following amine will react with BF_3 ?

(*a*) $(CH_3)_3N$ (*b*) $(C_6H_5)_3N$

(*c*) Both (*d*) None.

24. Glycine (aminoacetic acid) can best be prepared by the reaction of potassium phthalimide with

(*a*) chloroacetic acid (*b*) ethyl chloroacetate (*c*) either of the two (*d*) acetic acid.

25. How many alkenes can be formed when *n*-butylamine is treated with nitrous acid ?

(*a*) 1 (*b*) 2

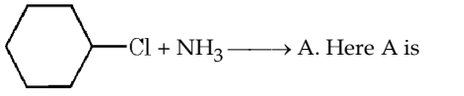
(*c*) 3 (*d*) 0.

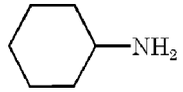
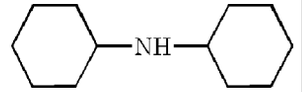
26. Predict the nature of P in the following reaction

$$Me_3CCH_2NH_2 \xrightarrow{HONO} P \text{ (main product)}$$

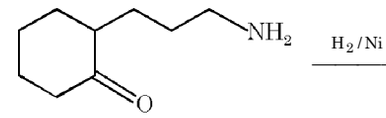
(*a*) Me_3CCH_2OH (*b*) $Me_2CCH=CH_2$

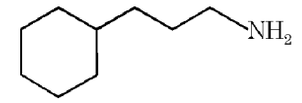
(*c*) $Me_2C(OH)C_2H_5$ (*d*) $Me_3CCH_2NH(NO)$.

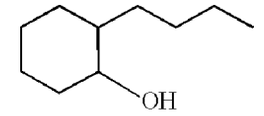
27.  A. Here A is

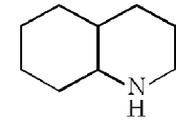
(*a*)  (*b*) 

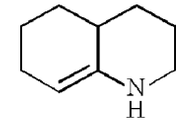
(*c*) Both (*a*) and (*b*) (*d*) 

28.  X. Here X is

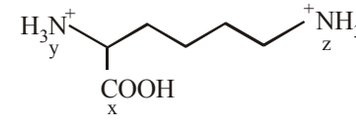
(*a*) 

(*b*) 

(*c*) 

(*d*) 

29. In the compound given below the correct order of the acidity of the positions X, Y and Z is



(a) Z > X > Y (b) X > Y > Z

(c) X > Z > Y (d) Y > X > Z

30. In the following reaction,

$$CH_3NH_2 + CHCl_3 + KOH$$

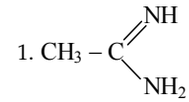
$$\longrightarrow \text{Nitrogen containing compound} + KCl + H_2O.$$

The nitrogen containing compound is

(a) $CH_3-NH-CH_3$ (b) $CH_3-C\equiv N$

(c) $CH_3\overset{+}{N}\equiv\overset{-}{C}$ (d) $CH_3-\overset{-}{N}\equiv\overset{+}{C}$

31. The correct order of basicities of the following compounds is

1.  2. $CH_3-CH_2-NH_2$

3. $(CH_3)_2NH$ 4. $CH_3-\overset{O}{\overset{\|}{C}}-NH_2$

(a) 2 > 1 > 3 > 4 (b) 1 > 3 > 2 > 4

(c) 3 > 1 > 2 > 4 (d) 1 > 2 > 3 > 4

32. Which one of the following is the strongest base in aqueous solution ?

(a) Methylamine (b) Trimethylamine

(c) Aniline (d) Dimethylamine.

33. The correct order of increasing basic nature for the bases NH_3, CH_3NH_2 and $(CH_3)_2$ NH is

(a) $(CH_3)_2NH < NH_3 < CH_3NH_2$

(b) $NH_3 < CH_3NH_2 < (CH_3)_2NH$

(c) $CH_3NH_2 < (CH_3)_2NH < NH_3$

(d) $CH_3NH_2 < NH_3 < (CH_3)_2NH$

34. Ethyl isocyanide on hydrolysis in acidic medium generates

(a) propanoic acid and ammonium salt

(b) ethanoic acid and ammonium salt

(c) methylamine salt and ethanoic acid

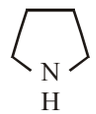
(d) ethylamine salt and methanoic acid

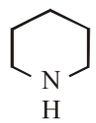
35. Which one of the following methods is neither meant for the synthesis nor for separation of amines?
(a) Curtius reaction (b) Wurtz reaction
(c) Hofmann method (d) Hinsberg method

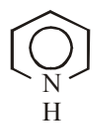
36. Introduction of a methyl group in ammonia markedly increases the basic strength of ammonia in aq. solution, introduction of the second methyl group increases only marginally the basic strength of methyl amine in water. This is due to
(a) different type of hybridisation in the two amines
(b) protonated dimethyl amine is more solvated than methyl amine
(c) protonated dimethyl amine is more solvated than the protonated methyl amine
(d) protonated dimethyl amine is less stable than the protonated methyl amine

37.  Z; Z is

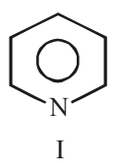
(a) 

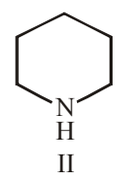
(b) 

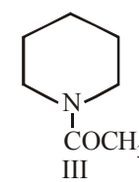
(c) 

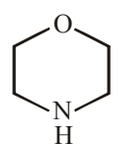
(d) 

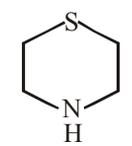
38. The relative order of basic character of the following compounds is


I


II


III


IV


V

(a) II > I > III > IV > V (b) II > III > IV > V > I
(c) II > V > IV > I > III (d) II > IV > V > III > I

39. In the following reaction, the reagent X should be

$$RCOOH + [X] \xrightarrow{\text{conc. } H_2SO_4} RNH_2$$

(a) NH_3 (b) HN_3
(c) either of the two (d) None of the two

40. Benzamide and benzyl amine can be distinguished by
(a) cold dil. NaOH
(b) cold dil. HCl
(c) both a & b
(d) $NaNO_2$, HCl, 0°C, then β-naphthol

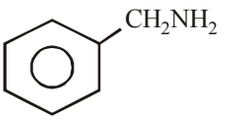
41. Which of the following is true regarding basic character of pyridine and pyrrole?
(a) Pyrrole is more basic because its nonbonding electrons occupy sp^3 orbital
(b) Pyridine is more basic because its nonbonding electrons is not a part of aromatic sextet.
(c) Both are equally basic
(d) Pyridine is less basic because it is 3° amine

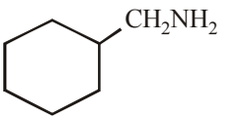
42. The correct order of decreasing basic character of the three aliphatic primary amines is


I II III

(a) I > II > III (b) III > II > I
(c) I > II ≈ III (d) I = II ≡ III

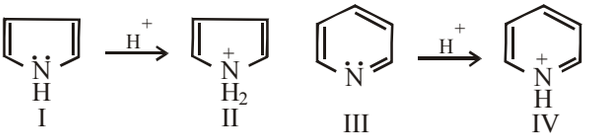
43. Which of the statement is true regarding the basicity of the following two primary amines ?


I


II

(a) Both are equally basic because both are 1° amines
(b) I > II because it is an aromatic amine
(c) II > I because it is an aliphatic amine
(d) I < II because of difference in the nature of β-carbon

44. Pyrrole and pyridine both are basic and form salts with acids?


I II III IV

Which of the following statement is true regarding the aromatic character of the four species?
(a) All the four are aromatic
(b) I, III and IV are aromatic
(c) I, II and III are aromatic
(d) I and III are aromatic

45. Which of the following leads to carbon-carbon double bond?
(a) 1° Amine + RCHO → (b) 2° Amine + R_2CO →
(c) 2° Amine + RCHO → (d) both b & c

46. Which of the following will react most readily with NaOH to form ethanol ?

(a) $(CH_3)_4 N^+ I^-$ (b) $(CH_3)_4 S^+ I^-$

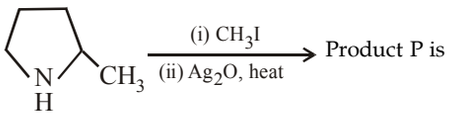
(c) $(CH_3)_3 CCl$ (d) CH_3OCH_3

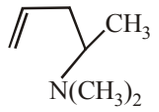
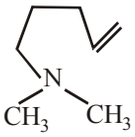
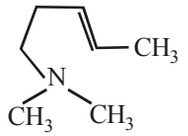
47. In Hofmann bromamide degradation, one of the important steps is the migration of
(a) an alkyl group without its electron pair to electron deficient N atom
(b) an alkyl group with its electron pair to electron deficient O atom
(c) an alkyl group with its electron pair to electron rich N atom
(d) an alkyl group with its electron pair to electron deficient N atom

48. $(CH_3)_3C-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[(ii)D_2O]{(i)\ OD^-/Br_2}$ Product P is

(a) $(CH_3)_3 CNH_2$ (b) $(CH_3)_3$ CNHD
(c) $(CH_3)_3CND_2$ (d) no reaction

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49.  Product P is

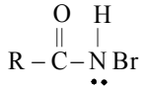
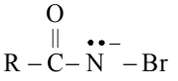
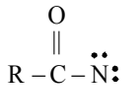
(a) 
(b) 
(c) 
(d) None

50. Which of the following is one of the intermediates in Hofmann, Curtius, Schmidt and Lossen reaction ?

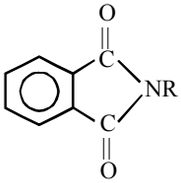
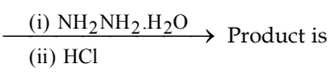
(a) $R\overset{+}{C}O$ (b) RNCO
(c) RCNO (d) $R\,CO\overset{-}{N}H$

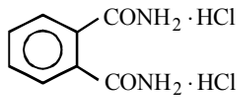
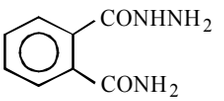
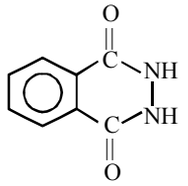
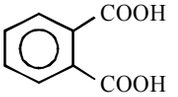
51. Which of the following is not formed as an intermediate in the Hofmann rearrangement?

$$R-CONH_2 \xrightarrow{Br_2/NaOH} RNH_2$$

(a) 
(b) 
(c) 
(d) All the three are formed

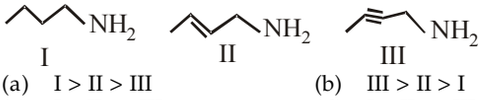
52. How many structural isomers of a Grignard reagent are possible for preparing *n*-butane by reaction with ethyl amine ?
(a) 1 (b) 2
(c) 3 (d) 4

53.   Product is

(a) 
(b) 
(c) 
(d) 

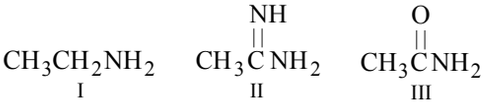
54. The basic character of ethyl amine, diethyl amine and triethyl amine in chlorobenzene is
(a) $C_2H_5NH_2 < (C_2H_5)_2NH < (C_2H_5)_3N$
(b) $C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$
(c) $(C_2H_5)_3N < (C_2H_5)_2NH < C_2H_5NH_2$
(d) $(C_2H_5)_3N < C_2H_5NH_2 < (C_2H_5)_2NH$

55. The correct order of decreasing basic character of the three aliphatic primary amines is



(a) I > II > III (b) III > II > I
(c) I > II ≈ III (d) I = II ≡ III

56. The correct order of increasing basicity is

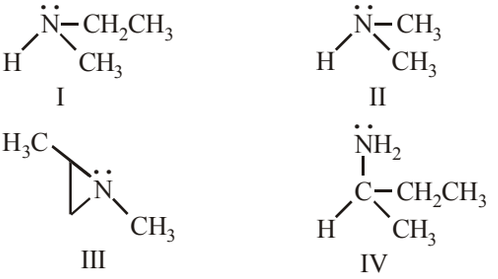


(a) II < III < I (b) I ≈ III < II
(c) I < II < III (d) III < I < II

57. $CH_3CH_2CH_2NH_2 \xrightarrow[0^\circ C]{NaNO_2,\ HCl} P$. P is

(a) $CH_3CH_2CH_2OH$ (b) $(CH_3)_2CHCl$
(c) Both (a) and (b) (d) Reaction not possible

58. Which of the following amines can be resolved into two enantiomers?

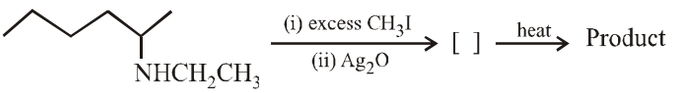


(a) I, IV (b) I, II
(c) I, III, IV (d) III, IV

59. Which of the following statement is false?
(a) Dimethyl amine as well as trimethyl amine are soluble in water
(b) Trimethyl amine forms hydrogen bond neither with itself nor with water.
(c) Trimethyl amine can act as hydrogen bond acceptor only, while dimethyl amine can serve as both a hydrogen bond donor and acceptor
(d) All the three statements are false

60. Which of the following leads to carbon-carbon double bond?
(a) 1° Amine + RCHO → (b) 2° Amine + R_2CO →
(c) 2° Amine + RCHO → (d) both b & c

61. Predict the possible number of alkenes and the main alkene in the following reaction.



(a) 2 and 
(b) 2 and 
(c) 3 and $H_2C=CH_2$
(d) 2 and $H_2C=CH_2$

62. In Hofmann bromamide degradation, one of the important steps is the migration of
(a) an alkyl group without its electron pair to electron deficient N atom
(b) an alkyl group with its electron pair to electron deficient O atom
(c) an alkyl group with its electron pair to electron rich N atom
(d) an alkyl group with its electron pair to electron deficient N atom

63. Identify (C) and (D) in the following series of reactions

$$CH_3NH_2 \xrightarrow[CH_3I]{\text{excess of}} [A] \xrightarrow{AgOH} [B] \xrightarrow{heat} [C]+[D]$$

(a) $(CH_3)_3COH$, CH_3NH_2 (b) $(CH_3)_2C=CH_2$, CH_3NH_2
(c) $(CH_3)_3N$, CH_3OH (d) $(CH_3)_2C=CH_2$, CH_3OH

64. Which of the following is hydrolysed to give secondary amine -

(a) Alkyl cyanide (b) 
(c) Nitro paraffins (d) Acid amide

65. Which of the following does not yield an amine -

(a) $R - X + NH_3 \rightarrow$

(b) $R - CH = N - OH + [H] \xrightarrow[C_2H_5OH]{Na}$

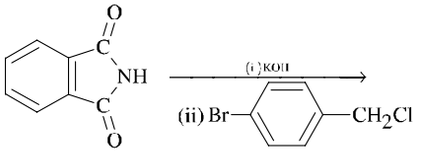
(c) $R - CN + H_2O \rightarrow$ (d) $RCONH_2 + 4[H] \rightarrow$

66. Which of the following amine does not react with Hinsberg reagent ?

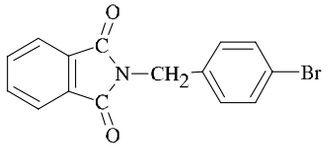
(a) Neopentylamine (b) Isopropylamine

(c) Triethylamine (d) Ethylmethylamine

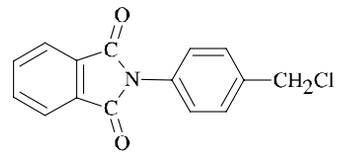
67. The major product of the following reaction is



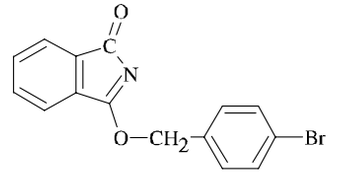
(a)



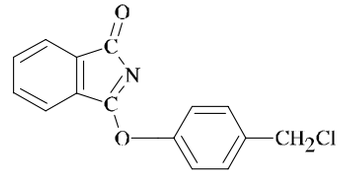
(b)



(c)



(d)



EXERCISE 19.2 (MCQ 1 or >1 option correct, Passage based, Matching, A/R)

DIRECTIONS for Q. 1 to Q. 22 : Multiple choice questions with one or more than one correct option(s).

1. Which of the following amine can be prepared by Gabriel method?

(*a*) $CH_3CH_2NH_2$ (*b*) $(CH_3)_2CHNH_2$

(*c*) $(CH_3)_3CNH_2$ (*d*) $C_6H_5NH_2$

2. Which of the following can't be used as an alkylating agent for an amine ?

(a) CH_3CH_2Cl (b) $CH_2 = CHCl$

(c) C_6H_5Cl (d) $(CH_3)_3CCl$

3. $(CH_3)_3CNH_2$ can't be prepared by

(*a*) reductive amination (*b*) oxime reduction

(*c*) Hofmann degradation (*d*) Gabriel synthesis.

4. Guanidine, $(NH_2)_2 C = NH$, is said to be the strongest nitrogen containing organic base because

(*a*) it has two —NH_2 groups

(*b*) it has three nitrogen atoms that can be protonated

(*c*) it is less stable as compared to the protonated species

(*d*) its conjugate acid is very much stable due to three equivalent structures.

5. Quaternary ammonium salts are used

(*a*) as phase transfer catalysts

(*b*) in preparing alkenes

(*c*) for preparing 3° amines

(*d*) preparing 2° amines

6. Which of the following is not true

Hinsberg test is applicable to

(*a*) all amines

(*b*) liquid amines soluble in water

(*c*) liquid amines insoluble in water

(*d*) solid amines insoluble in water.

7. Primary, secondary and tertiary amines may be separated by using

(a) benzene sulphonyl chloride

(b) diethyl oxalate

(c) sulphonyl chloride

(d) acetyl chloride

8. $CH_3CH_2CH_2NH_2 \xrightarrow{HNO_2} A(\text{mixture})$

Mixture can contain

(a) $CH_2CH_2CH_2OH$ (b) $CH_3\underset{\displaystyle OH}{\underset{|}{C}}H.CH_3$

(c) $CH_2 - CH_2$ with CH (d) $CH_3CH = CH_2$

9. $\underset{(x)}{C_4H_{11}N} + HNO_2 \longrightarrow C_4H_{10}O(3° \text{alcohol})$; hence X will give :

(a) carbyl amine reaction

(b) Hofmann mustard oil reaction

(c) diazonium salt (as the intermediate) with HNO_2

(d) none is correct

10. Mixture of 1°, 2° and 3° amines can be separated by :

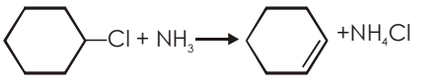
(a) Hinsberg's method

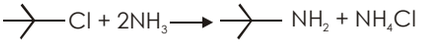
(b) Hofmann's method

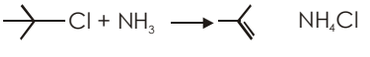
(c) distillation

(d) chromatography

11. Which is /are correct reaction(s) :

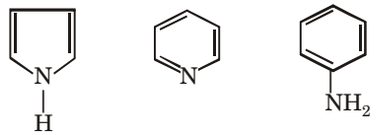
(a) 

(b) 

(c) 

(d) 

EBD_7091

12. 

pyrrole I pyridine II aniline III

which is/are correct statements?

(a) I is more basic than II
(b) II is more basic than I and III
(c) III is more basic than II
(d) all are aromatic bases

13. In the reaction $2\mathbf{X} + B_2H_6 \rightarrow [BH_2(\mathbf{X})_2]^+ [BH_4]^-$ the amine(s) **X** is (are)

(a) NH_3 (b) CH_3NH_2
(c) $(CH_3)_2NH$ (d) $(CH_3)_3N$

14. Reaction of $R-\overset{O}{\overset{\|}{C}}-NH_2$ with a mixture of Br_2 and KOH gives R-NH_2 as the main product. The intermediates involved in this reaction are :

(a) $R-\overset{O}{\overset{\|}{C}}-NHBr$ (b) $R-NHBr$

(c) $R-N=C=O$ (d) $R-\overset{O}{\overset{\|}{C}}-N<^{Br}_{Br}$

15. Which of the following compound can be methylated by diazomethane ?

(a) C_2H_5COOH
(b) $C_2H_5NH_2$
(c) C_6H_5OH
(d) $CH_3COCH_2COOC_2H_5$

16. Which of the following amine can be prepared by Gabriel method ?

(*a*) $CH_3CH_2NH_2$ (*b*) $(CH_3)_2CHNH_2$
(*c*) $(CH_3)_3CNH_2$ (*d*) $C_6H_5NH_2$

17. Which of the following can't be used as an alkylating agent for an amine ?

(a) CH_3CH_2Cl (b) $CH_2=CHCl$
(c) C_6H_5Cl (d) $(CH_3)_3CCl$

18. Which of the following can exist as inner salt ?

(*a*) *p*-Aminobenzenesulphonic acid
(*b*) *p*-Aminobenzoic acid
(*c*) Aminoacetic acid
(*d*) Alanine

19. Which of the following reacts with nitrous acid ?

(*a*) Acetamide
(*b*) 2-Nitrobutane
(*c*) 2-Methyl-2-nitropropane
(*d*) Diethylamine

20. Which of the following intermediates are likely to be formed when 2-methylpropyl amine is treated with nitrous acid ?

(a) $(CH_3)_2CH\overset{+}{C}H_2$ (b) $(CH_3)_3C\overset{+}{O}H_2$

(c) $(CH_3)_2CHCH_2\overset{+}{O}H_2$ (d) $(CH_3)_2\overset{+}{C}CH_3$

21. Carbenes are the reactive intermediates in

(a) Reimer Tiemann reaction
(b) Wittig reaction
(c) Hofmann bromamide reaction
(d) Carbylamine reaction

22. $\underset{(X)}{C_4H_{11}N} + HONO \longrightarrow \underset{(3^\circ \text{ alcohol})}{C_4H_{10}O}$

X should

(a) give carbylamine reaction
(b) undergo diazotisation
(c) react with water
(d) give Hofmann bromamide reaction

INSTRUCTION for Q. 23 to Q. 38 : Read the passages given below and answer the questions that follow.

PASSAGE 1

An optically active naturally occurring toxic liquid $C_8H_{17}N$ (X), in hemlock that was said to cause Socrates death dissolves in aq. HCl and gives no gas with nitrous acid. It gives a precipitate with benzenesulphonyl chloride in presence of NaOH. when treated with excess of methyl iodide, then with moist oxide and finally heated, it gives a compound (Y). Compound (Y) is treated similarly as (X) and which finally gives two nitrogen free compounds.

23. What conclusion you will draw when we say that the original compound does not give any precipitate with $C_6H_5SO_2Cl$ in presence of NaOH?

(a) It may be 1° amine (b) It may be 3° amine
(c) Either of the two (d) Neither of the two

24. The above set of reactions indicate that N is present in the

(a) side chain (b) ring
(c) either of the two (d) none of the two

PASSAGE 2

Primary aliphatic amines also react with nitrous acid to yield aliphatic diazonium salts. However, aliphatic diazonium salts are quite unstable and decompose spontaneously, even at low temperatures, by losing nitrogen to form carbocations (hence the reaction is commonly known as **deamination**). The carbocations, in turn, produce a mixture of alkenes, alcohols, and alkyl halides.

$$CH_3CH_2CH_2NH_2 \xrightarrow[HCl]{HONO} [CH_3CH_2CH_2N_2^+Cl]$$

$$\longrightarrow CH_3CH_2CH_2^+ + \mathbf{N_2} + Cl^-$$

$$CH_3CH=CH_2 \xleftarrow{-H^+} \mathbf{CH_3CH_2CH_2^+} \longrightarrow CH_3^+CHCH_3$$

$$\xrightarrow{-H^+} CH_3CH=CH_2$$

Propene

25. The reaction of $CH_3CH_2CH_2NH_2$ with nitrous acid is used in detecting the presence of $-NH_2$ group in amino acids and proteins because this test is based on the fact

(a) a green colour is obtained
(b) a red colour is obtained in the final stage
(c) a characteristic change in colour is observed
(d) nitrogen is evolved quantitatively

26. Which of the following product is also formed in the above reaction?

(a) $CH_3CH_2CH_2Cl$ (b) $CH_3CHOHCH_3$

(c) $CH_3CHClCH_3$ (d) All the three

27. Which type of product is likely to be formed when $CH_3CH_2CH_2NH_2$ in the above case is replaced by $C_6H_5CH_2NH_2$?

(a) An alkene (b) An alcohol

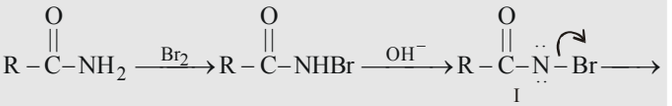
(c) Both (a) and (b) (d) None of the two

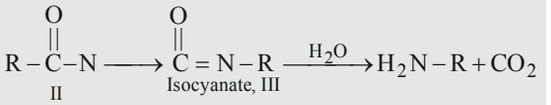
PASSAGE 3

The conversion of an amide to an amine with one carbon atom less by the action of alkaline hypohalite is known as Hofmann degradation.

$$RCONH_2 + Br_2 + 4KOH \longrightarrow RNH_2$$

The most important feature of the reaction is the rearrangement of N-bromamide anion to isocyanate :





Hofmann reaction is accelerated if the migrating group is more electron-releasing.

28. Which step is the driving force in the above reaction to proceed in right direction?

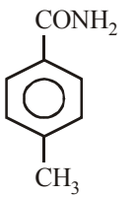
(a) conversion of I to II

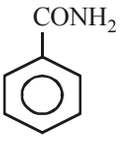
(b) conversion of II to III

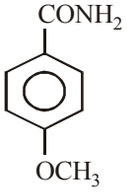
(c) conversion of III to RNH_2

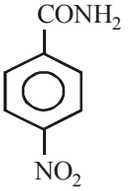
(d) All

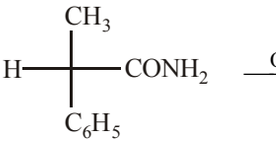
29. Which of the following can undergo Hofmann reaction most easily?

(a) 

(b) 

(c) 

(d) 

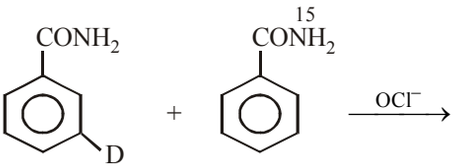
30.  Product amine will be

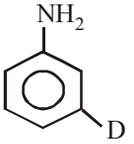
(+) – α-Phenylpropionamide

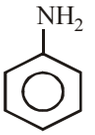
(a) (+) – (b) (–) –

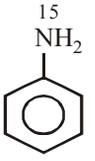
(c) 50 : 50 racemic (d) non-50 : 50 racemic

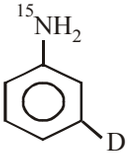
31. Predict the product in the following reaction :



(i) 

(ii) 

(iii) 

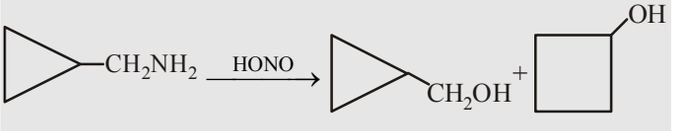
(iv) 

(a) (i) and (ii) (b) (ii) and (iii)

(c) (i) and (iii) (d) All the four

PASSAGE 4

Nitrous acid reacts with amines forming different products depending upon the type of amine. Aliphatic primary amines react with HONO forming alcohol as the major product, other products being alkene and alkyl halide. Certain cyclic primary amines can undergo ring expansion or ring contraction on treatment with HONO again forming alcohol as the major product.



Aromatic primary amines when treated with HONO undergo diazotization to form diazonium salt as the stable product.

32. Which of the following statement is not true ?

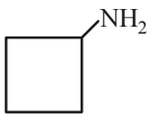
(a) All primary amines first form diazonium salt when treated with nitrous acid.

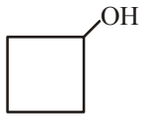
(b) All aliphatic primary amines when treated with nitrous acid form primary alcohols as the major product

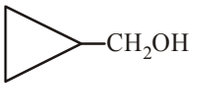
(c) The three classes of amines give different products on treatment with nitrous acid.

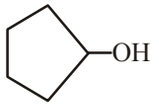
(d) None of the three

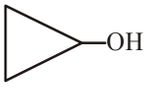
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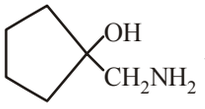
33.  $\xrightarrow{HONO}$ P. Product P may be

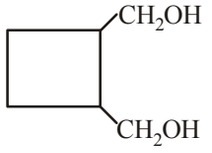
(a) 

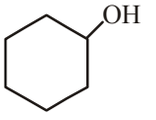
(b) 

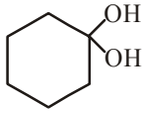
(c) 

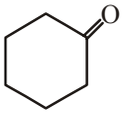
(d) 

34.  $\xrightarrow[HCl]{NaNO_2}$ Stable product Z may be

(a) 

(b) 

(c) 

(d) 

35. $(+)-CH_3\underset{\displaystyle NH_2}{\underset{|}{C}}HCH_2CH_3 \xrightarrow{HONO}$ Product is

(a) enantiomer of the original compound
(b) diastereomer of the original compound
(c) racemic mixture of the original compound
(d) (+) – isomer

PASSAGE 5

Like ammonia, an amine (1°, 2° or 3°) can react with an alkyl halide to form next higher class of amine. Here, again it is the presence of electron pair on nitrogen which makes amines to behave as nucleophile and alkyl halides thus undergo nucleophilic substitutions.

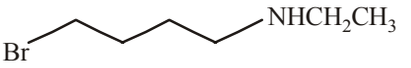
$$\underset{\text{1° Amine (Nucleophile)}}{R\ddot{N}H_2} + \underset{\text{1° Alkyl halide}}{R'CH_2X} \longrightarrow \underset{\displaystyle H}{\overset{\displaystyle H}{\underset{|}{\overset{|}{RN^+}}}}-CH_2R' \; X^-$$

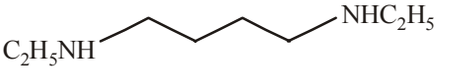
$$\longrightarrow \underset{\displaystyle H}{R\ddot{N}}-CH_2R' + HX$$

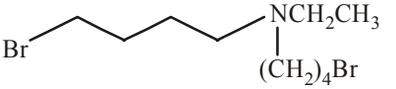
2° Amine

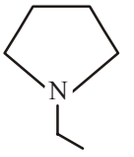
A second alkylation may follow, converting the secondary amine to a tertiary amine which may be alkylated to give a quaternary ammonium salt.

36. Identify the product(s) obtained when $Br(CH_2)_4Br$ is heated with 1 equivalent of ethyl amine

(a) 

(b) 

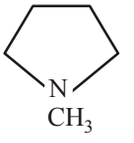
(c) 

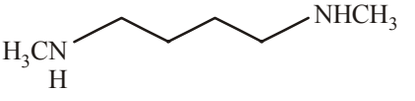
(d) 

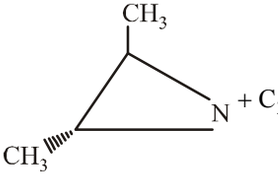
37. Identify the product(s) obtained when $Br(CH_2)_4Br$ is heated with excess of methyl amine

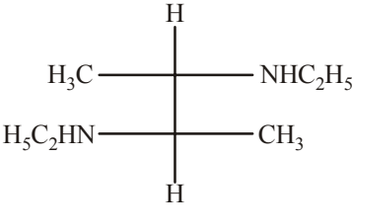
(a) $Br(CH_2)_3CH_2\underset{\displaystyle (CH_2)_4Br}{\underset{|}{N}}CH_3$

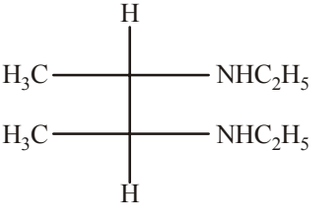
(b) $Br(CH_2)_3CH_2\underset{\displaystyle (CH_2)_4Br}{\underset{|}{\overset{|}{N^+}}}CH_3 \quad Br^-(CH_2)_4Br$

(c) 

(d) 

38.  $+ C_2H_5NH_2 \longrightarrow Z$, here Z is

(a) 

(b) 

(c) Both of these
(d) None of the two

Instructions for Q. 39 to Q. 45 : Following questions are Multiple Matching type Questions :

39.

	Column - I (Reagent/Reaction)	*Column - II* (Product)
(A)	Reductive amination	(a) 1° amines
(B)	Isonitriles	(b) 2° amines
(C)	Hofmann rearrangement	(c) 3° amines
(D)	Alkyl azides	(d) Isocyanate is formed as intermediate

40.

	Column - I	*Column - II*
(A)	Tertiamine oxide	(a) Regioselective
(B)	Hofmann elimination	(b) Stereospecific
(C)	Cope elimination	(c) Zwitterion
(D)	Mustard oil reaction	(d) Isothiocyanates

41. Match the following in which reactions match with the name given on RHS in any way, i.e reactant, product, intermediate or reagent.

	Column I	*Column II*
(A)	Beckmann rearrangement	(a) Isocyanate
(B)	Hofmann bromamide rearrangement	(b) Amide
(C)	Curtius reaction	(c) Amine
(D)	Fries reaction	(d) $AlCl_3$

42. Match each of the compounds in **Column I** with its characteristic reaction(s) in **Column II**.

	Column I	**Column II**
(A)	$CH_3CH_2\ CH_2CN$	(a) Reduction with Pd–C/H_2
(B)	$CH_3\ CH_2\ OCOCH_3$	(b) Reduction with $SnCl_2$/HCl
(C)	CH_3–CH= CH–CH_2OH	(c) Development of foul smell on treatment with chloroform and alcoholic KOH
(D)	$CH_3CH_2CH_2CH_2NH_2$	(d) Reduction with diisobutylaluminium hydride(DIBAL-H)
		(e) Alkaline hydrolysis

43.

	Column I	*Column II*
(A)	Allylic rearrangement	(a) Carbanions
(B)	Hofmann rearrangement	(b) Electron deficient species
(C)	Wittig reaction	(c) Carbocations
(D)	Carbylamine reaction	(d) Carbenes

44.

	Column - I	**Column - II**
(A)	Hofmann degradation	(a) Amides
(B)	Beckmann rearrangement	(b) Isocyanates
(C)	Curtius rearrangement	(c) $NaOH/Br_2$
(D)	Lossen rearrangement	(d) $RCON_3$

45. Match the column correctly –

	Column I	**Column II**
(A)	Conversion of amide	(a) Quaternary salt to amine
(B)	Conversion of primary amine to isocyanide	(b) Schmidt reaction
(C)	Tetraethylammonium iodide	(c) Carbylamine reaction
(D)	$RCOOH + N_3H + H_2SO_4$	(d) Hofmann's bromamide reaction.

Instructions for Q. 46 to 54 : Following questions are Assertion and Reasoning Type Questions :

Note : Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 5 choices (a), (b), (c), (d) and (e) out of which ONLY ONE is correct.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.

(c) Statement -1 is True, Statement-2 is False.

(d) Statement -1 is False, Statement-2 is True.

(e) Statement -1 is False, Statement-2 is False.

46. **Statement 1 :** Amines are basic in nature

Statement 2 : The lone pair of electron is present on nitrogen atom.

47. **Statement 1 :** In order to convert R – Cl to pure R–NH_2. Gabriel pthalimide synthesis can be used.

Statement 2: With proper choice of alkyl halides, pthalimide synthesis can be used to prepare 1°, 2° or 3° amines.

48. **Statement 1:** In Hofmann bromide reaction, the amine formed has one carbon atom less than the parent 1° amide.

Statement 2: N-methyl acetamide undergoes hofmann bromamide reaction.

49. **Statement 1:** Ammonia is less basic than water.

Statement 2 : Nitrogen is less electronegative than oxygen.

50. **Statement-1 :** 1° Amides react with Br_2 + NaOH to give 1° amines with one carbon atom less than the parent amide.

Statement-2 : The reaction occurs through intermediate formation of acylnitrene.

51. **Statement-1 :** In order to convert R–Cl to pure R–NH_2, Gabriel-phthalimide synthesis can be used.

Statement-2 : With proper choice of alkyl halides, phthalimide synthesis can be used to prepare 1°, 2° or 3° amines.

52. **Statement-1 :** Acetamide reacts with Br_2 in presence of methanolic CH_3ONa to form methyl N-methylcarbamate.

Statement-2 : Methyl isocyanate is formed as an intermediate which reacts with methanol to form methyl N-methylcarbamate.

53. **Statement-1 :** 1°, 2° and 3° amines are hydrogen-bonding donors, while 1° and 2° amines are hydrogen-bonding acceptors.

Statement-2 : Low molecular weight amines are soluble in water.

54. **Statement-1 :** Hofmann elimination gives alkene

Statement-2 : Alkenes are less acidic than NH_3

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EXERCISE 19.3 (Subjective Problems)

1. Write down the structures, names and type (1°, 2°, 3°) of

(*a*) the isomeric amines of the formula $C_4H_{11}N$

(*b*) the isomeric amines having benzene nucleus of the formula C_7H_9N.

(*c*) the five isomeric cyclic compounds having the molecular formula C_4H_9N.

2. Give the structural formulas of the following compounds.

(*a*) *sec*- Butylamine

(*b*) β-Phenylethylamine

(*c*) Diphenylamine

(*d*) N, N-Dimethylaminocyclohexane

(*e*) Tetra-isobutylammonium iodide

(*f*) *sec*-Butylammonium benzoate

(*g*) Ethyl 3-(N-methylamino)-2-butenoate.

3. Mention the sequence of reagents used in the preparation of *n*-propylamine from each of the following compounds.

(*a*) *n*-Propyl bromide (*b*) *n*-Propyl alcohol

(*c*) Ethanol (*d*) *n*-Butanol

(*e*) *n*-Butyramide

Mention which of the above corresponding compound can be used for preparing aniline and benzylamine ?

4. Prepare *n*-propylamine by

(*a*) alkyl halide amination

(*b*) reductive amination

(*c*) amide reduction

(*d*) nitrile reduction

(*e*) Hofmann rearrangement, and

(*f*) Curtius reaction.

5. Gabriel synthesis is not recommended for preparing following amines, explain.

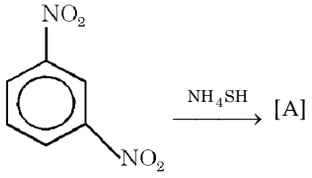
(*a*) *tert*-Butylamine

(*b*) Neopentylamine

(*c*) Diethylamine

(*d*) *p*-Toluidine.

6. Identify compounds A to D.

(*a*) 

(*b*) $CH_2 = CHCH_2Li \xrightarrow{NaN_3} [B] \xrightarrow[H_2/pt]{LiAlH_4} [C] \quad [D]$

7. Give the structures for the products of the reductive amination with H_2/Ni of

(*a*) CH_3CHO with (*i*) NH_3, (*ii*) $C_2H_5NH_2$, and (*iii*) $C_2H_5NHCH_3$

(*b*) $(CH_3)_2CO$ with (*i*) NH_3, (*ii*) $C_2H_5NH_2$, and (*iii*) $C_2H_5NHCH_3$.

8. (*a*) What are the advantages of reductive amination over the reaction of alkyl halides with amines.

(*b*) How can you ensure a good yield of RR′NH (a 2° amine) from RNH_2 and R′ X ?

9. Two α, ω-diamines have been isolated from the rotting flesh ; one has the molecular formula $C_4H_{12}N_2$ and the other $C_5H_{14}N_2$. Give two methods for preparing each of them from α, ω-dihalides.

10. Write chemical equations for the reactions of CH_3NH_2 with (*i*) H_2O, (*ii*) HCl(*g*), (*iii*) B $(CH_3)_3$.

11. Compare the basicities of

(*a*) $C_6H_5NH_2$, $(C_6H_5)_2NH$, NH_3, and cyclohexyl—NH_2.

(*b*) aniline, *p*-methyoxyaniline, *p*-nitroaniline

(*c*) benzylamine,*m*-chlorobenzylanine,*m*-ethylbenzylamine,

(*d*) *p*-chloro-N-methylaniline, 2, 4-dichloro-N-methylaniline, 2, 4, 6-trichloro-N-methylaniline.

12. Which is more basic : an aqueous solution of trimethylamine or an aqueous solution of tetramethylammonium hydroxide ?

13. What do you expect about the solubility of N-nitrosoamines in aq. HCl ?

14. Give the structure of the compound formed, if any, when ethylamine is treated with

(*a*) acetic acid (*b*) isobutyryl chloride

(*c*) dil. NaOH (*d*) benzyl bromide

(*e*) chlorobenzene (*f*) 2,4,6-trinitrochlorobenzene

(*g*) phthalic anhydride (*h*) acetone, H_2/Ni

(*i*) sodium chloroacetate.

15. Compare the behaviour of ethylamine, diethylamine and triethylamine with each of the following reagents.

(*a*) dil. HCl (*b*) methyl iodide

(*c*) acetic anhydride (*d*) benzenesulphonyl chloride

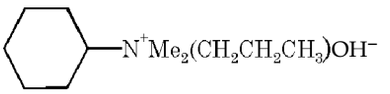
(*e*) $NaNO_2$ + aq. HCl.

16. Compare and account for the products obtained from thermal decomposition of following compounds.

(*a*) $[(CH_3)_3\,N^+C_2H_5]\,OH^-$

(*b*) $(CH_3)_4N^+OH^-$

(*c*) $C_6H_5N^+Me_3OH$

(*d*) 

17. Give structures and names of the principal products obtained from the action, if any, of sodium nitrite and hydrochloric acid on each of the following.

(*a*) *n*-Propylamine (*b*) 2-Amino-3-methylbutane

(*c*) 4, 4′-Diaminodiphenyl (*d*) N, N-Dimethylaniline

(*e*) Sulphanilic acid (*f*) Benzylamine.

18. Give the structures of all possible products obtained by the action of sodium nitrite and hydrochloric acid on

(*a*) isobutylamine, and (*b*) neopentylamine.

19. Write the equation involved in the formation of nylon-6, 6 when hexamethylenediamine is heated with adipic acid, Addition of a drop of HCl on the fabric nylon-6, 6 makes a hole, explain the chemistry involved.

20. Name the reagent or test used to distinguish between the following pairs.

(*a*) $n\text{-}C_3H_7NH_2$ and $(n\text{-}C_3H_7)_2NH$

(*b*) $(n\text{-}C_3H_7)_2$ NH and $(n\text{-}C_3H_7)_3N$

(*c*) Me_3NHCl and Me_4NCl

(*d*) $Me_2NCH_2CH_2OH$ and Me_4NOH

(*e*) $C_6H_5NH_2$ and $C_6H_5NHCOCH_3$

(*f*) $C_6H_5NH_3Cl$ and $p\text{-}ClC_6H_4NH_2$

(*g*) $C_6H_5NH_2$ and 2, 4, 6-trinitroaniline

(*h*) $C_2H_5NH_3Cl$ and $NH_2CH_2CH_2Cl$

(*i*) $C_2H_5NH_3HSO_4$ and $C_2H_5NHSO_2C_6H_5$.

21. Describe the simple chemical tests that can be used to distinguish among members of each of the following set :

(*a*) Aniline, benzylamine and N, N-dimethylbenzylamine

(*b*) Formamide, benzonitrile and N, N-dimethylaniline

(*c*) Nitrobenzene, *m*-tolunitrile and N, N-dimethyl-*m*-toluidine.

22. An organic solid compound A ($C_{13}H_{11}ON$) is insoluble in aqueous NaOH and aqueous HCl. However, its prolonged heating with aqueous NaOH gives a liquid (B) and a solution of compound (C). Compound B can be separated from C by steam distillation, its solution in hydrochloric acid gives a red solid on treatment with sodium nitrite followed by β-naphthol. Acidification of C gives white precipitate of the compound D ($C_7H_6O_2$) which on distillation with soda lime gives benzene. Identify compound A and give reactions to explain all reactions.

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SOLUTIONS

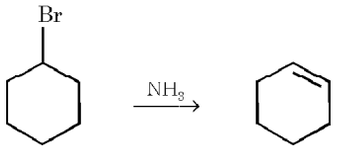
EXERCISE 19.1

1	(c)	**11**	(d)	**21**	(a)	31	(b)	**41**	(a)	**51**	(d)	**61**	(c)
2	(b)	**12**	(b)	**22**	(a)	**32**	(d)	**42**	(a)	**52**	(b)	**62**	(d)
3	(a)	**13**	(c)	**23**	(a)	**33**	(b)	**43**	(d)	**53**	(c)	**63**	(c)
4	(b)	**14**	(a)	**24**	(b)	**34**	(d)	**44**	(b)	**54**	(a)	**64**	(b)
5	(b)	**15**	(a)	**25**	(b)	**35**	(b)	**45**	(d)	**55**	(a)	**65**	(c)
6	(c)	**16**	(a)	**26**	(c)	**36**	(d)	**46**	(a)	**56**	(d)	**66**	(c)
7	(c)	**17**	(b)	**27**	(d)	**37**	(c)	**47**	(d)	**57**	(c)	**67**	(a)
8	(b)	**18**	(b)	**28**	(c)	**38**	(c)	**48**	(c)	**58**	(d)		
9	(b)	**19**	(c)	**29**	(b)	**39**	(b)	**49**	(b)	**59**	(b)		
10	(c)	**20**	(b)	**30**	(c)	**40**	(b)	**50**	(b)	**60**	(d)		

1. Methylaniline can be $C_6H_5NHCH_3$, *o*-, *m*- and *p*-$CH_3C_6H_4NH_2$.

2. $RX + NH_3$ (excess) $\longrightarrow RNH_2 + HX$; $NH_3 + HX \longrightarrow NH_4^+ + X^-$.

3. Reaction of 2° halide with ammonia (a base) is always accompanied by some elimination product.



4. In Hofmann's method, the starting material is amide (not amine). Reaction of alkyl halide with ammonia may lead to the formation of a mixture of amines (1°, 2° and 3°).

5. In option (*a*), $C_6H_5NH_2 + CH_3I$ may form 4° salt as a by product. In option (*c*), CH_2O is converted to CH_2O^+H which may cause electrophilic aromatic substitution.

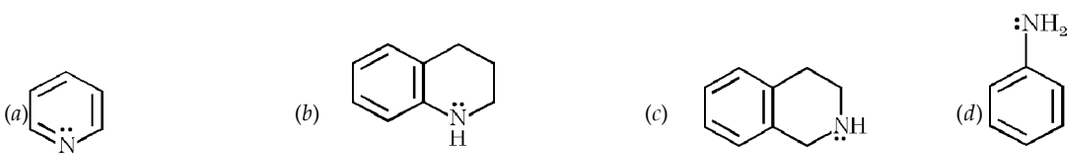
6. $CH_3CH_2CN \xrightarrow{H^+} CH_3CH_2COOH \xrightarrow{NH_3} CH_3CH_2COONH_4 \xrightarrow{heat} CH_3CH_2CONH_2 \xrightarrow{Br_2, OH^-} CH_3CH_2NH_2$.

7. Consult mechanism of Hofmann's Bromamide reaction.

8. Although N is also chiral but its three substituents interconvert due to lone pair of electrons on nitrogen, hence it should be non-resolvable due to chiral N.

9. $R_4N^+OH^-$ behaves like NaOH or KOH.

10. In options (*a*), (*b*) and (*d*), lone pair of electrons is involved in delocalization because of presence of π electrons in the conjugate position.



11. In gas phase, solvation effect is absent, hence basicity is due to alkyl group.

12. Steric factor. More is crowding near the $—NH_2$ group lesser is its capacity to accept H^+.

13. *tert*-Amine molecules can not associate because of absence of H-bonding.

14. Electronegativity of O, N and C follows the order : O > N > C.

15. (*i*) Fluorine decreases electron density on N. (*ii*) F stabilizes the conjugate acid, $FCH_2CH_2NH_3^+$, by dispersing +ve charge on N.

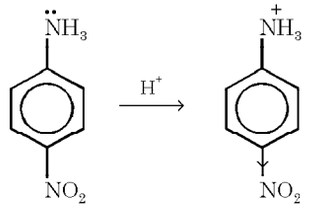
16. In $CH_3—\overset{\overset{O}{\|}}{C}—\ddot{N}H_2$, electron pair is delocalized.

17. $C_6H_5NHNH_2 + HCl \longrightarrow C_6H_5NHNH_3^+Cl^-$ $\qquad$ $CH_3NHNH_2 + HCl \longrightarrow CH_3N^+H_2NH_2Cl^-$.

Electron releasing character of the $—CH_3$ group increases electron density on the first N.

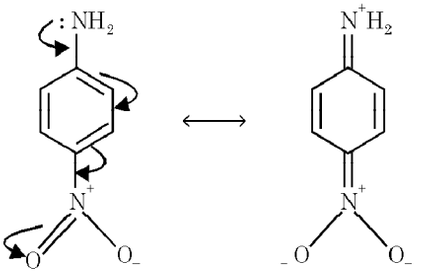
18. In II, intermolecular H-bonding between similar molecules is possible, while this is not so in I.

19. (*a*)



—M, —I effect of the $—NO_2$ group increases +ve charge on N, hence destabilize the intermediate

(*b*)

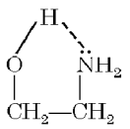


Delocalization of electron on N of the $—NH_2$ group stabilizes the amine

20. In NOCl, Cl^- is a weak base hence good leaving group.

21. H_2O is less basic, hence good leaving group than OH^-.

22. Intramolecular H-bonding decreases nucleophilicity and hence reactivity of the $—NH_2$ group.



23. $(C_6H_5)_3$ N: does not react with BF_3 because of delocalization of electrons on N to three benzene rings.

24. Chloroacetic acid protonates phthalimide.

25. $CH_3CH_2CH_2CH_2NH_2 \xrightarrow{HONO} CH_3CH_2CH_2\overset{+}{C}H_2 \longrightarrow CH_3CH_2\overset{+}{C}HCH_3$

1° carbocation 2° carbocation

$\longrightarrow CH_3CH = CHCH_3 + CH_3CH_2CH = CH_2$

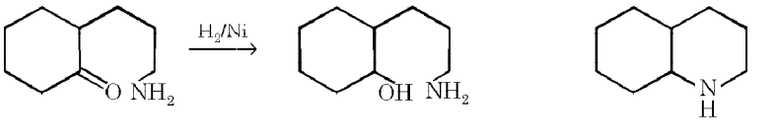
cis- and *trans*- Butene-2 Butene-1

26. $Me_3CCH_2NH_2 \xrightarrow{HONO} Me_3C\overset{+}{C}H_2 \longrightarrow Me_2\overset{+}{C}CH_2CH_3 \longrightarrow Me_2C(OH)CH_2CH_3.$

1° carbocation 3°carbocation

27. 2° Halides mainly undergo elimination with base like NH_3.

28.



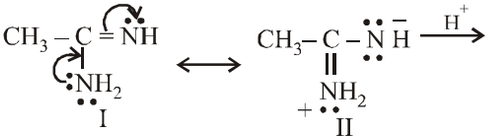
29. **(b)** (i) Position (X) is most acidic due to – COOH group.

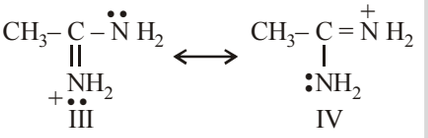
(ii) $-NH_3^+$ group at position Y is more acidic than at Z because of presence of electron withdrawing – COOH group in close proximity. Hence $-NH_3^+$ group at position Z is least acidic.

30. **(c)** This is an example of carbylamine reaction

$$CHCl_3 + RNH_2 + KOH \longrightarrow R - N^+ \equiv C^- + 3KCl + 3H_2O$$

31. **(b)**

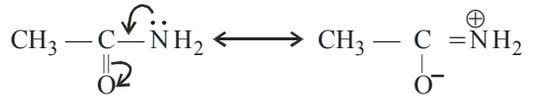




The protonated form of II would be III which is more stable because here the contributing structures (III) and (IV) are equivalent.

In $CH_3 - \ddot{N}H - CH_3$, the availability of electron pair increases due to the +I effect of two CH_3 groups while in $CH_3CH_2NH_2$, +I effect of only one ethyl group is operative.

In $CH_3 - \underset{\underset{O}{\|}}{C} - NH_2$, the electron availability on nitrogen decreases due to resonance as shown below



Therefore, the order of basic strength would be 1 > 3 > 2 > 4.

32. **(d)** Aromatic amines are less basic than aliphatic amines. Among aliphatic amines the order of basicity is 2° > 1° > 3°. The electron density is decreased in 3° amine due to crowding of alkyl group over N atom which makes the approach and bonding by a proton relatively difficult. Therefore the basicity decreases. Further Phenyl group show – I effect, thus decreases the electron density on nitrogen atom and hence the basicity.

$\therefore$ dimethylamine (2° aliphatic amine) is strongest base among given choices.

$\therefore$ The correct order of basic strength is

Dimethylamine > Methyl amine > Trimethyl amine > Aniline.

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33. **(b)** The alkyl groups are electron releasing group (+ I), thus increases the electron density around the nitrogen thereby increasing the availability of the lone pair of electrons to proton or lewis acid and making the amine more basic. Hence more the no. of alkyl group more basic is the amine. Therefore the correct order is

$NH_3 < CH_3NH_2 < (CH_3)_2N$

34. **(d)** Ethyl isocyanide on hydrolysis form primary amines.

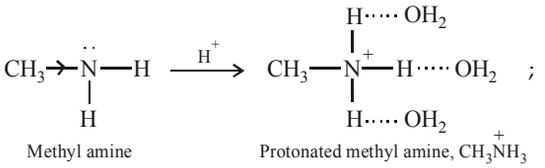
$$CH_3CH_2N\equiv C + H_2O \xrightarrow{H^+} CH_3CH_2NH_2 + HCOOH$$

Therefore it gives only one mono chloroalkane.

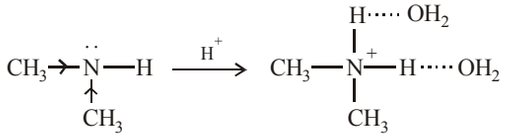
35. **(b)** Wurtz reaction is for the preparation of hydrocarbons from alkyl halide

$$RX + 2Na + XR \longrightarrow R - R + 2NaX$$

36. **(d)** The basic character of an amine in water is determined by (i) electron availability on the N atom and (ii) the extent of stabilization of the cation (protonated amine) due to solvation by hydrogen bonding

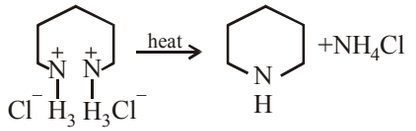


Methyl amine — Protonated methyl amine, $CH_3\overset{+}{N}H_3$ (Highly stabilized)

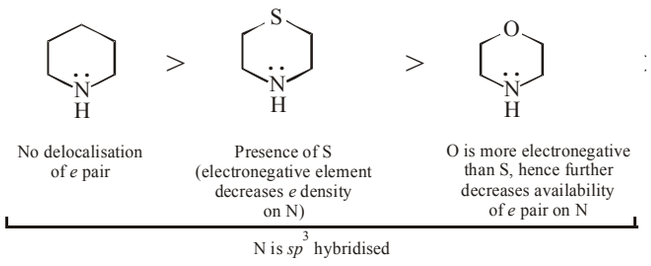


Dimethyl amine — Protonated dimethyl amine (Lesser stabilized than $CH_3\overset{+}{N}H_3$)

37. **(c)**

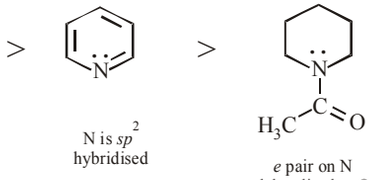


38. **(c)**



No delocalisation of *e* pair — Presence of S (electronegative element decreases *e* density on N) — O is more electronegative than S, hence further decreases availability of *e* pair on N

N is sp^3 hybridised



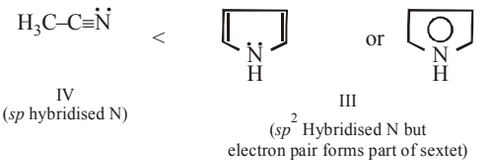
N is sp^2 hybridised — *e* pair on N delocalised to O

39. **(b)** Reaction is an example of **Schmidt reaction** in which carboxylic acids are heated with hydrazoic acid in presence of a mineral acid to form primary amines.

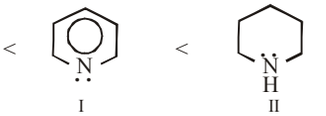
$$RCOOH + HN_3 \xrightarrow{\text{conc. } H_2SO_4} RNH_2 + CO_2$$

40. **(b)** Cold dil. NaOH does not attack to either of the compound, while cold dil. HCl reacts only with benzyl amine $C_6H_5CH_2NH_2$.

41. **(a)** The four compounds differ in two respects : Compounds II has sp^3 hybridised N, compounds I and III have sp^2 while compound IV has *sp* hybridised N. Now we know that greater the *s* character of an orbital, more tightly its electrons are held and hence lesser will be their availability for protonation causing weak basic character. Thus the basic character of the three N's is sp^3N > sp^2 N > *sp* N. However, in pyrrole electrons on N are part of aromatic sextet, i.e., these are delocalised and hence lesser available for protonation and thus pyrrole is a weaker base than pyridine because in pyridine nonbonding electrons present in sp^2 orbital do not form a part of aromatic sextet. Thus the basic character should be in the following order.

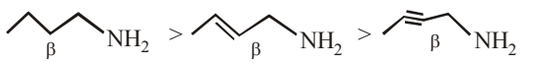


IV (*sp* hybridised N) — III (sp^2 Hybridised N but electron pair forms part of sextet)



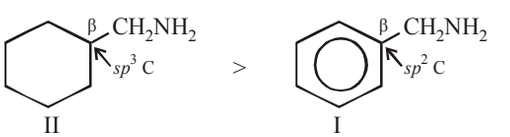
I (sp^2 Hybridised N; electron pair not a part of sextet) — II (sp^3 Hybridised N)

42. **(a)** Note the point of difference in the given compounds which here lies at β-carbon. In I, II, III, the β-carbon atoms are sp^3, sp^2 and *sp* hybridised respectively which in turn cause the difference in their *s* character. We know that more is the *s* character of an atom, greater will be its electron-withdrawing nature. Thus *sp* (50% *s* character) hybridised carbon is most electron-withdrawing, while sp^3 (25% *s* character) is least electron-withdrawing. Further, we know that presence of an electron-withdrawing group decreases basicity of an amine. Thus



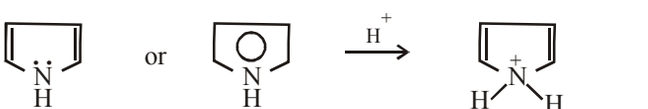
I (β – C sp^3 hybridised) — II (β – C sp^2) — III (β – C *sp*)

43. **(d)** Here again the two amines differ in the nature of β-carbon atom

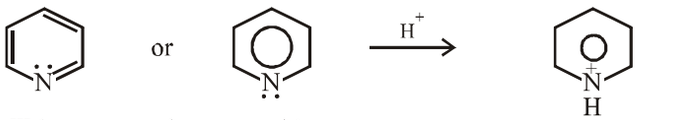


II — I

44. **(b)**



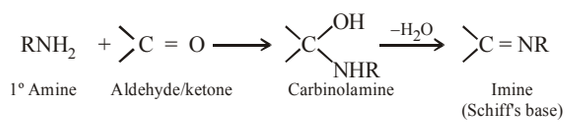
I (Sextet present, hence aromatic) (*e* pair on N forms a part of aromatic sextet) — II (not aromatic) (Aromatic sextet is not present because *e* pair is involved in protonation)



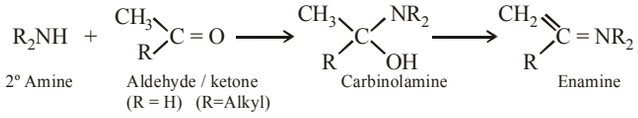
III (sextet present, hence aromatic)
(*e* pair on N, not a part of sextet)

IV (sextet present, hence aromatic)

45. (d)

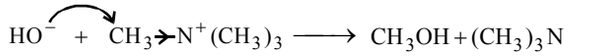


1° Amine Aldehyde/ketone Carbinolamine Imine (Schiff's base)

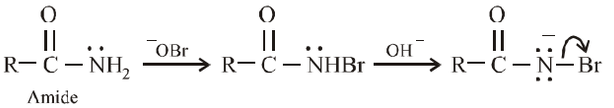


2° Amine Aldehyde / ketone (R = H) (R=Alkyl) Carbinolamine Enamine

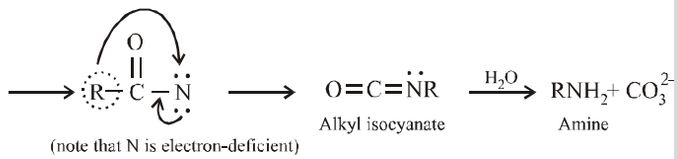
46. (a) Due to greater electronegativity of N over S, positive charge on N will make the methyl groups more electron- deficient than that on positively charged S. Therefore, $(CH_3)_4N^+I^-$ will undergo nucleophilic substitution more readily than the sulphur analogue.



47. (d) For this one should remember that Hofmann's degradation involves migration to electron deficient nitrogen atom, hence the alkyl group will migrate with its bonding pair of electrons.

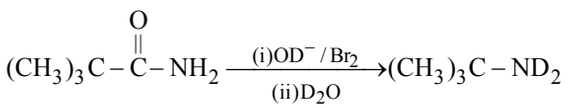


Amide

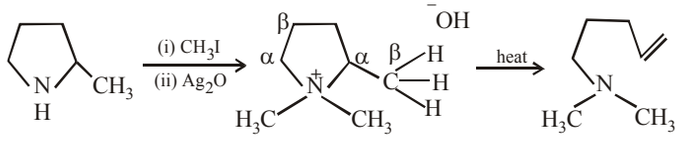


(note that N is electron-deficient) Alkyl isocyanate Amine

48. (c) Remember that in Hofmann rearrangement, the two original H atoms of the $-CONH_2$ group are removed by base (OH^-) and new H's are derived from H_2O.



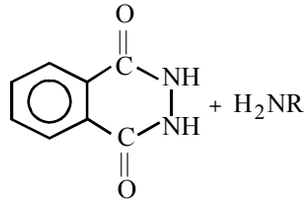
49. (b)



50. (b) $R-N=C=O$ (Alkyl isocyanate) is the common intermediate in the four reactions.

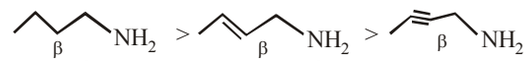
51. (d) All the three are formed.

53. (c) The reaction is an example of hydrazinolysis.



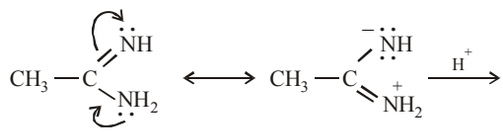
54. (a) In presence of chlorobenzene, hydrogen bonding is not possible between the protonated amine and the solvent and thus the stabilization factor (solvation effect) is absent. Hence basicity is explained on the basis of the number of electron releasing groups in an amine.

55. (a) Note the point of difference in the given compounds which here lies at β-carbon. In I, II, III, the β-carbon atoms are sp^3, sp^2 and *sp* hybridised respectively which in turn cause the difference in their *s* character. We know that more is the *s* character of an atom, greater will be its electron-withdrawing nature. Thus *sp* (50% *s* character) hybridised carbon is most electron-withdrawing, while sp^3 (25% *s* character) is least electron-withdrawing. Further, we know that presence of an electron-withdrawing group decreases basicity of an amine. Thus

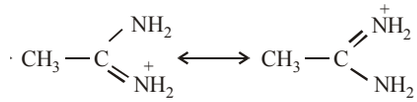


I (β – C sp^3 hybridised) II (β – C sp^2) III (β – C *sp*)

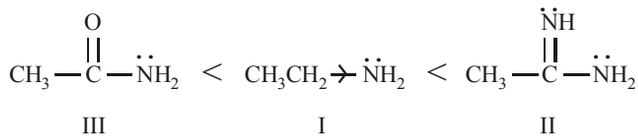
56. (d) II is most basic because delocalisation of electron pair leads to negative charge on N making it electron-rich and hence liable to be attacked by proton very easily. Moreover, the corresponding protonated species is very much stable because of equivalent contributing structures.



II



Species III is least basic because of delocalisation of electron pair on N, making it less available for protonation. Species I lies in mid-way, thus



III I II

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57. **(c)** Although aliphatic 1° amines form diazonium salts, these are unstable and decompose to alkyl carbocation which can form variety of normal as well as rearranged products

$$CH_3CH_2CH_2NH_2 \xrightarrow[0°C]{HONO} \underset{\text{Unstable}}{\left[CH_3CH_2CH_2\overset{+}{N}_2Cl^-\right]}$$

$$\rightarrow CH_3CH_2\overset{+}{C}H_2 + N_2 + Cl^-$$

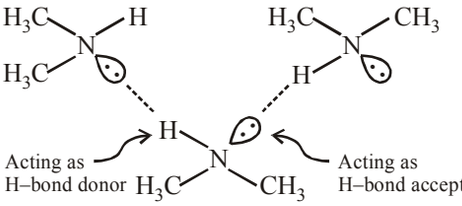
$$CH_3CH_2CH_2OH \xleftarrow{H_2O} \underset{\text{1° Carbocation}}{CH_3CH_2\overset{+}{C}H_2} \longrightarrow$$

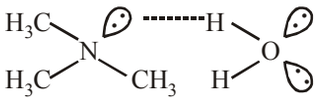
$$CH_3\overset{+}{C}HCH_3 \xrightarrow{Cl^-} CH_3\overset{Cl}{\overset{|}{C}}HCH_3$$

2° Carbocation

58. **(d)** Most of the simple amines those having smaller alkyl (groups) can't be resolved , although they may contain three different alkyl groups.

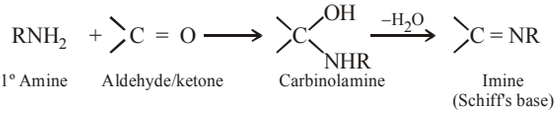
59. **(b)** Hydrogen bonding is a strong intermolecular attraction between an electrophilic O–H or N–H hydrogen atom and a pair of non-bonding electrons. Thus a hydrogen bond requires both a **hydrogen bond donor** (a molecule having O–H or N–H group) and a **hydrogen bond acceptor** (a molecule having lone pair of electrons). Thus dimethyl amine can serve as hydrogen bond donor due to N–H group as well as hydrogen bond acceptor due to lone pair of electrons on N. Such molecules can form hydrogen bond with themselves and also with water (or other hydrogen bond donor). On the other hand, trimethyl amine can serve only as hydrogen bond acceptor since it has lone pair of electrons but not hydrogen on N. Hence it can form hydrogen bond with water but not with themselves.

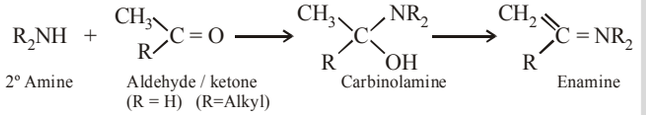




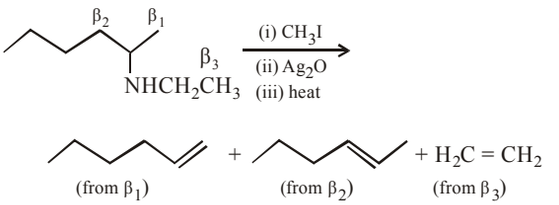
Trimethyl amine only as
H– bond acceptor

60. **(d)**



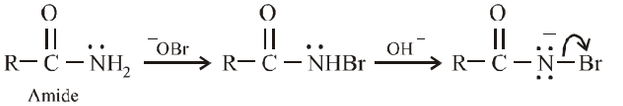


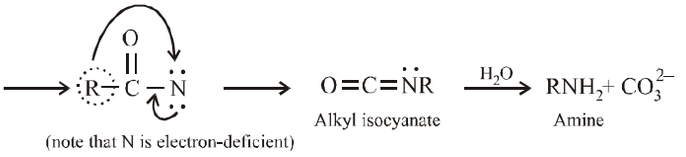
61. **(c)** The given amine has three β-hydrogens, hence it can form three alkenes of which least substituted ($H_2C=CH_2$) will be the major product (Hofmann product or Hofmann elimination).



In Hofmann elimination H atom (in the form of proton) is eliminated from that β carbon atom which has maximum number of H atom(s). This is due to the fact that Hofmann elimination (an example of E2 reaction) requires anti-coplanar arrangement of the β H atom and the leaving group. Further, higher the chances for this arrangement to remain in staggered conformation more will be the ease of elimination. Thus greater the number of H atom at β position, higher will be the chances for Me_3N^+– and H atom to remain in this particular conformation (anti-coplanar arragnement of Me_3N^+ – and H atom in staggered conformation).

62. **(d)** For this one should remember that Hofmann's degradation involves migration to electron deficient nitrogen atom, hence the alkyl group will migrate with its bonding pair of electrons.





63. **(c)** $CH_3NH_2 \xrightarrow[\text{excess}]{CH_3I} \underset{\text{(A)}}{(CH_3)_4N^+I^-} \xrightarrow{AgOH}$

$$\underset{\text{(B)}}{(CH_3)_4N^+OH^-} \xrightarrow{heat} \underset{\text{(C) and (D)}}{(CH_3)N + CH_3OH}$$

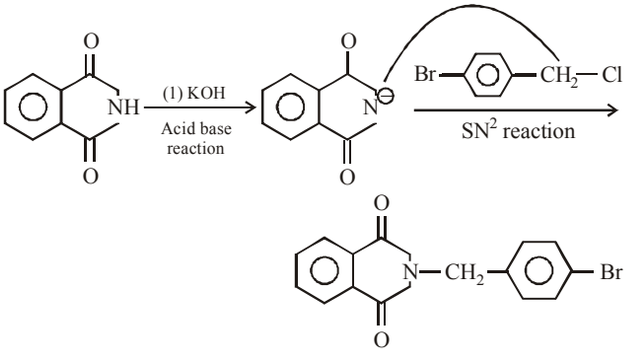
64. **(b)** Alkyl cyanides, nitroparaffins and acid amides on hydrolysis give carboxylic acids.

$$H-\overset{O}{\overset{\|}{C}}-N(CH_3)_2 \longrightarrow H-\overset{O}{\overset{\|}{C}}-OH + HN(CH_3)_2$$

65. **(c)** RCN on hydrolysis yields RCOOH (acid)

66. **(c)** **Hinsberg's reagent** is benzene sulphonyl chloride.
A **tertiary amine** does not react with **Hinsberg's** reagent and remains insoluble in aqueous KOH when it is treated with Hinberg's reagent in presence of excess of KOH.

67. (a)



EXERCISE 19.2

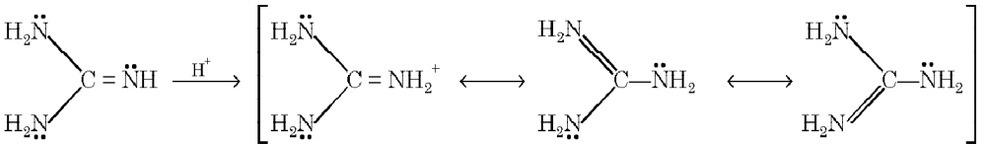
>1 CORRECT OPTION	**1**	(a,b)	**2**	(b,c,d)	**3**	(a,b,d)	**4**	(c,d)	**5**	(a,b,c)
	6	(a,b,d)	**7**	(a, b)	**8**	(a, b, c, d)	**9**	(a, b, c)	**10**	(a, b, c, d)
	11	(a, c, d)	**12**	(b, d)	**13**	(a, b, c)	**14**	(a, c)	**15**	(a, c, d)
	16	(a, b)	**17**	(b, c, d)	**18**	(a, c, d)	**19**	(a, b, d)	**20**	(b, d)
	21	(a, b, d)	**22**	(a, b, c)						
PASSAGE 1	**23**	(c)	**24**	(b)						
PASSAGE 2	**25**	(d)	**26**	(d)	**27**	(c)				
PASSAGE 3	**28**	(b)	**29**	(c)	**30**	(a)	**31**	(c)		
PASSAGE 4	**32**	(b)	**33**	(a, b)	**34**	(d)	**35**	(c)		
PASSAGE 5	**36**	(a, d)	**37**	(c, d)	**38**	(a)				
MATCH THE FOLLOWING	**39**	(A) - (a, b, c), (B) - (a, b), (C) - (a, d), (D) - (a)								
	40	(A) - (c), (B) - (a), (C) - (b, c), (D) - (d)								
	41	(A) - (b) ; (B) - (a, b, c) ; (C) (a, c) ; (D) - (d)								
	42	(A) - (a, b, d, e) ; (B) - (a, d, e) ; (C) a ; (D) - ©								
	43	(A) - (b, c) ; (B) - (b) ; (C)- (a) ; (D) - (b)								
	44	(A) - (a, b, b) ; (B) - (a) ; (C) -(b, d) ; (D) - (b)								
	45	(A) - (d) ; (B) - (c) ; (C)-(a) ; (D) - (b)								
A/R	**46**	(a)	**47**	(c)	**48**	(c)	**49**	(d)	**50**	(a)
	51	(c)	**52**	(a)	**53**	(b)	**54**	(b)		

1. For the preparation of Me_3CNH_2, the required alkyl halide is Me_3CX which will react with potassium phthalimide, a strong base, to form alkene rather than substituted product. For preparing $C_6H_5NH_2$, C_6H_5Cl will be the starting halide in which Cl is non-reactive.

2. Vinyl and aryl halides do not undergo S_N2 reactions, unless activated by electron withdrawing group (in the *o*- and *p*-position in case of aryl halides). 3° Halides form alkenes on elimination.

3. In **reductive amination method**, products can have only CH_3, a 1°C, or 2°C bonded to N as in CH_3NH_2, RCH_2NH_2 or R_2CHNH_2 respectively. In the **reduction of oxime**, amine formed can have only 1° or 2°C bonded to N. In **Gabriel phthalimide method**, the required Me_3CCl would undergo elimination (E2) rather than substitution (S_N2).

4. On the basis of hybridisation, N (sp^3) of NH_2 with less *s* character should be more basic than N (sp^2) of the imino (= NH) group. However, N of imino group is more basic and it is this nitrogen which is protanated because its conjugate acid is resonance hybrid of three equivalent structures which accounts its unusual stability.



Guanidine Conjugate acid of guanidine

Unusual stability of the conjugate acid of guanidine explains why guanidine is the strongest organic known base

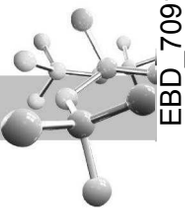
5. Consult text.

6. Hinsberg test is applicable to liquid amines which are insoluble in water because water solubility of the amine decreases nucleophilicity of nitrogen.

13. **(a,b,c)** Lower amines like NH_3, CH_3NH_2 and $(CH_3)_2NH$ break diborane molecule unsymmetrically, while larger amines like $(CH_3)_3N$, C_5H_5N break diborane in symmetrical manner.

$$B_2H_6 + 2NH_3 \longrightarrow [H_2B(NH_3)_2]^+[BH_4]^-$$

$$B_2H_6 + 2NH_3 \longrightarrow 2H_3B \longleftarrow N(CH_3)_3$$



14. **(a, c)** This is an example of Hoffmann degradation of amides.

$$R-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 \rightarrow R-\overset{\overset{O}{\|}}{C}-NHBr + HBr$$

$$R-\overset{\overset{O}{\|}}{C}.NHBr + KOH \rightarrow R-\overset{\overset{O}{\|}}{C}.N^-Br + H_2O + KBr$$

$$R-\overset{\overset{O}{\|}}{C}.N^-Br \xrightarrow{-Br^-} R-\overset{\overset{O}{\|}}{C}.N \xrightarrow{\text{rearrangement}} R-N=C=O \xrightarrow{H_2O} R-NH_2$$

15. **(a,c,d)** Diazomethane is used for methylating acidic groups ; compound IV has enolic —OH group, hence it can also be methylated by CH_2N_2.

16. **(a,b)** For the preparation of Me_3CNH_2, the required alkyl halide is Me_3CX which will react with potassium phthalimide, a strong base, to form alkene rather than substituted product. For preparing $C_6H_5NH_2$, C_6H_5Cl will be the starting halide in which Cl is non-reactive.

17. **(b,c,d)** Vinyl and aryl halides do not undergo S_{N^2} reactions, unless activated by electron withdrawing group (in the *o*- and *p*-position in case of aryl halides). 3° Halides form alkenes on elimination.

18. **(a,c,d)** In *p*-$NH_2C_6H_4COOH$, —COOH group is very weak so it can't transfer H^+ to the weakly basic amino group. All other three form zwitterions.

19. **(a,b,d)** *tert*-Nitro compounds (Me_3CNO_2) do not react with HONO because they do not have any α-H. The three others react with HONO as usual.

$$\underset{\text{2-Nitrobutane}}{CH_3-\overset{\overset{NO_2}{|}}{CH}CH_2CH_3} \xrightarrow{HONO} CH_3-\overset{\overset{NO_2}{|}}{\underset{\underset{NO}{|}}{C}}-CH_2CH_3$$

Pseudonitrol (**blue**)

28. **(b)** Species II (acylnitrene) is electron-deficient (N has only 6 electrons), hence it has a tendency to get its octet completed by the migration of alkyl group.

29. **(c)** $-OCH_3$ is more electron-releasing hence when the migrating aryl group has $-OCH_3$ in the para postion, its migration is accelerated.

30. **(a)** The migrating group (the group attached to C of the $-CONH_2$ part) never becomes free, so optical activity of the reactant is maintained.

31. **(c)** Since phenyl group (migrating group) does not become free, no cross product [i.e., (ii) and (iv)] is formed.

43. **A-b, c; B-b; C-a; D-b, d**

(A) Allylic rearrangements involve the migration of the double bond (and the functional group, if present) from one position to other. These reactions proceed through SN^1, SN^2, SE^1 and SE^2 mechanism; SN^1 involves carbocations (electron-deficient species), while SE^1 involves carbanion.

(B) Hofmann rearrangement involves nitrene $\left(R-\overset{\overset{O}{\|}}{C}-\ddot{N}:\right)$ intermediate in which nitrogen is electron deficient.

(C) Aldol condensation involves the attack of base on aldehyde or ketone, the reaction will involve the formation of carbanion.

(D) Carbylamine reaction involves the formation of dichlorocarbene ($:CCl_2$) as intermediate which is electron deficient.

50. **(a)** **R** is the correct explanation of **A**.

51. **(c)** **Correct R :** Only primary aliphatic amines can be prepared by Gabriel phthalimide reaction.

52. **(a)** **R** is the correct explanation of **A**.

EXERCISE 19.3

1. (*a*) 1° Amines **$CH_3(CH_2)_2CH_2NH_2$** $CH_3CH(NH_2)CH_2CH_3$ $(CH_3)_2CHCH_2NH_2$ **$(CH_3)_3CNH_2$**

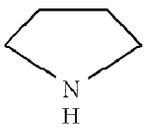
n-Butylamine; *sec*-Butylamine; Isobutylamine; *tert*-Butylamine

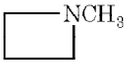
2° Amines $CH_3NHCH_2CH_2CH_3$ (Methylpropylamine); $CH_3NHCH(CH_3)_2$ (Methyl isopropylamine); $(CH_3CH_2)_2NH$ (Diethylamine)

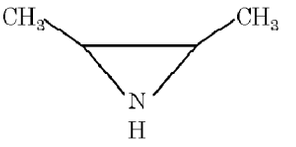
3° Amines $(CH_3)_2NCH_2CH_3$ (Ethyldimethylamine)

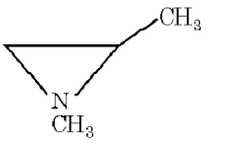
(*b*) **1° Amines** $C_6H_5CH_2NH_2$ (Benzylamine); *o*-, *m*-, and *p*-$CH_3C_6H_4NH_2$ (Toluidines)

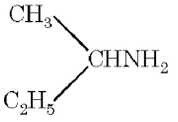
2° Amines $C_6H_5NHCH_3$ (N-Methylaniline)

(*c*) 
Pyrrolidine or Azacyclopentane (2° amine)


N-Methylazacyclobutane 3°(amine)

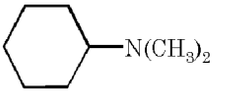

cis-and *trans*- 2, 3-Dimethylaziridine (2° amine)


N-Methyl-2-methylaziridine (3° amine)

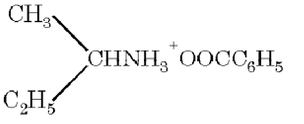
2. (*a*) 

(*b*) $C_6H_5CH_2CH_2NH_2$

(*c*) $C_6H_5—NH—C_6H_5$

(*d*) 

(*e*) $[(CH_3)_2CHCH_2]_4N^+I^-$

(*f*) 

(*g*) $CH_3C(NHCH_3)=CHCOOC_2H_5$

3. (*a*) excess of NH_3
(*b*) $C_6H_5NHCrO_3Cl$ (for oxidising —CH_2OH to —CHO), NH_3, H_2/Ni
(*c*) HBr, NaCN, H_2/Ni
(*d*) $K_2Cr_2O_7$, $SOCl_2$, NH_3, $Br_2/NaOH$
(*e*) $Br_2/NaOH$.

Aniline can be prepared only from C_6H_5Cl and that too under very vigorous conditions. Benzylamine can be prepared from all of the corresponding compounds except (*c*).

4. (*a*) $CH_3CH_2CH_2Br + NH_3\ (excess) \longrightarrow CH_3CH_2CH_2NH_2$

(*b*) $CH_3CH_2CHO + NH_3 \xrightarrow{H_2/Ni} CH_3CH_2CH_2NH_2$

(*c*) $CH_3CH_2CONH_2 \xrightarrow{LiAlH_4} CH_3CH_2CH_2NH_2$

(*d*) $CH_3CH_2CN \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} CH_3CH_2CH_2NH_2$

(*e*) $CH_3CH_2CH_2CONH_2 \xrightarrow{Br_2/KOH} CH_3CH_2CH_2NH_2$

(*f*) $CH_3CH_2CH_2COCl \xrightarrow{NaN_3} CH_3CH_2CH_2CON_3 \xrightarrow[H_2O]{heat} CH_3CH_2CH_2NH_2$

EBD_7091

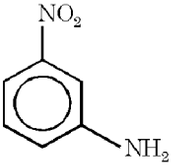
5. Recall that Gabriel phthalimide involves S_N2 reaction in one of the steps, so halides unreactive in S_N2 reaction (*e.g.* $CH_2 = CHX$, ArX) cannot be used.

(*a*) For preparing *tert*-butylamine, the corresponding *tert*-butyl chloride, being 3°, undergoes elimination reaction.

(*b*) For preparing neopentylamine, the corresponding alkyl halide (neopentyl chloride, Me_3CCH_2Cl) is sterically himdered at the carbon bearing Cl, so it can't undergo S_N^2 reaction.

(*c*) In potassium phthalimide, only one alkyl group can be introduced, hence Gabriel synthesis is used only for preparing 1° and not for 2° and 3° amines.

(*d*) For preparing *p*-toluidine, the corresponding halide would be *p*-$BrC_6H_4CH_3$ in which Br is not activated for nucleophilic substitution ; had there been an electron-withdrawing group as in *p*-$BrC_6H_4NO_2$, Br must have been replaced to form *p*-$NH_2C_6H_4NO_2$.

6. (*a*) 

(*b*) $CH_2 = CHCH_2N_3$, $CH_3CH_2CH_2NH_2$ $CH_2 = CHCH_2NH_2$

[A] [B] [C] [D]

7. (*a*) (*i*) $CH_3CH_2NH_2$, (*ii*) $CH_3CH_2NHC_2H_5$, (*iii*) $CH_3CH_2N(CH_3)C_2H_5$

(*b*) (*i*) $(CH_3)_2CHNH_2$, (*ii*) $(CH_3)_2CHNHC_2H_5$, (*iii*) $(CH_3)_2CHN(CH_3)C_2H_5$

8. (*a*) Although both processes give the same kind of products, in reductive amination successive amination is more easily controlled. Moreover, reductive amination can be successfully used for preparing amines having *sec*-alkyl group by taking corresponding ketone as one of the starting materials. Ammonolysis method can't be used for preparing such amines because the starting halide would be R_2CHX which may undergo E2 elimination under the given conditions.

(*b*) By using excess of RNH_2. However, this technique is useful only when the amine is relatively inexpensive.

9. Structural formula for the two α, ω-diamines (two —NH_2 groups present on the terminal carbon atoms) can be written as below.

$C_4H_{12}N_2$: $H_2NCH_2—[C_2H_4]—CH_2NH_2$ **or** $H_2NCH_2CH_2CH_2CH_2NH_2$ (Putrescine)

$C_5H_{14}N_2$: $H_2NCH_2—[C_3H_6]—CH_2NH_2$ **or** $H_2NCH_2CH_2CH_2CH_2CH_2NH_2$ (Cadaverine)

Synthesis of $C_4H_{12}N_2$.

(*i*) $Br(CH_2)_4Br \xrightarrow{NH_3} H_2N(CH_2)_4NH_2$

(*ii*) $BrCH_2CH_2Br \xrightarrow{KCN} NCCH_2CH_2CN \xrightarrow{Na/C_2H_5OH} H_2N(CH_2)_4NH_2$

Synthesis of $C_5H_{14}N_2$. (*i*) From $Br(CH_2)_5Br$; (*ii*) From $Br(CH_2)_3Br$.

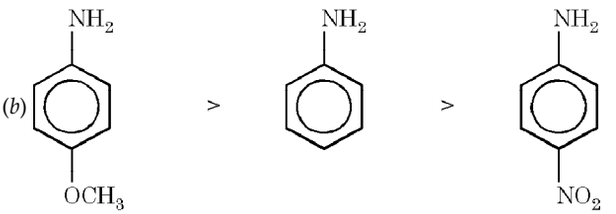
10. (*i*) $CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$

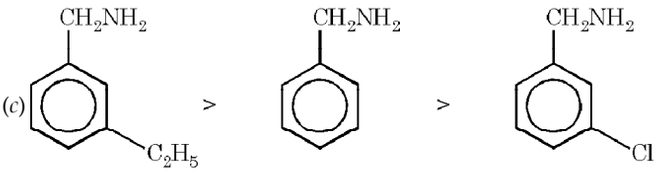
(*ii*) $CH_3NH_2 + HCl(g) \longrightarrow CH_3NH_3^+Cl^-(s)$

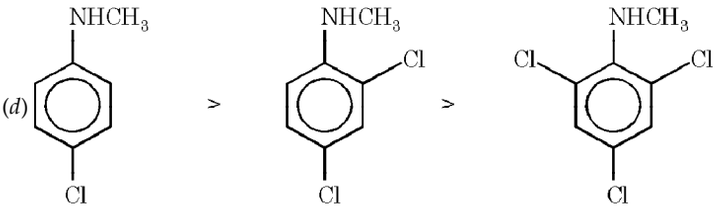
(*iii*) $CH_3\ddot{N}H_2 + B(CH_3)_3 \longrightarrow CH_3\underset{H_2}{N^+}—B^-(CH_3)_3$

11. Aliphatic amines are more basic than aromatic amines. Electron-releasing groups raise basicity, while electron-withdrawing groups lower basicity.

(*a*) *cyclo*-$C_6H_{11}NH_2$ > NH_3 > $C_6H_5NH_2$ > $(C_6H_5)_2NH$

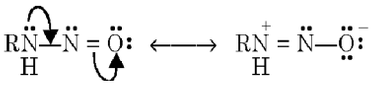
(*b*) 

(*c*) 

(*d*) 

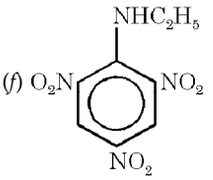
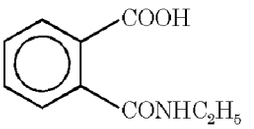
12. In aqueous solution of $(CH_3)_4N^+ OH^-$, the base is OH^-, which is much stronger than $(CH_3)_3N$.

13. N-Nitrosoamines are insoluble in aq. HCl because nitroso group (N = O) behaves like C = O in delocalizing electron density and weakening the basicity.



