

Trishna's

IIT JEE
Super Course in
Chemistry
ORGANIC CHEMISTRY



Super Course in Chemistry

**ORGANIC
CHEMISTRY**

for IIT-JEE

Volume 3

Trishna Knowledge Systems

*A division of
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Preface

The IIT-JEE, the most challenging amongst national level engineering entrance examinations, remains on the top of the priority list of several lakhs of students every year. The brand value of the IITs attracts more and more students every year, but the challenge posed by the IIT-JEE ensures that only the *best* of the aspirants get into the IITs. Students require thorough understanding of the fundamental concepts, reasoning skills, ability to comprehend the presented situation and exceptional problem-solving skills to come on top in this highly demanding entrance examination.

The pattern of the IIT-JEE has been changing over the years. Hence an aspiring student requires a step-by-step study plan to master the fundamentals and to get adequate practice in the various types of questions that have appeared in the IIT-JEE over the last several years. Irrespective of the branch of engineering study the student chooses later, it is important to have a sound conceptual grounding in Mathematics, Physics and Chemistry. A lack of proper understanding of these subjects limits the capacity of students to solve complex problems thereby lessening his/her chances of making it to the top-notch institutes which provide quality training.

This series of books serves as a source of learning that goes beyond the school curriculum of Class XI and Class XII and is intended to form the backbone of the preparation of an aspiring student. These books have been designed with the objective of guiding an aspirant to his/her goal in a clearly defined step-by-step approach.

- **Master the Concepts and Concept Strands!**

This series covers all the concepts in the latest IIT-JEE syllabus by segregating them into appropriate units. The theories are explained in detail and are illustrated using solved examples detailing the different applications of the concepts.

- **Let us First Solve the Examples—Concept Connectors!**

At the end of the theory content in each unit, a good number of “Solved Examples” are provided and they are designed to give the aspirant a comprehensive exposure to the application of the concepts at the problem-solving level.

- **Do Your Exercise—Daily!**

Over 200 unsolved problems are presented for practice at the end of every chapter. Hints and solutions for the same are also provided. These problems are designed to sharpen the aspirant’s problem-solving skills in a step-by-step manner.

- **Remember, Practice Makes You Perfect!**

We recommend you work out ALL the problems on your own – both solved and unsolved – to enhance the effectiveness of your preparation.

A distinct feature of this series is that unlike most other reference books in the market, this is not authored by an individual. It is put together by a team of highly qualified faculty members that includes IITians, PhDs etc from some of the best institutes in India and abroad. This team of academic experts has vast experience in teaching the fundamentals and their application and in developing high quality study material for IIT-JEE at T.I.M.E. (Triumphant Institute of Management Education Pvt. Ltd), the number 1 coaching institute in India. The essence of the combined knowledge of such an experienced team is what is presented in this self-preparatory series. While the contents of these books have been organized keeping in mind the specific requirements of IIT-JEE, we are sure that you will find these useful in your preparation for various other engineering entrance exams also.

We wish you the very best!

CHAPTER

1

BASICS OF ORGANIC CHEMISTRY

■■ CHAPTER OUTLINE

Preview

STUDY MATERIAL

Nomenclature of Organic Compounds

Electron Displacement Effects

- Concept Strands (1-17)

Isomerism

- Concept Strands (18-24)

Projection formulae

Stereoisomerism

- Concept Strands (25-28)

Chemical reactions and bond cleavages

Reaction intermediates

Hydrogen Bonding

TOPIC GRIP

- Subjective Questions (10)
- Straight Objective Type Questions (5)
- Assertion-Reason Type Questions (5)

- Linked Comprehension Type Questions (6)
- Multiple Correct Objective Type Questions (3)
- Matrix-Match Type Question (1)

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- Straight Objective Type Questions (80)
- Assertion-Reason Type Questions (3)
- Linked Comprehension Type Questions (3)
- Multiple Correct Objective Type Questions (3)
- Matrix-Match Type Question (1)

ADDITIONAL PRACTICE EXERCISE

- Subjective Questions (10)
- Straight Objective Type Questions (40)
- Assertion-Reason Type Questions (10)
- Linked Comprehension Type Questions (9)
- Multiple Correct Objective Type Questions (8)
- Matrix-Match Type Questions (3)

NOMENCLATURE OF ORGANIC COMPOUNDS

Two systems of nomenclature are generally used for naming organic compounds.

- (i) Trivial or common system
- (ii) IUPAC system

Trivial Names

In the early years, organic compounds were named after the source from which they were first isolated or on the basis of some of their properties. These names are called trivial names or common names.

e.g.,	Citric acid	:	Citrus (Source)
	Malic acid	:	Malus-apple
	Acetic acid	:	Acetum-vinegar

Names based on character

Glucose	(glykys-Sweet)
Acrolein	(acris-pungent)

Common or Trivial names are short and easy to remember, but the disadvantage is that a particular compound may have more than one name. For example, Methylalcohol is also called wood spirit or wood naptha or carbinol.

IUPAC Nomenclature

In order to clearly identify the large number of organic compounds, a systematic method of naming has been developed by the International Union of Pure and Applied Chemistry. This revised system is known as IUPAC system of nomenclature.

The IUPAC name of an organic compound is obtained by identifying the parent hydrocarbon and the functional groups attached to it. The name of the parent hydrocarbon is suitably modified by adding prefixes and suffixes.

The name of each compound has a word root which denotes the number of carbon atoms present in the principal chain of the molecule (i.e., the longest possible continuous chain of carbon atoms, including the functional groups and the multiple bonds). The word roots for chain length upto 12 carbon atoms are given below.

Table 1.1

Chain Length	Root Word
C ₁	meth-
C ₂	eth-
C ₃	prop-
C ₄	but-
C ₅	pent-
C ₆	hex-
C ₇	hept-
C ₈	oct-
C ₉	non-
C ₁₀	dec-
C ₁₁	undec-
C ₁₂	dodec-

IUPAC nomenclature of straight chain alkanes

The name of a straight chain alkane consists of two parts: word root and suffix. The suffix for alkanes is *-ane*. Names of some alkanes are given below.

Table 1.2

Molecular formula	Name	Molecular formula	Name
CH ₄	Methane	C ₇ H ₁₆	Heptane
C ₂ H ₆	Ethane	C ₈ H ₁₈	Octane
C ₃ H ₈	Propane	C ₉ H ₂₀	Nonane
C ₄ H ₁₀	Butane	C ₁₀ H ₂₂	Decane
C ₅ H ₁₂	Pentane	C ₂₀ H ₄₂	Icosane
C ₆ H ₁₄	Hexane	C ₃₀ H ₆₂	triacontane

Different types of carbon

Primary (1°) carbon: A carbon which is attached to one carbon.

e.g., Carbon atoms in CH₃ – CH₃

Secondary (2°) carbon: A carbon which is attached to two other carbons.

Tertiary (3°) carbon: A carbon which is attached to three other carbons.

Quaternary (4°) carbon: A carbon which is attached to four other carbons.



Alkyl (R-) groups

These groups are obtained by removing one hydrogen from the corresponding alkanes.

e.g.,

methyl (Me) CH_3- ethyl (Et) C₂H₅- (or) CH₃-CH₂-n-propyl (n-Pr) or propyl $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-}$

isopropyl (iso-Pr) $\text{CH}_3\text{—CH—CH}_3$

n-butyl (n-Bu) or butyl $\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--}$

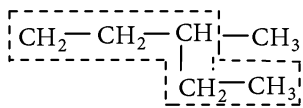
isobutyl (iso-Bu) $\text{CH}_3-\underset{\text{CH}_3}{\underset{|}{\text{CH}}}-\text{CH}_2-$

s-butyl (s-Bu) (s-secondary) $\text{CH}_3 - \underset{\text{CH}_3}{\underset{|}{\text{CH}}} - \text{CH}_2 - \text{CH}_3$

t-butyl (t-Bu) (t-tertiary) $\text{CH}_3 - \overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}} -$

Rules governing IUPAC nomenclature of branched chain alkanes

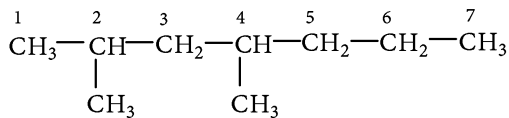
1. Longest continuous carbon chain is chosen as the parent chain and the compound is named as a derivative of that hydrocarbon.



Derivative of pentane

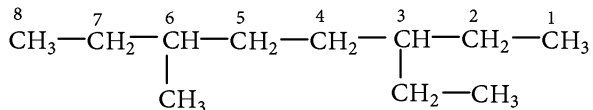
- Carbon atoms in the selected parent chain are numbered from one end in such a way that the carbon atoms carrying the substituents get the lowest possible numbers.

- For naming the compound, the position of each substituent and its name is prefixed to the name of the parent alkane.



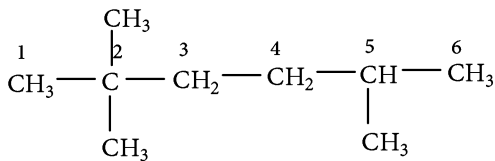
2,4-Dimethylheptane

4. If there are different alkyl substituents in the parent chain, their names are written in the alphabetical order.
5. When two or more substituents are present at equivalent positions in the carbon chain, lowest number is assigned to the one which is first in the alphabetical order.



3-Ethyl-6-methyloctane

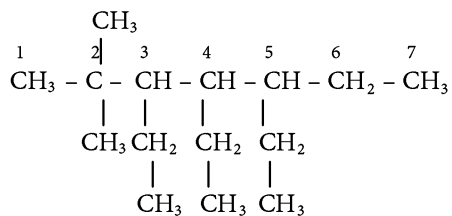
6. If two or more identical substituents are present in the molecule, then the positional number of each group is separated by commas and the appropriate suffix-di, tri, tetra, etc, is attached to the name of the substituent.



2,2,5-Trimethylhexane

The prefixes di, tri, etc., are not considered while deciding the alphabetical order of the substituent.

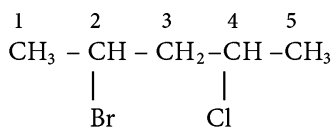
For example, the compound with the structure,



should be named as 3,4,5-Triethyl-2,2-dimethylheptane (and not as 2,2-dimethyl-3,4,5-trimethylheptane).

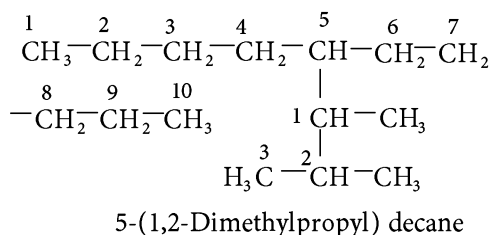
When substituents are other than alkyl groups, they are arranged in alphabetical order.

1.4 Basics of Organic Chemistry



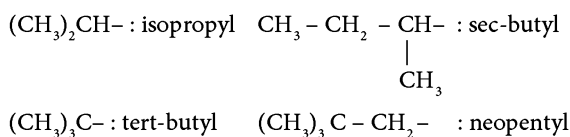
2-Bromo-4-chloropentane

7. When the substituent on the parent chain itself has a branched chain, then the carbon chain in the substituent is separately numbered in such a way that the carbon directly attached to the parent chain gets number 1. The name of such complex substituent is written in brackets to avoid confusion. For example,

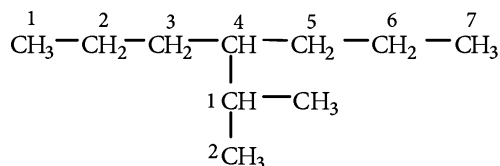


The present IUPAC rules permit the use of certain trivial names for unsubstituted radicals.

For example,



While writing the names of substituents in alphabetical order, the prefixes 'iso' and 'neo' are considered as part of the fundamental name of alkyl group while the prefixes 'sec' and 'tert' are not considered to be part of the fundamental name.

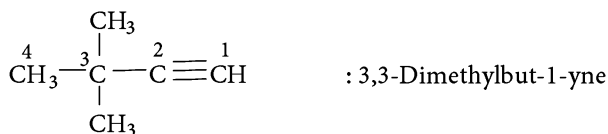
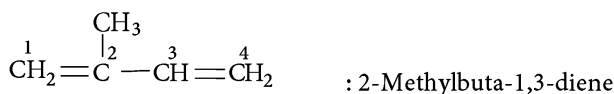
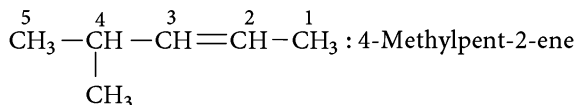


4-isopropylheptane or 4-(1-methylethyl)heptane

Nomenclature of alkenes and alkynes

The IUPAC name of alkene is derived from the name of the corresponding alkane by replacing the suffix *-ane* by *-ene*. Similarly, the name of alkyne is obtained by replacing *-ane*

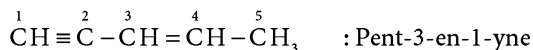
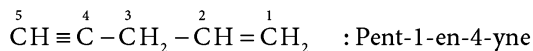
by *-yne*. In higher alkenes and alkynes, the carbon chain is numbered such that the C atoms containing the double or triple bond get the lowest number. In naming such compounds containing branched chain, the longest continuous chain containing the multiple bond is selected as the parent compound. For example,



If the hydrocarbon contains both double and triple bond, the following rules are used.

- The parent chain is numbered in such a way that the double bond and triple bond get the lowest possible numbers.
- If there is a choice, the double bond is given the lowest number.
- Such a hydrocarbon is named as a derivative of an alkyne.

For example,



Note: In the second case numbering from the other end will violate rule (i) Hence rule (ii) is not applicable

Nomenclature of compounds containing functional groups

When a functional group (other than C = C and C $\equiv$ C) is present in a molecule, it is indicated by adding secondary suffix after the primary suffix. The terminal 'e' of the primary suffix is removed before adding the secondary suffix if its name begins with *a*, *i*, *o*, *u* or *y*

Common suffixes used to represent functional groups

Table 1.3

No.	Functional Group	Generic Name	Formula	Suffix	Example
1.	Saturated hydrocarbon	Alk(+)ane	R - H	-ane	Methane
2.	Unsaturated hydrocarbon with carbon-carbon double bond	Alk(+)ene	$\text{>C}=\text{C}<$	-ene	Ethene
3.	Unsaturated hydrocarbon with carbon-carbon triple bond	Alk(+)yne	- C $\equiv$ C -	-yne	Ethyne
4.	Alcohol	Alkan(+)ol	- OH	-ol	Methanol
5.	Aldehyde	Alkan(+)al	- CHO	-al	Methanal
6.	Ketone	Alkan(+)one	- CO -	- one	Propanone
7.	Carboxylic acid	Alkan(+)oic acid	- COOH	-oic acid	Methanoic acid
8.	Carboxylic ester	Alkyl alkan(+)oate	- COOR'	- oate	Methyl ethanoate

Nomenclature of compounds containing more than one functional group

If a compound contains two or more different functional groups, the parent chain must contain maximum possible number of substituents. The carbon atoms in the parent chain are numbered in such a way that the functional group of higher priority gets the lowest number. The functional group with higher priority is indicated by suitable secondary suffix and other functional groups are treated as substituents. It may be noted that halo, nitro, and nitroso groups are not considered as functional groups: they are considered as substituents.

For example,

$\text{CH}_3 - \text{CH}_2 - \text{Cl}$ is known as chloroethane with chlorine as substituent.

$\text{CH}_3 - \text{NO}_2$ is known as nitromethane with $-\text{NO}_2$ as substituent.

The order of preference for functional groups in the decreasing order along with their prefix and suffix are given in table 1.3

Table 1.4

No.	Functional Group	Suffix	Prefix
1.	- COOH	- oic acid	Carboxy
2.	- SO_3H	- Sulphonic acid	-
3.	- COOR	- oate	Alkoxy carbonyl
4.	- COX	- oyl halide	Haloformyl
5.	- CONH_2	- amide	Carbamoyl

No.	Functional Group	Suffix	Prefix
6.	- CN	- nitrile	Cyano
7.	- CHO	- al	Formyl
8.	$\text{>C}=\text{O}$	- one	Oxo
9.	- OH	- ol	Hydroxy
10.	- SH	- thiol	Mercapto
11.	- NH_2	- amine	Amino
12.	$\text{>C}=\text{C}<$	- ene	Alkenyl
13.	- C $\equiv$ C -	- yne	Alkynyl
14.	- NO_2	-	Nitro
15.	- NO	-	Nitroso
16.	- X	-	Halo

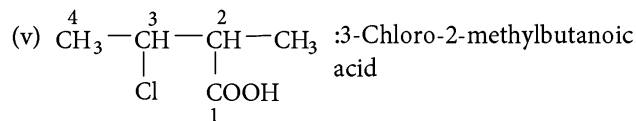
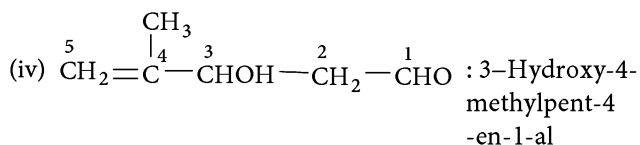
Examples

(i) $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CHO}$: 3-Butenal or But-3-en-1-al
(-CHO functional group gets preference over - C = C -)

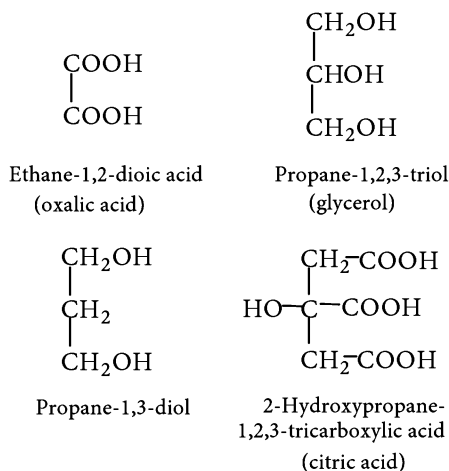
(ii) $\text{CH}_3-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{CH}_2-\text{CH}_2-\overset{\text{NH}_2}{\underset{2}{\text{CH}}}-\overset{1}{\text{CHO}}$: 2-Amino-5-oxohexanal

(iii) $\text{CH}_3-\overset{\text{OH}}{\underset{\text{OH}}{\text{CH}}}-\text{COOH}$: 2-Hydroxypropanoic acid
(Common name: Lactic acid)

1.6 Basics of Organic Chemistry

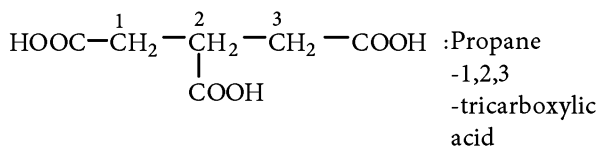


When the same functional group is present more than once in a compound, then the terms di, tri, tetra should be added to the prefix of the respective functional group.

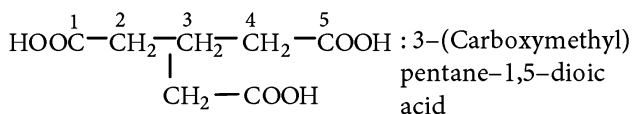


Polyfunctional compounds having more than two similar functional groups containing carbon

If more than two similar terminal functional groups containing carbon (e.g., $-\text{COOH}$, $-\text{CHO}$ and $-\text{CN}$) are directly linked to the principal chain, then none of these groups are considered as part of the parent chain. These are named by using suffix such as tricarboxylic acid (for three $-\text{COOH}$ groups), tricarbaldehyde (for three $-\text{CHO}$ groups) or tricarbonitrile (for three $-\text{CN}$ groups)



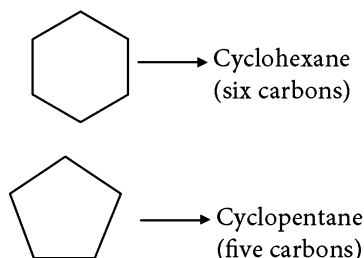
But if one of the three similar groups are not directly linked to the parent chain, then the carbon atoms of the two like groups are included in the parent chain while the third which forms the side chain is considered as a substituent group. For example



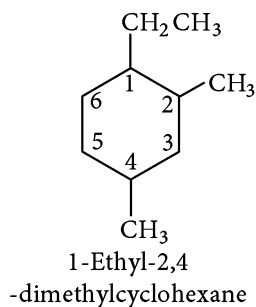
Nomenclature of alicyclic compounds

Alicyclic compounds are closed chain compounds resembling aliphatic compounds in their properties. Cycloalkanes, cycloalkenes and compounds with nonaromatic carbocyclic structures are classified as alicyclic.

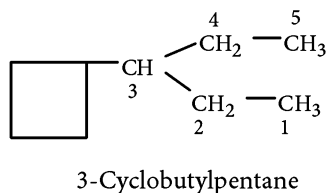
- (i) A saturated monocyclic compound is named by prefixing cyclo to the name of the corresponding hydrocarbon (cycloalkanes).



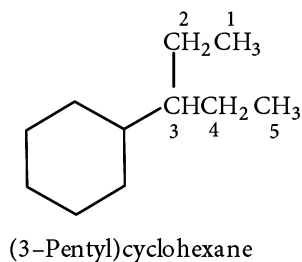
- (ii) If two or more substituents are present, numbering should start from the substituent which comes first in alphabetical order and the next substituent should get least possible number.



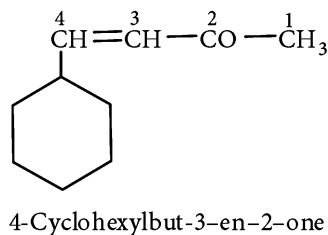
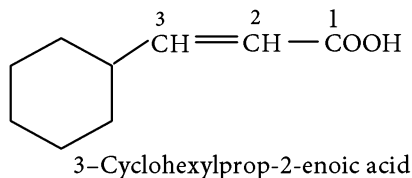
- (iii) If the alkyl group attached to the ring contains more number of carbon atoms than the ring, then it is termed as the derivative of alkane.



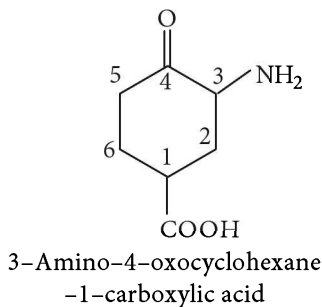
- (iv) If the alkyl group attached to the ring contains same or less number of carbon atoms, then it is termed as derivative of cycloalkane.



- (v) If the side chain contains a functional group, compound is termed as an acyclic one irrespective of the ring size. The alicyclic ring is considered as a substituent.



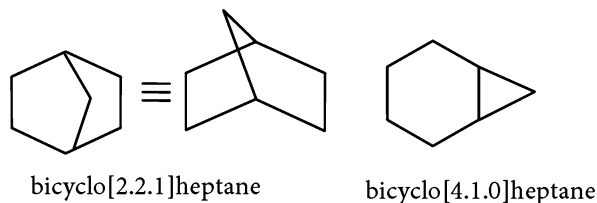
- (vi) If the functional groups are present as part of the ring system, then numbering is done such that functional group of highest priority gets least possible number.



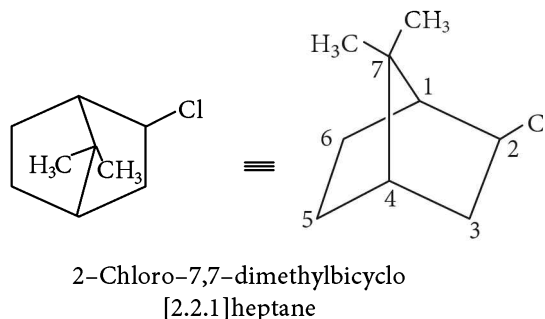
Nomenclature of bicyclic compounds

These are compounds with two fused rings joined by two tertiary carbon atoms. The prefix bicyclo is followed by the

name of the alkane containing the same number of total carbon atoms as that in the bicyclic compound. The number of carbon atoms in each of the three bridges is indicated in brackets in descending order.



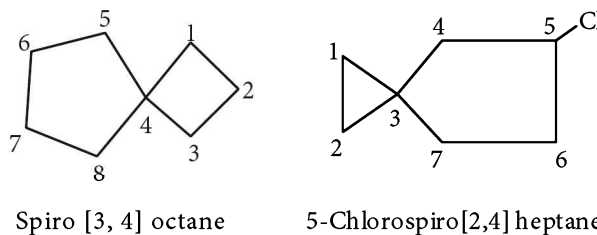
The numbering of ring should begin from one of the bridgeheads or ring junctions and proceed by the longest bridged ring to the second bridgehead followed by the numbering of next longest bridge and at last the shortest bridge.



Nomenclature of spiro compound

Spiro compounds are those in which two rings are joined by a common quaternary carbon at the apex. They are prefixed by the term spiro followed by the name of the alkane (containing same number of carbon atoms as part of the ring system(s)).

The numbering starts from the carbon atom next to the quaternary carbon at the apex in the smaller ring. Number of the carbon atoms in each bridge is written in ascending order in brackets.

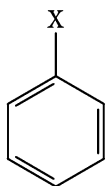


1.8 Basics of Organic Chemistry

Nomenclature of aromatic compounds

Aromatic compounds contain two parts

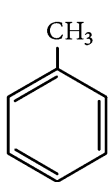
- (i) Benzene ring part
- (ii) Side chain or substituent part (group attached to benzene ring)



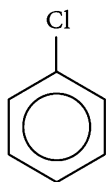
Monosubstituted benzene

If one of the hydrogens of benzene ring is replaced by some substituent, then it is called as monosubstituted benzene. It has no isomer, since all the nuclear carbons are identical.

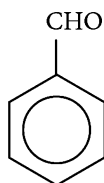
For example,



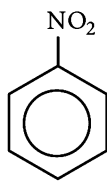
Toluene



Chlorobenzene



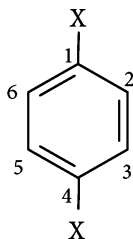
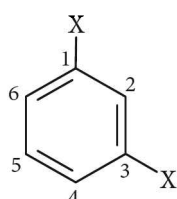
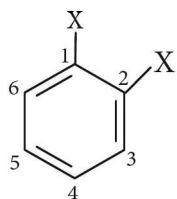
Benzaldehyde



Nitrobenzene

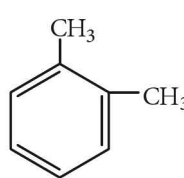
Disubstituted benzene

These are compounds having two substituents in the ring replacing hydrogens of the ring. For example,

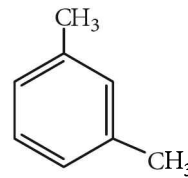


In the common system, these three isomers are called ortho(o-), meta (m-) and para (p-) according as the

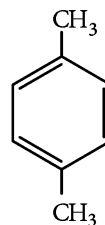
relative positions of the two substituents are 1,2; 1,3 and 1,4, respectively.



1,2-Dimethylbenzene
(o-xylene)

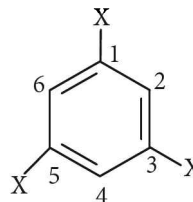
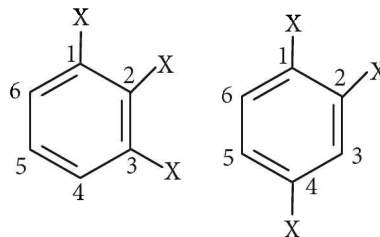


1,3-Dimethylbenzene
(m-xylene)

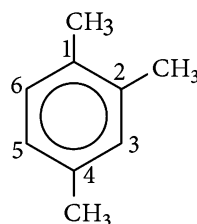


1,4-Dimethylbenzene
(p-xylene)

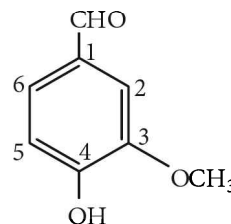
For trisubstituted compounds also positions are designated by numbers.



For example,

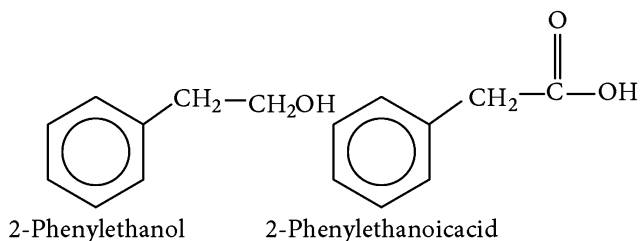


1,2,4-Trimethylbenzene

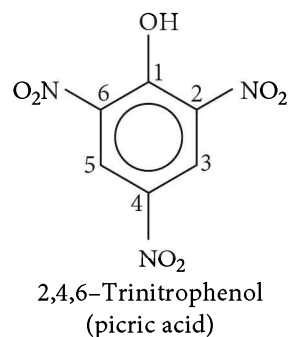


4-Hydroxy-3-methoxy
benzaldehyde
(common name: Vanillin)

If the side chain contains a functional group, then the phenyl ring is considered as a substituent.



Hydroxy derivative of benzene is phenol.

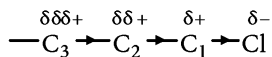


ELECTRON DISPLACEMENT EFFECTS

Inductive effect

It is the permanent partial polarization of sigma bonds in a molecule by the influence of an adjacent polar bond or group.

For illustration, let us consider a carbon chain in a molecule in which one terminal end is joined to a chlorine atom. Since chlorine atom is more electronegative than carbon, the sigma electrons of the C – Cl bond are displaced slightly towards the chlorine atom. As a result, the chlorine atom acquires a small negative charge and C₁ acquires a small positive charge, as shown below.

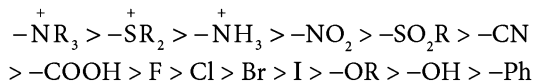


The small positive charge on C₁ in turn attracts the sigma electrons of C₁ – C₂ bond towards it. As a result C₂ will acquire a small positive charge, but the charge will be smaller than that on C₁. Similarly C₃ will also acquire a small positive charge which will be smaller than that on C₂. *This type of electron displacement of sigma electrons along a saturated carbon chain due to the presence of an electron withdrawing group (or electron donating group) is called inductive effect.*

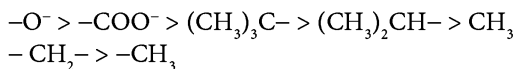
This effect decreases sharply with increasing distance from the substituent and becomes negligible after the third carbon in a chain.

For measurement of relative inductive effect, hydrogen is chosen as the reference standard. Atoms or groups which are more electronegative than hydrogen withdraw electrons from a chain and are said to have electron withdrawing inductive effect or –I effect. Atoms or groups which push or donate electrons to a carbon chain are said to have electron releasing inductive effect or +I effect. Some examples of groups showing –I and +I effects are given below in the order of their decreasing effect.

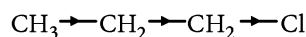
Groups with –I effect



Groups with +I effect



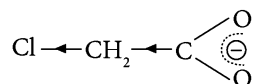
Inductive effect is generally represented by placing an arrow midway along the sigma bond in the direction of electron shift as shown below



Inductive effect is a permanent effect and it is quite useful in explaining many of the physical and chemical properties of organic molecules. Some of them are given below.

1. Acidity of substituted carboxylic acids

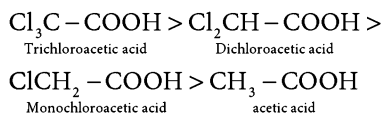
The presence of substituent groups with –I effect increases the acidity of carboxylic acids. For example, monochloro acetic acid (ClCH₂ – COOH) is a stronger acid than acetic acid. Due to the electron withdrawing nature (–I effect) of chlorine, the negative charge on the anion formed by ionization would get dispersed. This would stabilize the anion of chloroacetic acid more than that of acetic acid.



So chloroacetic acid ionizes more readily and is more acidic than acetic acid.

1.10 Basics of Organic Chemistry

Evidently, greater the number of groups having $-I$ effect, greater would be the dispersal of the negative charge on the anion and hence stronger will be the acid. For example,



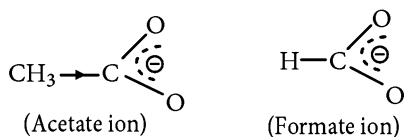
Electron withdrawing inductive effect ($-I$ effect) decreases rapidly with distance. So the effect of the substituent will diminish as it moves away from the carboxyl group. This is evident from the pK_a values of chlorobutanoic acid given below.

(Note: Greater the pK_a value, weaker is the acid)

Table 1.5

Compounds	Structural formula	pK_a
2-Chlorobutanoic acid	$\text{CH}_3\text{CH}_2\underset{\text{Cl}}{\text{CH}}-\text{COOH}$	2.86
3-Chlorobutanoic acid	$\text{CH}_3\underset{\text{Cl}}{\text{CH}}-\text{CH}_2\text{COOH}$	4.05
4-Chlorobutanoic acid	$\text{ClCH}_2-\text{CH}_2-\text{CH}_2-\text{COOH}$	4.52
Butanoic acid	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	4.82

The presence of electron releasing substituents (groups with $+I$ effect) decreases the acidic strength of carboxylic acid. For example, acetic acid is a weaker acid than formic acid. The methyl group intensifies the negative charge on the acetate ion and destabilizes it compared to formate ion.



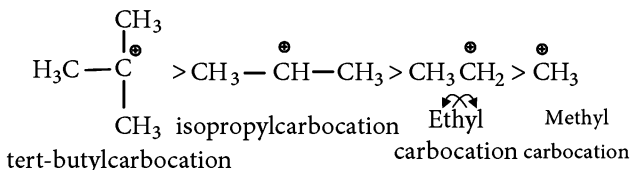
2. Basic character of amines

Amines are the alkyl or aryl derivatives of ammonia. e.g., $\text{CH}_3-\ddot{\text{N}}\text{H}_2$ (Methylamine or methanamine). The presence of a lone pair of electrons available for protonation on nitrogen makes amines basic.

Aliphatic amines are more basic than ammonia due to the $+I$ effect of alkyl groups. For example, CH_3-NH_2 is more basic than NH_3 . The alkyl group pushes electrons by $+I$ effect and increases the electron density on nitrogen for protonation.

3. Relative stabilities of carbocations

The stability of carbocations is of the order, $3^\circ > 2^\circ > 1^\circ > \text{CH}_3^+$

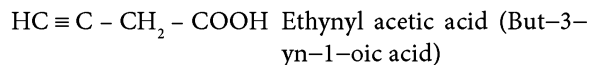
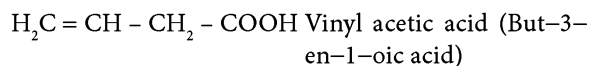


The relative stability of a carbocation is increased by the dispersal of the charge over a wider area.

An electron releasing substituent reduces the positive charge at the electron deficient carbon. An electron withdrawing substituent tends to intensify the positive charge on the electron deficient carbon and in doing so makes the carbocation less stable. Alkyl groups release electrons and greater the number of alkyl groups around an electron deficient carbon, more stable is the carbocation.

4. Acidity of unsaturated acids

Carbon-carbon double and triple bonds have significant electron attracting effect that is reflected in the enhanced acidity of vinyl acetic acid and ethynyl acetic acid.



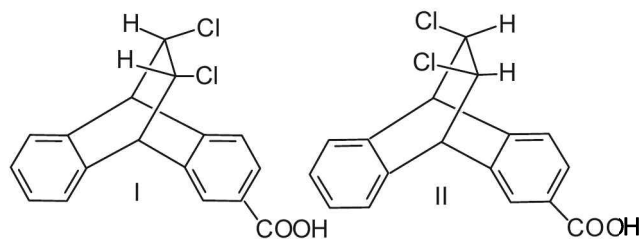
An sp hybridized carbon orbital with its greater s -character is effectively more electronegative than an sp^2 orbital which in turn is more electronegative than an sp^3 orbital with the least s -character.

5. Aromatic Electrophilic Substitution

In an aromatic electrophilic substitution, a substituent group affects both the reactivity and orientation by electron release or electron withdrawal by inductive effect.

Another similar effect operates not through bonds, but directly through space or solvent molecules and is called the field effect. While the field effect depends on the geometry of the molecule, the inductive effect depends on the nature of the bonds.

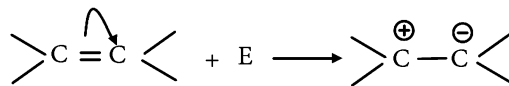
For example, in the two isomeric acids (I) and (II), (I) is more acidic than (II) due to field effect.



Electromeric effect

Electromeric effect is a temporary effect which involves the complete transfer of π electrons of a multiple bond to one of the bonded atoms in presence of an attacking reagent. The electromeric effect is brought about only at the requirement of the attacking reagent and the direction of the electromeric effect is that which facilitates the reaction.

When an electrophile is added to a multiple bonded substrate, there is a complete transfer of π electrons from one atom to the other to produce temporary polarity.



If the electrophile is removed, the charges residing at the carbon centres disappear and the substrate regains its original multiple bonded structure.

When the π electron transfer occurs in carbon-carbon bond, the process is called +E effect. When π electron transfer occurs to a more electronegative atom like oxygen, nitrogen or sulphur (when the carbon is connected to one of these atoms like

>C=O , $\text{-C}\equiv\text{N}$), then it is called -E effect.

CONCEPT STRANDS

Concept Strand 1

Rationalize the following statements

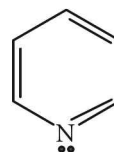
- Pivalic acid $(\text{CH}_3)_3\text{C} - \text{COOH}$ is a very weak acid compared to acetic acid.
- CCl_3NH_2 is a very weak base.
- The pK_a of acetic acid is 4.76 whereas that of Cl_3CCOOH is 0.63.
- Pyridine is a stronger base compared to methylcyanide.

Solution

- Pivalic acid $(\text{CH}_3)_3\text{C} - \text{COOH}$ is trimethylacetic acid. There are three methyl groups on the carbon adjacent to the carboxyl group. The cumulative effect of electron release by the three methyl groups makes the $-\text{COOH}$ group less acidic. The electron releasing influence of the methyl group in pivalic acid is three times greater than that of acetic acid which has only one methyl group.
- The strength of a base depends on the availability of the lone pair of electrons on nitrogen for protonation. Methyl amine (CH_3NH_2) is a stronger base than ammonia, because one of the hydrogen atoms of ammonia NH_3 is replaced by a methyl group. In the case of CCl_3NH_2 , the methyl group is replaced by a trichloromethyl group. There are three chlorine atoms which are powerfully electron withdrawing.

The lone pair of electrons are not readily available on nitrogen as they are drawn towards chlorine. Hence trichloromethyl amine CCl_3NH_2 is a much weaker base when compared to CH_3NH_2 .

- Comparison of the pK_a values of acetic acid and trichloroacetic acid reveals that the latter is a stronger acid. This is because the three chlorine atoms on the α -carbon of the $-\text{COOH}$ group in trichloroacetic acid strongly withdraw the electron, thereby stabilizing the anion, namely CCl_3COO^- . Hence trichloroacetic acid is a stronger acid. On the other hand because of the electron releasing effect of the methyl group in the acetate ion CH_3COO^- , acetic acid is poorly ionized. Hence acetic acid is a weak acid.
- Pyridine is a stronger base than methylcyanide. The strength of the base depends on the availability of lone pair of electrons on nitrogen as well as on the hybridization of the nitrogen involved. In the case of pyridine, nitrogen is sp^2 hybridized.



The lone pair of electrons of nitrogen in pyridine are in a plane perpendicular to the plane of the π electrons

1.12 Basics of Organic Chemistry

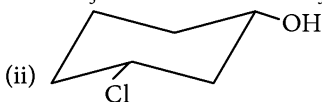
that contribute to the aromaticity of the pyridine ring. Hence the pair of electrons on nitrogen are available for protonation and not used for delocalization. Hence pyridine acts as a stronger base.

In the case of $\text{CH}_3 - \text{C} \equiv \text{N}$, the nitrogen is sp hybridized and is triply bonded to sp hybridized carbon. This means that the lone pair of electrons on nitrogen is firmly held with itself due to the greater percentage of s -character.

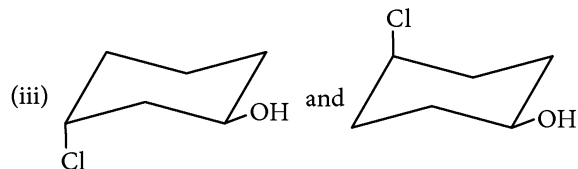
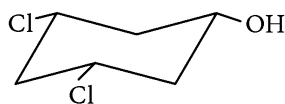
Concept Strand 2

For each of the following pairs of compounds, which is more acidic and why?

- (i) $\text{CH}_3\text{CHF}\text{COOH}$ and $\text{CH}_3\text{CHBr}\text{COOH}$

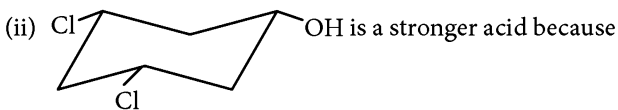


and

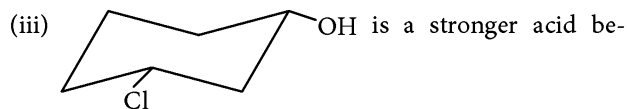


Solution

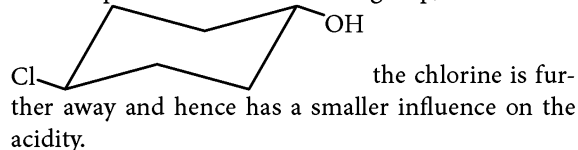
- (i) $\text{CH}_3\text{CHF}\text{COOH}$ is a stronger acid than $\text{CH}_3\text{CHBr}\text{COOH}$ because fluorine has greater $-I$ effect than bromine.



of the presence of two chlorine atoms in the structure and the cumulative inductive effect of two electron withdrawing chlorine atoms.

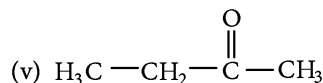
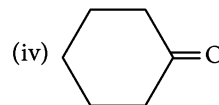
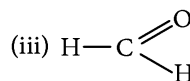
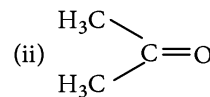
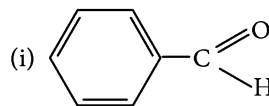


cause the chlorine atom is in the third carbon atom with respect to the functional group, whereas in



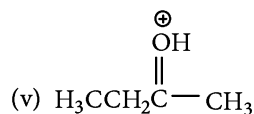
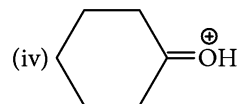
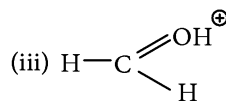
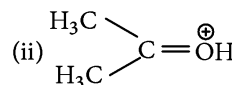
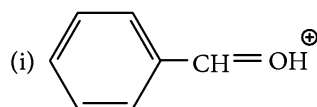
Concept Strand 3

Give the protonated forms of the following carbonyl compounds. Arrange them in the decreasing order of electrophilic nature of carbon.

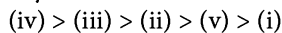


Solution

Protonated forms are:

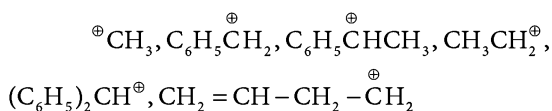


The decreasing order of electrophilic nature of the carbonyl carbon will be

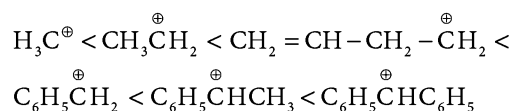


Concept Strand 4

Arrange the following in the increasing order of stability.



Solution



Resonance

There are certain compounds whose properties cannot be explained by a single electronic structure. Such compounds exist in a state which is a hybrid or combination of two or more structures. This phenomenon is known as resonance.

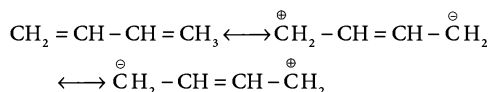
Molecules exhibiting resonance contain one or more bonding orbitals that are not restricted to two atoms, but are spread over three or more atoms. Such bonds or bonding electrons are said to be delocalized.

There are two main types of molecules that exhibit resonance.

1. Compounds containing double (or triple) bonds in conjugation

e.g., Buta-1,3-diene, benzene, etc.

Buta-1,3-diene is a resonance hybrid of the following structures

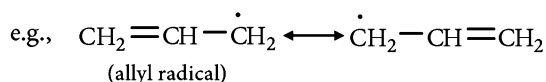


The various resonance structures (also known as canonical structures) drawn for any molecule are imaginary structures. The real molecule will be a resonance hybrid of the different canonical structures. The various canonical structures of a compound are separated by a double headed arrow ($\longleftrightarrow$)

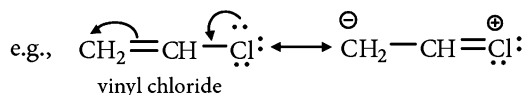
2. Compounds containing an atom having a p-orbital adjacent to a double bond

A p-orbital adjacent to a double bond allows the formation of an extended π bond. Such a p-orbital may contain one, two or no electrons as given below.

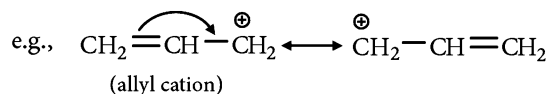
- (i) Atom having p-orbital containing one electron adjacent to the double bond



- (ii) Atom with p-orbital containing two electrons adjacent to the double bond.