14. (*a*) $C_2H_5NH_3^+ {}^-OCOCH_3$ (*b*) $(CH_3)_2CHCONHC_2H_5$ (*c*) No reaction

(*d*) $C_2H_5NHCH_2C_6H_5$, $C_2H_5N(CH_2C_6H_5)_2$, $C_2H_5N^+(CH_2C_6H_5)_3\ Br^-$

(*e*) No reaction (*f*)  (*g*) 

(*h*) $C_2H_5NHCHMe_2$ (*i*) $C_2H_5NHCH_2COO^-Na^+$

15. (*a*) All the three form soluble ammonium salts

$C_2H_5NH_2HCl$ or $C_2H_5NH_3^+Cl^-$, $(C_2H_5)_2NH_2^+Cl^-$, $(C_2H_5)_3N^+HCl^-$

(*b*) All the three form quaternary ammonium salts

(*c*)

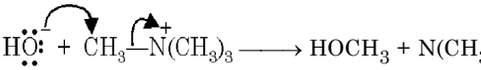
$C_2H_5NHCOCH_3$	$C_2H_5N(CH_3)COCH_3$	No reaction, $(C_2H_5)_3N$
Neutral amide	Neutral amide	Basic
Insoluble in dil. acid or base		Soluble in H^+, insoluble in base

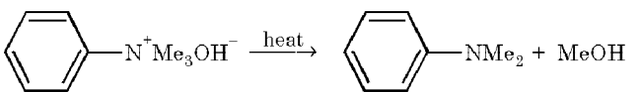
(*d*)

$C_2H_5NHSO_2C_6H_5$	$(C_2H_5)_2NSO_2C_6H_5$	$(C_2H_5)_3N$ (No reaction)
Acidic	Neutral	Basic
Soluble in aq.base	Insoluble in acid or base	Insoluble inbase, soluble in acid

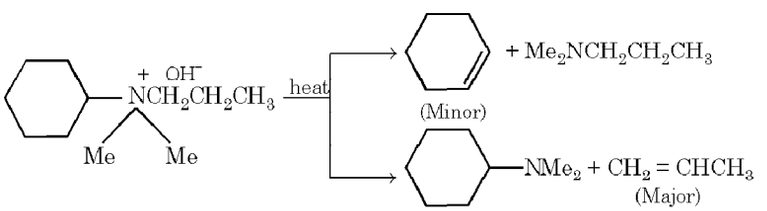
(*e*) $C_2H_5OH + N_2$ $(C_2H_5)_2N—N = O$ No reaction.

16. (*a*) $[(CH_3)_3 N^+C_2H_5]OH^- \xrightarrow{\text{heat}} (CH_3)_3N + CH_2 = CH_2 + H_2O$

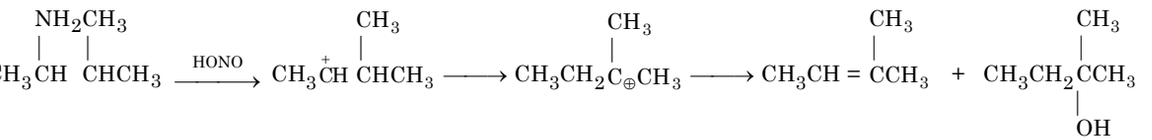
(*b*) 

(*c*) 

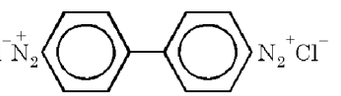
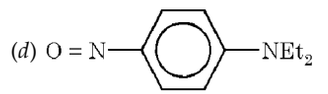
There is no β hydrogen, hence alkene is not formed.

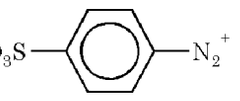
(*d*) 

17. (*a*) *n*-C_3H_7OH, $(CH_3)_2CHOH$, $CH_3CH = CH_2$, *n*-C_3H_7Cl, $(CH_3)_2CHCl$

(*b*) 

2° Carbocation 2-Methyl-2-butene *tert*-Pentyl alcohol (2-Methyl-2-butanol)

(*c*)  (*d*) 

(*e*)  (*f*) $C_6H_5CH_2OH + N_2$

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18. (*a*) $(CH_3)_2CHCH_2NH_2 \xrightarrow[(-N_2)]{HONO} CH_3-\overset{H}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-\overset{+}{C}H_2 \longrightarrow CH_3-\overset{\oplus}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3$

tert-Butyl cation

$(CH_3)_2CHCH_2OH + (CH_3)_2CHCH_2Cl + (CH_3)_2C=CH_2$ $\qquad$ $(CH_3)_2C=CH_2 + (CH_3)_3-COH + (CH_3)_3Cl$

(*b*) $CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2NH_2 \xrightarrow[(-N_2)]{HONO} CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2^+ \longrightarrow CH_3-\overset{+}{\underset{CH_3}{\overset{|}{C}}}-CH_2CH_3$

$\xrightarrow[\text{or } -H^+]{(i)\ OH^-} CH_3-\overset{OH}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2CH_3 + CH_3-\overset{CH_3}{\overset{|}{C}}=CHCH_3 + CH_2=\overset{CH_3}{\overset{|}{C}}-CH_2CH_3$

19. $HOOC(CH_2)_4COOH + H_2N(CH_2)_6NH_2 \longrightarrow Salt \xrightarrow[-H_2O]{heat} -\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-NH(CH_2)_6NH-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}NH(CH_2)_6NH-$

Adipic acid — Hexamethylenediamine — A polyamide (Nylon 6, 6)

Addition of HCl causes hydrolysis of the amide linkage and thus the polymer chain is cleaved which appears in the form of a hole.

20. (*a*) Hinsberg test $\qquad$ (*b*) Hinsberg test

(*c*) $Me_3N^+HCl^- \xrightarrow{OH^-} Me_3N$; $Me_4N^+Cl^- \xrightarrow{OH^-} Me_4N^+OH^-$

(odour or basic nature)

(*d*) CrO_3/H_2SO_4 positive only for $Me_2NCH_2CH_2OH$ which is an alcohol

(*e*) $C_6H_5NH_2$ (being basic) dissolves in aq. HCl ; $C_6H_5NHCOCH_3$ is neutral and hence insoluble in aq. HCl

(*f*) $AgNO_3$ gives AgCl only with $C_6H_5NH_3^+Cl^-$

(*g*) aq. HCl which dissolves only $C_6H_5NH_2$; 2, 4, 6-trinitroaniline being very very weak base does not dissolve in aq. HCl

(*h*) $AgNO_3$which gives AgCl only with $C_2H_5NH_3^+Cl^-$

(*i*) (*i*) $BaCl_2$ which gives $BaSO_4$ precipitate only with $C_6H_5NH_3^+HSO_4^-$

(*ii*) Water which dissolves only salt, *i.e* $C_6H_5NH_3^+HSO_4^-$.

21. (*a*)(*i*)Aniline gives red compound with HONO (cold) + β-naphthol.

(*ii*) Benzylamine ($C_6H_5CH_2NH_2$) and N, N-dimethylbenzylamine ($C_6H_5CH_2NMe_2$) can be differentiated by HONO or Hinsberg test

(*b*) Formamide ($HCONH_2$) is soluble in water, N, N-dimethylaniline is soluble in aq. HCl, but the neutral nitrile (C_6H_5CN) is insoluble

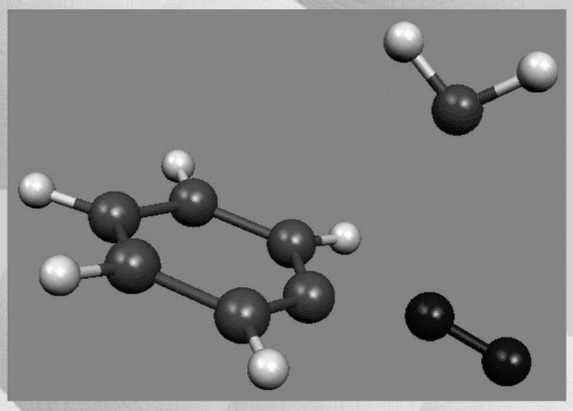
(*c*) Only N, N-dimethyl-*m*-toluidine is soluble in aq. HCl, hot aq. NaOH gives NH_3 with the nitrile (*m*-tolunitrile), while $C_6H_5NO_2$ is unreactive.

22. $C_6H_5NHCOC_6H_5 \xrightarrow[\text{heat}]{\text{aq. NaOH}} C_6H_5NH_2 + {}^+Na^-OOCC_6H_5$

Benzanilide (A) — (B) — (C)

$^+Na\ ^-OOCC_6H_5 \xrightarrow{H^+} HOOCC_6H_5 \xrightarrow[\text{lime}]{\text{Soda}} C_6H_6$

(C) — (D) — Benzene



20

Aromatic Amines and Diazonium Salts

CHAPTER HIGHLIGHTS

20.1 **Preparation of Aryl Amines**

20.2 **Properties of Aryl Amines**

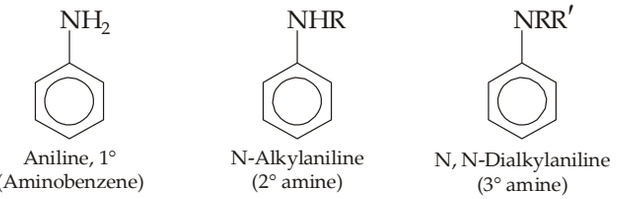
20.3 **Preparation and Reactions of Diazonium Salts**

20.4 **Illustrative Examples**

EXERCISES

SOLUTIONS

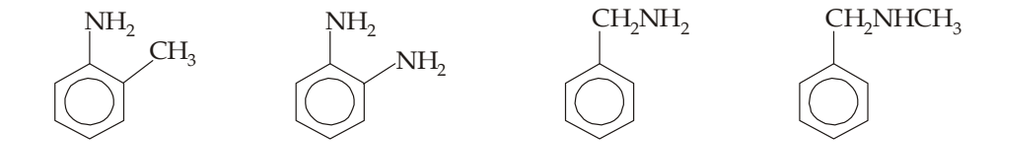
When 1°, 2°, or 3° amino group is directly attached to benzene nucleus, compunds are known as **aromatic amines** *or* **aryl amines**



Aniline, 1° (Aminobenzene) | N-Alkylaniline (2° amine) | N, N-Dialkylaniline (3° amine)

(R and R′ may be any alkyl or aryl (group)

One should note that when amino group is indirectly attached to benzene ring, the compound is called as aryl substituted aliphatic amine. In such compounds, —NH_2 group behaves as that of aliphatic amines.



o-Toluidine (*o*-Methylaniline) | *o*-Phenylenediamine | Benzylamine (1°) | N-Methylbenzylamine (2°)

Aromatic amines | Aryl substituted aliphatic amine



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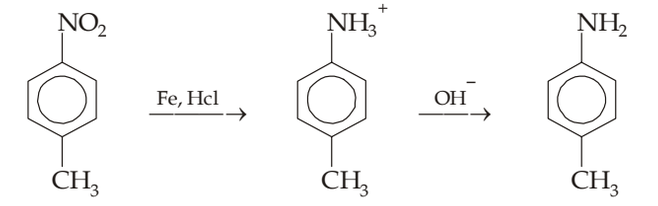
20.1 Preparation of Aryl Amines

Most of the methods used for preparing aromatic amines are very similar to that used for aliphatic amines.

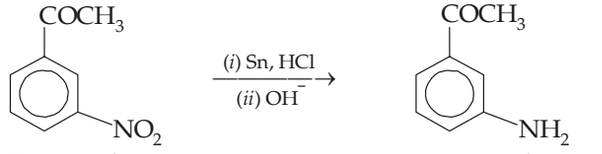
1. **Reduction of nitro compounds.** The most widely used method for preparing aromatic amines is the reduction of the nitro group to the amino group. This reduction can be achieved by catalytic hydrogenation, or most frequently with an acid and a metal (Fe, Zn, Sn) or a metal salt like $SnCl_2$.

$$C_6H_5NO_2 \xrightarrow[\text{or (i) Fe, HCl, (ii) } OH^-]{H_2\text{, Catalyst}} C_6H_5NH_2$$

Nitrobenzene — Aniline



p-Nitrotoluene — *p*-Toluidine



m-Nitroacetophenone — *m*-Aminoacetophenone

Remember that $LiAlH_4$ does not reduce $PhNO_2$ to $PhNH_2$.

Since nitro compounds are readily prepared by direct nitration, the primary aromatic amines obtained by the reduction of these nitro compounds are readily converted into diazonium salts ; the diazonium group, in turn, can be replaced by a large number of other groups. This route gives a common and most useful method for introducing different groups in benzene nucleus.

$$Ar—H \longrightarrow Ar—NO_2 \longrightarrow Ar—NH_2 \longrightarrow Ar—N_2^+ \longrightarrow \text{Other compounds.}$$

TEST YOUR UNDERSTANDING - 20.1

1. Give steps involved in the following conversions.

(*a*) Toluene to *p*-toluidine

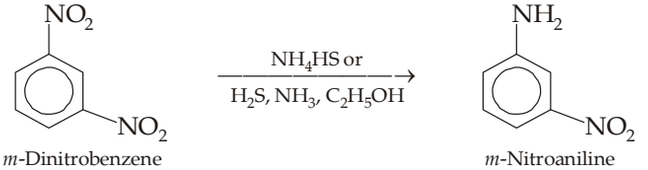
(*b*) *o*-Isopropylaniline from benzene

(*c*) *m*-Aminoacetophenone from benzene

(*d*) 4-Isopropyl-1, 3-benzenediamine from benzene.

(*e*) Toluene to *p*-aminobenzoic acid.

Selective reduction of one nitro group of a dinitro compound can often be achieved by NH_4HS or through the use of carefully measured amount of hydrogen sulphide in aqueous (or alcoholic) ammonia

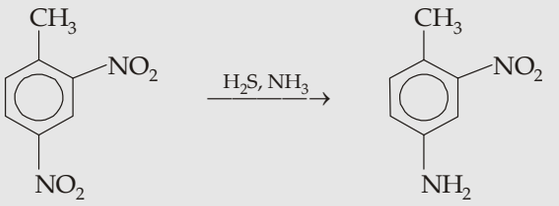


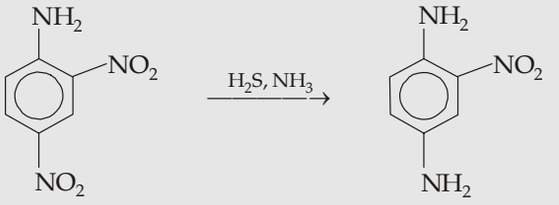
m-Dinitrobenzene — *m*-Nitroaniline

Remember that

(*i*) use of an excess amount of H_2S may result in the reduction of more than one nitro group.

(*ii*) it is always not possible to predict which —NO_2 group will be reduced, *e.g.*





2. Hofmann degradation.

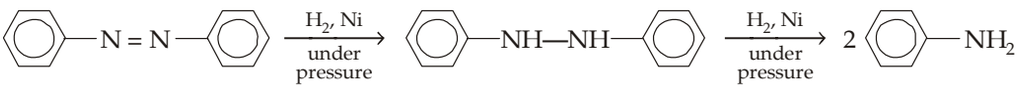
$$\underset{\text{Benzamide}}{C_6H_5CONH_2} \xrightarrow{Br_2/NaOH} \underset{\text{Aniline}}{C_6H_5NH_2}$$

3. Curtius reaction

$$C_6H_5COOH \xrightarrow[\text{heat}]{N_3H,\ \text{conc.}\ H_2SO_4} C_6H_5NH_2 + CO_2 + N_2$$

4. By acidic hydrolysis of isocyanides. $C_6H_5NC \xrightarrow{H_3O^+} C_6H_5NH_2 + HCOOH$

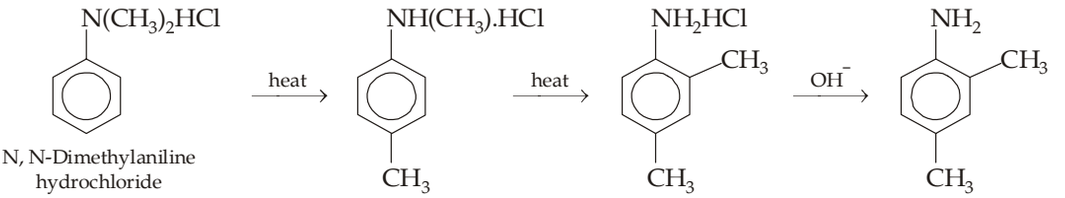
5. By reduction of azobenzene.



Azobenzene Hydrazobenzene Aniline

$$ArN = NAr \xrightarrow[\text{(mild reduction)}]{Sn,\ NaOH} ArNH—NHAr \xrightarrow[\text{(vigorous reduction)}]{(i)\ SnCl_2,\ H_3O^+,\ (ii)\ OH^-} 2ArNH_2$$

6. Hofmann Martius rearrangement. When a 3° or 2° aromatic amine hydrochloride is heated, it is converted into primary amine hydrochloride.



N, N-Dimethylaniline hydrochloride

7. Commercially, aniline is prepared by passing ammonia over chlorobenzene in presence of Cu_2O as catalyst and under pressure and at 200°C.

$$C_6H_5Cl + NH_3 \xrightarrow[\text{pressure, 200°C}]{Cu_2O} C_6H_5NH_2$$

Like aliphatic secondary amines, aromatic secondary amines can be prepared by reducing the corresponding isocyanide. $C_6H_5NC \longrightarrow C_6H_5NHCH_3$.



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20.2 Properties of Aryl Amines

Aryl amines give most of properties of aliphatic amines in exactly similar fashion, *viz*. solubility, basicity, alkylation, acetylation, benzoylation, carbylamine reaction, condensation with aldehydes to form Schiff base, oxidation etc. Two properties deserve special attention, *viz*. reaction with nitrous acid and electrophilic substitution.

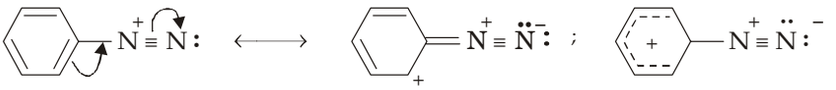
1. Reaction with nitrous acid. As is aliphatic amines, each class of aromatic amine yields a different kind of product when treated with nitrous acid, HONO. Primary aromatic amines react with nitrous acid to yield arene diazonium salts.

$$\underset{\text{1° Aromatic amine}}{ArNH_2} + NaNO_2 + 2HX \xrightarrow{\text{cold}} \underset{\text{Arenediazonium salt}}{Ar{-}N \equiv N^+X^-} + NaX + 2H_2O$$

Although arenediazonium salts are far more stable than aliphatic diazonium salts, especially at low temperatures (0–5°C), they slowly decompose even at low temperature, hence always used immediately after preparation.

Why arenediazonium ions are more stable than alkyldiazonium ions ? This is due to two factors.

(*a*) Electron-release from the *ortho* and *para* positions of the ring stabilizes the arenediazonium ions.



(*b*) The arene cation, Ar^+, is very difficult to be formed as compared to R^+ from $RN^+ \equiv N$.

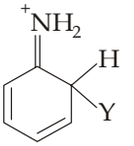
Secondary amines, both aliphatic and aromatic, react with nitrous to form N-nitrosamines which shown Libermann's nitroso reaction

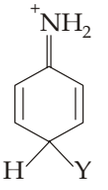
$$\underset{\text{N-Methylaniline}}{C_6H_5NHCH_3} + NaNO_2 + HCl \longrightarrow \underset{\text{N-Nitroso-N-methylaniline}}{C_6H_5N(NO)CH_3}$$

Tertiary aromatic amines undergo ring substitution discussed in electrophilic substitution.

2. Electrophilic Substitution. Arylamines contain two functional groups, the amino group and the aromatic ring. The reactivity of the amino group is affected by its aryl substituent, and the reactivity of the ring is affected by its amino group. The same electron delocalization that reduces the basicity and the nucleophilicity of an arylamine nitrogen increases the electron density in the aromatic ring and thus makes arylamines extremely reactive towards electrophilic aromatic substitution.

We know that the —NH_2, —NHR, and —NR_2 groups are ortho, para-directing and exceedingly powerful activating groups in electrophilic aromatic substitution. These effects are due to the formation of the especially stable intermediate carbocations I and II, in which every atom (except hydrogen) has a complete octet of electrons.

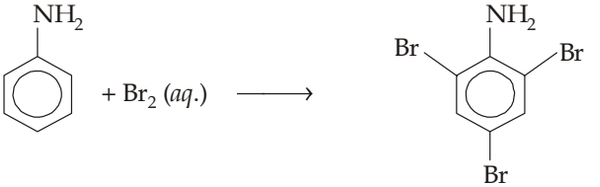




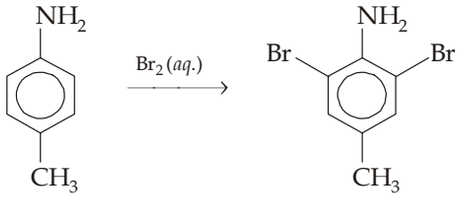
II

Thus the chief problem encountered in electrophilic substitution with aromatic amines is that *they are hightly reactive.* For example,

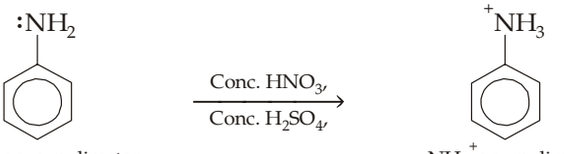
(*a*) In halogenation substitution tends to occur at every available *ortho* and *para* position and thus monohalogenated product can't be prepared



Aniline — 2, 4, 6-Tribromoaniline

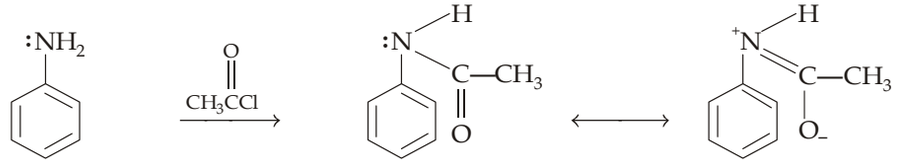


(*b*) Nitric acid not only nitrates, but also oxidizes the highly reactive ring as well, with loss of much material as dark-coloured tar. Furthermore, in the strongly acidic nitration medium, the amine is converted into anilinium ion ($—NH_3^+$) ; substitution is thus controlled not by the $—NH_2$ group but by the $—NH_3^+$ group which, because of its positive charge, directs the entering group to the *meta-* position instead of *ortho*, and *para-*.



$—NH_2$ gp. *o*, *p*-director $—NH_3^+$ gp. *m*-director

However, all these difficulties are overcome by protecting the amino group by acetylation, with either acetyl chloride or acetic anhydride. Acetylation ($—NH_2 \longrightarrow NHCOCH_3$) converts $—NH_2$ group to acetamido ($—NHCOCH_3$) group which is *o*, *p*-directing but lesser activating toward electrophilic aromatic substitution than the parent $—NH_2$ group.

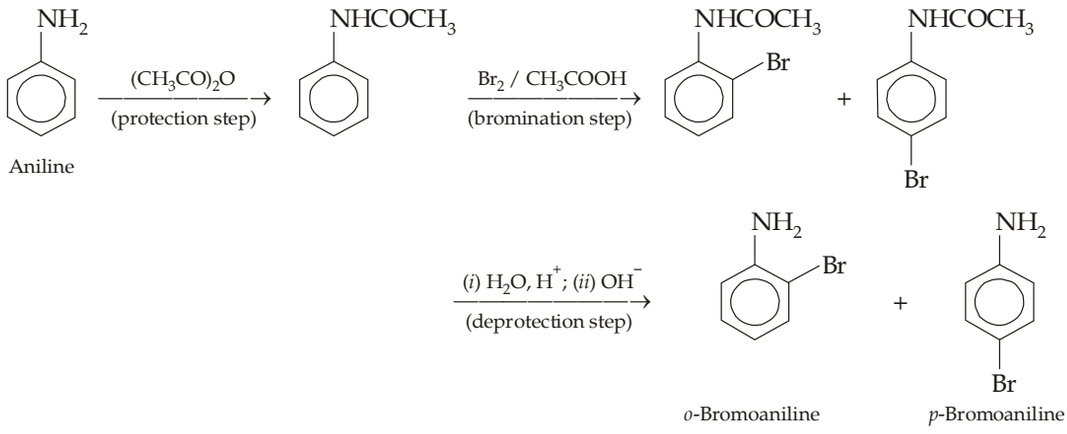


Aniline (electron pair can delocalize only to benzene ring making *o*, *p*-positions highly reactive)

Acetanilide Resonance in acetanilid due to amide group (note that electron pair on N can also delocalize to amide group, hence $—NHCOCH_3$ gp. becomes weak activator than the $—NH_2$ group)

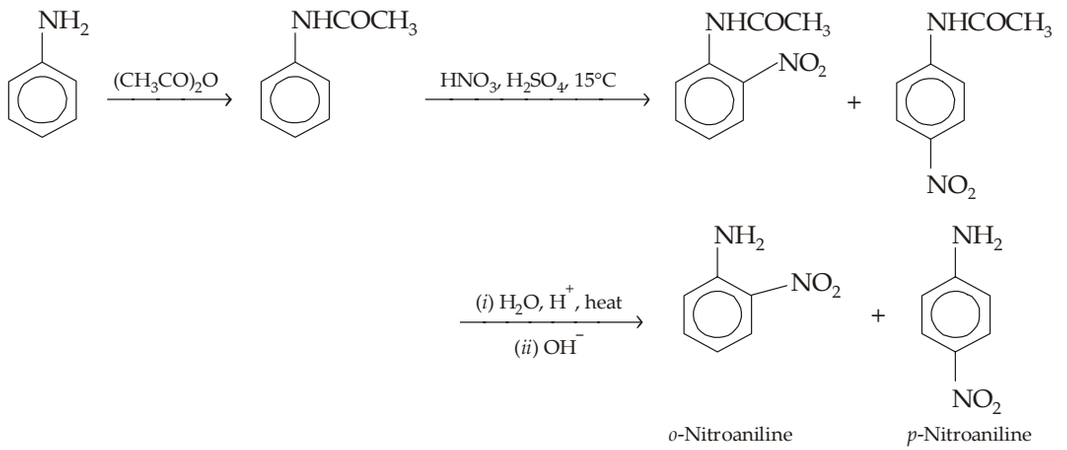
Thus protection of the amino group of an arylamine moderates the reactivity of the $—NH_2$ group and permits nitration (or halogenation) of the ring to be achieved in the required *o*, *p*-positions. Another important feature of the N-acetyl protecting group is that after it has served its purpose, it may be removed by hydrolysis (acidic or basic) liberating the parent amino group (*deprotection*).

Bromination



Aniline *o*-Bromoaniline *p*-Bromoaniline

Nitration

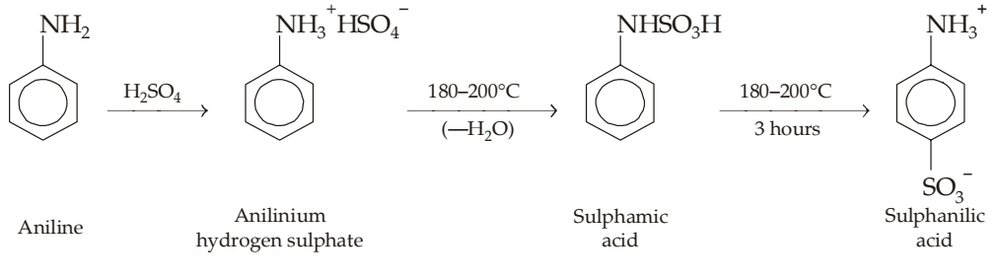


o-Nitroaniline *p*-Nitroaniline

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Sulphonation

Aniline is usually sulphonated by **"baking"** the salt, anilinium hydrogen sulphate at 180–200°C ; the main product is the *para* isomer-



Aniline — Anilinium hydrogen sulphate — Sulphamic acid — Sulphanilic acid

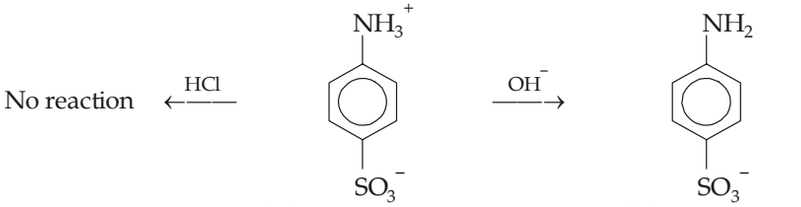
It is believed that sulphonation of amines proceeds by a mechanism that is entirely different from ordinary aromatic substitution.

Sulphanilic acid (*p*-Aminobenzenesulphonic acid) is a salt of special type, called a *dipolar ion** (*sometimes called a* Zwitterion). It is formed by the reaction of on acidic group (—SO_2OH) and a basic group (—NH_2) that are part of the same molecule, hence it is also called *inner salt.* It is interesting to note that its properties are different from that of a typical amine and a sulphonic acid. Such properties are (*a*) high melting point, (*b*) insolubility in water and organic solvents, (*c*) solubility in aqueous NaOH, and (*d*) insolubility in aqueous HCl. These properties can be explained on the basis of its structure.

(*a*) High melting point is due to its ionic nature.

(*b*) Insolubility in organic solvents is also due to its ionic nature. Its insolubility in water is typical of dipolar salts. Not all salts dissolve in water.

(*c*) Its solubility in aq. NaOH is because of transference of H^+ from the weakly acidic —NH_3^+ group to strongly basic OH^- ion to form *p*-aminobenzene sulphonate ion (II), which, like most sodium salts, is soluble in water.



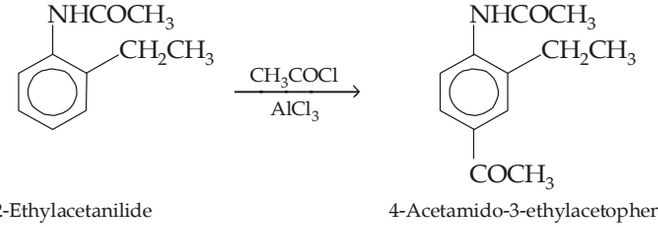
I (Insoluble in water) — II (Soluble in water)

(*d*) Its insolubility in aq. HCl is due to the fact that the —SO_3^- ion is too weak base to accept H^+ from strong acids (recall that sulphonic acids are strong acids, hence their anions are very weak bases).

TEST YOUR UNDERSTANDING - 20.2

1. Account for the fact that *p*-$NH_2C_6H_4COOH$, does not exist as a dipolar ion, although 2-aminoethanoic acid (glycine) exists as a dipolar ion.

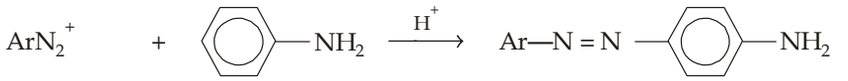
Friedel-Crafts reactions are normally not successful to unprotected anilines.



2-Ethylacetanilide — 4-Acetamido-3-ethylacetophenone

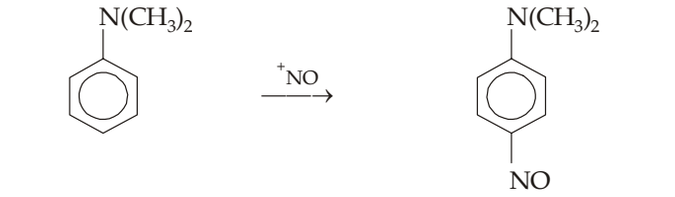
* A dipolar ion is formed only when a molecule contains both an amino as well as an acidic group, and the amine is more basic than the anion of the acid.

Coupling reaction. Aniline having a strongly activating (—NH_2) group undergoes coupling reaction with benzenediazonium salt (a weak electrophile).



A weak electrophile — A strongly activated ring — *p*-Aminoazobenzene

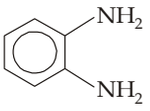
Nitrosation. In an electrophilic aromatic nitrosation, the attacking reagent is *nitrosonium ion.* The nitrosonium ion is a very weak electrophile and hence nitrosation can take place only in rings bearing powerfully activating dialkylamino (—NR_2) or hydroxy (—OH) group, *i.e.,* in *tert*-amines and phenols.

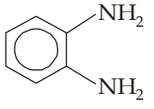


N, N-Dimethylaniline — *p*-Nitroso–N, N– dimethylaniline

TEST YOUR UNDERSTANDING - 20.3

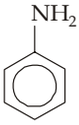
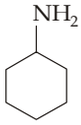
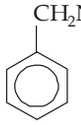
1. Complete the following reaction by supplying structure to the bracketed compounds.

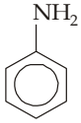
(*a*)  + Glyoxal ⟶ [E]

(*b*)  $\xrightarrow[\text{HONO, 5°C}]{\text{1 mol of}}$ [F]

(*c*) Aniline $\xrightarrow{C_6H_5CHO}$ [G] $\xrightarrow{HNO_3}$ [H] + [I] $\xrightarrow{H_3O^+}$ [J] + [K] + [L]

2. Arrange the following amines in their decreasing basic character.

(*a*)  ,  and 

(*b*)   and 

20.3 Preparation and Reactions of Diazonium Salts

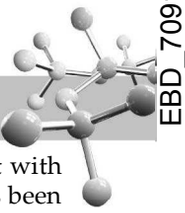
When a primary aromatic amine dissolved or suspended in cold aqeuous mineral acid, is treated with sodium nitrite, arenediazonium salts are formed.

$$\underset{\text{1° Aromatic amine}}{Ar—NH_2} + \underset{\text{A diazonium salt}}{NaNO_2 + 2HX} \xrightarrow{0–5°C} Ar—N \equiv N^+X^- + NaX + 2H_2O$$

As described earlier, aryl diazonium ions are substantially more stable than alkyl diazonium ions, and are of enormous synthetic value. The important synthetic reactions of diazonium salts may be divided into two classes. (*a*) *replacement reactions*, in which nitrogen is lost as N_2 and its place is taken by some other atom or group, and (*b*) *coupling reactions*, in which the nitrogen is retained in the product.

1. Reactions involving replacement of —$N^+ \equiv N$. Diazonium group can be replaced easily be any one of a number of groups or atoms like —F, —Cl, —Br, —I, —CN, —OH, —H, and —NO_2. Most of these replacement reactions do not require any special and drastic condition ; simply the requisite reagent is added to the solution of diazonium salt which is then gently warmed. The required substituted compound is formed along with the evolution of nitrogen.

$$Ar—N^+ \equiv N + :Z \longrightarrow Ar—Z + N_2$$



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(*a*) *Replacement of the —N_2^+ group by —Cl, —Br, or —CN (the Sandmeyer reaction*). Arenediazonium salts react with cuprous chloride, cuprous bromide, and cuprous cyanide to give products in which diazonium group has been replaced by —Cl, —Br, and —CN respectively. These reactions are known as **Sandmeyer reactions.**

$$Ar—N_2^+X^- \xrightarrow{CuX} Ar—X + N_2 \ (X = —Cl, —Br, —or—CN)$$

Sometimes the synthesis is carried out by a modification known as the **Gattermann reaction,** in which copper powder and hydrogen halide (HCl or HBr) are used in place of cuprous halide.

(*b*) *Replacement by —NO_2 group*

$$Ar—N^+_2Cl^- + NaNO_2 \xrightarrow[Cu^{2+} \text{ or } Cu_2O]{NaHCO_3} Ar—NO_2 + N_2$$

(*c*) *Replacement by —I.* This can simply be achieved by mixing the diazonium salt with potassium iodide at room temperature.

$$Ar—N_2^+X^- + I^- \longrightarrow Ar—I + N_2 + X^-$$

(*d*) *Replacement by —F*. The diazonium group can be replaced by fluorine by treating the diazonium salt with fluoroboric acid (HBF_4). The precipitated diazonium fluoroborate is isolated, dried and heated until decomposition occurs to yield the aryl fluoride. This reaction is known as **Balz-Schiemann reaction.**

$$Ar—N_2^+X^- \xrightarrow{HBF_4} Ar—N_2^+BF_4^-\downarrow \xrightarrow{heat} Ar—F + BF_3 + N_2$$

(*e*) *Replacement by —OH.* Diazonium salts react with water, of course slowly at low temperature, even ice cold, and vigorously at room or high temperature to yield phenols and this is the reason why these salts are used immediately after preparation.

$$Ar—N_2^+X^- + H_2O \xrightarrow{heat} Ar—OH + N_2 + H^+$$

This is the most general method for the preparation of phenols. Sulphuric acid is normally used instead of hydrochloric acid in the diazotization steps so as to minimise the competition with water for capture of the cationic intermediate ; HSO_4^- is less nucleophilic than Cl^-.

As we shall see later, the phenol so formed may undergo coupling reaction with the unreacted diazonium salt. Since this coupling takes place easily in alkaline medium, we can minimize this further by making the solution more acidic ; for which diazonium solution is added slowly to a large volume of boiling dil. H_2SO_4.

Diazonium group can be replaced by —OH group also by adding cuprous oxide to a dilute solution of the diazonium salt containing a large excess of cupric nitrate.

$$Ar—N_2^+ HSO_4^- \xrightarrow[Cu^{2+}, H_2O]{Cu_2O} Ar—OH$$

This variation of Sandmeyer reaction is a much simpler and safer procedure than the above older method for preparing phenol.

(*f*) *Replacement by hydrogen (deamination via diazotization).* This can be brought about by a number of reducing agents, *e.g.*, H_3PO_2, C_2H_5OH, $NaBH_4$, or Na_2SO_3; most useful of these is *hypophosphorous acid,* H_3PO_2.

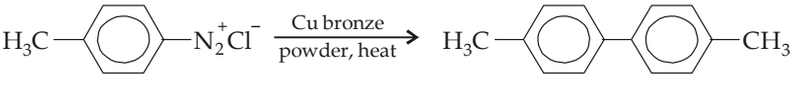
$$Ar—N_2^+X^- + H_3PO_2 + H_2O \longrightarrow Ar—H + H_3PO_3 + HX$$

Aniline can directly be converted to benzene by carrying out its diazotization in presence of hypophosphorous acid for which amine is dissolved in hypophosphorous acid and sodium nitrite is added (diazonium salt is reduced as fast as it is formed).

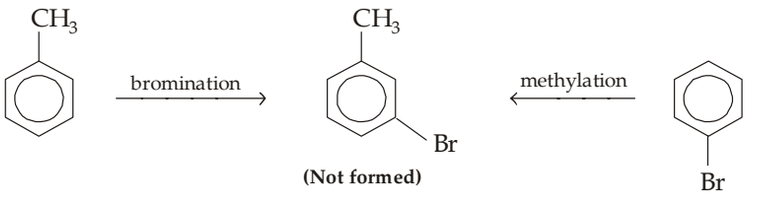
$$Ar—NH_2 \xrightarrow{H_3PO_2, NaNO_2} Ar—H + N_2 + H_2O$$

Replacement of —NH_2 group *via* the diazonium group by hydrogen is very useful reaction because introduction of —NH_2 group (precursor of —N_2X) can be used to introduce the new group in a *p*-position which is sometimes not possible by direct reaction as illustrated in the following preparation.

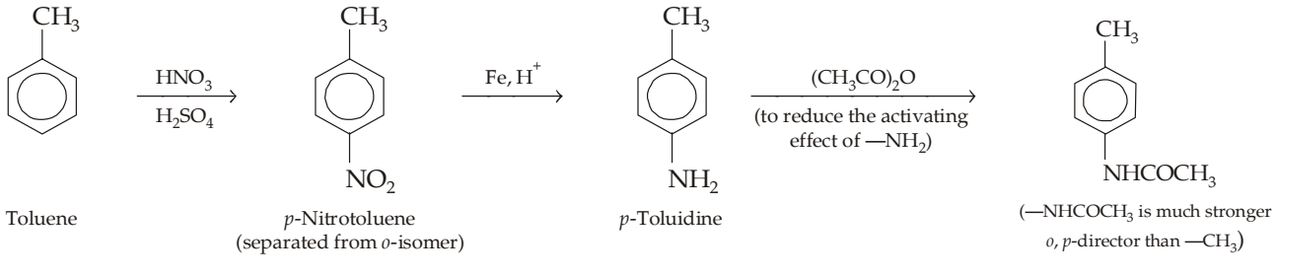
(*g*) *Replacement by phenyl group (Gattermann reaction) :*

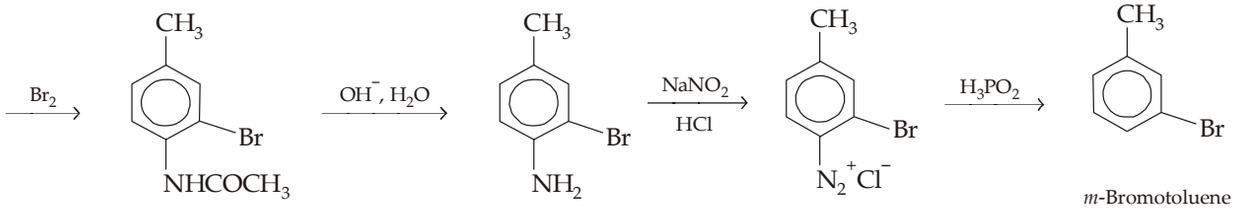


Preparation of *m*-bromotoluene : Here the two *o, p*-directing groups are situated *meta* for each other, hence neither bromination of toluene nor methylation of bromobenzne would yield the required *m*-bromotoluene.



However, this can be prepared from toluene in the following way.

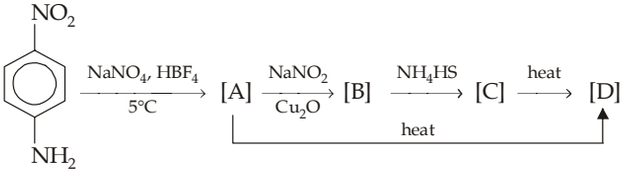


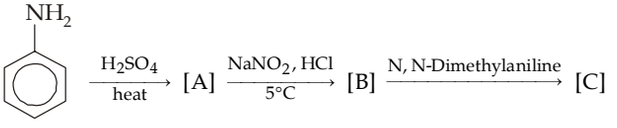


TEST YOUR UNDERSTANDING - 20.4

1. In diazotisation of arylamines, excess of mineral acid is used. Explain.

2. Complete the following by supplying structures to the bracketed compounds.

(*a*) 

(*b*) 

3. Give intermediate steps to carry out the following transformations.

(*a*) Toluene to *p*-toluic acid

(*b*) Nitrobenzene to *m*-bromophenol

(*c*) *p*-Nitroaniline to 1, 2, 3-tribromobenzene

(*d*) Benzene to 1, 3, 5-tribromobenzene

(*e*) Benzene to *m*-bromochlorobenzene

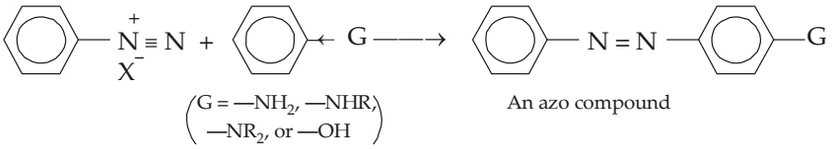
(*f*) Aniline to *p*-dinitrobenzene

(*g*) $C_6H_5NH_2$ to C_6H_5D.

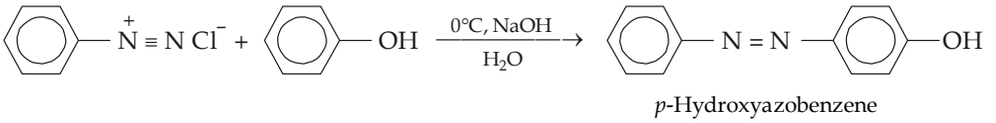
4. Direct bromination of toluene gives a mixture of *o*- and *p*-bromotoluenes which are very difficult to separate, so devise a scheme that can be used for converting toluene to *o*- and *p*-bromotoluenes.

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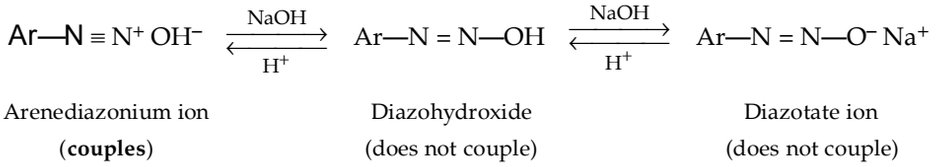
2. Coupling reactions of diazonium salts. Like nitrosonium ion (^+NO), arenediazonium ions (ArN_2^+) are weak electrophiles, and are thus capable of attacking only very reactive rings. Hence the aromatic ring undergoing attack by the diazonium ion must contain a powerfully electron-releasing group, generally —OH, —NR_2, —NHR, —or NH_2. Substitution mainly occurs *para* to the activating group.



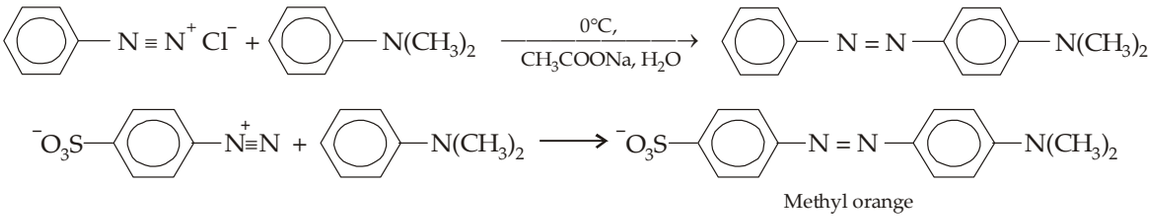
(*a*) Couplings between arenediazonium cation, and phenols take place most rapidly in *slighlty* alkaline solution. In alkaline medium, an appreciable amount of phenol is present as a phenoxide ion which is more reactive toward electrophilic substitution than the parent phenol.



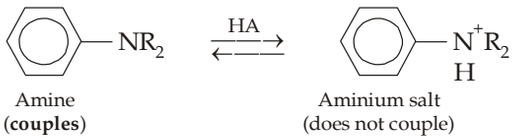
However, the solution should not be too alkaline because in strongly alkaline medium the arenediazonium ion exists in equilibrium with an un-ionized diazohydroxide and diazotate ; neither of these couple.



(*b*) Couplings between arenediazonium cation and amines take place mostly in *slightly* acidic solutions (pH 5–7).



The higher acidity increases the amount of protonated amine which is unreactive toward electrophilic substitution

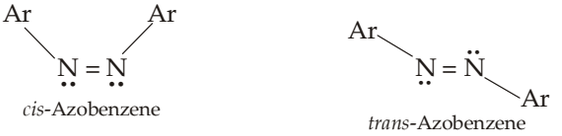


Azo compounds are usually intensely coloured because the azo linkage (—N = N—) brings the two aromatic rings into conjugation. This gives an extended system of delocalized π electrons and allows absorption of light in the visible region. Because of their intense colours, many azo compounds are extensively used as dyes. Azo compounds undergo reduction in the following manner.

(*i*) $Ar—N=N—Ar' \xrightarrow[\text{(mild reduction)}]{\text{Sn, NaOH}} Ar—\underset{H}{\overset{H}{N}}—\underset{H}{\overset{H}{N}}—Ar$ (A hydrazo compound)

(*ii*) $Ar—N=N—Ar' \xrightarrow[\text{(vigorous reduction)}]{\text{(i) } SnCl_2, H^+ \text{ ; (ii) } OH^-} ArNH_2 + H_2NAr'$

Azo compounds can exist in *cis* and *trans* forms ; the former being less stable due to steric strain.



3. **Reduction.** Arenediazonium salts are reduced to phenylhydrazine hydrochloride by means of $SnCl_2$ and HCl or with sodium sulphite.

$$\underset{\text{Benzenediazonium chloride}}{C_6H_5—N \equiv N^+ Cl^-} \xrightarrow[\text{or } Na_2SO_3]{SnCl_2, HCl} \underset{\text{Phenylhydrazine hydrochloride}}{C_6H_5NHNH_2 . HCl}$$

20.4 Illustrative Examples

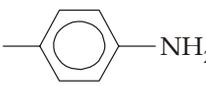
Example 1 :

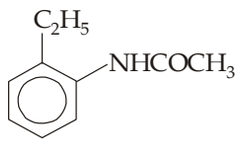
Supply the structure of bracketed compounds in each of the following conversions.

(a) [A] Acid $\xrightarrow{[B]/\text{ Conc. } H_2SO_4}$ [C] $\xrightarrow[5°C]{NaNO_2, HCl}$ [D] $\xrightarrow{CuCl}$ *p*-Nitrochlorobenzene

(b) $C_6H_6 \xrightarrow[AlCl_3]{C_2H_5Br}$ [A] $\xrightarrow[H_2SO_4]{HNO_3}$ [B] $\xrightarrow{NBS}$ [C] $\xrightarrow[NH_3]{\text{excess}}$ [D]

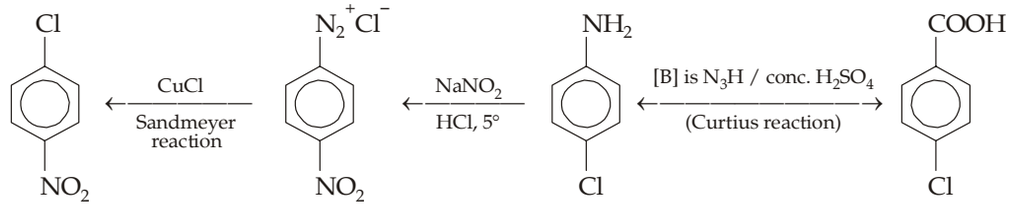
(c) $C_6H_5NH_2 \xrightarrow{(CH_3CO)_2O}$ [A] $\xrightarrow{ClSO_2OH}$ [B] $\xrightarrow{NH_3}$ [C] $\xrightarrow[(ii)\, OH^-]{(i)\, H_3{}^+O}$ [D]

(d) [B] $\xleftarrow[H^+]{C_6H_5N_2{}^+Cl^-}$  $\xrightarrow[OH^-]{C_6H_5N_2{}^+Cl^-}$ [A]

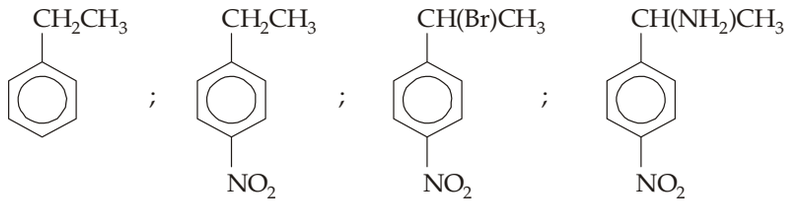
(e)  $\xrightarrow[H_2SO_4]{HNO_3}$ [A] $\xrightarrow{OH^-}$ [B] $\xrightarrow{Cl_2}$ [C]

Solution :

(*a*) Proceed backward with the structure of the knwon compound, *p*-nitrochlorobenzene and the knwon reagent.

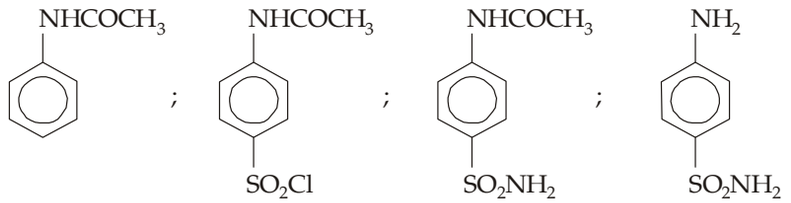


[D] [C] [A]

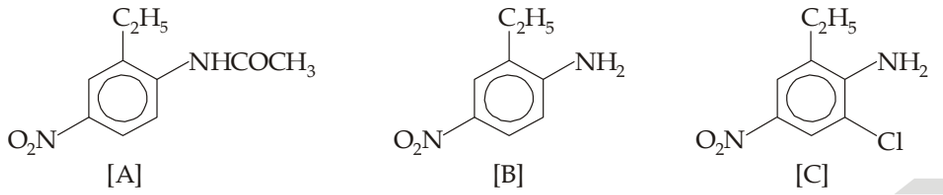
(*b*) 

[A] [B] [C] [D]

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(*c*) 

(*d*) 

(*e*) 

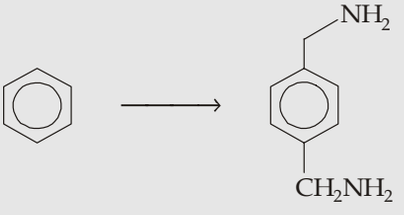
Example 2 :

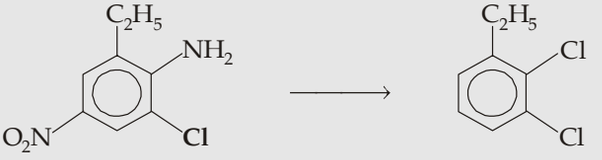
Give steps involved in the following conversions.

(a) **$C_6H_5NH_2$ to C_6H_5D**

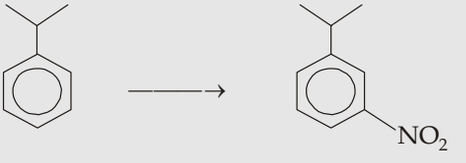
(b) **C_6H_6 to optically active *sec*-butylbenzene**

(c) **Aniline to benzoic acid.**

(d) 

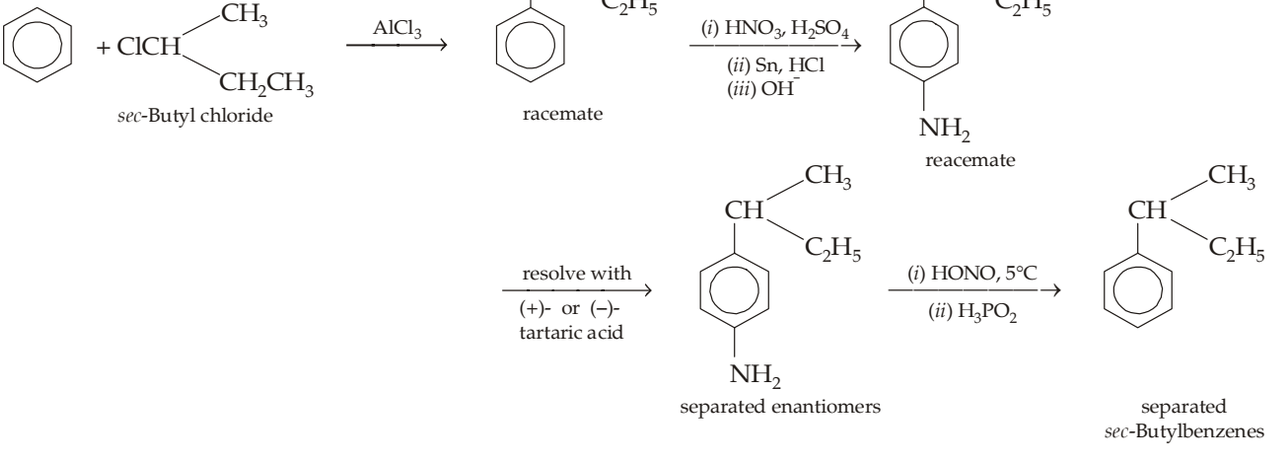
(e) 

(f) **Benzene to ethyl *m*-fluorophenyl ketone**

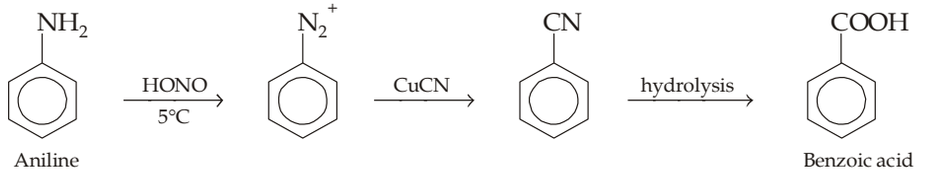
(g) 

Solution :

(*a*) $C_6H_5NH_2 \xrightarrow[HCl,\ 5°C]{NaNO_2} C_6H_5N_2^+Cl^- \xrightarrow{DPH_2PO_2} C_6H_5D$

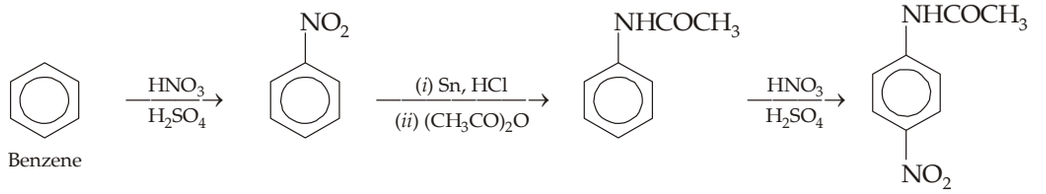
(*b*) 

(*c*)

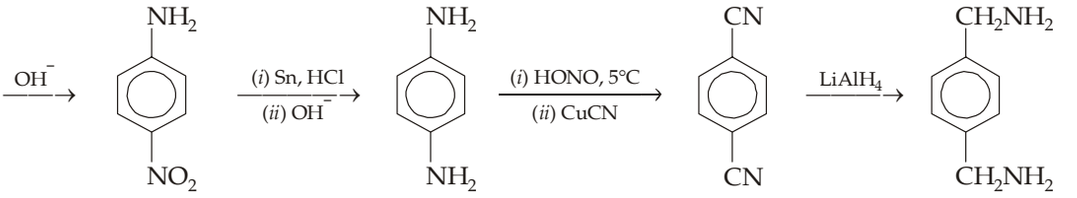


Aniline Benzoic acid

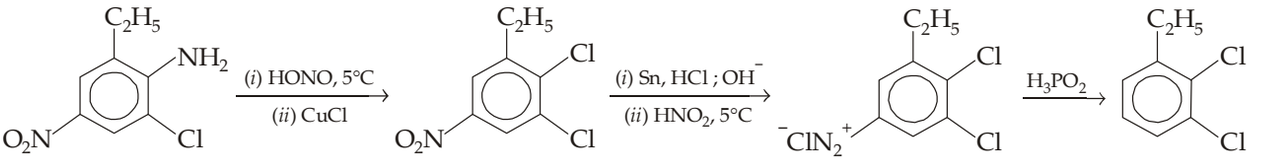
(*d*)



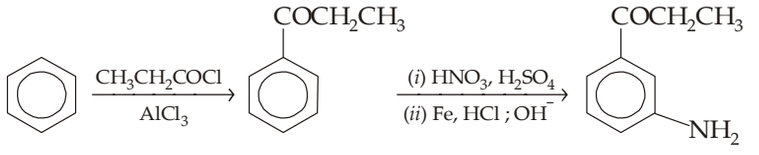
Benzene



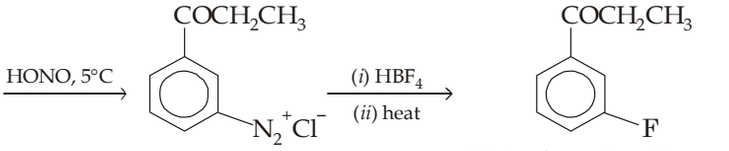
(*e*)



(*f*)

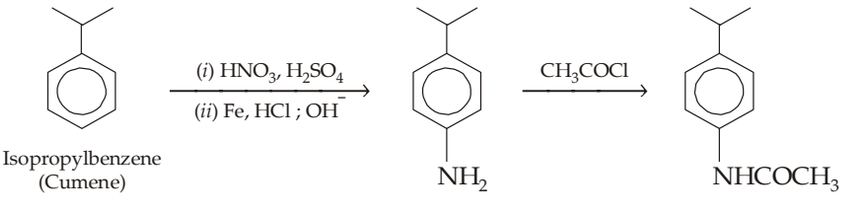


Benzene

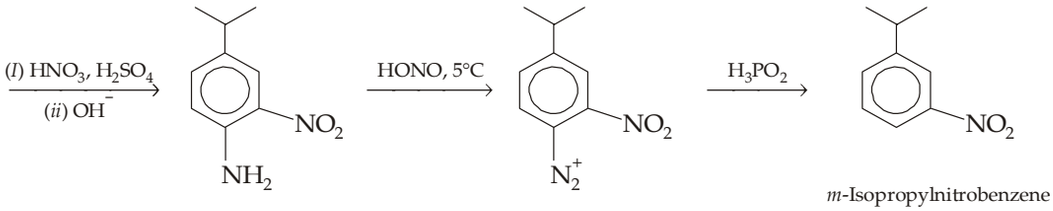


Ethyl *m*-fluorophenyl ketone

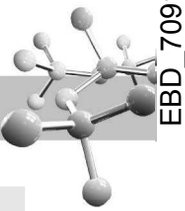
(*g*)



Isopropylbenzene (Cumene)



m-Isopropylnitrobenzene



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Example 3 :

An unknown compound X containing nitrogen and chlorine is readily soluble in water to give a solution that turns blue litmus red. Titration of X with standard sodium hydroxide gives a neutralization equivalent of 129.

When compound X is treated with aq.NaOH, a liquid containing nitrogen but no chlorine separates out. Liquid Y gives a red precipitate on treatment with nitrous acid and β-naphthol under suitable conditions. Assign structure to X and Y.

Solution :

Solubility of the compound X in water, and its reaction with NaOH to form Y with the loss of chlorine indicates that X is the hydrochloric acid salt. Further compound Y (not having chlorine) seems to be 1° primary aromatic amine due to its reaction with HCl (diazotisation) and β-naphthol (coupling) to form red precipitate. The 1° aromatic amine hydrochloride should be $C_6H_5NH_3^+Cl^-$, indicated by its N.E. 129.

$$\underset{\text{(X) NE = 129}}{C_6H_5NH_3^+Cl^-} + H_2O \longrightarrow \underset{\text{(Y)}}{C_6H_5NH_2} + H_2O + HCl$$

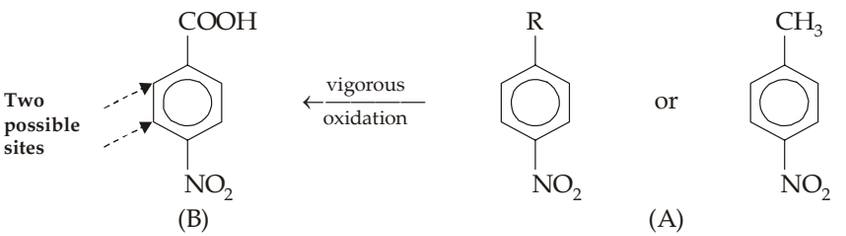
$$\underset{\text{(X)}}{C_6H_5NH_3^+Cl^-} + NaOH \longrightarrow \underset{\text{(Y)}}{C_6H_5NH_2} + H_2O + NaCl$$

Example 4 :

Deduce structure of the compound (A) of the formula $C_7H_7NO_2$ which is insoluble in dil. acid and base. On vigorous oxidation, it gives compound (B), $C_7H_5NO_4$ which is soluble in dil. aqueous $NaHCO_3$ and gives two isomeric monochloro substitution products.

Solution :

Since the compound (A), $C_7H_7NO_2$ is insoluble in dil. acid and base, and its nitrogen is not removed on oxidation, so it should contian —NO_2 group as one of the substitutents which is present as such in B. Hence the other substituent in B ($C_7H_5NO_4$) should be —COOH as indicated by its solubility in aq. $NaHCO_3$. So, the compound B, $C_7H_5NO_4$ is $C_6H_4(NO_2)COOH$. The two substituents must be present in *para* to each other so as to explain the formation of two isomeric monochloro substitution products. Thus (A) should be *p*-nitrotoluene



(B) (A)

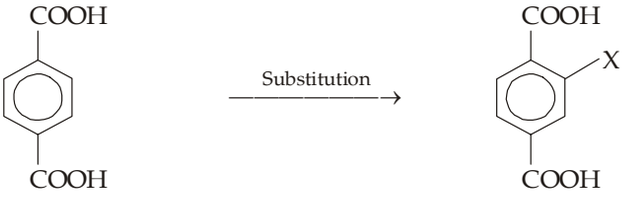
Example 5 :

Deduce a possible structure for the compund (A) of the formula C_8H_9NO which is insoluble in dil. acid and base. On treatment with $KMnO_4$ in H_2SO_4 , it gives compound B, which is free of nitrogen, soluble in aqueous $NaHCO_3$ and gives only one mononitro substitution product.

Solution :

$$\underset{C_8H_9NO}{[A]} \xrightarrow[H_2SO_4]{KMnO_4} \underset{\text{(soluble in aq. } NaHCO_3)}{[B]} \xrightarrow{\text{nitration}} \text{One mononitro derivative}$$

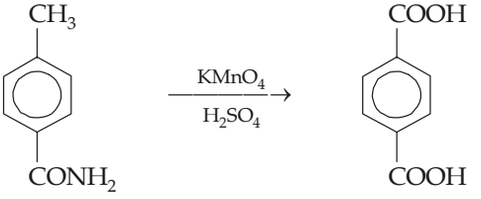
Students are advised to start the problem from any knwon reaction fact or strucutre given in the problem. For example, in the present question it is given that compound [B] is soluble in aq. $NaHCO_3$, so it must contain —COOH group. Further it is given that (B) forms only one mononitro derivative which indicates that it should contian two —COOH groups and that too in *para* to each other.



(B) All four positions are equivalent

Now since compound B is obtained by acidic $-KMnO_4$ oxidation of A, A should have two substituents and one substituent must contain nitrogen in such form which is insoluble in acids and bases and is liable to be converted to —COOH group by $KMnO_4 + H_2SO_4$.

The nitrogen containing group which coincides with all the given* characteristics is —$CONH_2$. Hence the other substituent in A (C_8H_9NO) should be —CH_3 and that too in *para* position to explain the formation of B.



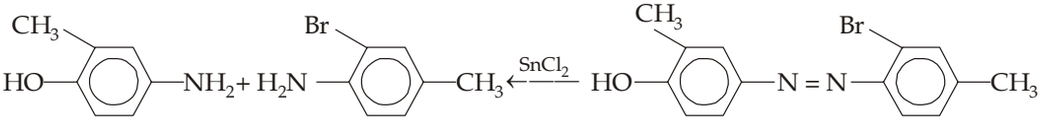
(A) C_8H_9NO (B)

Example 6 :

An azo compound (X) is cleaved by stannous chloride to form two amines, namely 2-methyl-4-aminophenol (A) and 3-bromo-4-aminotoluene (B). Deduce the structure of the azo compound. Can both of the amines (A and B) be used for preparing the parent azo compound by coupling reaction, if so give the synthesis of the azo compound.

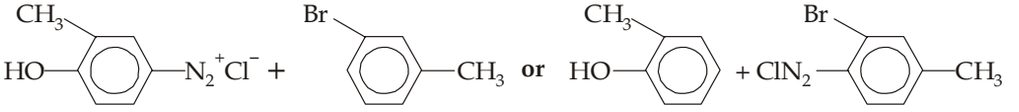
Solution :

In such questions, first draw structures of both of amines in such a way that their amino groups face each other. Now replace the two amino groups by azo linkage, —N = N—.



(A) (B) (X)

The two possible pairs that can be used for preparing the azo compound X by coupling are



(From amine A) (From amine B)

However, the first combination is not feasible because the benzene ring does not bear reactive —OH or —NH_2 group, *i.e.*, it is not sufficiently reactive to be attacked by the electrophilic diazonium cation.

* Other important N containing groups are —NO_2 (not removed by $KMnO_4 + H_2SO_4$), —NH_2, —$NHCOCH_3$, etc. (liable to destroy the benzene ring).

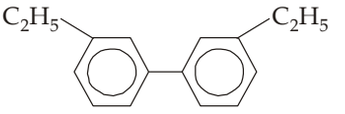
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Example 7 :

A nitrobenzene derivative (A) of the formula $C_8H_9NO_2$ when treated with metallic tin and NaOH, it forms compound (B). Compound B rearranges to an aromatic diamine (C) on treatment with strong mineral acid. Compound (C) is treated first with nitrous acid at low temperature and then heated with ethanol to give 3, 3′-diethyldiphenyl. Deduce the structure of the compound (A) and write the reactions involved.

Solution :

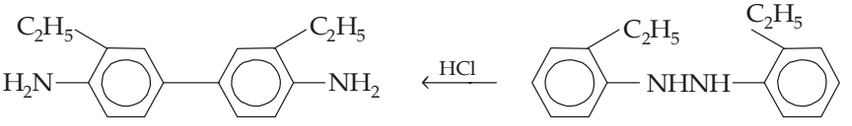
$$C_8H_9NO_2 \xrightarrow[NaOH]{Sn} [B] \xrightarrow{HCl} [C] \xrightarrow[(ii)\ C_2H_5OH,\ heat]{(i)\ HNO_2,\ 5°C}$$



[A] $C_6H_5NO_2.C_2H_4$

The above series of reactions lead to following points.

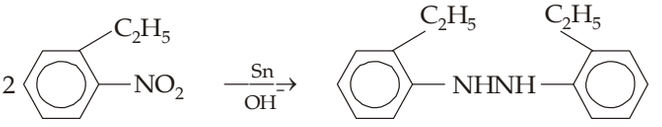
(*i*) Compound (C) is a diamine and is formed by treating [B] with strong HCl, involving rearrangement, [C] must have two —NH_2 groups in para positions.



[C] [B]

Thus the compound [B] must be a substituted hydrazobenzene with undergoes rearrangement (benzidine rearrangement) on treatment with strong mineral acid.

(*ii*) Formation of hydrazobenzene by the reduction of compound A with Sn and OH^- indicates that A must be 2-ethylnitrobenzene.



[A] [B]

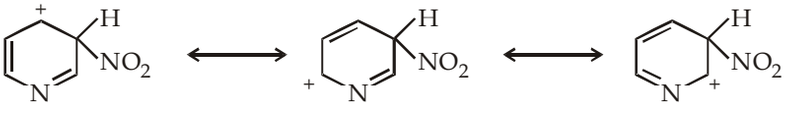
Example 8 :

Pyridine undergoes electrophilic substitution at position 3 rather than at 2 or 4. Explain.

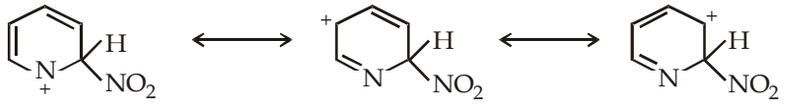
Solution :

Due to the presence of N in ring, pyridine behaves like a strongly deactivated benzene (e.g. nitrobenzene), thus positions 2 and 4 are deactivated towards electrophiles. This is evident by the fact that Friedel–Crafts reactions fail while other electrophilic substitutions require unusually strong conditions. Thus formation of 3-substituted product (the relatively less deactivated position) can be explained by higher stability of the corresponding intermediate.

Attack at 3-position :



Attack at 2-position :



No octet on N **(Unfavourable)**

Thus the intermediate corresponding to 2- (as well as 4-) substituted product is less stable than the 3-substituted intermediate.

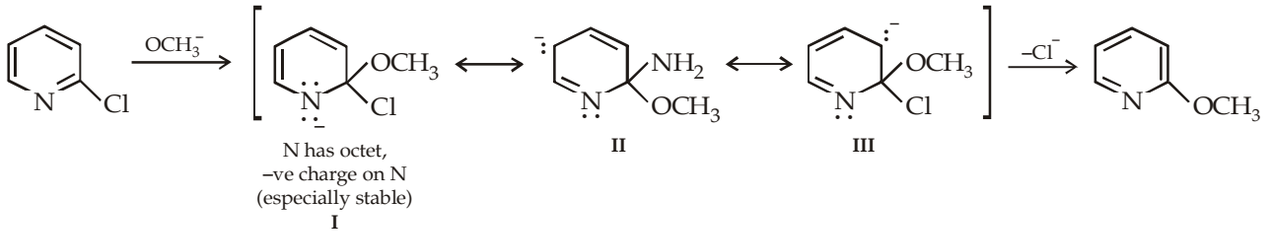
Example 9 :

2-Chloropyridine when treated with sodium methoxide gives 2-methoxypyridine, while no such reaction occurs with 3-chloropyridine. Explain.

Solution :

This is an example of nucleophilic substitution, recall that pyridine is deactivated toward attack by electrophiles, it is activated toward attack by nucleophiles. Thus if a good leaving group is present either at 2 or 4 position, a nucleophile can attack and displace the leaving group. The intermediate due to attack at 2 or 4 position is stabilized by delocalization of the negative charge, since this stabilization is not possible if attack occurs at the 3-position, 3-chloropyridine is not converted to 3-methoxypyridine.

Nucleophilic attack at C-2



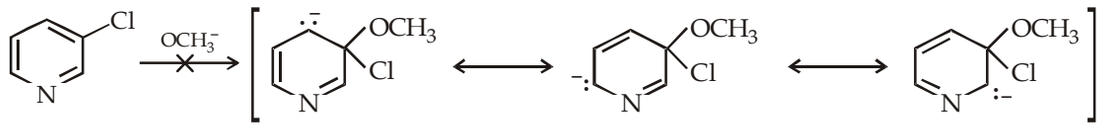
N has octet, –ve charge on N (especially stable)
I

II

III

Similar situation arises in case of 4-chloropyridine.

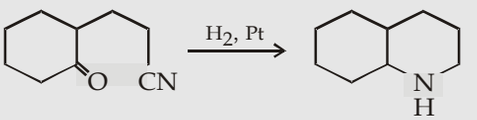
Nucleophilic attack at C-3 (not observed)



None of the structure has –ve charge on N (hence unfavouable situation)

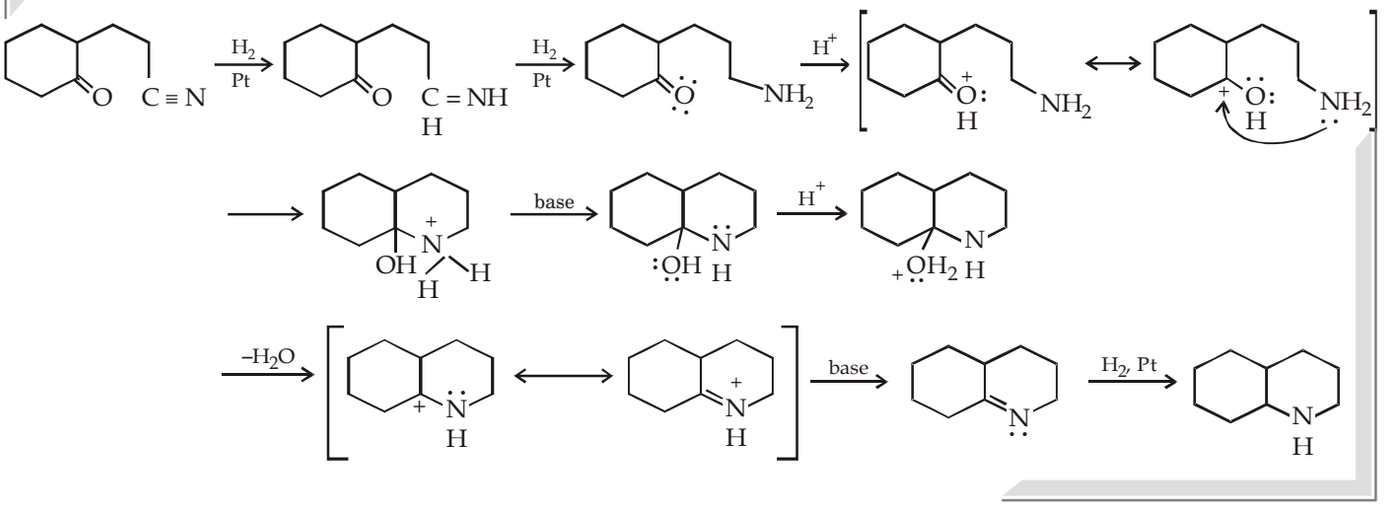
Example 10 :

Propose mechanism for the following reaction.



You may use an acid or a base, wherever you require.

Solution :

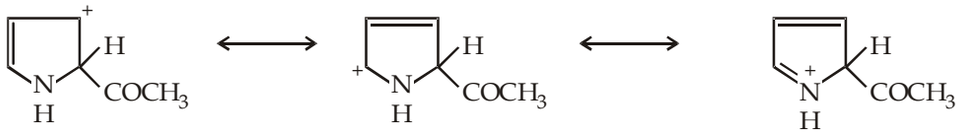


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Example 11 :

Draw all the resonating structures of the 2-substituted intermediate obtained by treating pyrrole in acetic anhydride (CH_3CO^+ is the electrophile). Is there any difference in the relative stability of these structures?

Solution :



Every atom has a full octet (especially stable)

Example 12 :

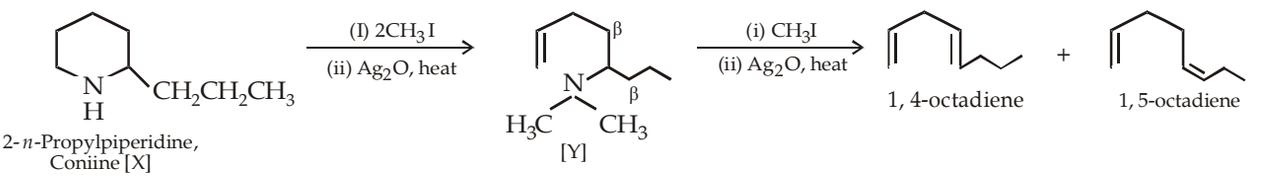
An optically active naturally occurring toxic liquid $C_8H_{17}N$ (X), in hemlock that was said to cause Socrates death dissolves in aq. HCl and gives no gas will nitrous acid. It gives a precipitate with benzenesulphonyl chloride in presence of NaOH. when treated with excess of methyl iodide, then with moist oxide and finally heated, it gives a compound (Y) $C_{10}H_{21}N$. Compound (Y) is treated similarly as (X) and finally gives 1, 4-octadiene and 1, 5-octadiene. Suggest structure to (X) and)(Y) and explain all the reactions. Is there any possible structural isomer of (X); if so give the complete set of reaction with this?

Solution :

(*i*) The given reactions (solubility in aq. HCl, no gas with HONO and a precipitate with $C_6H_5CO_2Cl$ / NaOH) indicate that the given compound is a secondary amine.

(*ii*) Since the given compound eliminates nitrogen by two sequence of Hofmann degradation, N must be present in the ring.

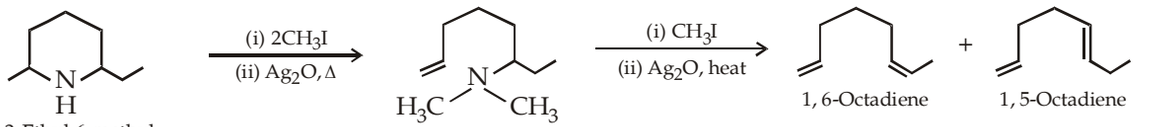
(*iii*) Formation of two unbranched alkenes as the final products indicates that the alkyl group or groups consisting of 3-C must be present on the α-carbons and it must be unbranched. Two possibilities arise : (a) one CH_3 and one C_2H_5 groups are present on the two α-carbons, (b) one *n*-C_3H_7 group is present on one of the α-carbons. However,



2-*n*-Propylpiperidine, Coniine [X]

[Y]

1, 4-octadiene + 1, 5-octadiene

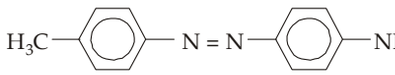


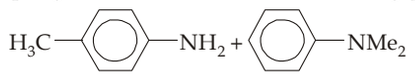
2-Ethyl-6-methyl piperidine, **isomer of (X)**

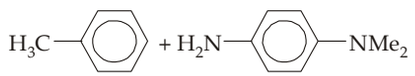
1, 6-Octadiene + 1, 5-Octadiene

EXERCISE 20.1 (MCQ - ONE option correct)

1. Which of the following is not a property of sulphanilic acid ?
(*a*) It is soluble in *aq*.NaOH
(*b*) It is soluble in *aq*. HCl
(*c*) It is insoluble in organic solvents
(*d*) It does not melt but decomposes.

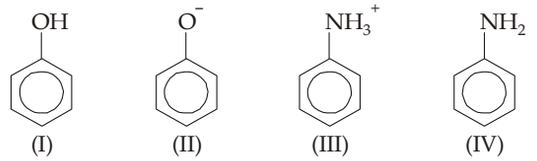
2.  can be produced by coupling reaction of which of the following pair?

(*a*) 

(*b*) 

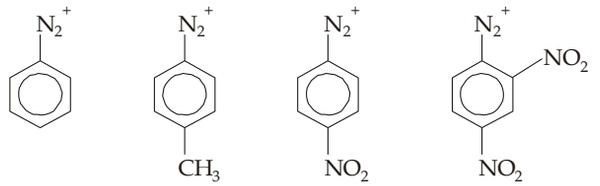
(*c*) Both (*a*) and (*b*)
(*d*) Neither of the two.

3. Arrange the following compounds in decreasing order of coupling with benzenediazonium chloride.



(*a*) IV > I > II > III
(*b*) II > I > IV > III
(*c*) II > IV > I > III
(*d*) II > III > IV > I.

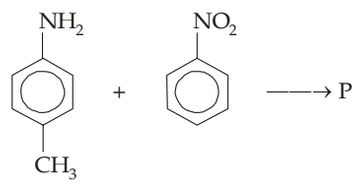
4. Arrange the following diazonium cation in decreasing order of coupling with phenol.

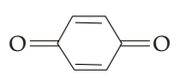
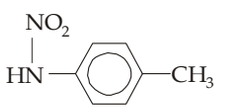


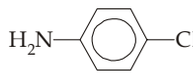
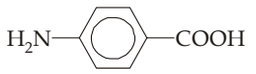
(I) (II) (III) (IV)

(*a*) I > II > III > IV
(*b*) IV > III > II > I
(*c*) IV > III > I > II
(*d*) II > I > III > IV.

5. Predict the nature of P in the following reaction.



(*a*)  (*b*) 

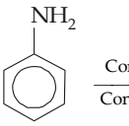
(*c*)  (*d*) 

6. Predict the product [B] in the following series of reactions.

$$C_6H_5NH_2 \xrightarrow[KOH]{CHCl_3} [A] \xrightarrow{H_3O^+} [B]$$

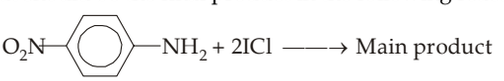
(*a*) $C_6H_5CH_2NH_2$ (*b*) C_6H_5COOH
(*c*) $C_6H_5NHCH_3$ (*d*) $C_6H_5NH_2$.

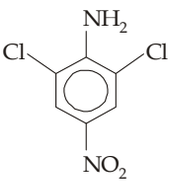
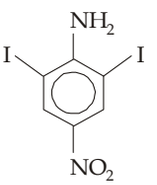
7. How many diazo group will be introduced when resorcinol is treated with excess of benzenediazonium chloride in alkaline medium ?
(*a*) 1 (*b*) 2
(*c*) 3 (*d*) Nil.

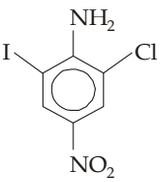
8.  $\xrightarrow[Conc.\ H_2SO_4]{Conc.\ HNO_3}$ X. Here X is mainly

(*a*) *o*-Nitroaniline
(*b*) *p*-Nitroaniline
(*c*) a mixture of (*a*) and (*b*)
(*d*) *m*-Nitroaniline.

9. What should be the final product in the following reaction ?

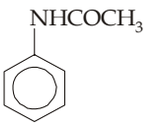
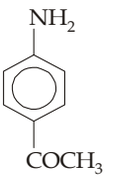


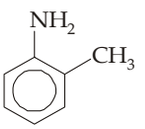
(*a*)  (*b*) 

(*c*)  (*d*) No reaction.

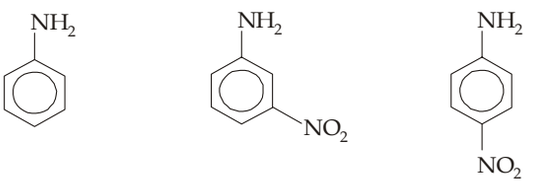
10. Which of the following has lowest pK_b value ?
(*a*) Benzylamine (*b*) Aniline
(*c*) Acetanilide (*d*) *p*-Nitroaniline

11. Which of the following is stronger than aniline ?

(*a*)  (*b*) 

(*c*)  (*d*) None.

12. The increasing order of pK_b values for the three anilines (I, II and III) is

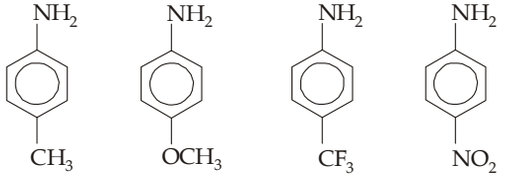


I II III

(*a*) I < II < III (*b*) III < II < I
(*c*) I < III < II (*d*) II < I < III.

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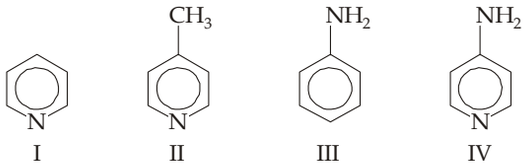
13. Arrange the following amines according to their decreasing K_b values.



I II III IV

(*a*) I > II > III > IV
(*b*) IV > III > II > I
(*c*) II > I > III > IV
(*d*) II > I > IV > III.

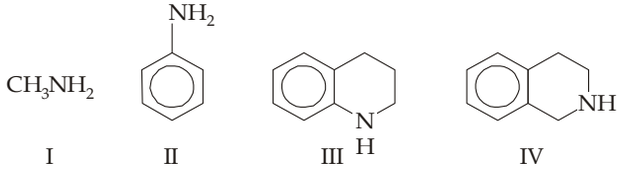
14. Of the four orders given below for the basic character of the four compounds, which one is correct order ?



I II III IV

(*a*) IV > III > II > I
(*b*) IV > I > II > III
(*c*) IV > II > I > III
(*d*) I > II > IV > III.

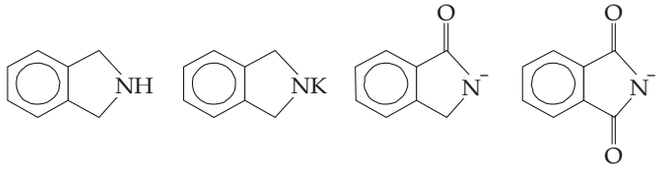
15. The correct order for decreasing basic character of the four amines I to IV is



I II III IV

(*a*) I > II > III > IV (*b*) I > IV > III > II
(*c*) I > II > IV > III (*d*) IV > I > III > II.

16. Which of the following is most basic, and which one is least ?



I II III IV

(*a*) II and IV respectively (*b*) II and I respectively
(*c*) I and II respectively (*d*) IV and I respectively.

17. When a 2°aromatic amine hydrochloride is heated, it leads to the formation of 1° amine hydrochloride, the reaction is known as
(*a*) Hofmann degradation
(*b*) Fries migration
(*c*) Hofmann Martius rearrangement
(*d*) None of the three.

18. Fluorobenzene can be prepared from aniline *via* diazotisation, the reaction is known as
(*a*) Sandmeyer reaction (*b*) Gattermann reaction
(*c*) Schiemann reaction (*d*) Modified Sandmeyer reaction

19. Benzenediazonium chloride on reaction with phenol in weakly basic medium gives
(*a*) diphenyl ether (*b*) *p*-hydroxyazobenzene
(*c*) chlorobenzene (*d*) benzene.

20. A positive carbylamine test is given by
(a) N, N-dimethylaniline
(b) 2,4-dimethylaniline
(c) N-methyl-*o*-methylaniline
(d) *p*-methylbenzyl amine

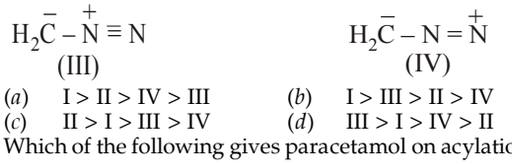
21. Which of the following statement is not correct regarding aniline?
(a) It is less basic than ethylamine
(b) It can be steam distilled
(c) It reacts with sodium to give hydrogen
(d) It is soluble in water

22. Benzenediazonium chloride on reaction with phenol in weakly basic medium gives
(a) diphenyl ether (b) *p*-hydroxyazobenzene
(c) chlorobenzene (d) benzene

23. The correct stability order of the following resonance structures is



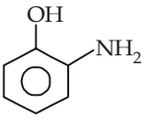
(I) (II)

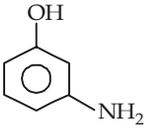


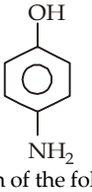
(III) (IV)

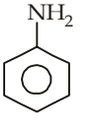
(*a*) I > II > IV > III (*b*) I > III > II > IV
(*c*) II > I > III > IV (*d*) III > I > IV > II

24. Which of the following gives paracetamol on acylation?

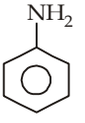
(*a*) 

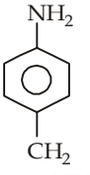
(*b*) 

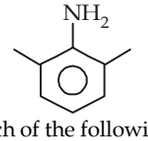
(*c*) 

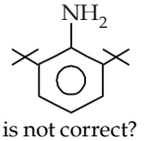
(*d*) 

25. Which of the following is strongly basic :

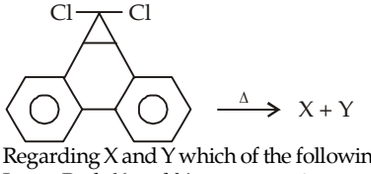
(*a*) 

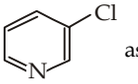
(*b*) 

(*c*) 

(*d*) 

26. Which of the following statements is not correct?
(*a*) Aliphatic amines are stronger bases than ammonia
(*b*) Aromatic amines are stronger bases than ammonia
(*c*) The alkyl group in alkyl ammonium ion stabilizes the ion more relative to the amine
(*d*) The aryl group in aryl ammonium ion stabilizes the ion less relative to the amine

27. 