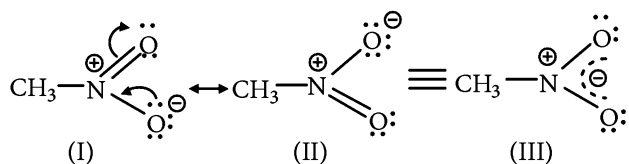


- (iii) Atom having vacant p-orbital adjacent to the double bond.



Few examples of resonance

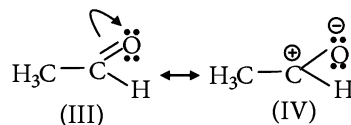
- (i) Two different Lewis electron dot structures can be drawn for nitromethane, CH_3NO_2 , as shown.



resonance hybrid

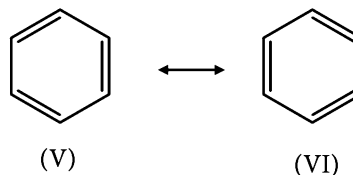
These two structures are not the same because nitrogen forms a double bond with two different oxygen atoms. The actual structure of nitromethane is a resonance hybrid of these two canonical structures (I) and (II). In reality, (I) and (II) are not existing.

- (ii) Acetaldehyde can be represented as



Out of these, (III) is a neutral structure and (IV) is a 1,2 dipolar structure.

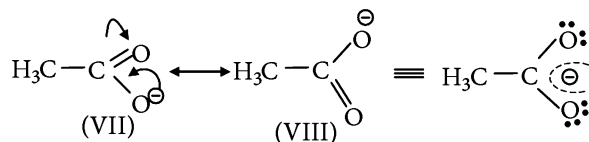
- (iii) Resonance is most often observed in cyclic conjugated molecules. The alternate single and double bonds present in a cyclic structure like benzene is an important example of resonance. Resonance theory tells us that benzene is a resonance hybrid of mainly the two Kekule structures (V) and (VI)



- (iv) The increased acidity of carboxylic acids compared to alcohols is attributed to resonance. The electron pair gets delocalized in an acetate ion (carboxylate anion of acetic acid) CH_3COO^- and hence gets stabilized by resonance. On the other hand, in ethoxide ion

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(anion of an alcohol) $\text{CH}_3\text{CH}_2\text{O}^-$, such delocalization of electrons is not possible.



(VII) and (VIII) are the contributing structures of acetate ion.

In the case of an ethoxide ion, $\text{C}_2\text{H}_5\text{O}^-$, electrons on oxygen are highly localized, cannot migrate to other positions making ethoxide ion is much less stable. In other words, resonance does not operate in an ethoxide ion.

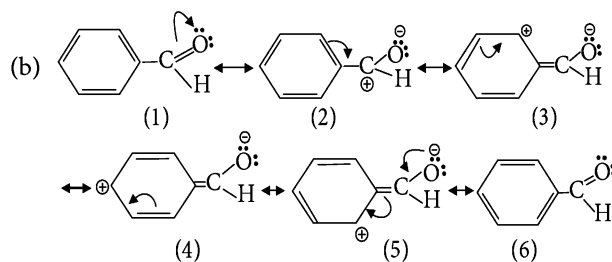
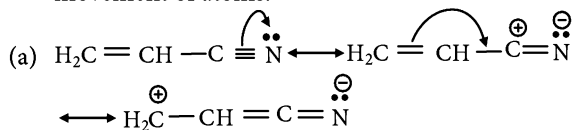
In the case of resonance, no single structural formula could satisfactorily explain all the properties of a compound. All the resonance structures drawn seem to be equally capable of describing most of the properties of the compound, but no single structure can explain satisfactorily all the properties of a compound. *The resonance hybrid is the real structure that is considered to be a blend of the contributing hypothetical structures.*

Resonance Energy (Delocalization Energy)

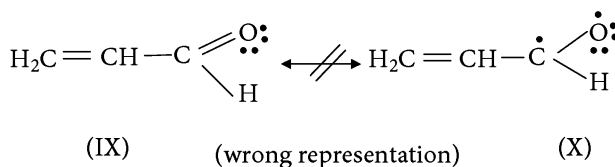
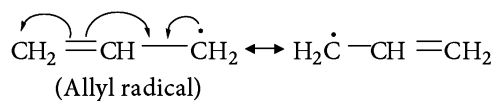
The energy of the hybrid is always lower than the energy of any of the individual resonance structures. The greater the number of contributing structures with similar energies, the more stable is the hybrid and lower is its energy. The difference between the energy of the most stable canonical structure, which is obtained by calculation, and the experimentally determined energy of an actual molecule or a resonance hybrid is termed as resonance energy or delocalization energy. Resonance energy is a measure of the stabilization due to resonance. The greater the resonance energy the greater is the stabilization due to resonance.

Rules of Resonance

- (i) Structures contributing to the hybrid must conform to one Lewis structure or other.
- (ii) Resonance structures are obtained by one or more shift of π electrons and/or nonbonded electrons.
- (iii) The various resonance structures are known as canonical forms and, in all these canonical structures, only movement of electrons are involved and not movement of atoms.



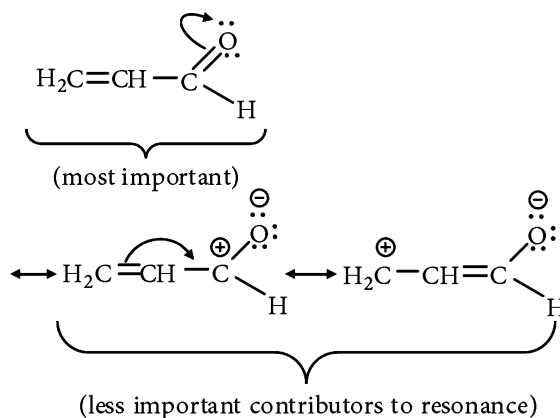
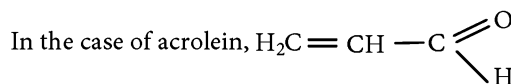
- (iv) Resonance structures must have the same number of paired or unpaired electrons.



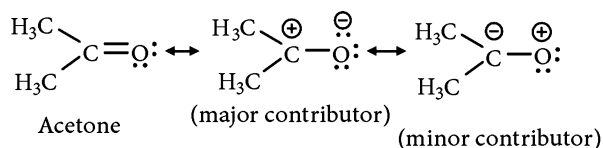
The structures (IX) and (X) do not have the same number of odd/even electrons, hence they are not resonance structures.

- (v) The more the covalent bonds in the structure, the greater is its stability and the greater is its contribution to the resonance hybrid.
- (vi) Dipolar structures are less stable than non-polar structures.
- (vii) Structures in which formal charges are separated make some contribution to the resonance hybrid of an electrically neutral or uncharged molecule. However, charged structures are less significant compared to neutral ones.

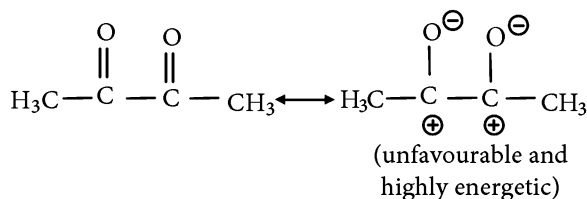
For example,



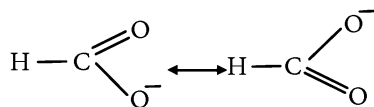
- (viii) The more nearly equal in stability are the resonance structures, the greater is the degree of resonance.
- (ix) When atoms of different electronegativities are connected, that resonance structure which places a negative charge on a more electronegative atom would be a major contributor to the resonance hybrid. Similarly, a structure with a positive charge on a more electropositive atom is comparatively more stable and its contribution to the resonance hybrid is significant. For example,



- (x) Resonance structures having like charges on adjacent atoms are unfavourable because they possess high energy. For example,



- (xi) Resonance gives rise to identical bond lengths in certain molecules. For example, formate ion is a resonance hybrid of the following two structures



Normally the $\text{C}=\text{O}$ double bond distance is $1.20 \text{ \AA}$ and $\text{C}-\text{O}$ single bond distance is $1.43 \text{ \AA}$. However, the $\text{C}-\text{O}$ bond length in the formate ion is found to be $1.34 \text{ \AA}$, the average of the $\text{C}=\text{O}$ and $\text{C}-\text{O}$ bond lengths, thereby showing that the bond lengths become identical because of delocalization of electrons.

- (xii) Delocalization of electrons within a molecule is most effective when the axes of the interacting 'p' orbitals of adjacent atoms are parallel. This means that the sigma framework of the conjugated portion of the molecule

should be planar. *Coplanarity of the molecule is one of the essential conditions for resonance.*

Resonance effect (Mesomeric effect)

Resonance effect (or mesomeric effect) may be defined as the electron displacement in a conjugated system creating polarity in the molecule due to the phenomenon of resonance.

Resonance effect may be positive or negative and is usually denoted as +R (or +M) or -R (or -M) respectively.

When atoms or groups containing lone pair of electrons are linked to an unsaturated system, they displace electrons towards the multiple bond or conjugated system. This type of resonance effect is called electron-releasing resonance effect and is represented as +R (or +M).

Examples of groups showing +R effect: halogens, -OH, -OR, -NH₂, -NHR, -NR₂, -NHCOR etc.

When certain groups are bonded to a conjugated system, they attract electrons from the multiple bond due to resonance. This is called electron-withdrawing resonance effect and is designated as -R (or -M)

Examples of groups showing -R effect:

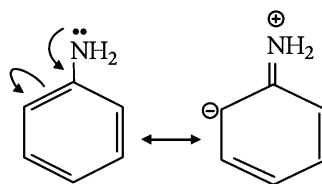
-NO₂, -COOH, -CHO, >C=O , -CN etc.

Resonance effect has been used to explain

- (i) The poor reactivity of halogen attached to an sp² carbon - in systems like aryl halides and vinyl halides.
- (ii) The stabilities of carbocations, carbanions and free radicals.
- (iii) The acidic nature of carboxylic acids, sulphonic acids and phenols.
- (iv) The high reactivity of phenols, aniline etc., in aromatic electrophilic substitution reactions.

Steric inhibition of resonance

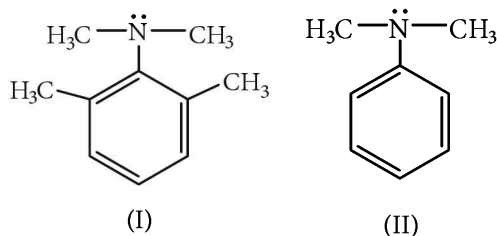
An aromatic amine like aniline (C₆H₅NH₂) is less basic than an aliphatic amine like dimethylamine (CH₃)₂NH, because the lone pair of electrons on nitrogen in aniline are delocalized into the benzene ring.



Such a type of delocalization is not possible in dimethylamine H₃C-NH-CH₃.

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Among the following amines, 2,6-dimethyl-N,N-dimethylaniline (I) is a stronger base than N,N-dimethylaniline (II).



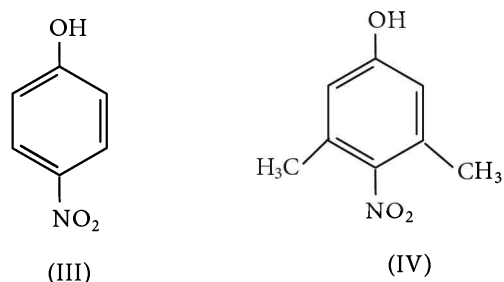
This is a clear effect of steric inhibition of resonance as explained below.

An essential condition for resonance is that all the atoms covered by the delocalized electrons must lie in a plane or nearly so. In (I), the presence of bulky methyl groups at the ortho positions causes $-\text{N}(\text{CH}_3)_2$ group to be out of plane with the benzene ring. This considerably reduces delocalization of the lone pair on nitrogen with the benzene ring. This phenomenon in which resonance gets restricted or inhibited because of steric factors of bulky group is known as steric inhibition of resonance. The net result is that the lone pair electrons are localized on nitrogen in (I) and it is more basic.

On the other hand, in the case of N,N-dimethylaniline (II), there is no steric restriction for resonance and

therefore electrons from nitrogen get delocalized easily into the aromatic ring. Therefore, (II) is a weaker base than (I).

Another example of steric inhibition of resonance is the comparison of acidities of 4-nitrophenol (III) ($\text{pK}_a = 7.15$) and 3,5-dimethyl-4-nitrophenol (IV) ($\text{pK}_a = 8.25$).



(IV) is a weaker acid than (III). In the case of (III), the phenoxide ion is resonance stabilized by delocalization due to the influence of the electron withdrawing $-\text{NO}_2$ group in the 4-position. Thus (III) exhibits stronger acidity. The presence of two methyl groups in the 3 and 5 positions in addition to the nitro group in the 4 position in (IV) sterically inhibits the coplanarity and the methyl and nitro groups are forced out of plane and resonance is prevented. Hence (IV) is a weaker acid compared to (III).

CONCEPT STRANDS

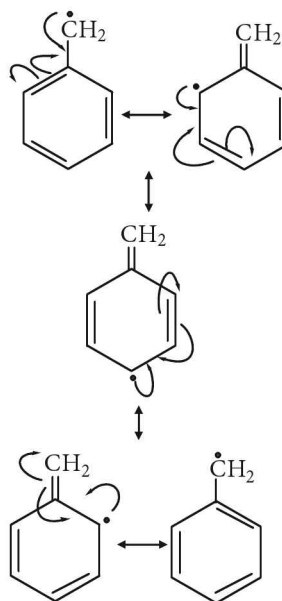
Concept Strand 5

Draw canonical resonance structures of the following—indicating the lone pair of electrons and the shift of electrons.

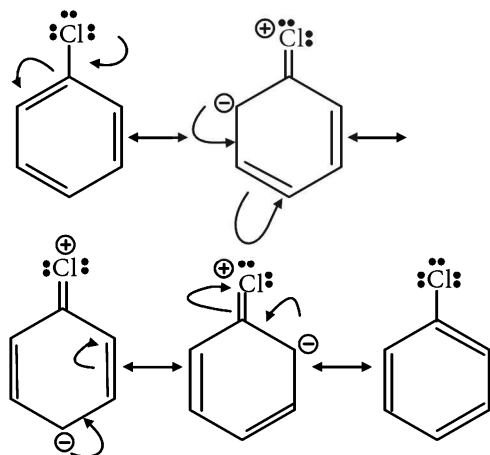
- Benzyl radical
- Chlorobenzene
- Phenoxide ion
- Benzyl cation
- Benzyl anion
- Diazomethane
- Tropolone

Solution

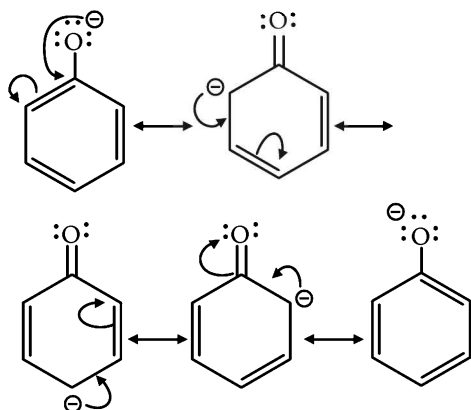
- Benzyl radical (movement of a single electron is indicated by a fish hook arrow or single headed arrow)



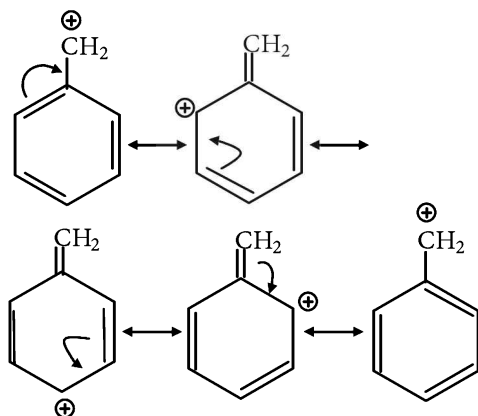
(ii) Chlorobenzene



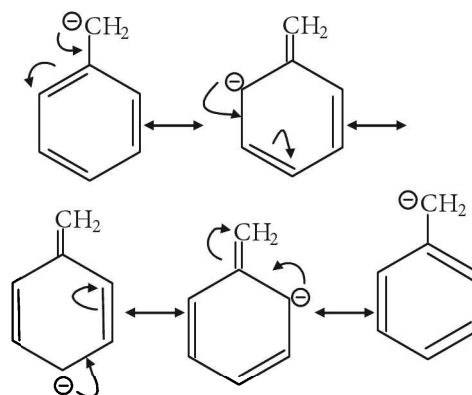
(iii) Phenoxide ion



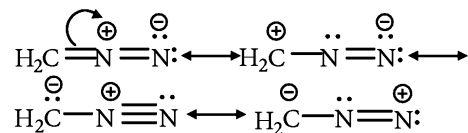
(iv) Benzyl cation



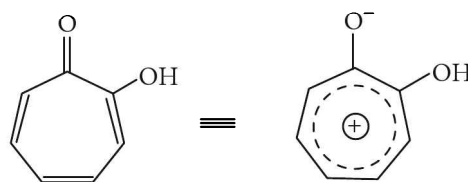
(v) Benzyl anion



(vi) Diazomethane

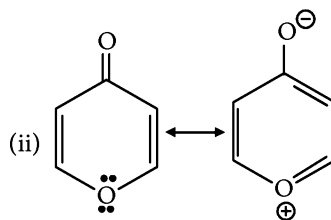
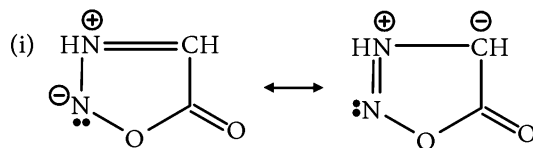


(vii) Tropolone

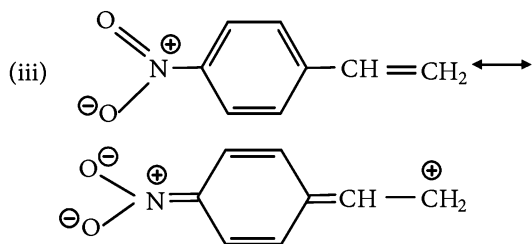


Concept Strand 6

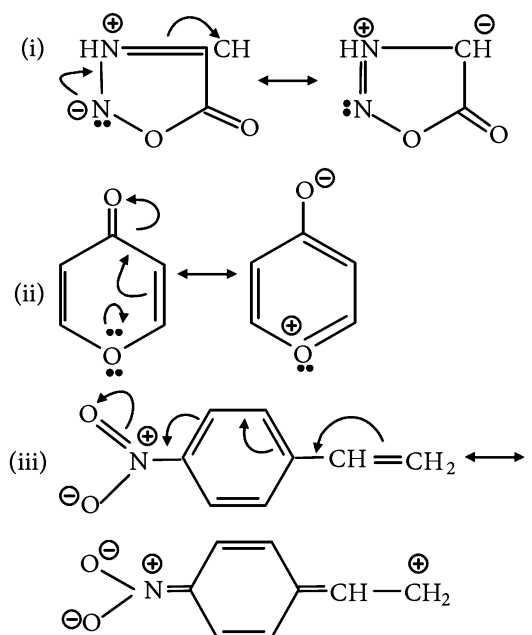
Draw the curved arrows necessary to convert the following structures from the first to the second.



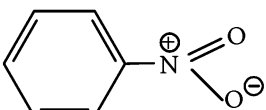
1.18 Basics of Organic Chemistry



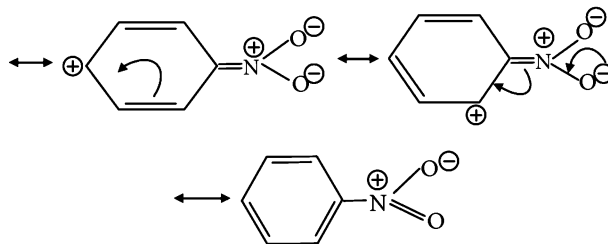
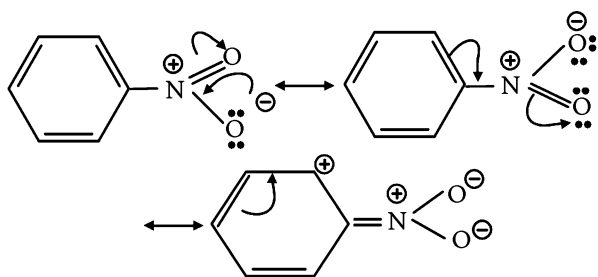
Solution



Concept Strand 7

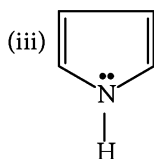
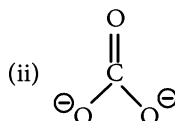
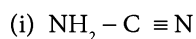
Draw the resonance structures of  (nitrobenzene)

Solution

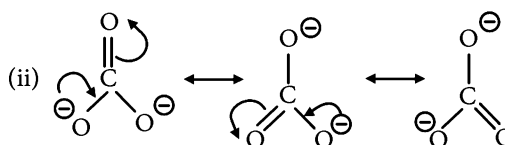
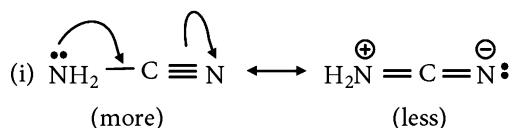


Concept Strand 8

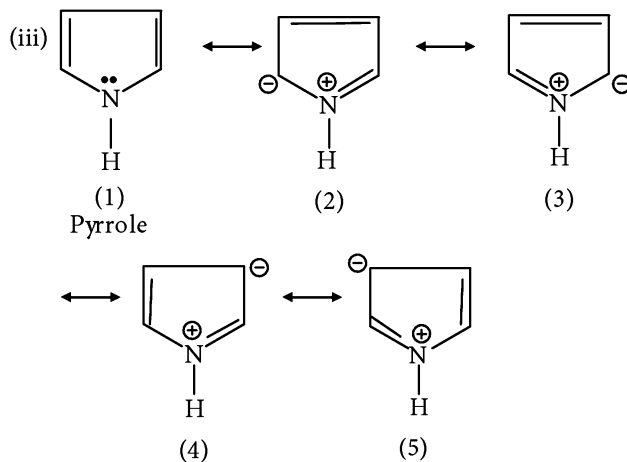
Draw resonance structures of the following and indicate their relative contribution to resonance hybrid.



Solution



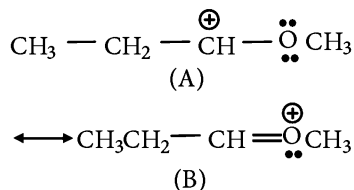
All the three structures are equal contributors to resonance hybrid.



Of the five structures represented for pyrrole (1) – (5), only the structure (1) is important as it is fully neutral, aromatic and stabilized. The other structures (2) – (5) are less important. As they are charged and –ve charge is on less electronegative 'c'.