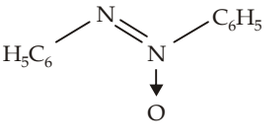
Regarding X and Y which of the following statement is/are correct?
I. Both X and Y are aromatic
II. One of them is anti-aromatic
III. All the carbon in X and Y are sp^2 hybridized
IV. One of the above species can give addition reaction with pyrrole and can produce  as a major product.

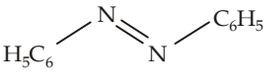
(*a*) I, III (*b*) I, III, IV
(*c*) III, IV (*d*) II, IV

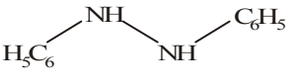
28. Benzenediazonium chloride forms coloured compound when treated with :
(*a*) Phenol (*b*) Cresol
(*c*) Resorcinol (*d*) All of the above

29. Which of the following statements is correct?
(*a*) Reaction of stereoisomeric alcohol with $SOCl_2$ in presence of pyridine gives the product with retention of configuration
(*b*) Solvolysis of secondary substrate is found to depend upon only the nucleophilic power of solvent not upon the ionization power of solvent.
(*c*) *p*-Aminobenzoic acid exists as Zwitterion in aqueous solvent
(*d*) Coupling of diazonium salt with phenol is carried out in mildly alkaline solution and with amines in mildly acidic solution

30. Which of the following substances represent a colourless substance?

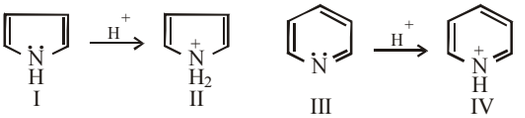
(*a*) 

(*b*) 

(*c*) 

(*d*) None of the above

31. Pyrrole and pyridine both are basic and form salts with acids?

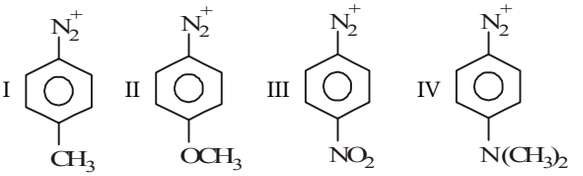


I II III IV

Which of the following statement is true regarding the aromatic character of the four species?
(a) All the four are aromatic
(b) I, III and IV are aromatic
(c) I, II and III are aromatic
(d) I and III are aromatic

32. Electrophilic aromatic substitution of pyridine resembles with
(a) benzene (b) aniline
(c) nitrobenzene (d) none of these

33. For the diazonium ions, the order of reactivity towards diazo-coupling with phenol in the presence of dil.NaOH is

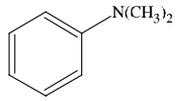
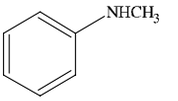


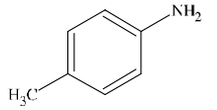
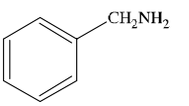
(a) I < IV < II < III (b) IV < II < I < III
(c) I < II < IV < III (d) III < IV < II < I

34. When aniline is treated with acetyl chloride in presence of anhydrous aluminium chloride, the main product is
(a) *o* - aminoacetophenone (b) *p*-aminoacetophenone
(c) both (a) and (b) (d) *m*-aminoacetophenone

35. Benzenediazonium chloride when treated with phenols gives azo dyes, to get best result the pH of the medium should be
(a) around 4 (b) around 8
(c) around 10 (d) 12

36. Amongst the compounds given, the one that would form a brilliant colored dye on treatment with $NaNO_2$ in dil. HCl followed by addition to an alkaline solution of β-naphthol is

(a)  (b) 

(c)  (d) 

EXERCISE 20.2 (MCQ 1 or >1 option correct, Passage based, Matching, A/R)

DIRECTIONS for Q. 1 to Q. 15 : Multiple choice questions with one or more than one correct option(s).

1. Which of the following reaction can be used for preparing aniline ?

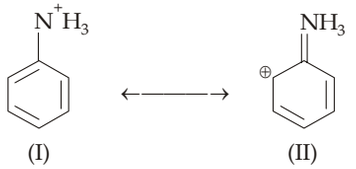
(*a*) $C_6H_5COOH \xrightarrow{N_3H,\ conc.\ H_2SO_4}$

(*b*) $C_6H_5NC \xrightarrow{H_3O^+}$

(*c*) $C_6H_5NC \xrightarrow{LiAlH_4}$

(*d*) $C_6H_5CONH_2 \xrightarrow{Br_2/NaOH}$

2. Examine the following two structures for the anilinium ion, predict which of the following statement is FALSE regarding the two canonical structures for anilinium ion ?

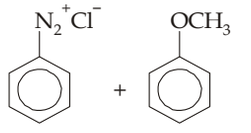


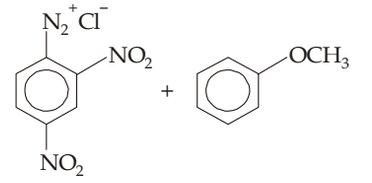
(I) (II)

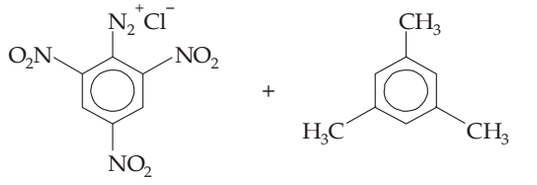
(*a*) II is not an acceptable canonical structure because carbocations are less stable than ammonium ions.
(*b*) II is not acceptable canonical structure because nitrogen has 10 valence electrons.
(*c*) II is not acceptable canonical structure because it is non-aromatic.
(*d*) II is acceptable structure.

3. Which of the following can exist as inner salt ?
(*a*) *p*-Aminobenzenesulphonic acid
(*b*) *p*-Aminobenzoic acid
(*c*) Aminoacetic acid
(*d*) Alanine

4. Which of the following pairs show coupling reaction ?

(*a*) 

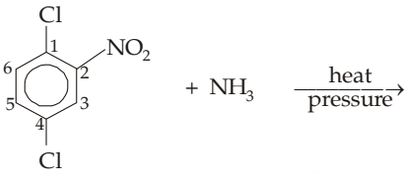
(*b*) 

(*c*) 

(*d*) Diazotised sulphanilic acid + Dimethylaniline

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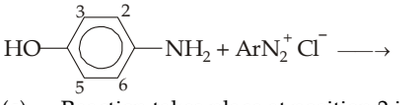
5. Which of the following statement is false regarding following reaction ?



(*a*) No reaction is possible because —Cl is present on benzene ring.
(*b*) A nucleophilic substitution will take place in which both —Cl will be replaced by two —NH_2 groups.
(*c*) A nucleophilic substitution will take place in which only —Cl attached on C_1 will be replaced by —NH_2.
(*d*) A nucleophilic substitution will take place in which only —Cl attached on C_4 will be replaced by —NH_2.

6. Libermann's nitroso reaction is used for testing
(*a*) 1° amine (*b*) 2° amine
(*c*) phenol (*d*) 3° amine.

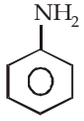
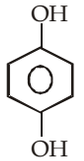
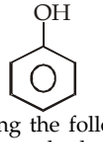
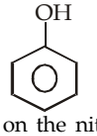
7. Which of the following statement is true regarding reaction of *p*-aminophenol with arenediazonium chloride?



(*a*) Reaction takes place at position 2 in presence of HCl.
(*b*) Reaction takes place at position 3 in presence of NaOH.
(*c*) No reaction occurs.
(*d*) Four azo groups can be introduced in the molecule.

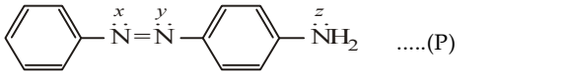
8. *p*-Chloraniline and aniline hydrochloride can't be distinguished by
(*a*) Sandmeyer reaction (*b*) $NaHCO_3$
(*c*) $AgNO_3$ (*d*) Carbylamine test.

9. Oxidation of A gives p-benzoquinone. A can be :

(a) 
(b) 
(c) 
(d) 

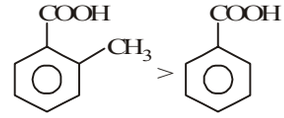
10. Among the following statements on the nitration of aromatic compounds, the correct ones are
(a) the rate of nitration of benzene is almost the same as that of hexadeutrobenzene.
(b) the rate of nitration of toluene is greater than that of benzene.
(c) the rate of nitration of benzene is greater than that of hexadeutrobenzene
(d) nitration is an electrophilic substitution reaction.

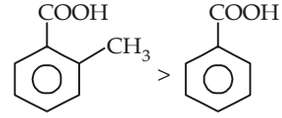
11. When nitrobenzene is treated with Br_2 in presence of $FeBr_3$, the major product formed is *m*-bromonitrobenzene. Statements which are related to obtain the *m*-isomer are
(a) The electron density on meta carbon is more than that on ortho and para positions
(b) The intermediate carbonium ion formed after initial attack of Br^+ at the meta position is least destabilised
(c) Loss of aromaticity when Br^+ attacks at the ortho and para positions and not at meta position
(d) Easier loss of H^+ to regain aromaticity from the meta position than from ortho and para positions.

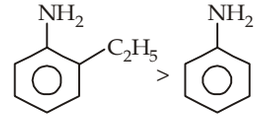
12.  .....(P)

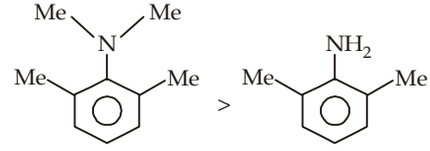
The correct statements about the compound (P) is/are :
(*a*) Nitrogen (*x*) is most basic in nautre
(*b*) The lone pair of electrons of nitrogen (*z*) is delocalized in the aromatic ring
(*c*) All the nitrogen atoms *x*, *y* and *z* are sp^2 hybridized
(*d*) The compound 'P' has stereoisomers

13. The correct orders are :

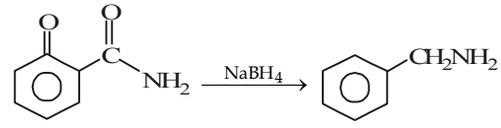
(*a*)  .....acid strength

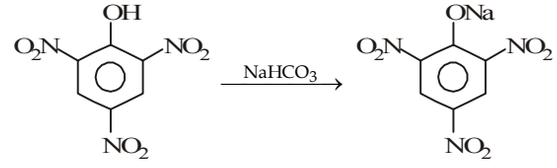
(*b*)  ..... rate of decarboxylation by soda lime

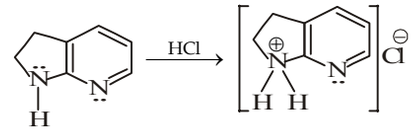
(*c*)  ..... basic strength

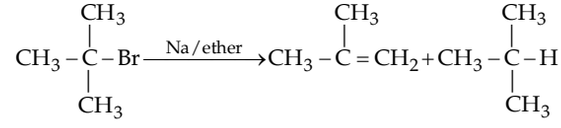
(*d*)  .... basic strength

14. The feasible reactions are :

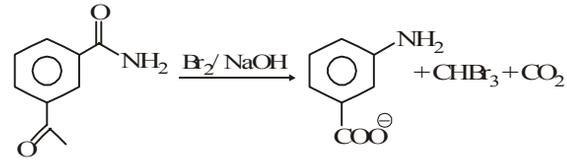
(a) 

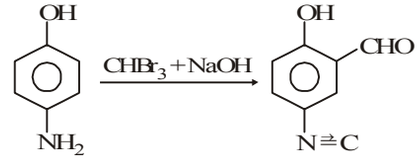
(b) 

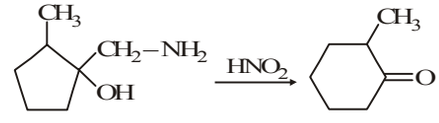
(c) 

(d) 

15. In which reaction, major product formed is correct

(a) 

(b) 

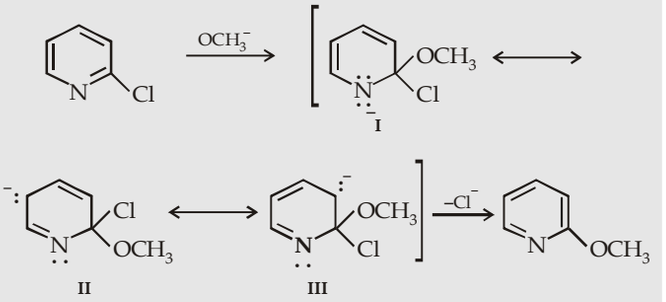
(c) 

(d)

INSTRUCTION for Q. 16 to 26 : Read the passages given below and answer the questions that follow.

PASSAGE 1

2-Chloropyridine when treated with sodium methoxide gives 2-methoxypyridine. The intermediate is stabilized by delocalization of the negative charge; since this type of stabilization is not possible if attack occurs at the 3-position, hence 3-chloropyridine is not converted into 3-methoxypyridine.



16. Which of the three resonating structures is especially stable?
(a) I (b) II
(c) III (d) none

17. The unstability of the corresponding intermediate from 3-chloropyridine is because of the fact that
(a) the intermediate has lesser number of canonical structures
(b) none of the canonical structure has negative charge on N
(c) both of the above reasons
(d) none of the two

18. What would happen if 2-chloropyridine is replaced by 4-chloropyridine?
(a) 2-Methylpyridine will be formed
(b) 3-Methoxypyridine will be formed
(c) 4-Methoxypyridine will be formed
(d) No reaction

PASSAGE 2

Primary aromatic amines react with nitrous acid to yield arenediazonium salts.

$$\underset{\text{1° aromatic aniline}}{ArNH_2} + NaNO_2 + 2HX \xrightarrow{\text{cold}} \underset{\text{Arenediazonium salt}}{Ar-N\equiv N^+X^-} + NaX + 2H_2O$$

Although arenediazonium salts are far more stable than aliphatic diazonium salts, especially at low temperature (0 - 5°), they slowly decompose even at low temperature, hence always used immediately after preparation.

Secondary amines, both aliphatic and aromatic, react with nitrous to form N-nitrosoamines which show Libermann's nitroso reaction

$$\underset{\text{N-Methylaniline}}{C_6H_5NHCH_3} + NaNO_2 + HCl \longrightarrow C_6H_5N(NO)CH_3$$

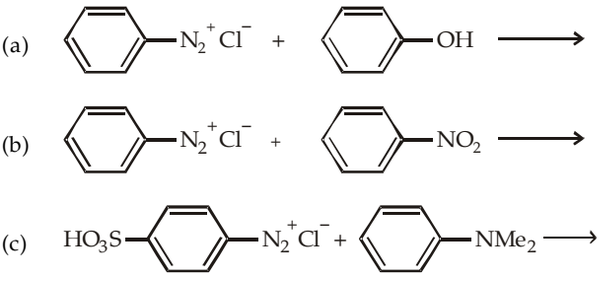
Aryldiazonium ions are substantially more stable than alkyldiazonium ions, and are of enormous synthetic value. The important synthetic reactions of diazonium salts may be divided into two classes. (a) replacement reaction, in which nitrogen is lost as N_2 and its place is taken by some other atom or group, and (b) coupling reactions, in which the nitrogen is retained in the product.

19. Arenediazonium ions are more stable than alkyldiazonium ions because
(a) resonance stabilization of the corresponding cation
(b) the arene cation, Ar^+ is very difficult to be formecd
(c) both the above factors
(d) none of the two

20. $C_6H_5NH_2 \longrightarrow C_6H_5N_2X^- \xrightarrow{H_2O} C_6H_5OH + N_2 + H^+$

In the preparation of the above diazonium salt, use of H_2SO_4 is preferred to HCl because
(a) sulphuric acid is a stronger acid
(b) HSO_4^- is less nucleophilic than Cl^-
(c) sulphuric acid absorbs water
(d) None of the three

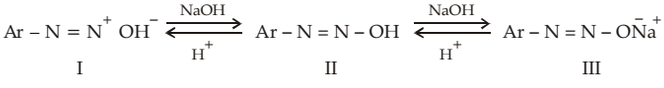
21. Coupling reaction is not in feasible in



(d) All are feasible

22. Which of the following statement is false?
(a) Coupling between arenediazonium cation and amines take place in strongly acidic conditions
(b) Coupling between arenediazonium cation and phenols takes place in slightly alkaline medium
(c) Both are correct
(d) Neither is correct

23. In strongly alkaline medium, the arenediazonium cation exists in the following equilibrium



Which of the above can undergo coupling reaction?
(a) I (b) II
(c) III (d) II and III

PASSAGE 3

p-Amino-*N*, *N*-dimethylaniline is added to a strongly acidic solution of **X**. The resulting solution is treated with a few drops of aqueous solution of **Y** to yield blue coloration due to the formation of methylene blue. Treatment of the aqueous solution of **Y** with the reagent potassium hexacyanoferrate(II) leads to the formation of an intense blue precipitate. The precipitate dissolves on excess addition of the reagent. Similarly, treatment of the solution of **Y** with the solution of potassium hexacyanoferrate (III) leads to a brown coloration due to the formation of **Z**.

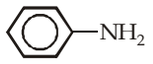
24. The compound **X** is
(a) $NaNO_3$ (b) NaCl
(c) Na_2SO_4 (d) Na_2S

25. The compound **Y** is
(a) $MgCl_2$ (b) $FeCl_2$
(c) $FeCl_3$ (d) $ZnCl_2$

26. The compound **Z** is
(a) $Mg_2[Fe(CN)_6]$ (b) $Fe[Fe(CN)_6]$
(c) $Fe_4[Fe(CN)_6]_3$ (d) $K_2Zn_3[Fe(CN)_6]_2$

Instructions for Q. 27 to 29 : Following questions are Multiple Matching type Questions :

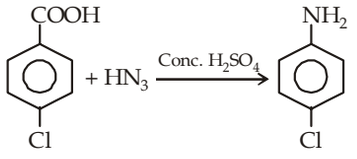
27.

	Column - I Basic compound		*Column - II* pK_a of ammonium ions
(A)		(a)	0.4
(B)	NH_3	(b)	4.63
(C)		(c)	5.25
(D)		(d)	9.26
(E)		(e)	11.27

28.

	Column - I		*Column - II*
(A)	Aldehyde + Zn(Hg) + conc. HCl	(a)	distinguish between primary and other amines
(B)	Carbylamine reaction	(b)	White precipitate
(C)	Schiff bases	(c)	Hydrocarbon
(D)	2, 4, 6-tri bromo-aniline	(d)	Antioxidation

29.

	Column - I	*Column - II*
(A)		(a) pH 5 - 7
(B)	$NH_2 + C_6H_5N_2^+ \longrightarrow$ Azo dye.	(b) Curtius reaction
(C)	$OH + C_6H_5N_2^+ \longrightarrow$ Azo dye.	(c) Sulphanilic acid
(D)	Methyl orange	(d) pH 9 - 10

Instructions for Q. 30 to 42 : Following questions are Assertion and Reasoning Type Questions :

Note : Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 5 choices (a), (b), (c), (d) and (e) out of which ONLY ONE is correct.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement -1 is True, Statement-2 is False.
(d) Statement -1 is False, Statement-2 is True.
(e) Statement -1 is False, Statement-2 is False.

30. **Statement-1 :** Benzene diazonium chloride does not give tests for nitrogen.
Statement-2 : Loss of N_2 gas takes place during heating.

31. **Statement-1 :** Anilinium chloride is more acidic than ammonium chloride.
Statement-2 : Anilinium ion is resonance-stabilized.

32. **Statement-1 :** p-O_2N—$C_2H_5COCH_3$ is prepared by Friedel Craft's acylation of nitrobenzene.
Statement-2 : Nitrobenzene easily undergoes electrophilic substitution reaction.

33. **STATEMENT - 1 :** Aniline on reaction with $NaNO_2$ / HCl at 0°C followed by coupling with β-naphthol gives a dark blue precipitate.
STATEMENT - 2 : The colour of the compound formed in the reaction of aniline with $NaNO_2$/HCl at 0°C followed by coupling with β-naphthol is due to the extended conjugation.

34. **Statement 1 :** pK_b for aniline is more than that of methylamine.
Statement 2 : Higher pK_b means less basic.

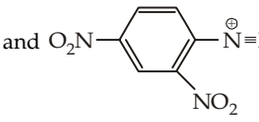
35. **Statement 1 :** Amino group is o- and p-directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline.
Statement 2 : Direct nitration of aniline gives a substantial amount of p-nitroaniline

36. **Statement 1 :** Diazonium salts of aromatic amines are more stable than those of aliphatic amines.
Statement 2 : Diazonium ion shows resonance.

37. **Statement 1 :** Ethylamine is soluble in water, whereas aniline is not.
Statement 2 : Ethylamine forms hydrogen bonds with water molecules.

38. **Statement 1 :** Aniline undergo Friedel-Crafts reaction.
Statement 2 : Aniline forms salt with aluminium chloride (a lewis acid) which is used as a catalyst.

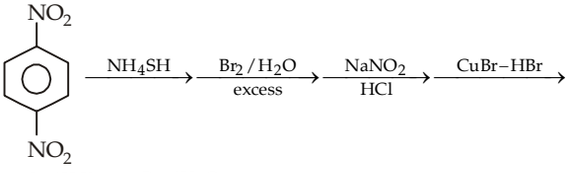
39. **Statement 1 :** Gabriel phthalimide synthesis is preferred for synthesising aliphatic primary amines.
Statement 2 : Aryl halides undergo nucleophilic substitution with the anion formed by phthalimide.

40. **Statement 1 :** Toluene undergoes diazo coupling with $Ph\overset{\oplus}{N}_2$ and  .
Statement 2 : $Ar\overset{\oplus}{N}_2$ is a weak electrophile and undergoes diazo coupling only with highly activated ring.

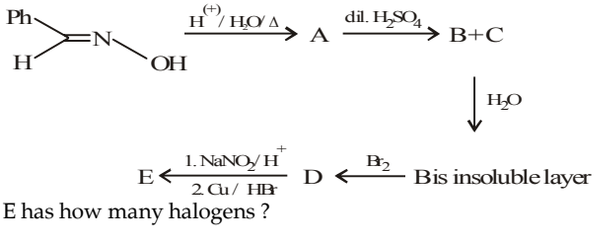
41. **Statement 1 :** In strongly acidic medium aniline becomes less reactive towards electrophilic reagent.
Statement 2 : NH_2 group is ortho and para directing.

42. **Statement - 1 :** In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagents.
Statement-2 : The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance.

Instructions for Q. 43 to 45 : Following questions are Integer Type Questions :

43. 
$\xrightarrow{Sn/HCl} \xrightarrow{Br_2/H_2O}$ major end product.
Find the total number of halogen atoms present in the major end product.

44. $Ph-NH_2 \xrightarrow[0-5°C]{NaNO_2/HCl} \xrightarrow[\text{dil. HCl}]{Ph-NH_2} (X)$
Find the sum of number of nitrogen atoms present in (X) and the total number of stereoisomers of (X) formed.

45. 
Find the total number of halogens in E.

EXERCISE 20.3 (Subjective Problems)

1. Write down structures of the following compounds.
(*a*) *p*-Toluidine (*b*) Anilinium chloride
(*c*) N, N-Diethylaniline (*d*) 2, 4-Dimethylaniline
(*e*) Benzylamine (*f*) Diphenylamine
(*g*) *p*, *p*′-Diaminodiphenyl (*h*) N-*n*-Propylaniline.

2. Compare the behaviour of aniline, N-methylaniline and N, N-dimethylaniline toward each of the following reagents.
(*a*) Dil. HCl (*b*) excess of CH_3I
(*c*) C_6H_5COCl + pyridine (*d*) $C_6H_5SO_2Cl$ + *aq*. KOH
(*e*) Bromine water.

3. Give structures and names of the principal organic products expected from the action of sodium nitrite and hydrochloric acid on each of the following compound.
(*a*) *o*-Toluidine (*b*) N-Methylaniline
(*c*) N, N-Dimethylaniline (*d*) 4, 4′-Diaminodiphenyl
(*e*) Benzylamine (*f*) Sulphanilic acid.

4. Write balanced equations for the following reactions.
(*a*) Benzanilide + *aq*. NaOH (boiling)
(*b*) Methyl formate + aniline
(*c*) *m*-Nitro–N–methylaniline + HONO
(*d*) *m*-Toluidine + *aq*. Br_2 (excess)
(*e*) *p*-Toluidine + *aq*. Br_2 (excess)
(*f*) $p\text{-}CH_3C_6H_4NHCOCH_3 + HNO_3 + H_2SO_4$
(*g*) Benzanilide + Br_2 + Fe.

5. Complete the following.

(*a*) $C_6H_5COOH \xrightarrow{PCl_5} [A] \xrightarrow{NH_3} [B] \xrightarrow{P_2O_5} [C] \xrightarrow{H^+,\ heat} [D]$

(*b*) $C_6H_5NH_2 + [E] + [F] \longrightarrow C_6H_5NHCONHC_6H_5$

(*c*) 2, 4-Dinitroaniline $\xrightarrow[5°C]{NaNO_2,\ HCl} [G] \xrightarrow{anisole} [H]$

(*d*) Aniline $\xrightarrow{Br_2\ water} [I] \xrightarrow[(ii)\ C_2H_5OH]{(i)\ NaNO_2,\ HCl,\ 5°C} [J]$

(*e*) $CH_3CONHC_6H_5 \xrightarrow{Br_2,\ Fe} [K] + [L]$.

SOLUTIONS

EXERCISE 20.1

1	(b)	**6**	(d)	**11**	(c)	**16**	(a)	**21**	(d)	**26**	(b)	**31**	(b)	**36**	(b)
2	(a)	**7**	(c)	**12**	(a)	**17**	(c)	**22**	(b)	**27**	(c)	**32**	(c)		
3	(c)	**8**	(d)	**13**	(c)	**18**	(c)	**23**	(b)	**28**	(d)	**33**	(b)		
4	(c)	**9**	(b)	**14**	(c)	**19**	(b)	**24**	(c)	**29**	(d)	**34**	(d)		
5	(c)	**10**	(a)	**15**	(d)	**20**	(b)	**25**	(c)	**30**	(c)	**35**	(b)		

1. In the Zwitterion of sulphanilic acid, the $—SO_3^-$ is too weakly basic (its conjugate acid $—SO_3H$ is a strong acid) to accept H^+ from strong acids, hence it does not dissolve in HCl.

2. Arenediazonium cation is a weak electrophile, hence it can couple only with those compounds which bear powerful electron-releasing group like —OH, $—NH_2$, —NHR, or $—NR_2$. Hence toluene, having weak electron-releasing $—CH_3$ group can't couple with diazonium cation.

3. Coupling reaction between arenediazonium cation and an aromatic compound is an electrophilic substitution reaction in which, $C_6H_5N_2^+$, a weak electrophile reacts with the benzene compound having highly activating group. More is the activating (electron-releasing) character of the group, easier will be coupling. Hence

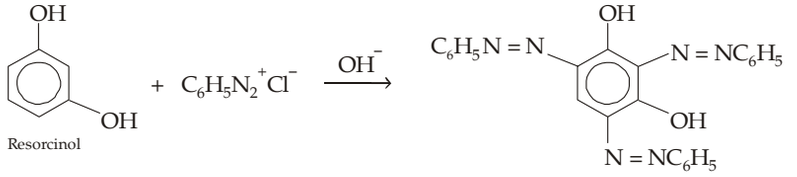
$$—O^- > —NH_2 > —OH > —NH_3^+.$$

4. Electorn-withdrawing groups (like $—NO_2$) make arenediazonium cation more electron-deficient, *i.e.*, strong electrophile, while electron-releasing group makes diazonium cation a weak electrophile.

5. $C_6H_5NO_2$ oxidizes CH_3 of $p\text{-}NH_2C_6H_4CH_3$ to CHO and itself reduced to $C_6H_5NH_2$.

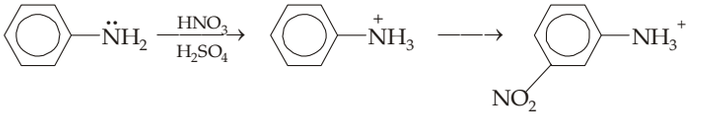
6. $C_6H_5NH_2 \xrightarrow{CHCl_3,\ KOH} C_6H_5NC \xrightarrow{H_3O^+} C_6H_5NH_2 + HCOOH$

7.



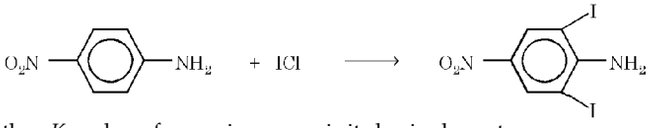
Resorcinol has one *para* and two *ortho* positions free.

8. Aniline in presence of acids undergoes protonation to form $C_6H_5NH_3^+$ in which $—NH_3^+$ group is *m*-directing.

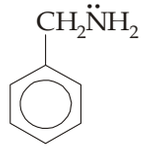


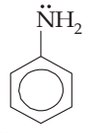
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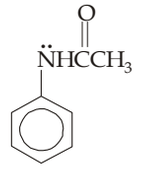
9. Iodine chloride is an electrophilic reagent and because of high electronegativity of Cl it gives rise to I^+ and Cl^-. Hence

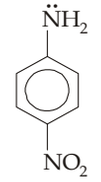


10. Lower the pK_b value of an amine, more is its basic character.

(*a*) 
Electron pair localized, hence most basic

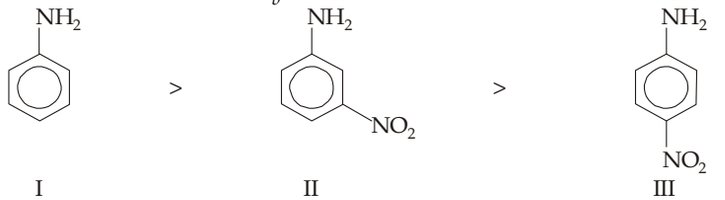
(*b*) 
Electron pair delocalized

(*c*) 
electron pair delocalized on ring as well as on —CO—gp.

(*d*) 
electron pair highly delocalized due to —NO_2 gp.

11. Presence of electron-withdrawing gp. (—$COCH_3$) in *o*, *p*-position decreases basicity while that of electron-releasing gp. (—CH_3) increases basic character of the aromatic amine. Acetanilide is weaker than aniline because here electron pair on N is also delocalized to the —CO— part in addition to benzene ring. The same is also true to *p*-$CH_3CO.C_6H_4.NH_2$.

12. The basic character and hence K_b values of the three anilines follows the order

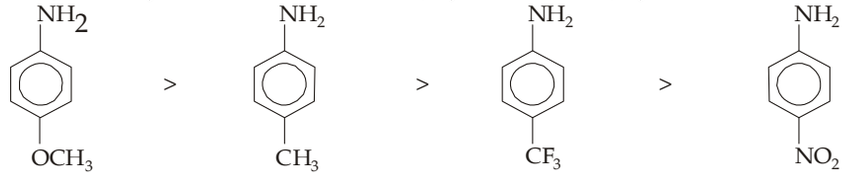


I
e pair is delocalized only to ring

II
e pair is delocalized only to ring, but —I effect of —NO_2 also decreases basicity

III
e pair is delocalized to ring as well as to —NO_2 gp. ; —I effect of —NO_2 further decreases basicity

Since higher the K_b value of an amine, lower is pK_b value ; thus the pK_b values of the three anilines will be of the order : I < II < III.

13. 

II
—OCH_3 increases basic character due to + M effect of the —OCH_3 gp.

I
—CH_3 increases basic character due to + I effect of the —CH_3 gp.

III
—CF_3 decreases basic character due to —I effect of the —CF_3 gp.

IV
–NO_2 decreases basic character due to —M and —I effects of the —NO_2 gp.

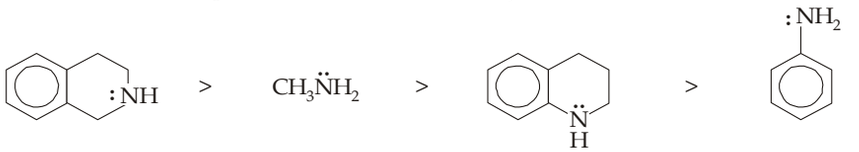
14. 

IV
e pair on N of the ring not involved in sextet ; also e pair on —NH_2 delocalized to N of the ring

II
e pair of N of the ring not involved in sextet; +I effect of —CH_3 further increases *e* density

I
e pair on N is not involved in sextet

III
e pair on N is delocalized to ring

15. 

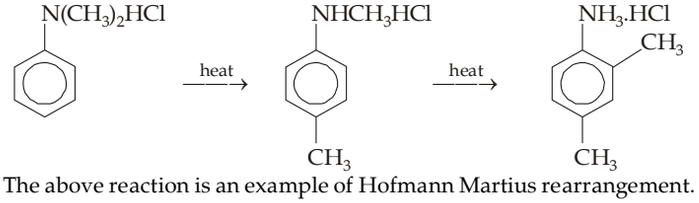
IV
2° Amine, *e* pair localized

I
1° Amine, *e* pair localized

III
2° Amine, *e* pair delocalized

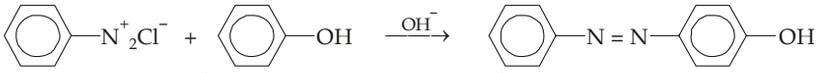
II
1° Amine, *e* pair delocalized

16. II has maximum electrons density on N and it is localized ; in IV electrons are delocalized due to two —C = O groups.

17. 

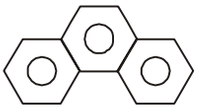
The above reaction is an example of Hofmann Martius rearrangement.

18. Theoretical question.

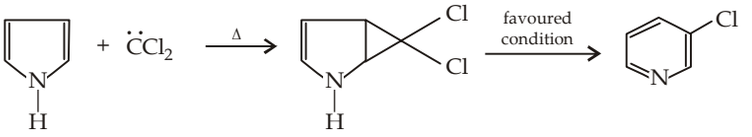
19. 

25. The conjugate acid of (d) exhibits steric inhibition of resonance.

26. Aromatic amines are less basic than ammonia.

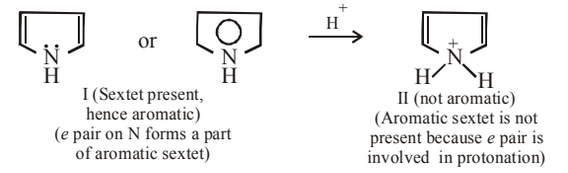
27.  $\ddot{C}Cl_2$ (Singlet carbon)

X Y



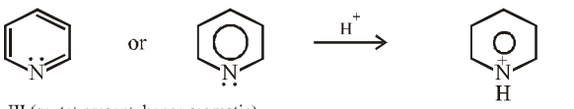
28. All have electron donating group attached to the ring which makes dye formation favourable.

31.



I (Sextet present, hence aromatic) (*e* pair on N forms a part of aromatic sextet)

II (not aromatic) (Aromatic sextet is not present because *e* pair is involved in protonation)



III (sextet present, hence aromatic) (*e* pair on N, not a part of sextet)

IV (sextet present, hence aromatic)

32. Pyridine resembles a strongly deactivated benzene, here the deactivation is due to electron-withdrawing effect of the electrongative N atom from 2-and 4 - positions making 3-positions to be more vulnerable for the attack of an electrophile. Remember that the nonbonding electrons on N are perpendicular to the π-system (they are present in sp^2 orbital), these are not involved in delocalisation, i.e., they can't stabilize the positively charged intermediate.

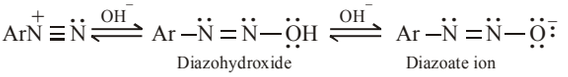
33. Presence of electron withdrawing group in arene diazonium ions enhances the electrophilic character of the ion and thus increases coupling.

34. In presence of $AlCl_3$ (a Lewis acid), aniline is converted into anilinium cation, which being *m*-directing gives *m*-aminoacetophenone.

35.(a) Couplings of arenediazonium cations and phenols take place most rapidly in slightly alkaline medium because

(i) acidic medium (pH < 7) will suppress the ionisation of C_6H_5OH to the more reactive $C_6H_5O^-$, while the alkaline medium (pH > 7) will enhance ionisation of phenol to phenoxide ion.

(ii) strongly alkaline medium (pH > 10) causes the arenediazonium salt to react with the OH^- ion to form a relatively unreactive diazohydroxide or diazoate ion.



Diazohydroxide Diazoate ion

36. (c) Only primary aromatic amines undergo diazotisation followed by coupling.

EXERCISE 20.2

>1 CORRECT OPTION	**1**	(a,b,d)	**2**	(a,c,d)	**3**	(a,c,d)	**4**	(b,c,d)	**5**	(a,b,d)	**6**	(b,c)
	7	(a,b,d)	**8**	(a,b,d)	**9**	(a, b, c)	**10**	(a,b,d)	**11**	(a, d)	**12**	(a, b, c, d)
	13	(a, d)	**14**	(b,d)	**15**	(a, b, c, d)						
PASSAGE 1	**16**	(a)	**17**	(b)	**18**	(c)						
PASSAGE 2	**19**	(c)	**20**	(b)	**21**	(b)	**22**	(a)	**23**	(d)		
PASSAGE 3	**24**	(d)	**25**	(c)	**26**	(b)						
MATCH THE FOLLOWING	**27**	(A) - b ; (B) - d ; (C) - e ; (D) - a ; (E) - C										
	28	(A) – (c); (B) – (a); (C) – (d); (D) – (b)										
	29	(A) - (b), (B) - (a), (C) - (d), (D) - (c)										
A/R	**30**	(a)	**31**	(b)	**32**	(d)	**33**	(d)	**34**	(a)	**35**	(c)
	36	(a)	**37**	(a)	**38**	(d)	**39**	(c)	**40**	(d)	**41**	(b)
	42	(d)										
INTEGER	**43**	**5**	**44**	**5**	**45**	**4**						

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1. Isonitriles (C_6H_5NC) on reduction give 2° amines ($C_6H_5NHCH_3$). All other three methods give aniline.

2. Nitrogen (N) has no *d* orbital, hence it can't have more than 8 electorns in the outermost shell. All other three options are false.

3. In *p*-$NH_2C_6H_4COOH$, —COOH group is very weak so it can't transfer H^+ to the weakly basic amino group. All other three form zwitterions.

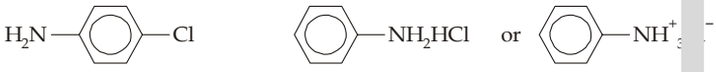
4. In $C_6H_5OCH_3$, —OCH_3 does not sufficiently increase electron density on the ring. Recall that C_6H_5OH undergoes coupling in weakly alkaline medium which converts C_6H_5OH to the more reactive $C_6H_5O^-$. In options (*b*) and (*c*), presence of electron-withdrawing —NO_2 groups increases electrophilic character to such an extent that these diazonium cations can couple even with the compounds having weak electron-releasing groups. Option (d) undergoes coupling reaction easily because –NMe_2 is sufficiently electron-releasing.

5. Recall that the —Cl group present in the *o*- and *p*- positions to the electron-withdrawing group is activated toward nucleophilic substitution, hence only —Cl present on the *o*- and/or *p*-position to the —NO_2 group will be replaced.

6. In Libermann's nitroso test 2° amine and phenol are used as reagents.

7. In *p*-aminophenol all the four positions (2, 3, 5 and 6) can be coupled (positions 2 and 6 in presence of H^+ and positions 3 and 5 in presence of OH^-).

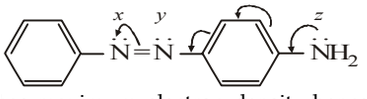
8.



p-Chloroaniline (—Cl is non-reactive) (—Cl is present as reactive)

It reacts with $AgNO_3$. The three other options (a, b and d) are not proper reagents to distinguish.

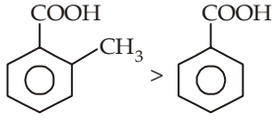
12. (*a,b,c,d*)



x has maximum electron density hence it is most basic. Lone pair of *z* is delocalised. All nitrogen atoms *x*, *y* and *z* are sp^2 hybridised.

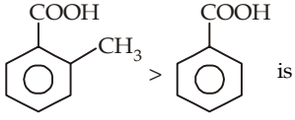
The compound has stereoisomerism along N = N.

13.(*a, d*) (a)



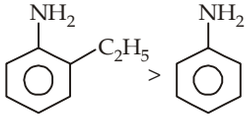
....K_a is correct.

(b)



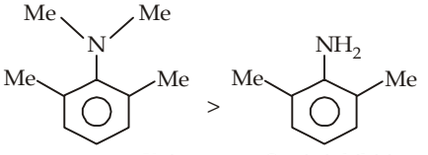
is incorrect

(c)



is incorrect.

(d)

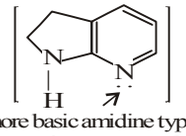


..... K_b is correct. Steric inhibition of resonance.

14.(*b,d*) (a) not feasible.

(b) is feasible.

(c) not feasible



more basic amidine type; electron pair not a part of sextet

(d) is feasible by-product in Wurtz reaction.

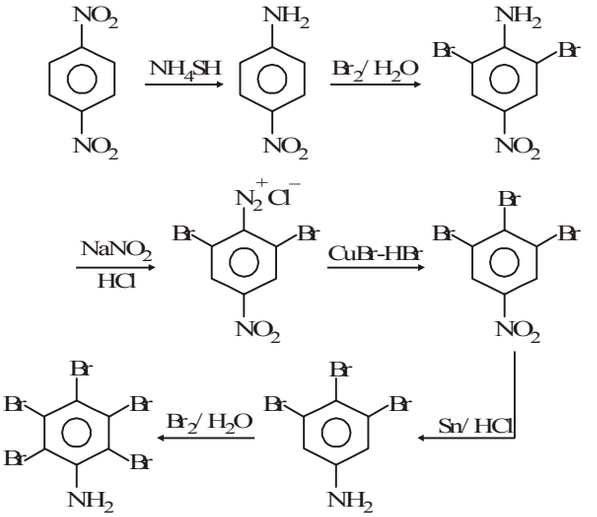
40. (*d*) Statement-1 false, statement-2 true.

41. (*b*) In presence of acid, –NH_2 group forms –NH_3^+, i.e. anilinium ion and shows *m*-directing nature. Thus, ring is deactivated for electrophilic substitution reaction.

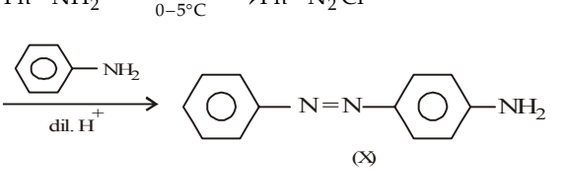
42. (*d*) Electron donating tendency to a double bond is called +M effect and the transfer of electrons take place towards the attacking reagent due to +E effect.

In strongly acidic conditions, aniline becomes protonated with the result lone pair of electrons is not available to produce +E and +M effects. Thus here aniline becomes less reactive towards electrophilic substitution. On the other hand, the $-\overset{\oplus}{N}H_3$ group exerts strong –I effect causing deactivation of the ring.

43. 5;



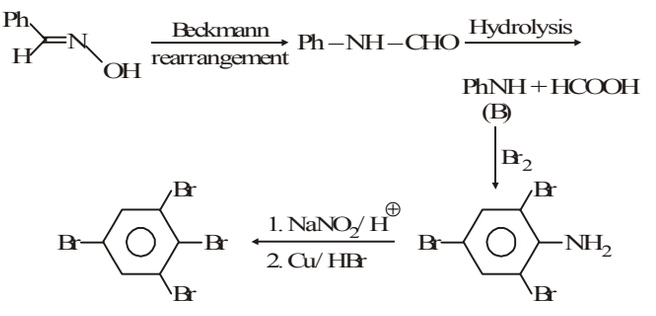
44. 5;



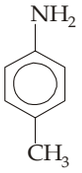
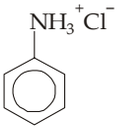
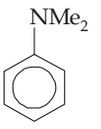
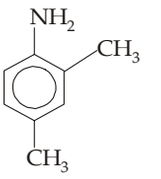
No. of N-atoms in X is 3.

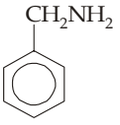
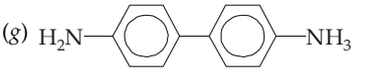
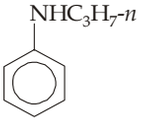
No. of stereoisomers = 2 (syn/anti).

45. 4;



EXERCISE 20.3

1. (*a*)  (*b*)  (*c*)  (*d*) 

(*e*)  (*f*) $C_6H_5NHC_6H_5$ (*g*)  (*h*) 

2. (*a*) All the three produce soluble ammonium salts.

$C_6H_5NH_2.HCl$, $C_6H_5N^+H_2CH_3Cl^-$, and $C_6H_5N^+H(CH_3)_2Cl^-$

(*b*) All the three produce same quaternary ammonium salt, $C_6H_5N^+Me_3I^-$, of course by taking different amount of CH_3I.

(*c*) $C_6H_5NH_2 \xrightarrow[\text{Pyridine}]{C_6H_5COCl} C_6H_5\overset{\overset{H}{|}}{\underset{\cdot\cdot}{N}}-\overset{\overset{O}{\|}}{C}-C_6H_5$ **Neutral** (due to delocalization of *e* on N to —C = O group),

insoluble in dil acid or base

$C_6H_5\overset{\overset{CH_3}{|}}{N}H \xrightarrow{C_6H_5COCl} C_6H_5\overset{\overset{CH_3}{|}}{\underset{\cdot\cdot}{N}}-\overset{\overset{O}{\|}}{C}-C_6H_5$ **Neutral,** insoluble in acid or base

$C_6H_5\overset{\overset{CH_3}{|}}{\underset{\cdot\cdot}{N}}-CH_3 \longrightarrow$ No reaction. **Basic,** soluble in acid, insoluble in base

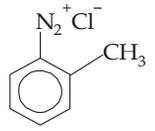
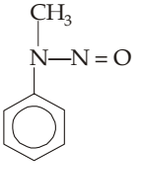
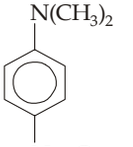
(*d*) $C_6H_5NH_2 \xrightarrow{C_6H_5SO_2Cl} \underset{\text{Acidic (Soluble in base)}}{C_6H_5NHSO_2C_6H_5} \xrightarrow[KOH]{aq.} \underset{\text{Soluble}}{C_6H_5N^-SO_2C_6H_5}$

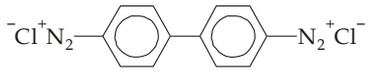
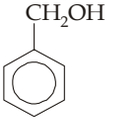
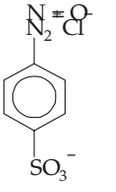
$C_6H_5\overset{\overset{CH_3}{|}}{N}H \longrightarrow \underset{\text{Neutral}}{C_6H_5\overset{\overset{CH_3}{|}}{N}SO_2C_6H_5} \xrightarrow[KOH]{aq.}$ No reaction *i.e.*, insoluble

(Insoluble in acid or base)

$C_6H_5\overset{\overset{CH_3}{|}}{N}-CH_3 \longrightarrow$ No reaction ; **Basic** (insoluble in base, soluble in acid)

(*e*) All the three undergo very fast ring bromination to give corresponding tribromo products.

3. (*a*)  (*b*)  (*c*) 

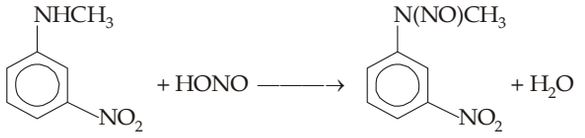
(*d*)  (*e*)  (*f*) 

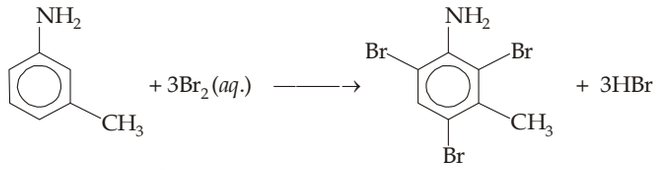
4. (*a*) $C_6H_5NHCOC_6H_5 + NaOH \xrightarrow{boil} C_6H_5NH_2 + C_6H_5COO^-Na^+$

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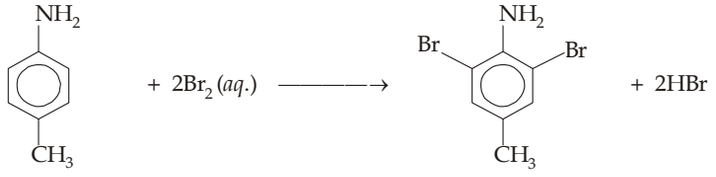
(*b*) $C_6H_5NH_2$ + $H_3CO-\overset{\overset{O}{\|}}{C}-H \longrightarrow C_6H_5NH-\overset{\overset{O}{\|}}{C}-H + CH_3OH$

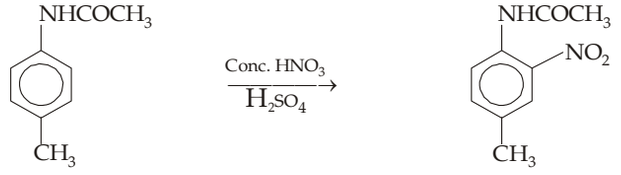
Aniline — Methyl formate

(*c*) 

(*d*) 

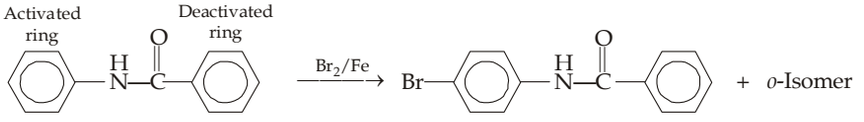
(—NH_2 is more activating than —CH_3)

(*e*) 

(*f*) 

(—$NHCOCH_3$ is more electron-releasing than —CH_3)

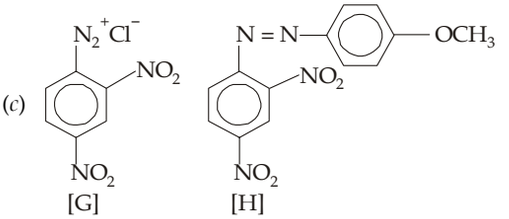
(Second —NO_2 is not introduced because the ring is deactivated due to —NO_2 group, already present)

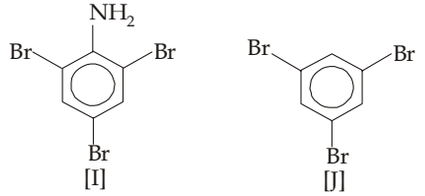
(*g*) 

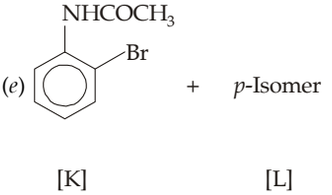
Benzanilide
(Ring having —NH—part is activated while other having —CO— is deactivated

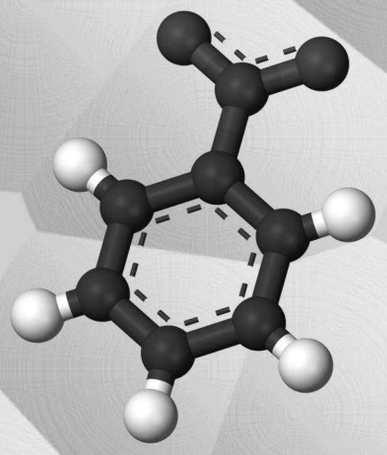
5. (*a*) C_6H_5COCl [A] $C_6H_5CONH_2$ [B] C_6H_5CN [C] C_6H_5COOH [D]

(*b*) $COCl_2 + C_6H_5NH_2$
[E] and [F]

(*c*) 

(*d*) 

(*e*) 



21

Other Nitrogen Containing Compounds

CHAPTER HIGHLIGHTS

21.1 Nitriles and Isonitriles

21.2 Alkyl Nitrites and Nitro Compounds

21.3 Aromatic Nitro Compounds

21.4 Illustrative Examples

EXERCISES

SOLUTIONS

21.1 Nitriles and Isonitriles

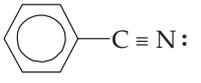
A nitrile has the formula R—C ≡ N: (or R—CN). The carbon and the nitrogen of a nitrile are *sp* hybridised. In IUPAC systematic nomenclature, acyclic nitriles are named by adding the suffix *nitrile* to the name of the corresponding hydrocarbon, the carbon atom of the —C ≡ N group is assigned number 1.

$\overset{2}{C}H_3—\overset{1}{C} \equiv N:$ Ethanenitrile (acetonitrile)

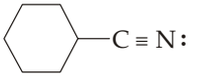
$\overset{3}{C}H_2 = \overset{2}{C}H—\overset{1}{C} \equiv N:$ Propenenitrile (acrylonitrile)

$\overset{5}{C}H_2 = \overset{4}{C}H\overset{3}{C}H_2\overset{2}{C}H_2—\overset{1}{C} \equiv N:$ 4-Pentenenitrile

Cyclic nitriles are named by adding the suffix *carbonitrile* to the name of the ring system to which the —CN group is attached.



Benzenecarbonitrile



Cyclohexanecarbonitrile (benzonitrile)

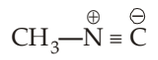
Common name of nitriles (given in parentheses) are derived by replacing the *-ic acid* or *-oic acid* ending of the corresponding carboxylic acid by *-onitrile*. Alternatively, nitriles are sometimes given **radicofunctional names** as *alkyl cyanides.*

Isonitriles are functional isomers of nitriles ; the latter being more stable than the former.

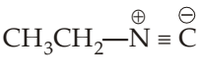
$$\underset{\text{Isonitriles}}{R—\overset{\oplus}{N} \equiv \overset{\ominus}{C}:} \xrightarrow{\text{heat}} \underset{\text{Nitriles}}{R—C \equiv N}$$

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These are commonly called by their common names, in which the prefix *iso* is added before the name of the isomeric nitrile. In IUPAC nomenclature, these are named as alkylcarbylamines.



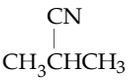
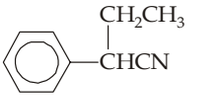
Methylcarbylamine
Methyl isocyanide
Methyl isonitrile
Acetoisonitrile



Ethylcarbylamine
Ethyl isocyanide
Ethyl isonitrile
Propionoisonitrile

TEST YOUR UNDERSTANDING - 21.1

1. Give IUPAC names for the following :

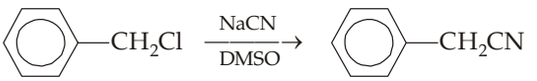
(*a*)  (*b*) CH_3CH_2NC (*c*) 

21.1.1 Preparation of Nitriles and Isonitriles

1. **From alkyl halides.** Aliphatic nitriles are prepared by treating alkyl halides with sodium cyanide in a solvent that dissolves both reactants ; in dimethyl sulphoxide (DMSO), reaction occurs rapidly and exothermically at room temperature.

$$\underset{\text{1° or 2° alkyl halide}}{R{-}X} + CN^- \longrightarrow R{-}CN + X^-$$

Remember that this reaction is of the S_{N^2} type and is limited to 1° and 2° alkyl halides ; 3° alkyl halides undergo exclusively elimination reaction because CN^- is a strong base (recall that HCN, conjugate acid of CN^- is a very weak acid).



Benzyl chloride — Benzyl cyanide



Cyclopentyl chloride — Cyclopenyl cyanide

In case silver cyanide is used in place of potassium cyanide, isonitrile is the main product, while nitrile is formed only in small amount.

$$CH_3I + AgCN \longrightarrow \underset{\text{Methylcarbylamine}}{CH_3NC} + AgI$$

Remember that aryl and vinyl halides are unreactive toward nucleophilic substitution reaction, hence aryl nitriles and vinyl nitriles can't be prepared by this method.

$$C_6H_5Cl \quad \text{or} \quad CH_2 = CHCl \xrightarrow[DMSO]{NaCN} \text{No reaction}$$

2. **From arenediazonium salts.** Aryl nitriles are prepared from diazonium salts by **Sandmeyer reaction** which involves the reaction of aryl diazonium salt with cuprous cyanide.

$$\underset{\text{Aryl diazonium halide}}{Ar{-}N_2^+X^-} \xrightarrow{CuCN} Ar{-}CN + N_2$$

3. **By dehydration of amides.** Amides react with P_4O_{10} (a compound that is often called phosphorus pentoxide and written P_2O_5) or with boiling acetic anhydride to form nitriles.

$$RCONH_2 \xrightarrow[\text{heat, } (-H_2O)]{P_4O_{10} \text{ or } (CH_3CO)_2O} RCN + H_3PO_4 \quad \text{or} \quad CH_3COOH$$

(R = alkyl or aryl group)

This method is useful for preparing nitriles which can't be prepared by nucleophilic substitution reaction between alkyl halides and cyanide ions.

4. **By the dehydration of aldoximes** with acetic anhydride or P_4O_{10}

$$\underset{\text{Aldoxime}}{RCH = NOH} \xrightarrow{(CH_3CO)_2O} \underset{\text{Nitrile}}{RC \equiv N} + H_2O$$

(R may be alkyl or aryl)

5. **From Grignard reagents.**

$$RMgX + \underset{\text{Cyanogen chloride}}{ClCN} \longrightarrow RCN + Mg(Cl)X$$

6. **Carbylamine reaction (***only for isonitriles***).**

$$C_2H_5NH_2 + CHCl_3 + 3KOH \longrightarrow C_2H_5NC + 3KCl + 3H_2O$$

TEST YOUR UNDERSTANDING - 21.2

1. (*a*) Try to convert ethanol to (*i*) CH_3CN, and (*ii*) CH_3CH_2CN

(*b*) Give steps involved in the synthesis of Me_3CCN from Me_3CCOOH.

21.1.2 Properties of Nitriles and Isonitriles

1. **Nitriles** are more polar than isonitriles, hence they have high dipole moment, high b.p. and are more soluble in water. Recall that carbylamines (isonitriles) are extremely unpleasant, while nitriles are pleasant smelling.

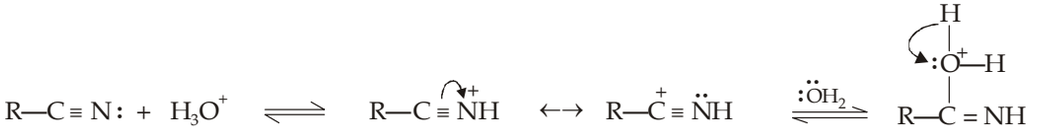
2. **Hydrolysis.** Since nitriles are converted to carboxylic acids on hydrolysis, *these are classified as carboxylic acid derivatives.*

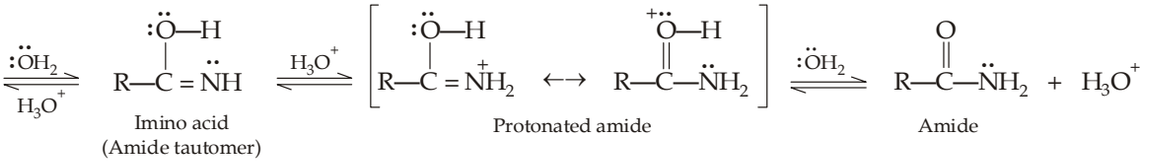
Like amides, nitriles when heated in aqueous acid or base for several hours give carboxylic acids. Further like amide hydrolysis, nitrile hydrolysis is irreversible.

$$R{-}C \equiv N + H_2O + H_3O^+ \longrightarrow RCOOH + NH_4^+$$

$$R{-}C \equiv N + H_2O + OH^- \longrightarrow RCOO^- + NH_3$$

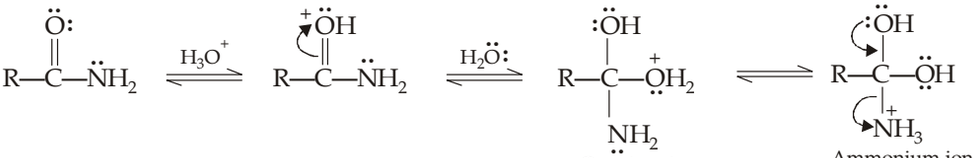
Mechanism for acidic hydrolysis of nitriles



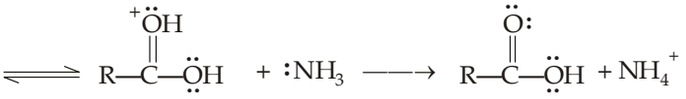


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In presence of concentrated H_2SO_4, the reaction stops at the protonated amide which constitutes a useful way for preparing amides from nitriles. In presence of dilute acids, amides undergo further hydrolysis to form carboxylic acids as the final product.

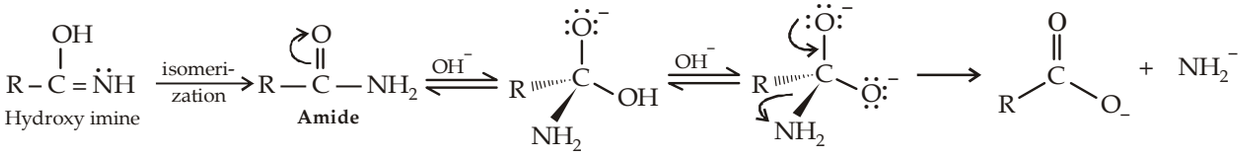


Amide | Protonated amide | Oxonium ion (a proton is lost from O and gained at N) | Ammonium ion



Protonated carboxylic acid

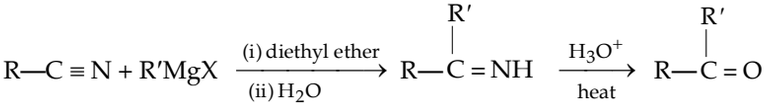
Mechanism for basic hydrolysis of nitriles

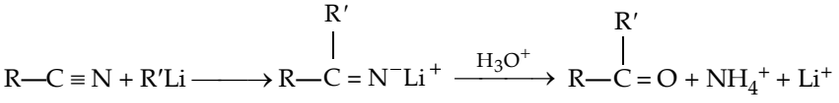


Hydroxy imine | Amide

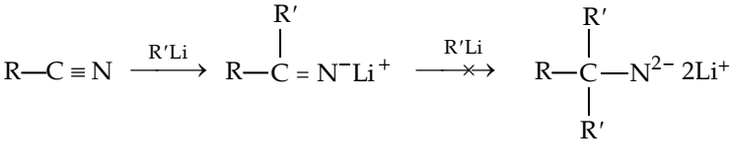
Here also, amides can be isolated under appropriate (milder) conditions.

3. **Addition of Grignard reagents.** Although the carbon-nitrogen triple bond of nitriles is much less reactive toward nucleophilic addition than is the carbon-oxygen double bond of aldehydes and ketones, strongly basic nucleophiles such as Grignard reagents and organolithium compounds easily add on nitriles to form ketones





Since nitriles are more reactive than ketones, the next molecule of R′MgX will add to fresh molecule of RC ≡ N to form ketone rather than with ketone to form a 3° alcohol. Although a nitrile has a triple bond, addition of the Grignard or lithium reagent takes place only once because if the addition takes place twice, nitrogen will get a double negative charge which is not possible.



(The dianion does not form)

TEST YOUR UNDERSTANDING - 21.3

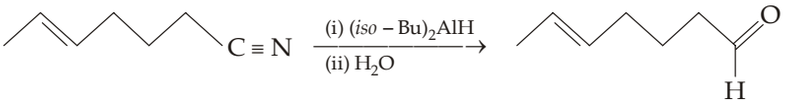
1. Compare the reaction of Grignard reagent with an ester and a nitrile, explain the difference between the intermediates formed in two cases when one molecule of the reagent adds on the compound (ester or nitrile).

4. Reduction of nitriles. Nitriles can be reduced to 1° amines by catalytic hydrogenation or $LiAlH_4$.

$$R—C \equiv N \xrightarrow{2H_2,\ \text{Raney Ni, } 140°C} R—CH_2NH_2$$

Nitriles can also be reduced to aldehydes by means disobutylaluminium hydride (DIBAL–H). This reaction is also known as **Stephen reduction.**

$$R—C \equiv N \xrightarrow{(iso\text{–}Bu)_2\ AlH} R—CH = NH \xrightarrow{H_2O} R—CHO + NH_3$$



5. Condensation with aldehydes. The α-hydrogens of nitriles are appreciably acidic, but less than those of aldehydes and ketones. The acidity constant for acetonitrile (CH_3CN) is about 10^{-25} ($pK_a \approx 25$). Other nitriles with α-hydrogens show comparable acidities, and consequently these nitriles undergo aldol type of condensations.

$$C_6H_5\overset{\overset{O}{\|}}{C}H + C_6H_5CH_2CN \xrightarrow[C_2H_5OH]{C_2H_5O^-} C_6H_5CH = \underset{\underset{C_6H_5}{|}}{C}CN$$

The note-worthy properties of alkyl isonitriles are hydrolysis, reduction and addition reactions.

(*a*) Alkyl isonitriles are hydrolysed only by dilute mineral acid (H_2SO_4 or HCl) to form **1° amines**

$$R—N \rightleftarrows C \xrightarrow[(+\ 2H_2O)]{H^+} R—NH_2 + HCOOH$$

Isonitriles do not undergo basic hydrolysis because of their inability to undergo the attack by OH^- ions.

(*b*) Catalytic hydrogenation or reduction with lithiumaluminium hydride gives 2° amines.

$$R—N \rightleftarrows C \xrightarrow{LiAlH_4} RNHCH_3$$

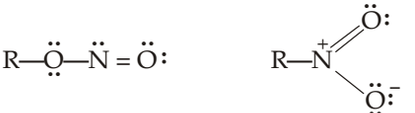
(*c*) Isonitriles undergo certain addition reactions in which addition takes place only on carbon.

$$RN = C = O \xleftarrow[\text{or } O_3]{2HgO} \mathbf{RN \rightleftarrows C} \xrightarrow{1/8\ S_8} RN = C = S$$

Alkyl isocyanate* **Alkyl isonitrile** Alkyl isothiocyanate

21.2 Alkyl Nitrites and Nitro Compounds

These are functional isomers, *e.g.*



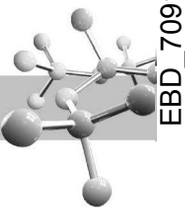
Alkyl nitrite Nitroalkane

Nitromethane, used as a high-energy fuel for race cars, is a liquid with a b.p. of 101°C, while methyl nitrite is a gas (b.p. –12°C) which causes dilation of blood vessels, on inhalation, hence it is used for the treatment of angina pectoris (a heart disease).

However, remember that alkyl nitrites are esters of nitrous acid (HONO) while nitro compounds are not esters because these can neither be prepared by the interaction of alcohol with an acid (HONO) nor they undergo hydrolysis to form alcohol and acid (nitrous acid). Actually, nitro compounds are regarded as nitro derivatives of the hydrocarbons.

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* Recall that methyl isocyanate, MIC was responsible for Bhopal tragedy in Dec. 1984.



21.2.1 Preparation and Properties of Alkyl Nitrites

1. By the action of nitrous acid on alcohol.

$$C_2H_5OH \xrightarrow[(+\ HONO)]{NaNO_2,\ H^+} C_2H_5ONO + H_2O$$

2. By the action of nitrogen trioxide (N_2O_3) on alcohols.

$$2C_2H_5OH + N_2O_3 \longrightarrow 2C_2H_5ONO + H_2O$$

Nitrogen trioxide is generated *in situ i.e.* it is prepared by the action of conc. HNO_3 on a mixture of conc. H_2SO_4 and alcohol and then adding copper turnings.

3. By the action of alkyl iodide and potassium nitrite.

$$C_2H_5I + KNO_2 \longrightarrow C_2H_5ONO + KI$$

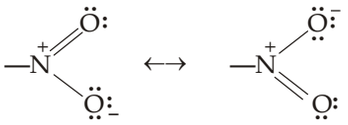
Properties. Its two worth-mentioning properties are hydrolysis and reduction.

$$C_2H_5—O—N = O \xrightarrow{H^+,\ OH^-,\ \text{or, neutral medium}} C_2H_5—OH + HONO$$

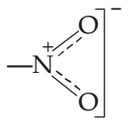
$$C_2H_5—O—N = O \xrightarrow{Sn + HCl} C_2H_5OH + H_2NOH\ (\text{or } NH_3 + H_2O)$$

21.2.2 Preparation and Properties of Nitroalkanes

Nitro group is found to be a resonance hybrid of the following two structures as evidenced by its equivalent bond length of the two N—O bonds.



Resonating structures of the – NO_2 group



Resonance hybrid of the —NO_2 group

Preparation.

1. By heating an alkyl halide with of solution of silver nitrite.

$$C_2H_5Br + AgNO_2 \longrightarrow C_2H_5NO_2 + AgBr$$

Some alkyl nitrite is also formed as a side-product ; however, the two compounds can be separated easily by fractional distillation.

2. By the vapour phase nitration of alkanes.

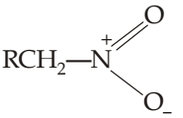
$$CH_3CH_3 + HNO_3\ (\text{fuming}) \xrightarrow{400°C} CH_3CH_2NO_2 + CH_3NO_2$$

The mixture of nitralkanes can be separated by fractional distillation.

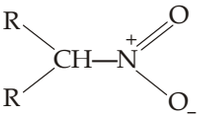
3. 3° Nitroalkanes can be prepared by the oxidation of the corresponding 3° amine with $KMnO_4$.

$$R_3CNH_2 \xrightarrow{KMnO_4} R_3CNO_2 + H_2O$$

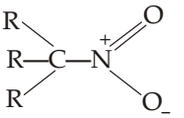
Properties. Presence of positive charge on N makes —NO_2 a powerful electron-withdrawing group which makes α-hydrogen atom acidic, much more than those of aldehydes and ketones. Further, the carbanion formed by the removal of α-H is stabilized due to resonance (see acidic character). Hence 1° and 2° nitroalkanes are very reactive as compared to 3° nitroalkanes having no α-hydrogen.



1° Nitroalkane



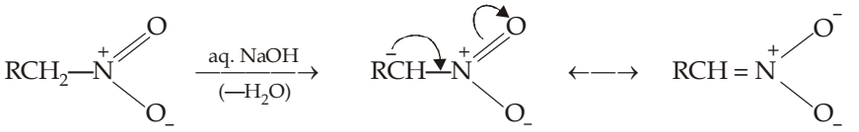
2° Nitroalkane



3° Nitroalkane

1. Properties of nitroalkanes due to α-H

(*a*) **Acidic nature.** Primary and secondary nitroalkanes dissolve in aq. NaOH to form salts.



(*b*) Action of alkaline halogen (X_2 + NaOH)

$$H_3CNO_2 \xrightarrow{Cl_2,\ NaOH} Cl_3CNO_2$$

Nitromethane — Nitrochloroform (Chloropicrin), a lachrymatory substance

(*c*) Action of nitrous acid.

(*i*) $RCH_2NO_2 \xrightarrow{HONO} R\overset{\overset{NOH}{\|}}{C}NO_2 \xrightarrow{NaOH} R\overset{\overset{NO^-Na^+}{\|}}{C}NO_2$

A 1° nitroalkane — Nitrolic acid — Sodium nitrolate (**red**)

(*ii*) $R_2CHNO_2 \xrightarrow{HONO} R_2\overset{\overset{N=O}{|}}{C}NO_2 \xrightarrow{NaOH}$ No reaction

A 2° nitroalkane — Pseudonitrol (**blue**)

(*iii*) $R_3CNO_2 \xrightarrow{NaOH}$ No reaction due to absence of α-H

A 3° nitroalkane

Recall that this difference of nitroalkanes toward nitrous acid forms the basis of the **Victor Meyer test** for the distinction of 1°, 2° and 3° alcohols.

(*d*) *Condensation with aldehydes and ketones.* Nitroalkanes having α-H undergo base catalyzed condensation with aldehydes and ketones.

$$C_6H_5CHO + CH_3NO_2 \xrightarrow{OH^-} C_6H_5CH = CHNO_2$$

TEST YOUR UNDERSTANDING - 21.4

1. Give the starting aldehyde/ketone, and nitroalkane used for synthesizing each of the following compounds.

(*a*) $C_6H_5CH = \overset{\overset{CH_3}{|}}{C}NO_2$ (*b*) $HOCH_2CH_2NO_2$.

(*e*) **Mannich reaction.** This is the condensation between formaldehyde and compound having active hydrogen and ammonia or a 1° or a 2° amine to form Mannich base.

$$R_2CHNO_2 + HCHO + R'NH_2 \xrightarrow{HCl} R_2\overset{\overset{NO_2}{|}}{C}CH_2\overset{\overset{R'}{|}}{N}H + H_2O$$

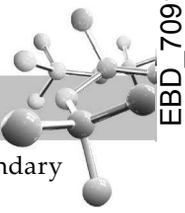
2. Reduction

(*a*) Reduction in acidic medium, like Sn + HCl, Fe + CH_3COOH ; $LiAlH_4$; or H_2—Ni, gives amines.

$$C_2H_5NO_2 + 6H \xrightarrow{Sn + HCl} C_2H_5NH_2 + 2H_2O$$

(*b*) Reduction in neutral medium, like Zn dust + NH_4Cl gives hydroxylamines.

$$C_2H_5NO_2 + 4H \xrightarrow{Zn\ dust + NH_4Cl} C_2H_5NHOH$$



3. **Hydrolysis.** Primary nitroalkanes are hydrolysed to hydroxylamine and carboxylic acid, while secondary nitroalkanes are hydrolysed to ketones.

$$CH_3CH_2NO_2 \xrightarrow{HCl} CH_3COOH + NH_2OH$$

$$2\,(CH_3)_2CHNO_2 \xrightarrow{HCl} 2(CH_3)_2CO + N_2O + H_2O$$

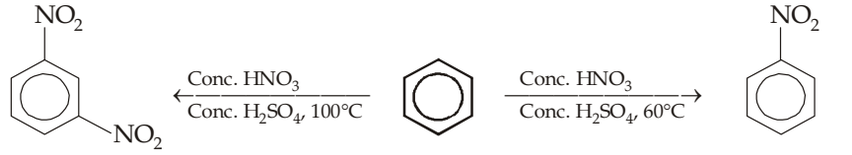
Tertiary amines do not undergo hydrolysis.

21.3 Aromatic Nitro Compounds

21.3.1 Preparation

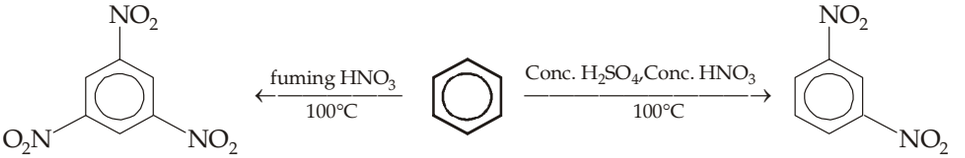
1. **Direct nitration.** This is the most important method for preparing aromatic nitro compounds. Nitration can be done by variety of reagents, like a mixture of conc. HNO_3 and conc. H_2SO_4, acetyl nitrate (N_2O_5 in acetic anhydride), fuming HNO_3 etc. Since —NO_2 group is deactivating, it is very difficult to introduce the second and third —NO_2 group, however this can be done by carrying out the reaction, at high temperature and with strong nitrating agent like fuming HNO_3. For example,

(*i*)



m-Dinitrobenzene **Benzene** Nitrobenzene

(*ii*)

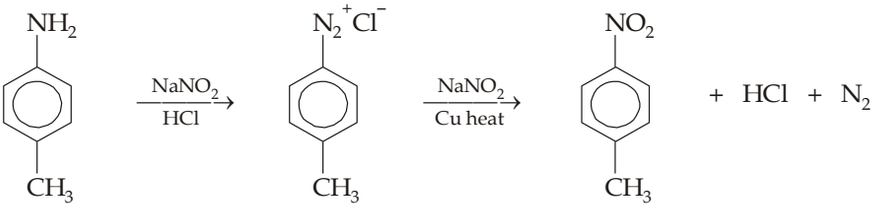


1, 3, 5-Trinitrobenzene **Benzene** *m*-Dinitrobenzene

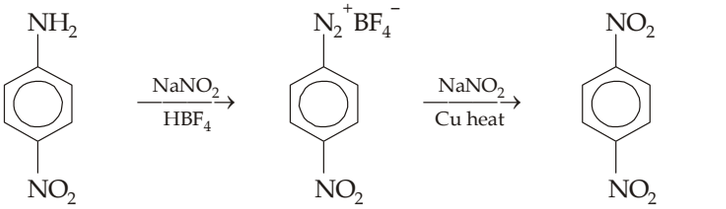
Recall that nitration is an electrophilic substitution hence presence of electron-releasing group like —OH, —NH_2, —CH_3, —OR etc., in the nucleus facilitates nitration. Thus aromatic compounds bearing these groups (*e.g.* toluene, aniline, phenol etc.) can be nitrated easily as compared to benzene.

2. **From diazonium salts (indirect method).** Since diazonium ion can be easily replaced by —NO_2 group, arenediazonium salts are used for preparing the aromatic nitro compounds which cannot be prepared by direct method.

(*i*)



(*ii*)



p-Nitroaniline *p*-Dinitrobenzene

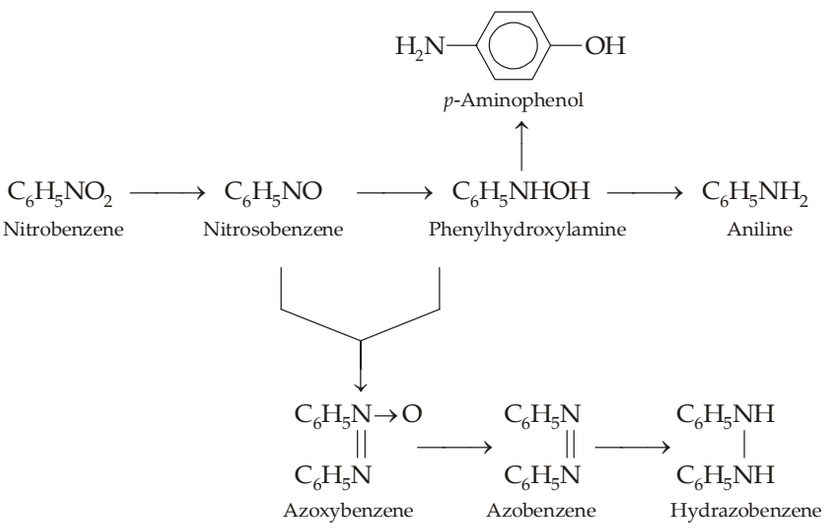
TEST YOUR UNDERSTANDING - 21.5

1. Give steps involved in the conversion of aniline to *o*-dinitrobenzene.

21.3.2 Properties of Aromatic Nitro Compounds

Nitro compounds are highly coloured (*yellow*, orange, red etc.), insoluble in water. Its three worth-mentioning properties are reduction, electrophilic substitution and nucleophilic substitution.

1. Reduction. Aromatic nitro compounds can be reduced to a variety of products through the following sequence.



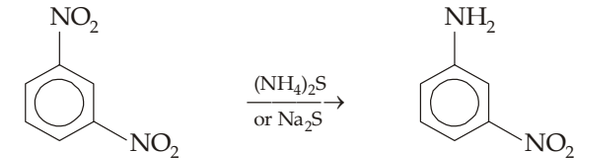
Each of the above product can be isolated depending upon the nature of the reducing agent. Following table lists the important products along with the corresponding reducing agent for that very particular compound.

Reduction of $C_6H_5NO_2$ under different conditions

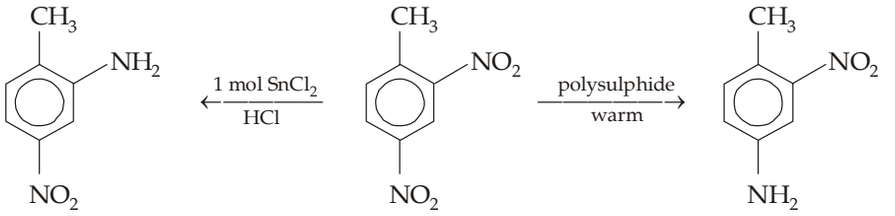
	Reagent	*Product*
1.	**Reduction in acidic medium**	
	Sn + HCl, Zn + HCl, $SnCl_2$ + HCl, Fe + H_2O + HCl	Aniline
2.	**Reduction in neutral medium**	
	Zn dust + NH_4Cl, Al-Hg couple + H_2O	Phenylhydroxylamine
3.	**Reduction in alkaline medium**	
	(*a*) Na_3AsO_3 + NaOH	Azoxybenzene
	(*b*) Zn + NaOH, CH_3OH	Azobenzene
	(*c*) Zn + NaOH ; C_2H_5OH	Hydrazobenzene
4.	**Reduction by metal hydrides and cata —H_2**	
	H_2 + Pt or Raney Ni ; or $LiAlH_4$	Aniline
5.	**Electrolytic reduction** in presence of dil.H_2SO_4	*p*-Aminophenol

EBD_7091

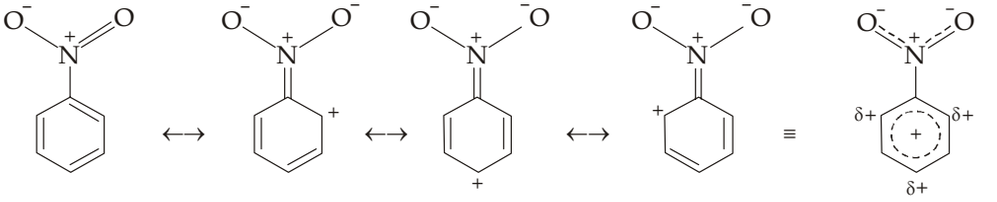
In case the compound contains two —NO_2 groups, selective reduction (reduction of only one —NO_2 group) can be achieved by using $(NH_4)_2S$ or Na_2S.



m-Dinitrobenzene *m*-Nitroaniline

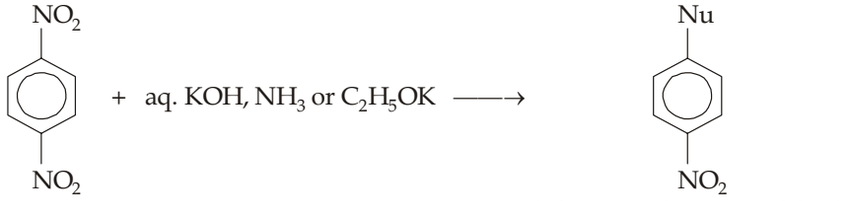


2. Substitution is benzene nucleus of nitrobenzene. Resonance in nitrobenzene imparts following characteristic features.



Resonating structures of nitrobenzene Resonance hybrid of nitrobenzene

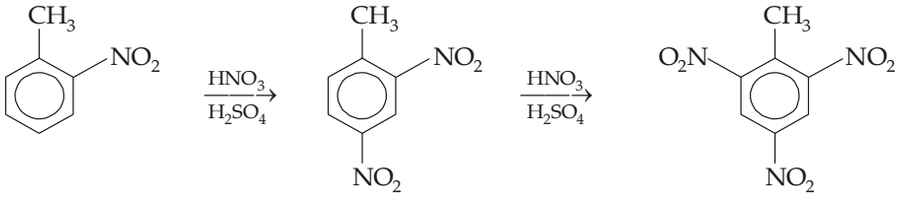
(*i*) It imparts partial double bond character to carbon-nitrogen bond causing replacement of —NO_2 a difficult task. However, if second —NO_2 group in present in the *ortho*- and *para* positions, one of them can be replaced **by a nucleophile.**



(Where, Nu = OH, NH_2, or OC_2H_5)

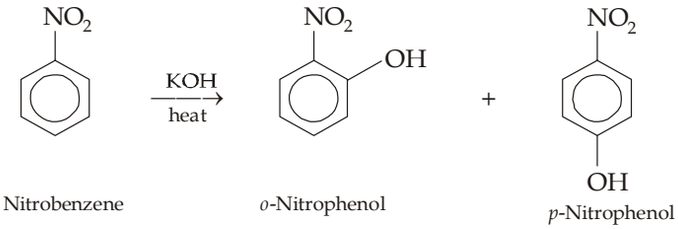
(*ii*) It imparts partial positive (especially *o*- and *p*-positions) charge on the ortho and para positions deactivating benzene nucleus for electrophiles and making the *ortho*- and *para*- positions reactive for nucleophiles. Thus nitrobenzene undergoes electrophilic substitution with difficulty and at *m*-position, however it undergoes nucleophilic substitution at *ortho*- and *para*-positions easily.

(*a*) **Electrophilic substitution.** As mentioned above, nitrobenzene undergoes electrophilic substitution only *under drastic conditions*, and at *meta* position. However, nitrobenzene having activating group like —R, —OR, —NH_2, etc. undergoes electrophilic substitutions relatively easily and at the position governed by the activating group rather than the nitro group.



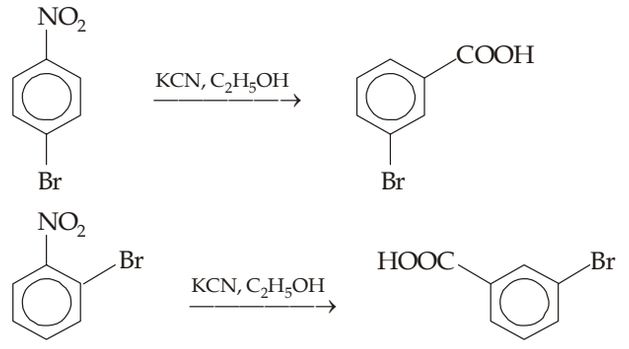
2, 4, 6-Trinitrotoluene
(**TNT**)

(*b*) **Nucleophilic substitution.** Recall that benzene is inert to nucleophiles ; however nitrobenzene undergoes nucleophilic substitution in *o*- and and *p*-positions, when fused with KOH.



Nitrobenzene *o*-Nitrophenol *p*-Nitrophenol

When nitrobenzene having electron-withdrawing group in *o*- or *p*-position is heated with ethanolic KCN—the —NO_2 group is eliminated and a —COOH group is introduced in the *ortho* position to the leaving —NO_2 group (**Von Richter reaction**).



21.4 ILLUSTRATIVE EXAMPLES

Example 1 :

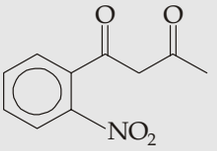
Supply structures to the bracketed compounds [A] to [L].