Concept Strand 9

Explain why (A) is less important than (B) as a contributor to resonance hybrid.



Solution

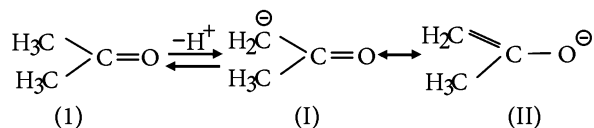
$\text{CH}_3\text{CH}_2\overset{\oplus}{\text{CH}} - \ddot{\text{O}}\text{CH}_3$ is less important than $\text{CH}_3\text{CH}_2\text{CH} = \overset{\oplus}{\text{O}}\text{CH}_3$ since it has a trivalent positive carbon. Structure (B), through contains a positive charge on an electronegative oxygen, has both carbon and oxygen atoms with octet of electrons.

Concept Strand 10

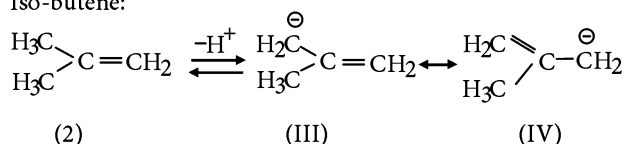
Compare the relative equilibria in the deprotonation reactions of acetone and isobutene. Explain the role of resonance in these two equilibria.

Solution

The application of resonance can be illustrated by referring to the relative equilibrium constants for the deprotonation of acetone and isobutene which can be shown as follows. Acetone:



Iso-butene:

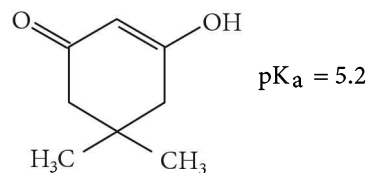


Deprotonation of acetone (1) is more favourable than the deprotonation of isobutene (2). The anion of acetone

(II) is of lower energy and more stable, since the negative charge is on the oxygen which is a more electronegative atom.

The anions (III) and (IV) generated from isobutene are comparatively less stable because the negative charge in these structures are on more electropositive carbon. On this basis, the equilibrium constant for the deprotonation of acetone is higher than that of isobutene.

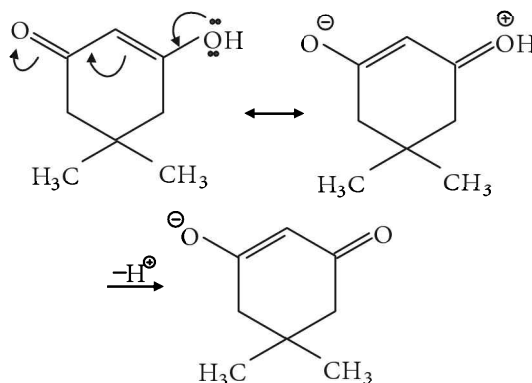
Concept Strand 11



Discuss the acidity of hydroxy group.

Solution

The acidity of the hydrogen of the hydroxy group is significant as the hydrogen is part of an enol system. The same compound has an α, β unsaturated carbonyl system which accounts for further stability.

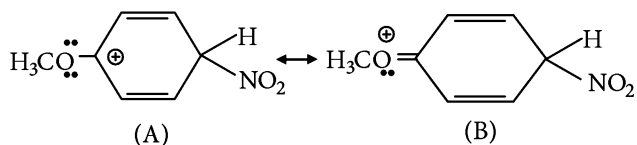


The hydrogen of the hydroxyl group is highly labile. The acidity of the hydrogen can be close to that of a carboxylic acid.

Concept Strand 12

Consider the two resonating structures (A) and (B) given below

1.20 Basics of Organic Chemistry



Explain the conflict, if any, in the stability of the two structures.

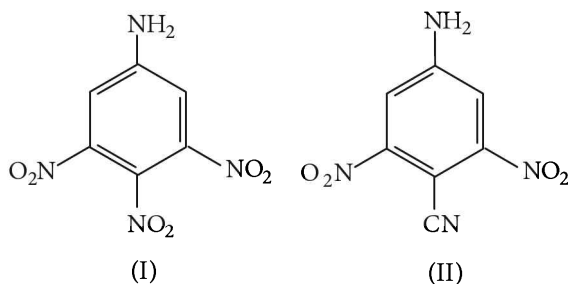
Solution

This is a case in which there is a conflict in the criteria exercised for resonance. Though it is generally believed that a resonance structure having a positive charge on a more electronegative atom should be a less favourable contributor to the resonance hybrid the latter structure (B) is more stable. These two structures are the intermediates (σ -complexes) in the nitration of anisole.

Structure (B) is more favourable because the positive charge on oxygen which is a more electronegative atom is compensated by an additional covalent bond in the structure (B) compared to (A). Further, all the atoms have complete octet.

Concept Strand 13

Account for the fact that 3,4,5-trinitroaniline (I) is a stronger base than 4-cyano-3,5-dinitroaniline (II).

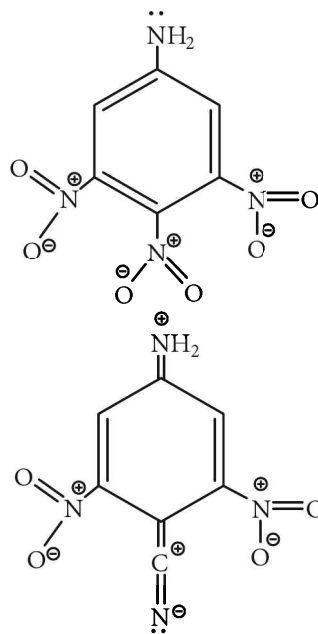


Solution

Nitro groups in (I) by their electron withdrawing effect should draw the lone pair of electrons on amine nitrogen thereby making it a weaker base than aniline.

However, this does not happen as the three bulky nitrogroups in adjacent positions 3, 4 and 5 in (I) sterically hinder the attainment of coplanarity, thereby preventing the delocalization of electrons to a certain extent and the result is that (I) is a stronger base than (II).

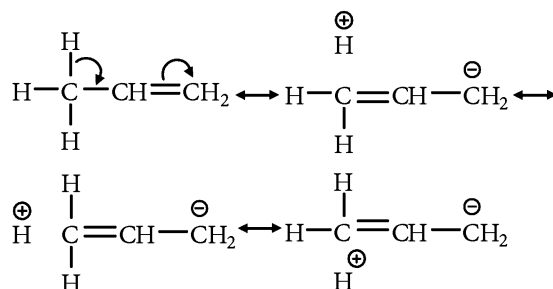
In the case of (II), the cyano group in the 4 position is a linear group and does not experience the steric restriction. Therefore, in the case of (II), the electrons from the amine are readily delocalized into the aromatic ring, thereby making (II) a weaker base.



Hyperconjugation

Hyperconjugation (or Baker-Nathan effect) is a special kind of resonance which involves delocalization of sigma electrons of C – H bond of an alkyl group directly joined to an unsaturated carbon atom or to an atom containing an unshared p-orbital. In such systems, the sigma electrons of the C – H bond of alkyl group enter into partial conjugation with the attached unsaturated system or with the unshared p-orbital.

Hyperconjugation is possible in alkenes, alkyl substituted arenes, carbocations and free radicals. For example, the hyperconjugation of propene can be represented as

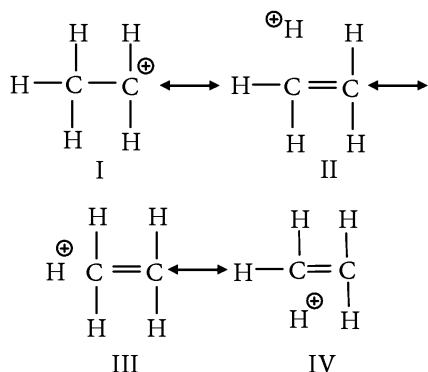


Hyperconjugation actually involves $\sigma - \pi$ conjugation. Since there is no bond between carbon and one of the hydrogen

atoms in hyperconjugation forms, hyperconjugation is also known as no bond resonance. The hydrogen atoms are not free but the effect is to increase the ionic character of the C – H bond.

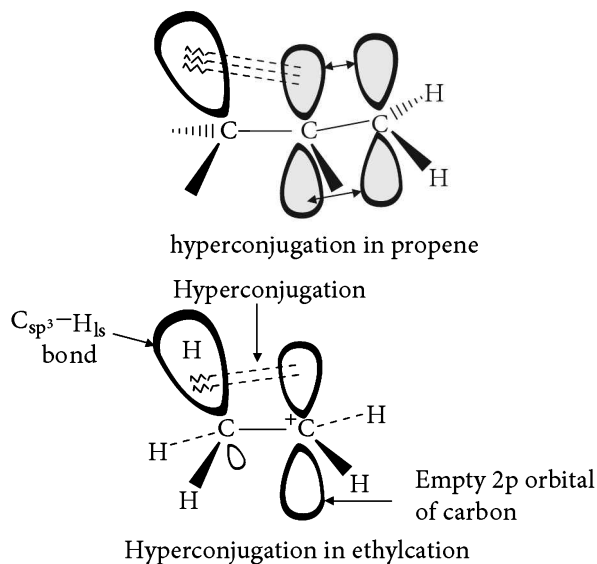
The concept of hyperconjugation arose from the discovery of anomalous electron release pattern for alkyl groups. When an alkyl group is attached to an unsaturated system containing double bond or to a benzene ring, the order of electron release is exactly opposite to that expected by inductive effect. Baker and Nathan used hyperconjugation to explain this anomalous electron release pattern.

Hyperconjugative structures of ethyl carbocation containing an empty p-orbital on the positively charged carbon are shown below

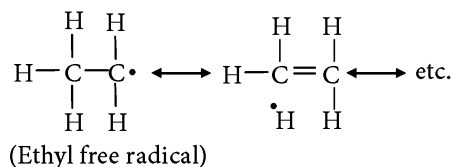


Individually each of these 'no bond' resonance structures II – IV mean that the C – H bond is something less than a single bond and the C – C bond has some double bond character and the positive charge is partly accommodated by the hydrogen atom.

Orbital diagrams showing hyperconjugation in propene and ethyl cation are given below



In the carbocations and free radicals, the canonical forms display no more charge separation than the main form. Mulliken has called this as *isovalent hyperconjugation*. (In such cases the number of covalent bonds in the various structures are the same).



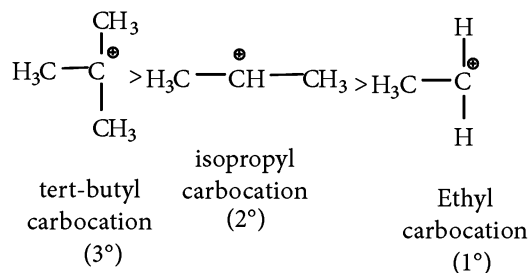
Even in these structures the main form of the cation or the radical contribute more to the hybrid compared to other structures.

As in the case of resonance, greater the number of equivalent hyperconjugative structures possible for a species greater is its stability.

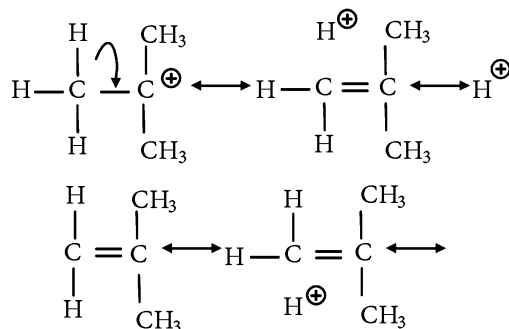
Application of hyperconjugation

1. Stability of carbocations and free radicals

The relative stability of carbocations and free radicals follows the order: tertiary (3°) > secondary (2°) > primary (1°).



tert-Butyl carbocation has nine α -hydrogens and hence it can have nine hyperconjugative structures as shown below.



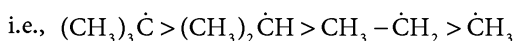
1.22 Basics of Organic Chemistry

Similarly six more energetically equivalent structures can be drawn for the other two methyl groups.

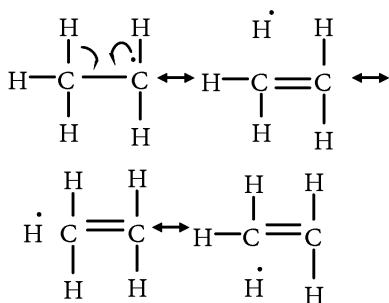
Since there are only six α -hydrogen atoms for isopropyl carbocation, it can have only six hyperconjugative structures. In a similar way three hyperconjugative structures can only be written for ethyl carbocation. Since methyl carbocation (CH_3^+) cannot have any hyperconjugative structure, it must be the least stable one. Thus, the order of stability of carbocations is



In a similar way, we can explain the stability order of free radicals,



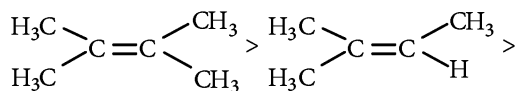
The three hyperconjugative structures possible for ethyl free radical are shown below.



2. Stability of alkenes

Heats of hydrogenation values show that greater the number of alkyl groups attached to the double bonded carbon atoms, greater is the stability of the alkene.

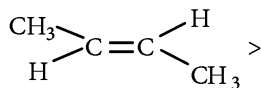
Among the following alkenes, the order of stability is



2,3-Dimethylbut-2-ene 2-Methylbut-2-ene

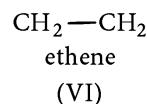
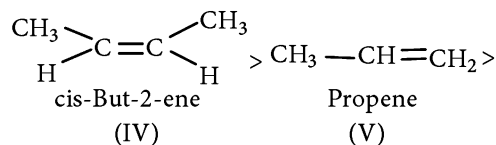
(I)

(II)



trans-But-2-ene

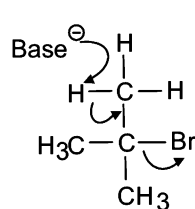
(III)



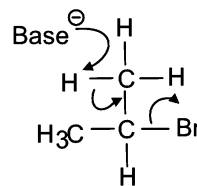
The number of hyperconjugative structures possible for alkenes I, II, III, IV, V and VI are respectively 12, 9, 6, 6, 3 and 0 (zero). Greater the number of hyperconjugative structures more stable is the alkene. Cis-but-2-ene is less stable than trans-but-2-ene because of steric repulsion.

3. Ease of formation of alkenes

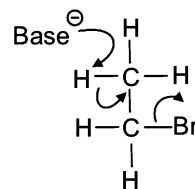
Hyperconjugative effect determines the stability of the alkenes produced in the elimination reactions. The ease of formation of the alkene from an alkyl halide by E2 mechanism under the influence of alcoholic alkali will be in the order, tertiary halide > secondary halide > primary halide.



Tertiary alkyl bromide
(Alkene stabilized by two methyl groups)



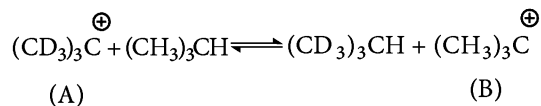
Secondary alkyl halide
(Alkene stabilized by one alkyl group)



Primary alkyl halide
(No methyl group for the stabilization of the alkene)

4. Isotope effect

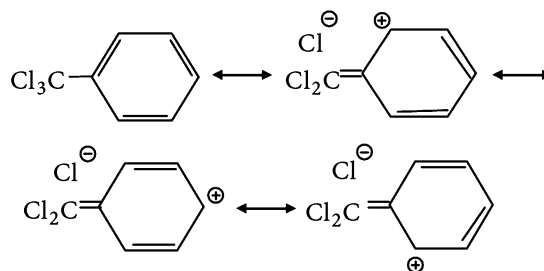
Evidence for hyperconjugative stability is provided by the equilibrium constant K for the reaction.



which is 1.97 indicating that (B) is more stable than (A). This means that there is less of hyperconjugative stability in (A) due to an isotope effect.

5. Meta orienting power of substituents

Hyperconjugation has been used to explain the meta orienting power of substituent like $-\text{CCl}_3$ as shown.



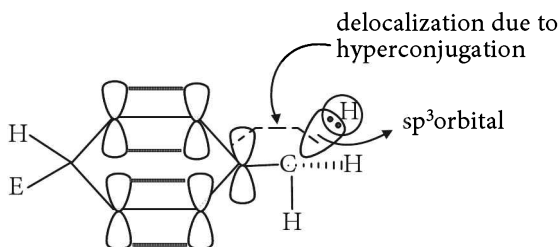
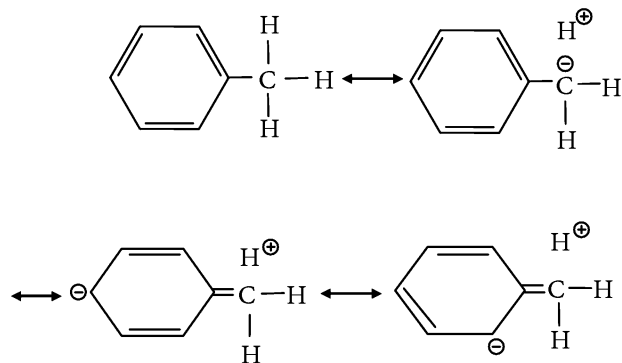
CONCEPT STRANDS

Concept Strand 14

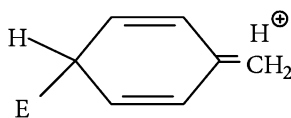
Account for the activating influence of methyl group in toluene in electrophilic substitution favouring ortho-para orientation.

Solution

Methyl group in toluene activates the benzene ring by electron release inductive effect. Another major contributing factor for activation is hyperconjugation as shown.



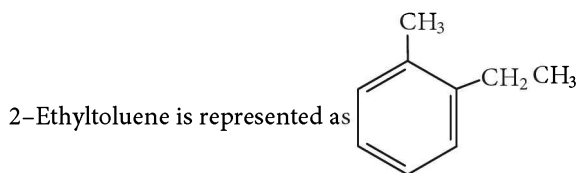
or



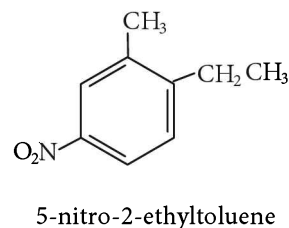
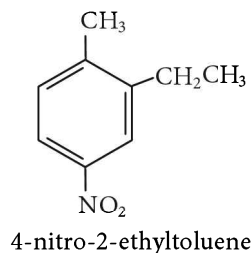
Concept Strand 15

What is the major product obtained when 2-ethyltoluene is nitrated? Is it 4-nitro-2-ethyltoluene or 5-nitro-2-ethyltoluene?

Solution



Hyperconjugation is more effective with a free methyl group which has three hydrogens, compared to an ethyl group, $-\text{CH}_2\text{CH}_3$, as ethyl group has only two hydrogens to interact with the ring. So a methyl group ($-\text{CH}_3$ group) is a better activator than an ethyl group. So the major product formed would be 4-nitro-2-ethyltoluene, which is activated by the methyl group than 5-nitro-2-ethyltoluene, which is activated by the ethyl group.

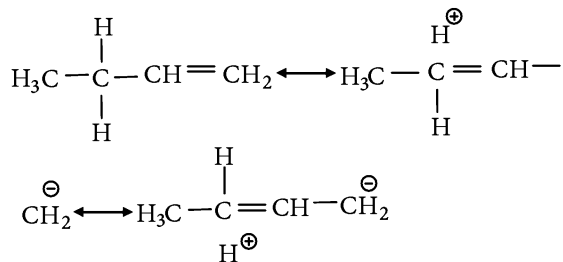


Concept Strand 16

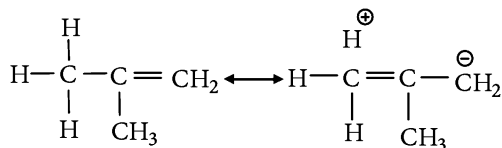
Account for the observation that ΔH (combustion) for 1-butene is $-2717 \text{ kJ mol}^{-1}$ whereas 2-methylpropene has the value $-2700 \text{ kJ mol}^{-1}$, although both are isomers.

Solution

Hyperconjugative stability of 1-butene can be represented only by two structures.



On the other hand, for the isomeric 2-methylpropene, six resonance or hyperconjugative structures are possible.



five other structures
are possible.

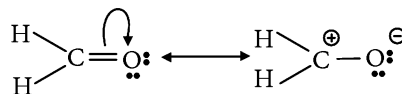
So delocalization of electrons (σ - π conjugation) is more effective in 2-methylpropene than in 1-butene. Further, six structures has a greater stabilizing influence over two structures. So 2-methylpropene has lower energy and more stable, and the combustion liberates less energy.

Concept Strand 17

Account for the fact that the dipole moment for CH_3CHO is 2.72 D whereas, for formaldehyde the dipole moment is 2.27 D.

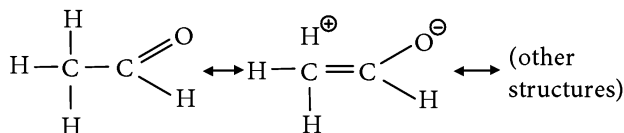
Solution

Only resonance effect is exhibited by formaldehyde as shown



The more electronegative oxygen acquires an extra pair of electrons on account of resonance. This accounts for its dipole moment of 2.27 D.

In the case of acetaldehyde in addition to the resonance of the carbonyl group, there is also hyper conjugative effect due to the adjacent $-\text{CH}_3$ group.



This accounts for greater polarization and hence the dipole moment of CH_3CHO is comparatively high ($\mu = 2.72$ D).

ISOMERISM

Two or more organic compounds which have the same molecular formula but different physical and chemical properties are called isomers and the phenomenon is known as isomerism.

Isomerism is mainly of two types: Structural isomerism and stereoisomerism.

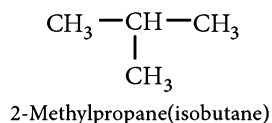
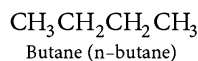
Isomers that differ from one another in the arrangement of atoms or groups within the molecule resulting in different structural formulae are known as structural isomers or constitutional isomers and the phenomenon is called structural isomerism. In other words, structural isomers have the same molecular formula but different structures or connectivity of atoms.

Classification of structural isomerism

Structural isomerism is further classified into the following types.