(*a*) $C_6H_5NO_2 \xrightarrow{Zn,\ aq.\ NH_4Cl} [A] \xrightarrow[NH_4OH]{AgNO_3} [B] \xrightarrow{CH_3MgI} [C]$

$\downarrow Pd/H_2$

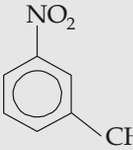
[D]

(*b*) $C_6H_5NO_2 \xrightarrow[\text{in presence of dil. } H_2SO_4]{\text{electrolysis}} [E] \xrightarrow[\text{(iii) heat, under pressure}]{\text{(i) NaOH, (ii) } CO_2} [F]$

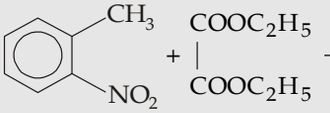
(*c*) 

$\xrightarrow[C_2H_5OH]{KOH,\ heat} [\ ] \longrightarrow [G]$

(*d*) $TNT + C_6H_5CHO \longrightarrow [H] + [I]$

(*e*) 

$\xrightarrow{Br_2.\ Fe} [J] \xrightarrow{KCN,\ C_2H_5OH} [K]$

(*f*) 

[L]

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Solution :

(*a*) C_6H_5NHOH — [A] formed by neutral reduction

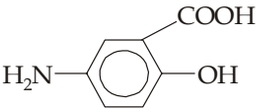
C_6H_5NO — [B] formed by oxi. of hydroxylamine

$C_6H_5N(CH_3)—OH$ — [C] Remember that N = O group behaves like C = O group

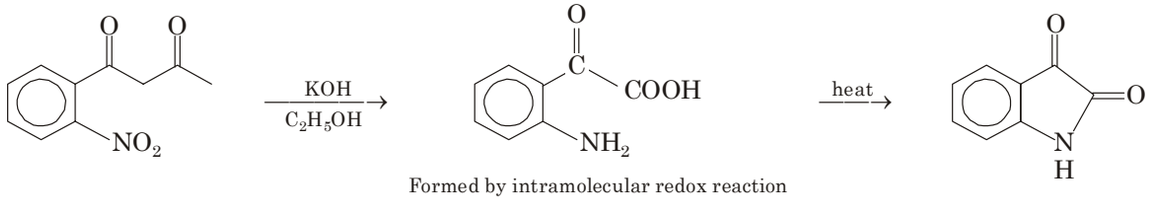
$C_6H_5N = NC_6H_5$ — [D] Reduction of nitrosobenzene

(*b*) 

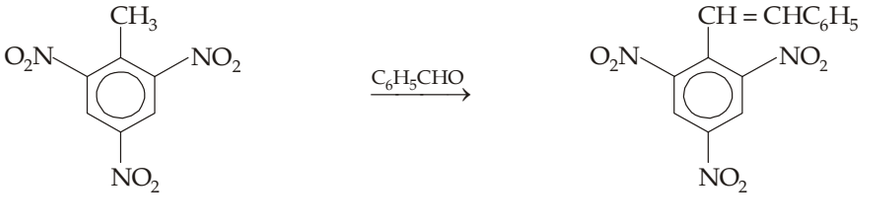
[E], Formed by electrolytic reduction



[F], Formed by Kolbe's reaction

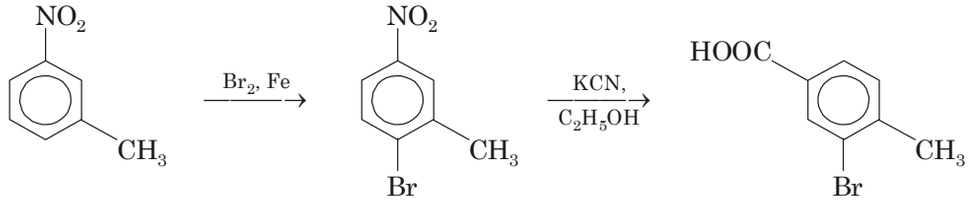
(*c*) 

Formed by intramolecular redox reaction

(*d*) 

Three —NO_2 groups in *o*-and *p*-positions make —CH_3 group reactive (acidic)

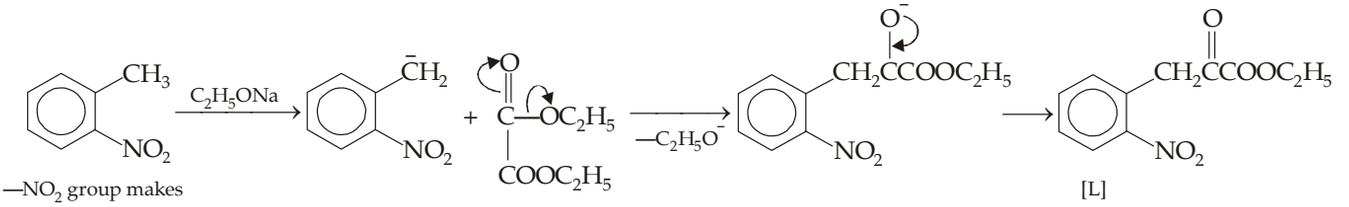
[H] and [I] *cis*- and *trans*-isomers

(*e*) 

—CH_3 is activating group

[j]

[k], Formed by Von Richter reaction

(*f*) 

—NO_2 group makes —CH_3 reactive

[L]

Example 2 :

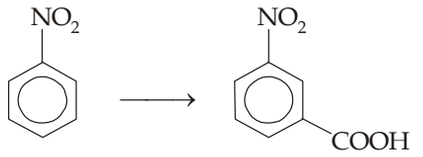
Give steps involved in the following conversions :

(a) Nitrobenzene to *m*-nitrobenzoic acid **(b) *p*-Nitrotoluene to *m*-nitrotoluene**

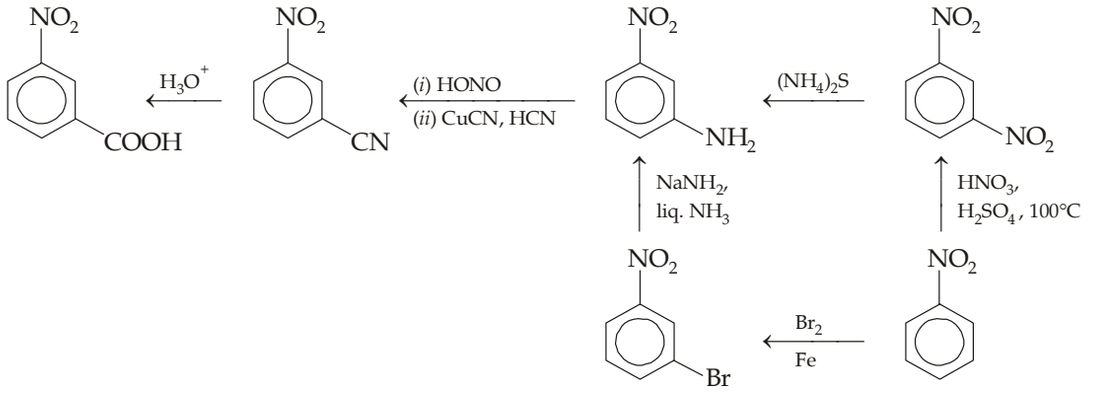
(c) Nitrobenzene into *sym*-tribromabenzene.

Solution :

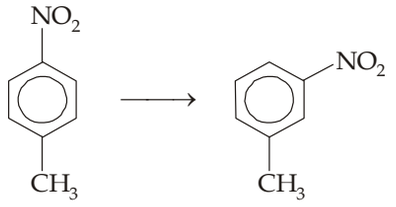
(*a*)



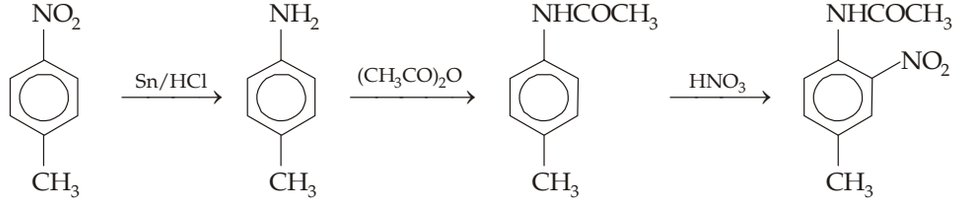
Although *m*-nitrobenzoic acid can be prepared easily by oxidising *m*-nitrotoluene, but it is very difficult to convert nitrobenzene to *m*-nitrotoluene because nitrobenzene does not undergo Friedel-Craft reaction. Hence indirect route is adopted, it is advisable to proceed backward for getting different steps.



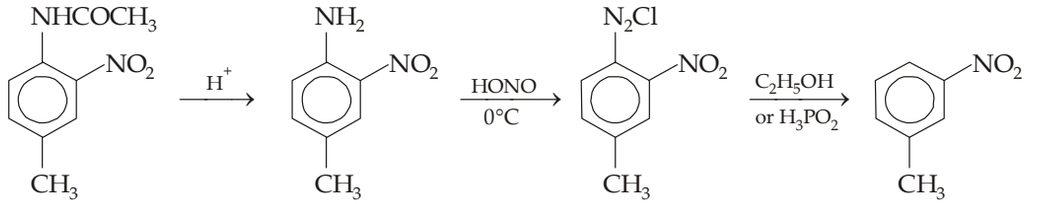
(*b*)



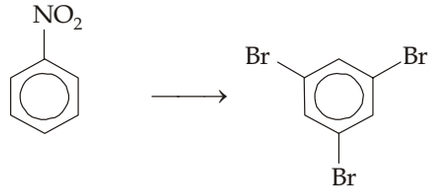
—NO_2 group in the *m*-position to —CH_3 *i.e.* in the *o*-position to the existing —NO_2 group can be introduced easily by converting existing —NO_2 group (*m*-directing) to the —NH_2 group (*o*, *p*-directing).



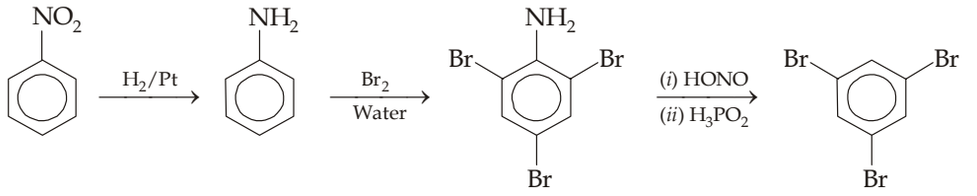
Now the —$NHCOCH_3$ group can be easily removed via diazotisation.



EBD_7091

(*c*) 

Remove —NO_2 group already present in the molecule (as in the above example) through diazotisation but by first introducing three Br.

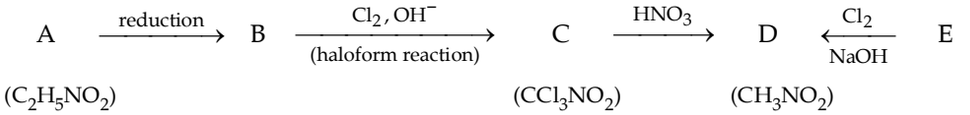


Example 3 :

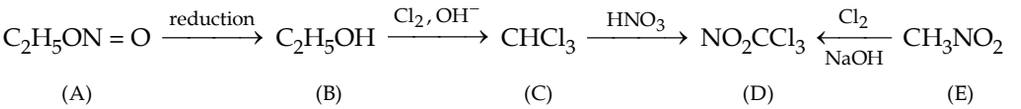
An organic compound A of the formula $C_2H_5NO_2$ on reduction gives compound B which undergoes haloform reaction to form compound C. The compound C when treated with nitric acid forms compound D of the formula CCl_3NO_2 ; compound D can also be obtained directly by the action of Cl_2 and NaOH on the compound E of the formula CH_3NO_2. Identify compounds A to D and explain the reactions involved.

Solution :

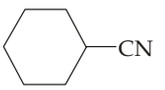
Let us summarise the given reactions.



Formation of D from E indicates that E (CH_3NO_2) is a nitromethane and hence D is trichloronitromethane, nitrochloroform or chloropicrin. Hence compound C should be chloroform, $CHCl_3$ consequently compound B should be CH_3CH_2OH and A as ethyl nitrite.

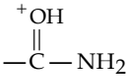
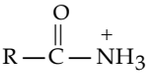


EXERCISE 21.1 (MCQ - ONE option correct)

1. Which of the following is not the correct name for 

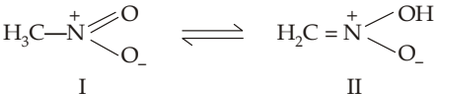
(*a*) Cyclohexanecarbonitrile (*b*) Cyclohexanenitrile
(*c*) Cyclohexanonitrile (*d*) None of the three.

2. Protonation of acid amides ($RCONH_2$) is likely to give

(*a*)  (*b*) 

(*c*) Both (*d*) None.

3. Methyl nitrite shows tautomerism



I II

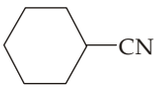
Predict their relative acidity.

(*a*) Both are equal in acidic character
(*b*) I is more acidic than II
(*c*) II is more acidic than I
(*d*) None of then is acidic.

4. The order of increasing boiling points among the three compounds is

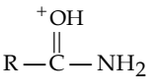
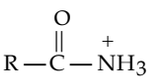
C_2H_5ONO(I), $C_2H_5NO_2$(II) C_2H_6(III)

EXERCISE 21.1 (MCQ - ONE option correct)

1. Which of the following is not the correct name for 

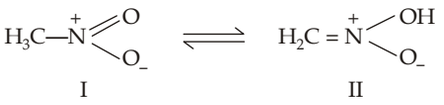
(*a*) Cyclohexanecarbonitrile (*b*) Cyclohexanenitrile
(*c*) Cyclohexanonitrile (*d*) None of the three.

2. Protonation of acid amides ($RCONH_2$) is likely to give

(*a*)  (*b*) 

(*c*) Both (*d*) None.

3. Methyl nitrite shows tautomerism



I II

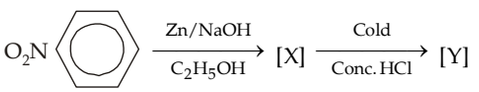
Predict their relative acidity.
(*a*) Both are equal in acidic character
(*b*) I is more acidic than II
(*c*) II is more acidic than I
(*d*) None of then is acidic.

4. The order of increasing boiling points among the three compounds is
C_2H_5ONO(I), $C_2H_5NO_2$(II) C_2H_6(III)
(*a*) III < II < I (*b*) I < II < III
(*c*) III < I < II (*d*) III < I ≈ II.

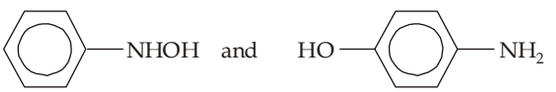
5. Which of the following gives a primary alcohol on reduction ?
(*a*) Alkyl carbylamine (*b*) Alkyl nitrite
(*c*) Nitroalkane (*d*) None of the three.

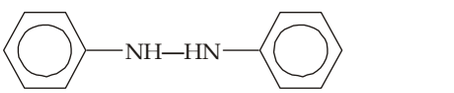
6. When a nitrogenous substance X is treated with nitrous acid, a blue colour is obtained. The compound X can be
(*a*) $CH_3CH_2NO_2$ (*b*) $(CH_3)_2CHNO_2$
(*c*) CH_3CH_2ONO (*d*) $(CH_3CH)_2ONO$.

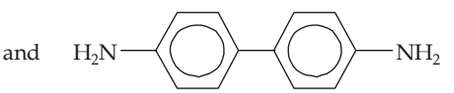
7. The compounds X and Y in the following reaction respectively are

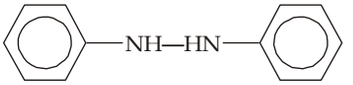


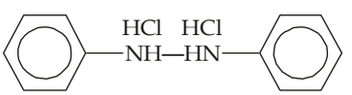
(*a*) 

(*b*) 

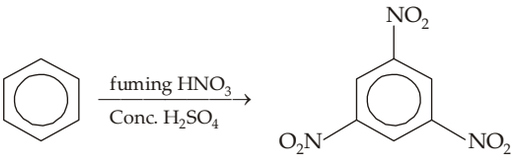
(*c*) 

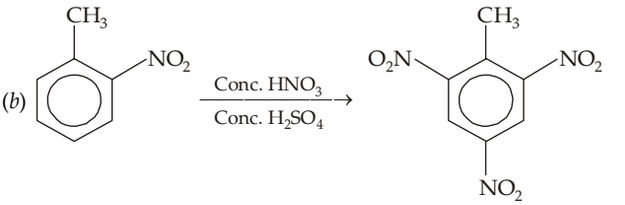
and 

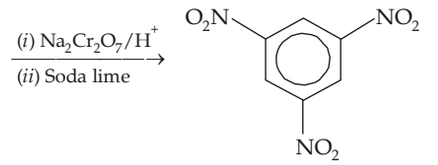
(*d*) 

and 

8. Which of the following method gives good yield for 1, 3, 5-trinitrobenzene, commonly known as TNB ?

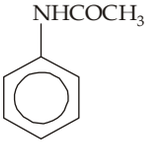
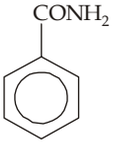
(*a*) 

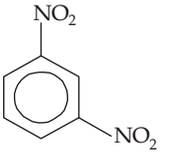
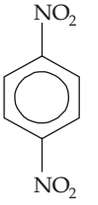
(*b*) 



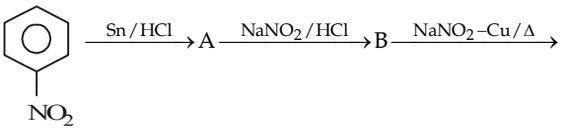
(*c*) Both are equally good
(*d*) None is suitable.

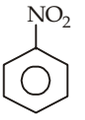
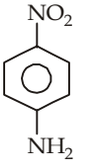
9. A neutral benzenoid nitrogenous organic compound has zero dipole moment, its probable structure is

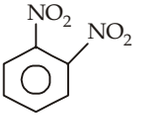
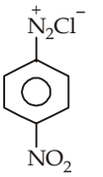
(*a*)  (*b*) 

(*c*)  (*d*) 

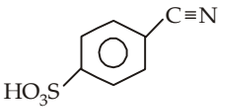
10. Predict the product for the following reaction



(*a*)  (*b*) 

(*c*)  (*d*) 

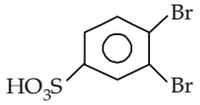
EBD_7091

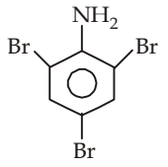
11. 

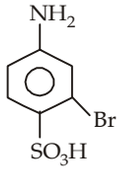
$\xrightarrow{\text{dilute NaOH}/\Delta}(C_7H_7NSO_4)$

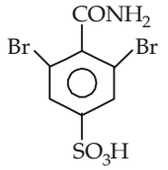
$\xrightarrow{KOBr/\Delta}$ Product $\xrightarrow{Br_2/H_2O}$ end product.

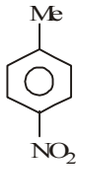
The end product is

(*a*) 

(*b*) 

(*c*) 

(*d*) 

12. 

$\xrightarrow{Br_2/Fe}\xrightarrow{Sn/HCl}\xrightarrow{NaNO_2/HCl}\xrightarrow{H_3PO_2}$

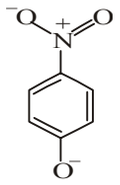
$\xrightarrow{KMnO_4/H^+}$ (P) Product.

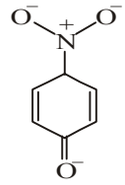
The product (P) is ..... bromobenzoic acid

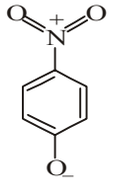
(*a*) ortho (*b*) meta

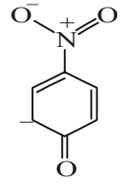
(*c*) para (*d*) ortho and para both

13. The most unlikely representation of resonance structures of *p*-nitrophenoxide ion is

(a) 

(b) 

(c) 

(d) 

14. Among the following statements on the nitration of aromatic compounds, the false one is

(a) the rate of nitration of benzene is almost the same as that of hexadeutereobenzene.

(b) the rate of nitration of toluene is greater than that of benzene.

(c) the rate of nitration of benzene is greater than that of hexadeutereobenzene

(d) nitration is an electrophilic substitution reaction.

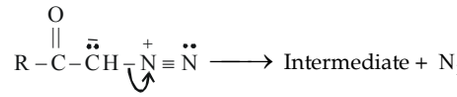
15. Nitrobenzene can be reduced to aniline by

$\underset{I}{H_2/Ni}$ $\underset{II}{Sn/HCl}$

$\underset{III}{Zn/NaOH}$ $\underset{IV}{LiAlH_4}$

(a) I, II and III (b) I and II

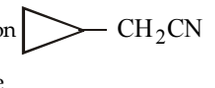
(c) I, II and IV (d) only II

16. 

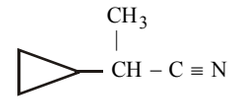
What is the nature of intermediate in this reaction ?

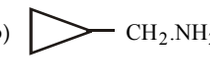
(a) Carbonium ion (b) Carbanion

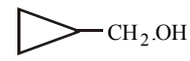
(c) Carbene (d) Free radial

17. In the reaction 

the products obtained are

(a) 

(b) 

(c) 

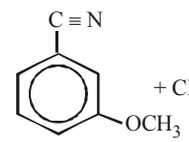
(d) None

18. In the reaction,

$CH_3CN + 2H \longrightarrow X \xrightarrow{\text{Boiling } H_2O} Y$, the term Y is

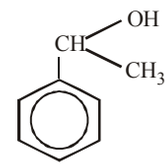
(a) Acetone (b) Ethanamine

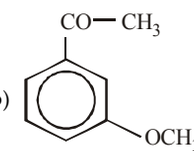
(c) Acetaldehyde (d) Dimethylamine

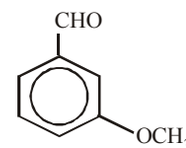
19. 

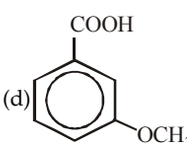
$+ CH_3MgBr \longrightarrow Q \xrightarrow{H_3O^+} P$

The product 'P' in the above reaction is

(a) 

(b) 

(c) 

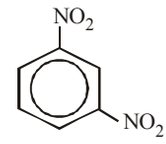
(d) 

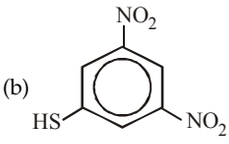
20. In the acidic reduction of nitrobenzene, which of the following is the intermediate?

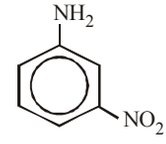
(a) $C_6H_5 - N = O$ (b) $C_6H_5NH - NHC_6H_5$

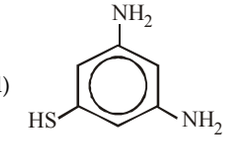
(c) $C_6H_5 - N = N - C_6H_5$ (d) $C_6H_5 - \overset{\uparrow}{N}(O) - C_6H_5$

21. The major product (70% to 80%) of the reaction between m-dinitrobenzene with NH_4HS is

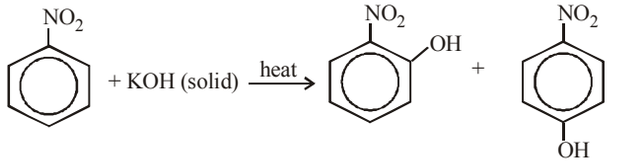
(a) 

(b) 

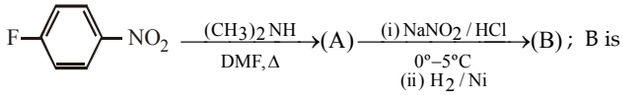
(c) 

(d) 

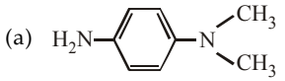
22. The following reaction is

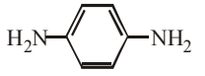


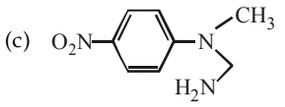
(a) nucleophilic substituton (b) electrophilic substitution
(c) free radical substitution (d) electrophilic addition

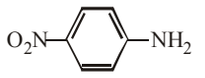
23. 

; B is

(a) 

(b) 

(c) 

(d) 

24. A nitro alkane reacts with HONO to give insoluble product in alkali which turns blue on treatment with an alkali. The nitro alkane is

(a) $CH_3CH_2NO_2$ (b) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2NO_2$

(c) $(CH_3)_2CHNO_2$ (d) $(CH_3)_3CNO_2$

25. Which nitro alkane will give ketone when boiled with HCl?

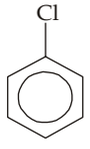
(a) $(CH_3)_2CHNO_2$ (b) $CH_3CH_2NO_2$

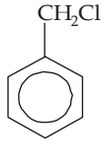
(c) $(CH_3)_3CCH_2NO_2$ (d) $(CH_3)_3CNO_2$

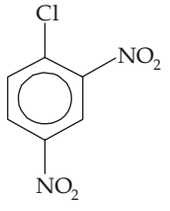
EXERCISE 21.2 (MCQ 1 or >1 option correct, Passage based, Matching, A/R)

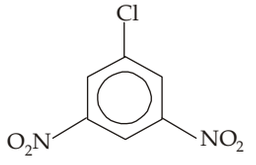
DIRECTIONS for Q. 1 to Q. 11 : Multiple choice questions with one or more than one correct option(s).

1. Which of the following reaction can form a nitrile when treated with NaCN in DMSO ?

(*a*) 

(*b*) 

(*c*) 

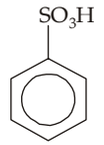
(*d*) 

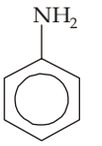
2. Which of the following shows tautomerism ?
(*a*) C_6H_5OH (*b*) CH_3NO_2
(*c*) $C_6H_5CH_2NO_2$ (*d*) $(CH_3)_3CNO_2$

3. Which of the following reacts with nitrous acid ?
(*a*) Acetamide
(*b*) 2-Nitrobutane
(*c*) 2-Methyl-2-nitropropane
(*d*) Diethylamine.

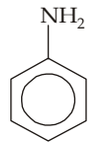
4. Which of the following compounds can reduce Tollen's reagent?
(a) CH_3CHO (b) $C_6H_5NO_2$
(c) C_2H_5NHOH (d) $CH_2OHCOCH_3$

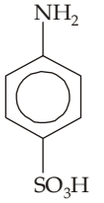
5. *p*-Nitroaniline can be obtained by

(*a*) 

$\xrightarrow[H_2SO_4]{HNO_3}$ (*b*) 

$\xrightarrow[(ii)\ H_2SO_4]{(i)\ HNO_3}$

(*c*) 

$\xrightarrow[\text{(ii) } HNO_3/H_2SO_4,\ \text{(iii) } H_3O^+]{\text{(i) } (CH_3CO)_2O}$ (*d*) 

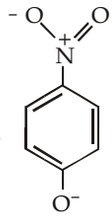
$\xrightarrow{HNO_3}$

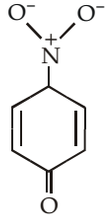
6. The products of reaction of alcoholic silver nitrite with ethyl bromide are
(a) ethane (b) ethene
(c) nitroethane (d) ethyl nitrite

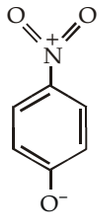
7. Which gases are poisonous?
(a) Lewisite (b) Mustard
(c) Phosgene (d) MIC

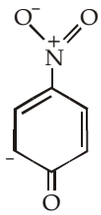
8. Butanonitrile may be prepared by heating
(a) Propyl alcohol with KCN
(b) Propyl magnesium chloride with Cyanogen chloride
(c) Butyl chloride with KCN
(d) Propyl chloride with KCN

9. The representations of resonance structures of p-nitrophenoxide ion are

(a) 

(b) 

(c) 

(d) 

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10. When nitrobenzene is treated with Br_2 in presence of $FeBr_3$, the major product formed is *m*-bromonitrobenzene. Statements which are related to obtain the *m*-isomer are

(*a*) The electron density on meta carbon is more than that on ortho and para positions

(*b*) The intermediate carbonium ion formed after initial attack of Br^+ at the meta position is least destabilised

(*c*) Loss of aromaticity when Br^+ attacks at the ortho and para positions and not at meta position

(*d*) Easier loss of H^+ to regain aromaticity from the meta position than from ortho and para positions.

11. Ethyl isocyanide on hydrolysis in acidic medium generates

(a) propanoic acid and ammonium salt

(b) ethanoic acid and ammonium salt

(c) methylamine salt and ethanoic acid

(d) ethylamine salt and methanoic acid

DIRECTIONS for Q. 12 to Q. 14 : Read the following passages and answer the questions that follows :

PASSAGE 1

The reduction of nitro compounds to primary amines occurs through the intermediate formation of nitroso compounds and hydroxylamines. Catalytic hydrogenation of reduction of a nitro compound with an active metal and concentrated hydrochloric acid always gives the corresponding primary amines. In the neutral medium, the nitro compounds are reduced to the corresponding hydroxylamines. However, in the basic medium, bimolecular reduction products are obtained which result through initial condensation of nitroso and hydroxylamine intermediates followed by its reduction to give different products depending upon the nature of the reducing agent used.

12. In the acidic reduction of nitrobenzene, which of the following is the intermediate?

(*a*) $C_6H_5 - N = O$

(*b*) $C_6H_5NH - NHC_6H_5$

(*c*) $C_6H_5 - N = N - C_6H_5$

(*d*) $C_6H_5 - \overset{\overset{O}{\uparrow}}{N} = N - C_6H_5$

13. The reagent that reacts with nitromethane to form methylhydroxylamine is ?

(*a*) Zn/HCl (*b*) Zn/NH_4Cl

(*c*) Zn/NaOH (*d*) Sn/HCl

14. Hydrazobenzene is formed when nitrobenzene is reduced with

(*a*) Zn/HCl (*b*) Zn/NaOH

(*c*) $Zn/NaOH–CH_3OH$ (*d*) Zn/NH_4Cl

Instructions for Q. 15 to 16 : Following questions are Multiple Matching type Questions :

15.

	Column - I		*Column - II*
(A)	Nitriles	(a)	1° amine
(B)	Isonitriles	(b)	2° amine
(C)	Ketones	(c)	Hydrolysis
(D)	Phthalimide	(d)	Reductive amination

16.

	Column - I		*Column - II*
(A)	Bromine water	(a)	Yellow precipitate
(B)	Nitrobenzene	(b)	Acetoacetic ester
(C)	CHI_3	(c)	1-Butyne
(D)	Acidic hydrogens	(d)	Lemon yellow oily liquid

Instructions for Q. 17 to Q. 22 : Following questions are Assertion and Reasoning Type Questions :

Note : Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 5 choices (a), (b), (c), (d) and (e) out of which ONLY ONE is correct.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.

(c) Statement -1 is True, Statement-2 is False.

(d) Statement -1 is False, Statement-2 is True.

(e) Statement -1 is False, Statement-2 is False.

17. **Statement-1 :** Alkyl isocyanides with acidified water gives alkyl formamide.

Statement-2 : In isocyanides, carbon first acts as a nucleophile and then as an electrophile.

18. **Statement-1 :** Methyl isocyanide reacts with ozone to form methyl isocyanate.

Statement-2 : Methyl isocyanate was responsible for Bhopal tragedy.

19. **Statement-1 :** Alkyl cyanide can be prepared by carbylamine reaction

Statement-2 : Ethyl amine when heated with chloroform in presence of alcoholic KOH, cyanide is formed.

20 **Statement-1 :** Nitrobenzene does not undergo Friedel Craft alkylation.

Statement-2 : Nitrobenzene is used as solvent in laboratory and industry.

21. **Statement-1 :** Alkyl isocyanides in acidified water give alkyl formamides.

Statement-2 : In isocyanides, carbon first acts as a nucleophile and then as an electrophile.

22. **Statement - 1:** Benzonitrile is prepared by the reaction of chlorobenzene with potassium cyanide.

Statement - 2 : Cyanide (CN^-) is a strong nucleophile.

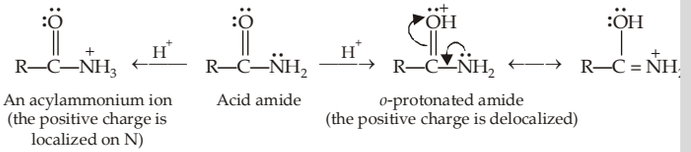
SOLUTIONS

EXERCISE 21.1

1	(c)	**6**	(b)	**11**	(b)	**16**	(c)	**21**	(c)
2	(a)	**7**	(c)	**12**	(a)	**17**	(a)	**22**	(a)
3	(c)	**8**	(b)	**13**	(c)	**18**	(c)	**23**	(a)
4	(c)	**9**	(d)	**14**	(b)	**19**	(b)	**24**	(c)
5	(c)	**10**	(a)	**15**	(c)	**20**	(a)	**25**	(a)

1. Cyclohexanenitrile is the wrong name.

2. The cation produced by the protonation of carbonyl group of amides is stabilized by resonance.



An acylammonium ion (the positive charge is localized on N) — Acid amide — *o*-protonated amide (the positive charge is delocalized)

3. The conjugate base of the *aci*-form (II) is more stable.

4. Nitro compounds, being relatively more polar than nitrites, have higher boiling points than the corresponding nitrites.

5. $R—O—N=O \xrightarrow{\text{reduction}} R—OH + H_2NOH$

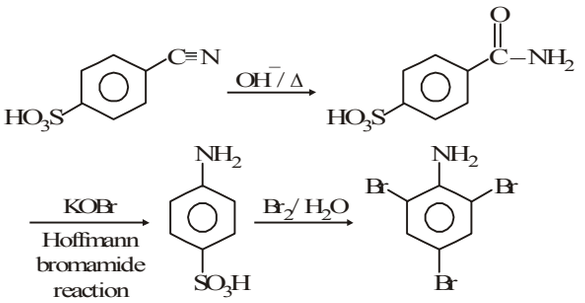
7. Reduction of nitrobenzene in alkaline medium gives hydrazobenzene which rearranges in presence of HCl to form 4, 4′-diaminodiphenyl, commonly known as benzidine (benzidine rearrangement).

8. Introduction of one $—NO_2$ group in benzene nucleus deactivates for further nitration. However, in option (*b*), nitration of *o*-nitrotoluene is not difficult because of the presence of activating $—CH_3$ group. Hence 2, 4, 6-trinitrotoluene is easily prepared from *o*-nitrotoluene. Further, $—CH_3$ group is easily oxidizable when $—NO_2$ groups are present in benzene nucleus as compared to oxidation of $C_6H_5CH_3$.

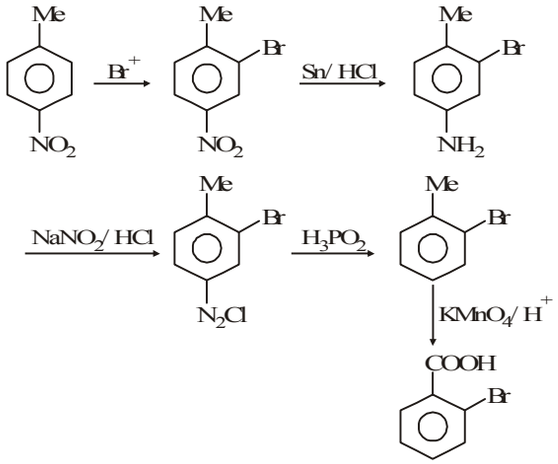
9. Neutral nature of the compound indicates that it should be a nitro compound. Further zero dipole moment indicates its symmetrical structure, *i.e.* it should be a benzene derivative having same group ($—NO_2$) in positions *p*- to each other.

10. (*a*)

11.(*b*)



12.(*a*)



13.(*c*) N can't have more than 8 electrons in its valence shell as it does not have any *d* orbital. In (c), N has 10 electrons.

14.(c) **Note :** As NO_2^+ is an electrophile so nitration is electrophilic substitution reaction.

Nitration in toluene is greater because of electron repelling (+I) nature of CH_3 group. Nitration of C_6H_6 and C_6D_6 takes place at the same rate because the rate determining step is the formation of carbocation which is same in both cases, in other words cleavage of C – H or C – D bond constitutes the fast step.

15.(*b*) $LiAlH_4$ does not reduce $–NO_2$ group to $– NH_2$ group.

16.(c) $R-\overset{O}{\overset{\|}{C}}-\ddot{C}H-\overset{+}{N}\equiv\ddot{N} \xrightarrow{-N_2} R-\overset{O}{\overset{\|}{C}}-\ddot{C}H \longrightarrow \overset{O}{\overset{\|}{C}}=CHR$

Ketene — Carbene (neutral)

17.(a) Nitriles having α -hydrogen atom form alkyl derivatives with RBr in presence of $NaNH_2 / NH_3$.

18.(c) $CH_3CN + 2H \rightarrow \underset{X}{CH_3CH=NH} \xrightarrow[Y]{H_2O,\ boil} CH_3CHO$

Note that cyanides are reduced only by 2H atoms, so reduction stops at aldimine stage which on hydrolysis with water gives aldehyde; it is an example of Stephen's reaction

19.(b)

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20.(a) Nitrobenzene is reduced in the following manner through various intermediates to form aniline as the final product.

$$C_6H_5NO_2 \xrightarrow{2[H]} C_6H_5NO \xrightarrow{2[H]}$$

nitrobenzene nitrosobenzene

$$C_6H_5NHOH \xrightarrow{2[H]} C_6H_5NH_2$$

phenylhydroxylamine aniline

21.(c)

22.(a) Although benzene does not undergo nucleophilic substitution, nitrobenzene undergoes such reaction due to the presence of electron withdrawing $-NO_2$ group which makes *o* - and *p* - carbon electron deficient and hence liable to be attacked by OH^- (a nucleophile)

23.(a)

24.(c) See action of HONO on P, S and T nitro alkanes.

25.(a) 1° nitro alkanes give aldehyde and 2 ° nitro alkanes give Ketones (See text)

EXERCISE 21.2

>1 CORRECT OPTION	**1**	(b,c)	**2**	(a,b,c)	**3**	(a,b,d)	**4**	(a,c,d)	**5**	(c,d)
	6	(c, d)	**7**	(a, b, c, d)	**8**	(b, d)	**9**	(a, b, d)	**10**	(a, d)
	11	(d)								
PASSAGE 1	**12**	(a)	**13**	(b)	**14**	(b)				
MATCH THE FOLLOWING	**15**	(A) – (a); (B) – (a,b,c); (C) – (a,b,d); (D) – (a)								
	16	(A) – (b, c); (B) – (d); (C) – (a); (D) – (b, c)								
A/R	**17**	(a)	**18**	(b)	**19**	(e)	**20**	(b)	**21**	(a)
	22	(d)								

1. $C_6H_5CH_2Cl$ (b) is arylsubstituted alkyl halide, hence it undergoes nucleophilic substitution ; while in (c) **Cl is activated by the presence of electron-withdrawing $-NO_2$ groups in** *ortho*- **and** *para*-**positions.**

2. *tert*-Nitroalkanes do not have labile H (H in α-position to the $-NO_2$ group) and hence can't exhibit tautomerism.

3. *tert*-Nitro compounds (Me_3CNO_2) do not react with HONO because they do not have any α-H. The three others reach with HONO as usual.

$$CH_3\overset{C_2H_5}{\overset{|}{C}}HNO_2 \xrightarrow{HONO} (CH_3)_2\overset{N=O}{\overset{|}{C}}NO_2$$

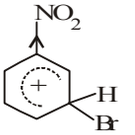
2° Nitroalkane Pseudonitrol (**blue**).

4. Aldehydes, α-hydroxyketones and hydroxylamines reduce Tollens' reagent.

5. $-SO_3H$ group present in *o*- and *p*-positions are easily replaced.

10. (*a,d*) Nitro group decreases the electron density at the *meta*-position in comparison to ortho and para position due to –I and –M effects.

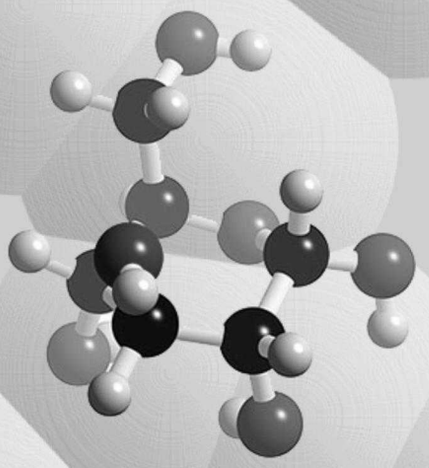
The above intermediate is a resonance hybrid of three structures, hence is more stable than the corresponding intermediate from *ortho* and *para*-attack.



11. (*d*) Ethyl isocyanide on hydrolysis forms primary amines.

$$CH_3CH_2N\equiv C + H_2O \xrightarrow{H^+} CH_3CH_2NH_2 + HCOOH$$

19. (*d*) Chlorobenzene is resonance stabilized. Thus aryl halides (chlorobenzene) do not undergo nucleophilic substitution. Statement-2 is correct.



22 Carbohydrates

CHAPTER HIGHLIGHTS

22.1 Definition and Classification
22.2 Importance of Carbohydrates
22.3 D and L Designations of Monosaccharides
22.4 D-(+)-Glucose
22.5 (–)-Fructose
22.6 (+)-Sucrose
22.7 Some Artificial Sweetners
22.8 Polysaccharides
22.9 Illustrative Examples
EXERCISE
SOLUTIONS

22.1 Definition and Classification

Historically, carbohydrates were once considered to be ''hydrates of carbon'' because molecular formulas of many carbohydrates (but not all) correspond to $C_x(H_2O)_y$ see examples (*a*). However, certain carbohydrates do not correspond to this general formula, see examples (*b*). Moreover, several compounds are although not carbohydrates, their molecular formula correspond to the above general formula, see examples (*c*).

(*a*) $C_6H_{12}O_6$ Glucose and Fructose; $C_{12}H_{22}O_{11}$ Sucrose; $(C_6H_{10}O_5)_n$ Cellulose and starch

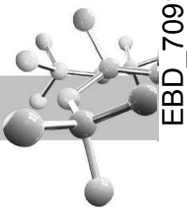
(*b*) $C_6H_{12}O_5$ Rhamnose; $C_7H_{14}O_6$ Rhamnohexose

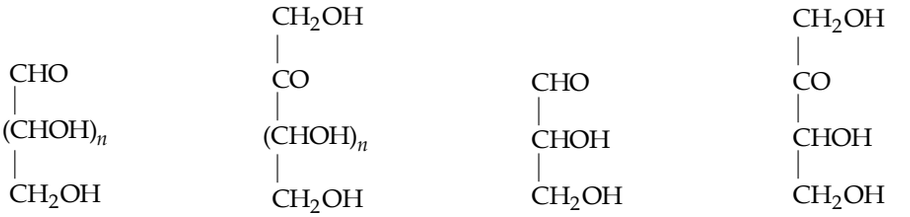
(*c*) CH_2O Formaldehyde; $C_2H_4O_2$ or CH_3COOH Acetic acid; $C_3H_6O_3$ Lactic acid; $C_6H_{12}O_6$ Inositol

Simple carbohydrates are also known as *sugars* or *saccharides,* and name of most sugars end in *–ose.*

Carbohydrates are polyhydroxyaldehydes, polyhydroxyketones or compounds that can be hydrolyzed to them. A carbohydrate that cannot be hydrolyzed to simpler compounds is called a **monosaccharide**. A carbohydrate that can be hydrolyzed to, two, three and indefinite monosaccharide molecules is called a **disaccharide,** a **trisaccharide**, and a **polysaccharide** respectively.

A monosaccharide may be further classified ; if it contains an aldehydic group it is called an **aldose,** and if it contains a ketonic group it is called a **ketose.** Alternatively, a monosaccharide may be classified on the basis of the number of carbon atoms present it it, *viz*. **triose, tetrose, pentose, hexose, heptose,** and so on. Most naturally occurring monosaccharides are pentoses or hexoses. These two classifications are frequently combined. A C_4 aldose, for example, is called on *aldotetrose*, a C_5 ketose is called a *ketopentose.*





An aldose | A ketose | An aldotriose | A ketotetrose

Glyceraldehyde (an aldotriose) is considered to be the simplest chiral carbohydrate.

Carbohydrates that reduce Fehling's or Benedict's or Tollens' reagent are known as **reducing sugars.** All monosaccharides, whether aldose or ketose, and *most* disaccharides are reducing sugars. However, the most common disaccharide, sucrose (also known as table sugar) is a **non-reducing sugar.**

TEST YOUR UNDERSTANDING - 22.1

1. What are oligosaccharides ? Classify the following carbohydrates as mono–, di–, tri–, or poly-saccharide. Which of the following can be considered as oligosaccharide.

(*a*) $C_{12}H_{22}O_{11}$ (*b*) $C_{18}H_{32}O_{16}$ (*c*) $C_{16}H_{26}O_{13}$ (*d*) $(C_5H_8O_4)_n$ (*e*) $C_6H_{12}O_6$.

2. Give the hydrolysis products for each of the above carbohydrate.

3. (*a*) Write a structural formula for (*i*) an aldotriose, and a (*ii*) ketohexose

(*b*) Classify the following monosaccharides

(*i*) $HOCH_2CHOHCOCH_2OH$ (*ii*) $HOCH_2(CHOH)_3CHO$ (*iii*) $HOCH_2(CHOH)_2CH_2CHO$.

4. Write molecular formula for (*i*) a hexose trisaccharide, (*ii*) a tetrose tetrasaccharide, and (*iii*) a pentose polysaccharide also known as polypentoside or pentosan.

22.2 Importance of Carbohydrates

Carbohydrates are the most abundant organic constituents of plants. They are the important source of chemical energy for living organisms (*e.g.* sugars and starches). Certain carbohydrates support the plant tissues, *e.g.* cellulose in wood, cotton, and flax ; carbohydrate, like chitin, forms the major constituent of the shells of crabs and lobsters. In addition to this, we encounter carbohydrate at almost every turn of our daily lives, *viz.* (*i*) sugars make fruits, sweet and yield alcohol on fermentation ; (*ii*) cellulose materials like cotton, linen, grass, wood, etc. supply clothes, paper, plastics, lacquers, paints and explosives, (*iii*) some glucose is converted into fatty acids and amino acids, (*iv*) ribose and deoxyribose (aldopentoses) are components of nucleic acids which determine human heredity.

Carbohydrates are synthesized in green plants by *photosynthesis*, a process that uses solar energy to reduce, or ''fix'', carbon dioxide.

$$x CO_2 + y\, H_2O + \text{Solar energy} \xrightarrow{\text{chlorophyll}} \underset{\text{Carbohydrate}}{C_x(H_2O)_y} + x O_2$$

This stored solar energy is released when animals or plants metabolize carbohydrates to carbon dioxide and water.

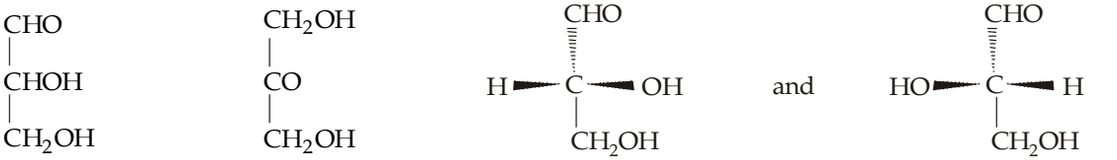
$$C_x(H_2O)_y + x\, O_2 \longrightarrow x\, CO_2 + y\, H_2O + \text{Energy}$$

Although some of the energy released in the oxidation of carbohydrates is converted into heat, much of it is conserved in the form of chemical compound mainly adenosine triphosphate (ATP) which is synthesized from adenosine diphosphate (ADP) and inorganic phosphate (P*i*). Plants and animals can use the conserved energy of ATP (or very similar substances) to carry out all of their energy-requiring processes like contraction of a muscle, the synthesis of a macromolecule, and so on.

$$ATP + H_2O \longrightarrow ADP + Pi + \text{Energy}$$

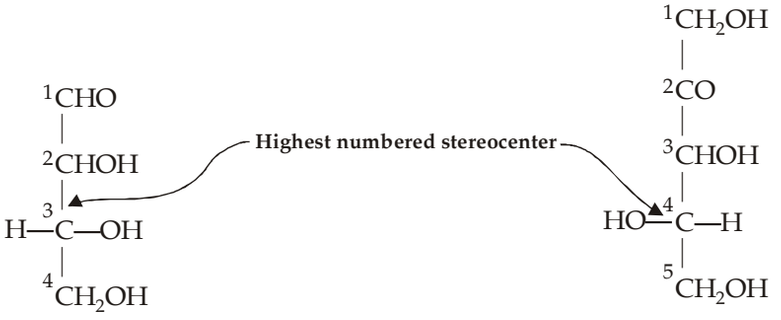
22.3 D and L Designations of Monosaccharides

The simplest monosaccharides are glyceraldehyde and dihydroxyacetone. Of these two compounds, only glyceraldehyde contains a **stereocenter** (a chiral carbon), hence it exists in two enantiomeric forms.



Glyceraldehyde (an aldotriose) | Dihydroxyacetone (a ketotriose) | (+)-Glyceraldehyde | (–)-Glyceraldehyde

Earlier in the 20th century, when the absolute configuration of any organic compound was not known, configuration of organic compounds were related to glyceraldehyde. (+)-Glyceraldehyde is designated as D-(+)-glyceraldehyde and (–)-glyceraldehyde is designated as L-(–)-glyceraldehyde. These two compounds serve as configurational standards for all monosaccharides. A monosaccharide whose highest numbered stereocenter (the penultimate carbon) has the same configuration as D-(+)-glyceraldehyde is designated as a D sugar, and similarly L sugar is related to L-(–)-glyceraldehyde.



A D-aldotetrose (The highest stereocenter, C_3 has –OH on right, and hence D–)

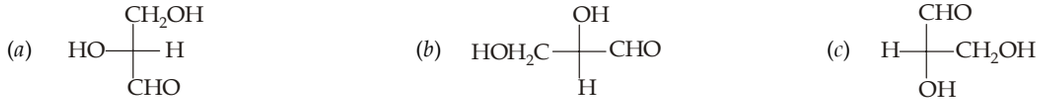
An L-ketopentose (The highest stereocenter, C_4 has –OH on left, hence L-)

Although the D, L-nomenclature is not unambiguous, while the modern R, S-nomenclature (Ch. 3) is unambiguous, this stereochemical designations is highly entrenched in the literature of carbohydrate and amino acid chemistry and hence its use in carbohydrate chemistry is not replaced by the modern Cahn-Ingold–Prelog system (R, S- nomenclature). This system has the disadvantage of specifying the configuration of only one stereocenter (the penultimate carbon).

Like R, S-designations, the D, L-designations are not necessarily related to the optical rotations of the sugars. Thus, one may encounter D-(+)-, (D)-(–)-, L-(+)- , or L-(–)-sugar.

TEST YOUR UNDERSTANDING - 22.2

1. Designate the following Fischer projections of glyceraldehyde as D or L



2. How many chiral carbon's are present in an aldotetrose ? Draw the Fischer formulas for all the possible stereoisomers of an aldotetrose and classify them as D and L sugars.

3. Assign the specification, R or S, to the following :

(*a*) D-(+)-Glyceraldehyde (*b*) D-(–)-Glyceric acid

(*c*) D-(–)-3-Bromo-2-hydroxypropionic acid (*d*) D-(–)-Lactic acid

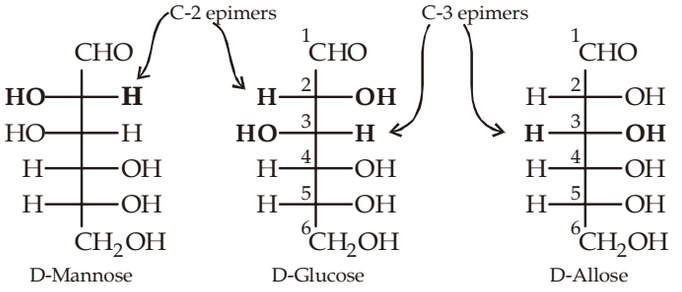
(*e*) L-(+)-Lactic acid.

4. (*a*) How many stereoisomers does an aldopentose have ?

(*b*) Is there any aldopentose, which can have only 4 stereoisomers ?

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Epimers : When the two sugars differ in the configuration of only one carbon atom, other than C-1, these are called **epimers**, and the carbon atom where they differ is generally mentioned. In case, the number of carbon atom is not specified, it is assumed to be C-2. Thus glucose and mannose are C-2 epimers, while glucose and D-allose are C-3 epimers.



22.4 D-(+)-Glucose

(+)-Glucose is the most important monosaccharide because it is a monomer of many important polysaccharides like starch, cellulose and glycogen and since it plays a vital role in biological processes. Glucose occurs in free as well as combined state, *viz*. disaccharide (sucrose), polysaccharides (*e.g*. cellulose, starch, glycogen) and glycosides. Important sources of free glucose are ripe grapes (hence it is also called **grape sugar**), honey, human blood, urine of diabetic patient, etc. In laboratory, glucose is prepared by the hydrolysis of sucrose, while commercially it is prepared by the hydrolysis of starch.

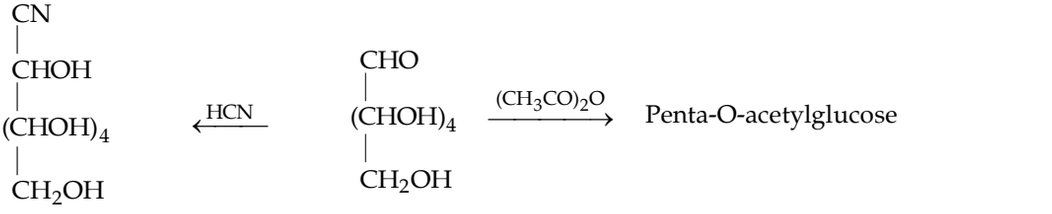
$$\underset{\text{Sucrose}}{C_{12}H_{12}O_{11}} \xrightarrow[\text{heat for 2 hrs.}]{\text{(i) alcohol (ii) dil. HCl, 50°C}} \underset{\text{Glucose (insoluble in alcohol)}}{C_6H_{12}O_6} + \underset{\text{Fructose (soluble in alcohol)}}{C_6H_{12}O_6}$$

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} \xrightarrow[\text{heat}]{\text{dil. } H^+} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

Glucose is a white crystalline substance (m.p. 160°C), soluble in water, sparingly soluble in alcohol. It is dextrorotatory, hence also called *dextrose*. It shows **mutarotation** (change in specific rotation in aqueous solution of the compound).

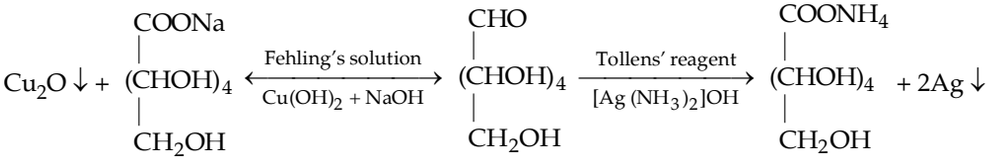
Chemical properties. (+)-Glucose is a typical monosaccharide, hence study on the structure and reactions of monosaccharides is mainly due to (+)-glucose. Following chemical reactions of glucose reveal that (+)-glucose is a six-carbon, straight-chain, pentahydroxyaldehyde, *i.e.* it is an aldohexose.

(*i*)



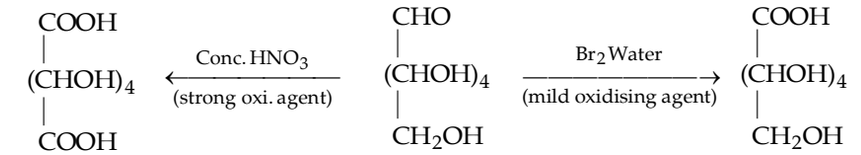
Glucose cyanohydrin (indicates presence of —CHO group) **(+)-Glucose** Glucose pentaacetate (indicates presence of 5 –OH groups)

(*ii*)



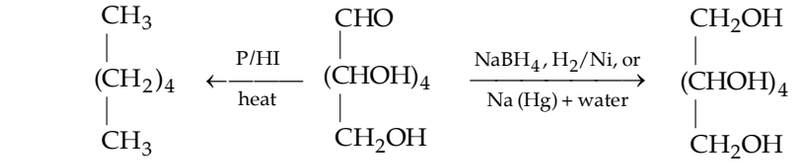
Red ppt. **(+)-Glucose** Silver mirror

(*iii*)



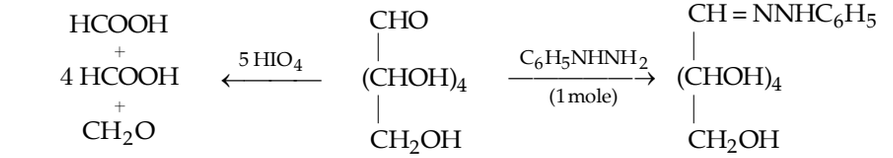
Glucaric acid (Saccharic acid) — **(+)-Glucose** — Gluconic acid

(*iv*)



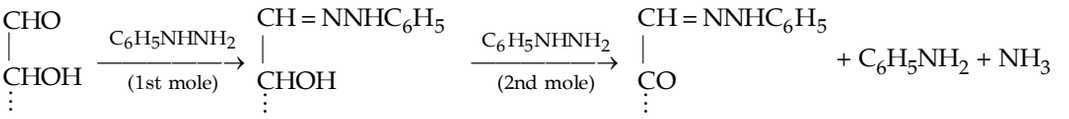
n-Hexane (indicates presence of a striaght chain of 6 C′s) — **(+)-Glucose** — Glucitol (Sorbitol)

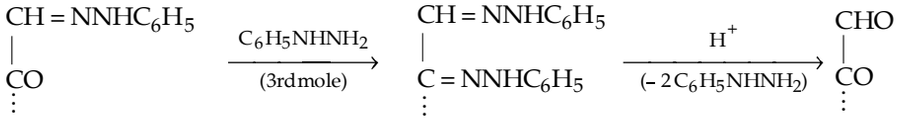
(*v*)



5 moles of formic acid, 1 mole of formaldehyde — **(+)-Glucose** — Glucose phenylhydrazone

Reaction of carbohydrates with phenylhydrazine requires special attention. At first stage, carbohydrates react with phenylhydrazine to form phenylhydrazones. However, if an excess of phenylhydrazine is used, the reaction proceeds further to yield products known as **osazone,** which contain two phenylhydrazine residues per molecule.

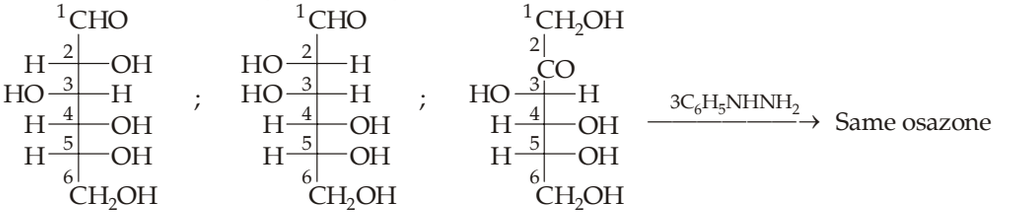




Osazone — Osone

Both of the phenylhydrazine residues of osazone can be removed to form dicarbonyl compounds, known as **osones.**

Osazones are highly coloured, crystalline compounds and can be readily identified, isolated and purified. Hence formation of osazone is used in the identification of carbohydrates. Osazone formation is not limited to carbohydrates, but in general it is a typical reaction of α-hydroxyaldehydes and α-hydroxyketones (*e.g.* benzoin, although not a carbohydrate, $C_6H_5CHOHCOC_6H_5$, it forms osazone). Further osazone formation involves only the first two carbon atoms, *i.e.* CHOCHOH— in aldoses and CH_2OHCO— in ketoses, of a compound without affecting the configuration of the rest of the molecule. Thus hexoses having similar configuration on C_3, C_4 and C_5 will form same osazone, *e.g.* glucose, mannose and fructose.



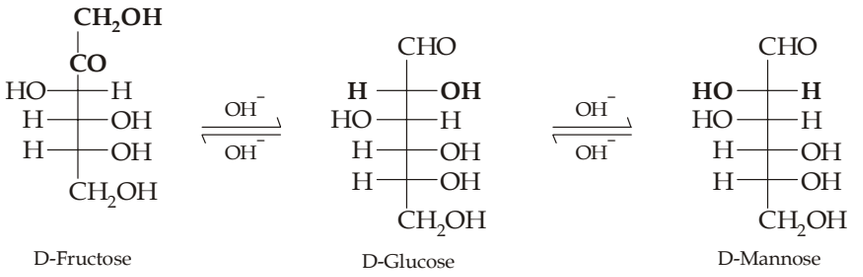
Glucose — Mannose — Fructose

22.4.1 Structural relation between glucose, mannose and fructose.

A pair of diastereomeric aldoses that differ only in the configuration about one of its chiral carbon are called epimers, e.g. glucose and mannose are examples of C–2 epimers ; while glucose and fructose, similarly mannose and fructose are simply isomers.

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(*vi*) When monosaccharides are dissolved in aqueous base, they undergo isomerization. For example, aqueous solution of D-glucose in presence of base undergoes isomerization to form D-mannose and D-fructose. This type of reaction is called the **Lobry de Bruyn van Ekenstein rearrangement.**



D-Fructose D-Glucose D-Mannose

This is the reason why D-fructose (not having an —CHO group) reduces Tollens' reagent (ammonical solution of silver nitrate), Fehling's solution (an alkaline solution cupric tartrate) and Benedict's reagent (an alkaline solution of cupric citrate). Actually, in presence of alkaline solution, ketoses (*e.g.* fructose) are converted to aldoses which reduce the above mentioned reagents.

TEST YOUR UNDERSTANDING - 22.3

1. Give the configuration of (–)-glucose, (–)-mannose, and (+)-fructose.

2. Compare the reactions of an aldohexose and a 2-ketohexose with (*i*) Tollens' reagent, (*ii*) Fehling solution, (*iii*) Benedict's reagent, and (*iv*) Bromine water.

3. (*a*) Give the products of oxidation with periodic acid with each of the following compound :

(*i*) Glycerol, (*ii*) Glyceraldehyde, (*iii*) Dihydroxyacetone, (*iv*) Propane-1, 3-diol.

(*b*) Describe how oxidation with periodate can be used in a simple way to distinguish between an aldohexose and a ketohexose?

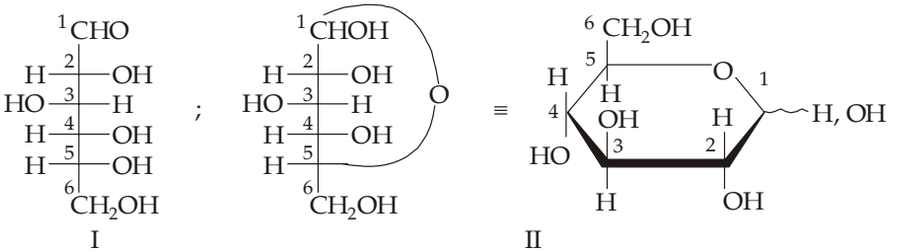
4. Establish the structure of the following glucose derivatives from their periodate oxidation products given against each of them.

(*a*) A + 5 HIO_4 ⟶ 2 HCHO + 4 HCOOH (*b*) B + 4 HIO_4 ⟶ CHOCOOH + 4 HCOOH

(*c*) C + 3 HIO_4 ⟶ 2 CHOCOOH + 2 HCOOH.

22.4.2 Structure of (+)-Glucose

Structure of (+)-glucose, an aldohexose, is not so simple as drawn above. An aldohexose with four stereogenic centers will have 2^4 = 16 stereoisomeric compounds ; 8 belongs to D series and 8 to the L series. All are known, either as naturally occurring substances or as the product of synthesis. Of these 16 stereoisomeric aldohexoses, only one is the (+)-glucose, second is its enantiomer (–)-glucose, and the other 14 isomers are diastereomers of (+)-glucose, namely mannose, galactose, talose, etc. As expected, these other aldohexoses undergo the same set of reactions that has been described for glucose. However, remember that they undergo these reactions at different rates (characteristics of diastereomers). Specific configurations of the four stereogenic carbons of glucose, C_2 to C_5, was assigned by Emil Fischer in 1900, see structure I. In IUPAC nomenclature and with the Cahn-Ingold-Prelog system of designations, the Fischer's open chain structure of D-(+)-glucose is (2R, 3S, 4R, 5R)-2, 3, 4, 5- pentahydroxyhexanal.



I II

D-(+)-Glucose (Open-chain structure)

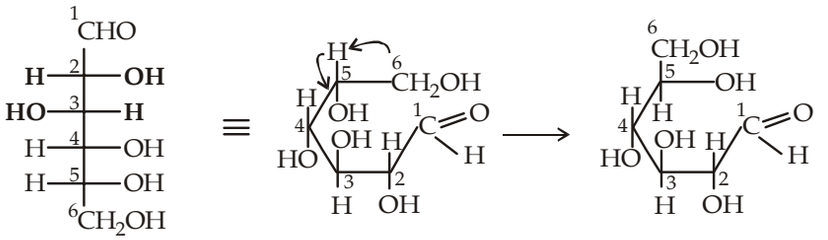
Cyclic structure of D-(+)-glucose

Fischer formula Haworth formula

(Substituents that are to the right in a Fischer projection are "*down*" in the corresponding Haworth formula)

Drawing Haworth structure for cyclic hemiacetals of sugars :

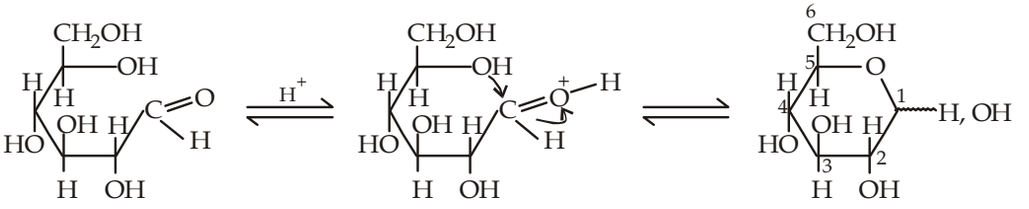
(i) Lay down the Fischer projection : right → down and left → up.



Glucose

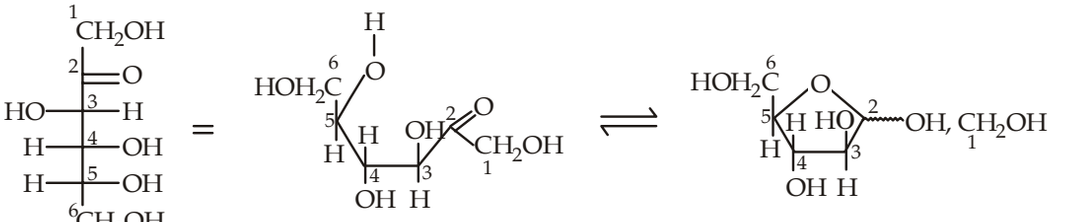
(ii) Rotate the C_4–C_5 bond to put the –OH in place so that it can form a part of the ring. For a sugar of the D series, this rotation puts the terminal –CH_2OH upward.

(iii) Close the ring and draw the result. The –OH group at C-1 can be either up or down giving two stereomers, henc groups at C-1 are denoted by wavy line, ~~~~.



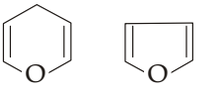
Haworth structure

Since some sugars exist in five-membered rings. Formation of five-membered ring of fructose is shown below.



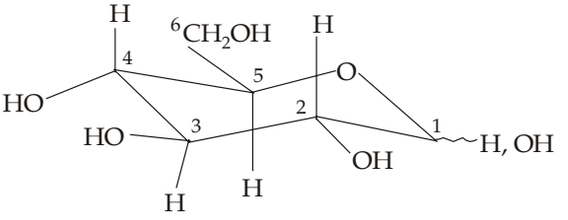
Haworth cyclic form for fructose

Significance of the word pyranose and furanose in carbohydrates. We have observed that the formation of hemiacetal of D-(+)-glucose involves —CHO and the —OH group at C_5 to form a six-membered ring (see structures I and II). However, it is not true for all carbohydrates, some carbohydrates (and even glucose, to a small extent) exist in the five membered ring where the hemiacetal formation involves —CHO group and the —OH group at C_4. Because of this variation, a system of nomenclature has been introduced to allow designation of the ring size. If the monosaccharide ring is 6 membered the compound is called a **pyranose** (derived from the 6-membered heterocylic compound, *pyran*) ; and if the ring is 5 membered, the compound is designated as a **furanose** (derived from the five-membered heterocylic compound, *furan*).



Pyran Furan

Thus the full name for the two isomeric D-(+)-glucoses is α-D-(+)-glucopyranose and β-D-(+)-glucopyranose. Remember that glucose mainly exists as pyranose (six membered ring). Further although Haworth formulas are widely used in carbohydrates, they do not give an accurate picture of the shape of the six-membered ring for which conformational formula (III) is the best description.



III

D-(+)-Glucopyranose

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However, the cyclic structure although explains most of the above mentional reactions, it does not explain following important reactions of D-(+)-glucose.

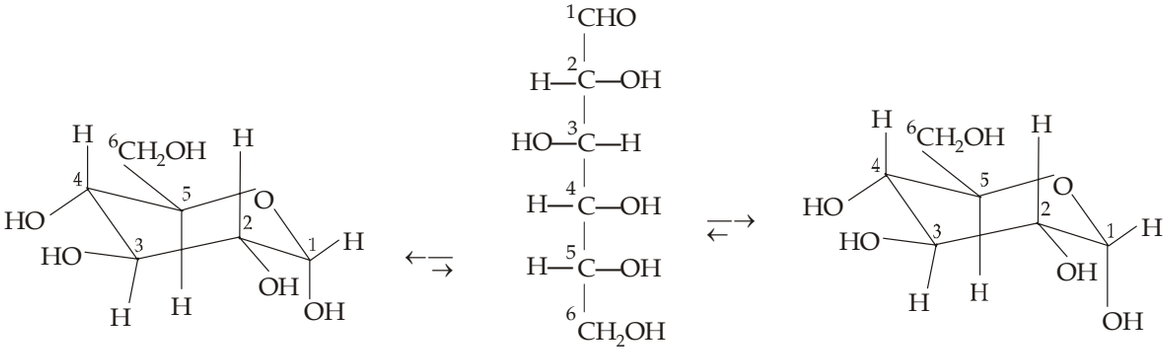
(*i*) It neither forms a bisulphite addition product with $NaHSO_3$ nor responds Schiff's test (both are reactions of —CHO group).

(*ii*) It forms two isomeric methyl D-glucosides when treated with methanol and HCl.

(*iii*) It exists in two isomeric forms both of which undergo **mutarotation.**

To explain above reactions, tremendous studies was done on the structure of D-(+)-glucose which led to a cyclic structure, II (rather than open chain structure). The cyclic forms of D-(+)-glucose are cyclic hemiacetals* formed by an intramolecular reaction of the —OH group at C_5 with the aldehyde group. Note that cyclization of the open chain structure of D-(+)-glucose has created a new stereocenter at C_1 which explains the existence of two cyclic forms of D-(+)-glucose, namely α– and β–. These two cyclic forms are *diastereomers, such diastereomers which differ only in the configuration of chiral carbon developed on hemiacetal formation* (it is C_1 in glucose and C_2 in fructose) *are called* **anomers** and the hemiacetal carbon (C_1 or C_2) is called the **anomeric carbon.** Remember that the prefixes α and β describe relative configuration. The configuration of the anomeric carbon (C_1) is said to be α when its —OH group is on the same side as the —OH group at the highest numbered stereogenic center (which is C_5 here) of the Fischer projection, in case the —OH group at the anomeric carbon and the highest numbered stereogenic center are on opposite sides of a Fishcer projection, the configuration at the anomeric carbon is β. Existence of two D-(+)-glucose and hence its cyclic hemiacetal structure is proved by isolation of the two D-(+)-glucoses under different conditions. When crystallized from ethanol, D-(+)-glucose yields α–D-(+)-glucose (better to name α–D-(+)-glucopyronose), m.p. 146° C, $[\alpha]_D$ = 112.2°. Crystallization from a water-ethanol mixture produces β–D-(+)-glucopyranose, m.p. 150°, $[\alpha]_D$ = + 18.7°. In the solid state the two forms do not interconvert and are stable indefinitely. Their structures have been unambiguously confirmed by X-ray crystallography. The optical rotations cited above for each isomer are those measured *immediately* after each one is dissolved in water.

Like hemiacetals, α- and β-D-(+)-glucose are readily hydrolyzed by water. In aqueous solution either anomer is converted, *via* the open chain form, into an equilibrium mixture containing both cyclic isomers.



α–D-(+)-Glucopyranose
m.p. 146°C ; $[\alpha]_D$ = + 112.2°
(36% at equilibrium)

Open chain form
of D-(+)-glucose
(negligible % at equbilibrium)

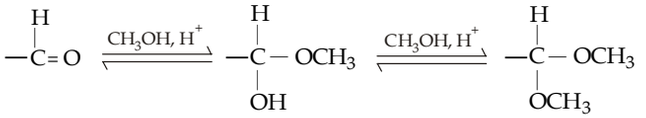
β–D-(+)-Glucopyranose
m.p. 150°C ; $[\alpha]_D$ = + 18.7°
(64% at equilibrium)

Thus when an aqueous solution of either form is allowed to stand, its rotation changes from + 112.2° (in case of α-) or + 18.7° (in case of β-) to a constant value of + 52.5°. *This change in rotation toward an equilibrium value is called mutarotation.*

The distribution between the α and β anomeric forms at equilibrium is readily calculated from the optical rotations of the pure isomers and the final optical rotation of the solution ; in case of D-(+)-glucose it is found to be 36 percent α and 64 percent β. The concentration of open chain D-(+)-glucose in solution at equilibrium is very small and

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* Acetals are the products formed by the reaction of an aldehyde or ketone with two moles of methanol in the presence of anhydrous HCl.



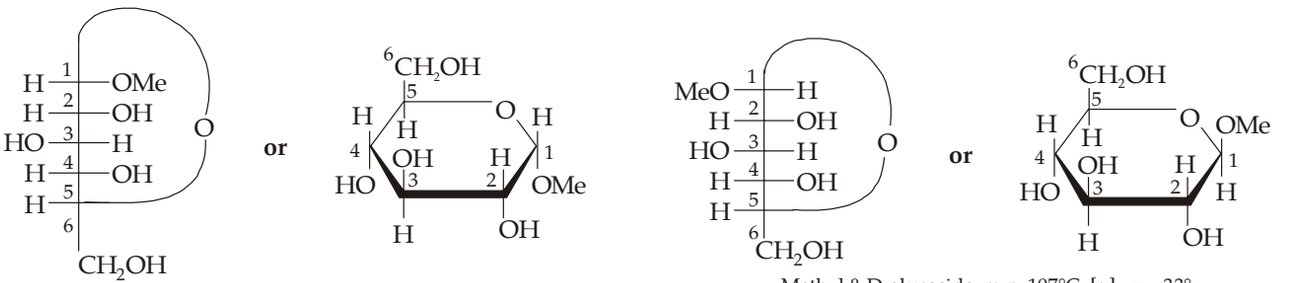
Aldehyde Hemiacetal Acetal

In glucose, both, —CHO as well as —OH group are provided by the same molecule, cyclization takes place leading to the formation of cyclic hemiacetal.

responsible for its reaction with Tollens' reagent, Fehling solution, and phenylhydrazine. Solutions of D-(+)-glucose give a negative test with Schiff's reagent and $NaHSO_3$ because reaction with these reagents are reversible, and the equilibrium favours unreacted hemiacetal form. On the other hand, osazone formation and Fehling reactions are irreversible, equilibrium is shifted to restore the low concentration of the open-chain structure.

22.4.3 Methyl D-Glucosides

Since two isomeric D-(+)-glucoses exist, there may be two isomeric methyl D-glucosides (obtained by reacting D-glucose with methanol in presence of HCl). The glucosides are full acetals, fairly stable in aqueous solution ; hence they do not undergo mutarotation. When heated with aq. acids, they are hydrolysed to yield the original hemiacetals (α- or β-glucose) ; however they are not readily hydrolyzed to hemiacetals and to open-chain aldehyde by alkalies hence they do not reduce Tollens' or Fehling's reagent (alkaline reagents), hence **glucosides are non-reducing sugars.**



Methyl α-D-glucoside, m.p. 165°C, $[\alpha]_D = +158°$

Methyl β-D-glucoside, m.p. 107°C, $[\alpha]_D = -33°$

TEST YOUR UNDERSTANDING - 22.4

1. Differentiate between epimers and anomers.
2. Name the enantiomer of α-D-(+)-glucose.
3. Do the anomers of D-glucose have specific rotations of the same magnitude but opposite signs ?
4. Can inverting the configuration of C_5 of D-glucose give L–glucose ?
5. Give two products of the reaction of an aldohexose with excess of $(MeO)_2SO_2$, dimethyl sulphate or CH_3I in concentrated NaOH.
6. Explain the following :
   (*a*) (+)-Glucose reacts with Fehling's solution and phenylhydrazine, but not with $NaHSO_3$.
   (*b*) Although glucose reacts with Fehling's solution, methyl glucosides do not react.
   (*c*) (+)-Glucose reacts with acetic anhydride to give two isomeric pentaacetyle derivatives neither of which reduces Fehlings' or Tollens' reagent.
   (*d*) Glycosides show mutarotation in acidic solution but not in neutral or basic aqueous solution.

22.5 (–)-Fructose

(–)-Fructose is the most important example not only of 2-ketohexoses but of all ketoses. It occurs widely in fruits and, combined with glucose, in the disaccharide sucrose (common table sugar). Commercially, fructose is obtained by the hydrolysis of the polysaccharide, inulin.

$$(C_6H_{10}O_5)_n + n\,H_2O \xrightarrow[\text{heat}]{H_2SO_4} n\,C_6H_{12}O_6$$

Inulin Fructose

Fructose is a white crystalline compound (m.p. 104°C), soluble in water and alcohol, but insoluble in ether (remember that nearly all carbohydrates are insoluble in ether). It is sweetest of all sugars and exhibits mutarotation; the $[\alpha]_D$ for α-, β-, and equilibrium mixture of fructose are – 21°, + 133.5° and – 92.3° respectively. It responds most of the usual reactions of the ketonic and hydroxyl groups. Its worth-mentioning properties are oxidation, reduction and osazone formation.

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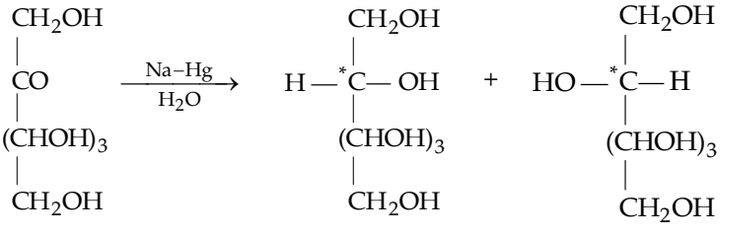
1. **Oxidation of fructose.** Fructose, although, does not have an —CHO group, it reduces Tollens' reagent, Fehling's solution and Benedict solution (similarity with glucose), **but not bromine water** (difference from glucose). The reason being the fact that the first three reagents (being alkaline in nature) provide alkaline medium to fructose which isomerises to glucose (*Lo bry de Bruyn van Ekeinstein rearrangement*), and hence reacts with the three reagents.

$$\text{Fructose} \underset{}{\overset{OH^- \text{ from the reagents}}{\rightleftharpoons}} \text{Glucose} \overset{\text{Reagent}}{\rightleftharpoons} \text{Gluconic acid}$$

(Here reagent means Tollens' reagent, Fehling solution or Benedict reagent.)

Since bromine water does not provide OH^- ions, fructose can't change to glucose in presence of bromine water, hence it is not oxidized by aqueous solution of bromine.

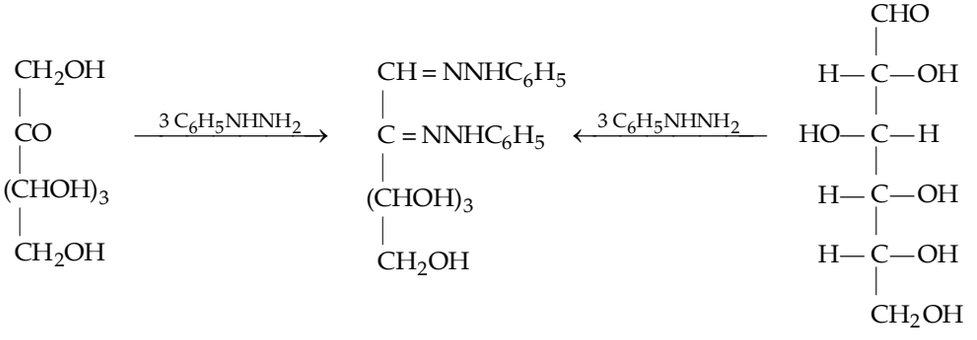
2. **Reduction.** Fructose, on reduction with Ni/H_2, Na–Hg and water or $LiAlH_4$ gives two alcohols, *viz*. sorbitol and mannitol (difference from glucose which on reduction gives only one alcohol, sorbitol).



Fructose Sorbitol Mannitol

The reason is very clear : reduction of fructose ($>C=O \longrightarrow -\overset{*}{C}HOH$) develops one more chiral carbon atom leading to two isomers, while reduction of glucose does not develop any additional chiral carbon [$-CHO \longrightarrow -CH_2OH$)].

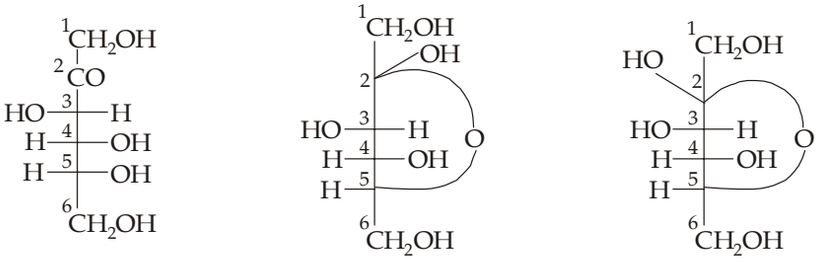
3. **Osazone formation.** Fructose reacts with excess of phenylhydrazine [3 moles of the reagent per mole of fructose) to form osazone hich is same as that formed by glucose.



Fructose Osazone Glucose

Now as we know from our previous discussion that osazone formation involves only first two carbon atoms, formation of same osazone from glucose (of known configuration) and fructose indicates that the two sugars have same configuration at C_3, C_4 and C_5 and differ only in the nature of the first two carbon atoms.

Thus by knowing the structure of D-glucose, we can write down the open chain structure of D-fructose as IV. However, like aldoses (*e.g*. glucose), ketoses (*e.g*. fructose) exist mainly as cyclic hemiacetals, better known as cyclic hemiketals (see structures V and VI).



D-Fructose IV α-D-Fructofuranose V β-D-Fructofuranose VI

Note that the configuration of the anomeric carbon, which is C_2 in fructose, is said to be α when its OH group is on the same side as the OH group at the highest numbered stereogenic center which is C_5 here.

TEST YOUR UNDERSTANDING - 22.5

1. (*a*) How many ketotetroses are possible ?

(*b*) How many chiral carbon centers are present in (–)– fructose ? Name the number of stereoisomers of fructose.

(*c*) Which is the anomeric carbon in fructose ? (*d*) What are deoxysugars ?

2. Differentiate between hemiacetal and acetal.

22.6 (+)-Sucrose

Ordinarily table sugar is a disaccharide (carbohydrates that yield two monosaccharide molecules on hydrolysis), called *sucrose. Sucrose*, the most widely occurring disaccharide, is formed in all photosynthetic plants. Commercially, it is obtained from sugarcane or sugar beets. It is colourless, crystalline, water soluble, sweet compound, dextrorotatory $[\alpha]_D$ + 66.5° compound **that does not show mutarotation.** Sucrose, on hydrolysis by dil. aqueous acid, or by the enzyme (*invertase*) gives D-(+)-glucose and D-(–) fructose.

$$\underset{\text{(+)-Sucrose}}{C_{12}H_{12}O_{11}} + H_2O \xrightarrow[\text{or invertase}]{H^+} \underset{\text{D-(+)-Glucose}}{C_6H_{12}O_6} + \underset{\text{D-(–)-Fructose}}{C_6H_{12}O_6}$$

Structurally, the two monosacchaide units (D-glucose and D-fructose) of sucrose are joined at their anomeric carbons, *i.e.*, C_1 of glucose is joined to C_2 of fructose through their —OH groups. Thus the disaccharide (sucrose) does not have free anomeric hydroxyl group and hence it can't have free —CHO or >C = O group is its structure. Consequently sucrose is found to be **non-reducing sugar,** and neither shows mutarotation nor forms osazone.

Disaccharides in which anomeric hydroxyl group of either of the monosaccharide is free can regenerate its —CHO or >C = O, hence such disaccharides are **reducing**, and exist in α- and β- forms which undergo mutarotation, common examples are lactose, maltose, cellobiose etc.

Specific rotation of (+)-sucrose and its hydrolysate. (+)-Sucrose has a specific rotation of + 66.5°, while its hydrolyate (a mixture of equal amounts of D-(+)-glucose and D-(–)-fructose) has a specific rotation of –19.9°. Since the specific rotation of the hydrolysis product is opposite to that of (+)-sucrose, hydrolysis of sucrose is commonly called as *inversion of sucrose* and the hydrolysis product is called *invert sugar*. The inversion in rotation is due to the presence of equal amount of D-(–)-fructose with a large negative specific rotation of –92.4°.

$$\underset{\substack{\text{Sucrose}\\ [\alpha]_D = +66.5°}}{C_{12}H_{12}O_{11}} + H_2O \xrightarrow[\text{or invertase}]{H^+} \underbrace{\underset{\substack{\text{D-(+)-Glucose}\\ [\alpha]_D = +52.7°}}{C_6H_{12}O_6} + \underset{\substack{\text{D-(–)-Fructose}\\ [\alpha]_D = -92.4°}}{C_6H_{12}O_6}}_{\text{Invert sugar, } [\alpha]_D = -19.9°}$$

Honey mainly contains invert sugar, the bees supply the enzyme invertase.

Remember the following order of sweetness of the common sugars (mono- and oligo- saccharides are called sugars, while polysaccharides are called *non-sugars*)

Fructose > Invert sugar > Sucrose > Glucose > Maltose > Lactose

One of the interesting reactions of sucrose is its reactions with conc. H_2SO_4 to give free carbon (commonly known as **sugar charcoal**, a very pure form of carbon) along with water ; the reaction is known as dehydration. A part of carbon is oxidised by conc. H_2SO_4 to form CO_2 and SO_2, the latter is detected due to its characteristic smell.

$$\underset{\text{Sucrose}}{C_{12}H_{12}O_{11}} + H_2SO_4 \longrightarrow \underset{\text{Sugar charcoal}}{12\,C} + 11\,H_2O$$

$$C + 2H_2SO_4 \longrightarrow 2\,SO_2 + CO_2 + 2H_2O$$

TEST YOUR UNDERSTANDING - 22.6

1. Can you calculate the specific rotation of invert sugar, given $[\alpha]_D$ = + 52.7° for D-glucose, and $[\alpha]_D$ = – 92.4° for D-fructose ?



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22.7 Some Artificial Sweetners

Sucrose and fructose are the most common natural sweeteners. Since they add to our calorie and promote tooth decay, some artificial sweetening agent were developed. Important artificial sweetening agents are mentioned below.

1. **Aspartame.** It is the most successful and widely used artificial sweetner. It is the methyl ester of a dipetide formed from phenylalanine and aspartic acid. It is roughly 100 times as sweet as sucrose. Its limitations are its slow hydrolysis in solution and decomposition with heat.
2. **Alitame.** It is a compound related to aspartame, but with important properties like more stability and more sweetness. It is nearly 2000 times as sweet as sucrose.
3. **Sucralose.** It is a trichloro derivative of sucrose. It looks and tastes like sugar, it is stable at the temperatures used for cooking and baking, and neither causes tooth decay nor provides calories. It is 600 times sweeter than sucrose.
4. **Cyclamate and Saccharin.** These were popular sweetners at one time, a mixture of 10 part of cyclamate and 1 part of saccharin proved sweetner than either compound individually. However, this mixture produced tumours in animals, hence its use was banned. Saccharin is still used is some products.
5. **Sucronic acid.** It is reported to be 200,000 times as sweet as sucrose.
6. **L-Glucose.** L-Sugars are also artificial sweetners and they provide nearly zero calories because our enzymes selectively metabolize only the D-sugars.

22.8 Polysaccharides

Polysaccharides are naturally occurring polymers of aldoses or ketoses. The most common polysaccharides are the polymers of aldohexoses or ketohexoses, and have the general formula $(C_6H_{10}O_5)_n$. Common examples are cellulose, starch, glycogen, inulin etc. ; all of these on hydrolysis give indefinite number of monosaccharides of the formula $C_6H_{12}O_6$ which may be glucose, fructose or other hexose depending upon the individual polysaccharide.

$$(C_6H_{10}O_5)_n + nH_2O \longrightarrow n\,C_6H_{12}O_6$$

Cellulose, starch and glycogen are the polysaccharides of D-(+)-glucose ; they differ in the point of linkage of the glucose units, of molecular size and shape. Further starch contains two different monosaccharides : (*a*) a water-soluble fraction (20%) called *amylose* and (*b*) a water-insoluble fraction (80%) called *amylopectin. Dextrin* is one of the intermediate hydrolysis products of starch.

$$\text{Starch} \xrightarrow{\text{hydrolysis}} \text{Dextrin} \xrightarrow{\text{hydrolysis}} \text{(+)-Maltose} \xrightarrow{\text{hydrolysis}} \text{D-(+)-glucose}$$

Glycogen is the form of a polysaccharide of (+)-glucose which is stored in animals (hence also called *animal starch*). It is released from liver (where it is stored) upon metabolic demand and hydrolysed in the system to (+)-glucose. **Inulin** is a polysaccharide of fructose.

22.9 ILLUSTRATIVE EXAMPLES

Example 1 :

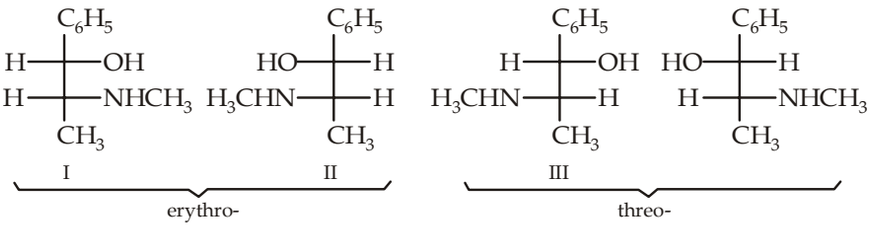
(a) Draw the Fischer projection formulas for the possible stereoisomer of 2-(methylamino)-1-phenylpropan-1-ol.

(b) The erythro stereoisomers of the above compound represent ephedrine (a bronchodilator), while the threo stereoisomers represent pseudoephedrine (a decongestant). Which structure you will give for ephedrine and pseudoephedrine?

(c) Label the structure for (–)-ephedrine and (+)-pseudoephedrine?

Solution :

(a)



(b) Structures I and II represent enantiomers of ephedrine, while structures III and IV represent enantiomers of pseudoephedrine.

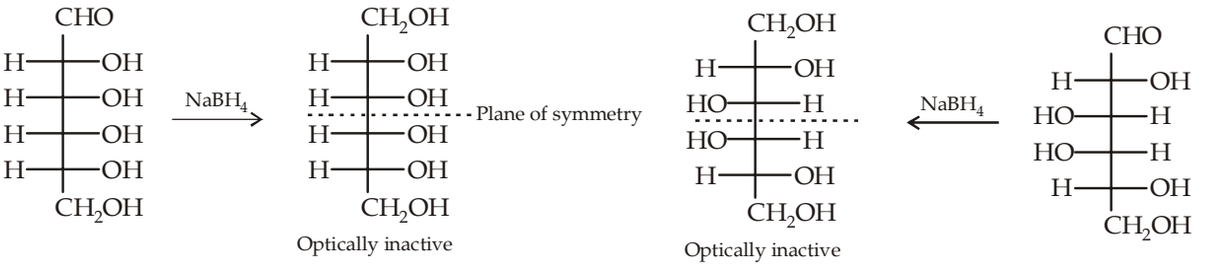
(c) The direction of optical rotation has no relation with the D or L designation (except for glyceraldehyde) so it is not possible to assign the (–)– or (+)– sign for structures. The optical rotation can only be determined with the help of polarimeter.

Example 2 :

Aldohexoses have four chiral carbon atoms, and hence it exists in eight enantiomeric pairs. Out of the eight D-aldohexoses, how many are expected to yield optically inactive alditols on reduction, write the Fischer projection formulas for such D-aldohexoses?

Solution :

Only those alditols would be optically inactive, whose molecules possess a plane of symmetry. There are two such D-alditols and hence two D-aldohexoses.



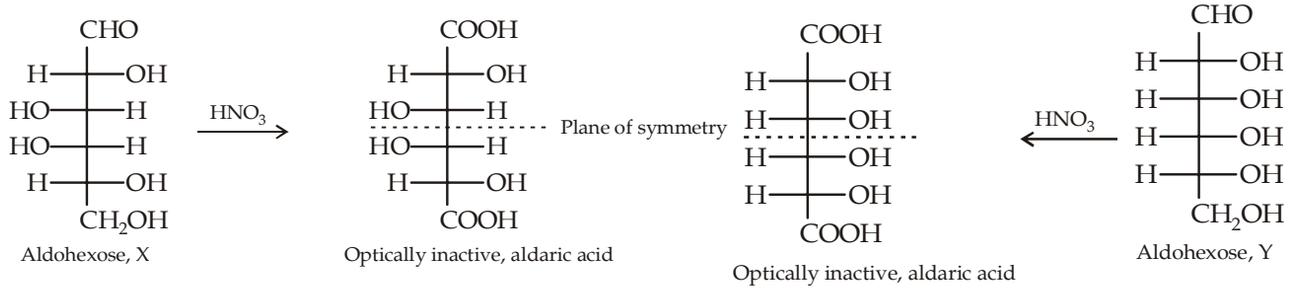
These two aldohexoses are D-allose and D-galactose.

Example 3 :

Two D-aldohexoses *A* and *B* are oxidised with nitric acid to form optically inactive aldaric acids. Compound *A* is degraded to an D-aldopentose which on oxidation with HNO_3 gives an optically active aldaric acid. However, on similar treatment aldohexose B gives optically inactive aldaric acid.Determine the structures of *A* and *B*.

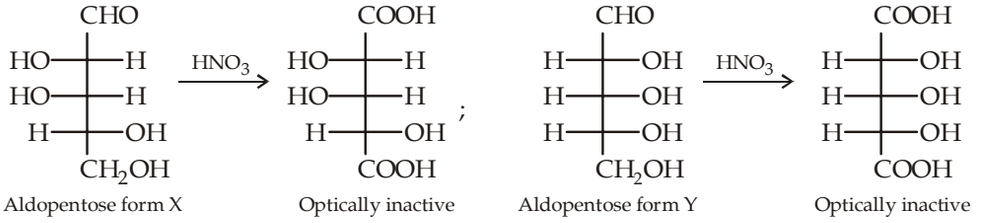
Solution :

Only following two configurations of aldohexose will give optically inactive acid, on oxidation.



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Now let us take the lower homologue of the two aldohexoses and observe the optical activity of their corresponding aldaric acids.

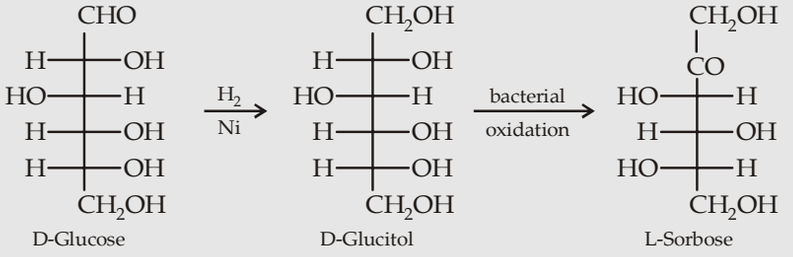


Aldopentose form X — Optically inactive — Aldopentose form Y — Optically inactive

Hence X is **A** and Y is **B.**

Example 4 :

Observe the following reactions carefully, and answer the question given below :

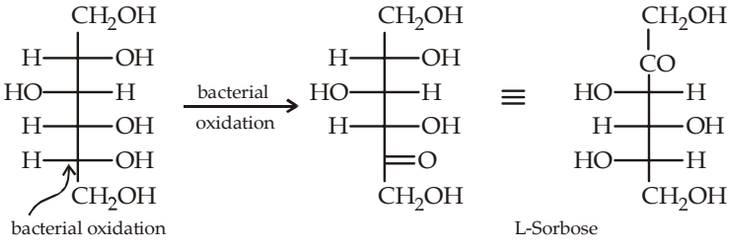


D-Glucose — D-Glucitol — L-Sorbose

Explain the conversion of D-glucitol to L-sorbose.

Solution :

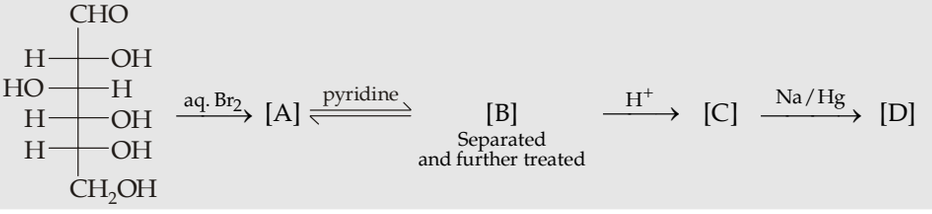
Bacterial oxidation of D-glucitol is specific, it selectively oxidises the –CHOH group of D-glucitol that corresponds to C-5 of D-glucose.



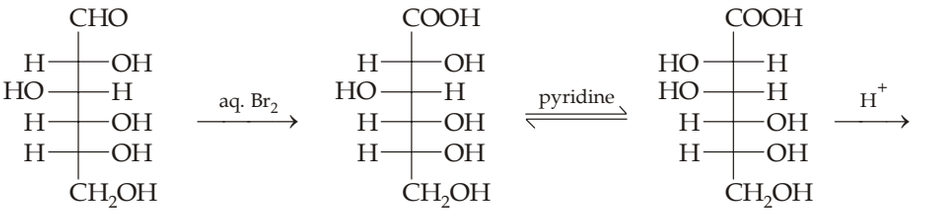
bacterial oxidation — L-Sorbose

Example 5 :

Supply structures for A to D in the following series of reactions.

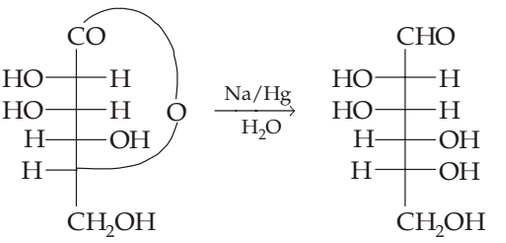


Solution :



[A] [B]

Epimerisation (in presence of base)

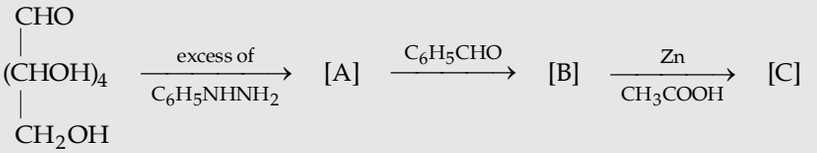


[C]
A δ-lactone,
(more stable than γ-lactone)

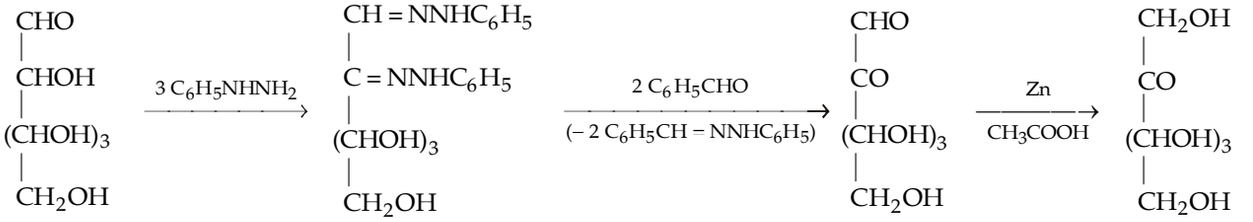
[D]
A, C–2 epimer of the
starting compound

Example 6 :

Identify compounds A, B and C in the following reactions.



Solution :



[A] [B] [C]

In the conversion of [B] to [C], the more reactive aldehyde group of the osone is reduced.

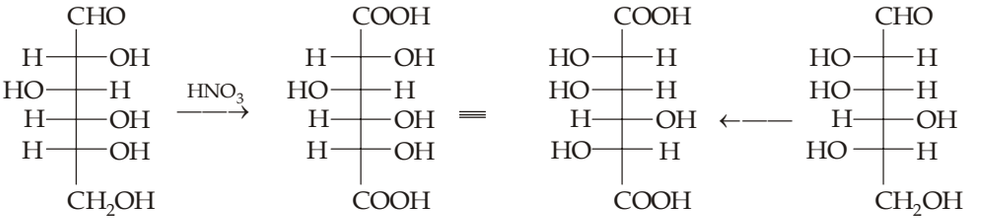
Example 7 :

Can you imagine a carbohydrate, other than D-(+)-glucose, which on oxidation with HNO_3 gives same aldaric acid as D-(+)-glucose ?

Solution :

First of all, write down the reaction involving oxidation of D-(+)-glucose with HNO_3. Now write the equivalent structure of the aldaric acid (aldaric acids are dicarboxylic acids obtained by oxidation of the two terminal carbon atoms of the monosaccharide to —COOH groups).

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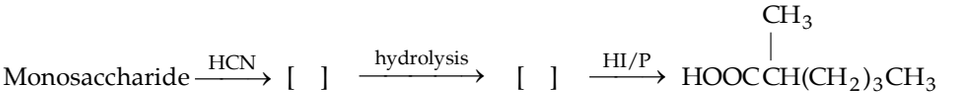
(D)-(+)-Glucose Aldaric acid

Example 8 :

A monosaccharide is treated with HCN, the product hydrolyzed and reduced to 2-methylhexanoic acid by heating with HI and P. Establish the structure of the monosaccharide.

Solution :

Summarise the given facts in the form of equation



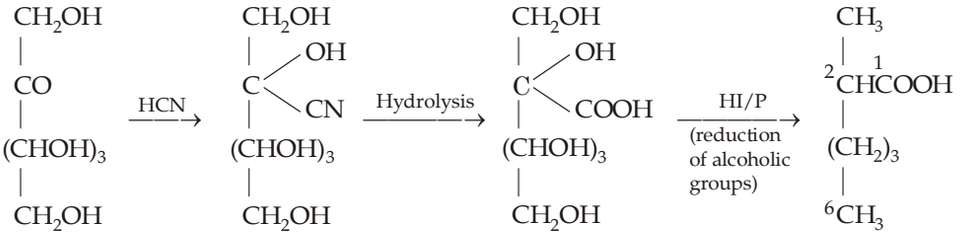
2-Methylhexanoic acid

Above reactions lead to following conclusions.

(*i*) Since the starting compound is a monosaccharide, it must have a —CHO or >C = O group.

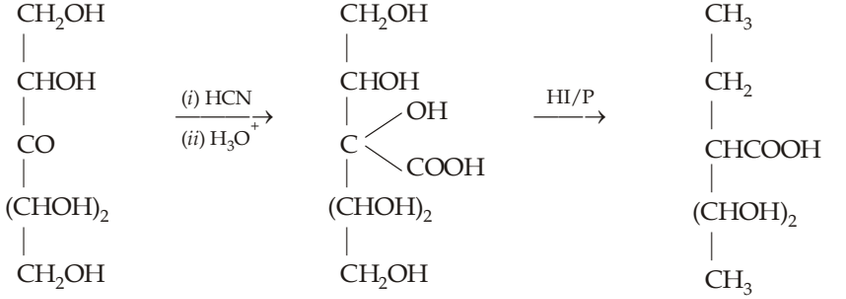
(*ii*) Formation of carboxylic acid, having a branched alkyl chain indicates that the monosaccharide is a ketose. Position of ketonic group is indicated by the nature of alkyl group, which is —CH_3, here.

Hence the above reactions can be explained by taking 2-ketohexose as the monosaccharide.



A 2-ketohexose (*e.g.* fructose) 2-Methylhexanoic acid

Had the keto group been on C_3 wrt to the upper CH_2OH group, the final product would have been 2-ethylpentanoic acid.



A 3-ketohexose 2-Ethylpentanoic acid

Example 9 :

The specific optical rotations of pure α- and β-D-mannopyranose are + 29.3° and –17.0, respectively. When either form is dissolved in water, specific optical rotation of the equilibrium mixture is found to be + 14.2°. Calculate the percentage of each isomer at equilibrium.

***Solution* :**

Let fraction of α-anomer = x

$\therefore$ Fraction of β-anomer = $(1 - x)$

Hence $x\,(+ 29.3°) + (1 - x)\,(- 17.0°) = + 14.2°$

$29.3°\,x + (- 17° + 17°x) = + 14.2°$

$29.3°x + 17°x = 14.2° + 17°$

$46.3°x = 31.2°$

$x = 0.67$

$\therefore$ Fraction of α-anomer = 0.67 or 67%

and fraction of β-anomer = 0.33 or 33%.

Example 10 :

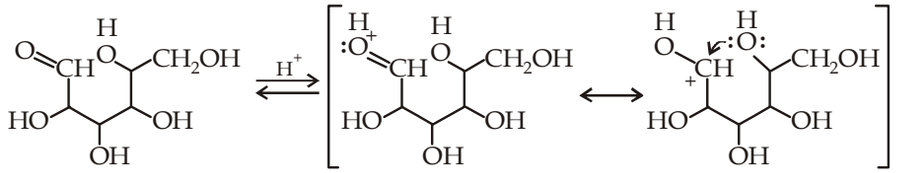
Interconversion of the open chain and cyclic hemiacetal forms of glucose is catalysed by either acid or base.

(a) Propose a mechanism for the cyclization, in presence of a trace of acid.

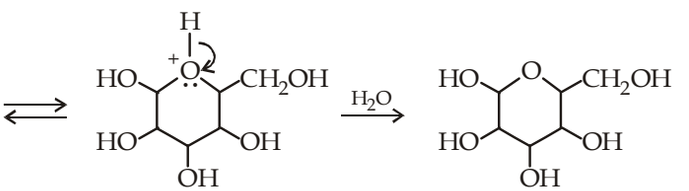
(b) The cyclic hemiacetal form of glucose is more stable than the open chain form, so at equilibrium very little of the open chain form is present. When Tollens reagent is added to glucose solution, what do you expect about the amount of the cyclic form of glucose with time.

Solution :

(a)

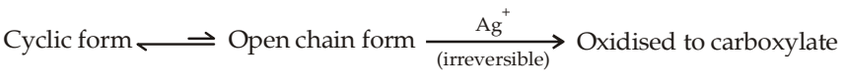


Open chain form of glucose



Cyclic form (hemiacetal)

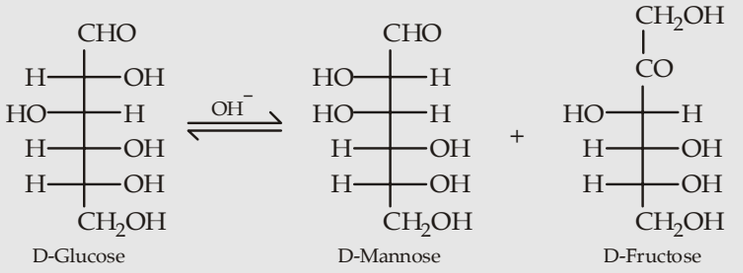
(b) In the basic solution of the Tollens reagent, an equilibrium exists between the hemiacetal (cyclic) form and open chain form, of course the former is present in larger concentration. However, the Tollen's reagent oxidises the open chain form to a carboxylate ion causing conversion of further amount of cyclic form to open chain which is again oxidised to carboxylate, thus more and more amount of cyclic form is converted to carboxylate with the time and ultimately all the cyclic form is converted to the carboxylate (**Le Chatelier principle**).



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Example 11 :

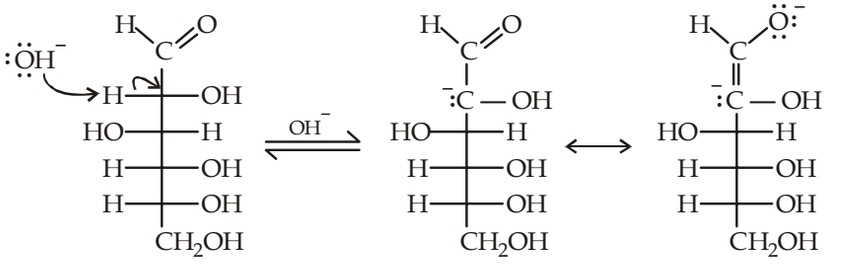
When glucose is treated with a base, a mixture of glucose, mannose and fructose is obtained. Explain by giving proper mechanism.



D-Glucose D-Mannose D-Fructose

Solution :

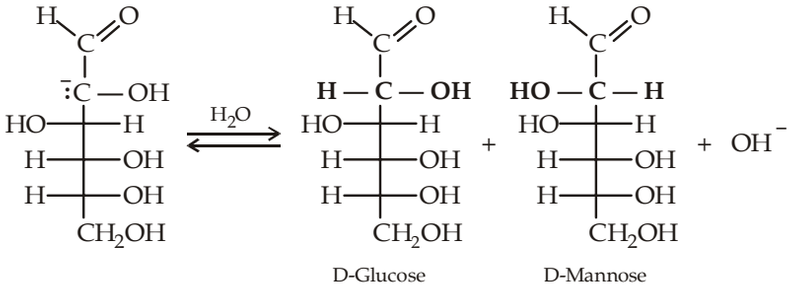
Under basic conditions, the proton alpha to the aldehyde (or ketone) carbonyl group is reversibly removed to form corresponding enolate.



Enolate

The enolate so formed may undergo two different reactions forming two different compounds.

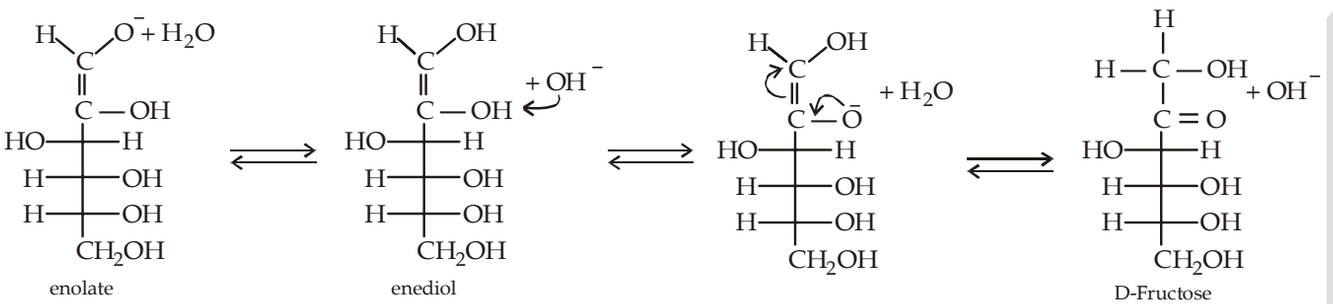
(a) **Reprotonation of enol at C_2 :** Since C_2 of enolate is no longer asymmetric, reprotonation can occur on either face of the enolate, giving a mixture of the original sugar and its C_2 epimer.



D-Glucose D-Mannose

Since this reaction leads to a mixture of epimers, it is called **epimerization**.

(b) **Reprotonation of enol on the C_1 oxygen :** This leads to an **enediol** intermediate which is easily converted into a ketose (fructose) by a series of reactions.



enolate enediol D-Fructose

Since this reaction leads to isomer, it is known as **isomerization**.

EXERCISE 22.1 (MCQ - ONE option correct)

1. The general formula for most of carbohydrates is $C_n(H_2O)_m$; in this formula the value of n and m may be

(*a*) $n > m$ (*b*) $n < m$

(*c*) Both (*d*) None.

2. The molecular formula for a pentose tetrasaccharide should be

(*a*) $C_{24}H_{42}O_{21}$ (*b*) $C_{20}H_{32}O_{16}$

(*c*) $C_{20}H_{36}O_{18}$ (*d*) $C_{20}H_{34}O_{17}$.

3. (+)-Glucose is oxidised in the tissues to CO_2 and H_2O with the release of energy. This energy is

(*a*) first formed and then stored inside the tissue

(*b*) originally supplied by enzymes present in the tissues

(*c*) originally supplied by sun

(*d*) None of the above is true.

4. (+)-Glucose and (–)-fructose can be differentiated by

(*a*) Tollen's reagent (*b*) Fehling solution

(*c*) Bromine water (*d*) None of the three.

5. D-(+)-Glucose $\xrightarrow{5(CH_3CO)_2O}$ D-(+)-Glucose pentaacetate

Which statement is true about glucose pentaacetate ?

(*a*) It will react with phenylhydrazine but not with Tollens' reagent.

(*b*) It will react with Tollens' reagent but not with phenylhydrazine.

(*c*) It will react with both of the above mentioned reagents.

(*d*) It will react neither with phenylhydrazine nor with Tollens' reagent.

6. Which of the following is not possible in glucose ?

(*a*) (+)-form (*b*) (–)-form

(*c*) *rac*-form (*d*) *meso* form.

7. Which of the following statement is true ?

(*a*) Epimers are also anomers

(*b*) Anomers are also epimers

(*c*) Both of the above statements are true

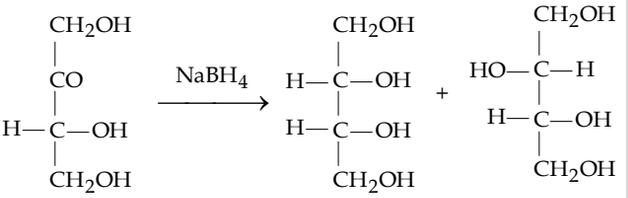
(*d*) Neither of the two statement is true

8. The enantiomer of α-D-(+)-glucose is

(*a*) β-D-(+)-glucose (*b*) α-D-(–)-glucose

(*c*) α-L-(–)-glucose (*d*) β-L-(–)-glucose.

9. A D-ketotetrose is reduced to give two products



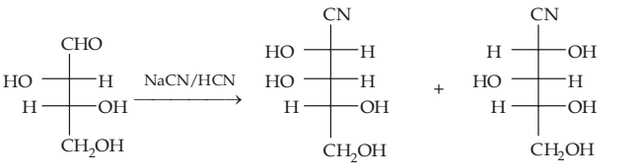
I II

The two products I and II are

(*a*) enantiomers (*b*) diastereomers

(*c*) anomers (*d*) none of the three.

10.



I II

Compounds I and II may be grouped as

(*a*) diastereomers (*b*) epimers

(*c*) C–2 epimers (*d*) all of the three.

11. Which one is the absolutely specific term ?

(*a*) A diastereomer (*b*) An epimer

(*c*) An anomer (*d*) None of the three.

12. Pick up the correct statement.

(*a*) α- and β-D-glucoses are diastereomers

(*b*) α- and β-D-glucoses are anomers

(*c*) α- and β-D-glucoses are epimers

(*d*) All the above statements are correct.

13. When an aqueous solution of D-glucose is treated with a base, it is converted into D-fructose and D-mannose, this conversion (isomerisation) involves

(*a*) enolization (*b*) tautomerization

(*c*) both (*a*) and (*b*) (*d*) none of the two.

14. The anomeric carbon atom in glucose and fructose is

(*a*) C_1 (*b*) C_2 (*c*) C_5

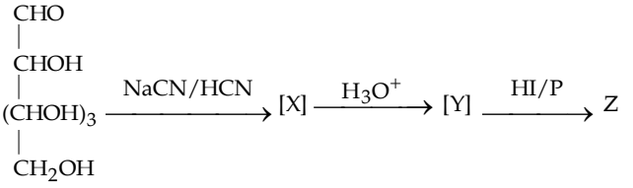
(*d*) C_1 in glucose and C_2 in fructose.

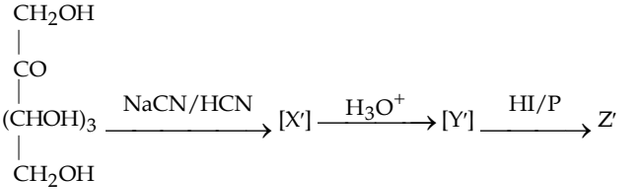
15. Fructose on reduction gives a mixture of two alcohols which are related as

(*a*) diastereomers (*b*) epimers

(*c*) both (*a*) and (*b*) (*d*) anomers.

16. Predict the nature of the products Z and Z′ in the following series of reactions





(*a*) Both are *n*-heptane

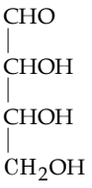
(*b*) Both are *n*-heptanoic acid

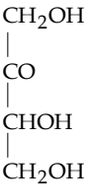
(*c*) Both are 7-iodoheptanoic acid

(*d*) Z is *n*-heptanoic acid, and Z′ is a substituted hexanoic acid.

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17. Which of the following evolves carbon dioxide, on oxidation with periodate ?

(*a*) 

(*b*) 

(*c*) Both (*d*) None.

18. Which of the following pairs can be distinguished by Fehling's solution ?

(*a*) Glucose and fructose

(*b*) Glucose and sucrose

(c) Methanal and ethanal

(*d*) Hydroxypropanone and benzaldehyde.

19. Benedict's reagent is reduced by which type of carbohydrates?

(*a*) Acetals (*b*) Hemiacetals

(*c*) Glucose pentacetate (*d*) None of the three.

20. What will happen when D-(+)-glucose is treated with methanolic —HCl followed by Tollens' reagent ?

(*a*) A black ppt. will be formed

(*b*) A red ppt. will be formed

(*c*) A green colour will appear

(*d*) No characteristic colour or ppt. will be formed.

21. Pick the up the false statement.

(*a*) Ketoses show the phenomenon of mutarotation.

(*b*) Glycosides show the phenomenon of mutarotation

(*c*) There is a relationship between the ability of a sugar to mutarotate and reduce Tollens' reagent.

(*d*) None of the above statement is false.

22. Which is true about the acidic character of hydroxyl groups of sugars and hydroxyl group of an alcohol ?

(*a*) The OH's of sugars are more acidic than that of a typical alcohol.

(*b*) The OH's of sugars are less acidic than that of a typical alcohol.

(*c*) Both have similar acidic character.

(*d*) The OH's of sugars are neutral while that of an alcohol is acidic.

23. Honey is more sweet than glucose because it has

(*a*) pure glucose

(*b*) sucrose which is sweeter than glucose

(*c*) invert sugar

(*d*) none of the above three is correct.

24. Which of the following carbohydrate in not related to (+)glucose?

(*a*) Amylopectin (*b*) Amylose

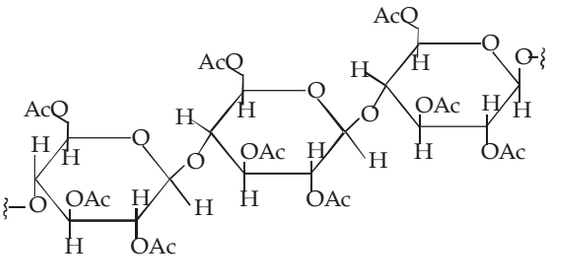
(*c*) Inulin (*d*) Glycogen.

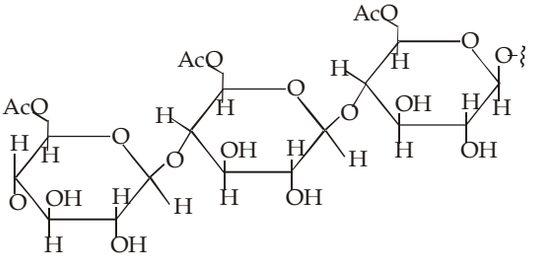
25. Which of the following is (are) not polysaccharide(s)?

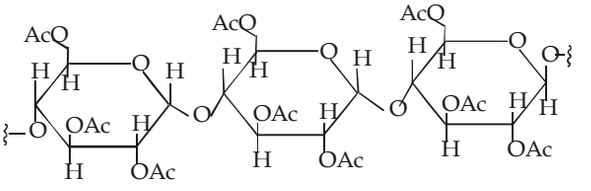
(a) Amylose (b) Amylopectin

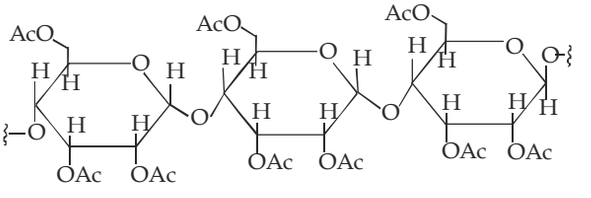
(c) Inulin (d) Sucrose

26. Cellulose upon acetylation with excess acetic anhydride/H_2SO_4 (catalytic) gives cellulose triacetate whose structure is

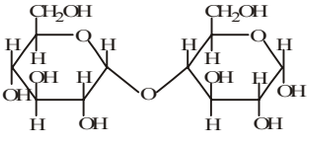
(A) 

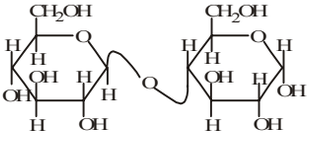
(B) 

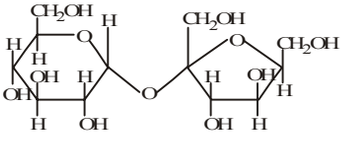
(C) 

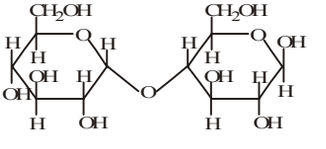
(D) 

27. Which compound will not give the Tollen's test

(a) 

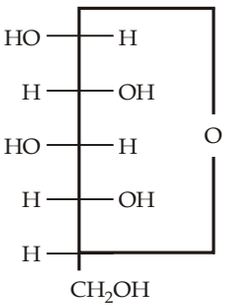
(b) 

(c) 

(d) 

28. Glucose reduces
(*a*) Tollen's reagent (*b*) Fehling's solution
(*c*) Benedict's solution (*d*) All

29. S_1 : Sucrose has $C_1 - C_2$ glycosidic linkage between β-D-glucose & α-D-fructose.
S_2 : Glucose does not give positive test with 2, 4-DNP.
S_3 : Pentacetate of glucose does not form oxime.

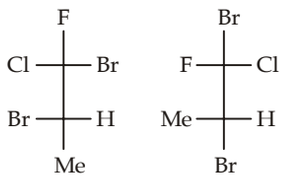
S_4 :  is structure of β-D(+) glucose.

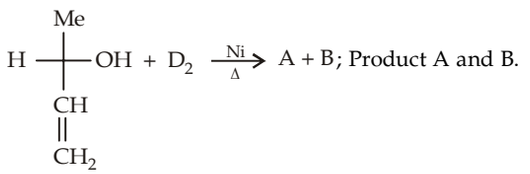
Which of the following is correct statements (F = False, T = True)
(*a*) FFTT (*b*) FFTF
(*c*) FFFT (*d*) TTTT

30. Methyl-α-D-glucoside and methyl-β-D-glucoside are
(*a*) Epimers
(*b*) Anomers
(*c*) Enantiomers
(*d*) Conformational diastereomers

31. The term anomers of glucose refers to
(*a*) A mixture of (D)-glucose and (L)-glucose
(*b*) Enantiomers of glucose
(*c*) Isomers of glucose that differ in configuration at carbon one (C-1)
(*d*) Isomers of glucose that differ in configurations at carbons one and four (C-1 and C-4)

32. Which of the following pairs are enantiomers ?
(i) D-Glucose and L-glucose.
(ii) R-Tartaric acid and S-tartaric acid

(iii) 

(iv) 

(*a*) I, II (*b*) I, II, III
(*c*) I, II, III, IV (*d*) II, IV

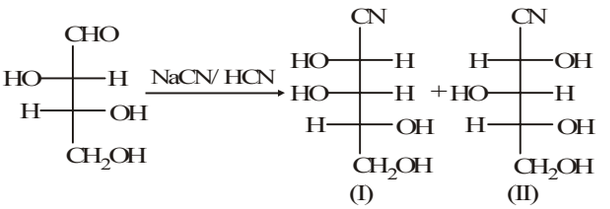
33. If C-5 carbon of D-glucose is inverted, the new compound is related with parent compound as
(I) Diastereomer
(II) Enantiomer
(III) Epimer
(IV) Anomer
(*a*) I and III (*b*) II and III
(*c*) IV and I (*d*) I only

34. The pair of compounds in which both the compounds give positive test with Tollen's reagent is
(a) Glucose and Sucrose
(b) Fructose and Sucrose
(c) Acetophenone and Hexanal
(d) Glucose and Fructose

35. The two forms of D-glucopyranose obtained from the solution of D-glucose are called
(a) Isomers (b) Anomers
(c) Epimers (d) Enantiomers

36. Among cellulose, poly (vinyl chloride), nylon and natural rubber, the polymer in which the intermolecular force of attraction is weakest is
(a) Nylon (b) Poly (vinyl chloride)
(c) Cellulose (d) Natural rubber

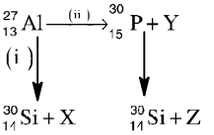
37. The two functional groups present in a typical carbohydrate are:
(a) – CHO and – COOH
(b) > C = O and – OH
(c) – OH and – CHO
(d) – OH and – COOH

38. 

Compounds I and II may be grouped as
(a) diastereomers (b) epimers
(c) C–2 epimers (d) all of the three.

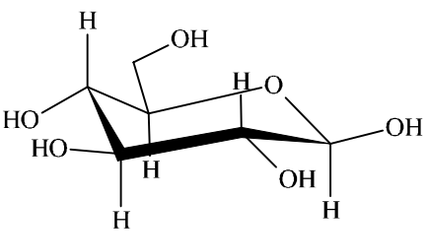
39. When an aqueous solution of D-glucose is treated with a base, it is converted into D-fructose and D-mannose, this conversion (isomerisation) involves
(a) enolization (b) tautomerization
(c) both (a) and (b) (d) none of the two.

40. Bombardment of aluminium by α-particle leads to its artificial disintegration in two ways, (i) and (ii) as shown. Products X, Y and Z respectively are,



(A) proton, neutron, positron
(B) neutron, positron, proton
(C) proton, positron, neutron
(D) positron, proton, neutron

41. The following carbohydrate is



(a) a ketohexose (b) an aldohexose
(c) an α-furanose (d) an α-pyranose

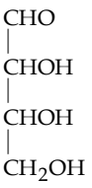
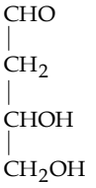
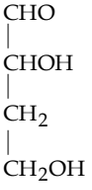
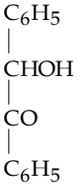
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EXERCISE 22.2 (MCQ 1 or >1 option correct, Passage based, Matching, A/R)

DIRECTIONS for Q. 1 to Q. 9 : Multiple choice questions with one or more than one correct option(s).

1. Which of the following statement is correct ?
(*a*) Fruit mainly contains glucose as carbohydrate
(*b*) Honey mainly contains invert sugar
(*c*) Blood sugar and grape sugar mainly contain glucose
(*d*) Sucrose is an oligosaccharide.

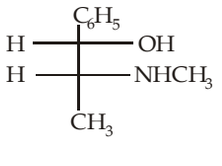
2. Which of the following can form osazone ?

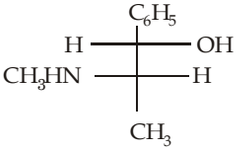
(a) 
(b) 
(c) 
(d) 

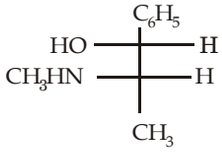
3. Which of the following statement(s) is(are)
(a) Glucose and fructose forms same compound on heating with P and hydriodic acid
(b) Glucose and fructose differ in the configuration only at C_1 and C_2
(c) Both form two isomeric cyanohydrins
(d) The two are epimers

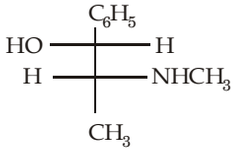
4. Which of the following are correct statements?
(a) Invert sugar is the sweetest sugar
(b) Fructose is a reducing sugar
(c) Fructose is a ketohexose
(d) Fructose has four chiral centers

5.


I

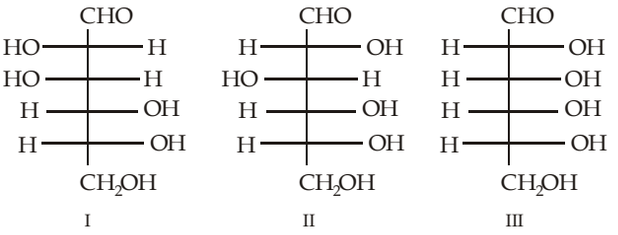

II


III


IV

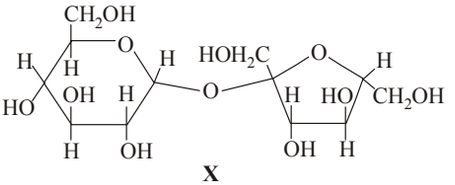
(a) I and III are enantiomers
(b) II and IV are enantiomers
(c) I and III are erythro isomers
(d) II and IV are threo isomers

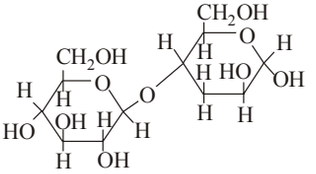
6.


I II III

(a) I and II are epimers (b) II and III are epimers
(c) all the three are epimers (d) No one is epimer to other

7. The correct statement(s) about the following sugars **X** and **Y** is(are)

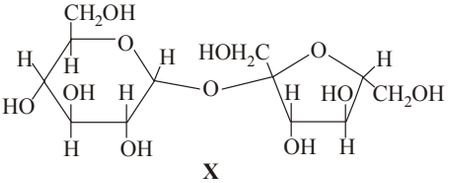

X

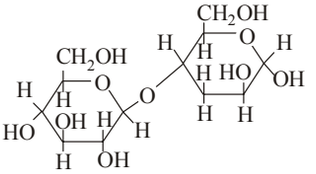


(a) **X** is a reducing sugar and **Y** is a non-reducing sugar
(b) **X** is a non-reducing sugar and **Y** is a reducing sugar
(c) The glucosidic linkages in **X** and **Y** are *a* and *b*, respectively
(d) The glucosidic linkages in **X** and **Y** are *b* and *a*, respectively

8. Which of the following statement is (are) correct?
(*a*) Glucose requires three moles of phenylhydrazine to give osazone
(*b*) Glyceraldehyde on oxidative cleavage with HIO_4 will give three different products
(*c*) Through Killiani - Fischer synthesis if we add two more C-atoms in a chain of (D)-glyceraldehyde, total number of possible compounds will be four
(*d*) Hydrolysis of lactose gives one unit of β-D-glucose and one unit of α-D-galactose

9. The correct statement(s) about the following sugars **X** and **Y** is(are)

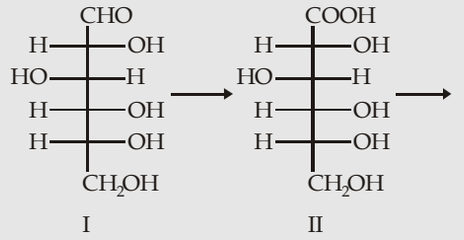

X

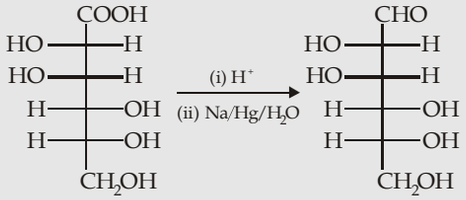


(a) **X** is a reducing sugar and **Y** is a non-reducing sugar
(b) **X** is a non-reducing sugar and **Y** is a reducing sugar
(c) The glucosidic linkages in **X** and **Y** are α and β, respectively
(d) The glucosidic linkages in **X** and **Y** are β and α, respectively

INSTRUCTION for Q. 10 to Q. 29 : Read the passages given below and answer the questions that follow.

PASSAGE 1





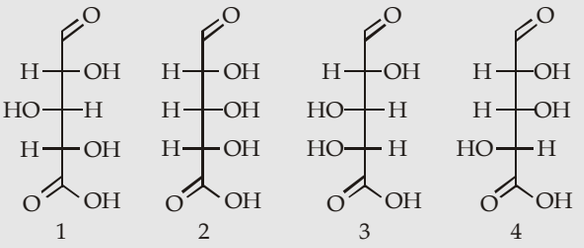
10. Compound I can be converted to II by using
(a) HNO_3 (b) $KMnO_4$
(c) NaOH -Br_2 (d) Br_2

11. Conversion of II to III can be affected by
(a) H^+ (b) pyridine
(c) heat (d) irradiation to U V light

12. Which of the following are epimers?
(a) I and IV (b) II and III
(c) Both (d) None

PASSAGE 2

Carbohydrates are polyhydroxyaldehydes or polyhydroxyketones. However, in actuality, the carbonyl groups are often present as hemiacetals and acetals. Below are the structures of some carbohydrates



13. The stereochemical relationship of compounds (3) and (4) is that they are
I. diastereomers II. enantiomers III. epimers
(a) III only (b) I and II
(c) I and III (d) II and III

14. The (-) enantiomer of each compound is oxidized by bromine water to yield the corresponding dicarboxylic acid, which will still be optically active. This is possible in
(a) 2 and 3 (b) 3 and 4
(c) 1 and 2 (d) 1 and 4

15. To convert these compounds to riboses (five-carbon sugars), one must
(a) cyclize the chain by forming a hemiacetal with the C-4 hydroxyl and the C-1 aldehyde
(b) oxidize the C-1 aldehyde to a carboxylic acid
(c) reduce the C-5 carboxylic acid to an alcohol
(d) reduce the C-5 carboxylic acid to an aldehyde

PASSAGE 3

Carbohydrates are optically active polyhydroxy aldehydes or ketones or substances which on hydrolysis give such compounds (although there are few exceptions to this definition). Certain carbohydrates can be hydrolysed to simpler carbohydrates, while the others are not hydrolysed to simpler products; the former are called oligo- or poly-saccharides, while the latter are known as monosaccharides. Monosaccharides are further classified as aldoses and ketoses which in turn are classified on the basis of number of carbon atoms like aldopentoses, ketohexoses, etc.

Although major function of carbohydrates is to provide energy to living organisms, certain carbohydrates like cellulose support the plant tissues, while ribose and deoxyribose (aldopentoses), constituents of nucleic acids (RNA and DNA), are responsible for protein synthesis and human heredity.

16. The first member of aldose sugars is
(a) aldodiose (b) aldotriose
(c) aldotetrose (d) glucose

17. The first member of ketose sugars is
(a) ketodiose (b) ketotriose
(c) ketotetrose (d) fructose

18. How many enantiomeric pairs are possible for a carbohydrate of the formula, $CHO(CHOH)_5CH_2OH$?
(a) 8 (b) 16
(c) 32 (d) 64

19. A carbohydrate of five carbon atoms has two asymmetric carbon atoms and found to be constituent of nucleic acids. It is
(a) $C_5H_{10}O_5$ (b) $C_5H_{10}O_4$
(c) both (d) none

20. How many chiral carbon atoms are present in the carbohydrate molecule which is found to be constituent of nucleic acids?
(a) 1 (b) 2
(c) 3 (d) 4

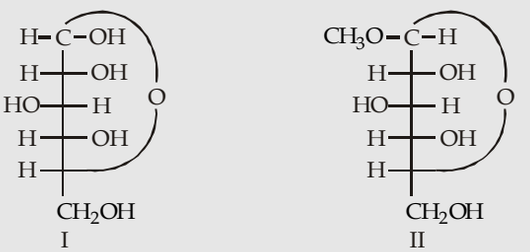
PASSAGE 4

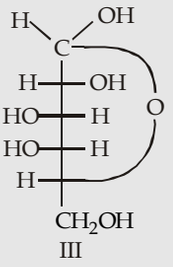
Read the following defintions :

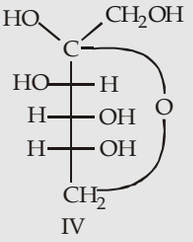
(i) Carbohydrates which differ in configuration at glycosidic carbon (aldehydic or ketonic carbon atom involved in ring formation) are called anomers; when H is on left and OH is on right, the anomer is α-, while when H is on right and OH is on left, the anomer is β-

(ii) Carbohydrates which differ in configuration at any asymmetric carbon atom other than glycosidic carbon are called epimers.

(iii) Optical isomers which are not enantiomers are called diastereomers.




III


IV

21. In which of the above structures glycosidic carbon is present at C-2 position?
(a) II (b) III
(c) IV (d) None

22. Which of the following is β-anomer?
(a) II (b) IV
(c) II and IV (d) None

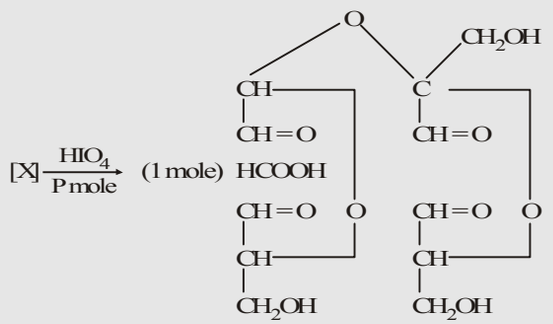
23. Which of the following constitute anomeric pair?
(a) I and III (b) I and IV
(c) III and IV (d) None

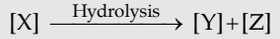
24 Which of the following constitute epimeric pair?
(a) I and III (b) I and IV
(c) III and IV (d) None

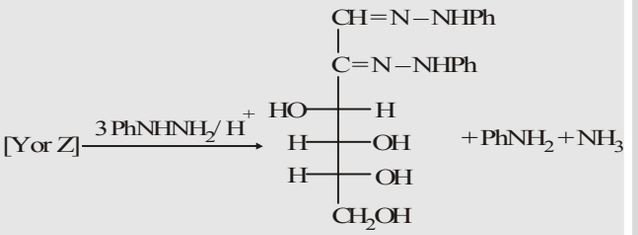
25. Which of the following constitute diastereomeric pair?
(a) I and III (b) I and IV
(c) III and IV (d) All the three

26. Which of the following has different ring, with respect to size, than others?
(a) II (b) III
(c) IV (d) None

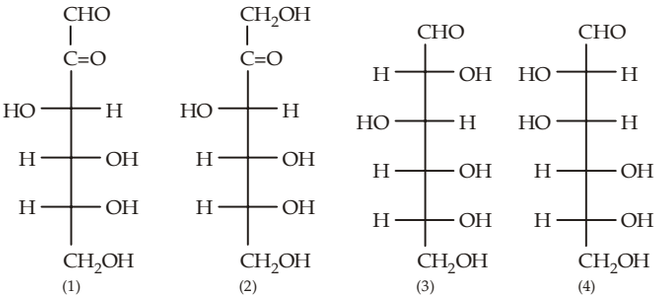
PASSAGE 5







27. Compounds Y and Z can be :


(1) (2) (3) (4)

(*a*) 1 only (*b*) 2, 3
(*c*) 1, 4 (*d*) 2, 3, 4

28. The value of P is :
(*a*) 2 (*b*) 3
(*c*) 4 (*d*) 5

29. The true characteristics about X, Y and Z are :
(*a*) Oligosaccharide - X, Reducing - X, Monosaccharide - Y, Z, Mutarotation - Y, Z
(*b*) Oligosaccharide - X, Reducing - Y, Z, Monosaccharide - Y, Z, Mutarotation - Y, Z
(*c*) Oligosaccharide - Y, Z, Reducing - Y, Z, Monosaccharide - X, Mutarotation - Y, Z
(*d*) Oligosaccharide - Y, Z, Reducing - X, Monosaccharide - X, Mutarotation - X

Instructions for Q. 30 to Q. 37 : Following questions are Multiple Matching type Questions :

30.

	Column - I Reactant		*Column - II* Product
(A)	Glucose + OH^-	(a)	Fructose
(B)	Fructose + $3C_6H_5NHNH_2$	(b)	Glucosazone
(C)	Mannose + OH^-	(c)	Mannose
(D)	Glucose + $3C_6H_5NHNH_2$	(d)	Fructosazone

31.

	Column - I		*Column - II*
(A)	Reducing sugar	(a)	Frutose
(B)	Non-reducing sugar	(b)	Sucrose
(C)	Epimer of glucose	(c)	Mannose
(D)	Isomer of glucose	(d)	Ribose

32.

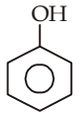
	Column - I		*Column - II*
(A)	α-Glucopyranose	(a)	Mutarotation
(B)	β-Methylglucoside	(b)	Artificial sweetner
(C)	L-Glucose	(c)	Non-reducing sugar
(D)	Sucrose	(d)	Natural sweetner

33. Match the chemical substances in **Column I** with type of polymers/type of bonds in **Column II**. Indicate your answer by darkening the appropriate bubbles of the 4 × 4 matrix given in the ORS.

	Column I		**Column II**
(A)	cellulose	(a)	natural polymer
(B)	nylon-6, 6	(b)	synthetic polymer
(C)	protein	(c)	amide linkage
(D)	sucrose	(d)	glycoside linkage

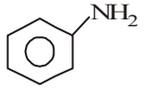
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34. ***Column I*** ***Column II***

(A)  (a) reacts with Br_2 water

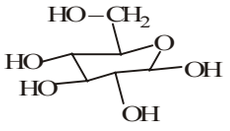
(B) $CH_3 - CH = CH_2$ (b) oxidised by $KMnO_4$

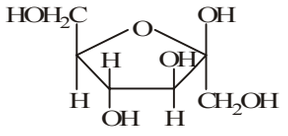
(C) D-Glucose (c) reacts with $CHCl_3$ / KOH to give cyclo compound

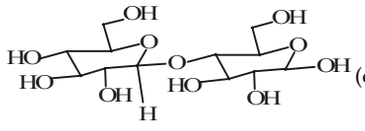
(D)  (d) H_2O soluble in high amount

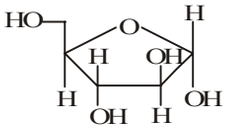
(e) reacts with acetic anhydride

35. ***Column I*** ***Column II***

(A)  (a) Aldohexoses

(B)  (b) Hemiacetals

(C)  (c) Mutarotates in H_2O

(D)  (d) Reducing sugars

(e) Glycosides

36. Match the reaction in Column I with corresponding products in column II.

	Column I	***Column II***
(A)	D-glucose $\xrightarrow{OH^-}$	(a) D-glucose
(B)	D-fructose $\xrightarrow{OH^-}$	(b) D-fructose
(C)	On reaction with HIO_4, gives 5 moles of HCOOH and 1 mole of HCHO	(c) D-Mannose (C-2-epimer of D-glucose)
(D)	On reaction with phenylhydrazine forms same osazone	(d) D-galactose (C-4 epimer of D-glucose)

37. Match the chemical substances in **Column I** with type of polymers/type of bonds in **Column II**.

	Column I	***Column II***
(A)	Cellulose	(p) Natural polymer
(B)	Nylon-6, 6	(q) Synthetic polymer
(C)	Protein	(r) Amide linkage
(D)	Sucrose	(s) Glycoside linkage

Instructions for Q. 38 to Q. 45 : Following questions are Assertion and Reasoning Type Questions :

Note : Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 5 choices (a), (b), (c), (d) and (e) out of which ONLY ONE is correct.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.

(c) Statement -1 is True, Statement-2 is False.

(d) Statement -1 is False, Statement-2 is True.

(e) Statement -1 is False, Statement-2 is False.

38. **Statement 1 :** Reducing sugars undergo mutarotation.

Statement 2 : During mutarotation, one pure anomer is converted into an equilibrium mixture of two anomers.

39. **Statement 1 :** Galactose is the C_4-epimer of glucose.

Statement 2 : Glucose and galactose differ in configuration at C_4.

40. **Statement 1 :** A solution of sucrose in water is dextrorotatory but on hydrolysis in presence of little hydrochloric acid, it becomes laevorotatory.

Statement 2 : Sucrose on hydrolysis gives unequal amounts of glucose and fructose as a result of which change in sign of rotation is observed.

41. **Statement 1 :** Hydrolysis of sucrose is known as inversion of cane sugar.

Statement 2 Sucrose is a disaccharide.

42. **Statement 1 :** Sucrose is a non-reducing sugar.

Statement 2 : It has glycosidic linkage.

43. **Statement 1 :** Maltose is a reducing sugar which gives two moles of D-glucose on hydrolysis.

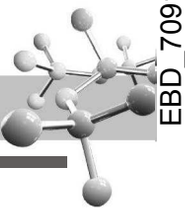
Statement 2 : Maltose has a 1, 4-β-glycosidic linkage

44. **Statement 1** : Glucose gives a reddish-brown precipitate with Fehling's solution.

Statement 2 : Reaction of glucose with Fehling's solution give CuO and gluconic acid.

45. **Statement 1 :** Glucose gives a reddish-brown precipitate with Fehling's solution.

Statement 2 : Reaction of glucose with Fehling's solution give CuO and gluconic acid.

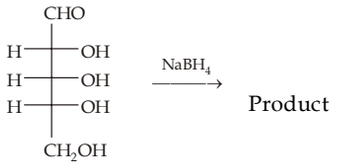


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EXERCISE 22.3 (Subjective Problems)

1. Write the Fischer projection formula for L-(+)-arabinose, obtained by the hydrolysis of a polysaccharide, found in a natural gum ; configuration of D-(–)-arabinose is given on the right side.

2. (*a*) Establish the optical nature of the reactant and product.



(*b*) Write down the structure of the compound A in the following reaction.



3. Differentiate between hemiacetals and acetals with reference to carbohydrates.

4. Which of the following can show mutarotation ?

(*a*) L-(–)-Glucose (*b*) Methyl α-glucopyranoside
(*c*) Glucose penta-acetate (*d*) Methyl β-glucofuranoside
(*e*) α-Glucopyranose (*f*) β-Glucofuranose.

5. The rate of oxidation of reducing sugars by cupric ions is found to be proportional to sugar and $[OH^-]$, but independent of $[Cu^{2+}]$. What does this kinetic suggest about the mechanism of oxidation ?

6. An optically inactive carbohydrate *bio-inonose*, $C_6H_{10}O_6$ shows following reactions.

(*i*) It reduces Benedict's solution but does not react with bromine water.

(*ii*) It reacts with acetic anhydride to form penta-acetate.

(*iii*) On reduction with sodium borohydride, it gives two isomeric compounds of the formula $C_6H_{12}O_6$ which gives six moles of HCOOH on oxidation with periodic acid.

Identify the nature of functional groups present in bio-inonose and explain its conversion to two isomeric compounds. Also explain the given oxidation of isomeric compounds.

7. When galactose is dissolved in water, its specific rotation gradually changes to +80.2°, if the specific rotation of α-anomer is +150.7° and that of β-anomer is +52.8°, determine the percentage of the two anomers at equilibrium.

SOLUTIONS

EXERCISE 22.1

1	(a)	**6**	(d)	**11**	(d)	**16**	(d)	**21**	(b)	**26**	(c)	**31**	(c)	**36**	(d)	**41**	(b)
2	(d)	**7**	(b)	**12**	(d)	**17**	(b)	**22**	(a)	**27**	(d)	**32**	(a)	**37**	(c)		
3	(c)	**8**	(c)	**13**	(c)	**18**	(b)	**23**	(c)	**28**	(a)	**33**	(a)	**38**	(d)		
4	(c)	**9**	(b)	**14**	(d)	**19**	(b)	**24**	(c)	**29**	(b)	**34**	(d)	**39**	(c)		
5	(d)	**10**	(d)	**15**	(c)	**20**	(d)	**25**	(d)	**30**	(c)	**35**	(b)	**40**	(a)		

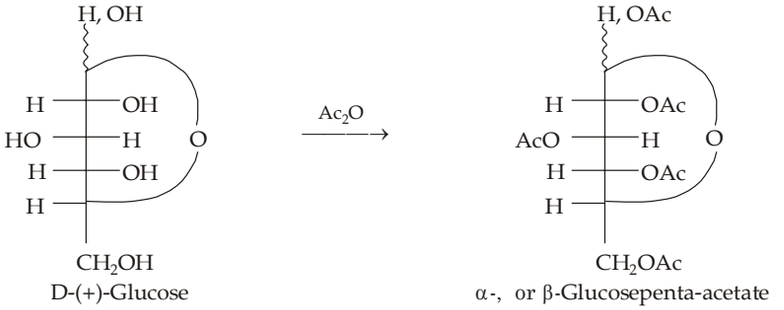
1. The value of n in $C_n(H_2O)_m$ may be either same as m as in monosaccharides or more than m as in oligosaccharides, but never less than m.

2. The general formula for oligosaccharides is $(C_5H_{10}O_5)_n + (n-1)\ H_2O$.

3. Photosynthesis takes place in presence of sunlight, the light energy is stored in the form of chemical energy in carbohydrates. It is this energy that is released when glucose is oxidised.

4. Bromine, a mild oxidising agent, oxidises only glucose (aldoses, in general) to gluconic acid. Tollens' reagent and Fehling solution, being alkaline in nature, cause isomerization of fructose to glucose hence both of them react with these reagents.

5. During acetylation of (+)-glucose, it is the C_1 —OH of the hemiacetal that is acetylated and not the C_5—OH that forms the ring (cyclic structure). Since equilibrium with the open-chain aldehyde is prevented, the penta-acetate does not respond the aldehydic reactions.



6. Since the two ends of the glucose molecule are dissimilar, *meso* form is not possible.

7. Epimers are those diastereomers which differ in the configuration of only one chiral carbon which may be C_1, C_2, C_3, etc. ; while anomers are diastereomers that differ in the configuration of a specific chiral carbon which is C_1 in aldoses and C_2 in ketoses.

8. In the D family the more dextrorotatory anomer is named α-D-. In the L family the more laevorotatory anomer is named α-L-.

9. Diastereomers are isomers which are not enantiomers. Since structures I and II are not non-superimposable mirror-image of each other, these are not enantiomers.

10. When structures I and II are C–2 epimers, it implies that these are epimers and diastereomers too.

11. Since diastereomers are all those isomers which are not enantiomers, there may be more than one diastereomer of a compound. An epimer differs in the configuration of only one chiral carbon, so an epimer can be C—2, C—3, C–4, etc. An anomer may be α- or β- ; so no term is absolutely specific.

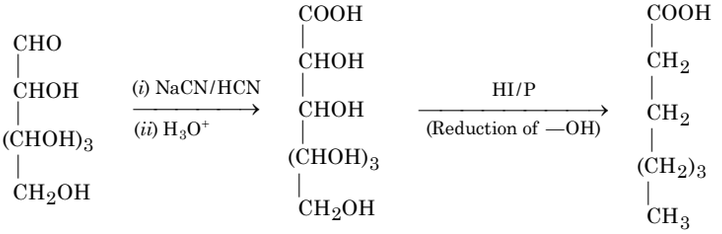
12. Same as for Q. 11.

13. When an aqueous solution of D-glucose, D-mannose or D-fructose is treated with a base, it undergoes enolization and a series of keto-enol tautomerization to form a mixture of the three monosaccharides (*Lobry de Bruyn van Ekenstein transformation*). For reactions, consult text.

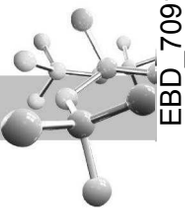
14. An anomeric carbon is that which is developed by intramolecular reaction between carbonyl group and —OH group of the same molecule. Thus it should be C_1 in glucose and C_2 in fructose.

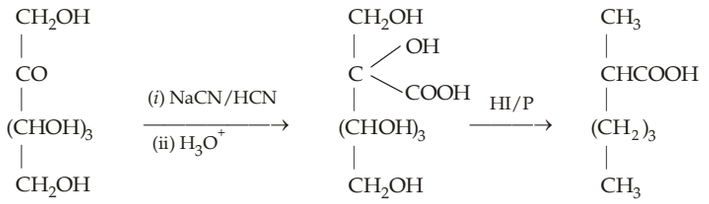
15. Ketoses on reduction produce a new chiral carbon leading to the formation of two isomeric alcohols which are diastereomeric as well as C–2 epimers.

16.



Z (*n*-Heptanoic acid)





Z′ (2-Methylhexanoic acid)

17. A ketonic group having —OH group on both sides is removed as CO_2 during oxidation with periodate.

18. Glucose is a hemiacetal, so in presence of a base (alkaline medium is provided by Fehling's solution) it can develop —CHO group in the form of open chain structure which responds Fehling's solution. Sucrose is a glycoside, *i.e.* its hemiacetal OH groups (one due to glucose and another due to fructose) are not free, so it can't attain —CHO group. Hence it will not respond Fehling's solution.

19. Same explanation as that of Q. 18. Also see Q. 5.

20. Reaction of D-(+)-glucose with methanolic —HCl leads to formation of methyl glucoside (C_1—OH group is methylated) which, being acetal, is not hydrolysable by base, so it will not respond Tollens' reagent.

21. Carbohydrates having hemiacetal type of structures, which is observed in all monosaccharides, show mutarotation. Further the reduction of Tollens' reagent and mutarotation both depend on the presence of the free carbonyl form. Glycosides do not mutarotate because here the OH group of hemiacetal is blocked.

22. The OH's of sugars are more acidic than that of a typical alcohol because of their mutual electron-withdrawing inductive effect.

23. Honey has mainly invert sugar which is more sweet than ordinary sugar (sucrose), and glucose.

24. Inulin is a polysaccharide of fructose, while all others are polysaccharides of glucose ; although all the four has same molecular formula, $(C_6H_{10}O_5)_n$.

1. Fruit mainly contains fructose, hence the latter is commonly known as fruit sugar.

2. α-Hydroxyaldehydes and α-hydroxyketones form osazone. In compound II, aldehydic and —OH groups are separated by CH_2, *i.e.*, it is β-hydroxyaldehyde hence it will not form osazone.

27. Compound given in option (a), (b) and (d) do not have any hemi-acetal group so can't be oxidised by Tollen's regent and will not give Tollen's test.

31. (*c*) Due to cyclic hemiacetal or cyclic hemiketal structures, all the pentoses and hexoses exist in two stereoisomeric forms i.e., α form in which the OH at C_1 in aldoses and C_2 in ketoses lies towards the right and β form in which it lies towards left. Thus glucose, fructose, ribose etc., all exist in α and β form. Glucose exists in two forms α-D-glucose and β-D-glucose.

$$\underset{\text{Glucose}}{\alpha-D-(+)} \rightleftharpoons \text{equilibrium mixture} \rightleftharpoons \underset{(+)\text{ Glucose}}{\beta-(D)-}$$

As a result of cyclization, anomeric carbon (C-1) becomes asymmetric and the newly formed –OH group may be either on left or on right in Fischer projection thus resulting in the formation to two isomers (anomers). The isomers having –OH group on the left of the C-1 designated β-D-glucose and the other having –OH group on the right as α-D-glucose.

32. (III) is identical pair; in (IV) products A and B are distereomers.

34. Glucose being an aldose responds to Tollen's test while fructose, although a ketose, undergoes rearrangement in presence of basic medium (provided by Tollen's reagent) to form glucose, which then responds to Tollen's test.

35. The two isomeric forms (α – and β –) of D-glucopyronose differ in configuration only at C–1; hence these are called anomers.

36. Nylon and cellulose, both have intermolecular hydrogen bonding, polyvinyl chloride has dipole-dipole interaction, while natural rubber has van der Waal forces which are weakest.

37. Glucose is considered as a typical carbohydrate which contains –CHO and –OH group.

38. When structures I and II are C–2 epimers, it implies that these are epimers and diastereomers too.

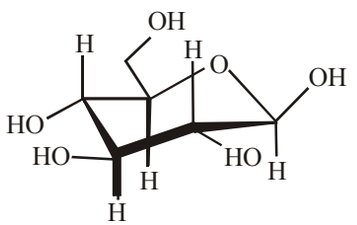
39. When an aqueous solution of D-glucose, D-mannose or D-fructose is treated with a base, it undergoes enolization and a series of keto-enol tautomerization to form a mixture of the three monosaccharides (*Lobry de Bruyn van Ekenstein transformation*). For reactions, consult text.

40. (a) $_{13}A\ell^{27} + {}_2\alpha^4 \longrightarrow {}_{14}Si^{30} + \underset{(X)}{{}_1p^1}$

$$_{13}A\ell^{27} + {}_2\alpha^4 \longrightarrow {}_{15}p^{30} + \underset{(Y)}{{}_0n^1}$$

$$_{15}p^{30} \longrightarrow {}_{14}Si^{30} + \underset{(Z)}{{}_1\beta^0}$$

41. (b)

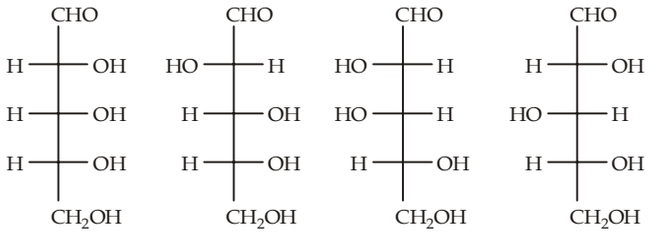


It is a β-pyranose hence it is an aldohexose.

EXERCISE 22.2

>1 CORRECT OPTION	**1**	(b,c,d)	**2**	(a,c,d)	**3**	(a, b, c)	**4**	(b, c)	**5**	(c, d)
	6	(a, b)	**7**	(b,c)	**8**	(a, c)	**9**	(b, c)		
PASSAGE 1	**10**	(d)	**11**	(b)	**12**	(c)				
PASSAGE 2	**13**	(a)	**14**	(c)	**15**	(c)				
PASSAGE 3	**16**	(b)	**17**	(b)	**18**	(b)	**19**	(b)	**20**	(b,c)
PASSAGE 4	**21**	(c)	**22**	(c)	**23**	(d)	**24**	(a)	**25**	(d)
	26	(d)								
PASSAGE 5	**27**	(d)	**28**	(b)	**29**	(b)				
MATCH THE FOLLOWING	**30**	(A) –a, c ; (B) – b, d ; (C) – a, c ; (D) –b, d								
	31	(A) – a, c, d; (B) – b; (C) – c; (D) – a, c								
	32	(A)-a, d ; (B)-c ; (C)-a, b ; (D)-c, d								
	33	A-(a) & (d) ; (B)-(b) &(c) ; (C)-(a) & (c); D-(d)								
	34	A-(a, b, e); (B)-(a, b, c); (C)-(a, b, d, e); D-(a, b, e)								
	35	A-(a, b, c) ; (B)-(b, c, d) ; (C)-(b, c, d, e); D-(b, c, d)								
	36	A-(a, b, c) ; (B)-(a, b, c) ; (C)-(a, c, d); D-(a, b, c)								
	37	A-(a, d) ; (B)-(b, c) ; (C)-(a, c); D-(d)								
A/R	**38**	(b)	**39**	(b)	**40**	(d)	**41**	(a)	**42**	(a)
	43	(c)	**44**	**(c)**	**45**	**(c)**				

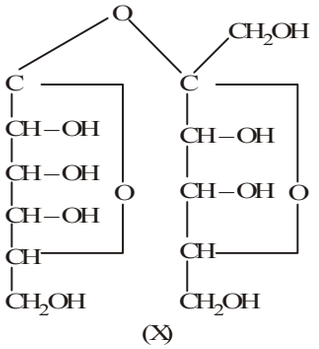
8. Glucose requires 3 moles of phenylhydrazine to give osazone. Glyceraldehyde on cleavage with HIO_4 gives 2 moles of HCOOH + 1 mole of HCHO
Through Killiani - Fischer synthesis, we will be able to get following four products.



Hydrolysis of lactose gives one unit of β-D-glucose and α-D-glucose.

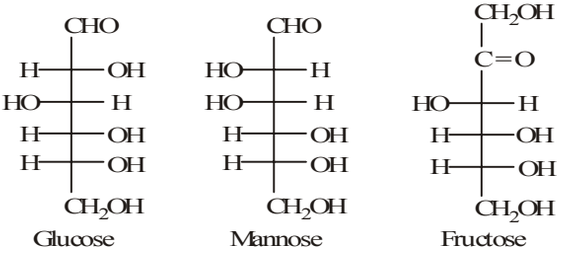
9. We know that carbohydrates having acetal linkage are non-reducing while that with hemiacetal linkage are reducing. In the given structure,
X has acetal linkage, hence non-reducing.
Y has hemiacetal linkage, hence reducing.
Further **X** is α-anomer, while **Y** is β-anomer of D-(+)- glucose.

Sol. 27-29.

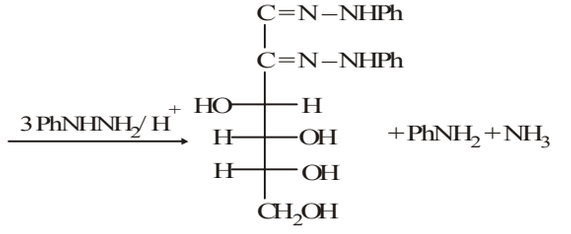


(X)

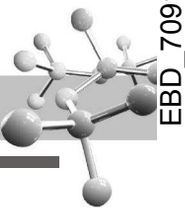
[X] $\xrightarrow{\text{Hydrolysis}}$ Glucose or Mannose (Y) + Fructose (Z)



Glucose Mannose Fructose

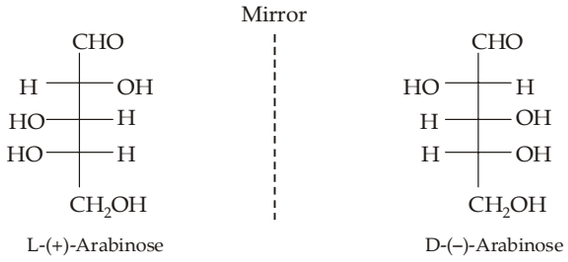


34. (A)-a,b,e; (B)-a,b,c; (C)-a,b,d,e; (D)-a,b,e;
35. (A)-a,b,c, d; (B)-b,c,d; (C)-b,c,d,e; (D)-b,c,d;
36. (A)-a,b,c; (B)-a,b,c; (C)-a,c,d; (D)-a,b,c;
37. (A) : (p, s) Cellulose is a natural polymer and has a $C_1 - C_4$ β-glycosidic linkage.
(B) : (q, r) Nylon-6, 6 is a synthetic polymer of hexamethylenediamine and adipic acid and has amide linkages.
(C) : (p, r) Proteins are natural polymers of α amino acids joined by amide linkages (peptide bonds).
(D) : (s) Sucrose is a disaccharide of α-D glucose and β-D-fructose and has an α, β-glycosidic linkage.
45. Statement-1 is correct, but statement-2 is incorrect because glucose on reaction with Fehling solution gives Cu_2O and not CuO.



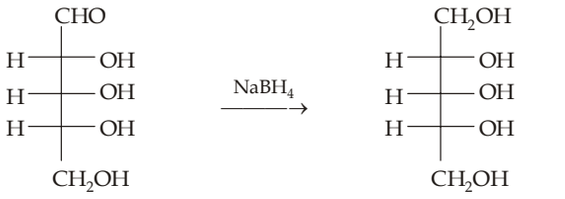
EXERCISE 22.3

1.

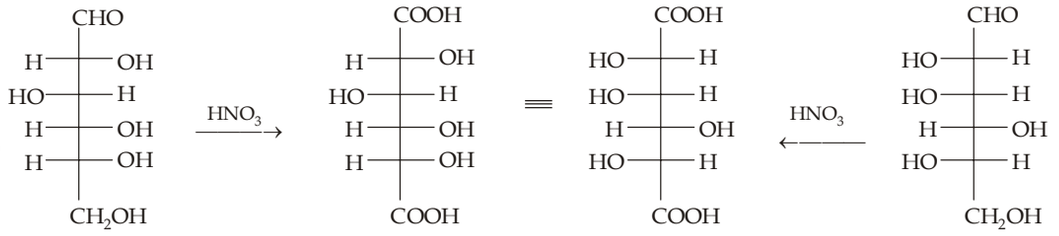


The two are enantiomers

2. (*a*)



(*b*)



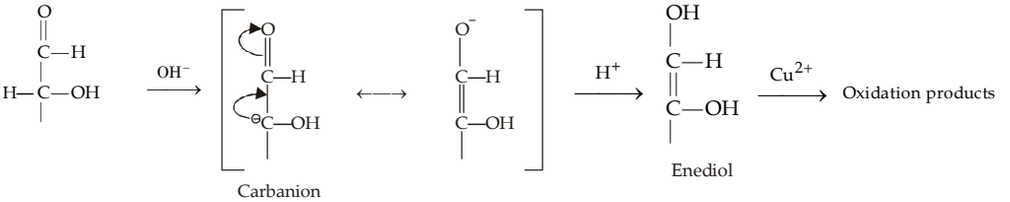
3. Hemiacetals are the condensation products obtained by the interaction of a carbonyl group and an alcoholic group. In case of carbohydrates both these groups are provided by the same molecule, so here a cyclic hemiacetal is formed. Hemiacetals are easily hydrolysed by aqueous solution and by alkalis. These are reducing in nature and undergo mutarotation. Glucose, fructose, and monosaccharides, in general, are examples of hemiacetals.

Acetals are the products obtained by the reaction of hemiacetal with another molecule of alcohol. Since here the —OH group of hemiacetal has reacted with the alcoholic group of another molecule, it is not free. Hence it can't be converted into open-chain structure, hence it is non-reducing and does not undergo mutarotation. It is stable to alkali but can be hydrolysed by acids. Alkyl glucoside and sucrose are examples of acetals.

4. When the anomeric hydroxyl group of a sugar is free *i.e.*, when the sugar is hemiacetal, one anomer (α- or β-) is converted to another (β- or α-) and thus such sugars show mutarotation.

In the compounds (*a*), (*e*) and (*f*), the anomeric —OH group is free, *i.e.*, these are hemiacetals, hence will show mutarotation. In compounds (*b*), (*c*) and (*d*), the anomeric —OH group is not free, it is present in the form of —OCH_3, —OAc and —OCH_3 respectively, so α- or β- form can't be converted to another, hence no possibility of mutarotation.

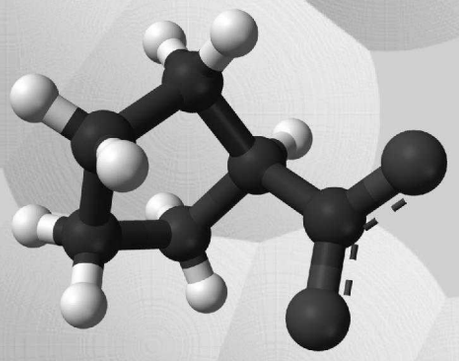
5. The kinetics of the reaction suggest that the rate-determining step involves the reaction with OH^- prior to the reaction with Cu^{2+}. Reaction of reducing sugars with OH^- probably involves abstraction of H^+ leading to the formation of enediol.



6. (*i*) Positive reaction with Benedict solution and negative reaction with Br_2 water indicate that bio-inonose has either an —CHO group or an α-hydroxy ketonic group which is converted to —CHO group in presence of OH^- ions provided by Benedict solution.

(*ii*) Molecular formula of the saturated open-chain compound corresponding to the carbonyl compound, $C_6H_{10}O_6$ will be $C_6H_{14}O_6$ which indicates that the compound has 2° of unsaturation, 1° of unsaturation is in the form of carbonyl group, so the 2nd unsaturation must be in the form of one ring (double bond is discarded due to negative reaction with Br_2 water).

Thus the compound bio-inonose should have following structure.



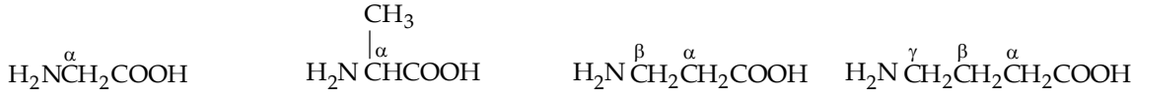
23 Amino Acids & Polymers

CHAPTER HIGHLIGHTS

23.1 Introduction
23.2 Configuration of Natural Amino Acids
23.3 Preparation of Amino Acids
23.4 Acid-Base Properties
23.5 Reactions of Amino Acids
23.6 Peptides
23.7 Polymer
23.8 Illustrative Examples
EXERCISE
SOLUTIONS

23.1 Introduction

Amino acids are the compounds having amino as well as carboxyl group in the same molecule. These are classified as α, β, γ, and so on, depending the relative position of the two groups.



α-Amino acids β-Amino acid γ-Amino acid

Of the different types of amino acids, α-amino acids are most important as they constitute the building blocks of **proteins** (naturally occurring polymers of α-amino acids). A single protein molecule contains indefinite number of amino acid units which can be of 22 different types. It is the number of different combinations of these amino acids which gives rise to infinite number of protein molecules. However, human body is capable of synthesizing *only some of these 22 amino acids,* and hence the remaining amino acids, which our body can't biosynthesize must be supplied from outside in the form of diet, such amino acids are called **essentail amino acids.** On the whole, there are 10 essential amino acids, although this number is eight for adult humans. Thus the other amino acids which are synthesized in the body are known as **non-essential amino acids.** All of the 22 amino acids contain a primary amino group, except two (proline and hydroxyproline) which are secondary amines, and also known as *imino acids.*



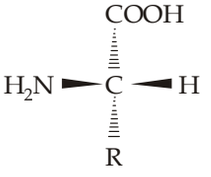
Proline Hydroxyproline

EBD_7091

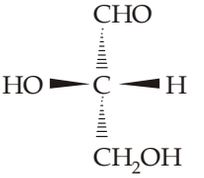
In addition to the carboxyl group and the amino group *alpha* to it, some amino acids contain a second carboxyl group (*e.g.* aspartic acid and glutamic acid) or a potential carboxyl group in the form of a carboxyamide (*e.g.* asparagine) ; these are called **acidic amino acids.** Similarly, there are some **basic amino acids** too, which contain an additional basic group in the form of an amino group (*e.g.* lysine), a guanido group (*e.g.* arginine), or an imidazole ring (*e.g.* histidine). Some of the amino acids contain benzene or heterocyclic ring systems, phenolic or alcoholic —OH groups, halogens or sulphur atoms.

23.2 Configuration of Natural Amino Acids

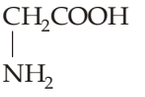
With the exception the simplest amino acid, glycine, all amino acids contain a chiral center. Further, *almost* all naturally occurring amino acids have L-configuration at the α-carbon, *i.e.* they have the same relative configuration as L-glyceraldehyde. Since the group R nearly always happens to have lower Cahn-Infold-Prolog priority than COOH, most of these have the S configuration.



An L-α-amino acid



L-Glyceraldehyde



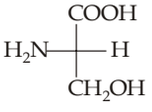
Glycine

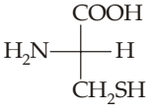
TEST YOUR UNDERSTANDING - 23.1

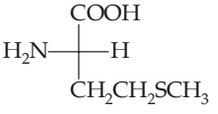
1. Draw the Fischer projection formulas for the following amino acids. Designate these as R or S.

(*a*) $CH_3CH(NH_2)COOH$ (*b*) $CH_2OHCH(NH_2)COOH$ (*c*) $H_2NCH(CH_2C_6H_5)COOH$

2. What is the absolute configuration (R or S) at the α carbon atom in each of the following L amino acids ?

(*a*) 

(*b*) 

(*c*) 

3. How many chiral carbon atoms are present in threonine, $H_3\overset{+}{N}CH(CH(OH)CH_3)COO^-$? Write the Fischer projection formulas for its stereoisomers.

23.3 Preparation of Amino Acids

1. **Direct ammonolysis of α-halo acids.** This is simply a nucleophilic substitution.

$$CH_3CH(X)COOH \xrightarrow{NH_3\ (excess)} CH_3CH(\overset{+}{N}H_3)COO^-$$

(X = Cl or Br)

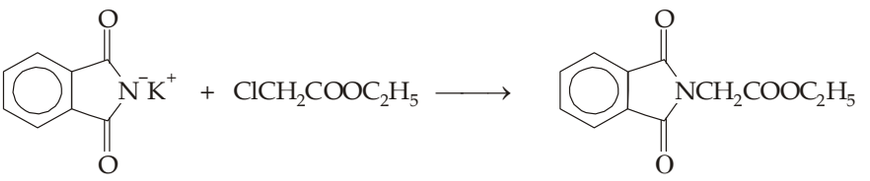
The required α-halo acids or esters can be prepared by (*a*) **Hell-Volhard-Zelinsky halogenation** of the unsubstituted acids or by (*b*) a modification of the **malonic ester synthesis.**

(*a*) $CH_3CH_2COOH \xrightarrow{Cl_2 \text{ or } Br_2/P} CH_3CH(Br)COOH$

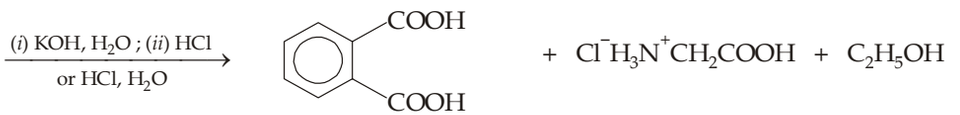
(*b*) $^{+}Na^{-}CH(COOC_2H_5)_2 \xrightarrow{RCl} RCH(COOC_2H_5)_2 \xrightarrow[(ii)\ HCl]{(i)\ KOH} RCH(COOH)_2$

$$\xrightarrow[\text{reflux}]{Br_2,\ \text{ether}} RC(Br)(COOH)_2 \xrightarrow{\text{heat}} R\,CH(Br)COOH$$

2. From potassium phthalimide. This method is a modification of the *Gabriel synthesis of amines.* The yields are usually high and the products are easily purified. Here α-halo esters are used instead of α-acids, used in the above method.

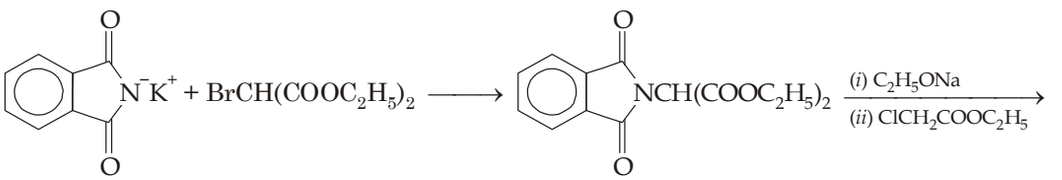


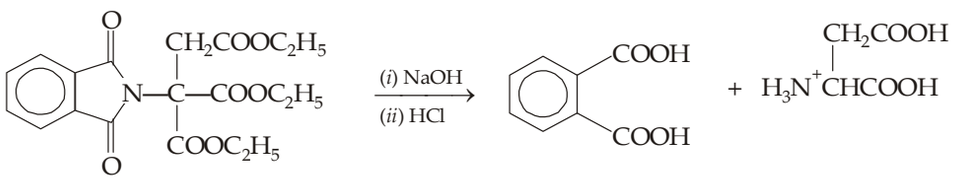
Potassium phthalimide Ethyl chloroacetate



Phthalic acid Glycine hydrochloride

A further modification of this method uses potassium phthalimide and diethyl bromomalonate, hence the method is sometimes named as **phthalimidomalonic ester method.**





3. The Strecker synthesis. In the strecker synthesis, an aldehyde is converted to an α-amino acid with one more carbon atom.

$$CH_3CHO \xrightarrow[\text{or } NH_4Cl/NaCN]{NH_3/HCN} CH_3CH(NH_2)CN \xrightarrow{H_3O^{+},\ \text{heat}} CH_3CH(NH_3^{+})COO^{-}$$

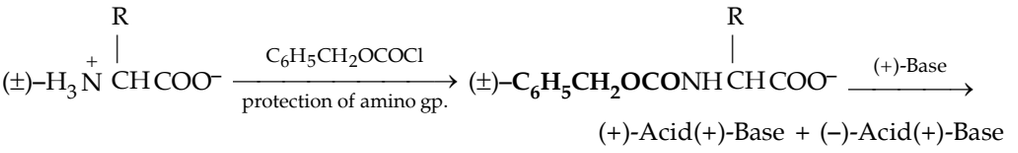
An α-aminonitrile α-Amino acid

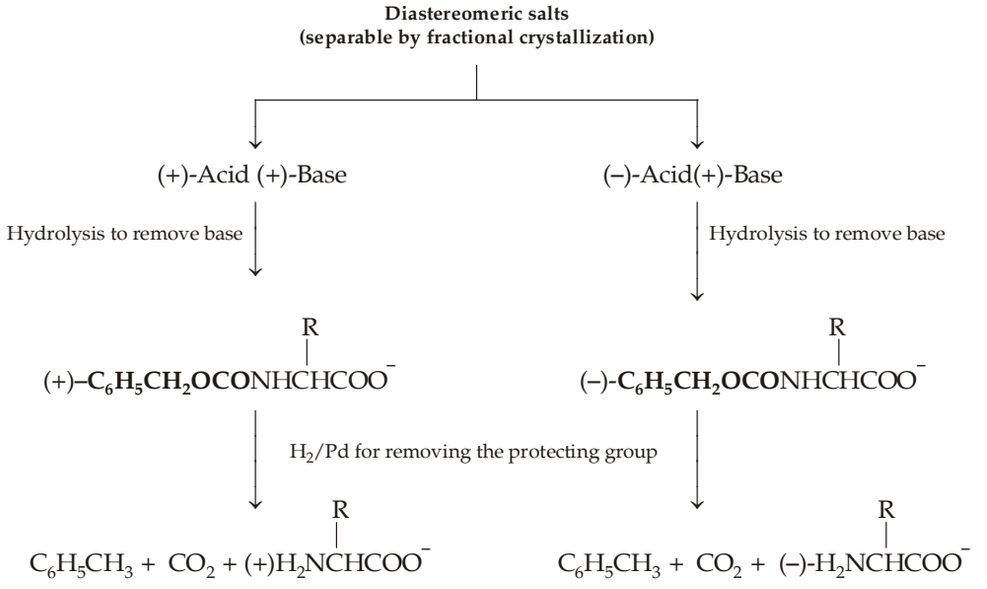
4. Reductive amination of α-keto acids (*Knoop synthesis*).

$$CH_3C(=O)COOH + NH_3 \longrightarrow CH_3C(=NH)COOH \xrightarrow[\text{or } NaBH_4]{H_2/Pd} CH_3CH(^{+}NH_3)COO^{-}$$

EBD_7091

All of the above methods give optically inactive amino acids, and hence these must be resolved if the active materials are desired for comparison with the naturally occurring L acids or for synthesis of peptides. An optically active amino acid may directly be obtained, *i.e.*. without the use of resolution, such synthesis is better known as **enantioselective synthesis.** Enantioselective synthesis, *i.e.* when one of the enatiomer is in excess amount than the other, may be achieved by using an optically active reagent or catalyst at some point in the process. Remember that amino acids synthesized in living systems are 100 percent enantioselective because of the involvement of enzymes as catalyst.