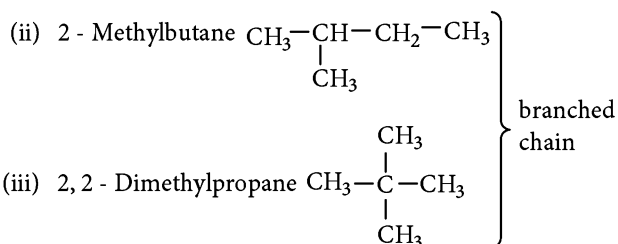
Chain isomerism or Nuclear isomerism

Isomers that differ in the arrangement of carbon chain within the molecule are called chain or nuclear isomers and the phenomenon is called chain or nuclear isomerism. The simplest compound showing chain isomerism is butane (C_4H_{10}). There are two chain isomers for butane



Pentane (C_5H_{12}) has three chain isomers

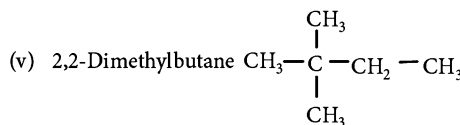
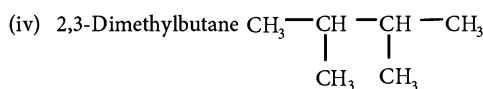
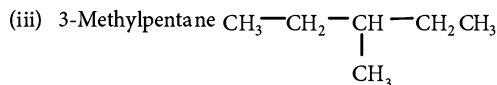
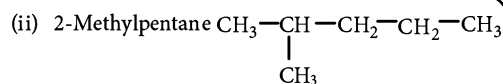
(i) Pentane (n-pentane) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
(straight chain)



Hexane (C_6H_{14}) has five chain isomers. They are

(i) Hexane (n-hexane) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

(straight chain)



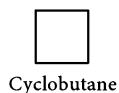
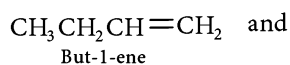
Heptane (C_7H_{16}) has nine chain isomers.

Ring chain isomerism

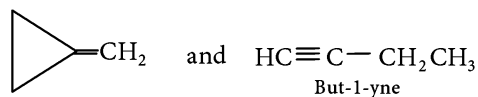
Ring chain isomers differ from each other in that one of the isomers will be an open chain compound while the other will have a ring structure.

For example

(i) C_4H_8



(ii) C_4H_6



(Methylene cyclopropane)

Position Isomerism

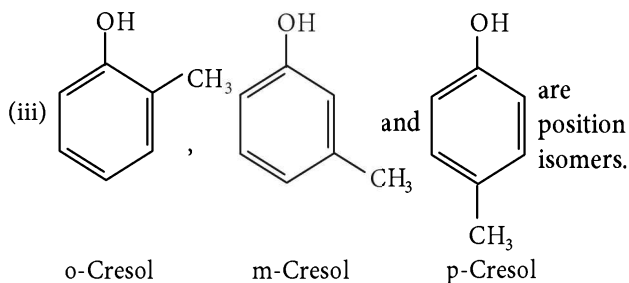
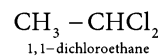
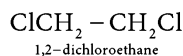
Position isomerism arises due to the difference in the positions occupied by the same functional groups or substituents in the molecule.

For example,

(i) $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$ and $\text{CH}_3\text{CH}=\text{CHCH}_3$ are
 But-1-ene But-2-ene

position isomers.

(ii) 1,2-Dichloroethane and 1,1-dichloroethane are
 position isomers.

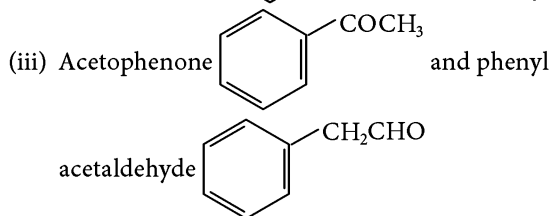
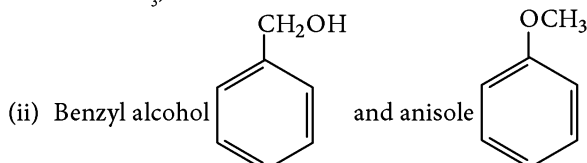


Functional isomerism

Compounds having the same molecular formula but different functional groups are called functional isomers and the phenomenon is called functional isomerism.

Some examples of functional isomers

(i) Acetic acid ($\text{CH}_3 - \text{COOH}$) and methyl formate ($\text{H} - \text{COOCH}_3$)



Metamerism

Compounds having the same molecular formula but different arrangement of alkyl groups on either side of the same functional group are called metamers and the phenomenon is called metamerism. For example

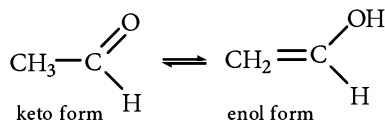
- (i) Diethyl ether, $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ and methyl propyl ether, $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3$.
- (ii) 3-Pentanone $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$ and 2-pentanone $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$.
- (iii) Methyl n-propylamine $\text{CH}_3 - \text{NH} - \text{CH}_2\text{CH}_2\text{CH}_3$ and diethylamine $\text{CH}_3\text{CH}_2\text{NHCH}_2\text{CH}_3$.

Tautomerism

Tautomerism is the phenomenon in which two isomeric forms, having different functional groups and are spontaneously interconvertible, exist in dynamic equilibrium.

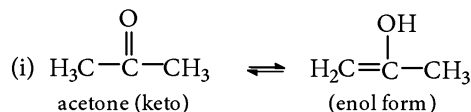
Keto-enol tautomerism

An important example of tautomerism is the keto-enol tautomerism shown by carbonyl compounds. For example, the keto and enol forms of acetaldehyde are shown below.

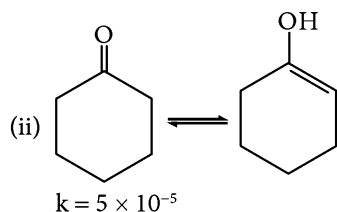


The two structures are called tautomers which coexist in dynamic equilibrium. The percentage of enol form in acetaldehyde is negligibly small. The greater stability of the keto form with respect to the enol form is mainly due to the greater strength of $\text{C} = \text{O}$ as compared to $\text{C} = \text{C}$.

Some other examples of keto-enol tautomerism

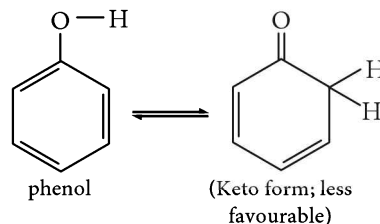


$$k = \frac{[\text{enol}]}{[\text{keto}]} \quad k = 1.5 \times 10^{-7}$$

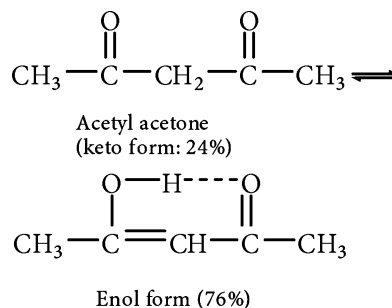


Although the percentage of enol isomer is quite small in the above examples, enol forms are very important in many reactions.

In the case of phenol, enol form is more favourable, as the ring maintains its aromaticity which imparts extra stability to the enol form. On the other hand, the keto form of phenol is more energetic and less favourable stability wise.

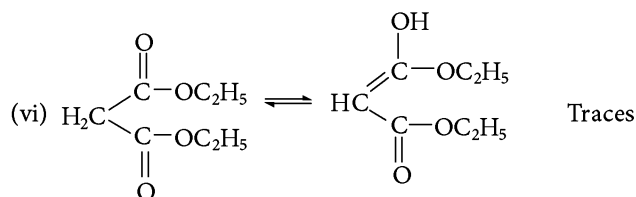


In certain dicarbonyl compounds, the enol form is stabilized by intramolecular hydrogen bonding. Such compounds exist mainly in the enolic form. For example, the percentage of enol form is about 76% in acetyl acetone.



Keto-enol equilibria of a few systems

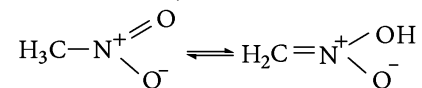
System	Percentage of enol content
(i) $\text{CH}_3 - \text{C}(=\text{O}) - \text{CH}_2 - \text{C}(=\text{O}) - \text{OCH}_3 \rightleftharpoons \text{CH}_3 - \text{C}(\text{OH}) = \text{CH} - \text{C}(=\text{O}) - \text{OCH}_3$	4.8
(ii) $\text{CH}_3 - \text{C}(=\text{O}) - \text{CH}_2 - \text{C}(=\text{O}) - \text{OC}_2\text{H}_5 \rightleftharpoons \text{CH}_3 - \text{C}(\text{OH}) = \text{CH} - \text{C}(=\text{O}) - \text{OC}_2\text{H}_5$	7.5
(iii) $\text{CH}_3 - \text{C}(=\text{O}) - \text{CH}_2 - \text{C}(=\text{O}) - \text{CH}_3 \rightleftharpoons \text{CH}_3 - \text{C}(\text{OH}) = \text{CH} - \text{C}(=\text{O}) - \text{CH}_3$	76
(iv) $\text{CH}_3 - \text{C}(=\text{O}) - \text{CH}(\text{CH}_3) - \text{C}(=\text{O}) - \text{CH}_3 \rightleftharpoons \text{CH}_3 - \text{C}(\text{OH}) = \text{C}(\text{CH}_3) - \text{C}(=\text{O}) - \text{CH}_3$	31
(v) $\text{C}_6\text{H}_5 - \text{C}(=\text{O}) - \text{CH}_2 - \text{C}(=\text{O}) - \text{C}_6\text{H}_5 \rightleftharpoons \text{C}_6\text{H}_5 - \text{C}(\text{OH}) = \text{CH} - \text{C}(=\text{O}) - \text{C}_6\text{H}_5$	96



The very high enol content in some of the examples given above is due to the extra stabilization of the enol form due to intramolecular hydrogen bonding.

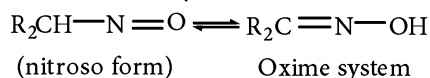
Other types of tautomerism—Examples

1. Nitro-acinitro system



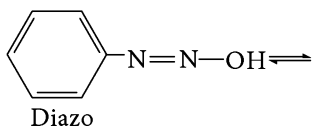
Nitromethane (nitro form)
(aci form)

2. Nitroso-oxime system

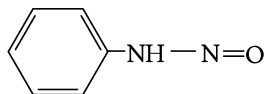


(nitroso form) Oxime system

3. Diazo-nitrosoamine system

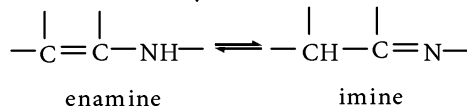


Diazo



Nitroso amine

4. Enamine-imine system

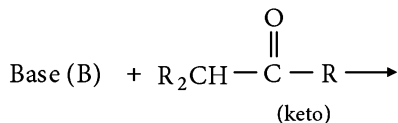


enamine

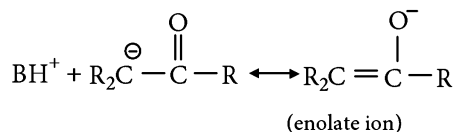
imine

Catalyzed enolization of a ketone.

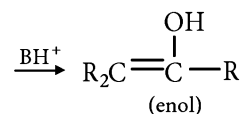
The conversion of the keto form to enol can be catalyzed by base or acid as shown below.



(keto)

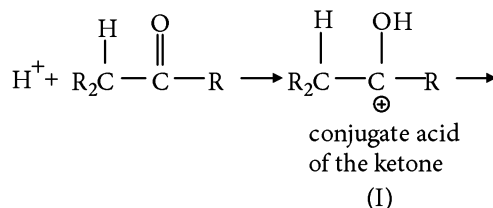


(enolate ion)

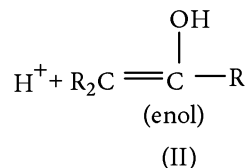


(enol)

Acid catalyzed enolization involves the initial protonation of the carbonyl oxygen to give an intermediate (I) from which a proton is removed to form the enol (II)



conjugate acid of the ketone
(I)



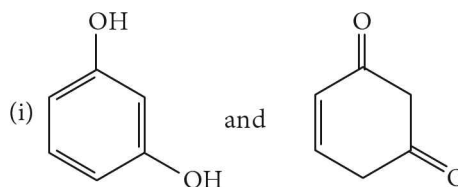
(enol)

(II)

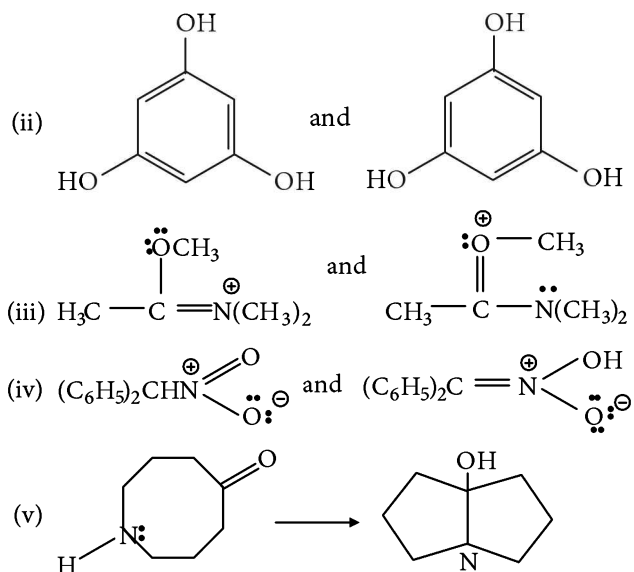
CONCEPT STRANDS

Concept Strand 18

Indicate whether the following pairs of structures are tautomers or resonance structures.



1.28 Basics of Organic Chemistry



Solution

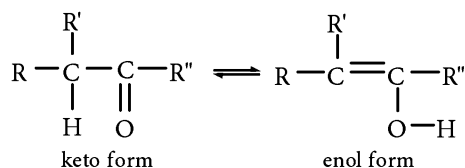
- (i) Tautomers
- (ii) Resonance structures
- (iii) Resonance structures
- (iv) Tautomers
- (v) Tautomers (transannular-which means across the ring)

Concept Strand 19

Why is keto form generally more stable than the enol form?

Solution

The keto and enol form of a carbonyl compound containing an α -hydrogen is shown below:

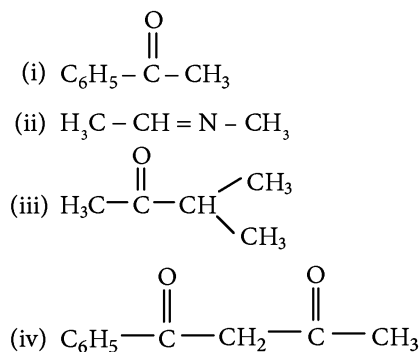


The keto form differs from the enol form in possessing a C-H, C-C and a C=O bond while the enol form has a C=C, C-O and an O-H bond. The sum of the bond enthalpies of the first three bonds is greater than the sum of the bond enthalpies of the other three bonds. This

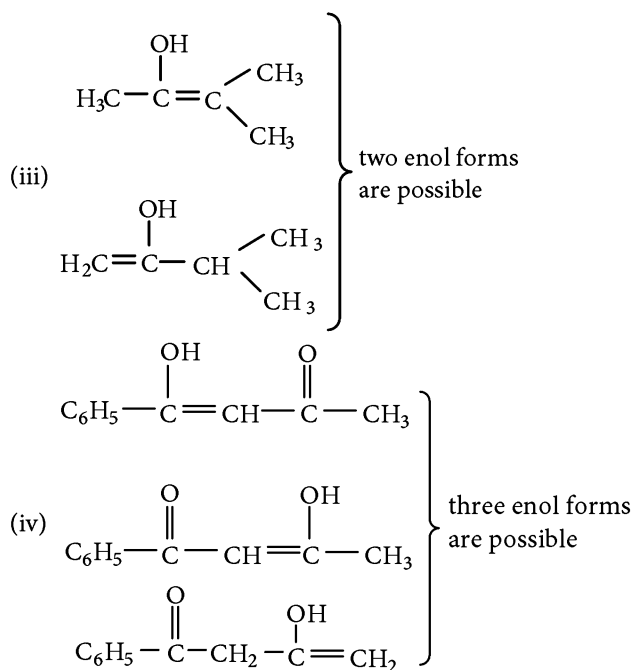
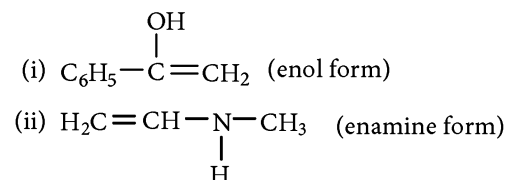
means that the keto form is thermodynamically more stable than the enol form.

Concept Strand 20

Give the structures of the corresponding tautomers in the following species.

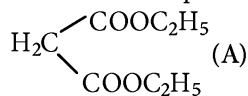


Solution



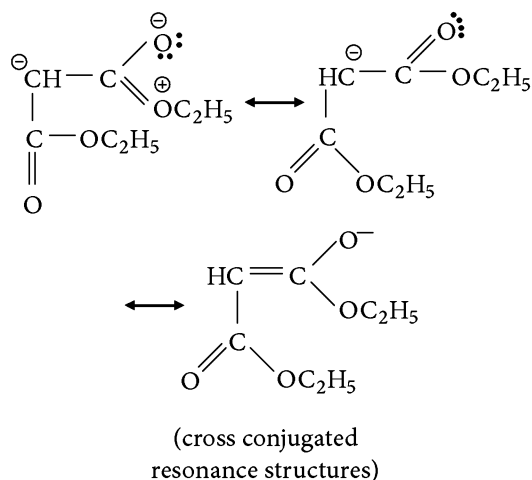
Concept Strand 21

Account for the poor enol content (traces) of



Solution

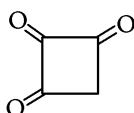
Cross conjugation is observed in (A) which is diethylmalonate as shown



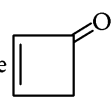
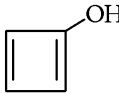
Cross conjugated resonance retards the ability of the $\text{C}=\text{O}$ of the ester group to stabilize the enol form.

Diethylmalonate has two ester groups and therefore has much lower enol content.

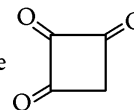
Concept Strand 22

Account for the fact that  does not enolize whereas the triketone  is more easily enolized?

Solution

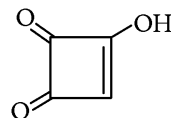
The enol of the ketone  cyclobutenone, which has the structure  does not exist, because it is a flat ring with 4π electrons and is antiaromatic.

The enol of the triketone



is easily formed

because the enol form

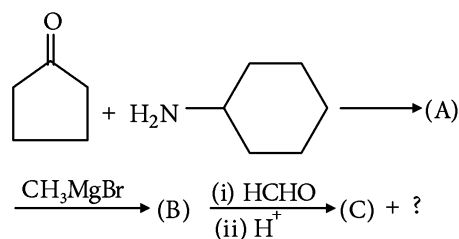


has 2π electrons

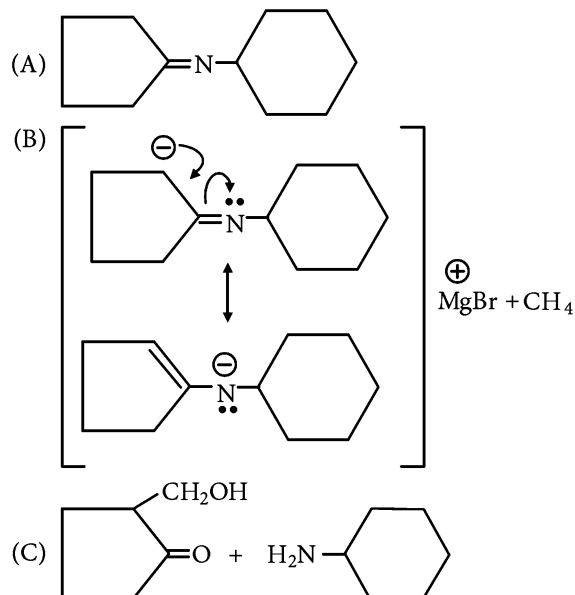
($4n + 2\pi$ electrons) required for aromaticity and is stabilized.

Concept Strand 23

Identify the structures of the lettered compounds



Solution

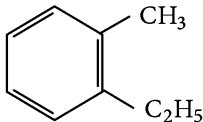
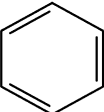
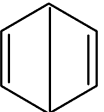
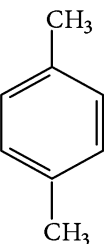
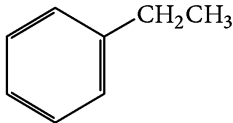


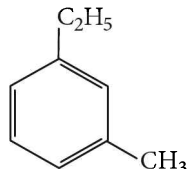
Concept Strand 24

Consider the following compounds. Pick out the isomeric pairs from the list and identify the type of isomerism exhibited by each pair.

1.30 Basics of Organic Chemistry

Table 1.6

1. CH_3COCH_3	2. α - hydroxy butyric acid
3. $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3$	4. $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$
5. $\text{CH}_2\text{ClCH}_2\text{Cl}$	6. $\text{CH}_2=\text{CH}-\text{OH}$
7. 	8. 
9. $\text{CH}_2=\text{CHCH}_2\text{OH}$	10. 
11. $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$	12. 
13. $\text{CH}_3\text{COCH}(\text{CH}_3)_2$	14. $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$
15. $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$	16. $\text{CH}_3\text{CHClCH}_2\text{CH}_2\text{CH}_3$
17. $(\text{CH}_3)_4\text{C}$	18. $\text{CH}_3\text{CH}(\text{OH})\text{H}_2\text{C}-\text{COOH}$
19. Methyl cyanide	20. CH_3NC
21. $\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5$	22. CH_3CHO
23. 	24. $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_2-\text{CH}_3$

25. 	26. $\text{H}_2\text{C}=\text{C}=\text{CH}-\text{CH}_3$
27. $(\text{CH}_3)_3\text{CCH}_2\text{Cl}$	28. Cyclobutane
29. $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$	30. CH_3CHCl_2

Solution

The pairs are

Table 1.7

(a)	1 and 9	Functional isomerism
(b)	3 and 21	Metamerism
(c)	5 and 30	Position isomerism
(d)	7 and 25	Position isomerism
(e)	11 and 24	Functional isomerism
(f)	13 and 29	Metamerism
(g)	15 and 28	Ring chain isomerism
(h)	14 and 17	Chain isomerism
(i)	19 and 20	Functional isomerism
(j)	12 and 23	Chain isomerism
(k)	16 and 27	Position isomerism
(l)	2 and 18	Position isomerism
(m)	4 and 26	Position isomerism
(n)	6 and 22	Functional isomerism and tautomerism
(o)	8 and 10	Ring isomerism

PROJECTION FORMULAE

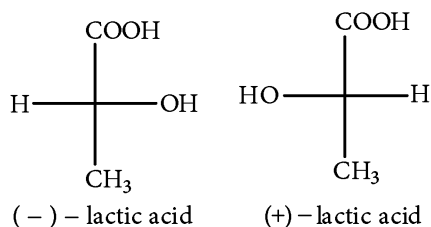
Fischer projection formula

A three dimensional formula on paper would be helpful to depict the exact configuration of a molecule. Fischer projection formula is an attempt to represent a three dimensional structure on paper.

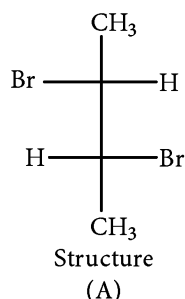
In Fischer projection, two lines crossed at right angles to each other are drawn to represent a chiral carbon (A carbon

joined to four different atoms or groups is called a chiral carbon). The chiral carbon is believed to lie at the intersection of these lines. The four groups attached to the chiral carbon are placed on the four ends of the cross. The horizontal lines represent bonds directed towards the viewer and the vertical lines represent bonds directed away from the viewer.

For example, lactic acid is represented in the Fischer projection formula as



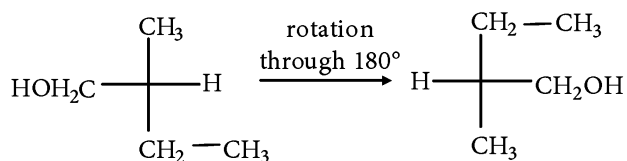
The Fischer projection formula of one isomer of 2,3-dibromobutane (a compound containing two chiral centers) is shown below.



But it may be noted that a molecule may be represented by different Fischer projections. Then it becomes necessary to find out whether two projections are same or not. The following are the points to be remembered in rotating a Fischer projection formula.

- (i) Rotation by 180° in the plane of the paper will not change the configuration of the molecule.

For example,

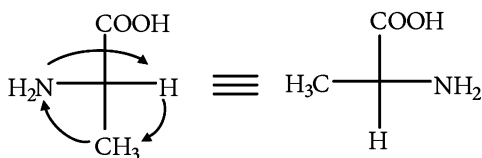


(A)

(B)

The two Fischer projections (A) and (B) shown above are identical and represent the same isomer.

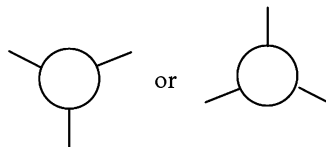
- (ii) It is also permissible to keep any one group fixed and to rotate the other three clockwise or anti-clockwise. This will not change the configuration



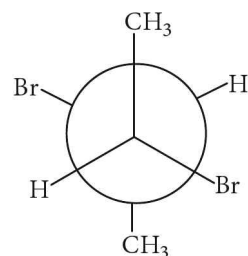
- (iii) Interchange of two pairs of groups in the Fischer projection will not change the configuration.

Newmann projection formula

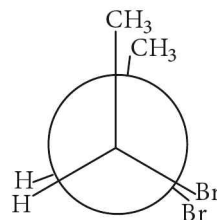
In writing the Newmann projection formula we imagine that we are viewing the molecule from one end directly along the carbon-carbon bond axis. The bonds of the front carbon atom are represented as or and the bonds of the rear carbon atom is shown as



Newmann structure is useful only for structures with two chiral carbon centers. The three dimensional structure of 2,3-dibromobutane $\text{CH}_3\text{CHBrCHBrCH}_3$, in Newmann form is shown below:



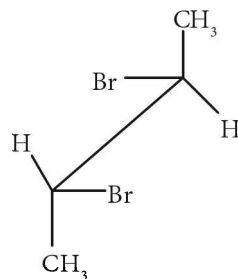
The most stable conformation of 2,3-dibromobutane is the staggered form shown above while the least stable form is the eclipsed form, shown below.



Sawhorse projection formula

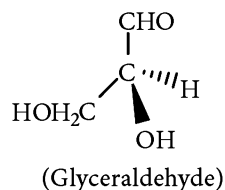
Another kind of projection formula is the Sawhorse projection formula.

The Sawhorse representation of the staggered conformation of 2,3-dibromobutane is shown below.



Wedge and dash formula

It is a convenient mode of representing three dimensional structures of simple molecules. A solid wedge represents a bond projecting above the plane and a dashed line represents a bond below the plane.



STEREISOMERISM

Stereoisomers are isomers that have the same connectivity but differ in the arrangement of their atoms in space. So stereoisomers have the same structural formula but differ in the relative arrangement of atoms or groups in space. The spatial arrangement of atoms or groups in a molecule is referred to as its configuration. Thus stereoisomers have the same molecular structure but different configurations.

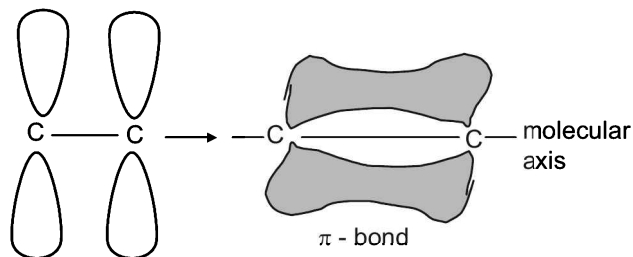
Stereoisomerism is divided into three major groups.

- (i) Geometric isomerism
- (ii) Optical isomerism
- (iii) Conformational isomerism

Geometrical isomerism

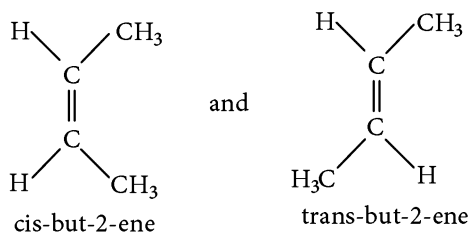
Geometrical isomerism normally arises because of the spatial geometry of atoms or groups associated with a double bond. Carbon atoms forming part of the double bond system and the various atoms or groups attached to these two carbons remain in the same plane.

The lateral overlap of the two 'p' atomic orbitals to give a π orbital completely prevents the rotation of the groups attached to the two carbons. The net result is that free rotation about a double bond is restricted or prevented as it involves a high energy around 60 kcal mol^{-1} .



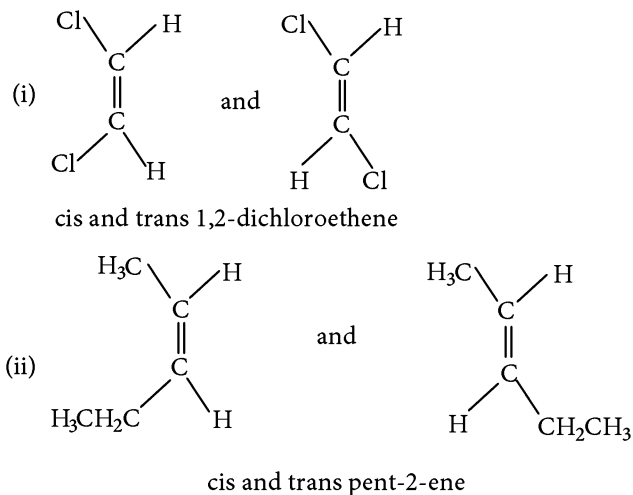
The isomers which have the same structural formula but differ in spatial arrangement of atoms or groups about the double bond are known as geometrical isomers.

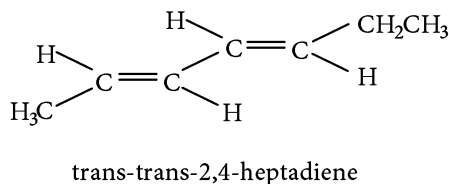
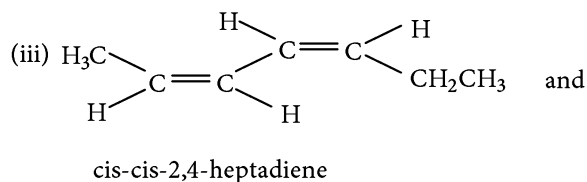
For example, But-2-ene ($\text{CH}_3\text{CH}=\text{CHCH}_3$) can exist in the form of two geometrical isomers.



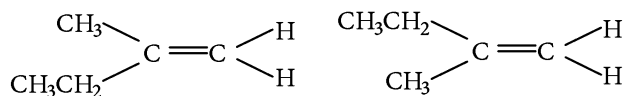
When the two methyl groups are on the same side of the molecule, the compound is assigned the cis configuration, while the trans configuration is assigned when the two methyl groups are on the opposite sides of the molecule. In the cis isomer, the two methyl groups are located close enough to cause steric crowding, while in the trans isomer, the same two groups are well separated. From this, we can expect the cis isomer to be less stable and more energetic than the trans.

Few other examples of compounds which exhibit geometrical isomerism are



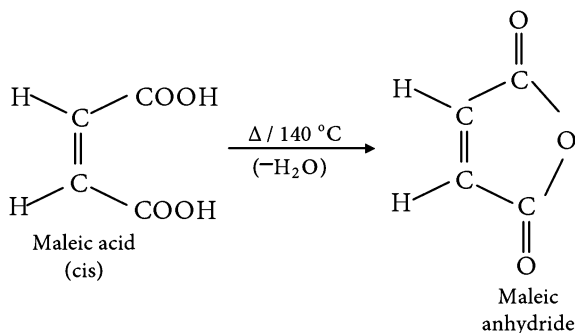


Not all double bonded compounds exhibit geometric isomerism. Only molecules in which each carbon of the double bond is bonded to two different groups can exist as cis-trans isomers.

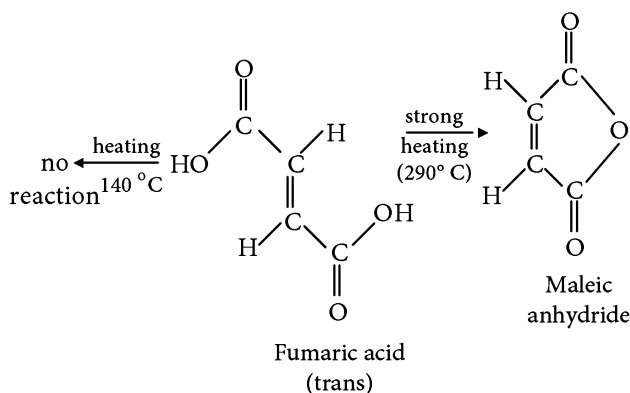


For example, 2-Methyl-but-1-ene cannot exist as geometric isomers as shown above as both the structures represent the same compound.

Restricted rotation about a carbon-carbon double bond may influence the chemical reactivity of certain geometric isomers. For example, the cis isomer of butenedioic acid, namely maleic acid on heating to 140°C , loses water to form maleic anhydride.



In contrast, the trans isomer of the same compound, namely fumaric acid does not lose water readily on heating, but on very strong heating to about 290°C , first isomerizes to give the cis isomer which then loses water to give the anhydride.

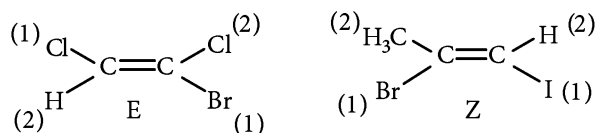


The high temperature provides sufficient energy to overcome the barrier of rotation about the carbon-carbon double bond and gives the cis-configuration which is required to form the anhydride.

E and Z notation of geometrical isomers

When all the four substituents attached to the double bonded carbon atoms are different, the geometrical isomers cannot be labeled as cis and trans. So a new notation known as E and Z notation has been developed to designate geometrical isomers. In this system, the two substituents attached to each of the double bonded carbon is assigned priorities in accordance with the sequence rules given by Cahn, Ingold and Prelog. According to these rules, the groups are arranged in order of decreasing atomic number of the atoms with which they are bonded to carbon and assigned priority 1 and 2 accordingly. If the groups are linked by identical atoms, priority is decided by comparison of the next atoms in the groups. Thus between $-\text{CH}_3$ and $-\text{CH}_2-\text{CH}_3$ groups, the latter gets priority.

The geometrical isomer is assigned the configuration E if the two groups of higher priority on each carbon are on the opposite sides of the double bond. If groups of higher priority are on the same side of the double bond, the isomer is assigned the configuration Z. For example

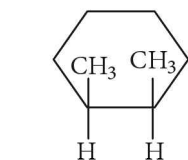


Geometrical isomerism in cyclic system

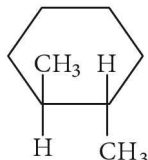
Geometrical isomerism can also be observed because of some type of structural rigidity of the molecule.

1.34 Basics of Organic Chemistry

For example, the molecule 1,2-dimethylcyclohexane can exhibit geometrical isomerism, the isomers are cis and trans 1,2-dimethylcyclohexane.



cis-1,2-
dimethylcyclohexane



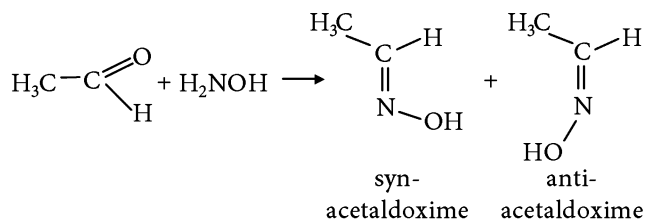
trans-1,2-
dimethylcyclohexane

In the above two structures freedom of rotation about a carbon-carbon single bond is restricted because of the cyclic nature of the system and inter conversion of cis and trans would mean the breaking of the bond.

Geometrical isomerism in oximes

Oximes are the products when the aldehydes and ketones react with hydroxylamine (H_2NOH).

For example, acetaldehyde reacts with H_2NOH to form acetaldoxime, which exist as two geometrical isomers

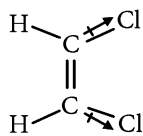


The geometric isomers of oximes are known as syn and anti isomers instead of the conventional names used in geometrical isomerism as cis and trans.

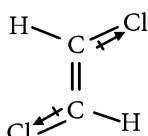
Dipole moment of geometrical isomers

Dipole moment is an additive property. The cis isomer generally has a larger dipole moment than the trans isomer.

For example,



cis-1,2-dichloroethene
 $\mu = 1.89 \text{ D}$



trans-1,2-dichloroethene
 $\mu = 0$

Difference in other Physical properties

Cis and trans isomers also differ in many other physical properties such as melting point, boiling point, solubility etc.

In general, the melting point of a trans isomer is higher than that of the corresponding cis isomer. This is because the molecules of a trans isomer are more symmetrical and hence fit more closely in the crystal lattice as compared to the molecules of the cis isomer. So more energy is needed to separate the molecules of the trans isomer in the solid state.

In general, solubility of a cis isomer is higher than that of the trans isomer. This is because molecules of a cis isomer are less tightly held in the crystal lattice and hence it is easier to break the crystal lattice of the cis isomer.

The boiling point of a cis isomer, in general, is higher than that of the trans isomer. This is because of higher dipole moment and hence higher dipole-dipole interaction among the molecules of the cis isomer in the liquid state.

Optical Isomerism

Optical isomerism is a kind of stereoisomerism in which isomers differ only in their behaviour towards plane polarized light. Under ordinary conditions, monochromatic light waves vibrate in a number of planes passing through the line of propagation. When a monochromatic light is passed through a Nicol prism (a special prism made from calcite) the emerging light will have vibrations in one plane only. Such a beam of light which has vibrations only in one plane is called plane polarized light.

When plane polarized light is passed through solutions of certain organic compounds, the plane of polarization gets changed or rotated through a certain angle. Such compounds which rotate the plane of polarized light are called optically active compounds.

If the rotation of the plane of polarised light is to the right (clockwise), the substance is said to be dextrorotatory and if the rotation is to the left, the substance is laevorotatory. The symbols (+) and (-) are used to indicate the directions of rotations to the right or to the left, respectively.

The optical rotation is measured using an instrument known as polarimeter. Specific rotation is the degree of rotation observed for a compound of concentrations 1 g mL^{-1} taken in a tube of 10 cm. (1 decimetre).

$$\begin{aligned} \text{Specific rotation } [\alpha]_D^{20} \\ = \frac{\text{observed rotation } (\alpha) \text{ in degrees}}{\text{length (dm)} \times \text{concentration (g mL}^{-1})} \end{aligned}$$

20 represents the temperature 20°C and D is the sodium light used (monochromatic).

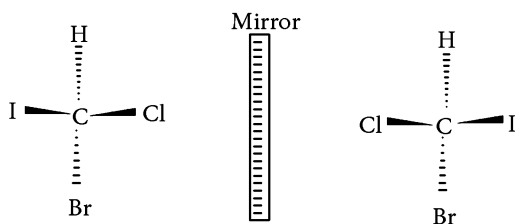
Cause of optical activity: Chirality

The study of the molecular structures of optically active compounds reveals that the molecules of all these compounds are chiral. A molecule (or object) is said to be chiral if it is not superimposable on its mirror image.

The property of non-superimposability of a structure on its mirror image is called chirality.

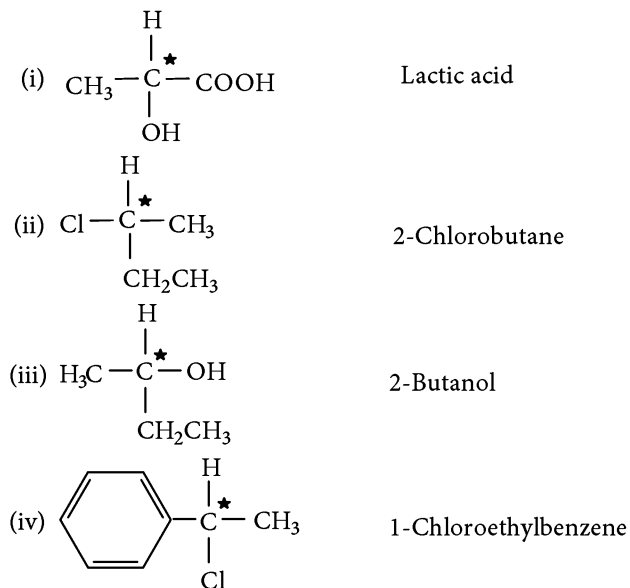
It has been observed that most of the chiral organic compounds have at least one chiral carbon or asymmetric carbon in the molecule. An asymmetric carbon is one in which all the four valencies are satisfied by four different atoms or groups.

For example, the molecule of bromochloriodomethane (CHBrCl) is chiral because it contains a chiral carbon. It can have two arrangements as shown below.

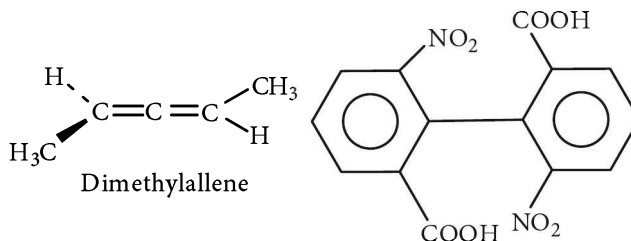


The two structures are related to each other as an object is related to its mirror image. The two structures are non-superimposable and represent the two optical isomers of the compound. One of the isomers will rotate the plane of polarized light to the right and the other will rotate it to the left through an equal angle.

Examples of few compounds which are chiral (those which have an asymmetric centre) are given below. The chiral centers are marked by an asterisk (*). All these compounds are optically active.



It may be noted that the necessary condition for chirality is not just the presence of asymmetric carbon atoms but the asymmetry of the molecule as a whole. There are certain organic molecules which are chiral and show optical activity even though they do not contain any asymmetric carbon atom. Substituted allenes and ortho substituted biphenyls are common examples of this type.



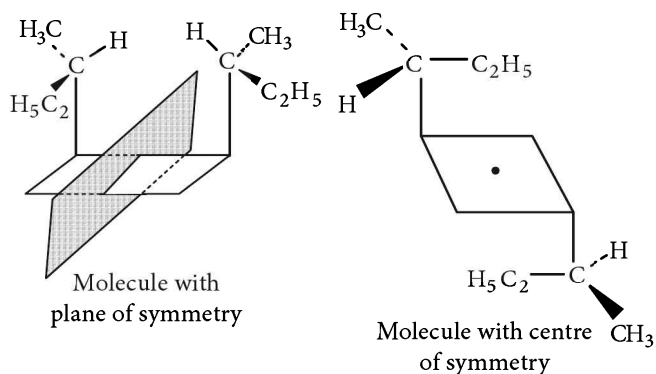
Elements of symmetry and chirality

A simple method to decide whether a molecule is chiral or not is to ascertain whether it contains elements of symmetry such as a *plane of symmetry*, a *centre of symmetry* or an *alternating axis of symmetry*. If any one of these is present in a molecule, it is symmetrical or achiral and will not exhibit optical activity.

A plane of symmetry is defined as an imaginary plane which divides the molecule into two equal halves such that one half of the molecule is a mirror image of the other.

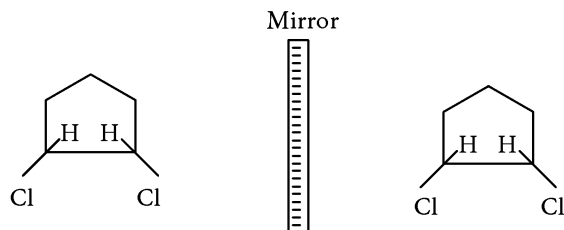
A centre of symmetry is defined as a point from which lines, when drawn on one side and produced an equal distance on the other side, will meet identical points (atoms or groups) in the molecule.

A molecule is said to possess an n -fold alternating axis of symmetry if rotation through an angle of $\frac{360^\circ}{n}$ about this axis and then followed by reflection in a plane perpendicular to the axis, gives a molecule that is indistinguishable from the original one.



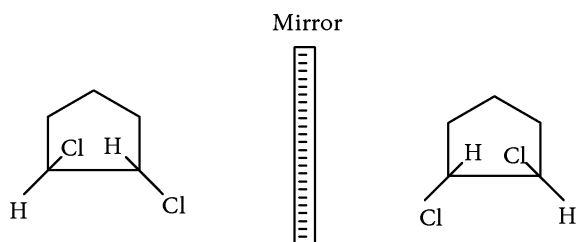
1.36 Basics of Organic Chemistry

In the cyclic compounds—cis and trans isomers of 1,2-dichlorocyclopentane can be taken as example.



cis - 1,2 - dichlorocyclopentane.

These two are superimposable mirror images—they are identical. The molecule has a plane of symmetry. They are not chiral. They do not show optical activity.



trans-1,2-dichlorocyclopentane

These two are non-super imposable mirror images. They are not identical. They are chiral. They are enantiomers. They can exhibit optical activity.

Enantiomers

Optical isomers whose molecular structures are non-superimposable mirror images of each other and which rotate the plane of polarized light equally but in opposite directions are called enantiomers or enantiomorphs. Eg., (+) lactic acid and (–) lactic acid are enantiomers.

Racemic mixture

A mixture containing equal amounts of enantiomers (i.e., dextro and laevo forms) is called a racemic mixture. A racemic mixture is denoted by putting a prefix ($\pm$) or dl before the name of the compound. A racemic mixture is optically inactive due to external compensation.