Alternatively, the carboxylic group is protected by esterification and an optically active acid is used as resolving reagent which reacts with the free amino group to form two diasteromeric ammonium salts. Fractional crystallization, hydrolysis of the salt to remove acid, and hydrolysis of the ester to remove protecting group completes resolution.

TEST YOUR UNDERSTANDING - 23.2

1. Give steps involved in the preparation of valine, $Me_2CHCH(NH_2)COOH$ from isobutanol by a Strecker reaction.

2. Prepare valine by (*a*) a HVZ reaction, (*b*) a reductive amination, and (*c*) a Gabriel synthesis.

3. Try to develop a scheme for synthesizing glycine from methyl chloride.

4. Account for the stereochemical specificity of enzymes with chiral substrates.

23.4 Acid-Base Properties

The usual structure of amino acids ($H_2NCH(R)COOH$) shown to contain a free amino and a free cerboxyl group is not in consistent with certain physical and chemical properties.

(*i*) Unlike amines and the lower aliphatic carboxylic acids, all amino acids even the simplest one (glyine) are crystalline solids and **melt with decomposition** at fairly high temperature.

(*ii*) They are **fairly soluble in water,** but insoluble in non-polar solvents like petroleum ether, benzene, or ether.

(*iii*) Amino acids have much **larger dipole moments** than simple amines and simple acids.

$H_3N^+ - CH_2 - COO^-$ Glycine, μ=14D $CH_3CH_2CH_2NH_2$ Propylamine, μ=1.4D CH_3CH_2COOH Propanoic acid, μ=1.7D

(*iv*) Amino acids are **less acidic than most carboxylic acids and less basic than most amines.** In fact, the acidic part of the amino acid molecule is the $-NH_3^+$ group, not a –COOH group, while the basic part of the amino acid is the $-COO^-$ group, and not a free $-NH_2$ group.

$R-COOH$ (pK_a=5) $R-NH_2$ (pK_b=4) $H_3\overset{+}{N}-\underset{R}{\underset{|}{C}}H-COO^-$ (pK_a=10; pK_b=12)

The above properties point out toward the salt like character (dipolar ion structure) to amino acids. Actually, in the dry state, amino acids exist as **dipolar ions** (also known as **zwitterions** or **inner salts**), a form in which the carboxyl group is present as a carboxylate ion, —COO^-, and the amino group as an aminium ion, —NH_3^+.

$H_2N\underset{R}{\underset{|}{C}}HCOOH \rightleftharpoons H_3\overset{+}{N}\underset{R}{\underset{|}{C}}HCOO^-$

Dipolar ions, I

The dipolar ionic (salt like) structure of amino acids explains all of its above properties.

In aqueous solution, the dipolar ionic structure is not stable and equilibrium exists between the dipolar ionic and the monoionic (cationic and anionic) forms of an amino acid.

$H_3\overset{+}{N}\underset{R}{\underset{|}{C}}HCOOH \xrightleftharpoons{H_2O\text{ (as an acid)}} H_3\overset{+}{N}\underset{R}{\underset{|}{C}}HCOO^- \xrightleftharpoons{H_2O\text{ (as a base)}} H_2N\underset{R}{\underset{|}{C}}HCOO^- + H_2O$

Cationic form (Dominates in strongly acidic solutions, *e.g.* at pH ≈ 0) Dipolar ion **Anionic form** (Dominates in strongly basic solutions, *e.g.* pH ≈ 14)

The predominant form of the amino acid (cationic, zwitterionic, or anionic) in the solution depends upon the pH of the solution and also on the nature of the side chain (R) of the amino acid. In strongly acidic solutions (pH ≈ 0), all amino acids are present mainly as cations,* while is stronlgy basic solutions (pH ≈ 14), they are present mainly as anions. At some intermediate pH (called the **isoelectric point, pI**), the concentration of the dipolar ion is at its maximum and the concentrations of the anions and cations are low but equal. Isoelectric point is a constant for an amino acid and depends upon the structure of the particular amino acid. Since at the isoelectric point, the cationic and anionic forms of an amino acid are equal, at this point the amino acid practically behaves as a neutral species as indicated by the fact that the amino acid neither migrates to anode nor to cathode when an electric current is passed through its aqeuous solution.

Determination of the isoelectric point. Let us consider the strongly acidic solution of alanine which primarily contains $H_3N^+CH(CH_3)COOH$. As the pH of the solution is raised by adding a base, a proton is removed from the —COOH group of the species to form zwitterion. This dissociation constant of the species is designated as pK_{a1}, and found to be 2.3 for the conjugate acid of alanine.

$H_3\overset{+}{N}\underset{CH_3}{\underset{|}{C}}HCOOH \underset{H^+}{\overset{-H^+}{\rightleftharpoons}} H_3\overset{+}{N}\underset{CH_3}{\underset{|}{C}}HCOO^- \xrightleftharpoons{-H^+} H_2N\underset{CH_3}{\underset{|}{C}}HCOO^-$

Cationic form ($pK_{a_1} \approx 2.3$) Dipolar ion ($pK_{a_2} \approx 9.7$) Anionic form

If the deprotonation of alanine would have involved the $-\overset{+}{N}H_3$ rather than —COOH, the pK_{a_1} value for the conjugate acid of alanine would have been higher than 5 (pK_a value for a typical RCOOH ≅ 5), (a *typical* ammonium ion has $pK_a \cong 9$).

* Existence of amino acids as cation ($H_3N^+CH(R)COOH$) in strongly acidic medium, and as an anion ($H_2NCH(R)COO^-$) in stronlgy basic medium explains why reactions of amino acids involving acidic group (*e.g.* esterification) and those involving —NH_2 group (*e.g.* acetylation) speed up in presence of strong acid and strong base respectively.

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When pH is further raised $-\overset{+}{N}H_3$ group of zwitterion is deprotonated (second deprotonation step) to form anionic species. This dissociation constant is designated as pK_{a_2} and found to be 9.7 for the zwitterion of alanine. The isoelectric point (pI) of an amino acid having one $-NH_2$ and one —COOH group is the average of pK_{a_1} and pK_{a_2}. Thus the pI for alanine is 6.0.

$$pI = \frac{2.3 + 9.7}{2} = 6.00$$

pK_{a1} corresponds to ionization of the carboxyl group.

pK_{a2} corresponds to ionization of the ammonium ion.

TEST YOUR UNDERSTANDING - 23.3

1. (*a*) Write the most stable structural formula for the amino acid, *p*-$OHC_6H_4CH_2\underset{\displaystyle NH_2}{\underset{|}{C}}HCOOH$, in its

(*i*) zwitterionic form (*ii*) cationic form (*iii*) anionic form (*iv*) dianionic form

(*b*) Supply the structure of the species I to IV

$$\overset{NH_2}{\underset{|}{}}{}^{-}OOCCHCH_2COO^{-} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} \text{I} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} [\text{II} \rightleftarrows \text{III}] \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} \text{IV}$$

2. Write structrual formulas for the principal species present in the solution of the amino acid lysine,

$$\overset{NH_2}{\underset{|}{}}H_2N(CH_2)_4\underset{|}{C}HCOOH$$ at pH 1, 9 and 13.

3. Draw the two possible dipolar structures for the amino acid, $H_2N(CH_2)_4CH(NH_2)COOH$. Which one is more likely to be correct ?

4. Explain the following

(*a*) *p*-Aminobenzoic acid or *o*-aminobenzoic acid does not exist as the zwitterion, while *p*-aminobenzene-sulphonic acid (sulphanilic acid) exists as zwitterion.

(*b*) Sulphanilic acid, a zwitterion dissolves in alkalies but not in acids.

5. To which electrode, an amino acid migrates at a

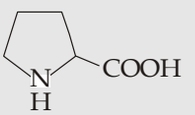
(*a*) pH > pI, (*b*) pH < pI, and (*c*) pH = pI.

6. What happens when an electric current is passed through an aqueous solution, buffered at pH = 6.0, containing three amino acids A, B, and C ? The isoelectric points for the three amino acids are 6.0, 3.0 and 10.0 respectively.

Example 1 :

Draw the structure of the predominant form of following amino acids at pH mentioned below them.

(a) $H_2N-\underset{|}{\overset{CH(CH_3)_2}{C}}H-COOH$ Valine at pH 11

(b)  Proline at pH 2

(c) $H_2N-\underset{|}{\overset{(CH_2)_3-NH-\overset{NH}{\overset{\|}{C}}-NH_2}{C}}H-COOH$ Arginine at pH 7

(d) a mixture of alanine, lysine, and aspartic acid at (i) pH 2, (ii) pH 6, and (iii) pH 11.

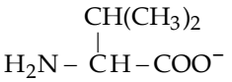
$H_2N-\underset{|}{\overset{CH_3}{C}}H-COOH$ Alanine

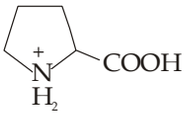
$H_2N-\underset{|}{\overset{(CH_2)_4NH_2}{C}}H-COOH$ Lysine

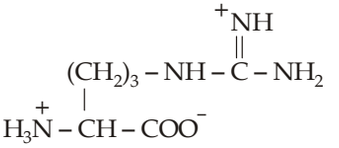
$H_2N-\underset{|}{\overset{CH_2COOH}{C}}H-COOH$ Aspartic acid

Solution :

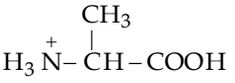
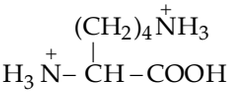
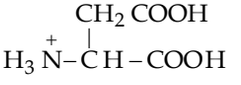
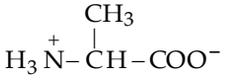
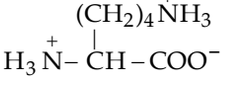
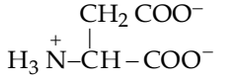
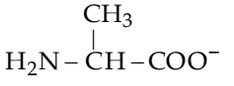
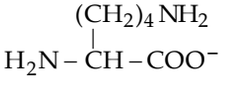
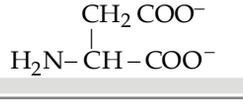
The first ionization constant (pK_{a1}) of α-amino acids is nearly 2.3, while the pK_{a2} is about 9.6. Hence in a strongly acidic medium (*p*H below 2), the amino acids exist in cationic form, while in a strongly alkaline medium (*p*H above 10), the amino acids exist in anionic form; the zwitterionic form is predominant at *p*H value ranging between 2 to 9. Thus at the pH below 2, the amino acids exist mainly as the cation, as the pH value exceeds 2.3, the –COOH group starts convering into $-COO^-$ and thus zwitterionic form starts appearing. Higher the *p*H, greater number of –COOH will be converted into $-COO^-$, and finally as the *p*H increases beyond pK_{a2} (9.6), the $-\overset{+}{N}H_3$ group is converted into $-NH_2$ and thus the amino acid mainly exists as an anion.

(a) 
Valine at pH 11

(b) 
Proline at pH 2

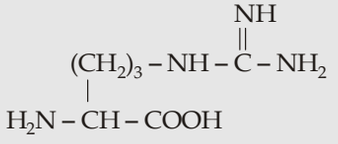
(c) 
Arginine at pH 7

(d)

		Alanine	Lysine	Aspartic acid
(i)	**pH 2**			
(ii)	**pH 6**			
(iii)	**pH 11**			

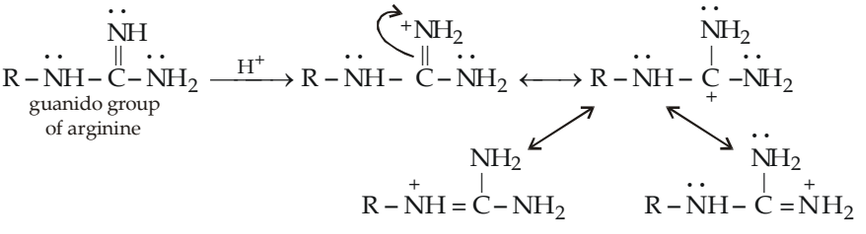
Example 2 :

Arginine has a strongly basic isoelectric point (10.7), while other amino acids have pI between pK_{a_1} (2.3) and pK_{a2} (9.7). Explain.



Solution :

The strongly basic isoelectric point (10.7) of arginine is due to unusual basicity of its guanido group which in turn is due to resonance stabilization of its protonated form.

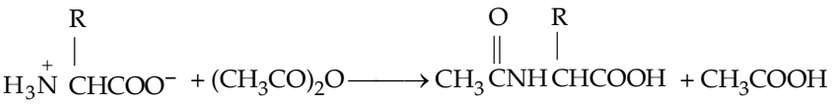

guanido group of arginine

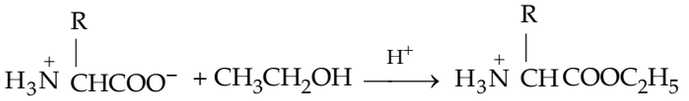
Protonation of the $-C=\ddot{N}H$ group in preference to $-\ddot{N}H_2$ groups is also because of high stability of the corresponding conjugate acid whose three of the resonating structures are identical.



23.5 Reactions of Amino Acids

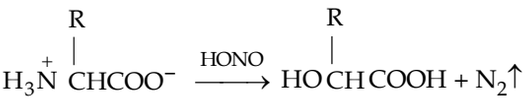
Amino acids undergo reactions characteristics of both their amino and carboxylic groups. Acylation is a typical reaction of the amino group, while esterification is a typical reaction of the carboxyl group.





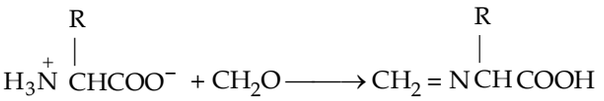
Other important reactions of α-amino acids are given below.

(*a*) **Reaction with nitrous acid** (*Similarity with 1° amines*).



This reaction forms the basis of the **Van Slyke** method for estimation of amino acid or amino group because one mole of N_2 is evolved per —NH_2 group in the amino acid.

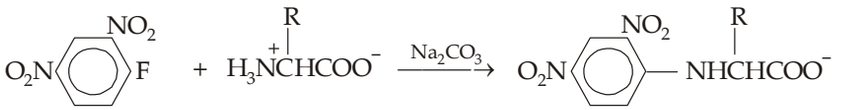
(*b*) **Reaction with formaldehyde**



N-Methyleneamino acid

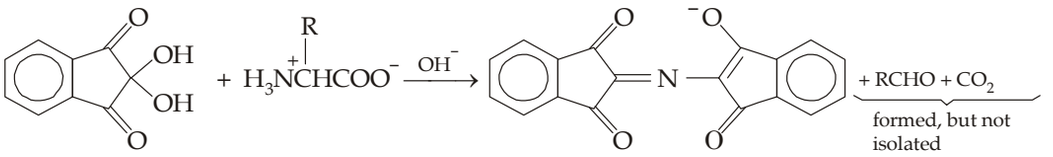
This reaction is used for estimating the —COOH group by titration (**Sorenson titration method**).

(*c*) **Reaction with 2, 4-dinitrofluorobenzene** (DNFB, commonly known as Sanger's reagent).



DNFB — Yellow coloured dinitrophenyl amino acid

(*d*) **Reaction with ninhydrin.** This is used as a test for detecting the presence of α-amino acids.



Ninhydrin — Ruhemann's purple (Violet colour)

Note that only N of the amino acid appears in the Ruhemann's purple, the side chain is lost as RCHO and —COO^- part as CO_2. Further, proline and hydroxyproline do not react with ninhydrin because they have secondary amino group.

(*e*) Heating of α-amino acids with copper sulphate in presence of dil. NaOH gives *deep blue colour.*

TEST YOUR UNDERSTANDING - 23.4

1. Give the products of reaction of glycine with

(*a*) aq. KOH (*b*) aq. HCl (*c*) C_6H_5COCl + NaOH (*d*) $Ba(OH)_2$, heat

2. (*a*) Give the products of the reaction of nitrous acid with $H_3\overset{+}{N}CH(R)COO^-$. What is the special importance of this reaction ?

(*b*) Can you name any amino acid that does not evolve N_2 with nitrous acid ?

(*c*) Determine the volume of N_2 evolved at STP when

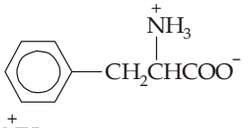
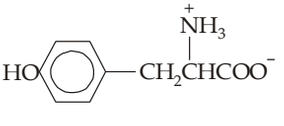
(*i*) 0.01 mole of a mono aminomonocarboxylic acid,

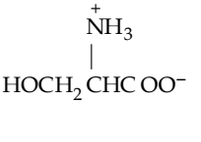
(*ii*) 0.001 mole of a diaminomonocarboxylic acid is treated with nitrous acid.

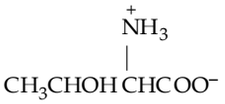
3. (*a*) What is the effect of heating on α-amino acids ?

(*b*) When the methyl ester of *rac*-alanine is heated, two diastereomers are obtained, only one of them is resolvable. Explain.

4. Give the reagent used for distinguishing following pairs of α-amino acids.

(*a*)  and 

(*b*) 

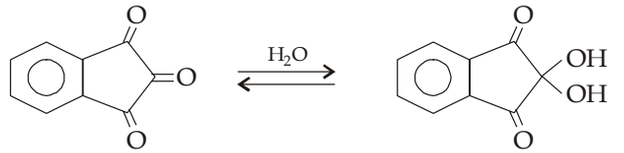
and 

Phenylalanine Tyrosine Serine Threonine

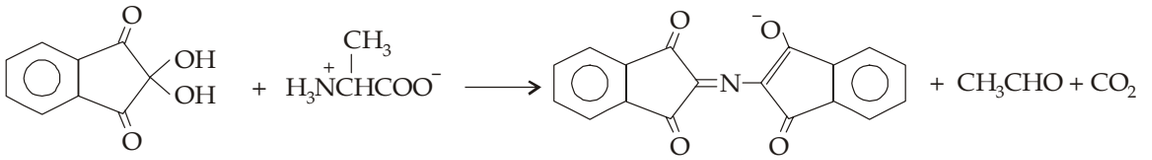
Example 3 :

Ninhydrin is the hydrate of indane-1,2,3-trione. Give its reaction with alanine, $CH_3CH(NH_2)COOH$ and draw the important resonating structures of the anion formed.

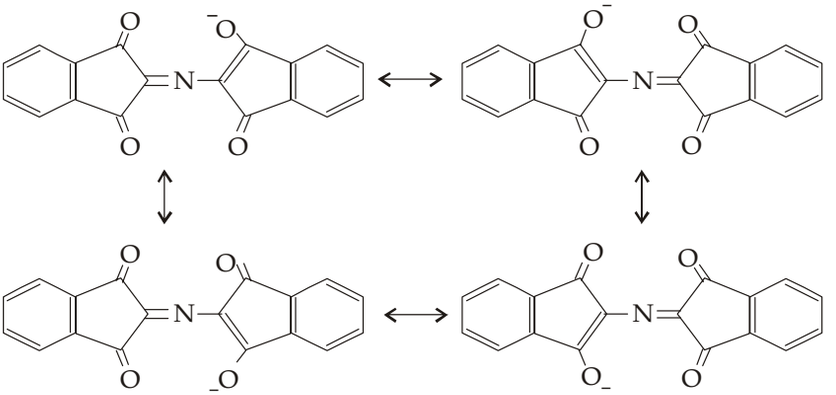
Solution :



Indane-1,2,3-trione Ninhydrin



Ninhydrin Alanine Ruhemann's purple



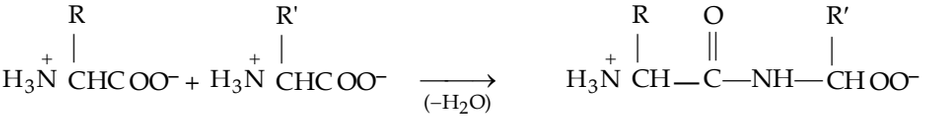
These are the most significant resonance contributors where the negative charge is present on the electronegative oxygens. In addition to these there will be two contributors in which negative charge is on the carbons bonded to the nitrogen, plus the Kekule structures of the benzene rings.



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23.6 Peptides

Peptides are polyamides formed by interaction between amino and carboxyl groups of amino acids. The amido group —NHCO—, in such compounds is often referred to as the **peptide linkage.** The peptides are classified into various groups depending upon the number of the amino acid residues in it, *e.g.* a peptide derived from two molecules of the same or different amino acids is known as dipeptide, from three, four or indefinite molecules of amino acids as **tripeptide, tetrapeptide,** and **polypeptide** respectively.



A dipeptide (it has one peptide bond)

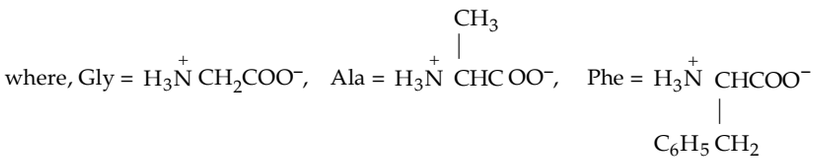
Thus the number of peptide bonds in di-, tri-, tera- and penta- peptide is 1, 2, 3 and 4 respectively.

Formula of peptides is written by using the three-letter amino acid abbreviations for the respective amino acids and connecting them by hyphens ; *e.g.* Gly– Gly is a dipepide having 2 molecules of glycine. Further, according to convention, the amino acid written at the left end of a peptide formula is considered to have free amino group hence it is commonly known as **N-terminal amino acid** ; while the amino acid written at the right end is considered to have free carboxyl group, hence it is known as **C-terminal** amino acid.

TEST YOUR UNDERSTANDING - 23.5

1. Write structural formulas for each of the following dipeptides.

(*a*) Gly–Ala (*b*) Ala–Gly (*c*) Ala–Phe (*d*) D-Ala-D-Ala



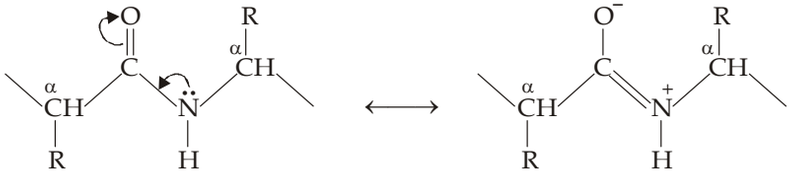
2. Write the structural formula for (*a*) Gly–Ala–Ala, and (*b*) phenylalanylalanylalanine.

3. You are given two α-amino acid molecules, and asked to prepare dipetide. Can you get a specific dipeptide ?

4. (*a*) List and name all the different dipeptides that can be synthesised from glycine and alanine ?

(*b*) How many tripeptides are possible using three different amino acids ?

The peptide bond is flat : carbonyl carbon, nitrogen, and the four atoms attached to them all lie in a plane. The short (1.32 Å) C—N distance of peptide linkage than the usual C—N single bond (1.47 Å) indicates that the C—N bond in peptides has considerable double bond character which in turn is due to delocalization of nonbonding electrons to the O of C = O. As a result the angles of the bonds to nitrogen are similar to the angles to the trigonal carbon atom.



Due to partial double bond character of the peptide bond, rotation about the amide linkage is not free. Further, the most stable conformation with respect to the peptide bond is that in which the two α carbon atoms are anti to each other.

23.7 Polymers

The macromolecules formed by the union between same or different molecules are known as polymers.

Polymerisation : The process of joining together the simple molecules is known as polymerisation.

MONOMERS : Small molecules which are joined together to form polymers are known as monomers.

DEGREE OF POLYMERISATION : The number of monomolecules (n) which combine to form a given macromolecule is called the degree of polymerisation.

HIGH POLYMERS : Such polymers have high degree of polymerisation.

OLIGOMERS : They have low degree of polymerisation.

DISTINCTION BETWEEN POLYMERS AND MACROMOLECULES : Polymers have repeat units and a macromolecule may or may not have repeat units eg chlorophyll and polythene.

HOMOPOLYMERS : Polymers containing one type of monomer units.

COPOLYMERS : Polymers containing two or more types of monomer units.

CLASSIFICATION : They may be divided into two categories.

(i) ***Natural polymers*** **-** They are obtained from natural sources eg **poly saccharides** (starch, cellulose), **Proteins** (polymers of amino acids), gums, resins (cross linked polymers formed by compounds containing double or triple bonds slowly oxidised by atmospheric oxygen). **natural rubber** (polymer of isoprene), **Nucleic acids** (polymers of nucleotides) silk and wool (polymers of amino acids).

(ii) ***Synthetic polymers*** **-** Polymers prepared by synthesis (man made), are known as synthetic polymers eg. polystyrene, nylon, PVC etc.

CLASSIFICATION BASED ON STRUCTURE :

(i) ***Linear polymers*** **-** Polymers containing the monomeric units linked together to form long straight chains stacked over one another to give packed structure.

Such polymers have high tensile strength, high densities, high m.p. and b.p. Examples - fibres and plastics.

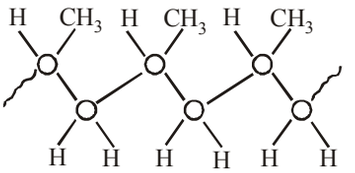
(ii) ***Branched polymers*** **-** Long chain of monomer units containing side chains of different length forms branched polymers. The chains are loosely packed, hence polymers have low density, low m.p. and low tensite strength. Examples - Amylopectin and glycogen.

(iii) ***Cross - linked*** or three dimensional polymers - Such polymers have three dimensional network and are hard, brittle and rigid. Examples - Bakelite, melamine.

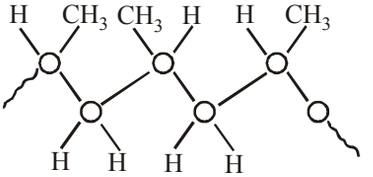
STEREOCHEMICAL CLASSIFICATION :

Polymers of propylene can be classified into

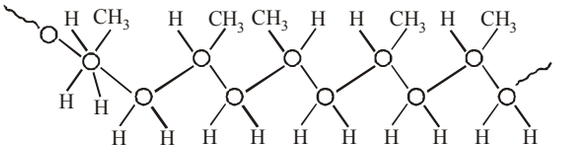
(i) ***Isotactic*** - with all methyl groups on one side of extended chain



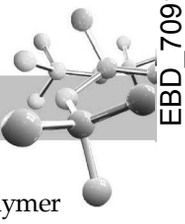
(ii) ***Syndiotactic,*** with methyl groups alternating regularty side to side



(iii) ***Atactic***-with random distribution of methyl groups



(Above polymers are obtained by coordination polymerisation)



CLASSIFICATION BASED UPON MODE OF SYNTHESIS :

(i) ***Addition polymers*** **-** Polymers formed without the elimination of any elements and the molecular weight of the polymer is the exact multiple of the monomer unit are known as addition polymers

$$n\left(\underset{\text{Alkene}}{\overset{R}{\overset{|}{CH=CH_2}}}\right) \rightleftarrows \underset{\text{Polyalkene}}{+\overset{R}{\overset{|}{CH-CH_2}}+_n}$$

(ii) ***Condensation polymers*** - They are formed with elimination of certain elements in the form of H_2O, C_2H_5OH, NH_3 etc. and molecular weight of polymer is not exact multiple of monomer unit eg. terephthalic acid condenses with ethylene glycol to give polyester

$$n\ HOOC-C_6H_4-COOH + n\ HO(CH_2)_2OH \longrightarrow -(OC-C_6H_4-\overset{O}{\overset{\|}{C}}-O-(CH_2)_2-O)_n + (n-1)H_2O$$

Terephthalic acid — ethylene glycol — Polyester

CHAIN GROWTH AND STEP GROWTH POLYMERS :

(i) ***Chain growth polymers*** **-** In chain growth polymerisation each step consumes a reactive particle and produces another similar particle.

$$A^{\bullet} + \overset{R}{\overset{|}{CH}}=CH_2 \rightarrow A-\overset{R}{\overset{|}{CH}}-\overset{\bullet}{CH_2}$$

$$A-\overset{R}{\overset{|}{CH}}-\overset{\bullet}{CH_2} + \overset{R}{\overset{|}{CH}}=CH_2 \rightarrow A-\overset{R}{\overset{|}{CH}}-CH_2-\overset{R}{\overset{|}{CH}}-\overset{\bullet}{CH_2}$$

(ii) ***Step growth polymers*** **-** Polymerisation proceeds through various steps independent of each other and it happens when monomer units contain more than one functional group. For example formation of nylon 66, bakelite etc proceed by step growth polymerisation.

$$n\,H_2N-(CH_2)_6-NH_2 + n\,HOOC(CH_2)_4COOH \rightarrow -(NH-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}})_n + (n-1)H_2O$$

Heaxamethylene diamine — Adipic acid — Nylon 66

CLASSIFICATION ON THE BASIS OF PHYSICAL PROPERTIES AND INTERPARTICLE FORCES :

(i) ***Elastomers*** **-** They can be easily stretched and can be made rigid to some extent by adding cross linking agents eg vulcanised rubber. They possess weakest intermolecular forces.

(ii) ***Thermoplastics*** - They become soft on heating and harden on cooling. eg polythene, polystyrene. They can be worked up again and again. Forces between molecules are intermediate of elastomers and fibers.

(iii) ***Thermosetting*** - Such polymers undergo chemical changes when heated and set to hard mass when cooled eg Bakelite. Such polymers can not be reworked. There is excessive cross linking on heating and three dimensional net work of bonds.

(iv) ***Fibres*** - Linear polymers containing polymeric units joined by hydrogen bonding. They can be woven into fabrics. Rayons, nylons are the examples.

FORMATION OF ADDITION POLYMERS :

They can be obtained by

(i) Free radical polymerisation

(ii) Cationic polymerisation

(iii) Anionic polymerisation

(iv) Ziegler - Natta polymerisation or coordination polymerisation

VULCANIZATION OF RUBBER :

Heating of rubber with sulphur which causes formation of sulphur bridges between molecules which are then cross linked is known as vulcanization of rubber. The vulcanised rubber is more elastic than natural rubber.

Vulcanization may be brought about by free radical generators (peroxides, azo compounds) and metal oxides (ZnO or MgO) also.

ANTI OXIDANTS :

Natural rubber is very sensitive to oxidation by air and ozone which can be inhibited by adding anti oxidants. They undergo easy oxidation and prevent the oxidative degradation of rubber. Examples are N - phenyl - β - naphthylamine and Di - β - naphthyl - p - phenylenediamine.

MOLECULAR MASS OF POLYMERS :

It is of two types

(i) Number average molecular mass $(\overline{Mn})$ given by

$$\overline{Mn} = \frac{N_1M_1 + N_2M_2 + N_3M_3 + ...}{N_1 + N_2 + N_3 + ...} = \frac{\sum N_iM_i}{\sum N_i}$$

Where N_1 number of molecules having molecular mass M_1 and so on. It is measured by osmotic pressure measurement.

(ii) Mass - average molecular mass $(\overline{Mw})$ given by

$$\overline{Mw} = \frac{N_1M_1^2 + N_2M_2^2 + N_3M_3^2 + ...}{N_1M_1 + N_2M_2 + N_3M_3 + ...} = \frac{\sum N_iM_i^2}{\sum N_iM_i}$$

It is determined by ultra centrifugation or sedimentation.

POLYDISPERSITY INDEX :

It is the ratio of mass average molecular mass $\overline{M}_w$ to the number average molecular mass $\overline{M}_n$

$$PDI = \frac{\overline{M}_w}{\overline{M}_n}$$

When PDI = 1 or nearly 1, we have monodisperse system in which all molecules have identical molecular mass. Natural polymers are monodisperse and synthetic polymers are polydisperse i.e. PDI > 1 for such polymers

IMPORTANT ADDITION POLYMERS :

(i) ***Polyethylene***

$$n\,CH_2 = CH_2 \xrightarrow[1500\,atm;\,150-250^oC]{\text{Traces of } O_2} \underset{\substack{\text{Polythene}\\ \text{or Polyethylene}}}{(-CH_2 - CH_2-)_n}$$

Free radical initiator gives low density polythene and ionic catalyst gives high density polythene. It is white, transluscent, rigid, linear, used for making tubes, pipes, coated wires, insulator parts. etc.

(ii) ***Polypropylene***

$$n\,CH_3 - CH = CH_2 \xrightarrow[Al(C_2H_5)_3 + TiCl_3]{\text{Ziegler Natta Catalyst}} \underset{\text{Polypropylene}}{(-\overset{\overset{CH_3}{|}}{CH} - CH_2-)_n}$$

It has good hardness, stiffness, resistance. Used for making ropes, carpets, washing machine parts etc.

(iii) ***Polystyrene***

$$n\,C_6H_5 - CH = CH_2 \xrightarrow{\text{Benzoyl Peroxide}} (-\overset{\overset{C_6H_5}{|}}{CH} - CH_2-)_n$$

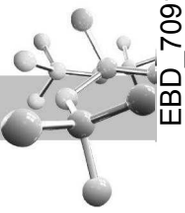
It is transparent, light, moisture resistant used for battery cases, refrigerator parts, electric insulators, combs, buttons TV cabinets. Its trade name is **Styrofoam** or **styron**.

(iv) Polymethyl methy acrylate, **Lucite** or **Plexiglass**.

$$n\,CH_2 = \underset{\substack{|\\ CH_3}}{\overset{\overset{|}{COOCH_3}}{C}} \xrightarrow[\text{or } H_2O_2]{\text{Acetylperoxide}} (-CH_2 - \underset{\substack{|\\ CH_3}}{\overset{\overset{|}{COOCH_3}}{C}} -)_n$$

Methylmeth acrylate (MMA) PMMA

It is hard, fairly rigid. It is used for making lenses, artificial eyes, dentures, aircraft windows.



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(v) ***Polyvinyl chloride (PVC)***

$$n\ CH_2 = CH - Cl \xrightarrow[\text{Under pressure}]{\text{Benzoyl peroxide or } H_2O_2} \left(CH_2 - \underset{|}{\overset{Cl}{CH}}\right)_n$$

It is resistant to light, atmopheric oxygen, chemically inert. It is used for electrical insulators, floor covering, safety helmets etc.

(vi) ***Teflon, Polytetrafluoroethylene (PTFE) of Fluon***

$$\underset{\text{Tetrafluoro ethene}}{n\ CF_2 = CF_2} \xrightarrow[\text{Amm.–peroxosulphate } (NH_4)_2S_2O_8]{\text{Benzoyl peroxide or}} \left(\underset{|}{\overset{F}{\overset{|}{C}}} - \underset{|}{\overset{F}{\overset{|}{C}}}\right)_n$$

It is extremely tough, resistant to heat and chemicals. It is used for making gaskets, pump parts, coating utensils, high frequency insulator

(vii) ***Polyacrylonitrile (PAN), acrilon or orlon***

$$\underset{\text{Acrylonitr ile}}{n\,CH_2 = \overset{CN}{\overset{|}{CH}}} \longrightarrow \underset{\text{orlon}}{(CH_2 - \overset{CN}{\overset{|}{CH}})_n}$$

It is hard used in preparing cloths, carpets

RUBBERS

(i) ***Buna - S* or SBR or GSR (Government styrene rubber)**

$$n\ \underset{\text{Styrene}}{\overset{C_6H_5}{\overset{|}{CH} = CH_2}} + n\,\underset{\text{Butadiene}}{CH_2 = CH - CH = CH_2} \xrightarrow[\Delta]{Na} \underset{\text{Buna–S}}{\left(\overset{C_6H_5}{\overset{|}{CH}} - CH_2 - CH_2 - CH = CH - CH_2 - \right)_n}$$

It is used for manufacture of tyres, floor tiles, gaskets, cable insulators etc.

(ii) ***Nitrile rubber*** (GR-A or Buna - N)

$$n\ \underset{\text{Butadiene}}{CH_2 = CH - CH = CH_2} + n\ \underset{\text{Acrylonitr ile}}{CH_2 = \overset{CN}{\overset{|}{CH}}} \longrightarrow \underset{\text{Nitrile rubber}}{\left(CH_2 - CH = CH - CH_2 - CH_2 - \overset{CN}{\overset{|}{CH}}\right)_n}$$

Excellent resistant to heat and chemicals. It is used for making conveyer belts, printing rollers, automobile parts.

(iii) ***Neoprene***

$$\underset{\text{Chloroprene}}{n\,CH_2 = CH - \overset{Cl}{\overset{|}{C}} = CH_2} \xrightarrow{K_2S_2O_8} \underset{\text{Neoprene}}{\left(CH_2 - CH = \overset{Cl}{\overset{|}{C}} - CH_2\right)_n}$$

It is resistant to heat and chemicals. It is used for making protective clothing, reaction vessels, floor tiles etc.

(iv) ***Heavy rubber*** - It is cis poly isoprene having length of repeat unit 8.1 A°.

(v) ***Gutta percha*** - It is trans poly isoprene having length of repeat unit 4.72A°.

IMPORTANT CONDENSATION POLYMERS :

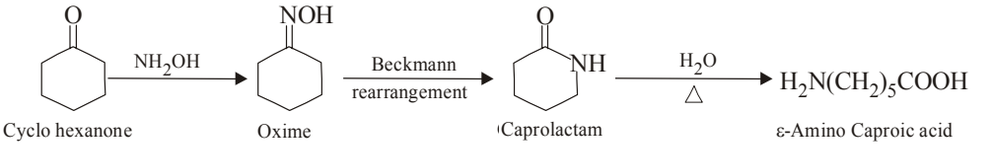
(A) Nylons - Synthetic polyamids are known as Nylons

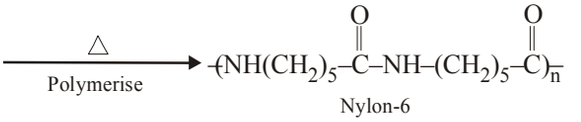
(i) ***Nylon 66:*** Copolymer of adipic acid (6C) and hexamethylene diamine (6C).

$$\underset{\text{Adipic acid}}{n\ HOOC(CH_2)_4COOH} + \underset{\text{Hexamethylene diamine}}{nH_2N(CH_2)_6NH_2} \rightarrow \underset{\text{Nylon 66}}{\left(\overset{O}{\overset{\|}{C}} - (CH_2)_4 - \overset{O}{\overset{\|}{C}} - NH - (CH_2)_6 - NH\right)_n}$$

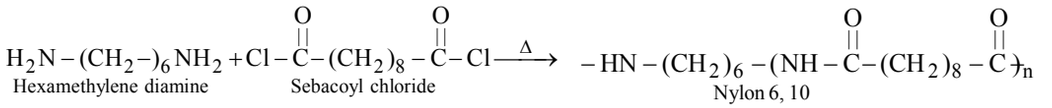
It has high tenacity and elasticity. It is resistant to abrasion and not affected by sea water. It is used for reinforcement of rubber tyres, manufacture of parachute, safety belts, carpets and fabrics.

(ii) ***Nylon 6:*** Homopolymer of caprolactam (6C)



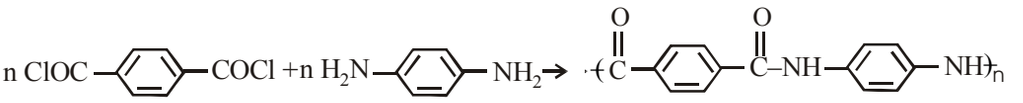


(iii) ***Nylon 6, 10*** - Copolymer of hexamethylene diamine (6C) and sebacoyl chloride (10C)



It is used for making brush bristlers

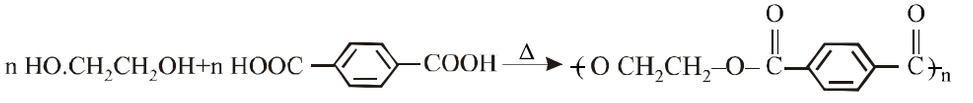
(iv) ***Kevlar:*** It is aromatic polyamide resembling nylons



It is used in aircraft industries, bullet proof vests, helmets, ropes cables.

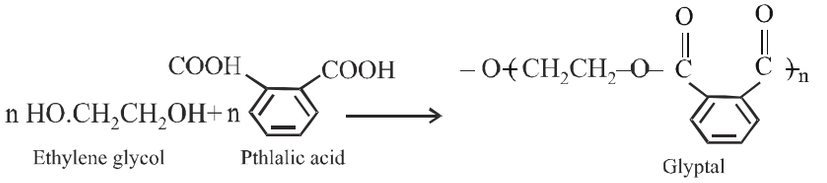
(B) Polyesters: Condensation polymers of a dibasic acid and a diol

(i) ***Terylene*** (dacron) / Polyethylene Terephthalate (PET)



It is resistant to mineral and organic acids. It is used for blending with wool to provide better crease, in safety helmets and aircraft battery boxes.

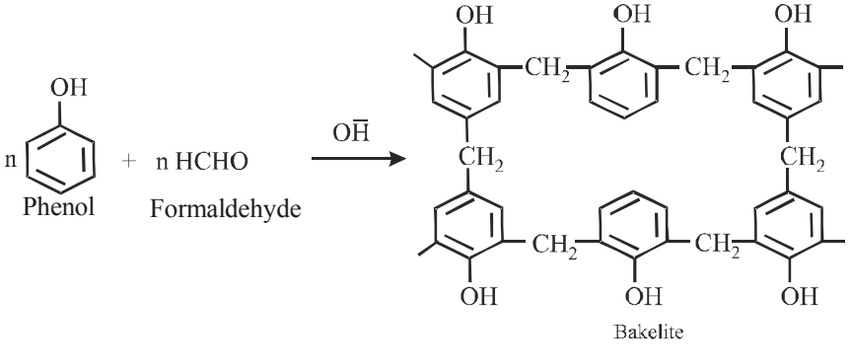
(ii) ***Glyptal or Alkyd resin*** (general name) **:** Condensation polymers of dibasic acids and polyhydroxy alcohols



Cross linked copolymer; For making good insulators, Sheets, rods switches lacquers and adherant paints.

(C) Thermo setting resins:

(i) ***Bakelite:*** Phenol formaldehyde resin

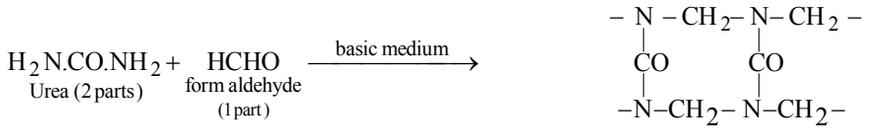


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High degree polymerisation leads to rigid, hard, scratch resistant, infusible, attacked by alkalies phenolic resins. They are used for making switches, plugs telephone parts. Sulphonated bakelites are used as ion - exchange resins in water softening.

Low degree polymerisation gives bonding glue, preparation of varnishes and lacquers.

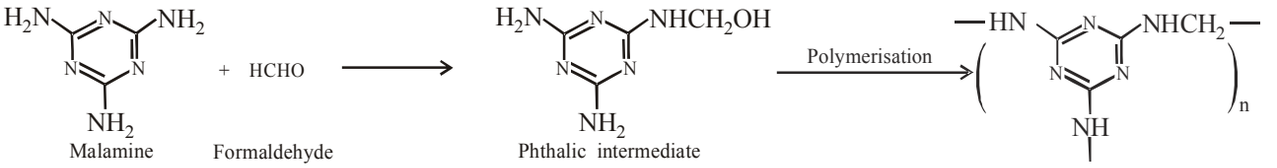
(ii) ***Urea formaldehyde resin***



Urea formaldehde resin (Crosslinked polymer)

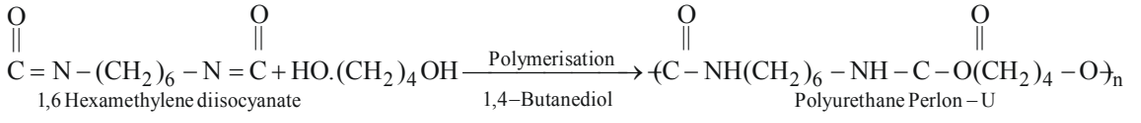
It is used for bonding grinding wheels, insulation, cation exchanger and decorative articles.

(iii) ***Melamine formaldehyde resins*** (MF resin)***:***



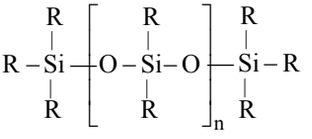
It is better than UF resin and used in making decorative laminates crockery under the trade name melmac, plywood industry as adhesive.

(iv) ***Polyuresthanes*** **-** Polymers of diisocyanate and diol eg. : Perlon-U



It is substitute of leather. They are used as foams, films adhesives, gaskets etc.

SILICON RESINS : Different organo-silicon chlorides can be polymerised by carefully controlled hydrolysis giving silicon resins. They contain alternate silicon oxygen structure.



where R = alkyl or phenyl radical

Silicones may be (a) liquid silicones or silicone oils (b) silicon greases (c) silicon rubbers (d) solid silicones.

RESIN : Resin is a low molecular weight polymer used as binder, fusible and mouldable. It changes into infusible cross - linked form during moulding in presence of catalyst.

RAYON : It is artificial silk. Actually the term includes all synthetic fibres manufactured from cellulose. The manufacturing can be carried out by

(i) Acetate process (ii) Viscose process.

PLASTICIZERS : The substances added to resins to increase their plasticity and flexibility are known as plasticizers. Examples are, vegetable oils (non drying), phosphates (tributyl phosphate, triphenyl phosphate etc), esters of oleic, stearic or phthalic acids and camphor etc.

RECLAIMED RUBBER: Rubber obtained from waste rubber articles.

REINFORCED RUBBER OR PLASTIC: They are obtained by adding solid fillers. They are also known as filled plastics or rubbers.

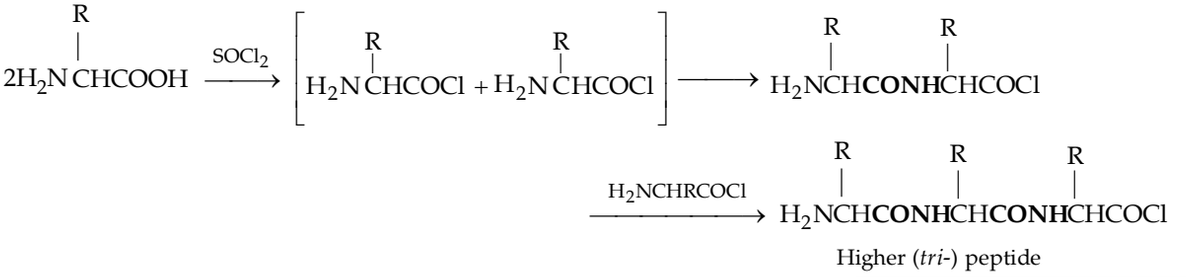
23.8 ILLUSTRATIVE EXAMPLES

Example 4 :

Give the product obtained when an α-amino acid is treated with $SOCl_2$.

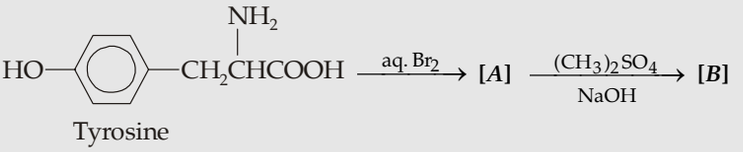
Solution :

Like carboxylic acids, α-amino acids react with $SOCl_2$ to form acid chlorides. However, acid chlorides are not isolated as the final product, because as soon as these are formed, two or more molecules react with each other to form peptides.



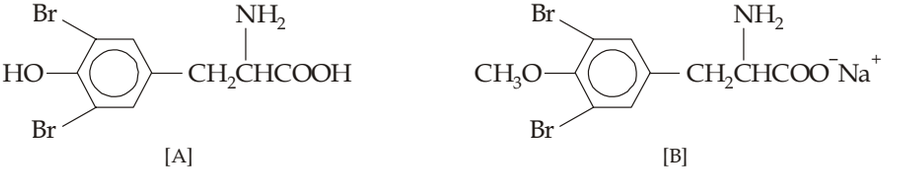
Example 5 :

Identify the products A and B in the following reactions



Solution :

The first step involves electrophilic substitution of the benzene, while in the second step phenolic —OH group is methylated.



Example 6 :

Identify the bracketed compounds in the following reactions.

(a) $CH_3COOC_2H_5 + \begin{matrix} COOC_2H_5 \\ | \\ COOC_2H_5 \end{matrix} \xrightarrow{NaOC_2H_5} [A] \xrightarrow{dil.\ H_2SO_4} [B] \xrightarrow[H_2/Pt]{NH_3} [C]$

(b) $CH_2 = CHCHO \xrightarrow{CH_3SH} [D] \xrightarrow[(ii)\ H_3O^+]{(i)\ NH_3,\ HCN} [E]$

(c) $C_6H_5N = C = S + Me_2CH\underset{|}{\overset{COO^-}{CH}}NH_3^+ \xrightarrow{OH^-} [F] \xrightarrow{H^+} [G]$

(d) $CH_3CH = CH_2 \xrightarrow{NBS} [H] \xrightarrow[(ii)\ H^+]{(i)\ KCN} [I] \xrightarrow[(ii)\ NH_3]{(i)\ P/Br_2} [J] \xrightarrow{HONO} [K] \xrightarrow{heat} [L]$

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Solution :

(*a*) $CH_3COOC_2H_5 + \begin{matrix}COOC_2H_5\\|\\COOC_2H_5\end{matrix} \xrightarrow[\text{(Crossed Claisen condensation)}]{NaOC_2H_5} \begin{matrix}COOC_2H_5\\|\\CO\\|\\CH_2COOC_2H_5\end{matrix}$

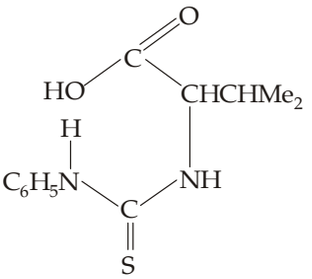
[A]

$\xrightarrow[\text{(i) ester hydrolysis}\\\text{(ii) —}CO_2\text{ from }\beta\text{-keto acid}]{H_2SO_4} \begin{matrix}COOH\\|\\CO\\|\\CH_3\end{matrix}$ [B] $\xrightarrow[\text{reductive amination}]{NH_3, H_2/Pt} \begin{matrix}COO^-\\|\\CH\overset{+}{N}H_3\\|\\CH_3\end{matrix}$ [C]

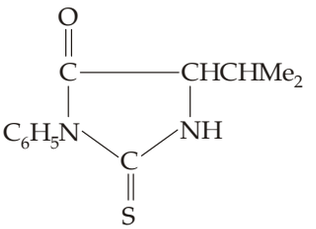
(*b*) $CH_2 = CH—CHO \xrightarrow[\text{(Michael addition)}]{CH_3SH} CH_3SCH_2CH_2CHO \xrightarrow[(ii)\ H_3O^+]{(i)\ NH_3, HCN} CH_3SCH_2\underset{[E]}{\underset{|}{\overset{+}{N}H_3}\underset{|}{CH}COO^-}$

[D]

(*c*)

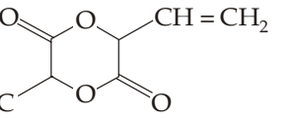


[F]



[G]

(*d*) $BrCH_2CH = CH_2$ [H] , $HOOCCH_2CH = CH_2$ [I] , $HOOC\underset{|}{\overset{NH_2}{CH}}CH = CH_2$ [J]

$HOOC\underset{|}{\overset{OH}{CH}}CH = CH_2$ [K] $\xrightarrow[\text{(intermolecular cyclization)}]{\text{heat}}$  Lactone (*cf.* lactams)

Example 7 :

Identify the bracketed compounds in the following reactions.

(a) $H_3\overset{+}{N}CH_2COO^- \xrightarrow[(ii)\ HCl]{(i)\ p\text{–}CH_3C_6H_4SO_2Cl, NaOH}$ [A] $\xrightarrow{Na/NH_3(liq.)}$ [B] + [B′]

(b) $H_2N\underset{|}{\overset{CH_3}{CH}}COOC_2H_5 \xrightarrow{p\text{–}CH_3C_6H_4SO_2Cl}$ [C] $\xrightarrow{Na/liq.\ NH_3}$ [D] + [D′]

(c) $H_2N\underset{\displaystyle CH_3}{\underset{|}{C}}HCOOH \xrightarrow{C_6H_5CH_2OCOCl} [E] \xrightarrow{H_2/Pd} [F] + [G]$

(d) $[G] \xrightarrow{heat} [H]$

(e) $PhthN\text{–}CH(COOC_2H_5)_2 \xrightarrow{OC_2H_5^-} [I] \xrightarrow[(ii)\,H_3O^+]{(i)\,CH_2=CHCOOC_2H_5} [J] \xrightarrow{H^+} [K]$

(where Phth = Phthalyl group)

(f) $CH_3CH(OH)CCl_3 \xrightarrow{NaN_3/OH^-} [L] \xrightarrow{H_2O} [M] \xrightarrow{H_2/Pd} [N]$

Solution :

(a) $\underset{[A]}{p\text{-}CH_3C_6H_4SO_2NHCH_2COOH}$; $\underset{[B]}{p\text{-}CH_3C_6H_4SO_2OH} + \underset{[B']}{H_2NCH_2COOH}$

(Na in liq. NH_3 reduces preferentially aromatic sulphonyl group, leaving —COOH as such)

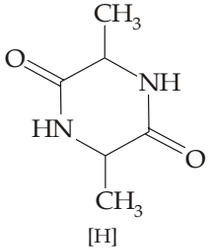
(b) $\underset{[C]}{p\text{-}CH_3C_6H_4SO_2NH\underset{\displaystyle CH_3}{\underset{|}{C}}HCOOC_2H_5}$ $\underset{[D]}{p\text{-}CH_3C_6H_4SO_2OH} + \underset{[D']}{H_2N\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2OH}$

(Na in liq. NH_3 reduces both $—SO_2Cl$ as well as —COOR group)

(c) $\underset{[E]}{C_6H_5CH_2OCONH\underset{\displaystyle CH_3}{\underset{|}{C}}HCOOH}$, $\underset{[F]}{C_6H_5CH_3} + CO_2 + \underset{[G]}{H_2N\underset{\displaystyle CH_3}{\underset{|}{C}}HCOOH}$

(H_2/catalyst does not reduce —COOH although it reduces —COOR)

(d)



[H]

(e) $\underset{[I]}{PhthN\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}(COOC_2H_5)_2} \xrightarrow[\text{Michael addition}]{(i)\,CH_2=CHCOOC_2H_5,\,(ii)\,H_3O^+} PhthN\text{—}\underset{\displaystyle COOC_2H_5}{\underset{|}{\overset{\displaystyle COOC_2H_5}{\overset{|}{C}}}}CH_2CH_2COOC_2H_5$

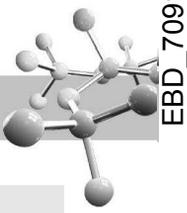
[J]

$\xrightarrow{H^+} H_3\overset{+}{N}\underset{\displaystyle COO^-}{\underset{|}{C}}HCH_2CH_2COOH$ + Phthalic acid

[K], Glutamic acid

(f) $CH_3\text{—}\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle O^-}{\overset{|}{C}}}}\text{—}\underset{\displaystyle Cl}{\underset{|}{C}}\text{—}Cl \xrightarrow[(-Cl^-)]{OH^-} CH_3\text{—}\underset{\displaystyle H}{\underset{|}{C}}\text{—}\underset{\displaystyle Cl}{\underset{|}{C}}\text{—}Cl \xrightarrow[(-Cl^-)]{N_3^-} CH_3\text{—}\underset{\displaystyle N_3}{\underset{|}{C}}\text{—}\overset{\displaystyle O}{\overset{\|}{C}}Cl \xrightarrow{H_2O} CH_3\text{—}\underset{\displaystyle N_3}{\underset{|}{C}}\text{—}\overset{\displaystyle O}{\overset{\|}{C}}OH \xrightarrow{H_2/pd} CH_3\text{—}\underset{\displaystyle NH_3^+}{\underset{|}{C}}\text{—}COO^-$

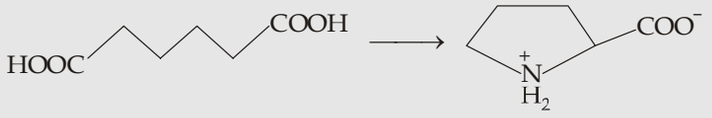
[L] [M] [N]



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Example 8 :

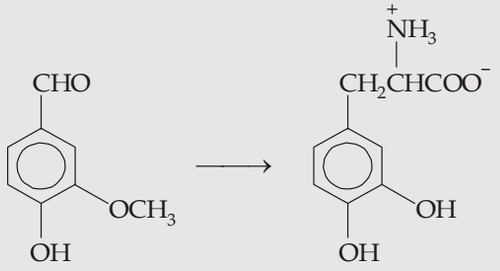
Give steps involved in the following conversions.

(a) 

Adipic acid proline

(b) Acrylic acid ⟶ β-Aminopropanoic acid (Pantothenic acid)

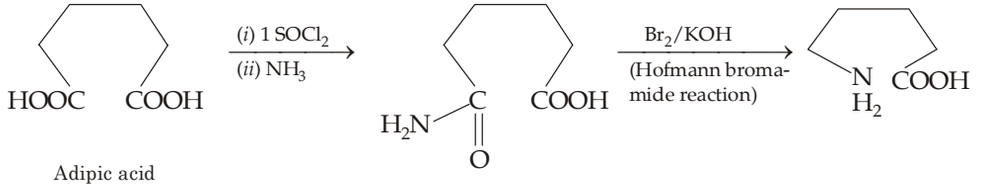
(c) Acrylic acid ⟶ γ-Aminobutyric acid (GABA)

(d) 

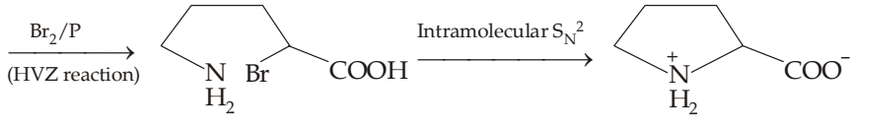
Vanillin 3, 4-Dihydroxyphenylalanine

Solution :

(*a*) The required compound has 5 C's with an amino group, while the starting compound has 6 C's without any amino group ; so this required set can be obtained by converting one of the —COOH groups of adipic acid to NH_2 via a Hofmann rearrangement. The remaining —COOH group is brominated by HVZ reaction.



Adipic acid



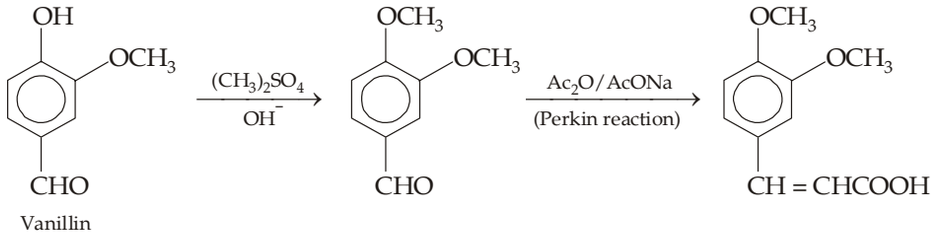
Proline

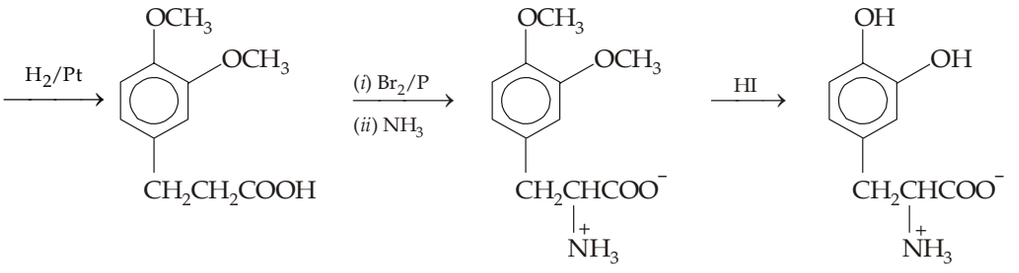
Remember that adipic acid can be easily obtained by the ozonolysis of cyclohexene.

(*b*) $\underset{\text{Acrylic acid}}{CH_2=CHCOOH} \xrightarrow[(ii)\,H^+]{(i):NH_3\ \text{(Michael addition)}} \underset{\beta\text{-Alanine}}{H_2NCH_2CH_2COOH}$

(*c*) $CH_2=CHCOOH \xrightarrow[\text{(Michael addition)}]{CN^-} NCCH_2\bar{C}HCOOH \xrightarrow{H^+} NCCH_2CH_2COOH \xrightarrow{H_2/Pd} \underset{\text{GABA (a neurotransmitter)}}{H_2NCH_2CH_2CH_2COOH}$

(*d*)





Example 9 :

An organic compound of the molecular formula $C_3H_4O_3$ gives following reactions :

(i) It evolves carbon dioxide with $NaHCO_3$ solution, and can undergo iodoform reaction.

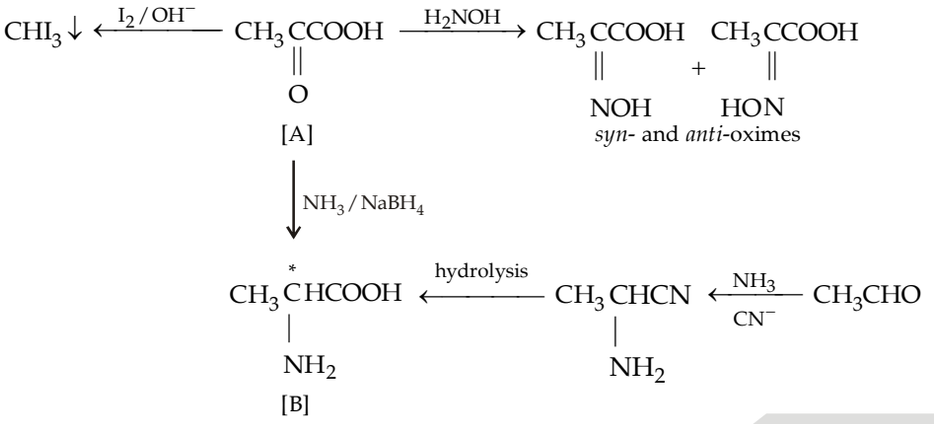
(ii) On treatment with hydroxylamine, it gives two isomeric oximes.

(iii) On treatment with ammonia followed by reduction with $NaBH_4$, it gives an acid B having chiral carbon. The acid B can also be produced by reaction of ethanal with ammonia in presence of potassium cyanide followed by hydrolysis.

Identify compounds A and B and explain the reactions involved.

Solution :

The given reactions of compound A indicate the presence of a —COOH and a —$COCH_3$ group. Thus the compound A should be $CH_3COCOOH$ which explains all the given reactions.



Example 10 :

An organic compound (A), of the formula $C_5H_{11}O_2N$ found in beet sugar molasses, shows following characteristics. It is water-soluble solid and melts with decomposition. It reacts with HCl to form compound B ($C_5H_{12}O_2NCl$), but it is not affected by base. Compound A can be synthesized easily by the reaction of chloroacetic acid and trimethylamine. Establish the structure of A and suggest another possible method for synthesising it.

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Solution :

Synthesis of compound A by the reaction of chloroacetic acid and trimethylamine leads to its following structure.

$$Me_3N + ClCH_2COOH \longrightarrow \underset{[A]}{Me_3N^+CH_2COO^-} + HCl$$

The above structure of A, being a dipolar explains its solid nature, solubility in water and melting with decomposition. Its reaction with acid involves the —COO^- group.

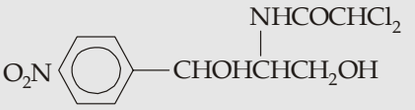
$$\underset{\text{A (Betaine)}}{Me_3N^+CH_2COO^-} + H^+ \longrightarrow Me_3N^+CH_2COOH$$

Another synthesis of A.

$$\underset{\text{Glycine}}{H_3N^+CH_2COO^-} \xrightarrow{3MeI} Me_3N^+CH_2COO^- + 3HI$$

Example 11 :

Chloramphenicol, commonly known as chloromycetin, is a broad-spectrum antibiotic with the following structure



(a) Name all the functional groups present in it

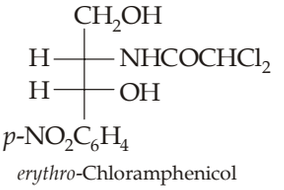
(b) How many stereoisomers are possible for this, draw their structures ?

(c) Give the hydrolysis products of chloramphenicol in acidic and basic medium.

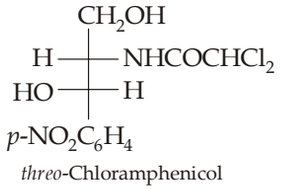
Solution :

(a) —NO_2 (nitro), 2° alcoholic, 1° alcoholic, amide, and halogen.

(b) It has two chiral carbons, hence can exist in four stereoisomeric forms, i.e. two enantiomeric pairs (drawn below).

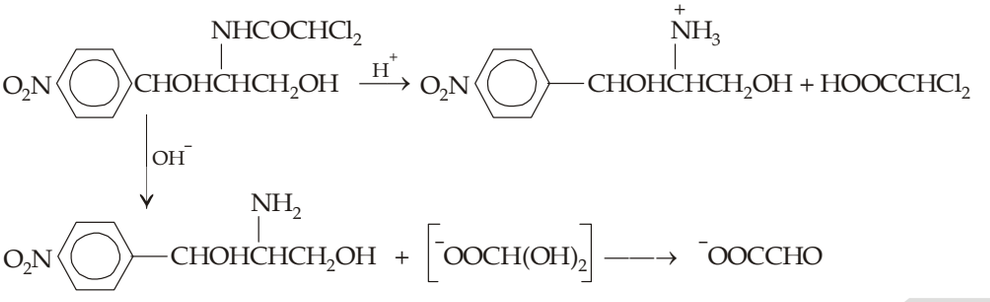


erythro-Chloramphenicol



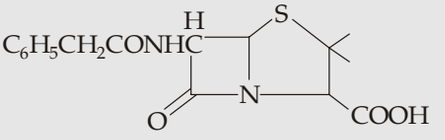
threo-Chloramphenicol

(*c*)



Example 12 :

Penicillin, the common antibiotic, has following structure :



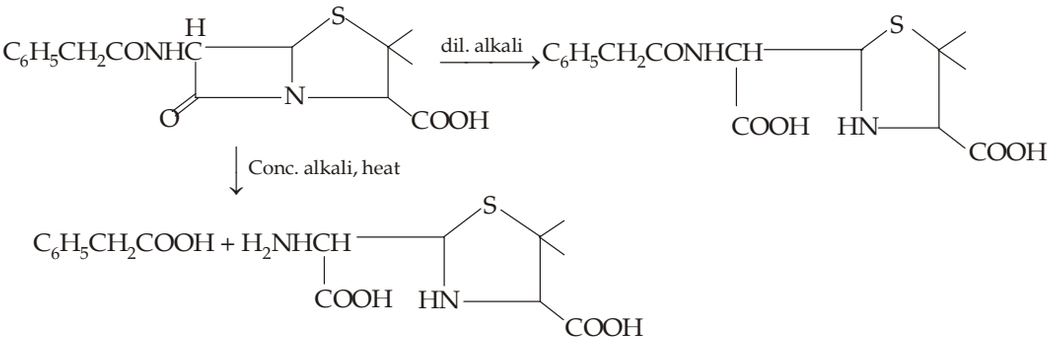
(a) List the different functional groups present in it.

(b) Write down the hydrolysis products obtained in presence of dil. alkali at room temperature.

Solution :

(a) Amide, lactam, carboxylic and thioether linkage.

(b) When hydrolysed by dilute alkali and at room temperature, lactam group (but not the amide) undergoes hydrolysis.



Example 13 :

The enzyme cytochrome C, involved in oxidation-reduction processes in the living system, has 0.43% Fe and 1.48% S. Determine the minimum molecular weight of the enzyme. Also determine the ratio of Fe : S in the enzyme.

Solution :

The minimum atom of Fe in the enzyme is **one.**

0.43 g of Fe is present in 100 g of enzyme

56 g of Fe is present in $\frac{100}{0.43} \times 56 = 1.3 \times 10^4$ g of enzyme

Thus the minimum mol. wt. of the enzyme = 13000

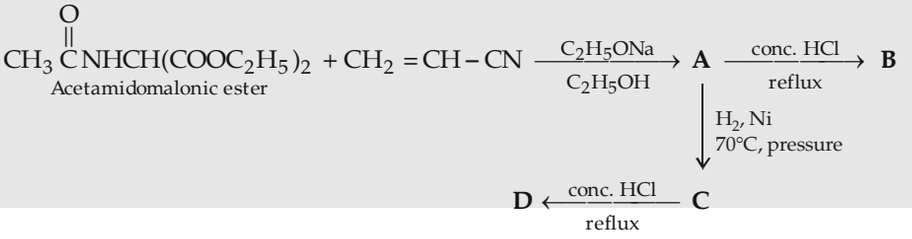
Similarly, 32 g of S is present in $\frac{100 \times 32}{1.48} = 2.16 \times 10^3$

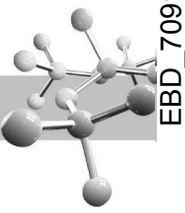
Thus the minimum mol. wt. corresponding to 1 S atom = 2160

$\therefore$ No of S atoms in the enzyme per Fe atom $= \frac{13000}{2160} \approx 6$

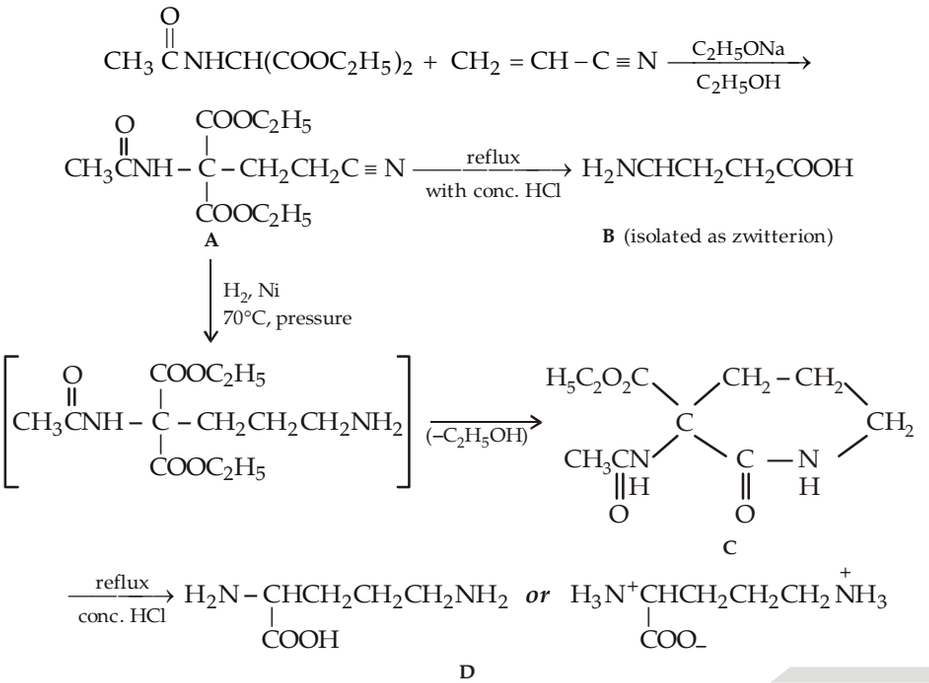
Example 14 :

Complete the following set of reactions by supplying structures to the compounds A to D.





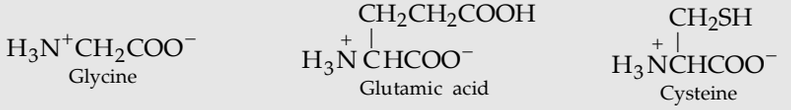
Solution :



A **B** (isolated as zwitterion) **C** **D**

Example 15 :

(a) Glutathione is a tripeptide composed of following three amino acids



Partial acid-hydrolysis of glutathione gives two dipeptides: Cys. Gly and Glu. Cys. Determine the possible structure(s) of the tripeptide, glutathione.

(b) On the basis of the above established structure explain the function of glutathione as a free radical scavanger in the cells.

Solution :

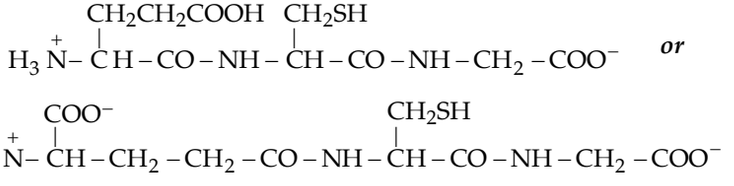
(a) Try to locate the point of overlap from the structures of the two dipeptides

Cys. Gly.

Glu. Cys.

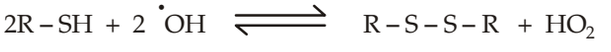
Thus the tripeptide should be : Glu. Cys. Gly.

This indicates that glutamic acid constitutes N-terminus and glycine constitutes C-termium. Now since glutamic acid has two –COOH groups, each of which may form peptide bond with the $-NH_2$ group of cysteine. Thus on the basis of the above points, glutathione may have either of the two structures.



or

(b) Due to the presence of $-CH_2SH$ group in glutathione it reduces the free radicals $^{\cdot}OH$ and $^{\cdot}O_2^-$ to H_2O and itself oxidised to a disulphide.



Example 16 :

A nonapeptide of molecular formula, Arg_2, Gly, Phe_2, Ser, Pro_3 has arginine (Arg) residue on both ends. On partial hydrolysis, it gives following peptides.

Phe. Ser + Phe. Arg + Pro. Pro + Arg. Pro + Pro. Gly. Phe + Ser. Pro. Phe

Establish the sequence of amino acids in this nonapeptide.

Solution :

Observe the points of overlap, keeping in mind that you should attach the peptides having Arg at ends.

Phe. Ser

Ser. Pro. Phe

Pro. Gly. Phe Phe. Arg

Pro. Pro.

Arg. Pro.

Complete structure of the nonapeptide

Arg. Pro. Pro. Gly. Phe. Ser. Pro. Phe. Arg.

EBD_7091

EXERCISE 23.1 (MCQ - ONE option correct)

1. Which of the following statement(s) is (are) true ?
(*i*) All amino acids contain one chiral center.
(*ii*) Some amino acids contain one, while some contain more chiral center or even no chiral center.
(*iii*) All amino acids found in proteins have L configuration.
(*iv*) All amino acids found in proteins have 1° amino group.
(*a*) (*ii*), (*iii*) and (*iv*) (*b*) (*ii*) and (*iii*)
(*c*) (*i*), (*iii*) and (*iv*) (*d*) (*i*) and (*iv*).

2. The nature of carboxylic group in the solid glycine is
(*a*) acidic (*b*) basic
(*c*) both (*d*) none.

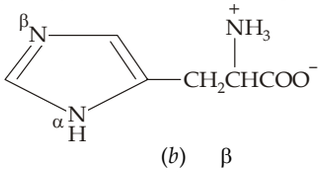
3. Which of the following is more acidic ?
(*a*) H_2NCH_2COOH (*b*) $H_3\overset{+}{N}CH_2COOH$
(*c*) CH_3COOH (*d*) Equal.

4. A strongly alkaline solution of a monoaminodicarboxylic acid contains how many basic groups ?
(*a*) 1 (*b*) 2
(*c*) 3 (*d*) 4.

5. Which of the following dipolar structure of the amino acid is considered more correct ?

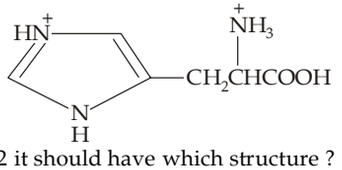
(*a*) $H_3\overset{+}{N}CH(CH_2COOH)COO^-$ (*b*) $H_3\overset{+}{N}CH(CH_2COO^-)COOH$
(*c*) Both (*d*) None.

6. Which of the nitrogen of histidine is first protonated ?



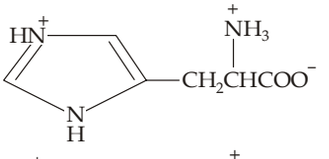
(*a*) α (*b*) β
(*c*) both (*d*) None.

7. Histidine, a heterocyclic amino acid has following structure at pH < 1.82,

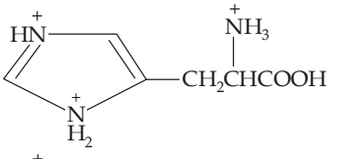


at pH > 1.82 it should have which structure ?

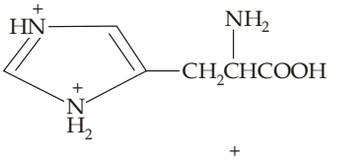
(*a*)



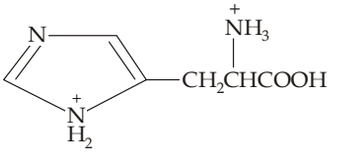
(*b*)



(*c*)



(*d*)



8. Which of the following statement is false ?
(*a*) All amino acids, including glycine, are ampholyte.
(*b*) An amino acid may be neutral, acidic or basic.
(*c*) The basic functional group in amino acids is —COO^-.
(*d*) None of the above statement is false.

9. An electric current is passed through an aqueous solution (buffered at pH = 6.0) of alanine (pI = 6.0) and ariginine (pI = 10.2). The two amino acids can be separated because
(*a*) alanine migrates to anode, and arginine to cathode.
(*b*) alanine migrates to cathode, and arginine to anode.
(*c*) alanine does not migrate, while arginine migrates to cathode.
(*d*) alanine does not migrate, while arginine migrates to anode.

10. A mixture of two amino acids having pI 9.60 and 5.40 can be separated
(*a*) by adjusting the pH of the solution at 9.60
(*b*) by adjusting the pH of the solution at 4.20
(*c*) by adjusting the pH of the solution at 7.0
(*d*) by adjusting the pH of the solution at 7.5.

11. Preparation of glycine by Strecker synthesis involves..... as one of the starting compounds.
(*a*) Formaldehyde (*b*) Acetaldehyde
(*c*) Methanol (*d*) Either (*a*) or (*c*).

12. In the following series of reactions, compound Z can be

$$Z + NH_3 \xrightarrow{H_2\ (catayst)} CH_3CH(\overset{+}{N}H_3)COO^-$$

(*a*) CH_3CHO (*b*) CH_3COCH_3
(*c*) $CH_3COCOOH$ (*d*) None of the three.

13. How many dipeptides are possible from two molecules of a typical α-amino acid ?
(*a*) 1 (*b*) 2
(*c*) 3 (*d*) 4.

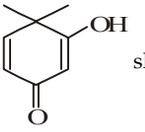
14. Which one of the following statement is false ?
(*a*) Gly-Ala and Ala-Gly have same structure.
(*b*) A dipeptide bond has two peptide bonds.
(*c*) Glycine and alanine form two dipeptides.
(*d*) All the above three statements are correct.

15. A molecule of haemoglobin, a protein found in blood, contains four atoms of Fe (56 g-atoms/mol), if the haemoglobin contains 0.35% Fe, the molecules weight of haemoglobin will be
(*a*) 64×10^5 (*b*) 128×10^5
(*c*) 64×10^3 (*d*) 128×10^3.

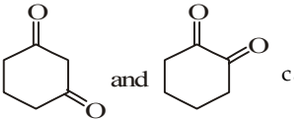
16. Select the correct statement(s).

(a) $HOOC-CH_2-NH-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-NH_2$ is a dipeptide of

(Glycine & Alanine, whose abbreviated name is GLY-ALA)

(b)  shows keto-enol tautomerism

(c) Phenol and benzoic acid can be distinguished by $NaHCO_3$

(d)  can be distinguished by iodoform test

17. Formation of polyethylene from calcium carbide takes place as follows

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

$$C_2H_2 + H_2 \longrightarrow C_2H_4$$

$$nC_2H_4 \longrightarrow (-CH_2 - CH_2 -)_n$$

The amount of polyethylene obtained from 64.1 kg of CaC_2 is
(a) 7 kg (b) 14 kg
(c) 21 kg (d) 28 kg

18. Which one of the following monomers gives the polymer neoprene on polymerization?

(a) $CCl_2 = CCl_2$ (b) $CH_2 = \underset{\displaystyle Cl}{\overset{\displaystyle |}{C}} - CH = CH_2$

(c) $CF_2 = CF_2$ (d) $CH_2 = CHCl$

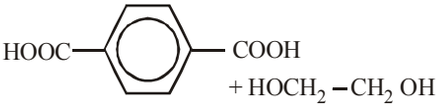
19. Plexiglas (PMMA) is a polymer of
(a) Acrylic acid (b) Methyl acrylate
(c) Methyl methacrylate (d) None of these

20. Urethane is

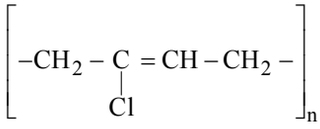
(a) $H_2N - C \equiv N$ (b) $H_2N - \underset{\displaystyle O}{\overset{\displaystyle ||}{C}} - OH$

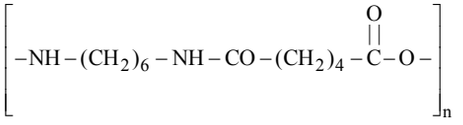
(c) $HO - C \equiv N$ (d) $H_2N - \underset{\displaystyle O}{\overset{\displaystyle ||}{C}} - OC_2H_5$

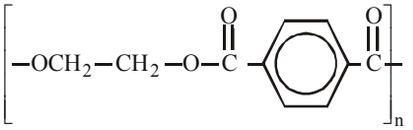
21. Which compound/set of compounds is used in the manufacture of nylon-66?
(a) $HOOC(CH_2)_4\,COOH + H_2N(CH_2)_6NH_2$
(b) $CH_2 = CH–C(CH) = CH_2$
(c) $CH_2 = CH_2$

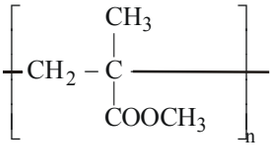
(d) 

22. Which of the following is not correctly matched?

(a) neoprene; 

(b) nylon-66: 

(c) terylene; 

(d) PMMA : 

23. Match List-I (Monomer) with List II (Polymer) and select the correct answer using the codes given below the lists:

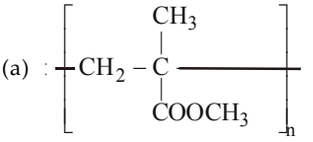
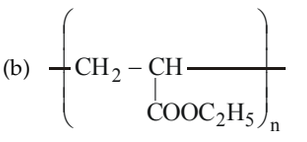
List I	List II
I. Hexamethylenediamine	A. Bakelite
II. Phenol	B. Dacron
III. Phthalic acid	C. Glyptal
IV. Terephthalic acid	D. Melamine
	E. Nylon

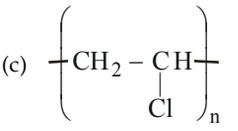
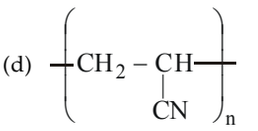
Codes:
(a) I-E, II-A, III-B, IV-C (b) I-E, II-A, III-C, IV-B
(c) I-D, II-C, III-A, IV-B (d) I-D, II-C, III-A, IV-B

24. Which one of the following is used to make 'non-stick' cookware?
(a) PVC (b) Polystyrene
(c) Poly (ethylene terephthalate)
(d) Polytetrafluoroethylene

25. Synthetic human hair wigs are made from a copolymer of vinyl chloride and acrylonitrile and is called
(a) PVC (b) Polyacrylonitrile
(c) Cellulose (d) Dynel

26. Acrilan is a hard, horny and a high melting material. Which of the following represents its structure?

(a)  (b) 

(c)  (d) 

27. Polymer formation from monomers starts by
(a) condensation reaction between monomers
(b) coordinate reaction between monomers
(c) conversion of monomer to monomer ions by protons
(d) hydrolysis of monomers.

28. Nylon threads are made of
(a) polyester polymer (b) polyamide polymer
(c) polyethylene polymer (d) polyvinyl polymer

29. Which of the following is a polyamide?
(a) Bakelite (b) Terylene
(c) Nylon-66 (d) Teflon

30. Which of the following is fully fluorinated polymer ?
(a) PVC (b) Thiokol
(c) Teflon (d) Neoprene

31. Bakelite is obtained from phenol by reacting with)
(a) HCHO (b) CH_3CHO
(c) CH_3COCH_3 (d) $(CH_2OH)_2$

32. Among cellulose, poly (vinyl chloride), nylon and natural rubber, the polymer in which the intermolecular force of attraction is weakest is
(a) Nylon (b) Poly (vinyl chloride)
(c) Cellulose (d) Natural Rubber

33. Among the following substituted silanes the one which will give rise to cross linked silicone polymer on hydrolysis is
(a) R_4Si (b) RSiCl
(c) R_2SiCl_2 (d) R_3SiCl

34. Buna-N synthetic rubber is a copolymer of
(a) $H_2C = CH - CH = CH_2$ and $H_5C_6 - CH = CH_2$
(b) $H_2C = CH - CN$ and $H_2C = CH - CHCH_2$
(c) $H_2C = CH - CN$ and $H_2C = CH - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}} = CH_2$

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EXERCISE 23.2 (MCQ 1 or >1 option correct, Passage based, Matching, A/R)

DIRECTIONS for Q. 1 to Q. 9 : Multiple choice questions with one or more than one correct option(s).

1. Which forms *Zwitter* ion ?
(a) glycine (b) sulphanilic acid
(c) anthranilic acid (d) salicyclic acid

2. Peptide linkage is present in :
(a) protein (b) γ-butyrolactam
(c) Zwitter ion (d) phthalimide

3. Alanine forms *Zwitter* ion which exists as :

(a) $CH_3-\underset{\oplus NH_3}{\underset{|}{CH}}-COO^{\ominus}$ in acidic medium

(b) $CH_3-\underset{\oplus NH_3}{\underset{|}{CH}}-COOH$ in medium of pH = 4

(c) $CH_3-\underset{NH_3}{\underset{|}{CH}}-COO^{\ominus}$ in a medium of pH = 13

(d) $CH_3-\underset{NH_3}{\underset{|}{C}}HOO^{\ominus}$ in a medium of pH = 2

4. Which is true about polymers?
(a) Polymers do not carry any charge
(b) Polymers have high viscosity
(c) Polymers scatter light
(d) Polymers have low molecular weight

5. On the basis of mode of formation, polymers can be classified?
(a) as addition polymers only
(b) as condensation polymers only
(c) as copolymers
(d) as homopolymers

6. Which of the following polymer(s) involve cross linkages?
(a) Melmac (b) Bakelite
(c) Polythene (d) Vulcanised rubber

7. Which of the following is/are example(s) of addition polymer ?
(a) Polystyrene (b) Nylon
(c) PVC (d) Polypropylene

8. Which of the following is/are example(s) of chain growth polymer?
(a) Neoprene (b) Buna-S
(c) PMMA (d) Glyptal

9. The correct functional group X and the reagent/reaction conditions Y in the following scheme are

$$X-(CH_2)_4-X \xrightarrow[\text{(ii) heat}]{\text{(i) Y}} \text{condensation polymer}$$
$$\text{(ii) } HO-C(=O)-(CH_2)_4-C(=O)-OH$$

(a) $X = COOCH_3$, $Y = H_2/Ni/heat$
(b) $X = CONH_2$, $Y = H_2/Ni/heat$
(c) $X = CONH_2$, $Y = Br_2/NaOH$
(d) $X = CN$, $Y = H_2/Ni/heat$

INSTRUCTION for Q. 10 to Q. 17 : Read the passages given below and answer the questions that follow.

PASSAGE 1

With the exception the simplest amino acid, glycine, all amino acids contain a chiral center. Further almost all naturally occurring amino acids have L-configuration at the α-carbon, i.e., they have the same relative configuration as L-glyceraldehyde.

In the dry state, amino acids exist as dipolar ions (also known as zwitterions) or inner salts, a form in which the carboxyl group is present as a carboxylate ion $-COO^-$, and the amino group as an aminium ion, $-NH_3^+$.

$$\underset{|}{\overset{R}{}}H_2NCHCOOH \qquad \overset{R}{\underset{|}{\overset{+}{}}}H_3N\,CHCOO^-$$

The dipolar ionic (salt like) structure of amino acids explains all of its above properties.

10. In aqueous solution, glycine is present as
(a) $H_3N^+CH_2COO^-$ (b) $H_3N^+CH_2COOH$
(c) $H_2NCH_2COO^-$ (d) All the three

11. In aqueous solution, the basic character of amino acids is due to
(a) $-NH_2$ group (b) $-\overset{+}{N}H_3$ group
(c) –COOH group (d) $-COO^-$ group

12. Amino acids constitute one of the important class of organic compounds. These are
(a) Fairly soluble in organic solvents like ether, benzene, etc.
(b) Fairly soluble in water
(c) Insoluble in both
(d) Soluble in both

13. $^-OOC-\underset{|}{\overset{NH_2}{C}}HCH_2COO^- \overset{H^+}{\rightleftharpoons}$ Product

Product in the above reaction is

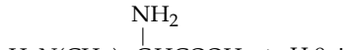
(a) $HOOC-\underset{|}{\overset{NH_2}{C}}HCH_2COOH$

(b) $HOOC-\underset{|}{\overset{NH_2}{C}}HCH_2COO^-$

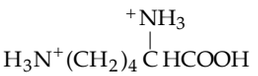
(c) $^-OOC-\underset{|}{\overset{^+NH_3}{C}}HCH_2COO^-$

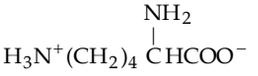
(d) Any of the three

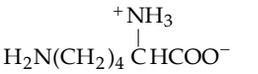
14. The principle species present in the solution of lysine,

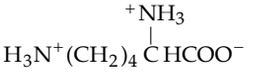


at pH 9 is

(a) 

(b) 

(c) 

(d) 

PASSAGE 2

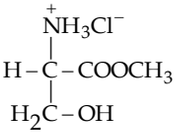
An α-amino acid 'A' has molecular formula $C_3H_7NO_3$. 'A' on treatment with methanol in presence of HCl yields 'B' $[C_4H_{10}NO_3Cl]$. 'B' on further treatment with PCl_5 yields 'C' $[C_4H_9NO_2Cl_2]$ which on acidic hydrolysis yields 'D' $[C_3H_6NO_2Cl]$. 'D' on reduction with Na(Hg) in dilute acidic medium yields alanine.

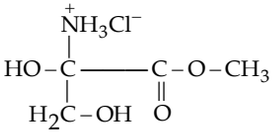
15. Compound 'A' has how many functional groups ?

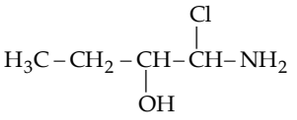
(a) 1 (b) 2

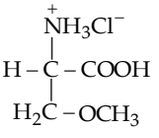
(c) 3 (d) 4

16. Compound 'B' should be

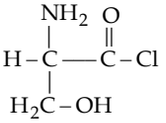
(a) 

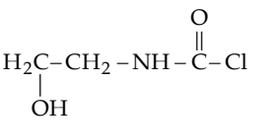
(b) 

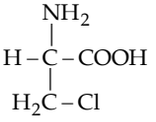
(c) 

(d) 

17. Compound 'D' is

(a) 

(b) 

(c) 

(d) (a) and (b) both are possible

Instructions for Q. 18 to Q. 20 : Following questions are Multiple Matching type Questions :

18.

	Column - I		*Column - II*
(A)	Anthranilic acid	(a)	Fuel
(B)	Sulphanilic acid	(b)	Body building
(C)	Amino acids	(c)	Diazotisation
(D)	Carbohydrates	(d)	Zwitterion

19.

	Column - I		*Column - II*
(A)	Ninhydrin	(a)	CH_2O
(B)	Sanger's reagent	(b)	HONO
(C)	Van Slyke method	(c)	Yellow coloured compound
(D)	Sorensen method	(d)	Violet colour

20. Match the chemical substances in **Column I** with type of polymers/type of bonds in **Column II**.

Column I		*Column II*	
(A)	cellulose	(p)	Natural polymer
(B)	nylon-6, 6	(q)	Synthetic polymer
(C)	protein	(r)	Amide linkage
(D)	sucrose	(s)	Glycoside linkage

Instructions for Q. 21 to 22 : Following questions are Assertion and Reasoning Type Questions :

Note : Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 5 choices (a), (b), (c), (d) and (e) out of which ONLY ONE is correct.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.

(c) Statement -1 is True, Statement-2 is False.

(d) Statement -1 is False, Statement-2 is True.

(e) Statement -1 is False, Statement-2 is False.

21. **Statement-1 :** The melting and solubility of amino acids are generally higher than that of corresponding halo acids.

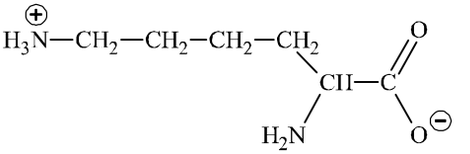
Statement-2 : The amino acids exist in zwitter ionic forms and behave like salts rather simply as amines of carboxylic acids.

22. **Statement-1 :** At the isoelectric point of an amino acid, it does not migrate under the influence of an electrifield.

Statement-2 : An amino acid at the isoelectric point exists as a zwitter ion.

Instructions for Q. 23 to 24 : Following questions are Integer Type Questions :

23. The total number of basic groups in the following form of lysine is



24. A decapeptide (Mol. Wt. 796) on complete hydrolysis gives glycine (Mol. Wt. 75), alanine and phenylalanine. Glycine contributes 47.0% to the total weight of the hydrolysed products. The number of glycine units present in the decapeptide is

EBD_7091

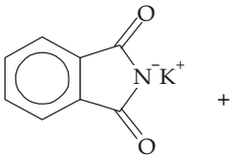
EXERCISE 23.3 (Subjective Problems)

1. Give steps involved in the synthesis of phenylalanine, $C_6H_5CH_2\underset{}{\overset{+}{N}H_3}CHCOO^-$, from toluene according to each of the following methods

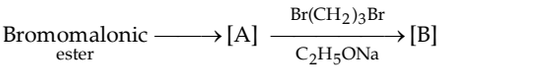
(*a*) Malonic ester synthesis (*b*) Gabriel synthesis

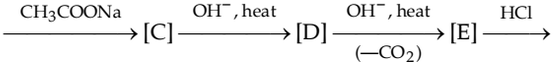
(c) Strecker synthesis (*d*) Reductive amination.

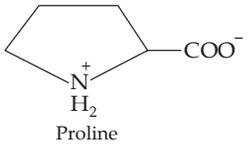
2. Supply the structures to the compounds A to E in the following reactions.



+

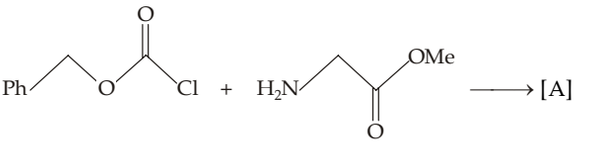


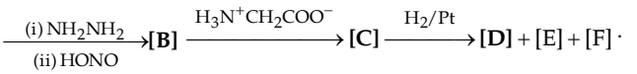




Proline

3. Identify compounds A to F in the following reactions.





4. Write down the structures obtained when each of the following amino acids is heated ?

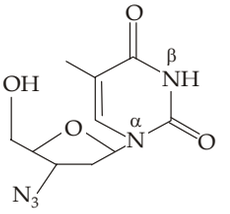
(*a*) An α-Amino acid (*b*) A β-amino acid

(*c*) A γ-amino acid (*d*) A δ-amino acid

(*e*) An ε-amino acid.

5. An organic compound A of the formula $C_5H_{10}N_2O_3$, when hydrolysed gives two compounds B and C. Compound B is optically active while C is optically inactive. However, both B and C give violet colour with nindhydrin and react with sodium nitrite in presence of HCl to give compounds D and E respectively. Assign structures from A to E and give the effect of heating on D and E.

6. Azidothymine, also known as AZT, is thedrug used for AIDS patients. It has following structure.



(*a*) Name the different functional groups present in it

(*b*) It can show lactam-lactium type of tautomerism, draw the different possible structures for this.

(*c*) Predict the relative basic/acidic character of the two N's (α- and β).

SOLUTIONS

EXERCISE 23.1

1	(b)	**6**	(b)	**11**	(d)	16	(a)	**21**	(a)	**26**	(d)	**31**	(a)
2	(b)	**7**	(a)	**12**	(c)	17	(d)	**22**	(b)	**27**	(a)	**32**	(d)
3	(b)	**8**	(d)	**13**	(a)	18	(b)	**23**	(b)	**28**	(b)	**33**	(c)
4	(c)	**9**	(c)	**14**	(d)	19	(c)	**24**	(d)	**29**	(c)	**34**	(b)
5	(a)	**10**	(a)	**15**	(c)	20	(d)	**25**	(d)	**30**	(c)		

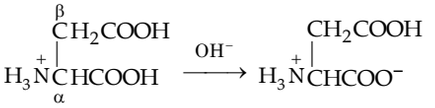
1. Although D-alanine is a constituent of a bacterial cell walls, it is not found in proteins.

2. In solid state, amino acids exist as zwitterions, which contain $—NH_3^+$ (acidic in nature) and $—COO^-$ (basic in nature).

3. $—\overset{+}{N}H_3$ increases acidity because of its electron-withdrawing inductive effect. Further, the electron-withdrawing nature of $—\overset{+}{N}H_3$ group stabilises the corresponding $—COO^-$.

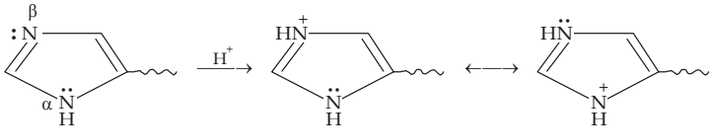
4. In strongly alkaline solution of an amino acid, all of its —COOH groups are converted into $—COO^-$. Thus a strongly alkaline solution of a monoaminodicarboxylic acid will have one $—NH_2$ and two $—COO^-$ groups, all of which are basic in nature. Further remember that a $—NH_2$ is more basic than a $–COO^-$ group.

5. Consider the parent compound of the species adding H^+ to —COO^-, and then observe the relative acidic character of the two —COOH groups keeping in mind that —$\overset{+}{N}H_3$ group is electron-withdrawing and hecne acid-strengthening.



(—COOH on α carbon is more acidic due to – I effect of $\overset{+}{N}H_3$).

6. Protonation at β–N leads to imidazolium ion, which is stabilized by two equivalent resonating structures.



Equivalent resonating structures

7. On increasing the pH by adding an alkali ; H^+ will be lost from —COOH.

8. Every amino acid has at least one basic and one acidic group, so it acts as an amphoteric compound (ampholyte). An amino acid may have one —NH_2 and one —COOH group (neutral amion acids), or two —NH_2 and one —COOH group (basic amino acids), or one —NH_2 and two —COOH groups (acidic amino acids). In amino acids, —$\overset{+}{N}H_3$ acts as an acid while —COO^- acts as a basic group.

9. At the given pH (6) of the solution, alanine (pI = 6.0), exists as a dipolar ion while arginine (pH = 10.2) exists as a cation. Hence on passing an electric current, alanine will not migrate to any electrode, while arginine will migrate to cathode.

10. Every amino acid exists exclusively as dipolar ion when the pH of the solution is equal to its isoelectric point (pI), hence at this pH it does not migrate to either electrode, while at other pH, an amino acid migrates either to cathode or to anode depending upon its pI. Thus at pH 9.60, amino acid with pI 5.40 will exist as an anion and migrate to anode ; while that with pI 9.60 will not migrate to any electrode.

11. Glycine has only two C's ; in Strecker synthesis one of which is supplied by CN^- so the second must be supplied by an aldehyde having one C only *i.e.* HCHO or its precursor CH_3OH ($CH_3OH \longrightarrow HCHO$).

12. The resulting compound is an α-amino acid and the reagent used for its synthesis are NH_3 and H_2/catalyst, so this is an example of preparation of α-amino acid by reductive amination for which α-keto acids are starting compounds.

13. Two molecules of an α-amino acid will form only one dipeptide, recall that four different dipeptides are formed when two α-amino acids are different.

14. In Gly-Ala, glycine is the N-terminal anino acid and alanine is C-terminal amino acid while opposite is the case with Ala-Gly. A dipeptide (peptide formed from two molecules of an α amino acid) has only one peptide bond. As mentioned above the number of dipeptides formed by two different amino acids is four.

15. Total weight of Fe in a molecule of haemoglobin = 56 × 4 = 224 g
0.35 g of Fe is present in 100 g of haemoglobin

224 g of Fe is present in $\frac{100}{0.35} \times 224 = 6.4 \times 10^4$ g haemoglobin.

17. (d) The concerned chemical reactions are

(i) $\underset{64\,kg}{CaC_2} + 2H_2O \rightarrow Ca(OH)_2 + \underset{\text{Ethyne, 26kg}}{C_2H_2}$ (ii) $C_2H_2 + H_2 \rightarrow \underset{\text{Ethylene, 28 kg}}{C_2H_4}$ (iii) $\underset{\substack{n\times 28\,kg\\ \text{or } 28\,kg}}{nC_2H_2} \rightarrow \underset{\substack{n\times 28\,kg\text{ polythene}\\ \text{or } 28\,kg}}{[-CH_2-CH_2-]_n}$

Thus 64 kg of CaC_2 gives 26 kg of acetylene which in turn gives 28 kg of ethylene whose 28 kg gives 28 kg of the polymer, polythene.

22. (b) Nylon-66 is a polyamide, hence it has only –CONH– linkage and no –COO– linkage

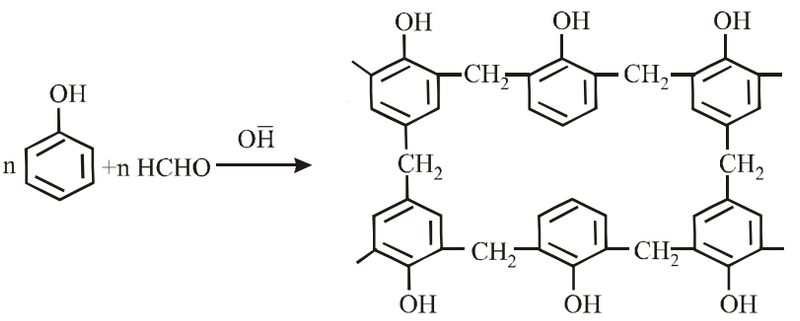
27. (a) Polymerisation starts either by condensation or addition reactions between monomers

28. (b) Nylon is a polyamide polymer

29. (c) Nylon is a general name for all synthetic fibres forming polyamides.

30. (c) Teflon is polymer of $CF_2 = CF_2$.

31. (a) Bakelite is formed by the reaction of formaldehyde (HCHO) and phenol so the correct answer is (1).



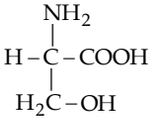
Bakelite

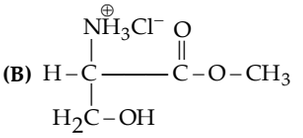
EXERCISE 23.2

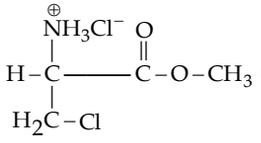
>1 CORRECT OPTION	1	(a, b, c)	2	(a, b, d)	3	(b, c)
	4	(a,b,c)	5	(a,b)	6	(a,b,d)
	7	(a,c,d)	8	(a,b,c)	9	(a, b, c, d)
PASSAGE 1	10	(d)	11	(d)	12	(b)
	13	(c)	14	(b)		
PASSAGE 2	15	(c)	16	(a)	17	(c)
MATCH THE FOLLOWING	18	(A)-c ; (B)-c, d ; (C)-b, c, d ; (D)-a				
	19	(A) - d, (B) - c, (C) - b, (D) - a				
	20	(A) - a, d, (B) - b, c, (C) - a, c, (D) - d				
A/R	21	(a)	22	(a)		
INTEGER	23	2	24	6		

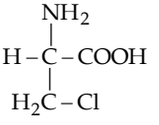
4. (a,b,c)
5. (a,b)
6. (a,b,d) Polythene is a linear polymer
7. (a,c,d) Nylon is a condensation polymer
8. (a,b,c) Glyptal is an example of a step growth polymer
9. (a, b, c, d)

Sol. (10-14) :

(A) 

(B) 

(C) 

(D) 

20. **(A)-(a, d) :** Cellulose is a natural polymer and has a $C_1 - C_4$ β-glycosidic linkage.
(B)-(b, c) : Nylon-6, 6 is a synthetic polymer of hexamethylenediamine and adipic acid and has amide linkages.
(C)-(a, c) : Proteins are natural polymers of a amino acids joined by amide linkages (peptide bonds).
(D)-(d) : Sucrose is a disaccharide of α-D glucose and β-D-fructose and has an α, β-glycosidic linkage.

22. (a) Zwitter ion is neutral, so it doesn't migrate under the influence of electric field.

23. **2.**
The basic groups in the given form of lysine is NH_2 (not $\overset{\oplus}{N}H_3$) and CO_2^-.

24. **6**
Molecular weight of decapeptide = 796 g/mol
Total bonds to be hydrolysed = (10 – 1) = 9 per molecule
Total weight of H_2O added = 9 × 18 = 162 g/mol
Total weight of hydrolysis product = 796 + 162 = 958 g
Total weight % of glycine (given) = 47%

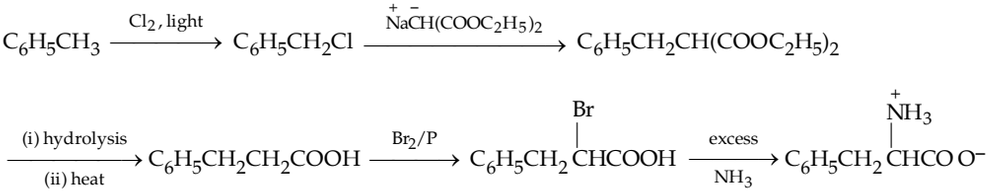
$$\text{Total weight of glycine in product} = \frac{958 \times 47}{100}\text{g} = 450\text{g}$$

Molecular weight of glycine = 75 g/mol

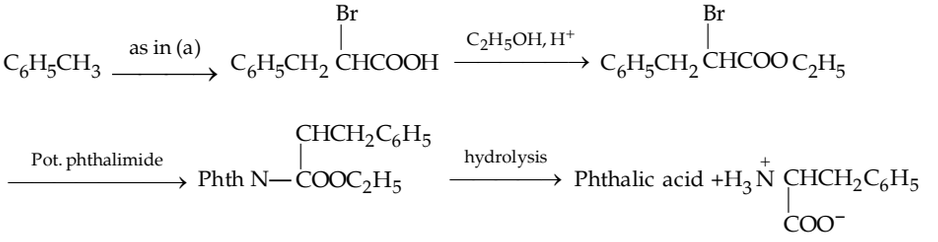
$$\text{Number of glycine molecule} = \frac{450}{75} = 6$$

EXERCISE 23.3

1. In such case recall the starting material, required for preparing phenylalanine in each of the method and then apply your mind for preparing that starting material from toluene.
(*a*) In malonic ester synthesis, the alkyl halide is treated with malonic ester to form α-halogeno acid.



(*b*) In Gabriel phthalimide synthesis, α-halogeno ester is treated with phthalimide.



(c) In Strecker synthesis, we require aldehyde ($C_6H_5CH_2CHO$) as the starting compound which can be obtained from toluene as below.

$$C_6H_5CH_3 \xrightarrow{Cl_2,\ light} C_6H_5CH_2Cl \xrightarrow[(ii)\ H_3O^+]{(i)\ NaCN} C_6H_5CH_2COOH \xrightarrow{SOCl_2} C_6H_5CH_2COCl \xrightarrow{LiAlH(OBu\text{-}tert)_3}$$

$$C_6H_5CH_2CHO \xrightarrow[NH_4^+]{CN^-} C_6H_5CH_2\underset{\displaystyle NH_2}{\underset{|}{C}}HCN \xrightarrow{H_3O^+} C_6H_5CH_2\underset{\displaystyle \overset{+}{N}H_3}{\underset{|}{C}}HCO\,O^-$$

(*d*) In reductive amination, the starting compound is α-keto acid, $C_6H_5CH_2COCOOH$, which can be obtained from toluene as follows.

$$C_6H_5CH_3 \xrightarrow{as\ in\ (c)} C_6H_5CH_2COOH \xrightarrow{C_2H_5OH,\ H^+} C_6H_5CH_2COOC_2H_5 \xrightarrow[(Dieckmann\ reaction)]{(COOC_2H_5)_2/C_2H_5ONa} C_6H_5\underset{\displaystyle CHCOOC_2H_5}{\underset{|}{C}}OCOOC_2H_5$$

$$\xrightarrow{H^+} C_6H_5\underset{\displaystyle CO\,COOH}{\underset{|}{\overset{\beta}{C}HC}}OOH \xrightarrow[(\beta\text{-keot acids eliminate } CO_2)]{heat} C_6H_5CH_2COCOOH \xrightarrow{NH_3,\ H_2/Pd} C_6H_5CH_2\underset{\displaystyle \overset{+}{N}H_3}{\underset{|}{C}}HCO\,O^-$$

2.

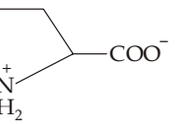
$$Phth{-}N^-K^+ + Br\underset{\displaystyle COOC_2H_5}{\underset{|}{C}}H\underset{\displaystyle COOC_2H_5}{\underset{|}{}} \xrightarrow{C_2H_5ONa} Phth{-}N\underset{\displaystyle COOC_2H_5}{\underset{|}{C}}H\underset{\displaystyle COOC_2H_5}{\underset{|}{}}$$

[A]

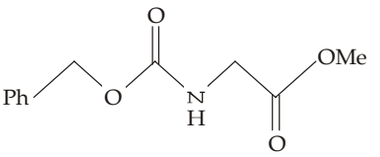
$$Phth{-}N\underset{\displaystyle COOC_2H_5}{\underset{|}{C}}H_2CH_2CH_2Br\ ,\quad Phth{-}N\underset{\displaystyle COOC_2H_5}{\underset{|}{C}}H_2CH_2CH_2OCOCH_3\ ,\quad Phthalic\ acid + H_2N\underset{\displaystyle COO^-}{\underset{|}{C}}H_2CH_2CH_2OH$$

[B] [C] [D]

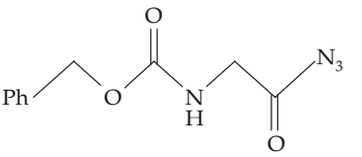
$$H_3\overset{+}{N}\underset{\displaystyle COO^-}{\underset{|}{C}}HCH_2CH_2CH_2OH\ ;\qquad \left[H_3\overset{+}{N}\underset{\displaystyle COO^-}{\underset{|}{C}}HCH_2CH_2CH_2Cl\right] \xrightarrow{-HCl}$$



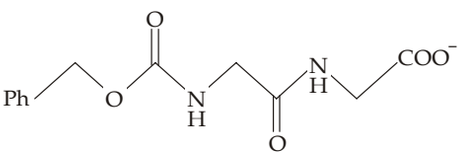
3.



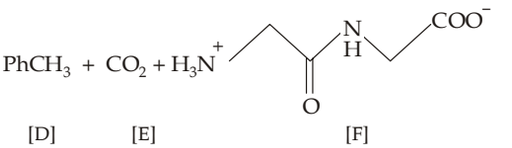
[A]



[B]



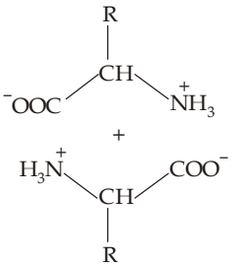
[C]



[D] [E] [F]

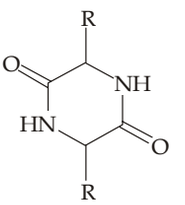
4. (*a*) α-Amino acids on heating undergo *intermolecular cyclization* to form diketopiperazine :
(*b*) β-amino acids on heating undergo deamination to form α, β-unsaturated carboxylic acids (in the form of ammonium salt).

(*a*)

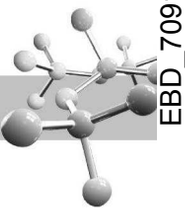


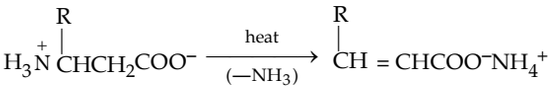
2 Moles of an a-amino acid

$\xrightarrow[(-2H_2O)]{heat}$

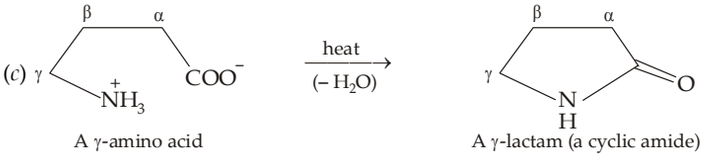


Diketopiperazine
(a cyclic diamide)

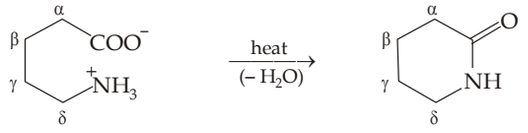


(*b*) 

A β-amino acid

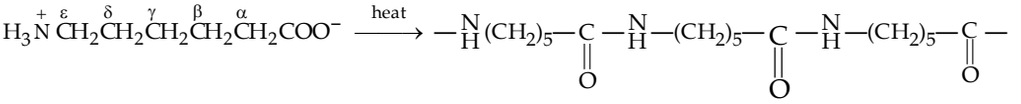
(*c*) 

A γ-amino acid A γ-lactam (a cyclic amide)

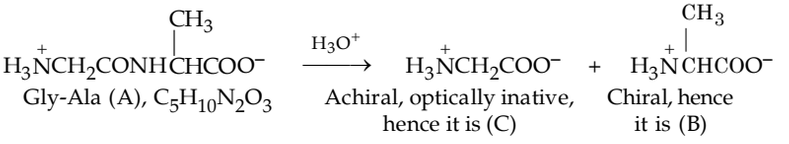
(*d*) 

A δ-amino acid A δ-lactam (a cyclic amide)

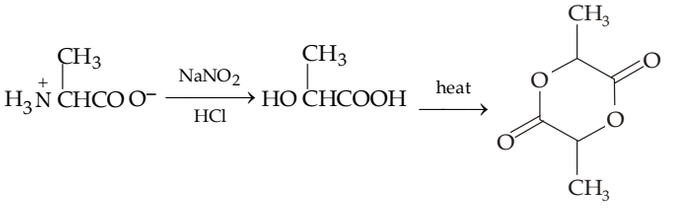
(*e*) γ- and δ- amino acids on heating undergo *intramolecular cyclization* to form stable 5- and 6-membered rings respectively. However, intramolecular cyclization of the ε-amino acids would give a seven-memebered ring which is formed with difficulty. Hence the more facile intermolecular reaction occurs, now since the substrate is bifunctional, polymerization occurs.



5. Since compounds B and C (hydrolysis products of the compound A) give purple colour with ninhydrin, these must be amino acids and hence the compound A is a dipeptide. Further since the dipeptide A is having 5 C's, its two constituent amino acids should be glycine (having 2 C's) and alanine (having 3 C's). Thus compound A should be Gly-Ala of Ala-Gly both of which explains all the given reactions.



Gly-Ala (A), $C_5H_{10}N_2O_3$ Achiral, optically inative, hence it is (C) Chiral, hence it is (B)

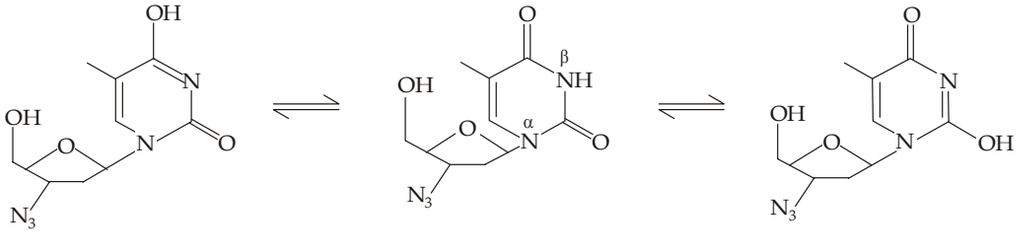


(B) (D)

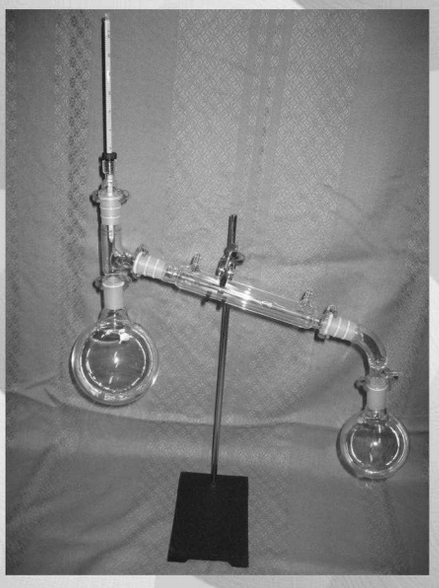


(C) (E)

6. (*a*) 1° alcoholic, azide, cyclic ether, lactam, ketonic group

(*b*) 

(*c*) α-N is basic, while β-NH having carbonyl group (electronegative group) on both sides is acidic in nature.



24

Practical Organic Chemistry

CHAPTER HIGHLIGHTS

24.1 Purification of Organic Compounds

24.2 Qualitative Analysis of Elements

24.3 Quantitative Analysis of Elements (Estimation of Elements)

24.4 Determination of Molecular Formula

EXERCISE

SOLUTIONS

24.1 Purification of Organic Compounds

In order to study the properties of organic compounds, we require pure compound which in turn can be achieved by any of the following methods.

1. **Crystallisation.** This method is applied for the purification of solid organic compounds. It is based on the fact that certain organic compounds dissolve partly in a solvent (*e.g.* water, alcohol, ether, benzene, acetone, etc.) and their solubility increases with increase in temperature. The filtrate (containing soluble organic compound) in cooled, when organic compound crystallises out ; sometimes crystal formation is initiated by adding a substance from outside, this process is known as **seeding**.

2. **Fractional crystallisation.** This method is used for the purification of a mixture of two components which are soluble in the same solvent but to different extents, *i.e.* one is more soluble than the other. When the hot saturated solution of such mixture is cooled, the less soluble component crystallises out earlier than the more soluble component. The two components are separated and process is repeated several times to get the two components in their respective pure form.

3. **Sublimation.** Certain organic substances change directly from solid to vapour state without passing through the liquid state and vice versa. This process, known as sublimation, is one of the important methods for purifying and separating *organic substances which sublime on heating* (like camphor, naphthalene, anthracene, benzoic acid, phthalic anhydride, ammonium chloride, iodine etc.) *from nonvolatile impurities.*

   Sublimation is based upon the fact that vapour pressure of substances which sublime becomes equal to the atmospheric pressure much before their respective melting points, hence liquid state escapes.

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4. **Distillation.** This method is based on the principle that at a constant pressure every pure liquid boils at a definite temperature, called its *boiling point.* This process is applied for the purification and separation of (*i*) liquids which boil, without decomposition, at atmospheric pressure from non-volatile impurities ; (*ii*) a mixture of two liquids whose boiling points differ by 30–50 K.

5. **Fractional distillation.** This method is used for the purification and separation of a mixture of two volatile liquids whose boiling points differ only by 10–15 K. The process involves the use of specially designed columns called *fractionating columns.* Common examples are (*i*) separation of acetone (b.p. 325 K) from methanol (b.p. 338 K), (*ii*) separation of petroleum into various fractions like gasoline, kerosene oil, diesel oil etc.

6. **Vacuum distillation** (*Distillation under reduced pressure*). This method is used for the purification of those liquids which decompose before their boiling points. We know that boiling point of a liquid is a point (temperature) at which its vapour pressure is equal to the atmospheric pressure, a liquid can thus be made to boil below its boiling point by reducing the pressure in the vicinity of the liquid. This is the principle applied in vacuum distillation. For example, under atmospheric pressure (760 mm) glycerol boils at 260°C with some decomposition, however it may be boiled at 180°C, without any decomposition, under reduced pressure (12 mm). Since boiling under reduced pressure, *i.e.* at lower temperature than usual, saves a lot of fuel, it is of great importance in industries, *e.g.* for the concentration of juice in sugar factories.

7. **Steam distillation** (*Co-distillation with water*). This method is used for the purification and separation of the organic solid or liquid compounds which are *immiscible with water, volatile in steam, contain non-volatile impurities and have high vapour pressure at 373 K* (boiling point of water). It is especially useful to purify essential oils and turpentine oil obtained from plants.

   Theory of steam distillation. We know that at the boiling point,

   Vapour pressure of the liquid = Atmospheric pressure (P).

   Let p_1 and p_2 be the vapour pressuer of water vapour (steam) and the liquid respectively at the distillation temperature, then at the boiling point,

   $$p_1 + p_2 = P \quad \text{or} \quad p_2 = P - p_1$$

   From the above relation, it is evident that when a liquid boils in the presence of steam, the vapour pressure of the liquid (p_2) is less than the atmospheric pressure (P), *i.e.* the substance is boiling under somewhat reduced pressure. Hence it will be boiling at a temperature lower than its usual boiling point and also below 373 K. For example, aniline which normally boils at 457 K boils in steam at 371.5 K. *Hence this process can be regarded as analogous to distillation under reduced pressure (here steam reduces the atmospheric pressure*).

   The relative amounts of the organic substance and water in the distillate depend upon their molecular weights and vapour pressures at the boiling point. In general,

   $$\frac{\text{Wt. of water distilled}}{\text{Wt. of susbtance distilled}} = \frac{\text{Mol. wt. of } H_2O \times p_1}{\text{Mol. wt. of substance} \times p_2}.$$

   The process of steam distillation can also be used to separate a mixture of two organic substances one of which is steam volatile while the other is not, *e.g.* when steam is passed through a mixture of *o*– and *p*– nitrophenols, vapours of *o*-nitrophenol are carried by steam leaving behind *p*-nitrophenol in the distillation flask.

8. **Azeotropic distillation.** Azeotropes are constant boiling mixtures, *i.e.* they distil off at a fixed temperature and without any change in composition. The most familiar example of azeotropic mixture is rectified spirit which contains 95.87 % ethanol and 4.13% water by weight and boils at 351.1 K. Since azeotropes distil off without change in composition, their components can't be separated by fractional distillation, hence these are separated by a special type of distillation called **azeotropic distillation.** Let us illustrate azeotropic distillation by taking example of separation of ethyl alcohol and water from rectified spirit. A suitable amount of benzene is added to the rectified spirit. Benzene forms two different azeotropes with the constituents of rectified spirit.

   (*a*) First of all it takes up all water present and some alcohol to form a ternary azeotrope. This azeotrope consists of 7.4% water, 74.1% benzene, and 18.5% alcohol. It distils at 337.8 K.

   (*b*) Remaining benzene takes up remaining alcohol and forms a binary azeotrope. This azeotrope consists of 67.6 % benzene and 32.4% alcohol. It distils at 341.2 K.

   Thus the mixture of rectified spirit and benzene consists of mainly three parts : (*i*) a ternary azeotrope, (*ii*) a binary azeotrope, and (*iii*) remaining pure ethyl alcohol. Since each part distils at different temperatures, these are separated by fractional distillation. The first fraction, *i.e.* ternary azeotrope, distils at 337.8 K, the second fraction, *i.e.* binary azeotrope at 341.2 K and the last fraction, *i.e.* pure ethyl alcohol at 351 K.

9. **Chromatography.** It is a modern and fast developing technique employed for the separation and purification of a complex *mixture of organic compounds especially carbohydrates, amino acids, plant pigments, terpenoids, vitamins, hormones, etc.* It was discovered by a *Russian botanist, Tswett* in 1906 and later developed by Kuhn, Winterstein and Karrer.

Chromatography is based on the principle of selective adsorption or distribution of the various components of a mixture between *two phases, one fixed and the other moving.* In general, the mixture to be separated is dissolved in a moving phase (liquid or gas) and passed over the fixed phase (solid or liquid). Different components are adsorbed (or distributed) at different levels of the fixed phase. When the fixed phase is solid, the basis of separation is *adsorption,** while when the fixed phase is liquid the basis of separation is *partition.*

Thus *chromatography is the technique of separating the components of a mixture in which separation is done by the differential movement of individual components through a stationary phase under the influence of a mobile phase.*

Classification of chromatography. On the basis of the principle operating in the technique, chromatography can broadly be classified into following two classes.

(*i*) *Adsorption or column chromatography*. In this technique, the stationary phase is solid while the mobile phase is liquid or gas. Thus this can further be divided into two types depending upon the nature of the mobile phase, *i.e. liquid-solid chromatography* (when mobile phase is liquid) and *gas-solid chromatography* (when mobile phase is gas). *Ion exchange chromatography,* using ion-exchange resins as the stationary phase, is also a type of adsorption chromatography. *Thin layer chromatography* (TLC) is a special case of absorption chromatography in which a glass strip coated with a thin layer of the adsorbent is used as a stationary phase.

(*ii*) *Partition chromatography.* In this technique, the stationary phase is a liquid supported on an inert solid while the mobile phase may be a liquid (*liquid-liquid partition chromatography*) or a gas (*gas-liquid partition chromatography*). Paper chromatography is the most important example of partition chromatography.

10. Chemical methods. Chemical methods of separation depend upon the nature of the functional group present in the components. Hence these can be applied to solid as well as liquid compounds. A chemical method can be applied only when one of the components of the mixture is soluble in a particular solvent while the other is insoluble in the same solvent. Few such examples are given below.

(*a*) ***Caboxylic acids,*** being soluble in $NaHCO_3$, can be separated from compounds which do not react with sodium bicarbonate solution like amines, nitro compounds, aldehydes, ketones, hydrocarbons, certain phenols etc.

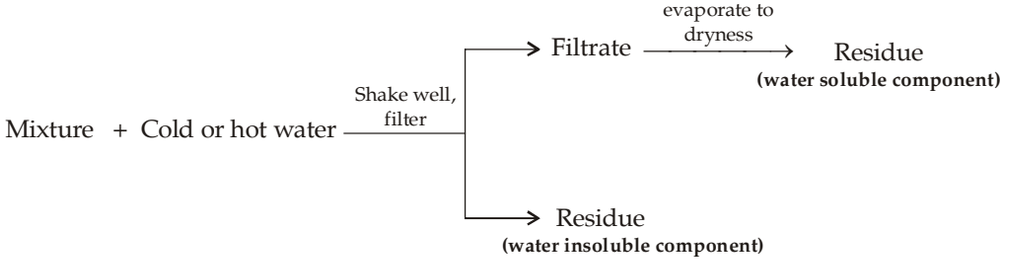
(*b*) ***Phenols,*** being soluble in strong alkalies like NaOH or KOH, can be separated from compounds which do not react with NaOH or KOH like amines, nitro compounds, aldehydes, ketones, hydrocarbons etc.

(*c*) ***Amines,*** being basic, are soluble in dil HCl. Hence these can be separated from compounds which do not react with HCl like carboxylic acids, phenols, aldehydes, ketones, hydrocarbons etc.

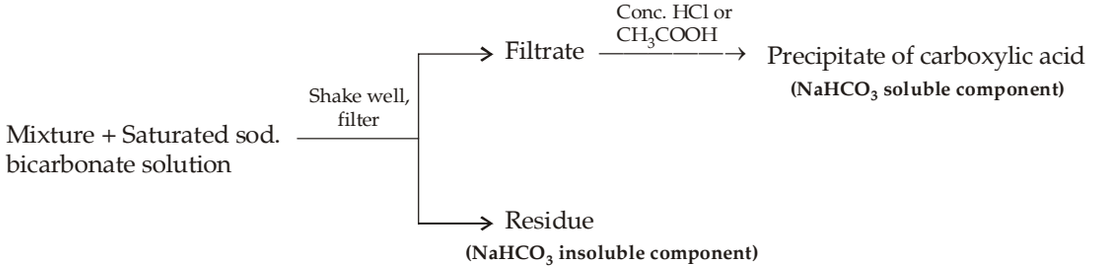
(*d*) ***Carbohydrates***, being insoluble in ether, can be separated from most of other organic compounds which are soluble in ether.

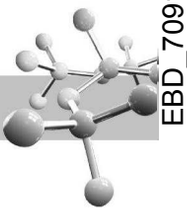
Schemes for separation of some binary mixtures are sketched below.

1. ***Separation with water.*** (Applied when one of the components is water soluble like phenols, certain carboxylic acids, alcohols etc.)

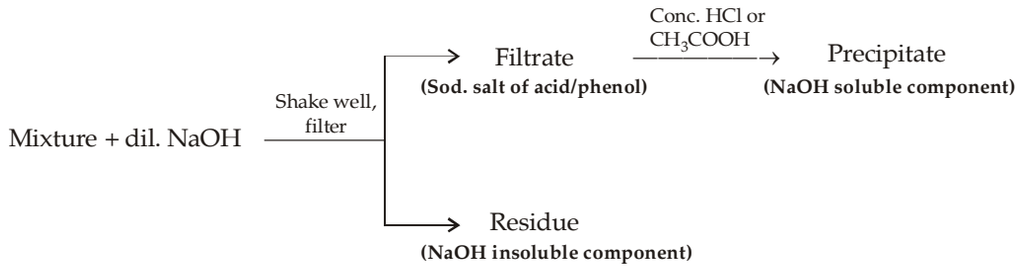


2. ***Separation with sodium bicarbonate.*** (Applied when one of the components is a carboxylic acid).

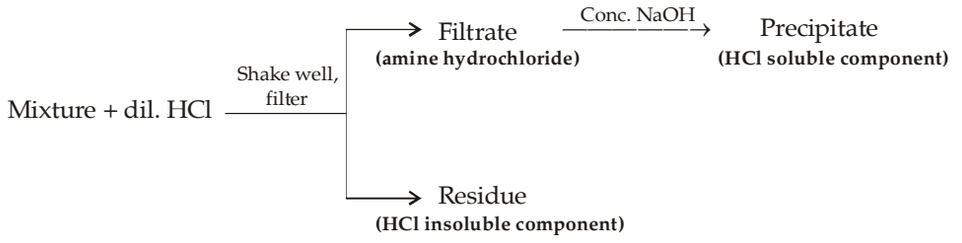




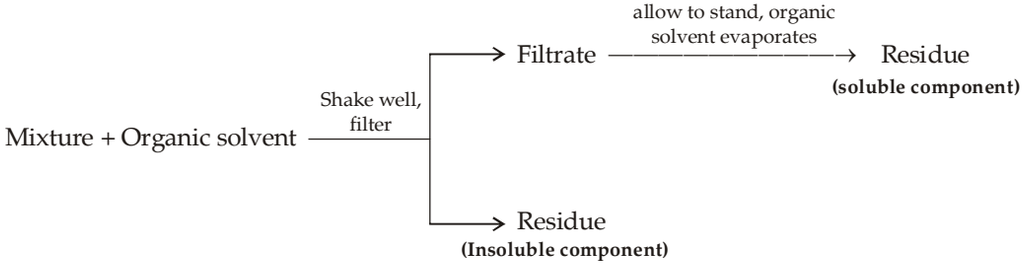
3. ***Separation with sodium hydroxide.*** (Applied when one of the components is a phenol)



4. ***Separation with hydrochloric acid.*** (Applied when one of the components is an amine).



5. ***Separation with organic solvents*** *like ether, benzene, alcohol, etc.* (Applied when only one of the components is soluble in a particular solvent)



TEST YOUR UNDERSTANDING - 24.1

1. Which method should be used for the purification of a liquid having non-volatile impurities ?

2. How will you separate a mixture of two organic compounds having different solubilities in the same solvent ?

3. What type of compounds are purified by sublimation ?

4. Suggest a method to purify

(*a*) kerosene containing water.
(*b*) iodine containing traces of common salt.
(*c*) a mixture of *o*– and *p*–nitrophenols.
(*d*) a substance which starts decomposing much below its b.p.
(*e*) a mixture of two liquids whose boiling points differ very much.
(*f*) a mixture of two liquids whose boiling points differ nearly by 10°C.

5. How will you purify an impure sample of (*i*) camphor, and (*ii*) aniline.

6. Define the terms chromatogram and elution.

7. Mention the reagent which can be used for separating each of the following mixtures.

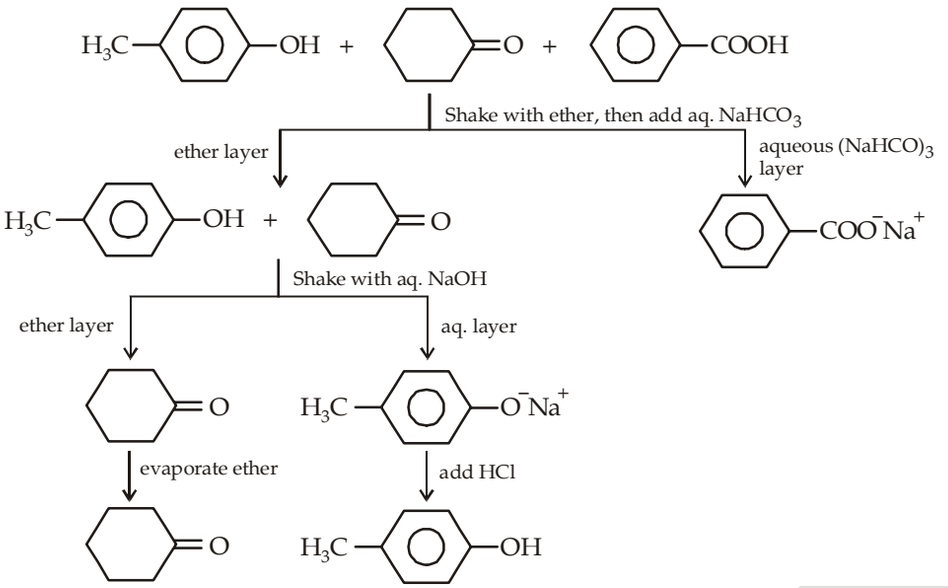
(*a*) Diphenyl and phenylacetic acid
(*b*) Naphthalene and *p*-bromobenzoic acid
(*c*) Anthracene and *p*-anisidine
(*d*) Mandelic acid and glucose
(*e*) α-Nitronaphthalene and lactose
(*f*) *p*-Hydroxybenzoic acid and *p*-aminobenzoic acid

ILLUSTRATIVE EXAMPLES

Example 1 :

Give a roadmap figure showing the separation of *p*-cresol, benzoic acid and cyclohexanone.

Solution :



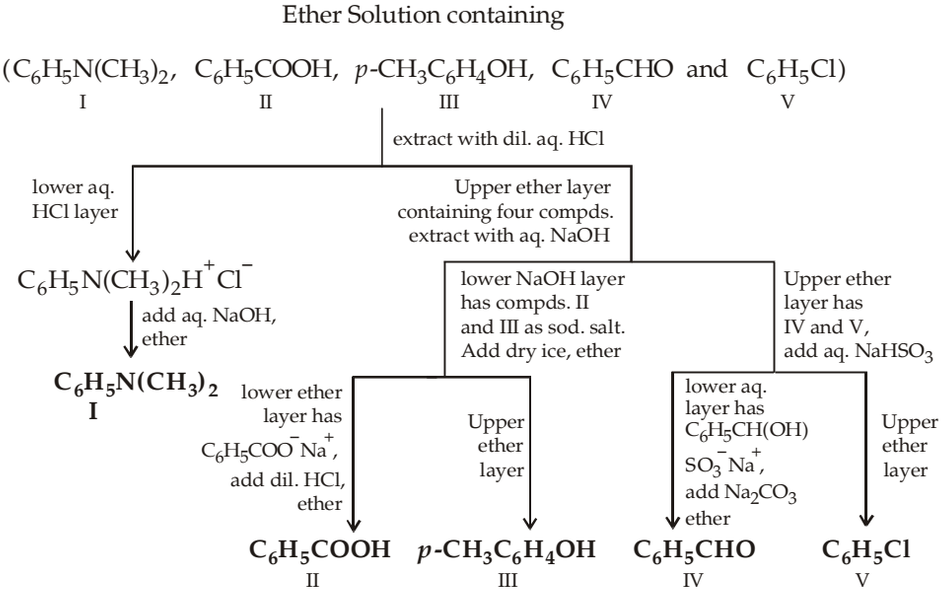
Example 2 :

Give a schematic diagram for the separation of the following water insoluble compounds present in a mixture.

C_6H_5Cl, C_6H_5CHO, C_6H_5COOH, *p*-$CH_3C_6H_4.OH$ and $C_6H_5N(CH_3)_2$

Solution :

The components can be separated on the basis of their specific reactivity with certain reagents, e.g. only $C_6H_5N(CH_3)_2$ reacts with dil. aq. HCl, only C_6H_5CHO reacts with $NaHSO_3$, phenols and –COOH react with aq. NaOH, only –COOH react with $NaHCO_3$.

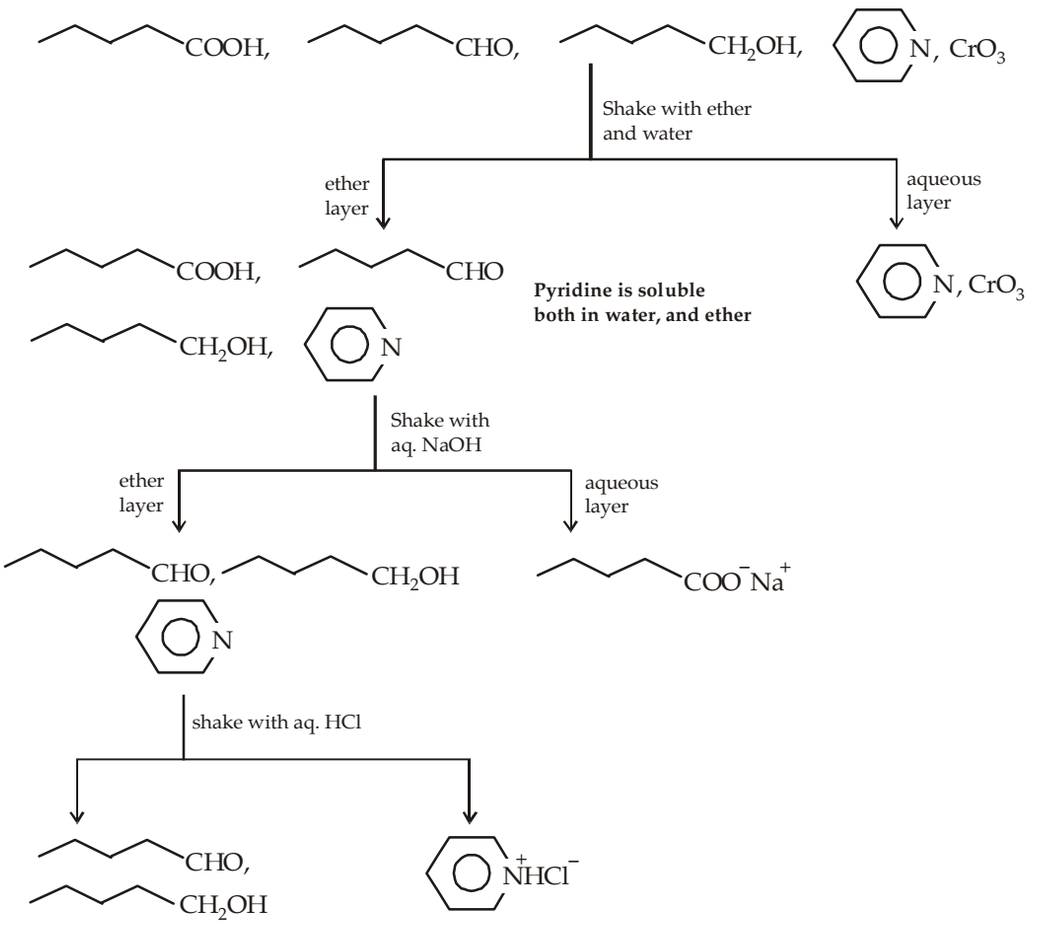


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Example 3 :

1-Pentanol is oxidised by PCC mainly to 1-pentanal. However, some overoxidation product, 1-pentanoic acid, although in very small amount is also formed. Give a scheme for separating the three organic compounds by acid-base extractions from each other.

Solution :



These two can't be separated by acid-base extraction. However distillation can be used to separate : alcohol has higher b.p. (137°C) than aldehyde (102°C)

24.2 Qualitative Analysis of Elements

1. **Detection of carbon and hydrogen.** Since all organic compounds contain carbon, and majority of them also contain hydrogen, in practice carbon and hydrogen are never detected (tested). However, if necessary these can be detected by heating a small quantity of the given *dry* organic compound with *dry* cupric oxide. Carbon and hydrogen, present in the compound,

$$2\,CuO + C \xrightarrow{heat} 2\,Cu + CO_2 \;;\; CuO + 2H \xrightarrow{heat} Cu + H_2O$$

are oxidised to CO_2 and H_2O respectively which in turn can be tested by their following reactions.

(*a*) Carbon dioxide turns lime water milky

$$\underset{\textbf{(Colourless)}}{Ca(OH)_2} + \underset{\text{(From C)}}{CO_2} \longrightarrow \underset{\textbf{(Milky)}}{CaCO_3\downarrow} + H_2O$$

(*b*) Water turns anhydrous copper sulphate (white in colour) to hydrated copper sulphate (blue in colour)

$$\underset{\textbf{(White)}}{CuSO_4} + \underset{\text{(From H)}}{5H_2O} \longrightarrow \underset{\textbf{(Blue)}}{CuSO_4.5H_2O}$$

2. **Detection of nitrogen, sulphur and halogens.** Nitrogen, sulphur and halogens are tested from the sodium fusion extract of the organic compound, which is more commonly known as **Lassaigne's extract.** For preparing Lassaigne's extract, a small quantity of the organic compound is fused with sodium metal in a fusion tube. The red hot tube is broken in distilled water, boiled and filtered. The filtrate is known as *Lassaigne's extract* or *sodium extract.*

Chemical reactions involved in the formation of Lassaigne's extract.

(*i*) When only N is present $Na + C + N \longrightarrow NaCN$

(*ii*) When only S is present $2\,Na + S \longrightarrow Na_2S$

(*iii*) When both N and S are present $Na + C + N + S \longrightarrow NaCNS$

(*iv*) When halogen is present $Na + X \longrightarrow NaX$

Lassaigne's extract, so prepared, is used for testing the presence of N, S and halogens.

(*a*) *Detection of nitrogen.* Generally, the Lassaigne's extract is alkaline in nature due to reaction of unreacted sodium with water ($2Na + 2H_2O \rightarrow 2NaOH + H_2$). If it is not so, it is made alkaline by adding sodium hydroxide. Now the extract is boiled with ferrous sulphate solution, and then acidified with dil. H_2SO_4 and dil. HCl, appearance of ***green* or *blue colour*** *confirms the presence of nitrogen.*

$$FeSO_4 + 2NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$$

$$Fe(OH)_2 + 6NaCN \longrightarrow \underset{\text{Sodium ferrocyanide}}{Na_4[Fe(CN)_6]} + 2NaOH$$

$$\underset{\substack{\text{(Formed by oxid. of } Fe^{2+} \text{ on} \\ \text{boiling in presence of } O_2)}}{4Fe^{3+}} + 3Na_4[Fe(CN)_6] \longrightarrow \underset{\substack{\text{Ferric ferrocyanide} \\ \textbf{(Prussian blue)}}}{Fe_4[Fe(CN)_6]_3} + 12\,Na^+$$

Sometimes, Fe^{3+} ions are provided by adding ferric chloride solution.

A less important test for nitrogen given by certain nitrogenous compounds is evolution of NH_3 by *heating of the compound with soda lime* (NaOH + CaO).

$$CH_3CONH_2 + NaOH \longrightarrow CH_3COONa + NH_3\uparrow$$

However, this test is not given by compounds containing —NH_2, —NO_2 and —N = N— groups.

(*b*) *Lassaigen's test for sulphur.* Sodium sulphide, if present in Lassaigne's extract can be detected by following tests.

(*i*) It gives purple colour with sodium nitroprusside solution.

$$Na_2S + \underset{\text{Sodium nitroprusside}}{Na_2[Fe(NO)(CN)_5]} \longrightarrow \underset{\substack{\text{Sodium thionitroprusside} \\ \textbf{(purple colour)}}}{Na_4[Fe(CN)_5NOS]}$$

(*ii*) It gives black precipitate with lead acetate solution.

$$Na_2S + (CH_3COO)_2Pb \longrightarrow 2\,CH_3COONa + \underset{\textbf{Black ppt}}{PbS\downarrow}$$

(*c*) *Lassaigen's test for nitrogen and sulphur, when present together*. In case the compound contains both N and S, sodium thiocyanate formed during fusion of organic compound with metallic sodium reacts with Fe^{3+} ions to form blood red coloured, ferric thiocyanate.

$$Fe^{3+} + \underset{\text{Sod. thiocyanate}}{3NaCNS} \longrightarrow \underset{\text{Ferric thiocyanate}}{Fe(CNS)_3} + 3Na^+$$

However, note that the absence of blood red colouration does not necessarily mean that sulphur is absent because in presence of excess of sodium, sodium thiocyanate decomposes to form sodium cyanide and sodium sulphide.

$$NaCNS + 2Na \longrightarrow NaCN + Na_2S$$

(*d*) *Lassaigne's test for halogens.* A small portion of the sodium fusion extract* is acidified with dil. nitric acid and then treated with silver nitrate solution. If a precipitate is formed, it indicates the presence of a halogen ; the colour of precipitate, in turn, indicates the nature of halogen, *viz.*

(*i*) white colour soluble in NH_4OH indicates chlorine.

(*ii*) pale yellow colour sparingly soluble in NH_4OH indicates bromine and

(*iii*) yellow colour insoluble in ammonia indicates iodine.

$$\underset{\substack{\text{Sod. halide} \\ \text{(Formed in Lassaigne's filtrate)}}}{NaX} + AgNO_3 \longrightarrow \underset{\text{Silver halide}}{AgX\downarrow} + NaNO_3$$

---

* In the preparation of sodium fusion extract used for the detection of halogens, fusion with sodium may be replaced by quicklime CaO, or a mixture of Na_2CO_3 and Zn dust or a mixture of Na_2CO_3 and sugar. These will avoid the formation of NaCN or Na_2S (in case N or S are present) hence step involving boiling with conc. HNO_3 (for the decomposition of NaCN or Na_2S) will be avoided.

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Note. Function of nitric acid. In case the compound under investigation is found to contain nitrogen and/or sulphur, the latter two must be destroyed, prior to treatment with $AgNO_3$, by boiling the extract with concentrated nitric acid which decomposes sodium cyanide and sodium sulphide (formed during sodium fusion) as volatile HCN and H_2S.

$$NaCN + HNO_3 \xrightarrow{boil} NaNO_3 + HCN \uparrow$$

$$Na_2S + 2HNO_3 \xrightarrow{boil} 2NaNO_3 + H_2S \uparrow$$

If NaCN and Na_2S are not removed, they will be forming precipitate on the addition of silver nitrate. The precipitate of AgCN (white) and Ag_2S (black) will make hindrance in the judgement of silver halide precipitate.

$$NaCN\ (Na_2S) + AgNO_3 \longrightarrow AgCN \downarrow + (Ag_2S\downarrow)$$

Copper wire test or Beilstein's test. A small quantity of the organic compound is taken on the flattened end of the pre-cleaned* copper wire. This end is now inserted in the Bunsen flame—if a *green colour* is developed (due to the formation of volatile cupric halides) in the flame, it indicates the presence of halogen in the compound. This test, although very sensitive, is not always reliable because some compounds containing no halogen (*e.g.* urea, thiourea, organic acids, pyridine, etc.) also respond this test due to the formation of volatile cupric cyanide. Therefore, we can say that a *negative Beilstein's test is the surety for the absence of halogens.*

Chloroform layer test for halogens. In case more than one halogen is present, these may be detected as in inorganic qualitative analysis with the help of chloroform (or carbon disulphide) and chlorine water. Moreover, this test is not interferred even in presence of N and/or S in the compound.

In practice, a small portion (about 2 ml.) of the sodium fusion extract is acidified with dilute HNO_3 or H_2SO_4 ; 1 c.c. of chloroform, carbon disulphide or carbon tetrachloride is added to it and the contents are now shaken with excess of chlorine water. On settling, if the carbon tetrachloride layer becomes : (*i*) *yellow or light brown*–bromine is indicated ; (*ii*) *violet*-iodine is indicated although in such case the compound may have both bromine as well as iodine. So in case, violet colour is obtained the contents are shaken with more chlorine, if violet colour disappears and yellow or brown colour is obtained bromine is also indicated in the compound.

Chemistry of the test. Chlorine oxidises NaI (formed in the fusion extract) to free iodine (*violet*) which when treated with excess of chlorine is further oxidised to iodic acid (*colourless*). Now excess of chlorine oxidises NaBr (formed in the fusion extract, if bromine is present in the compound) to fee bromine (*orange or brown*) which comes in the organic solvent (CS_2, CCl_4 or $CHCl_3$) layer.

$$\underset{\text{From fusion extract}}{2NaI} + Cl_2 \longrightarrow 2NaCl + \underset{\textbf{Violet}}{I_2}$$

$$I_2 + 5Cl_2 + 6H_2O \longrightarrow \underset{\text{Iodic acid } \textbf{(colourless)}}{2HIO_3} + 10HCl$$

$$2NaBr + Cl_2 \longrightarrow 2NaCl + \underset{\textbf{(Orange or brown)}}{Br_2}$$

In case chlorine is present along with other halogen (Br and/or I), the Lassaigne's extract is boiled with concentrated nitric acid till the evolution of brown coloured vapours ceases. It is now diluted and treated with silver nitrate; a ***curdy white precipitate*** soluble in excess of ammonium hydroxide and insoluble in nitric acid cofirms the presence of chlorine.

TEST YOUR UNDERSTANDING - 24.2

1. Can you expect any organic compound (*a*) without carbon, (*b*) without hydrogen ?

2. Can Na be replaced by K or Li for preparing Lassaigne's extract ?

3. Is it necessary to add H_2SO_4 or HCl in the test of nitrogen ? Explain.

4. It is proferred to add conc. H_2SO_4 rather than HCl during the test of nitrogen. Explain.

5. Urea, H_2NCONH_2, although contains nitrogen, *sometimes* it does not respond test for nitrogen.

6. Can you imagine any nitrogenous compound that does not respond Lassaigne's test for nitrogen ?

7. Beilestein's test is not given by which halogen ? Name it.

* Cleaning of copper wire. The copper wire is heated strongly in an oxidisng flame till it gives no colour to the flame.

24.3 Quantitative Analysis of Elements (*Estimation of Elements*)

After detecting various elements in an organic compound, the next step is to estimate the percentage composition of these elements. This is called *quantitative analysis* or *estimation of elements.* Accurate methods are known for the estimation of C, H, N and other elements but not for oxygen which is always determined by difference.

1. **Estimation of carbon and hydrogen** (*Liebig's method*). Carbon and hydrogen are always estimated simultaneously. The method is based upon the fact that when an organic compound is heated strongly with dry copper oxide in presence of oxygen or air, its carbon and hydrogen are oxidised to carbon dioxide and water vapours respectively.

$$\text{C (from org. compound)} + 2CuO \xrightarrow{\text{heat}} CO_2 + 2Cu$$

$$\text{2H (from org. compound)} + CuO \xrightarrow{\text{heat}} H_2O + Cu$$

The resultant CO_2 and H_2O vapours are absorbed separately in potash or ascarite (NaOH + CaO) a nd calcium chloride or magnesium perchlorate solutions respectively and hence the weights of absorbed gases (CO_2 and H_2O) is determined. From the weights of CO_2 and H_2O vapour formed, the weights of carbon and hydrogen in the known weight of the compound are obtained.

$$\textbf{Percentage of carbon} = \frac{\text{Wt. of } CO_2}{\text{Wt. of compound}} \times \frac{12}{44} \times 100$$

Similarly, $$\textbf{Percentage of hydrogen} = \frac{\text{Wt. of } H_2O}{\text{Wt. of compound}} \times \frac{2}{18} \times 100$$

Example 4 :

0.25 gm of an organic compound containing C, H and oxygen was analysed by the combustion method. The increase in weights of calcium chloride tube and potash bulbs at the end of the operation was found to be 0.15 gm and 0.1873 gm respectively. Calculate the percentage composition of the compound.

Solution :

Wt. of organic compound = 0.25 gm

Wt. of H_2O formed (increase in wt. of $CaCl_2$ tube) = 0.15 gm

Wt. of CO_2 (increase in wt. of potash bulbs) = 0.1873 gm

Now from our previous discussion we know that

$$\%\text{ of C} = \frac{12}{44} \times \frac{\text{wt. of } CO_2 \times 100}{\text{wt. of compound}}$$

$$= \frac{12}{44} \times \frac{0.1873 \times 100}{0.25} = \textbf{20.04\%}$$

Similarly, $$\%\text{ of H} = \frac{2}{18} \times \frac{0.15 \times 100}{0.25} = \textbf{6.66\%}$$

Hence percentage of oxygen = 100 – (20.04 + 6.66) = **73.30**

Example 5 :

0.36 gm of an organic compound on combustion gave 0.01 mole of CO_2 and 0.005 mole of water. Calculate the percentage of carbon and hydrogen in the compound.

Solution :

First convert the given moles of CO_2 and H_2O into their respective weights, the rest of the procedure is same as usual.

Calculation of wt. of CO_2 and H_2O formed

Since 1 mole of CO_2 weighs = 44 gm

0.01 mole of CO_2 weighs = $\frac{44}{1} \times 0.01 = 0.44$ gm.

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Similarly, as 1 mole of H_2O weighs = 18 gm

0.005 mole of H_2O weighs = $\frac{18}{1} \times 0.005 = 0.09$ gm

$\therefore$ Percentage of C = $\frac{12}{44} \times \frac{0.44 \times 100}{0.36}$ = **33.33%**

and Percentage of H = $\frac{2}{18} \times \frac{0.09 \times 100}{0.36}$ = **2.77%**

2. Estimation of nitrogen. Nitrogen is generally estimated by two methods : (*A*) *Duma's method and (B) Kjeldahl's method.*

(A) Duma's method. This method can be applied to all nitrogenous organic compounds.

Principle. The method is based on the fact that when an organic compound is heated with copper oxide, its carbon, hydrogen, sulphur and nitrogen contents are converted into CO_2, H_2O, SO_2 and N_2 respectively. In case any traces of nitrogen oxides are formed, these are reduced back to free nitrogen by passing it over bright reduced copper gauze. Carbon dioxide, water vapour and sulphur dioxide are absorbed in caustic potash solution and free nitrogen is collected over KOH in a nitrometer. From the volume of nitrogen collected over caustic potash, percentage of nitrogen can be calculated.

$$C + 2CuO \xrightarrow{heat} CO_2 + 2Cu$$

$$2H + CuO \xrightarrow{heat} H_2O + Cu$$

$$2N + CuO \xrightarrow{heat} N_2 + \text{Oxides of N}$$

$$\text{Oxides N} + Cu \xrightarrow{heat} N_2 + CuO$$

Room temperature and atmospheric pressure are also recorded in order to convert the volume of nitrogen collected under given conditions to volume of N_2 at N.T.P.

$\therefore$ Percentage of nitrogen = $\frac{28 \times \text{Vol. of } N_2 \text{ collected at N.T.P.} \times 100}{22400 \times \text{Wt. of organic compound}}$

= $\frac{\text{Wt. of nitrogen} \times 100}{\text{Wt. of organic compound}}$.

Example 6 :

0.290 gm of an organic compound containing nitrogen gave 50.00 ml of nitrogen at N.T.P. What is the percentage of nitrogen in the compound ?

Solution :

Wt. of organic substance = 0.290 gm.

Vol. of collected nitrogen at N.T.P. = 50 ml.

Now we know that percentage of nitrogen = $\frac{28 \times \text{Vol. of } N_2 \text{ collected at N.T.P.} \times 100}{22400 \times \text{Wt. of organic compound}}$

= $\frac{28 \times 50 \times 100}{22400 \times 0.290}$ = **21.55**

Example 7 :

In the determination of nitrogen by Duma's method, 0.200 gm of compound gave 20.7 ml of moist nitrogen at 15°C and 776 mm pressure. Calculate the percentage of nitrogen in the compound (Aq. tension at 15°C = 16 mm ; 1 litre of nitrogen of N.T.P. weighs 1.25 gm).

Solution :

Conversion of volume of N_2 collected to N.T.P. conditions

At given conditions	$P_1 = 776 - 16 = 760$ mm	$V_1 = 20.7$ ml	$T_1 = 15 + 273 = 288$ A
At N.T.P. conditions	$P_2 = 760$ mm	$V_2 = ?$	$T_2 = 273$ A

Applying the general gas equation

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \text{or} \quad V_2 = \frac{P_1V_1 \times T_2}{T_1 \times P_2}$$

$$\therefore \qquad V_2 = \frac{760 \times 20.7 \times 273}{288 \times 760} = 19.62 \text{ ml.}$$

Calculation of percentage of nitrogen

Since one litre (1000 ml) of nitrogen at N.T.P. weighs = 1.25 gm

$\therefore$ 19.62 ml. of nitrogen at N.T.P. weigh $= \frac{1.25}{1000} \times 19.62$ gm

Hence Percentage of nitrogen in the compound $= \frac{1.25}{1000} \times 19.62 \times \frac{100}{0.200} =$ **12.26 %.**

(B) Kjeldahl's method. This method is simpler and convenient, and can be used in compounds in which nitrogen is directly linked to carbon and hydrogen. Therefore, this method is largely used for the estimation of nitrogen in food, fertilizers and drugs. However, the method fails in compounds containing nitrogen joined either to other nitrogen or to oxygen as in nitro, nitroso, azo (N = N), azoxy, diazo, hydrazones, oximes, etc. The method is not applicable to compounds containing nitrogen in ring (*e.g.* pyridine, quinoline etc.)

Principle. This method is based on the fact that most of the nitrogenous compounds when heated with concentrated sulphuric acid in a long-necked flask called *Kjedahl's flask* in the presence of potassium sulphate* and a little copper sulphate **(Kjeldahlisation or digestion),** its nitrogen is quantitatively converted into ammonium sulphate. The ammonium sulphate so obtained is decomposed with excess of NaOH solution to give ammonia which is absorbed in an excess of a standard HCl or H_2SO_4 solution. The residual mineral acid is now titrated against a standard sodium hydroxide solution and thus the amount of HCl consumed for the neutralisation of ammonia, and hence the amount of ammonia produced from the known weight of the organic compound is determined.

$$\text{Organic compound containing N} + H_2SO_4 \xrightarrow{\text{heat}} (NH_4)_2SO_4$$

$$(NH_4)_2SO_4 + 2NaOH \xrightarrow{\text{heat}} Na_2SO_4 + 2NH_3 + 2H_2O$$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

Hence percentage of nitrogen in the compound $= \frac{14 \times \text{Vol. of acid used} \times \text{Normality of acid}}{1000 \times \text{Wt. of organic compound}} \times 100$

Type I. *When the ammonia evolved completely neutralises the standard acid taken.*

Example 8 :

If the ammonia obtained from 0.2160 gm of an organic compound by Kjeldahl method of analysis neuralises 23.85 ml of 0.1150 N acid, what is percentage of nitrogen in the compound?

Solution :

Wt. of substance taken = 0.2160 gm

Vol. of acid neutralised by NH_3 = 23.85 ml

Normality of the acid = 0.1150 N

$\therefore$ Percentage of nitrogen $= \frac{1.4 \times N \times V}{\text{Wt. of substance}} = \frac{1.4 \times 0.1150 \times 23.85}{0.2160}$ gm = **17.77**

* Potassium sulphate raises the boiling point of H_2SO_4 and thus ensures complete reaction.

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Type II. *When the ammonia evolved neutralises part of the standard acid and the acid left unused is titrated against standard NaOH.*

Example 9 :

0.445 gm of an organic compound was treated according to Kjeldahl method. The ammonia evolved was absorbed in 100 ml of N/2 sulphuric acid. The excess of the acid required 65.5 ml. N/2 alkali solution for neutralisation. Find the percentage of nitrogen in the compound.

Solution :

Wt. of organic compound = 0.445 nm

Vol. of N/2 H_2SO_4 taken = 100 ml.

Vol. of N/2 alkali required for the neutralisation of the excess of the acid = 65.6 ml.

Let the vol. of N/2 unused acid = V_1 ml.

Calculation of the volume of N/2H_2SO_4 used

(For acid) *(For alkali)*

$$\frac{N_1}{2} \times V_1 = \frac{N_2}{2} \times 65.5$$

$\therefore$ V_1 (vol. of unused acid) $= \frac{1}{2} \times 65.5 \times \frac{2}{1} = 65.5$ ml

$\therefore$ Vol. of N/2 acid used for neutralising NH_3 = 100 – 65.5 ml. = 34.5 ml.

Hence, percentage of nitrogen in the compound $= \frac{1.4 \times N \times V}{\text{Wt. of substance}} = \frac{1.4 \times 1 \times 34.5}{2 \times 0.445} =$ **54.33%**

Type III. *When the residual acid in the conical flask is diluted to a known volume with water and then titrated against standard alkali solution.*

Example 10 :

0.6 gm of an organic compound was Kjeldahlised and the ammonia evolved was passed into 100 ml of seminormal H_2SO_4. The residual acid was diluted to 500 ml with distilled water ; 25 ml. of diluted acid required 20.4 ml decinormal caustic soda solution for complete neutralisation. Calculate the percentage of nitrogen in the compound.

Solution :

Weight of substance taken = 0.6 gm

Vol. of N/2 H_2SO_4 taken = 100 ml

Let the vol. of N/2 H_2SO_4 unused = V_1 ml

Now 25 ml of the diluted acid solution = 20.4 ml N/10 NaOH

$\therefore$ Normality of the diluted acid $= 20.4 \times \frac{1}{10} \times \frac{1}{25} = \frac{51}{625}$ N

500 ml. of $\frac{51}{625}$ N of diluted acid $\equiv$ V_1 ml of N/2 H_2SO_4 (unused)

Applying the normality formula

(For unused acid) *(For diluted acid)*

$$\frac{N}{2} \times V_1 = \frac{51}{625} N \times 500$$

$\therefore$ $V_1 = \frac{51}{625} \times 500 \times \frac{2}{1} = 81.6$ ml.

$\therefore$ Vol. of N/2 acid used for ammonia = 100 – 81.6 ml = 18.4 ml.

Hence percentage of nitrogen $= \frac{1.4 \times N \times V}{w} = \frac{1.4 \times 1 \times 18.4}{2 \times 0.6} =$ **21.46**

3. **Estimation of halogens (Carius method). Principle.** Carius method is based on the fact that when an organic compound containing halogen is heated in a sealed tube with fuming nitric acid in presence of silver nitrate ; C, H and S of the compound are oxidised to their respective volatile oxides, while halogen is converted to the silver halide. From the weight of the silver halide formed, percentage of halogen in the organic compound can be calculated.

In general, % of halogen = $\frac{\text{At. wt. of halogen} \times \text{Wt. of AgX} \times 100}{\text{Mol. wt. of AgX} \times \text{w}}$.

Note (*i*) The method does not give satisfactory results with iodine because silver iodide is slightly soluble in nitric acid and some molecular iodine is also produced even in presence of excess of silver nitrate.

(*ii*) The method does not give correct result for highly halogenated aromatic compounds.

4. **Estimation of sulphur** (*Carius method*)**.** Sulphur is estimated like halogens but with a slight modification (*here $AgNO_3$ crystals used in halogen estimation are not used*). A weighed amount of organic substance (let it be *w* gm) is heated with conc. HNO_3 when its C, H and S are oxidised CO_2, H_2O (steam) and H_2SO_4 respectively. The contents of the Carius tube are transferred to a beaker and then treated with excess of barium chloride solution when whole of the sulphuric acid is precipitated as barium sulphate. From the weight of $BaSO_4$ (say *x* gm), percentage of S canbe calculated.

$$C + 2O \text{ (from } HNO_3) \xrightarrow{\text{heat}} CO_2 \; ; \; 2H + O \text{ (from } HNO_3) \xrightarrow{\text{heat}} H_2O$$

$$S + H_2O + 3O \text{ (from } HNO_3) \xrightarrow{\text{heat}} H_2SO_4$$

$$H_2SO_4 + BaCl_2 \longrightarrow BaSO_4 \downarrow + 2HCl$$

$\therefore$ Percentage of S in the compound = $\frac{32 \times x \times 100}{233 \times w}$.

Example 11 :

0.2595 gm of an organic compound containing sulphur was heated in a Carius tube with fuming nitric acid and the sulphuric acid formed was precipitated as $BaSO_4$ with $BaCl_2$. The weight of dry $BaSO_4$ was 0.350. Find the percentage of sulphur in the substance.

Solution :

$$\% \text{ of sulphur} = \frac{32}{233} \times \frac{\text{Wt. of } BaSO_4 \times 100}{\text{Wt. of compound}} = \frac{32}{233} \times \frac{0.350 \times 100}{0.2595} = \mathbf{18.52}$$

5. **Estimation of oxygen.** There is no satisfactory method for the direct estimation of oxygen in an organic compound. Hence, it is usually calculated by difference. In case, the sum of percentages of all other elements present in the organic compound is less than 100, the remainder gives the percentage of oxygen, *i.e.*,

% of oxygen = 100 – Sum of percentages of all other elements

24.4 Determination of Molecular Formula

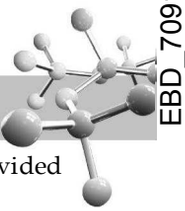
Knowing the percentage composition of a substance we proceed further for knowing the actual number of constituent atoms present in one molecule of the compound, *i.e.* the molecular formula of the compound. Determination of molecular formula of a compound involves the following three important steps.

(*i*) Calculation of empirical formula. (*ii*) Determination of molecular weight.

(*iii*) Calculation of molecular formula.

1. **Calculation of empirical formula.** *The empirical formula of a compound is the simplest formula which expresses the relative number of atoms present in the molecule.* It is calculated from the percentage composition of the compound by the following steps.

(*i*) *Determination of relative number of atoms.* For this, the percentage composition of each element is divided by its atomic weight. The different numbers so obtained are the relative numbers of different atoms present in the molecule.



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(*ii*) *Determination of simplest ratio.* The relative numbers of different atoms obtained in the above step are divided by the lowest one among them.

(*iii*) *Whole number.* The numbers expressing the simplest atomic ratio may or may not be whole numbers. In case any of the number is not nearly whole number then all the numbers are multiplied by a suitable common factor to get the smallest possible whole numbers. Minor fractions are neglected.

(*iv*) *Empirical formula.* The symbols of each element present in the compound are written in a line side by side. The whole numbers of each element obtained in step (*iii*) are put as subscripts to the lower right hand corner of each respective element. This gives the *empirical* or *simplest formula* of the compound.

2. Determination of molecular weight. *The molecular weight of a compound is the relative mass of one molecule of it as compared with the mass of atom of carbon* (^{12}C isotope) *taken as 12 amu.* It is only a number. If we say that molecular weight of a substance is 48, it means that the molecule of this substance is 48/12 = 4 times as heavy as an atom of carbon.

Gram-molecular weight. *When molecular weight is expressed in grams, it is known as gram molecular weight.* For example, the molecular weight of carbon dioxide is 44, but it gram molecular weight is 44 grams.

Gram-molecular volume. *The volume occupied by the vapour of a gram-molecular weight of substance at N.T.P. is called the gram molecular volume.* Its volume at N.T.P. is 22.4 litres or 22400 ml.

The methods employed for the determination of molecular weights can be divided into two groups.

(*i*) *Physical methods for volatile compounds.* In these methods a known weight of the organic compound is vaporised and the volume so obtained is reduced to N.T.P. From the volume of the vapours of the compound at N.T.P. from a given amount of the compound, weight of 22.4 litres of vapours is calculated. This weight will be the molecular weight of the compound. In short, these methods are based on the fact that 22.4 *litres of every gas or vapours at N.T.P. weigh equal to its molecular weight in gm.* (gram molecule). The important physical method is Victor Meyer's method.

(*ii*) *Physical methods for non-volatile compounds.* (*a*) Freezing point depression method and (*b*) boiling point elevation method.

(*iii*) *Chemical methods.* (*a*) Silver salt method for acids, (*b*) platinichloride method for bases, and (*c*) volumetric method for acids as well as bases.

(A) Victor Meyer's method. Mol. wt = $\dfrac{\text{Weight of compound} \times RT}{PV}$

Where V is the volume in litres collected at pressure P atmosphere and temperature T (in Kelvin) from w g of solute, $R = 0.082$ L atom mol^{-1} K^{-1}.

(B) Cryosopic or depression of freezing point method. This method is based on the fact that freezing point of a solvent is lowered on the addition of a soluble non-electrolyte. Depression in freezing point is found to be proportional to the amount of the solute added to a known weight of the solvent. In other words, freezing point of a solvent is depressed to the same extent when equimolecular quantities of different non-electrolytes are added to a fixed weight of the solvent.

The molecular weight of a non-volatile organic compound can be easily determined by dissolving a definite weight of the substance in a known weight of the solvent. Mathematically,

$$m = \frac{100\,K_f w}{\Delta T W}$$

where, m = Mol. wt. of the solute; W = Weight of the solvent
w = Weight of the solute; K_f = Molecular depression constant
ΔT = Depression of freezing point.

The **molecular depression constant or the freezing point constant** *is defined as the depression of freezing point which would be produced by dissolving one gram-molecule of the solute in 100 gm. of the solvent.* The molar depression constants for some common solvents are given below.

Water	18.6°C or 1.86	Acetic acid	38.2°C or 3.82
Benzene	51.2°C or 5.12	Phenol	73°C or 7.3

On the other hand, depression of freezing point may be determined experimentally.

(C) Ebullioscopic or Elevation of boiling point method. This method is similar to cryoscopic method and based on the fact that the normal boiling point of a solvent increases (elevates) on the addition of a soluble non-electrolyte. The elevation of boiling point is found to be proportional to the amount of the solute (and not the nature of the solute) added to a known weight of the solvent. The elevation of boiling point produced by adding a known amount of the solute (w) to a known amount of the solvent (W) can be used for determining the molecular weight of the solute (m).

$$m = \frac{100\,K_b w}{\Delta\, TW}$$

where, K_b = Molecular elevation constant ΔT = Elevation of boiling point.

Molecular elevation constant or boiling point constant *is defined as the elevation of boiling point which would be produced by dissolving one gram molecule of the solute in 100 gm. of the solvent.* The molecular elevation constants for some common solvents are given below.

Water	5.2°C or 0.52	Acetone	16.7°C or 1.67
Benzene	26.7°C or 2.67	Acetic acid	25.3°C or 2.53
Ether	21.0°C or 2.10	Ethyl alcohol	11.5°C or 1.15

Again, elevation of boiling point is determined experimentally.

(D) **Silver salt method (***For organic acids, RCOOH***).** This method is based on the fact that most of the organic acids form insoluble silver salts which on ignition decompose to give residue of pure metallic silver.

$$RCOOH \xrightarrow{NH_4OH} RCOONH_4 \xrightarrow{AgNO_3} RCOOAg\downarrow \xrightarrow{\text{ignite}} Ag\downarrow$$

From the known weight of the silver salt of the acid taken for ignition and from the weight of metallic silver obtained, the equivalent weight of the silver salt of the acid (let it be E) can be calculated with the help of following relation.

		RCOOAg $\xrightarrow{\text{ignite}}$	Ag
	Eq. wt.	E	108
	or Weight	w g	x g

Mathematically, $\dfrac{\text{Eq. wt. of the silver salt (say } E)}{\text{Eq. wt. of silver (108)}} = \dfrac{\text{Wt. of silver salt taken } (w)}{\text{Wt. of silver obtained } (x)}$

$$\therefore \quad E = \frac{w}{x} \times 108$$

Relation between formulae of RCOOH and RCOOAg

$$RCOOH = RCOOAg - Ag + H$$

Thus Eq. wt. of RCOOH $= E - 108 + 1$

or Eq. wt of RCOOH $= E - 107$

Thus Eq. wt. of RCOOH $= \left(\dfrac{w}{x} \times 108\right) - 107$

and hence Mol. wt. of RCOOH = Eq. wt. of the acid × Basicity

$$= \left[\left(\frac{w}{x} \times 108\right) - 107\right] \times n$$

(E) **Platinum salt method (***For organic bases, RNH_2***).** This method is based on the fact the platinichlorides, also known as chloroplatinates, of organic bases ($B_2H_2PtCl_6$) when ignited strongly give a residue of platinum.

$$2B \xrightarrow{HCl} 2BHCl \xrightarrow{PtCl_4} B_2H_2PtCl_6 \xrightarrow{\text{heat}} Pt$$

From the weight of the platinum salt taken (say w g) for ignition and from the weight of platinum obtained on ignition (say x g), equivalent weight of the base can be calculated.

	$B_2H_2PtCl_6$ $\longrightarrow$	Pt
	2B + 2 + 195 + 213 = 2B + 410	195
or	w g	x g

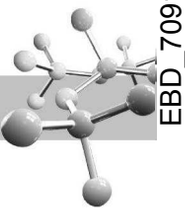
Thus $\dfrac{\text{Mol. wt. of chloroplatinate}}{\text{At. wt. of platinum}} = \dfrac{\text{Wt. of chloroplatinate}}{\text{Wt. of platinum}}$

$$\frac{2B + 410}{195} = \frac{w}{x}$$

$$B = \frac{1}{2}\left[\frac{w}{x} \times 195 - 410\right]$$ where B is the equivalent weight of the base

$\therefore$ Mol. wt. of the base = Eq. wt. of the base × Acidity

$$= B \times n$$



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(F) Volumetric method for acids and bases

This method is based on the following two facts.

(*i*) Acids and bases always react with each other (*i.e.* neutralise) in equivalent proportions. Thus 1 litre on N-acid is equivalent to 1 litre of N-alkali.

(*ii*) Since one litre of N solution of a substance contained 1 gm. equivalent of the substance, the amount of acid (or base) neutralised by one litre of N-alkali (or N-acid) would be the equivalent weight of the acid (base).

A known weight of the acid (or base) (say *w* g) is dissolved in water or alcohol and titrated against a standard alkali (or acid) solution (say N/10) using phenolphthalein as indicator. From the amount of the alkali (or acid) required to neutralise the acid (or base), the equivalent weight and hence molecular weight of the acid (or base) is calculated.

$$E = \frac{1000\,w}{NV}$$

Example 12 :

0.25 gm of a dibasic organic acid was dissolved in water and the volume was made to 100 ml., 10 ml. of this solution required 24.6 ml. of N/60 NaOH for neutralisation. Calculate the molecular weight of the acid.

Solution :

24.6 ml. of N/60 NaOH ≡ 10 ml. of acid

∴ 246 ml. of N/60 NaOH ≡ 100 ml. of acid ≡ 0.25 gm of acid

∴ 1000 ml. of N/NaOH $= \frac{0.25}{246} \times \frac{60}{1} \times 1000$

∴ Eq. wt. of the acid $= \frac{0.25 \times 60 \times 1000}{246} = 60.97$

Hence mol. wt. of the acid = 60.97 × 2 (basicity) = **121.94**

Example 13 :

0.184 gm of a diacid organic base required 25.6 ml. of N/8 sulphuric acid for complete neutralisation. Calculate the molecular weight of the base.

Solution :

25.6 ml. of N/8 H_2SO_4 ≡ 0.184 gm of the base

∴ 1000 ml. of N–H_2SO_4 $\equiv \frac{0.184}{25.6} \times \frac{8}{1} \times 1000$ gm = 57.5 gm.

∴ Eq. wt. of the base = 57.5

Hence, Mol. wt. of the base = 57.5 × 2 (acidity) = **115.0**

3. Calculation of molecular formula. *The formula which represents the actual number of atoms of various elements present in one molecule of the substance is termed as molecular formula.* It is either the same as the empirical formula of the substance or a simple multiple of it, *i.e.*

$$\text{Molecular formula} = (\text{Empirical formula})_n$$

Where *n* is a whole number and is the ratio between the molecular weight and the empirical formula weight of the substance, *i.e.*

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}.$$

Example 14 :

Determine the empirical and molecular formula of dibasic acid from the following data.

(a) 0.3192 gm of the acid gave on combustion 0.4224 gm of CO_2 and 0.512 gm of H_2O.

(b) It contained 10.52% nitrogen.

(c) The V.D. of its dimethyl ester is 80.50.