Racemization

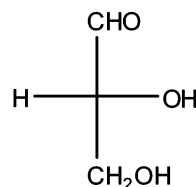
The process of converting the (+) or (–) form of a compound into the racemic mixture is known as racemization.

Designation of configuration

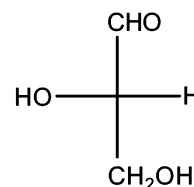
The spatial arrangement of atoms or groups in a molecule is referred to as its configuration. There are two systems for designation of configuration.

The D, L system

This is an old system in which the standard chosen for assigning relative configuration is glyceraldehyde. Fischer assigned the following configurations to the (+) and (–) enantiomers of glyceraldehyde arbitrarily and denoted them by the letters D and L respectively.

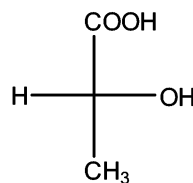


D (+) glyceraldehyde

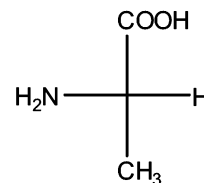


L (–) glyceraldehyde

If the configuration at the asymmetric carbon atom of a molecule can be related to D(+) glyceraldehyde, it belongs to the D-series and if it can be related to L(–) glyceraldehyde, the molecule belongs to the L-series. For example



D(–) lactic acid



L(+) alanine

It must be noted that this D and L notation shows only the configuration at the asymmetric carbon atom and does not indicate the direction of optical rotation.

The R, S system

This method was proposed by Cahn, Ingold and Prelog. The procedure involves the following steps.

1. The four atoms or groups attached to the chiral carbon atom are assigned priorities by using the sequence rules given by Cahn, Ingold and Prelog (CIP rules).
2. The molecule is then visualized in such a way that the atom or group of lowest priority is directed away from us. Then, if the other groups in the order of priority

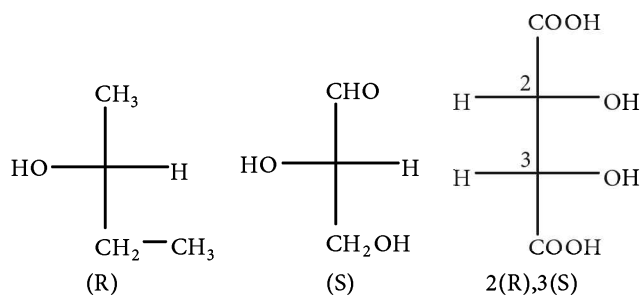
(1 $\rightarrow$ 2 $\rightarrow$ 3) are oriented clockwise, the molecule is designated R and if counter clockwise S.

Cahn-Ingold-Prelog rules

- (i) If the four atoms/groups directly bonded to the chiral carbon atom are different, the priority depends on the atomic number. The atom of higher atomic number gets higher priority.
- (ii) If two groups bonded to chiral carbon have identical first atoms, the priority order is determined by considering the atomic numbers of the second atom in the group. If they are also identical, the third atoms along the chain are compared. For example, between $-\text{CH}_3$ and $-\text{CH}_2-\text{CH}_3$ groups, ethyl group gets higher priority.
- (iii) A doubly or triply bonded atom is considered as equivalent to two or three such atoms respectively.

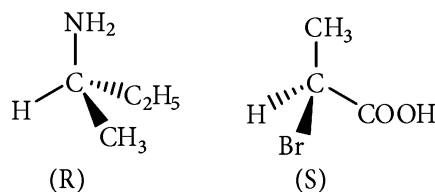
Assigning R and S configuration from Fischer projection

- (i) Assign priority order to the four atoms or groups using CIP rules.
- (ii) Perform any of the allowed rotations to place the group of lowest priority in any of the vertical positions (i.e., top or bottom). If the lowest priority group is at the vertical position, no rotation of groups is needed.
- (iii) Then determine the sequence of arrangement of groups 1 $\rightarrow$ 2 $\rightarrow$ 3 and assign R or S.



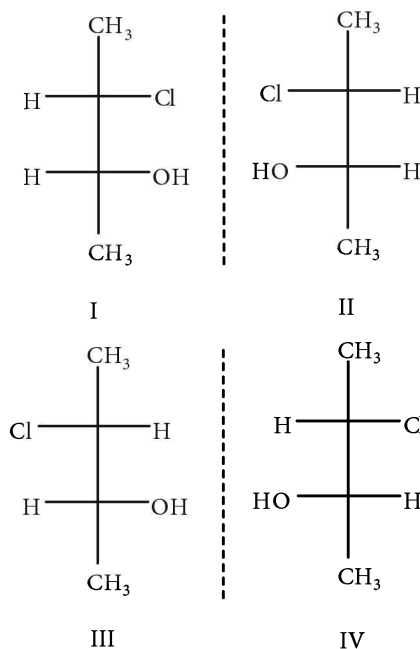
Assigning R and S configuration from Wedge and dash formula

The procedure is similar to the above. After assigning priority, interchange two pairs of groups and bring the group of lowest priority in the position shown by dotted line. Then find out the sequence 1 $\rightarrow$ 2 $\rightarrow$ 3 and assign R or S. If the group with lowest priority is given at the position shown by dotted line, then there is no need of interchange of groups.



Optical isomerism of compounds containing two dissimilar chiral centres

A compound containing two different chiral centres can have four stereoisomers. E.g., 3-Chlorobutan-2-ol.



There are two pairs of enantiomers: I and II, III and IV. The isomers I and III are not mirror images. Same is the case with II and IV. They are called diastereoisomers or diastereomers.

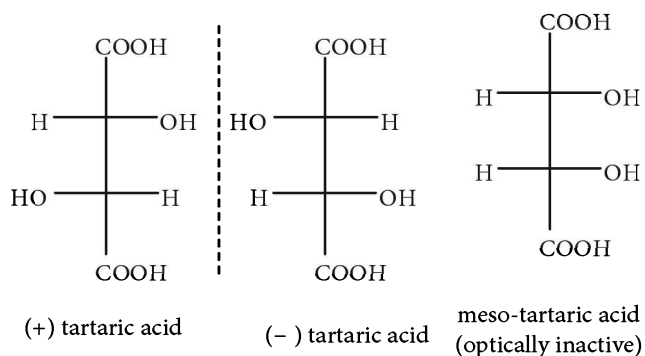
The stereoisomers which are not mirror images of each other are called diastereoisomers or diastereomers

Even geometrical isomers can be considered as diastereomers. Diastereomers differ in some of their physical properties such as melting point, boiling point etc. (But enantiomers have same physical properties except in their direction of rotation of plane polarized light).

In general, the total number of optical isomers possible for a compound containing n different chiral carbon atoms is 2^n .

Optical isomerism of compounds containing two similar chiral carbon atoms

When a molecule of a compound contains two similar chiral carbon atoms, the number of optical isomers possible is only three. e.g., tartaric acid.



Meso-tartaric acid molecule has a plane of symmetry. So it is achiral and optically inactive. Meso-tartaric acid is a diastereomer of (+) and (-) tartaric acid. Meso compound is optically inactive due to internal compensation.

Resolution of a racemic mixture

The process of separation of a racemic mixture into its enantiomers is called resolution.

Special methods are used for the resolution of racemic mixture.

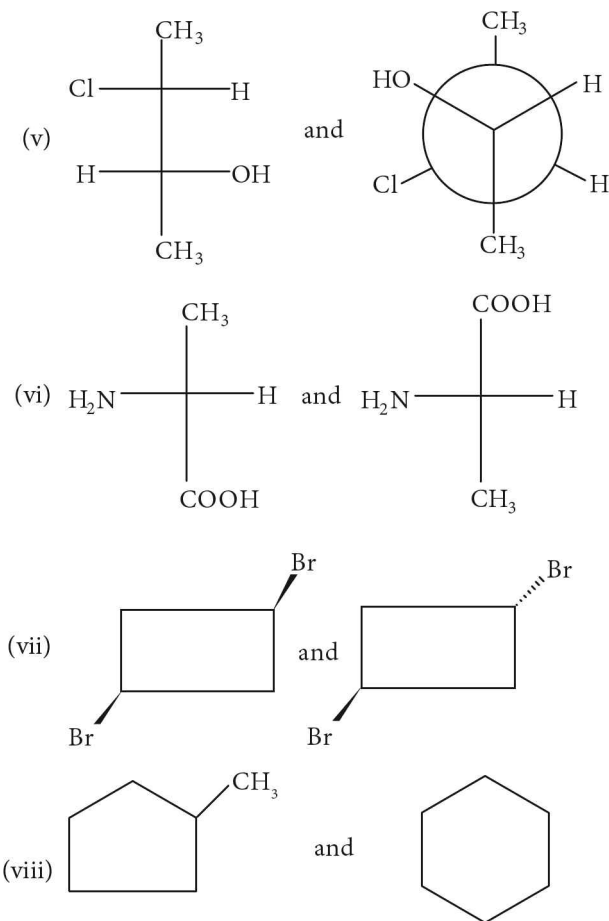
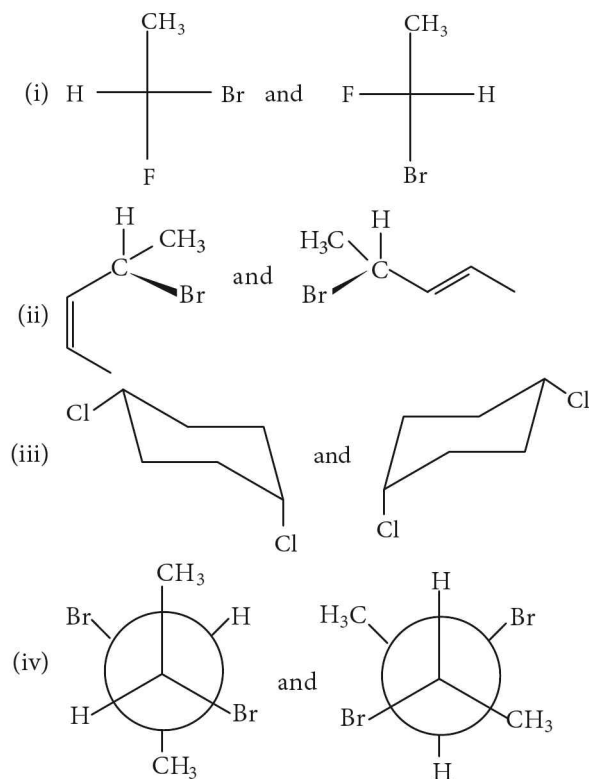
Inversion of configuration

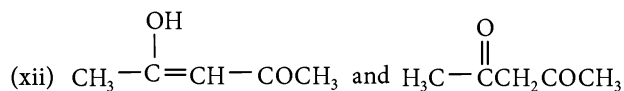
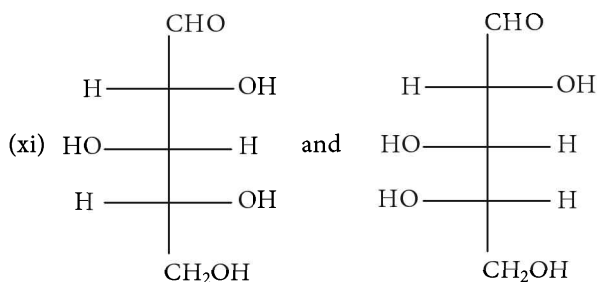
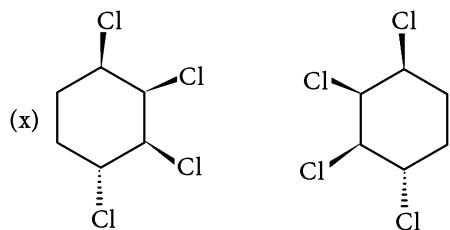
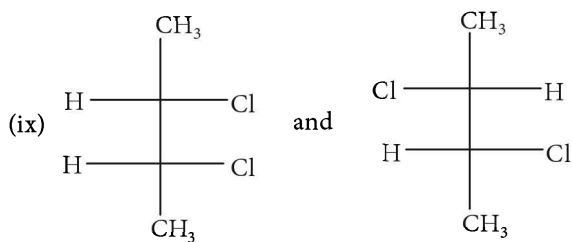
If the starting material and the product have opposite configurations, the reaction is said to proceed with inversion of configuration. If the product has the same configuration as the starting material, then the reaction is said to proceed with retention of configuration.

CONCEPT STRANDS

Concept Strand 25

Identify the following pairs of compounds as enantiomers, diastereomers, constitutional (or structural) isomers and two representations of the same compound.





Solution:

- Two exchanges are needed to make the two structures identical. Hence (even number of changes), the two structures are representations of the same compound (identical).
- They are cis-trans isomers or geometric isomers. They can also be considered as diastereomers.
- Both have plane of symmetry and represent the same compound.
- Two representations of the same compound (identical).
- Enantiomers
- Enantiomers
- Diastereomers as well as cis and trans isomers
- Constitutional or structural isomers (ring isomers)
- Diastereomers
- Enantiomers
- Diastereomers
- Tautomers

Concept Strand 26

What is the percentage composition of a mixture of two enantiomers, when the specific rotation of one of the enantiomers is $+12^\circ$ and that of the mixture is -9° ?

Solution:

The optical purity or percentage composition of an enantiomer is given by the relationship $(OP) = (-9^\circ / -12^\circ) \times 100 = 75\%$. This means that 75% of the mixture contains the (-) enantiomers whose specific rotation is -12° . The remaining 25% is the racemate which is a mixture of (+) and (-). So the percentage of the (+) enantiomer is half of 25% or 12.5%. i.e., 12.5% (+) isomer and 87.5% of (-) isomer.

Concept Strand 27

The specific rotation of a pure enantiomer is $+24^\circ$. What will be its observed rotation if it is isolated from a reaction with

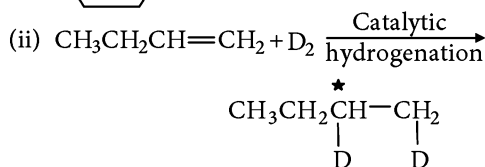
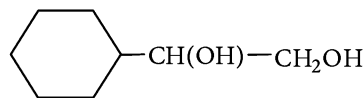
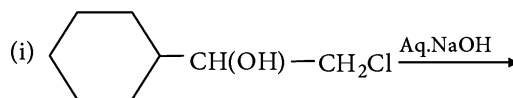
- 25% racemization and 75% retention of configuration.
- 75% racemization and 25% retention of configuration.

Solution:

- Observed rotation $= 0.75(+24) \Rightarrow \alpha = 18^\circ$
The observed rotation with 75% retention and 25% racemization $= 18^\circ$
- Observed rotation $(\alpha) = (0.25)(-24) = 6^\circ$
The observed rotation with 25% retention and 75% racemization $= 6^\circ$

Concept Strand 28

Predict whether the reactions given below occur with retention or inversion of configuration or with racemization.



Solution:

- (i) The reaction would give a product with retention of configuration, as the reaction site is not a chiral centre.
- (ii) The product obtained has a chiral centre in the carbon atom marked (*). Racemization is expected as the

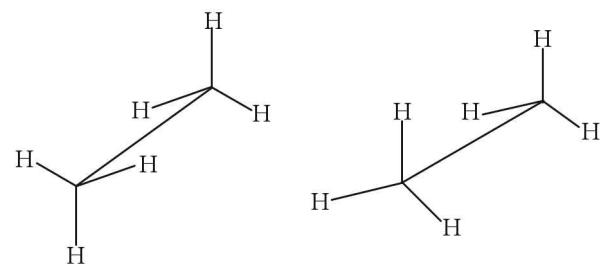
attack by the reagent (D_2) occurs on a planar carbon centre (an sp^2 centre) where there is possibility of an attack by direction from the top and bottom of the plane to give equal quantitative of (+) and (-) products. Hence racemization is expected.

Conformational isomerism**Sigma bonds and bond rotation**

Atoms and groups linked only by a sigma bond—that is by a single bond—can undergo free rotation about the bond axis with respect to each other. The various spatial arrangements which result on account of rotation of groups about a single bond are called conformational isomers or conformers or rotational isomers.

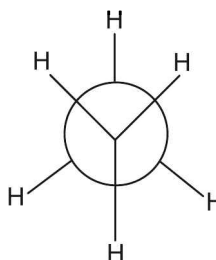
Conformations of ethane

In ethane molecule ($H_3C - CH_3$) the two carbon atoms are bonded by a sigma bond. If one of the carbon atoms in ethane molecule is kept fixed and the other is rotated around the $C - C$ bond, a large number of spatial arrangements of hydrogen atoms of one carbon with respect to the hydrogen atoms of the other carbon can be obtained. These different spatial arrangements are called conformations of ethane. Out of these infinite number of possible conformations of ethane, the conformation with minimum and maximum energies are the staggered conformation and the eclipsed conformations. The Sawhorse and Newmann projection formulae of these two conformations are given below.

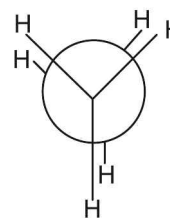
Sawhorse model

Staggered
conformation
of ethane

Eclipsed
conformation
of ethane

Newmann projections for ethane

Staggered form of
ethane



Eclipsed form of ethane

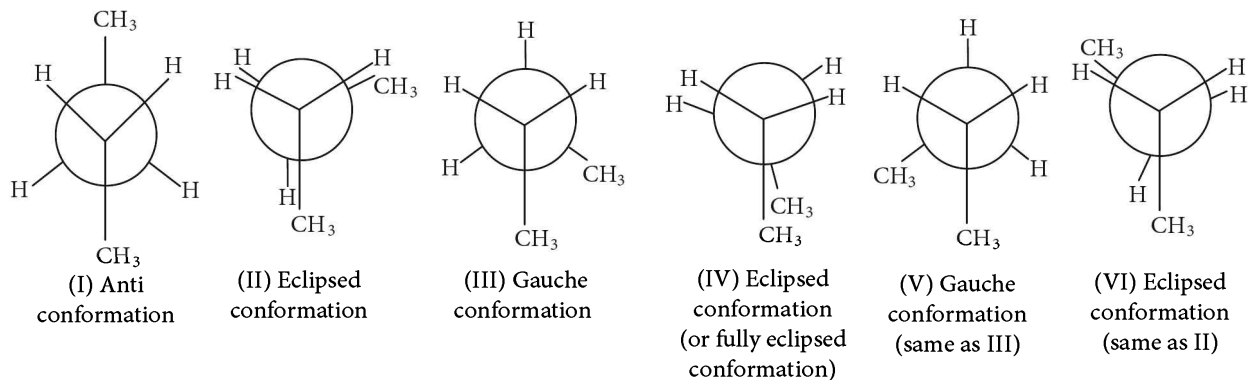
In ethane, the difference in energy between staggered and eclipsed conformations is 12 kJ mol^{-1} . This small barrier to rotation is called the energy barrier of the single bond. The least stable conformation of ethane is the eclipsed conformation. When viewed from one end along the carbon carbon bond axis, the hydrogen atoms attached to each carbon atom in the eclipsed conformation are in direction opposite to each other. This eclipsed conformation experiences the maximum repulsive interaction between electrons of the six $C - H$ bonds. Eclipsed conformation has the highest energy and least stability.

The conformation in which the hydrogen atoms attached to each carbon atom are perfectly staggered, is the most stable conformation and this conformation has the lowest energy. This is explained in terms of least repulsive interactions between bonding pairs of electrons.

Ethane will spend most of its time at the lowest energy staggered conformation. When the energy of an ethane molecule is raised, it can rotate, surmount the energy barrier of 12 kJ mol^{-1} and exist in the eclipsed conformation. However, the difference in energy between the eclipsed and staggered forms of ethane is not quite significant and it can easily interconvert from one form to the other. Therefore, it is not possible or easy to isolate any one of the specific conformer unless, the molecule is brought to an extremely low temperature, say -250°C , or frozen so that flipping from one conformational state to another is prevented.

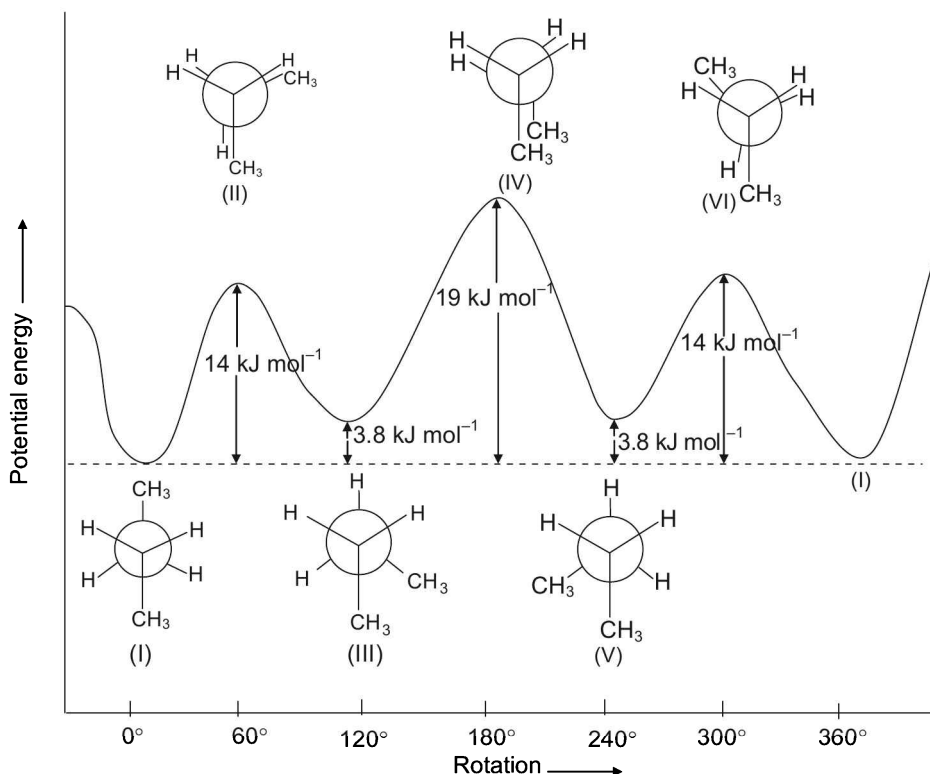
Conformations of *n*-butane ($^1\text{CH}_3 - ^2\text{CH}_2 - ^3\text{CH}_2 - ^4\text{CH}_3$)

Considering the rotation about $\text{C}_2 - \text{C}_3$ bond, an infinite number of conformations are theoretically possible. Out of these, the main conformations are given below.



The anti-conformation (I) of *n*-butane does not have any torsional strain as the two methyl groups are far apart. Therefore, the anti-conformer (I) is the most stable and has the least energy. The two methyl groups in the gauche or skew [(III) and (V)] conformations are fairly close to each other, consequently the non bonded van der Waals

interaction is appreciable. Hence the energy is slightly higher than the anti form. The eclipsed conformations (II), (IV) and (VI) have high energy. Out of these the conformation (IV) has the highest energy as the two bulky methyl groups are closest.