Solution :

(*a*) *Calculation of percentage composition*

$$\text{Percentage of C} = \frac{12}{44} \times \frac{0.4224}{0.3192} \times 100 = 36.09$$

$$\text{Percentage of H} = \frac{2}{18} \times \frac{0.512}{0.3192} \times 100 = 5.26$$

Percentage of N (given) = 10.52

Percentage of O (by difference) = 100 − (36.09 + 5.26 + 10.52) = 48.13

(*b*) *Calculation of empirical formula*

Element	Percentage	At.wt.	Relative No. at atoms	Simplest ratio
C	36.09	12	36.09/12 = 3.008	3.008/0.751 = 4
H	5.26	1	5.26/1 = 5.26	5.26/0.751 = 7
N	10.52	14	10.52/14 = 0.751	0.751/0.751 = 1
O	48.13	16	48.13/16 = 3.008	3.008/0.751 = 4

Hence the empirical formula of the acid = $\mathbf{C_4H_7NO_4}$

(*c*) *Calculation of the molecular formula*

Empirical formula wt. of the acid = 48 + 7 + 14 + 64 = 133

Mol.wt. of the dimethyl ester = 2 × V.D. = 2 × 80.50 = 161

Now let the dibasic acid in question = R $(COOH)_2$

∴ Its dimethyl ester is = $R(COOCH_3)_2$

Mol. wt. of the acid = Mol. wt. of ester − Wt. of two methyl (CH_3) groups + Wt. of two hydrogen (H) atoms

= 161 − 2(3 + 12) + 2 = 133

$$\therefore \; n \text{ (of acid)} = \frac{\text{Mol. wt.}}{\text{Empirical formula wt.}} = \frac{133}{133} = 1$$

∴ Molecular formula of the acid = Empirical formula × n

= $C_4H_7NO_4 \times 1 = \mathbf{C_4H_7NO_4}$

TEST YOUR UNDERSTANDING - 24.3

1. An 11.75 g sample of a hydrocarbon is volatilized at 1 atm pressure and 100°C to a gas that occupies 5.0 L. What is its molecular weight ? (R = 0.0821 L atm/mol K).

2. Complete combustion of 0.858 g of compound X gives 2.63g of CO_2 and 1.28 g of H_2O. Find the percentage composition of X. What is the lowest molecular weight it can have ?

EBD_7091

EXERCISE 24.1 (MCQ - ONE option correct)

1. In steam distillation of aniline, function of steam is
(*a*) to increase the vapour pressure of the liquid to be distilled
(*b*) to decrease the vapour pressure of the liquid to be distilled
(*c*) to carry vapours of the liquid with it, it has nothing to do with the vapour pressure of the liquid
(*d*) to dissolve the liquid due to high temperature

2. In steam distillation
(*a*) the liquid to be distilled starts boiling at 373 K
(*b*) the liquid to be distilled starts boiling above 373 K
(*c*) the liquid to be distilled starts boiling below 373 K
(*d*) any of the three temperatures.

3. Which of the following is not used for the purification of solid impurities ?
(*a*) Distillation (*b*) Sublimation
(*c*) Crystallisation (*d*) None of these.

4. Steam distillation is used for the extraction of
(*a*) fatty acids (*b*) mineral oils
(*c*) essential oils (*d*) higher alkanes.

5. A mixture of *o*-nitrophenol and *p*-nitrophenol can be separated by
(*a*) sublimation (*b*) steam distillation
(*c*) fractional distillation (*d*) fractional crystallisation.

6. Which of the following technique is most suitable for the purification of cyclohexanone from its mixture containing cyclohexane, benzoic acid and isoamyl alcohol as other components?
(*a*) Crystallisation (*b*) Sublimation
(*c*) Chromatography (*d*) None of the three

7. Gas chromatography is suitable for types of compounds which are
(*a*) liquids
(*b*) highly volatile
(*c*) vaporised without decomposition
(*d*) soluble in water

8. Diazo compounds, sometimes do not respond Lassaigne's test for nitrogen because
(*a*) these are quite stable compounds and do not decompose to elemental nitrogen
(*b*) these contain very little carbon
(*c*) these form organometallic compounds with sodium
(*d*) their nitrogen contents is removed, during heating, in the form of nitrogen gas

9. Sometimes, the colour observed in Lassaigne's test for nitrogen is green. It is because
(*a*) of green colour of ferrous sulphate
(*b*) ferric ferrocyanide is also green
(*c*) of green colour of copper sulphate
(*d*) of excess of Fe^{3+} ions whose yellow colour makes the blue colour of ferric ferrocyanide to appear green.

10. Which of the following compound will give white precipitate on heating with HNO_3 followed by addition of silver nitrate ?
(*a*) $(C_2H_5)_3NHCl$ (*b*) 2, 4, 6-Trinitrochlorobenzene
(*c*) Both (*a*) and (*b*) (*d*) None.

11. Lassaigne's extract of thiourea, $SC(NH_2)_2$ is boiled with ferrous sulphate and then acidified with HCl, the colour of the resulting solution will be
(*a*) prussian blue (*b*) green
(*c*) black (*d*) red.

12. In an organic compound, sulphur can be estimated by
(*a*) Carius method (*b*) Messenger method
(*c*) both (*d*) Lasaisgne's method.

13. The best criteria for testing the purity of a solid organic compound is
(*a*) melting point (*b*) mixed melting point
(*c*) both (*d*) mixed boiling point.

14. The function of sodium during preparation of Lassaigne's extract is to
(*a*) decrease the melting point of the compound
(b) increase the ionisation of the compound
(*c*) convert the covalent compound into ionic compounds
(*d*) increase the reactivity of the compound.

15. Positive Beilstein test for halogens shows that
(*a*) halogen is definitely present
(*b*) a halogen may be present
(*c*) a halogen is absent
(*d*) none of these.

16. There is no direct test for the detection of which element in an organic compound ?
(*a*) N (*b*) S (*c*) Cl (*d*) O

17. One g of an organic nitrogen-containing compound, on heating, decomposes to give 0.2 g of nitrogen. What should be nature of the compound ?
(*a*) $C_3H_7N_2Cl$ (*b*) $C_6H_5N_2Cl$
(*c*) $(CH_3)_3N$ (*d*) Datas are insufficient.

18. It percentage of selenium (at. wt. = 78.4) in peroxidase anhydrase enzyme is 0.5% by weight, then the minimum molecular weight of the enzyme should be
(*a*) 1.568×10^3 (*b*) 2.136×10^4
(*c*) 1.568×10^4 (*d*) 2.136×10^3.

19. If two compounds have the same empirical formula but different molecular formulae, they must have
(*a*) different percentage composition
(*b*) different molecular mass
(*c*) same vapour density
(*d*) same viscosity.

20. Empirical formula of hydrocarbon containing 80% C and 20% H is
(*a*) CH_4 (*b*) CH_3 (*c*) CH_2 (*d*) C_2H.

21. A hydrocarbon has 4 g carbon per g of hydrogen, it can be
(*a*) CH_4 (*b*) C_2H_6 (*c*) C_2H_2 (*d*) C_2H_4.

22. The simplest ratio of number of C and H atoms in a hydrocarbon is found to be 1 and 2.37 respectively. The molecular weight for the hydrocarbon should be
(*a*) 42 (*b*) 43 (*c*) 84 (*d*) 86

23. The empirical formula of a carboxylic acid is CH_2O_2, the probable molecular formula of the simplest acid may be
(*a*) CH_2O (*b*) CH_2O_2 (*c*) $C_2H_4O_4$ (*d*) $C_3H_6O_6$.

24. *p*-Chloroaniline and anilinium hydrochloride can be distinguished by
(a) Sandmeyer reaction (b) $NaHCO_3$
(c) $AgNO_3$ (d) Carbylamine test

25. If two compounds have the same empirical formula but different molecular fomulae they must have
(a) different percentage composition
(b) different molecular weight
(c) same viscosity
(d) same vapour density

EXERCISE 24.2 (MCQ 1 or >1 optic correct, Passage based, Matching, A/R)

DIRECTIONS for Q. 1 to Q. 15 : Multiple choice questions with one or more than one correct option(s).

1. The boiling point of a compound depend upon
(*a*) hydrogen bonding (*b*) polarity of the molecule
(*c*) size of the molecule (*d*) its solubility in water.

2. Which of the following is true?
(*a*) A liquid has same boiling point at all conditions
(*b*) A liquid can be made to boil at a temperature lower than its usual boiling point
(*c*) A liquid can be made to boil at a temperature higher than its usual boiling point
(*d*) Steam distillation means distillation under reduced pressure

3. During steam distillation of a mixture of *o*-nitrophenol and *p*-nitrophenol, which of the statement is false
(*a*) vapours of *o*-nitrophenol are carried by steam because of its lower boiling point due to chelation.
(*b*) vapours of *o*-nitrophenols are carried by steam because of its lower boiling point and solubility in steam.
(*c*) vapours of *o*-nitrophenol are carried by steam because its boiling point is reduced by steam.
(*d*) vapours of *p*-nitrophenol are carried by steam because of its lower boiling point.

4. Simple distillation can't be used to separate
(*a*) a mixture of ether (b.p. 308 K) & toluene (b.p. 383 K)
(*b*) a mixture of benzene (b.p. 353 K) & thiophene (b.p. 357 K)
(*c*) a mixture of ethyl alcohol (b.p. 351 K) & water (b.p. 373 K)
(*d*) essential oils

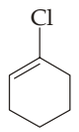
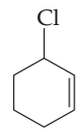
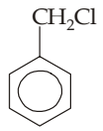
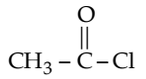
5. A mixture of sugar and common salt can't be separated by
(*a*) water (*b*) alcohol
(*c*) petroleum ether (*d*) sublimation

6. Lassaigne's test for nitrogen is negative for which compound ?
(*a*) NH_2OH (*b*) NH_2NH_2
(*c*) H_2NCONH_2 (*d*) H_2NCSNH_2

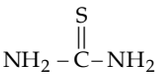
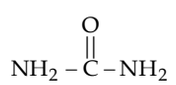
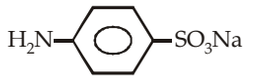
7. Lassaigne's extract of *p*-nitrochlorobenzene is acidified with dil.HNO_3 and then treated with silver nitrate solution, the white precipitate formed is due to
(*a*) AgCl (*b*) AgCN
(*c*) both (*a*) and (*b*) (*d*) no white ppt. is obtained.

8. Carius method is reliable for the estimation of
(*a*) Cl (*b*) Br (*c*) I (*d*) S.

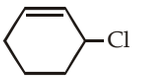
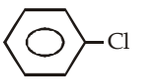
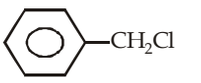
9. An organic compound is boiled with HNO_3, cooled and then treated with $AgNO_3$, a white precipitate is obtained. The compound can be

(*a*) 
(*b*) 
(*c*) 
(*d*) 

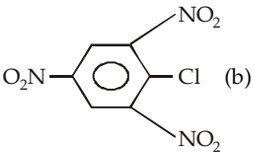
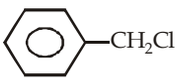
10. Which of the organic compound will give red colour in Lassaigne test :

(a) NaCNS (b) 
(c)  (d) 

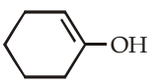
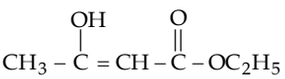
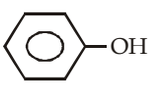
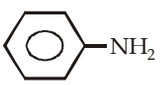
11. Organic compound A $\xrightarrow{HNO_3/AgNO_3}$ white ppt. A can be :

(a) NH_4Cl (b) 
(c)  (d) 

12. Detection of the chlorine is possible without preparing sodium extract in :

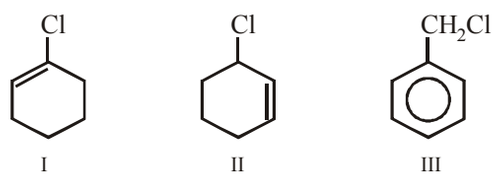
(a)  (b) $CHCl_3$
(c)  (d) $CH_2 = CH - CH_2Cl$

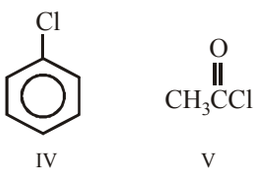
13. Which will give colour with $FeCl_3$?

(a)  (b) 
(c)  (d) 

14. *p*-Chloroaniline and anilinium hydrochloride can be distinguished by
(a) Sandmeyer reaction (b) $NaHCO_3$
(c) $AgNO_3$ (d) Carbylamine test

15. An organic compound is boiled with HNO_3, cooled and then treated with $AgNO_3$, a white precipitate is obtained. The compound can be


I II III

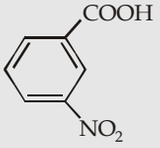
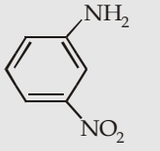
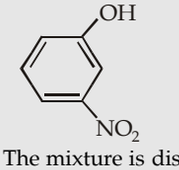

IV V

(a) I, II, III or IV (b) II, III or V
(c) only V (d) Any of the five

INSTRUCTION for Q. 16 to 27 : Read the passages given below and answer the questions that follow.

PASSAGE 1

In various scientific pursuits, it is important to be able to purify substances so that they can be better studied or better used. Common methods of separating substances are extraction, recrystalization, distillation, and chromatography. A mixture contains the three compounds shown in the table below

		Solubility (g/100 mL) in H_2O	in ether
(i)		0.31	25.0
(ii)		0.11	5.5
(iii)		3.02	106

16. The mixture is dissolved in a small amount of ether. To this is added an equal volume of 0.01 M HCl(aq). After shaking, two layers are formed: an aqueous layer and an ether layer. The layers are then separated. Which of the compounds will be found in the aqueous layer?
(a) (i) only (b) (ii) only
(c) (iii) only (d) (ii) and (iii)

17. To the ether layer is added an equal volume of 0.01 M NaOH(aq). Again, two layers are formed. After separating them, which of the compounds will be found in the aqueous layer?
(a) (i) only (b) (iii) only
(c) (i) and (iii) (d) (ii) and (iii)

18. This aqueous layer is evaporated to dryness leaving a solid residue of mass 0.31 g. Ten milliliters of aqueous acid of pH 3 are added. After stirring, the residue is smaller. What is the identity of the residue?
(a) (i) only (b) (ii) only
(c) (iii) only (d) (i) and (iii)

PASSAGE 2

Nitrogen, sulphur and halogens are tested from the sodium fusion extract of the organic compound, which is more commonly known as Lassaigne's extract. For preparing Lassaigne's extract, a small quantity of the organic compound is fused with sodium metal in a fusion tube. The red hot tube is broken in distilled water, boiled and filtered. The filtrate is known as Lassaigne's extract or sodium extract.

Generally, the Lassaigne's extract is alkaline in nature due to reaction of unreacted sodium with water

$$(2Na + 2H_2O \longrightarrow 2NaOH + H_2)\cdot$$

If it is not so, it is made alkaline by adding sodium hydroxide. Now the extract is boiled with ferrous sulphate solution, and the acidified with dil. H_2SO_4 or dil. HCl, appearance of green or blue colour confirms the presence of nitrogen.

Lassaigne's test for halogens. A small portion of the sodium fusion extract is acidified with dil. nitric acid and then treated with silver nitrate solution. If a precipitate is formed, it indicates the presence of a halogen; the colour of precipitate, in turn, indicates the nature of halogen.

19. Which of the following compound does not undergo Lassanigne's test for nitrogen?
(a) Urea (b) Hydrazine
(c) Methylamine (d) *p*-Nitroaniline

20. Lassaigne's extract of an organic compound containing C, N, S and Cl is for tested for chlorine with $AgNO_3$, the precipitate formed will be of
(a) AgCl (b) Ag_2S
(c) AgCN (d) All the three

21. The colour of precipitate in the above case will be
(a) White (b) Black
(c) Yellow (d) No precipitate

22. For testing chlorine in the Lassaigne's extract containing NaCN, Na_2S, and NaCl; the extract is first boiled with conc. HNO_3 and then treated with $AgNO_3$. What is the function of conc. HNO_3?
(a) It dissolves the precipitate of Ag_2S and AgCN
(b) It dissolves the white precipitate of AgCN
(c) It dissolves the precipitate of AgCl
(d) It decomposes NaCN and Na_2S

23. Lassaigne's extract, containing NaCN and Na_2S, when treated with ferric chloride generally gives blood red colour, indicating the presence of N and S (both) in the compound. However, sometimes the blood red colour does not appear, the reason being that
(a) Sodium thiocyanate is not formed
(b) The sodium thiocyanate is decomposed by means of sodium
(c) The Fe^{3+} ions are deactivated
(d) The ferric thiocyanate decomposes

PASSAGE 3

Characteristic reactions of some of the important groups are given below :

I. Phenols and carboxylic acids are soluble in dil. NaOH, however only carboxylic acids are soluble in very diute (5%) aqueous $NaHCO_3$ solution with the evolution of CO_2 gas.

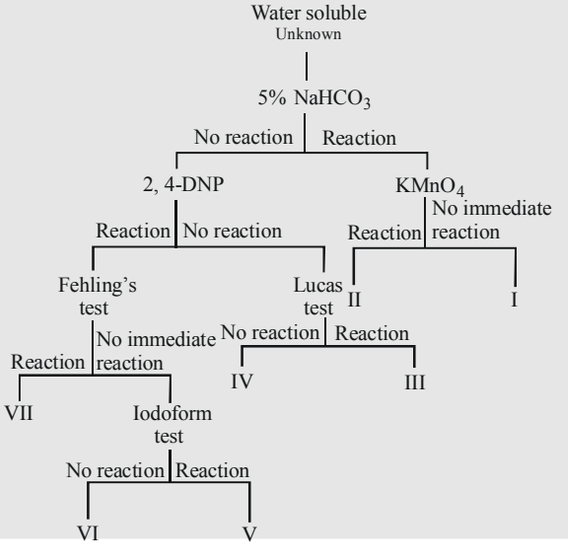
II. Lower alcohols containing five or less carbon atoms react with Lucas reagent, while the higher alcohols do not react with the reagent.

III. Aldehydes and ketones react with 2, 4 dinitrophenylhydrazine to give orange coloured crystals, however only aldehydes reduce Fehling solution.

IV. Acetaldehyde gives yellow precipitate with alkaline iodine

$$CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow{I_2/OH^-} CHI_3\downarrow + HCOO^-$$

The following flow-sheet diagram was prepared on the basis of the above reactions.



24. Compound II should have
(a) – COOH group (b) an alcoholic group
(c) Both (a) and (b) (d) A phenolic –OH group

25. Compound III is
(a) C_6H_5OH (b) $C_6H_{11}OH$
(c) C_2H_5OH (d) Any of the three

26. Which of the following compound can be an aldehyde?
(a) V (b) VI
(c) VII (d) IV

27. Compound V can be
(a) CH_3CHO (b) CH_3COCH_3
(c) $CH_2ICOC_2H_5$ (d) Any of the three

Instructions for Q. 28 to 34 : Following questions are Multiple Matching type Questions :

28.

	Column - I	*Column - II*
(A)	Acetoacetic ester	(a) Blue litmus test
(B)	2, 4, 6- trinitrophenol	(b) Evolves CO_2 with $NaHCO_3$ solution
(C)	Fructose	(c) Reduces Tollen's reagent
(D)	Acetone	(d) Forms 2, 4-DNP derivatives

29.

	Column - I	*Column - II*
(A)	Molisch test	(a) Glucose
(B)	Tollen's reagent	(b) CH_3CHO
(C)	Carbylamine test	(c) $C_6H_5NH_2$
(D)	Reaction with I_2 + NaOH	(d) $CHCl_3$

30.

	Column - I	*Column - II*
(A)	Lassaigne's extract	(a) N-atom
(B)	Sodium carbonate extract	(b) Halogen atom
(C)	Beilstein's test	(c) Halide ion
(D)	Chloroform test	(d) Sulphur atom

31.

	Column - I	*Column - II*
(A)	Lassaigne's test for detection	(a) C_6H_6
(B)	Dumas method for estimation	(b) $C_6H_5NO_2$
(C)	Kjeldahl's method for estimation	(c) Urea
(D)	Liebig's method for estimation	(d) Pyridine

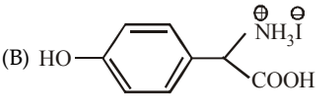
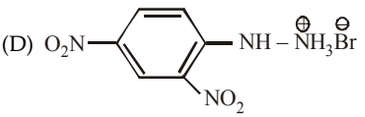
32.

	Column - I	*Column - II*
(A)	Baeyer's reagent	(a) Milkiness
(B)	Lucas reagent	(b) Alk. $KMnO_4$
(C)	Tollen's reagent	(c) Aldehydes
(D)	Phenylhydrazine hydrochloride	(d) Fructose

33.

	Column - I *Mixture*	*Column - II* *Method applied for separation*
(A)	Glucose + Fructose	(a) Sodium bicarbonate solute
(B)	Glucose + Benzoic acid	(b) Fractional distillation
(C)	Iodine + Chlorine	(c) Sublimation
(D)	Kerosene oil + Diesel oil	(d) Chromatography

34.

	Column I	**Column II**
(A)	$H_2N-\overset{\oplus}{N}H_3\,\overset{\ominus}{Cl}$	(p) sodium fusion extract of the compound gives Prussian blue colour with $FeSO_4$
(B)		(q) gives positive $FeCl_3$ test
(C)		(r) gives white precipitate with $AgNO_3$
(D)		(s) reacts with aldehydes to form the corresponding hydrazone derivative

Instructions for Q. 35 to 37 : Following questions are Assertion and Reasoning Type Questions :

Note : Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 5 choices (a), (b), (c), (d) and (e) out of which ONLY ONE is correct.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(c) Statement -1 is True, Statement-2 is False.
(d) Statement -1 is False, Statement-2 is True.
(e) Statement -1 is False, Statement-2 is False.

35. **Statement - 1 :** Aniline on reaction with $NaNO_2$ / HCl at 0^oC followed by coupling with β-naphthol gives a dark blue precipitate.
and
Statement - 2 : The colour of the compound formed in the reaction of aniline with $NaNO_2$/HCl at 0^oC followed by coupling with β-naphthol is due to the extended conjugation.

36. **Statement-1** : Duma's method is more applicable to nitrogen containing organic compounds than Kjeldahl's method.
Statement-2 : Kjeldahl's method does not give satisfactory results for compounds in which nitrogen is linked to oxygen.

37. **Statement-1** : Diazonium salts do not respond Lassaigne's test for nitrogen.
Statement-2 : Diazonium compounds lose N_2 on heating before they combine with sodium.

EBD_7091

EXERCISE 24.3 (Subjective Problems)

1. How will you differentiate each of the following pair on the basis of their solubility?

(a) 4-Chlorophenol and 4-chloro-1-methylbenzene

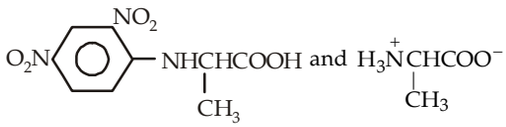
(b) 4-Methylphenol and 2,4,6-trinitrophenol.

(c) Phenol and 2,4-dinitrophenol.

(d) $C_6H_5SO_2NHCH_3$ and $C_6H_5CONHCH_3$

(e) 2-Hexanone and hexane

(f) $CH_3CH_2NH_2$ and CH_3CONH_2

(g)  and

2. How will you distinguish between

(a) toluene and cyclohexene with bromine

(b) $(CH_3)_2CHOH$ and $(CH_3)_2CHSH$ by a chemical test

(c) $(CH_3)_2C(OH)CH_2CH_3$ and $CH_3CH_2CH(OH)CH_2CH_3$ by a chemical test.

(d) Cyclopentyl chloride and cyclopentanol by solubility test.

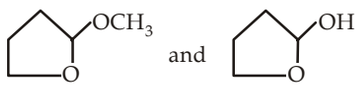
(e) $CH_2{=}CHCH_2OH$ and $CH_3CH_2CH_2OH$ by Lucas test.

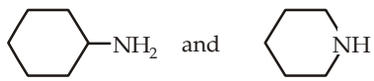
(f) $(COOH)_2$ and $CH_2(COOH)_2$ by a chemical test.

(g) RCOCl and RCOOH by aq. $AgNO_3$ test.

(h) $(CH_3CO)_2O$ and $CH_3COOC_2H_5$ by a chemical test.

(i) $C_6H_5SO_2NHCH_3$ and $C_6H_5CONHCH_3$ by NaOH.

(j) 

(k) 

(l) $(C_2H_5)_3N$ and $(C_2H_5)_2NH$

(m) $(C_2H_5)_3N^+HCl$ and $(C_2H_5)_4N^+Cl^-$

(n) $(C_2H_5)_4N^+Cl$ and $(C_2H_5)_4N^+OH^-$

3. What is hydroxamic acid test for esters?

4. Show the scheme to separate a mixture of organic compounds containing following components; benzyl alcohol, phenol, aniline and benzoic acid.

Hint : Treat the ether extract in the following sequence (i) with aq. HCl (for removing aniline), (ii) with aq. $NaHCO_3$ (for removing benzoic acid), and (iii) with aq. NaOH (for removing phenol). Finally benzyl alcohol will remain in ether.

5. 1.325 g sample of a fertilizer is treated in Kjeldahl's apparatus and the evolved ammonia gas is passed into 50 mL of 0.203 NH_2SO_4. The unused acid required 25.32 mL of 0.198 N NaOH. Calculate the percentage of nitrogen in the fertilizer.

6. Determine the molecular weight of the two given compounds from the following datas :

(*a*) 0.369 g of a bromo derivative when vaporised occupied 67.2 mL at NTP.

(*b*) 1.49 g of an organic compound gave 448 mL of vapour at STP.

7. An organic compound contains 69.4% C and 5.8%H ; 0.303 g of this compound was analysed for nitrogen, and the ammonia evolved was absorbed in 50 mL of 0.05 M sulphuric acid. The excess of acid required 25 mL of 0.1 M NaOH for neutralisation. Determine the empirical formula for the compound.

8. 0.450 g of an organic compound on ignition gives 0.905 g CO_2 and 0.185 g H_2O. 0.350 g of the same compound on boiling with HNO_3 and adding $AgNO_3$ solution gives 0.574 g of AgCl. If the vapour density of the compound is 87.5, what should be the molecular formula for the compound ?

9. The boiling point of the solution of 5.5 g of an organic compound, containing 42.86% C, 2.40% H, and 16.67% nitrogen, in 45 g of benzene is 1.84°C higher than that of pure benzene. If the molal boiling point elevation constant of benzene is 2.53 K kg mol^{-1}, what will be the molecular formula of the compound?

10. 0.1413 g of a monoacid organic base gave 0.3582 g CO_2 and 0.1904 g water ; 0.1237 g of the substance gave 17.85 mL of dry nitrogen at 27°C and 750 mm pressure. If the chloroplatinate of the base containing 33.4% platinum, determine the molecular formula of the base.

11. A dibasic organic acid gave the following results on analysis. (*a*) 0.236 g of the acid gave 0.352 g of CO_2 and 0.108 g of H_2O. (*b*) 0.177 g of acid required 30 mL of 0.1 N NaOH solution for complete neutralisation. Determine the molecular formula of the acid.

12. 0.4 g of a carboxylic acid on combustion gave 0.08 g of water and 0.39 g of CO_2. The silver salt of the acid weighing 1.0 g on ignition gave 0.71 g of silver. Determine the molecular formula of the acid.

13. An acid A contains 40%C, 5.1% H and rest oxygen. Its silver salt contains 65.1% silver. The ethyl ester of A has VD of 87. Determine the molecular formula for A.

14. A monobasic acid contains 68.8% C and 4.9% H. 0.610 g of the acid requires 25 mL of M/10 diacidic base for neutralisation. Determine the molecular formula of the acid.

15. 0.20 g of an organic compound, containing 60% C and 13.3% H, displaced 74.66 mL of air at NTP. Determine its molecular formula.

16. A monobasic acid gave following results.

(*a*) 0.236 g of it gave 0.528 g CO_2 and 0.324 g water, an combustion.

(*b*) In nitrogen determination, 0.295 g of it gave 56 mL of N_2 at NTP.

(*c*) Its platinichloride contains 36.93 % platinum.

Determine its molecular formula.

SOLUTIONS

EXERCISE 24.1

1	(b)	**6**	(c)	**11**	(d)	**16**	(d)	**21**	(b)
2	(c)	**7**	(c)	**12**	(c)	**17**	(b)	**22**	(d)
3	(d)	**8**	(d)	**13**	(b)	**18**	(c)	**23**	(b)
4	(c)	**9**	(d)	**14**	(c)	**19**	(b)	**24**	(c)
5	(b)	**10**	(c)	**15**	(b)	**20**	(b)	**25**	(b)

1, 2. In steam distillation of aniline, steam decreases vapour pressure of the liquid which in turn starts boiling below its usual boiling point. Hence steam distillation is considered analogous to distillation under reduced pressure.

3. All the three processes can be applied for the removal of solid impurities.

4. Essential oils are volatile, hence carried along with steam during steam distillation.

5. Steam distillation can be applied only when one of the components has b.p. less than bp. of water.

6. A mixture having more than two components can best be separated by chromatography.

7. Gas chromatography is suited for compounds which are not highly volatile and which form vapours without decomposition.

8. Since diazo compounds may lose nitrogen in the form of *nitrogen gas*, they sometimes do not respond Lassaigne's test for nitrogen.

9. Although blue coloured ferric ferrocyanide is formed but due to the presence of yellow coloured Fe^{3+} salts, the blue colour gives the shade of green.

10. $(C_2H_5)_3N^+HCl^-$ is an ionic compound, so it will form precipitate of AgCl on adding $AgNO_3$. In 2, 4, 6-trinitro-chlorobenzene, —Cl is activated due to the presence of three —NO_2 groups in *o*- and *p*-positions, so it will be very reactive leading to formation of AgCl on adding HNO_3 and $AgNO_3$.

11. Compounds having both N and S will form NaCNS leading to red coloured $Fe(CNS)_3$ during Lassaigne's test for nitrogen.

12. Sulphur can be estimated as $BaSO_4$ by Carius as well as Messenger method. In Messenger method, organic compound containing sulphur is heated (oxidised) with alkaline potassium permanganate to form sulphuric acid which is estimated as barium sulphate by adding barium chloride.

$$2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + O$$

$$\underset{\text{Thiourea}}{H_2N\overset{\overset{S}{\|}}{C}NH_2} + 4O + H_2O \longrightarrow H_2SO_4 + \underset{\text{Urea}}{H_2N\overset{\overset{O}{\|}}{C}NH_2}$$

$$H_2SO_4 + BaCl_2 \longrightarrow BaSO_4\downarrow + 2HCl$$

13. In mixed melting point, the sample whose purity is to be tested is mixed with the pure sample of the compound and the melting point of the mixture is determined, in case the melting point of the mixture is exactly same as the melting point of the pure sample, the compound in question is said to be pure, otherwise impure.

14. Fusion of the organic compound with Na converts organic compound into inorganic compounds.

15. A positive Beilstein's test for halogens does not always indicate the presence of halogen since some halogen free compounds *viz.* urea, thiourea, amides etc. also respond this test. The reason being the fact that these halogen free compounds form cuprous cyanide which is volatile and decomposes to copper which burns with green flame.

16. Oxygen is always detected indirectly, *i.e.* in the form of functional groups like —COOH, —CHO, —NO_2, —$CONH_2$ etc.

17. $\underset{2\text{ g}}{\text{N-containing compound}} \xrightarrow{\text{heat}} \underset{0.4\text{ g}}{N_2}$

0.4 g of N_2 is obtained from 2 g of compound

28 g of N_2 is obtained from $\frac{2}{0.4} \times 28 = 140$

Hence molecular weight of the compound is 140 which coincides with $C_6H_5N_2Cl$ (72 + 5 + 28 + 35.5 = 140.5).

18. 0.5 g of Se = 100 g of enzyme

78.4 g of Se = $\frac{100}{0.5} \times 78.4 = 1.568 \times 10^4$ g.

19. Molecular mass of a compound depends upon its molecular formula, hence when molecular formulae of the two compounds differ, they will have different molecular weights.

20. Ratio of C : H = $\frac{80}{12} : \frac{20}{1} = \frac{20}{3} : 20 = 1 : 3$

$\therefore$ Expirical formula = CH_3.

21. Ratio of C : H = 4 : 1 = $\frac{4}{12} : \frac{1}{1} = \frac{1}{3} : 1 = 1 : 3$

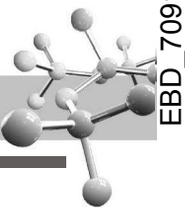
$\therefore$ Empirical formula = CH_3 or Molecular formula = C_2H_6.

22. Simplest ratio of C : H = 1 : 2.37 or 3 : 7

$\therefore$ Empirical formula = C_3H_7

But C_3H_7 does not coincide to any hydrocarbon ; remember that a hydrocarbon can't have odd number of H atoms. Hence the molecular formula for the hydrocarbon should be C_6H_{14} whose molecular weight will be 72 + 14 = 86.

23. A carboxylic acid should contain —COOH ; hence CH_2O_2 should coincide with H—COOH *i.e.* molecular formula and empirical formula for the simplest carboxylic acid is CH_2O_2.



EXERCISE 24.2

MCQ > 1 CORRECT OPTION	1	(a,b,c)	2	(b,c,d)	3	(b,c,d)	4	(b,c,d)	5	(a,c)
	6	(a,b)	7	(a,b)	8	(a,b,d)	9	(b,c,d)	10	(b, d)
	11	(b, d)	12	(a, c, d)	13	(a, b, c)	14	(c)	15	(b)
PASSAGE 1	16	(d)	17	(a)	18	(a)				
PASSAGE 2	19	(b)	20	(d)	21	(b)	22	(d)	23	(b)
PASSAGE 3	24	(c)	25	(c)	26	(c)	27	(d)		
MATCH THE FOLLOWING	28	(A)-a, d ; (B)-a, b ; (C)-c, d ; (D) -d								
	29	(A) – a; (B) – a, b; (C) – c, d; (D) – b								
	30	(A) - a,b,c,d; (B) - c; (C) - b,c; (D) - b,c								
	31	(A) – b,d; (B) – b,c,d; (C) – b,c; (D) – a								
	32	(A) – b; (B) – a; (C) – c, d; (D) – c, d								
	33	(A)-d ; (B)-a, c ; (C)-c ; (D)-b								
	34	(A)-c, d ; (B)-a, b ; (C)-a, b, c ; (D)-a, d								
A/R	35	(d)	36	(b)	37	(a)				

1. Boiling point of a liquid has no concern with its solubility; however all the other three factors affect the boiling point of a compound.

2. A liquid has a constant boiling point at atmospheric pressure, however the boiling point of a liquid may be (*a*) decreased by boiling it under reduced pressure, or (*b*) increased by boiling it at pressure higher than atmospheric pressure. Steam reduce atmospheric pressure, hence can be regarded as distillation under reduced pressure.

3. Only *o*-nitrophenol is capable of forming intramolecular H-bonding (chelation) which leads to its lower b.p. (less than 100°C) and also lower solubility in water (steam), all other statements (b, c and d) are false.

4. Simple distillation is applied when boiling points of the two components differ by more than 10°C. Ethanol and water both are capable of forming intermolecular H-bonds with each other, so they distil together. The constituents of essential oils have nearly similar boiling point.

5. Sugar and water, both are soluble in water and both are insoluble in petroleum ether, hence these two solvents can't be used. On the other hand, sugar is soluble in alcohol while sodium chloride is insoluble, hence the two can be separated by alcohol. Sodium chloride undergoes sublimation.

6. Hydroxylamine and hydrazine, both do not have carbon, hence NaCN will not be formed in Lassaigne's extract leading to negative test for nitrogen.

7. Lassaigne's extract for the compound *p*- nitrochlorobenzene contains both NaCN as well as NaCl, so on treatment with $AgNO_3$, the extract gives precipitate of AgCN as well as AgCl unless it is boiled with HNO_3 which will remove NaCN as gaseous HCN.

8. Silver iodide is somewhat soluble in nitric acid.

9. Only compounds containing reactive chlorine, *i.e.* when attached to sp^3 hybrid carbon will react with $AgNO_3$ forming white precipitate of AgCl. Unreactive chlorine (chlorine attached to sp^2 C) can give positive reaction with $AgNO_3$ when the compound is first fused with metallic sodium.

$$CH_3COCl \xrightarrow{H_2O} CH_3COOH + HCl \xrightarrow{AgNO_3} AgCl\downarrow$$

14. **(c)** Anilinium hydrochloride has ionisable chlorine whereas chlorobenze has non ionizable chlorine. Thus anilium hydrochloride gives white precipitate of AgCl with $AgNO_3$.

$$C_6H_5NH_3^+Cl^- + AgNO_3 \rightarrow C_6H_5NH_3^+NO_3^- + AgCl\downarrow$$

In chloroaniline, –Cl is directly attached to benzene ring, hence it is non-reactive.

15. **(b)** Only compounds containing reactive chlorine, i.e. when attached to sp^3 hybrid carbon will react with $AgNO_3$ forming white precipitate of AgCl. Unreactive chlorine (chlorine attached to sp^2 C) can give positive reaction with $AgNO_3$ when the compound is first fused with metallic sodium.

$$CH_3COCl \xrightarrow{H_2O} CH_3COOH + HCl \xrightarrow{AgNO_3} AgCl\downarrow$$

24. **(c)** Since the II is soluble in aq. $NaHCO_3$ and oxidised by $KMnO_4$, it should have a $-COOH$ group and an alcoholic group (1° or 2°).

25. **(c)** Compound III reacts with Lucas reagent, so it should be an alcohol with less than six carbon atoms.

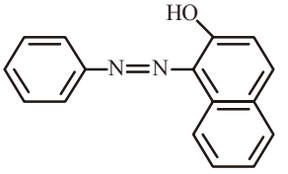
26. **(c)** Among the three given options, Fehling test is given only by VII.

27. **(d)** From the flow-sheet diagram, it is evident that compound V undergoes iodoform reaction. Since all the three compounds can undergo iodoform reaction, all the three options are correct.

$$ICH_2-\overset{\overset{O}{\|}}{C}-CH_2CH_3 \xrightarrow{I_2} I_3C-\overset{\overset{O}{\|}}{C}-CH_2CH_3 \xrightarrow{OH^-} CHI_3\downarrow + CH_3CH_2COO^-$$

34. **(A) - r, s; (B) - p, q; (C) - p, q, r; (D) - p, s**
compound (A) does not have carbon, hence does not responds (*p*) test.

35. **(d)** The colour of the azo dye formed will be orange red but not blue. However, the colour of dye can said to be due to extended conjugation due to presence of azo group.



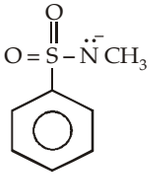
EXERCISE 24.3

1. (a) Only 4-chlorophenol is soluble in aqueous sodium hydroxide

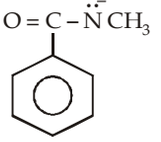
(b) 2,4,6-Trinitrophenol is exceptionally stronger acid and thus soluble in aq. $NaHCO_3$

(c) Only 2, 4-dinitrophenol is soluble in aq. $NaHCO_3$

(d) $C_6H_5SO_2NH\,CH_3$ is soluble in aq. NaOH, while in $C_6H_5CONHCH_3$, N is not acidic enough to dissolve in NaOH. Observe the structure of the conjugate base of the two compounds.



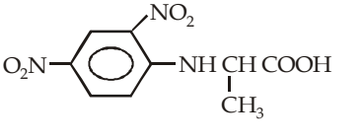
(more stable)



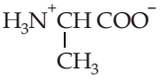
(e) Hexane is soluble in conc. H_2SO_4

(f) $CH_3CH_2NH_2$ is soluble in dil. acids.

(g)



Insoluble in aq. HCl
(2, 4-dinitrophenyl group reduces basic character of the –NH group)



soluble in HCl

2. (a) Toluene reacts with bromine to evolve HBr, while no HBr is evolved in case of cyclohexene. Thus if the reaction is performed in organic solvent, bubbles of HBr can be observed, further the escaping HBr gas will react with moist air forming a cloud. In case, the reaction is performed in water, the HBr (now in the form of acid) can be tested by adding moist litmus paper.

(b) Thiols give a precipitate with heavy cations like Hg^{2+}, Pb^{2+} and Cu^{2+}.

(c) The 2° ROH is oxidized by a Cr (VI) reagent, thus changing its colour from orange to green.

(d) Conc. H_2SO_4 dissolves the alcohol with the evolution of heat. In case of chloride, two different layers will be formed on addition of conc. H_2SO_4.

(e) Allyl alcohol, although a 1° alcohol, behaves like 3° alcohol because its carbocation (allyl cation) is as stable as 3° cations, hence it will react as fast as 3° alcohols, while propanol will not react with Lucas reagent.

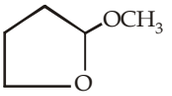
(f) Oxalic acid is oxidised by acidic $KMnO_4$, thus it discharges $KMnO_4$ solution.

(g) $RCOCl \xrightarrow{H_2O} RCOOH + HCl\,;\ HCl \xrightarrow{AgNO_3} \underset{\text{Insoluble in } HNO_3}{AgCl\downarrow}\ ;\ RCOOH \xrightarrow{AgNO_3} \underset{\text{Soluble in } HNO_3}{RCOOAg\downarrow}\ ;$

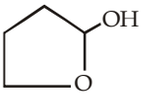
(h) $(CH_3CO)_2O \xrightarrow[\text{warm}]{H_2O} \underset{\text{turns blue litmus red}}{CH_3COOH}\ ;\ CH_3COOC_2H_5 \xrightarrow[\text{warm}]{H_2O} \text{No reaction}$

(i) $C_6H_5SO_2NHCH_3$ is more acidic, hence it dissolves easily in NaOH than $C_6H_5CONHCH_3$.

(j)



An acetal



Hemiacetal (positive test with Tollen's reagent)

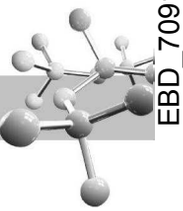
(k) $\underset{\text{Hinsberg reagent}}{-NH_2 + C_6H_5SO_2Cl} \xrightarrow{KOH} \underset{\text{(soluble)}}{-N^{\ominus}K^{\oplus}SO_2C_6H_5} \xrightarrow{H_3O^+} \underset{\text{precipitate}}{-NH\,SO_2\,C_6H_5}$

$>NH + C_6H_5SO_2Cl \xrightarrow{KOH} \underset{\text{precipitate}}{>N\,SO_2C_6H_5} \xrightarrow{H_3O^+} \text{Precipitate}$

(l) $(C_2H_5)_2NH$ responds Hinsberg test, while $(C_2H_5)_3N$ does not respond Hinsberg test.

(m) $(C_2H_5)_3N^+HCl + NaOH(aq.) \longrightarrow \underset{\text{water insoluble}}{(C_2H_5)_3N}$

$\underbrace{(C_2H_5)_4N^+Cl^- + NaOH^-(aq.)}_{\text{solution}} \longrightarrow \text{No reaction}$



EBD_7091

(n) $(C_2H_5)_4N^+Cl^- + H_2O \longrightarrow \underbrace{(C_2H_5)_4N^+OH^- + HCl}_{\text{neutral}}$

$\underbrace{(C_2H_5)_4N^+OH^-}_{\text{basic solution}} + H_2O \longrightarrow$ No reaction

3. An ester when treated with NH_2OH gives a hydroxamic acid (RCONHOH) which produces a red-violet colour with $FeCl_3$.

$$R-\overset{\overset{O}{\|}}{C}-OR' + H_2NOH \longrightarrow \underset{\text{Hydroxamic acid}}{R-\overset{\overset{O}{\|}}{C}-NHOH} + R'OH$$

Anhydrides also respond this test.

5. Meq of unused acid = Meq of NaOH = 25.32 × 0.198 = 5 meq
No. of meq of acid taken = 50 × 0.230 = 10.15 meq
Meq of acid used = 10.15 − 5 = 5.15 meq
or 1.325 g of sample of the fertilizer = 5.15 mL of 1 NH_2SO_4
According to Kjeldahl's method

$$\% \text{ of nitrogen} = \frac{1.4 \times \text{Normality of acid} \times \text{Vol. of acid used (mL)}}{\text{Wt. of compound}} = \frac{1.4 \times 1 \times 5.15}{1.325} = \mathbf{5.44\%}$$

6. (*a*) 67.2 mL of compound at NTP = 0.369 g

22400 mL of compound = $\frac{0.369 \times 22400}{67.2}$ = 123 g

Mol. wt of the bromo derivative = 123

(*b*) 448 mL of vapour at STP are obtained from 1.49 g

22400 mL of vapour at STP = $\frac{1.49}{448} \times 22400 = 74.5$ g

∴ Mol. wt. of the compound = 74.5.

7. *Calculation of % of N.*

50 mL of 0.05 M H_2SO_4 = 50 mL of 0.1 NH_2SO_4 ($\because N_{H_2SO_4} = 2 \times M_{H_2SO_4}$)

Excess of acid requires 25 mL of 0.1 M or 0.1 N NaOH ($\because N_{NaOH} = M_{NaOH}$)

25 mL of 0.1 N NaOH = 25 mL of 0.1 N H_2SO_4

Vol. of 0.1 N H_2SO_4 used for the neutralisation of NH_3 = 50 − 25 = 25 mL

$$\therefore \quad \% \text{ of nitrogen} = \frac{1.4 \times \text{Normality of acid} \times \text{Vol. of acid}}{\text{Wt. of compound}} = \frac{1.4 \times 0.1 \times 25}{0.303} = 11.55\%$$

Hence % of O = 100 − (69.4 + 5.8 + 11.55) = 13.25

Calculation of empirical formula of the compound

Element	Percentage	Relative No. of atoms	Simplest ratio
C	69.4	69.4/12 = 5.8	5.8/0.825 = 7
H	5.8	5.8/1 = 5.8	5.8/0.825 = 7
N	11.55	11.55/14 = 0.825	0.825/0.825 = 1
O	13.25	13.25/16 = 0.825	0.825/0.825 = 1

Thus the empirical formula of the compound = C_7H_7NO.

8. % of C = $\frac{12}{44} \times \frac{0.905}{0.450} \times 100 = 54.85$

% of H = $\frac{2}{18} \times \frac{0.185}{0.450} \times 100 = 4.58$

% of Cl = $\frac{35.5}{143.5} \times \frac{0.574}{0.350} \times 100 = 40.57$

Since the sum of the three % is 100, the compound does not contain any oxygen.

Determination of empirical formula

Element	Percentage	Relative No. of atoms	Simplest ratio
C	54.85	54.85/12 = 4	4/1 = 4
H	4.58	4.58/1 ≈ 4	4/1 = 4
Cl	40.57	40.57/35.5 = 1	1/1 = 1

∴ Empirical formula of the compound = C_4H_4Cl

$$n = \frac{87.5 \times 2}{48 + 4 + 35.5} = \frac{175}{87.5} = 2$$

Thus, molecular formula = $(C_4H_4Cl)_2 = C_8H_8Cl_2$

9. *Determination of molecular formula*

Element	Percentage	Relative No. of atoms	Simplest ratio
C	42.86	42.86/12 = 3.57	3.57/1.19 = 3
H	2.40	2.40/1 = 2.40	2.40/1.19 = 2
N	16.67	16.67/14 = 1.19	1.19/1.19 = 1
O	38.07	38.07/16 = 2.38	2.38/1.19 = 2

Thus empirical formula of the compound = $C_3H_2NO_2$

Empirical formula weight = 36 + 2 + 14 + 32 = 84

Determination of molecular weight = $\frac{K_b \times \omega \times 1000}{\Delta T \times W} = \frac{2.53 \times 5.5 \times 1000}{1.84 \times 45} = 168$

Hence molecular formula = $(C_3H_2NO_2)_2$ ($\because$ $n = 168/84 = 2$)

= $C_6H_4N_2O_4$

10. Conversion of given volume of N_2 at given conditions to NTP

$$V_2 = \frac{P_1V_1 \times T_2}{T_1 \times P_2} = \frac{17.85 \times 750 \times 273}{300 \times 760} = 16.03 \text{ mL}$$

$$\% \text{ of nitrogen} = \frac{28 \times \text{Vol. of nitorgen at NTP} \times 100}{22400 \times \text{Wt. of compound}} = \frac{28 \times 16.03 \times 100}{22400 \times 0.1237} = 16.198$$

$$\% \text{ of carbon} = \frac{12}{44} \times \frac{0.3582}{0.1413} \times 100$$

$$\% \text{ of hydrogen} = \frac{2}{18} \times \frac{0.1904}{0.1413} \times 100$$

By usual calculations, as above, empirical formula of the compound is found to be $C_5H_{13}N$

Determination of the molecular weight of the organic base.

$$\frac{\text{Mol. Wt. of chloroplatinate } (B_2PtCl_6)}{\text{At. Wt. of platinum}} = \frac{\text{Wt. of chloroplatinate}}{\text{Wt. of platinum}}$$

$$\frac{2B + 410}{195} = \frac{100}{33.4}$$

$$2B = \left(\frac{100}{33.4} \times 195\right) - 410 = 173.8$$

B = 86.9 (where B is the eq. Wt. of the base)

Hence Mol. Wt. of the monoacidic base = 86.9 × 1 = 86.9

$\therefore$ Molecular formula = $\frac{\text{Mol. Wt.}}{\text{Emp. formula Wt.}} \times \text{Empirical formula} = \frac{86.9}{86.9} \times C_5H_{13}N = C_5H_{13}N$

11. $\% \text{ of C} = \frac{12}{44} \times \frac{0.352}{0.236} \times 100 = 27.05$

$\% \text{ of H} = \frac{2}{18} \times \frac{0.108}{0.236} \times 100 = 5.08$

% of O = 100 − (27.05 + 5.08) = 67.87

As usual and in above examples, empirical formula of the compound = $C_2H_3O_2$

Calculation of molecular weight of the compound

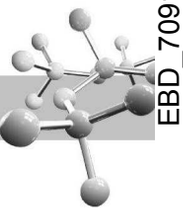
30.0 mL of 0.1 N NaOH = 0.177 g of acid

1000 mL of 1 N NaOH = $\frac{0.177}{30} \times \frac{1000 \times 1}{0.1} = 59$ g

$\therefore$ Eq. Wt. of the acid = 59

Mol. Wt. of the dibasic acid = Eq. Wt. × 2 = 59 × 2 = 118

$\% \text{ Mol formula} = \frac{118}{59} \times C_2H_3O_2 = C_4H_6O_4.$



12. % of C = $\frac{12}{44} \times \frac{0.08}{0.40} \times 100 = 2.22$

% of H = $\frac{2}{18} \times \frac{0.39}{0.40} \times 100 = 27.30$

% of O = 100 – (2.22 + 27.30) = 71.48

By usual calculations, empirical formula of the acid is found to be CHO_2

Determination of molecular weight

$$\text{Eq. Wt. of acid} = \frac{\text{Wt. of silver salt} \times 108}{\text{Wt. of silver}} - 107 = \left(\frac{1.0}{0.71} \times 108\right) - 107 = 45$$

Mol. Wt. of the diabasic acid= 45 × 2 = 90

$$\text{Mol. formula of the acid} = \frac{\text{Mol. Wt.}}{\text{Empirical formula Wt.}} \times \text{Empirical formula} = \frac{90}{45} \times CHO_2 = C_2H_2O_4$$

13. By usual calculations, empirical formula of the acid A = $C_2H_3O_2$

$$\text{Eq. Wt. of acid A} = \frac{\text{Wt. of Ag salt} \times 108}{\text{Wt. of Ag}} - 107 = \frac{100 \times 108}{65.1} - 107 = 59$$

Molecular weight of the ethyl ester of the acid = 2 × 87 = 174

Determination of molecular weight of the acid

Let the acid is monobasic, RCOOH, then the molecular weight of its ethyl ester ($RCOOC_2H_5$)

$$= RCOOH - H + C_2H_5 = 59 - 1 + 29 = 87$$

Thus the acid is not monobasic, now let it be dibasic, then the molecular wegiht of its ester

$$= (RCOOH)_2 - 2H + 2\,C_2H_5 = (59)2 - 2 + 2\,(29) = 118 - 2 + 58 = 174$$

Thus the acid is diabasic acid.

Hence its molecular formula= Empirical formula × Basicity = $C_2H_3O_2 \times 2 = C_4H_6O_4$.

14. Empirical formula of the acid from given percentages = $C_7H_6O_2$

Mol. Wt. of the acid

25 mL of $\frac{M}{10}$ diacidic base = 25 mL of $\frac{2N}{10}$ or $\frac{N}{5}$ or 0.2 N diacidic base

$$\text{Eq. Wt. of acid} = \frac{\text{Wt. of organic acid} \times 1000}{\text{Vol. of base required} \times \text{Normality of base}} = \frac{0.610 \times 1000}{25 \times 0.2} = 122$$

$\therefore$ Mol. Wt. of acid = Eq. wt × Basicity = 122 × 1 = 122

$\therefore$ Mol. formula of the acid = $\left(\frac{122}{84 + 6 + 32}\right) \times C_7H_6O_2 = C_7H_6O_2$

15. By usual calculations, empirical formula of the compound = C_3H_8O

Determination of molecular weight

$$\text{Mol. wt. of volatile compound} = \frac{\text{Wt. of compound} \times 22400}{\text{Vol. of air displaced at NTP}} = \frac{0.20 \times 22400}{74.66} = 60$$

$$\text{Molecular formula of the compound} = \frac{60}{36 + 8 + 16} \times C_3H_8O = C_3H_8O$$

16. Empirical formula calculated from percentage of elements = C_3H_9N

Determination of molecular weight

$$\frac{\text{Mol. Wt. of chloroplatinate } (B_2H_2PtCl_6)}{\text{At. Wt. of platinum}} = \frac{\text{Wt. of chloroplatinate}}{\text{Wt. of platinum}}$$

$$\frac{2B + 410}{195} = \frac{100}{36.93}$$

$$2B = \left(\frac{100}{36.93} \times 195\right) - 410 = 118.06$$

B = 59.03 (B is eq. Wt. of the base)

$\therefore$ Mol. wt. of the monoacidic base = 59 × 1 = 59

$$\text{Hence, molecular formula of the base} = \frac{59}{36 + 9 + 14} \times C_3H_9N = C_3H_9N$$

AMINES AND BIOMOLECULES

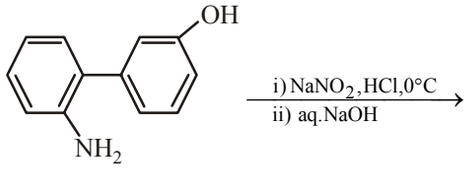
PAST YEAR QUESTIONS JEE ADVANCED/IIT-JEE (2013 - 2017)

MCQs with One Correct Answer

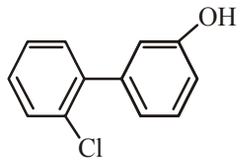
1. On complete hydrogenation, natural rubber produces **[JEE Adv. 2016]**

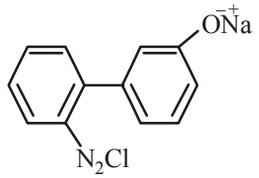
(a) ethylene–propylene copolymer
(b) vulcanised rubber
(c) polypropylene
(d) polybutylene

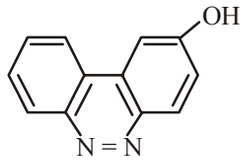
2. The major product of the following reaction is

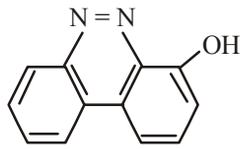


[JEE Adv. 2017]

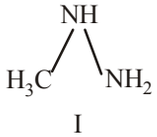
(A) 

(B) 

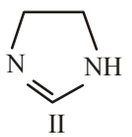
(C) 

(D) 

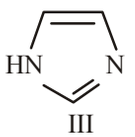
3. The order of basicity among the following compounds is **[JEE Adv. 2017]**



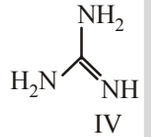
I



II



III



IV

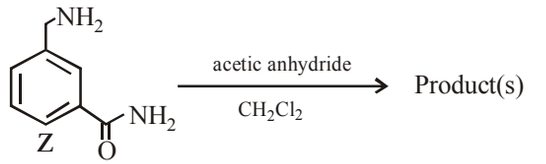
(A) II > I > IV > III
(B) IV > II > III > I
(C) IV > I > II > III
(D) I > IV > III > II

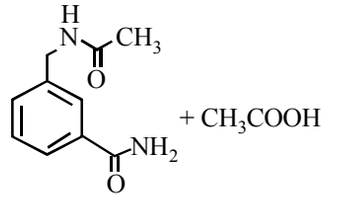
MCQs with One or More Than One Correct

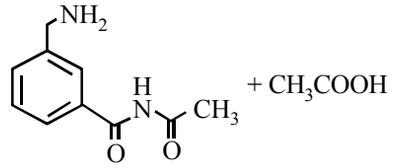
1. Hydrogen bonding plays a central role in the following phenomena **[JEE Adv. 2014]**

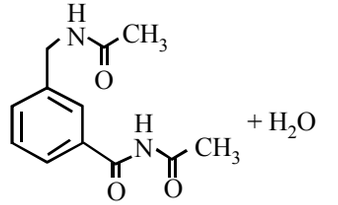
(a) Ice floats in water
(b) Higher Lewis basicity of primary amines than tertiary amines in aqueous solutions
(c) Formic acid is more acidic than acetic acid
(d) Dimerisation of acetic acid in benzene

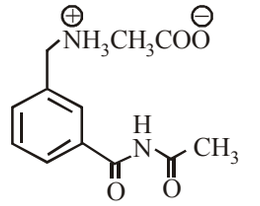
2. In the reaction shown below, the major product(s) formed is/ are **[JEE Adv. 2014]**



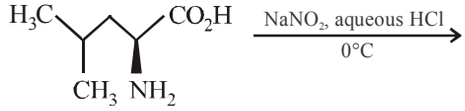
(a) 

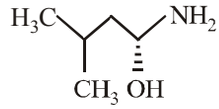
(b) 

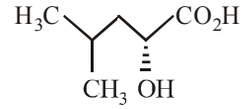
(c) 

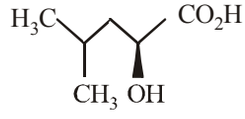
(d) 

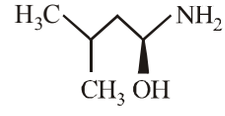
3. The major product of the reaction is **[JEE Adv. 2015]**



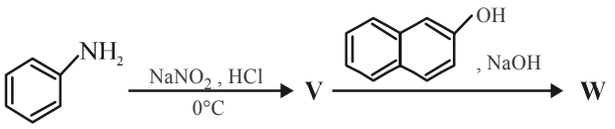
(a) 

(b) 

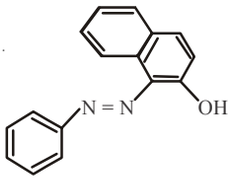
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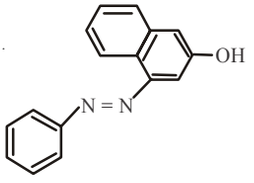
(d) 

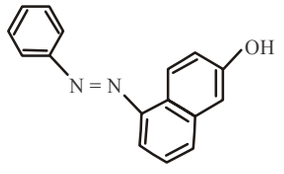
4. In the following reactions, the major product W is

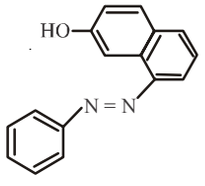


[JEE Adv. 2015]

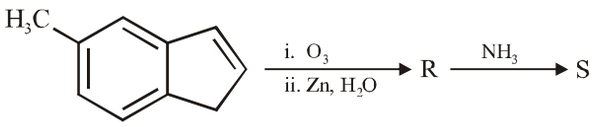
(a) 

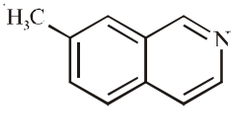
(b) 

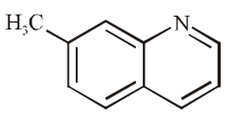
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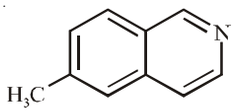
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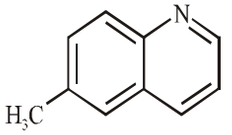
5. In the following reactions, the product S is **[JEE Adv. 2015]**



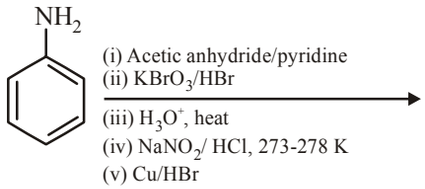
(a) 

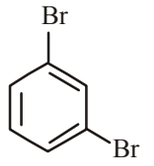
(b) 

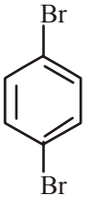
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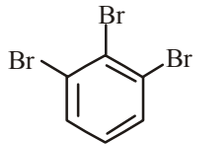
(d) 

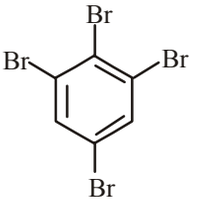
6. The product(s) of the following reaction sequence is(are) **[JEE Adv. 2016]**



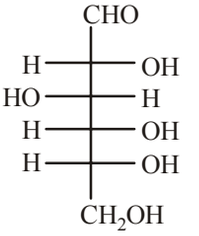
(a) 

(b) 

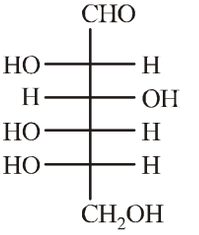
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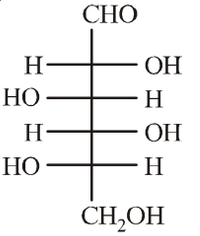
(d) 

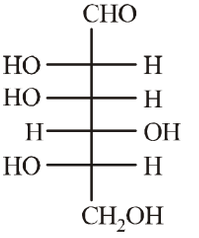
7. The structure of D-(+)-glucose is **[JEE Adv. 2015]**

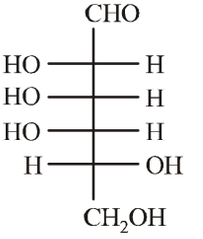


The structure of L-(–)-glucose is

(a) 

(b) 

(c) 

(d) 

8. For 'invert sugar', the correct statement(s) is(are)
(Given : specific rotations of (+) -sucrose, (+)-maltose, L-(-)-glucose and L-(+) fructose in aqueous solution are + 66°, +140°, –52° and +92°, respectively) **[JEE Adv. 2016]**

(a) 'invert sugar' is prepared by acid catalyzed hydrolysis of maltose

(b) 'invert sugar' is an equimolar mixture of D-(+)-glucose and D-(-)-fructose

(c) specific rotation of 'invert sugar' is –20°

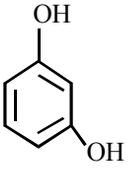
(d) on reaction with Br_2 water, 'invert sugar' forms saccharic acid as one of the products

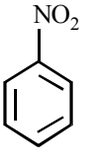
Match the following

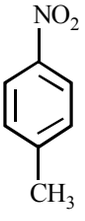
DIRECTIONS (Q. No. 2) : Match the four starting materials **(P, Q, R, S)** given in **List-I** with the corresponding reaction schemes **(I, II, III, IV)** provided in **List-II** and select the correct answer using the code given below the lists.

1. **List - I** **List - II** **[JEE Adv. 2014]**

P. 

Q. 

R. 

S. 

1. Scheme I

(i) $KMnO_4$, $HO^{\ominus}$, heat (ii) $H^{\oplus}$, H_2O
(iii) $SOCl_2$ (iv) NH_3 ? $\longrightarrow C_7H_6N_2O_3$

2. Scheme II

(ii) Sn/HCl (ii) CH_3COCl (iii) conc. H_2SO_4 (iv) HNO_3 (v) dil. H_2SO_4, heat (vi) $HO^{\ominus}$? $\longrightarrow C_6H_6N_2O_2$

3. Scheme III

(i) red hot iron, 873 K (ii) fuming HNO_3, H_2SO_4, heat
(iii) $H_2S.NH_3$ (iv) $NaNO_2$, H_2SO_4 (v) hydrolysis
? $\longrightarrow C_6H_5NO_3$

4. Scheme IV

(i) conc. H_2SO_4, 60°C
(ii) conc. HNO_3, conc. H_2SO_4
(iii) dil. H_2SO_4, heat ? $\longrightarrow C_6H_5NO_4$

Code:

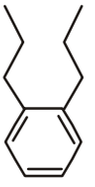
	P	Q	R	S		P	Q	R	S
(a)	1	4	2	3	(b)	3	1	4	2
(c)	3	4	2	1	(d)	4	1	3	2

Comprehension Based Questions

PASSAGE - 1

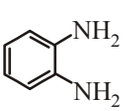
Treatment of compound O with $KMnO_4/H^+$ gave P, which on heating with ammonia gave Q. The compound Q on treatment with Br_2/NaOH produced R. On strong heating, Q gave S, which on further treatment with ethyl 2-bromopropanoate in the presence of KOH followed by acidification, gave a compound T.

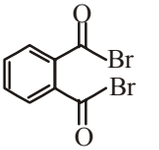
[JEE Adv. 2016]

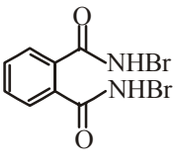


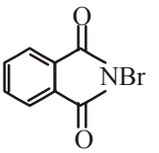
(O)

1. The compound R is

(a) 

(b) 

(c) 

(d) 

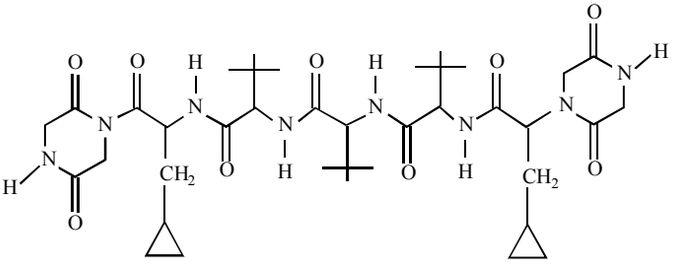
2. The compound T is

(a) glycine (b) alanine
(c) valine (d) serine

Integer Value Correct Type

1. A tetrapeptide has —COOH group on alanine. This produces glycine (Gly), valine (Val), phenyl alanine (Phe) and alanine (Ala), on complete hydrolysis. For this tetrapeptide, the number of possible sequences (primary structures) with — NH_2 group attached to a chiral center is **[JEE Adv. 2013]**

2. The total number of ***distinct naturally occurring amino acids*** obtained by complete acidic hydrolysis of the peptide shown below is **[JEE Adv. 2014]**



PAST YEAR QUESTIONS JEE MAIN/AIEEE (2013 - 2017)

1. A compound with molecular mass 180 is acylated with CH_3COCl to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is : **[JEE M 2013]**

(a) 2 (b) 5

(c) 4 (d) 6

2. An organic compound A upon reacting with NH_3 gives B. On heating B gives C. C in presence of KOH reacts with Br_2 to given $CH_3CH_2NH_2$. A is : **[JEE M 2013]**

(a) CH_3COOH (b) $CH_3CH_2CH_2COOH$

(c) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}-COOH$ (d) CH_3CH_2COOH

3. The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was : **[JEE M 2013]**

(a) Methyl isocyanate (b) Methylamine

(c) Ammonia (d) Phosgene

4. On heating an aliphatic primary amine with chloroform and ethanolic potassium hydroxide, the organic compound formed is: **[JEE M 2014]**

(a) an alkanol (b) an alkanediol

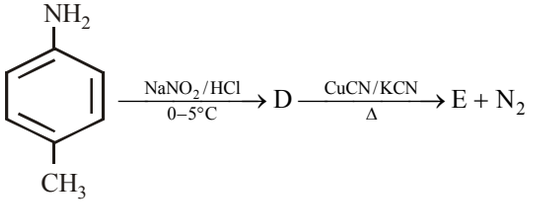
(c) an alkyl cyanide (d) an alkyl isocyanide

5. Considering the basic strength of amines in aqueous solution, which one has the smallest pK_b value? **[JEE M 2014]**

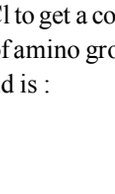
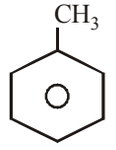
(a) $(CH_3)_2NH$ (b) CH_3NH_2

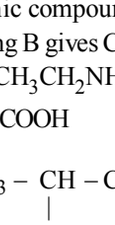
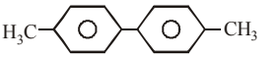
(c) $(CH_3)_3N$ (d) $C_6H_5NH_2$

6. In the reaction **[JEE M 2015]**



the product E is :

(a)  (b) 

(c)  (d) 

7. In the Hofmann bromamide degradation reaction, the number of moles of NaOH and Br_2 used per mole of amine produced are : **[JEE M 2016]**

(a) Two moles of NaOH and two moles of Br_2.

(b) Four moles of NaOH and one mole of Br_2.

(c) One mole of NaOH and one mole of Br_2.

(d) Four moles of NaOH and two moles of Br_2.

8. Synthesis of each molecule of glucose in photosynthesis involves : **[JEE M 2013]**

(a) 18 molecules of ATP (b) 10 molecules of ATP

(c) 8 molecules of ATP (d) 6 molecules of ATP

9. Which one is classified as a condensation polymer? **[JEE M 2014]**

(a) Dacron (b) Neoprene

(c) Teflon (d) Acrylonitrile

10. Which one of the following bases is **not** present in DNA? **[JEE M 2014]**

(a) Quinoline (b) Adenine

(c) Cytosine (d) Thymine

11. Which of the vitamins given below is water soluble ? **[JEE M 2015]**

(a) Vitamin E (b) Vitamin K

(c) Vitamin C (d) Vitamin D

12. Which of the following compounds is not an antacid ? **[JEE M 2015]**

(a) Phenelzine (b) Ranitidine

(c) Aluminium hydroxide (d) Cimetidine

13. Which polymer is used in the manufacture of paints and lacquers ? **[JEE M 2015]**

(a) Polypropene (b) Polyvinyl chloride

(c) Bakelite (d) Glyptal

14. The concentration of fluoride, lead, nitrate and iron in a water sample from an underground lake was found to be 1000 ppb, 40 ppb, 100 ppm and 0.2 ppm, respectively. This water is unsuitable for drinking due to high concentration of : **[JEE M 2016]**

(a) Nitrate (b) Iron

(c) Fluoride (d) Lead

15. Which of the following is an anionic detergent? **[JEE M 2016]**

(a) Cetyltrimethyl ammonium bromide.

(b) Glyceryl oleate.

(c) Sodium stearate.

(d) Sodium lauryl sulphate.

16. Which of the following statements about low density polythene is **FALSE**? **[JEE M 2016]**

(a) Its synthesis requires dioxygen or a peroxide initiator as a catalyst.

(b) It is used in the manufacture of buckets, dust-bins etc.

(c) Its synthesis requires high pressure.

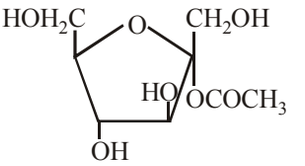
(d) It is a poor conductor of electricity.

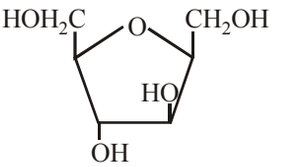
17. The formation of which of the following polymers involves hydrolysis reaction? **[JEE M 2017]**

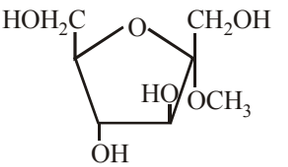
(a) Nylon 6 (b) Bakelite

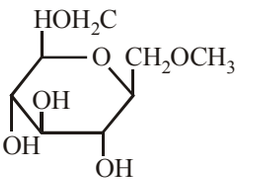
(c) Nylon 6, 6 (d) Terylene

18. Which of the following compounds will behave as a reducing sugar in an aqueous KOH solution? **[JEE M 2017]**

(a) 

(b) 

(c) 

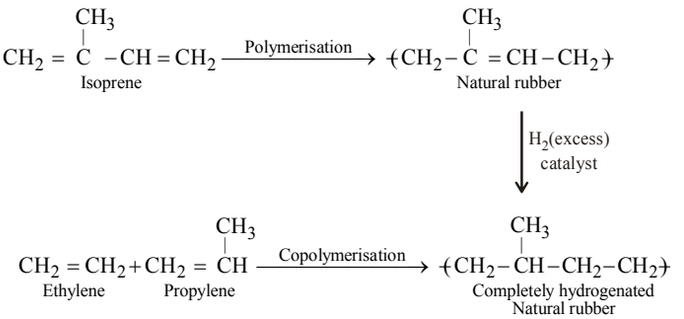
(d) 

SOLUTIONS

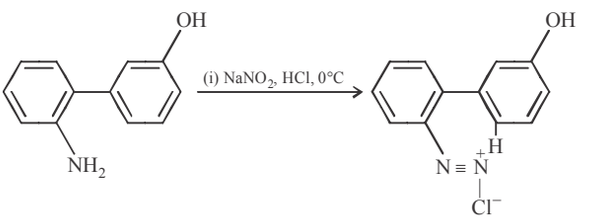
PAST YEAR QUESTIONS JEE ADVANCED/IIT-JEE (2013 - 2017)

MCQs with ONE Correct Answer

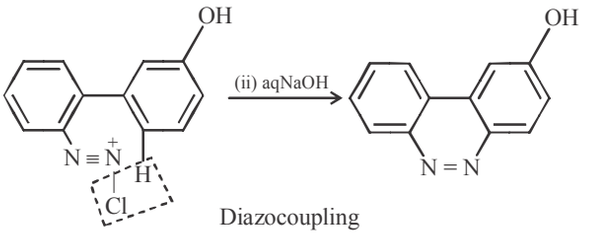
1. (a)



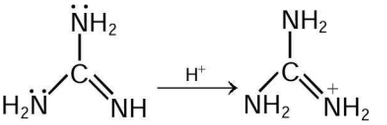
2. (c) **Step 1 :**



Step 2 :

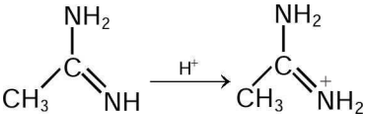


3. (c)



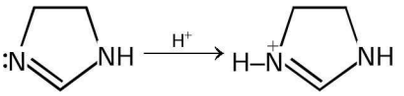
(IV)

The conjugate acid is stabilized by resonance with two different $-NH_2$ group. Hence electron density increases on N of = NH



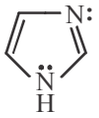
(I)

The conjugate acid is stabilized by resonance with one $-NH_2$ group. Hence as compared to IV lesser increase of electron density on N of = NH



(II)

Lone pair is not involvd in aromaticity. Hence more available



(III)

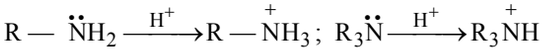
Lone pair is involved in aromatic sextet. Hence not available.

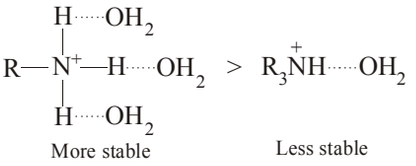
Hence the correct order of basic strength is

IV > I > II > III

MCQs with ONE or More Than One Correct

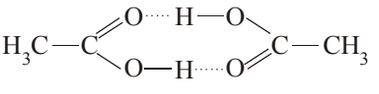
1. (a, b, d) In ice, water molecules are excessively H-bonded giving a cage-like structure which is lighter than water. Primary amines are more basic than tertiary amine, because the protonated 1° amines are extensively H-bonded and hence more stable than the corresponding protonated 3° amines.



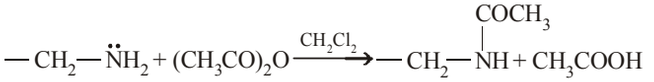


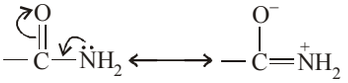
More stable Less stable

Acetic acid undergoes dimerisation in benzene.

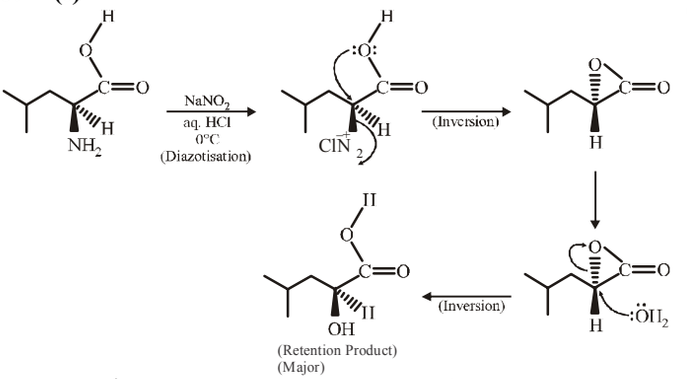


2. (a) $-\ddot{N}H_2$ group is acetylated by acetic anhydride in methylene chloride (solvent). Note that $-CONH_2$ group does not undergo acetylation because here lone pair of electrons is delocalised.



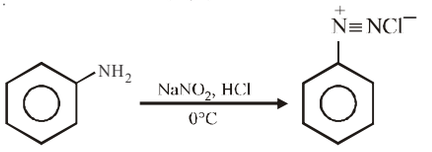


3. (c)

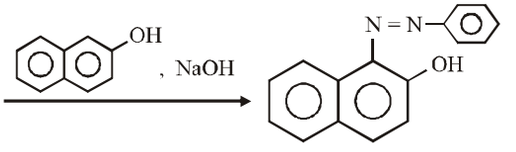


(Retention Product)
(Major)

4. (a)

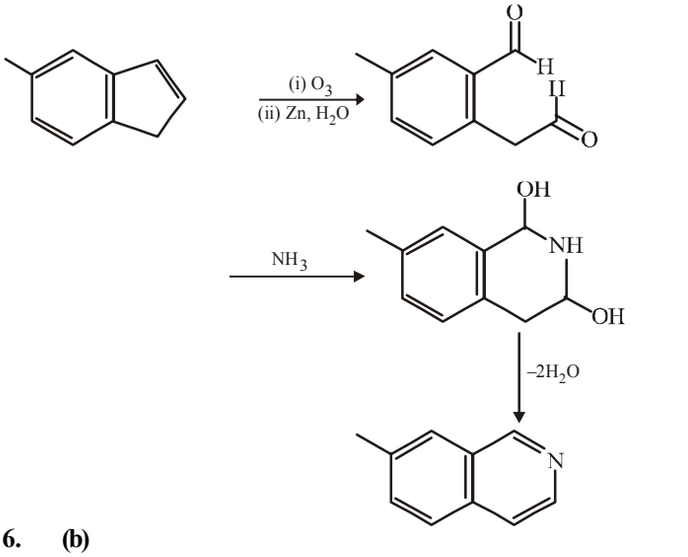


(V)

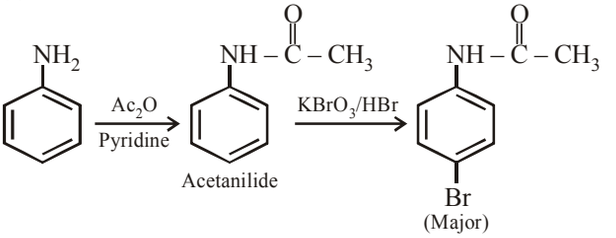


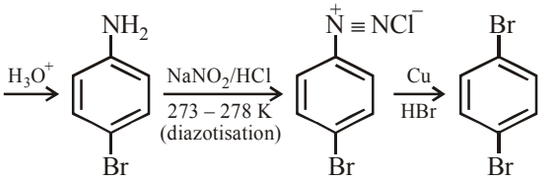
(W)

5. (a)

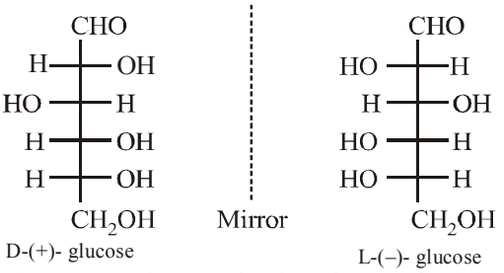


6. (b)

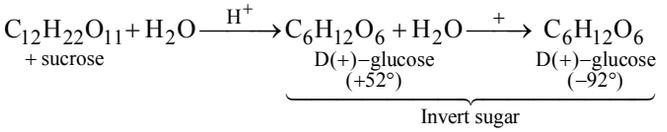




7. (a)



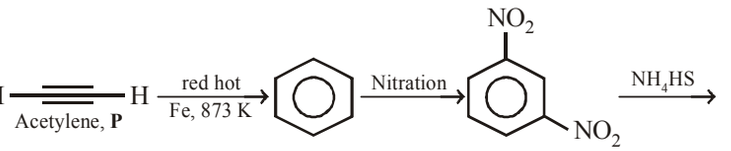
8. (b, c) Invert sugar is an equimolar mixture of D-(+) glucose and D(–) glucose.

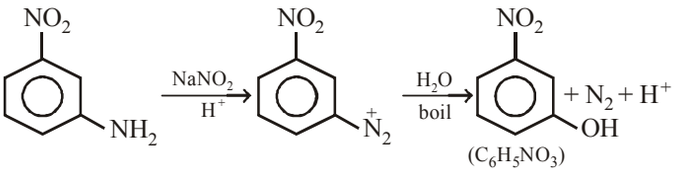


- Specific rotation of invert sugar = $\frac{-92° + 52°}{2} = -20°$
- D-glucose on oxidation with Br_2-water produces gluconic acid and not saccharic acid.

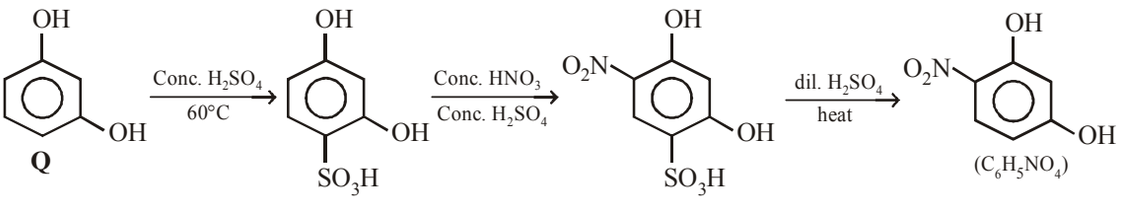
Match the Following

1. (c) **Scheme (III) :**

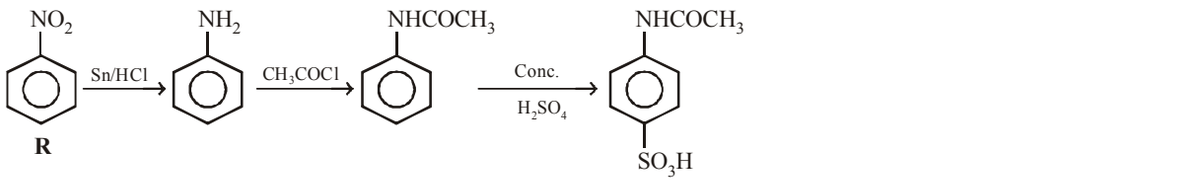


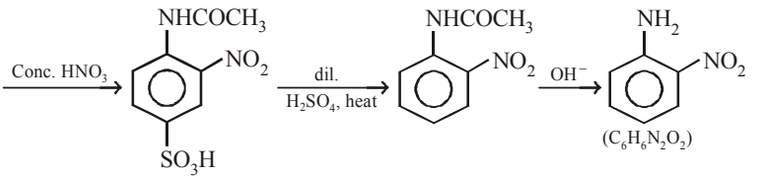


Scheme (IV) :

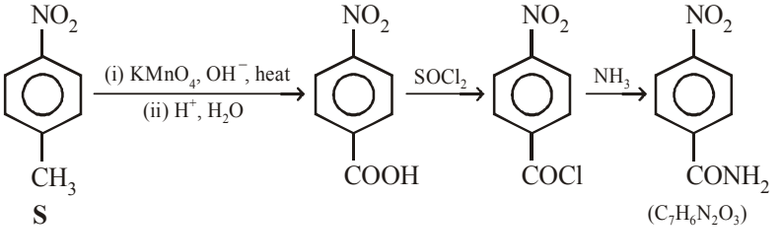


Scheme (II) :



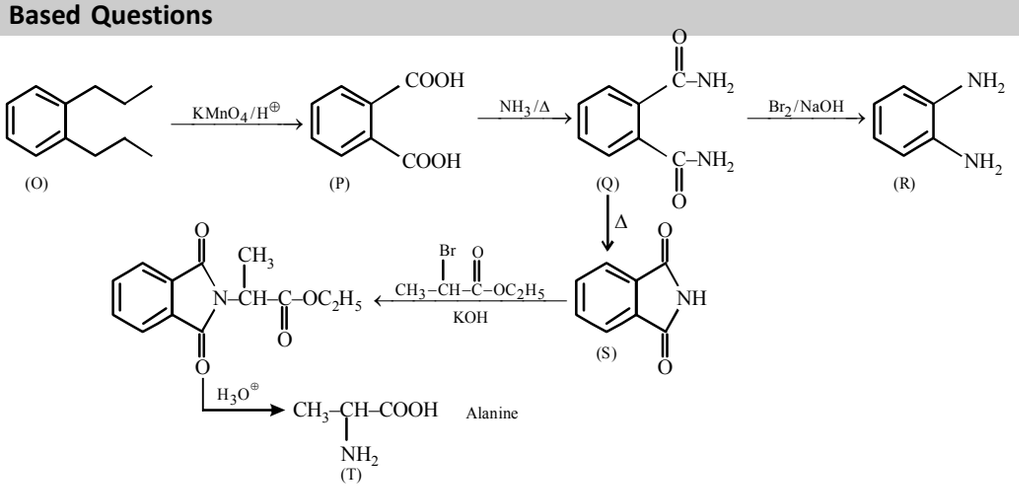


Scheme (I) :



Comprehension Based Questions

1. (a) 2. (b)



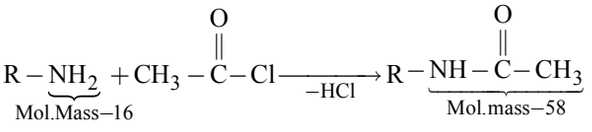
Integer Value Correct Type

1. (4) According to question C – Terminal must be alanine and N – Terminal do have chiral carbon means it should not be glycine. So possible sequence is : Val Phe Gly Ala ; Val Gly Phe Ala ; Phe Val Gly Ala ; Phe Gly Val Ala

2. (1) On hydrolysis, the given peptide gives only one naturally occurring amino acid (glycine).

PAST YEAR QUESTIONS JEE MAIN/AIEEE (2013 - 2017)

1. (b)

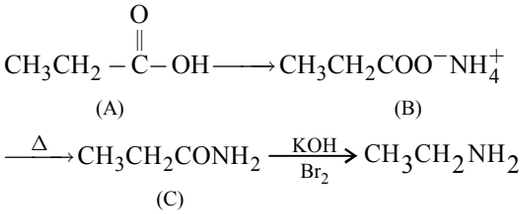


Now since the molecular mass increases by 42 unit as a result of the reaction of one mole of CH_3COCl with one-NH_2 group and the given increase in mass is 210. hence the number of $–NH_2$ group is = 210/42 = 5

2. (d) $A \xrightarrow{NH_3} B \xrightarrow{\Delta} C \xrightarrow[KOH]{Br_2} CH_3CH_2NH_2$

(I) (II) (III)

Reaction (III) is a Hofmann bromamide reaction formation of $CH_3CH_2NH_2$ is possible only from a compound $CH_3CH_2CONH_2$ which can be obtained from the compound $CH_3CH_2COO^- NH_4^+$ (B) in (II) reaction further propanic acid (CH_3CH_2COOH) on reaction with NH_3 produce $CH_3CH_2COO^-NH_4^-$ (reaction I) hence the reaction will be



3. (c) Water-soluble vitamins dissolve in water and are not stored by the body. The water soluble vitamins include the vitamin B-complex group and vitamin C.

4. (a) Phenelzine is an antidepressant, while others are antacids.

5. (d) Glyptal is used in the manufacture of paints and lacquers.

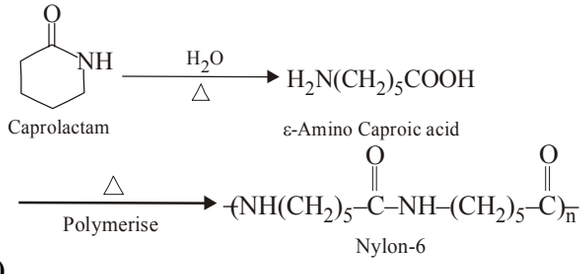
6. (a) The maximum limit of nitrate in drinking water is 50 ppm. Excess nitrate in drinking water can cause disease such as methemoglobinemia ('blue baby' syndrome).

7. (d) Sodium lauryl sulphate ($C_{11}H_{23}CH_2OSO_3^-Na^+$) is an anionic detergent. Glyceryl oleate is a glyceryl ester of oleic acid. Sodium stearate ($C_{17}H_{35}COO^-Na^+$) is a soap. Cetyltrimethyl ammonium bromide

$\left[CH_3(CH_2)_{15}\overset{+}{N}(CH_3)_3\right]Br^-$ is a cationic detergent.

8. (b) High density polythene is used in the manufacture of housewares like buckets, dustbins, bottles, pipes etc. Low density polythene is used for insulating electric wires and in the manufacture of flexible pipes, toys, coats, bottles etc.

9. (a) Formation of Nylon-6 involves hydrolysis of caprolactum, (its monomer) in initial state.



10. (b)