Although the energy barriers to free rotation in butane are considerably higher compared to ethane, still the energy differences between the conformers is very small and they are not sufficient enough to be separated and isolated.

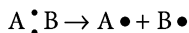
CHEMICAL REACTIONS AND BOND CLEAVAGES

A chemical reaction is one in which some of the existing bonds are broken and new bonds are made. So during a chemical reaction, covalent bonds get cleaved or broken.

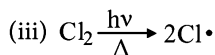
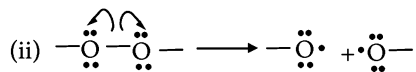
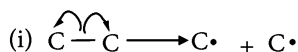
A covalent bond fission can occur in two ways.

Homolytic bond cleavage

When a covalent bond breaks in such a way that each fragment retains one electron of the bond, the process is called homolytic cleavage or homolysis.



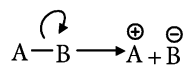
Cleavage of a covalent bond occurs in a symmetrical manner, so that each atom gets one electron from the bond pair. In a homolytic cleavage, free radicals or odd electron species are formed, which are very reactive and difficult to isolate. The movement of a single electron is shown by a single headed arrow (fish hook arrow).



Generally a homolytic cleavage occurs under thermal or photochemical conditions or under the influence of a catalyst or other radicals.

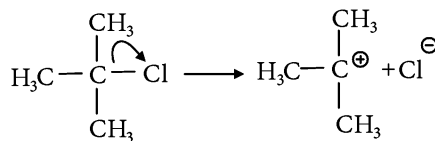
Heterolytic bond cleavage

When a covalent bond breaks in such a way that both the bonding electrons go to the same fragment, the mode of cleavage is called heterolytic cleavage or heterolysis.



The two electrons that form the bond between A and B move towards one of the atoms, say B, as a result of which B acquires the pair of electrons and gets a negative charge (B^-). The other element A from which the electrons have moved away, acquires a positive charge (A^+). Thus the breaking of the bond occurs in an unsymmetrical manner. Heterolysis of a neutral molecule generally results in an electron deficient positive ion and an electron rich negative ion.

A heterolytic cleavage is shown by a curved arrow showing the direction of movement of electrons. A heterolytic cleavage is generally observed when the bonded atoms are of different electronegativities.



When atoms combine to form a bond, energy is liberated or it is an exothermic process. When the same bond is broken to form the separate atoms, an equivalent quantity of energy is consumed or it is an endothermic process. The quantity of energy consumed or liberated when a bond is broken or formed is known as bond dissociation energy, which is characteristic of a particular bond.

For example, bond dissociation energies in kcal mol^{-1} for homolytic and heterolytic cleavages are given below.

Table 1.8

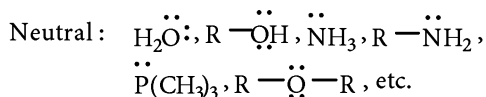
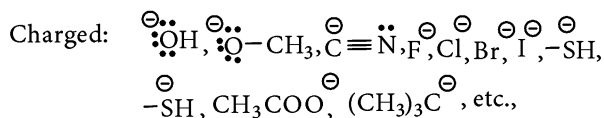
Bond type	Homolytic bond dissociation energy (in kcal mol^{-1})	Heterolytic bond dissociation energy (in kcal mol^{-1})
H-H	104	401
H-Cl	103	334
$\text{CH}_3\text{-H}$	104	313
$\text{CH}_3\text{-I}$	56	212

If we compare these two values (for homolytic and heterolytic cleavages) for the same type of bond, it can be observed that the heterolytic bond dissociation energy is considerably higher than the homolytic dissociation for the same bond. Heterolysis of a neutral molecule yields a positive and a negative ion. However, separation of these charges which are opposite requires a great amount of energy. In the gas phase, bond dissociation occurs by an easier route, namely homolysis. However in an ionizing solvent, heterolysis is the preferred kind of breakage.

Nucleophiles and Electrophiles

Nucleophiles are neutral or negatively charged species which can donate a pair of electrons to the substrate molecule. They attack electron deficient centres on the substrate molecule.

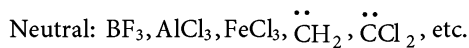
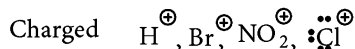
Examples of nucleophiles



Electrophiles are neutral or positively charged species which can accept a pair of electrons from the substrate

molecule. They attack electron rich centres on the substrate molecule.

Examples of electrophiles



Nucleophiles are Lewis bases (electron pair donors) and electrophiles are Lewis acids (electron pair acceptors).

REACTION INTERMEDIATES

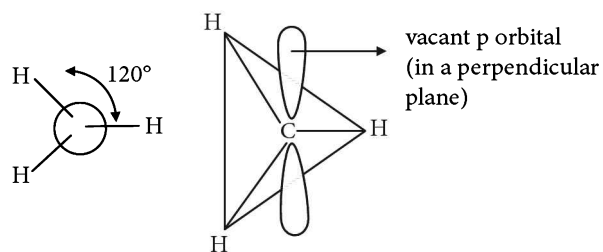
The reaction mechanism gives the exact route of a chemical reaction. The mechanism of a reaction is determined by considering all the possibilities that are consistent with the experimental observation. A great majority of the reactions proceed in several steps or multi steps which pass through intermediates whose lifetime is very short. A clear idea about the structure and properties of these intermediate structures is of great importance in arriving at the mechanism of a chemical reaction.

A few of these important intermediates and their chief characteristics are given in the following description.

Carbocations

A group of organic species having a positively charged carbon atom bearing only six electrons around the carbon are called carbocations. The simplest carbocation is methyl cation CH_3^+ .

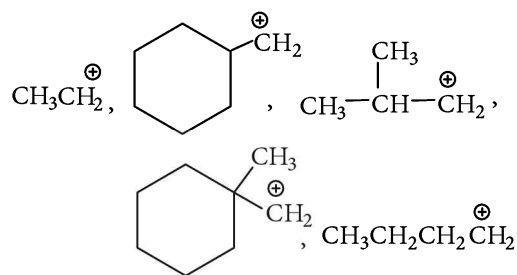
The central carbon atom of the carbocation is sp^2 hybridized. The three sp^2 orbitals are utilized in making three sigma bonds. Hence the carbocation possesses a planar configuration with a bond angle of 120° .



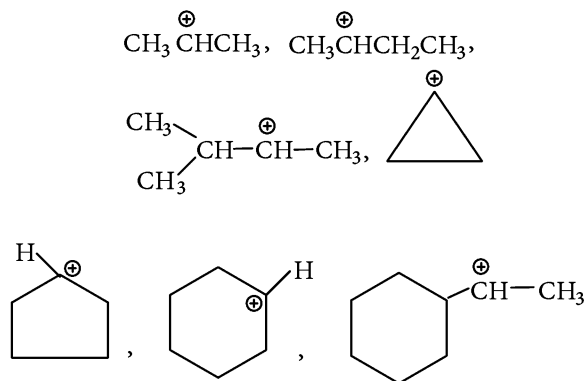
The empty p orbital is perpendicular to the plane. Since there are only six electrons around carbon and because of the strong tendency to attain an octet configuration, carbocations are highly reactive species.

Carbocations can be classified as primary (1°), secondary (2°) and tertiary (3°) carbocations based on the nature of the carbon on which the positive charge resides.

A few examples of 1° carbocations are

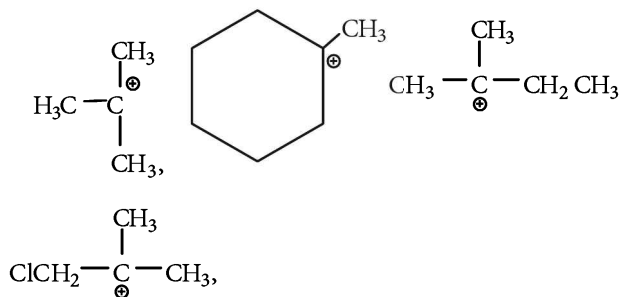


A few examples of 2° carbocations are



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A few examples of 3° carbocations are



Stability of carbocations

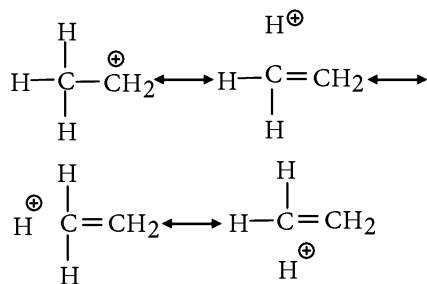
Several factors influence the stability of carbocations. They are

(i) Inductive effect

The electron releasing inductive effect (+I) exerted by an alkyl group attached to the carbon bearing the positive charge neutralizes a part of the positive charge. As a result the charge gets dispersed over the entire alkyl groups and the cation gets stabilized. Greater the number of alkyl groups or electron releasing groups attached to the carbocation centre, greater is the stability of the carbocation.

(ii) Hyperconjugation

Hyperconjugation has a stabilizing influence on the carbocation. An alkyl group attached to a carbocation centre can reduce the positive charge by hyperconjugation as shown in the case of an ethyl cation.

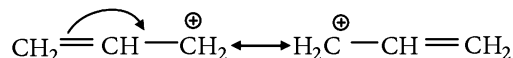


As the number of α -hydrogens or alkyl groups around the carbocation centre increases, the stability increases, as more structures can be proposed. For example there are three methyl groups around the carbocation in t-butyl cation and as such nine structures are possible and therefore a tertiary butyl cation (as shown) is more stable than a secondary or a primary carbocation.

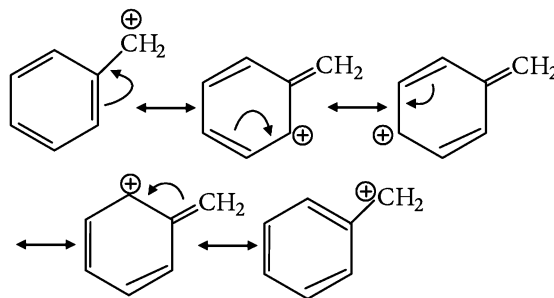
(iii) Resonance

Resonance plays a dominant role in the stability of carbocations. When the carbon bearing the positive charge is attached to a π system (a multiple bond), there is effective charge delocalization. Thus the positive charge gets stabilized by delocalization.

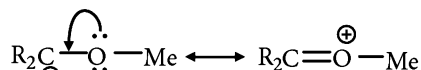
For example, in allyl cation, the positive charge is well stabilized by resonance, caused by an adjacent double bond.



The benzylic cation, though a primary cation, is well stabilized by resonance with the aromatic system.

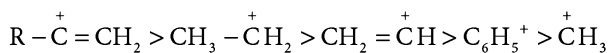
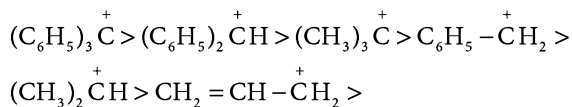


The presence of a hetero atom having an unshared pair (e.g., O, N or halogen) adjacent to the cationic centre also increases the stability of carbocations by resonance.



Stability order of carbocations

On the basis of the various factors discussed above, the stability order of some important carbocations is given below.

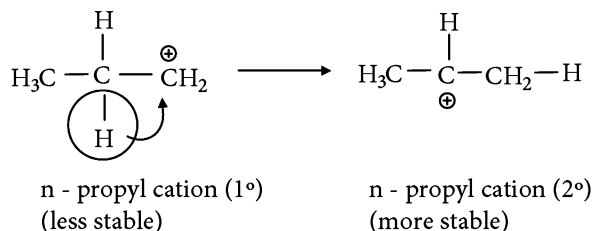


Rearrangement of carbocations

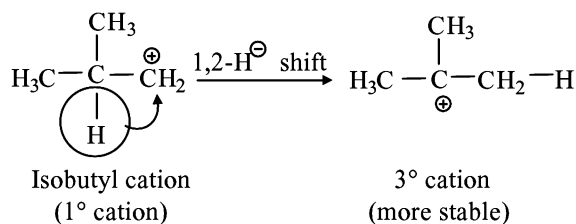
In the rearrangement of a carbocation, the electron deficient carbon gets a pair of electrons from a neighbouring carbon, preferably from a carbon centre which can accommodate a positive charge in a better way. In the rearrangement, a hydrogen atom or an alkyl group migrates with a pair of electrons from an adjacent carbon atom to the carbocation centre. The migration of hydrogen with a pair of

electrons is known as hydride shift. Similarly, when an alkyl group like $-\text{CH}_3$ group migrates, it is known as alkyl shift. In these rearrangements migrating group moves from one atom to the very next atom and hence this is known as 1, 2-shift.

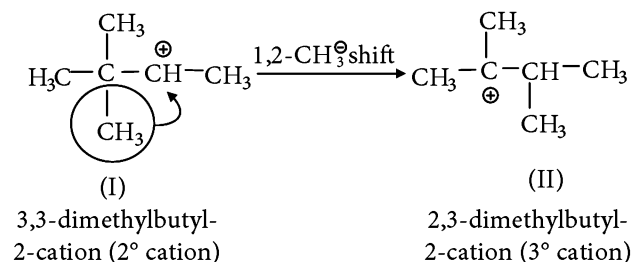
For example n-propyl cation rearranges to a more stable isopropyl cation by a 1,2 hydride shift.



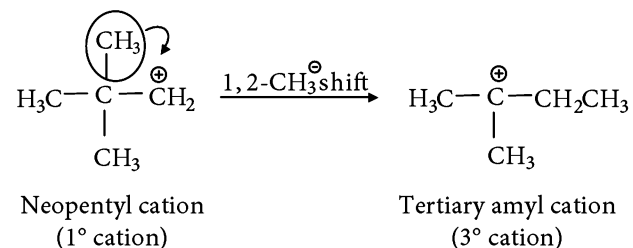
In the case of isobutyl cation, a 1,2-hydride shift occurs to give a more stable tertiary cation.



In the case of 3,3-dimethylbutyl-2-cation (I), a methyl shift is highly favourable and results in a tertiary cation (II).

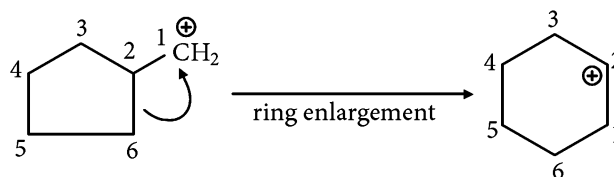


Neopentyl cation is a primary carbocation. This can undergo a 1,2-methyl migration to give a more stable 3° carbocation.



Rearrangement of carbocations in cyclic systems

A few cations in ring systems can undergo a rearrangement to give a ring enlarged structure or ring contracted structure which is energetically more favourable.



In this ring enlargement, C_2-C_6 bond in the five membered ring breaks and a new C_1-C_6 bond is formed in the newly formed six membered ring.

Reaction involving carbocations

(i) Acid catalyzed hydration of olefins

Olefins undergo electrophilic addition of H^+ to form carbocation, which then adds H_2O molecule to give alcohol.

(ii) Acid catalyzed dehydration of alcohols

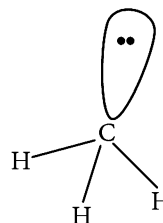
Alcohols form carbocation in presence of concentrated sulphuric acid which undergoes elimination to give alkenes.

(iii) Friedel Crafts alkylation

In Friedel Crafts alkylation, carbocations are the intermediates formed.

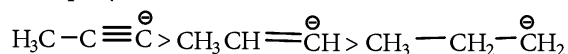
Carbanions

Carbanions are species containing a negatively charged carbon. The central carbon atom of a carbanion is sp^3 hybridized and it is surrounded by three bonding pair of electrons and one free pair of electrons not involved in any bonding. This unshared pair occupies one sp^3 orbital. Therefore, a carbanion has pyramidal shape.



Factors influencing the stability of carbanions

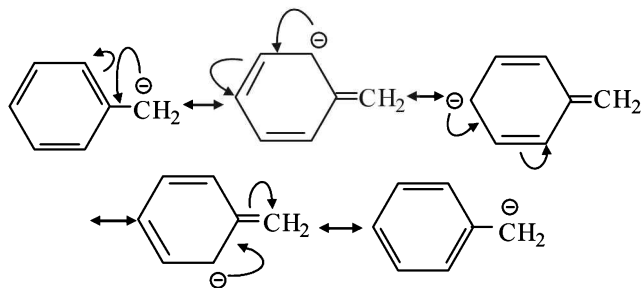
- (i) Carbanions with greater 's' character on the orbital (i.e., sp) attached to carbon bearing the negative charge are more stable comparable to those with sp^2 and sp^3 hybridized carbon at the carbanion site. Thus



- (ii) If groups with electron withdrawing inductive effect are attached to the carbon bearing the negative charge, the carbanion is stabilized by the greater dispersal of the negative charge. For example $CCl_3CH_2^\ominus$ is more stabilized than $CH_3CH_2^\ominus$ because of the presence of three chlorine atoms on the adjacent carbon. Groups having +I effect decrease the stability of carbanions.
- (iii) When there is a double bond or triple bond adjacent to the carbanion, then also the carbanion is stabilized. $H_2C=CH-CH_2^\ominus$ (allyl anion) is more stable than $H_3C-CH_2-CH_2^\ominus$ (n-propyl anion) because of resonance.

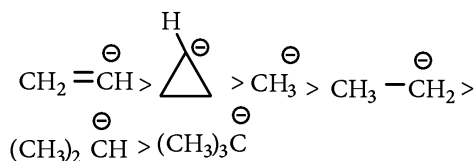
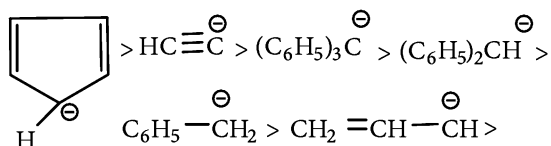


Benzylic carbanion is also well stabilized on account of resonance.



Order of stability of carbanions

The stability order of some carbanions is given below



Reactions involving carbanions

(i) Base catalyzed halogenation of ketones

The carbon adjacent to the carbonyl group becomes a carbanion under the influence of a base like OH^- . Then halogenation can occur.

(ii) Iodoform reaction

Compounds having CH_3CO- or $CH_3CH(OH)-$ groups give a yellow precipitate of iodoform when treated with iodine and alkali. This reaction involves a carbanion intermediate.

(iii) Aldol condensation

The carbanion generated from one molecule of aldehyde or ketone containing α -hydrogen, adds as a nucleophile to the carbonyl group of another aldehyde or ketone molecule.

Free Radicals

An atom or group of atoms which contain an unpaired electron is known as a free radical. Alkyl and aryl free radicals contain the odd electron on a carbon atom.

Alkyl free radicals are of three types: 1° , 2° and 3° free radicals. The decreasing order of stability of alkyl free radicals is $3^\circ > 2^\circ > 1^\circ$.

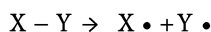
This order can be explained in terms of delocalization of the unpaired electron through hyperconjugation.

The carbon atom in simple alkyl radical is sp^2 hybridized and the unpaired electron lies in the unhybridized p-orbital.

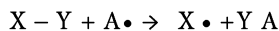
Formation of free radicals

Free radicals are formed by two routes.

- (i) Through the homolytic cleavage of bonds

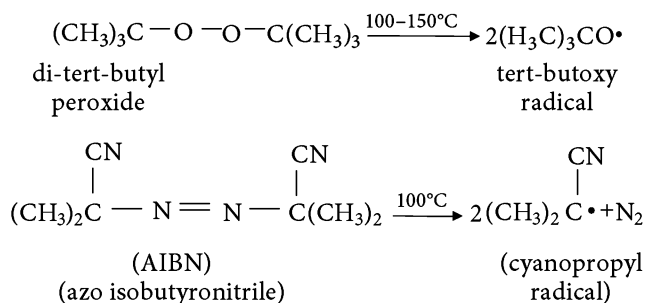


- (ii) By the reaction of neutral molecules with other free radicals.

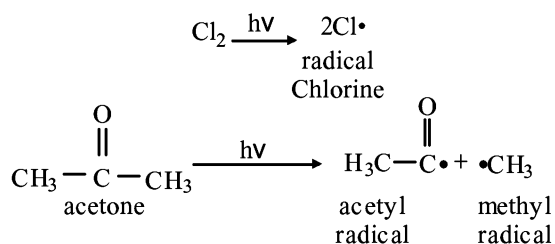


Free radicals are obtained by homolytic cleavage at high temperatures from peroxy and azo compounds whose bond energies are weak.

For example,

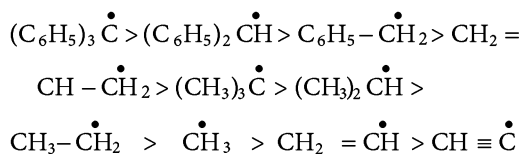


Free radicals can also be formed by photolysis under the influence of light energy.



Stability of free radicals

The order of stability of some free radicals is given below



Reactions involving free radicals

(i) Fragmentation

Free radicals undergo elimination reactions. A small neutral molecule is eliminated from a free radical to give another simpler free radical. These type of reactions are known as fragmentation reactions.

(ii) Substitution reactions of hydrocarbons

Substitution of a hydrogen in a hydrocarbon by a halogen in presence of light is one of the most important examples of a free radical reaction. These reactions proceed as a chain reaction.

(iii) Allylic bromination

Bromination in the allylic position of an alkene is a typical free radical reaction carried out under the influence of NBS (N – Bromosuccinimide).

(iv) Addition

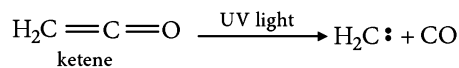
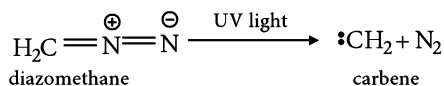
Anti Markownikoff addition of HBr to an olefin under the influence of peroxides occurs by a free radical mechanism. This is because only the HBr addition has favourable thermodynamics for both radical addition step and the hydrogen abstraction step that forms the product while propagating the chain reaction.

Carbenes

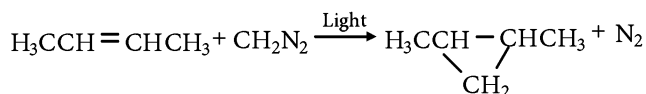
Carbenes are neutral intermediates having bivalent carbon in which the carbon atom is covalently bonded to two other atoms or groups and has two nonbonded electrons. When the two electrons are spin paired, the carbene is called a singlet carbene and if the spins of the electrons are parallel it is called a triplet carbene.

A singlet carbene possesses a bent structure with sp^2 hybridization in which the paired electrons occupy the vacant sp^2 orbital. A triplet carbene can be either bent sp^2 hybrid with an electron in each unoccupied orbital or a linear sp hybrid with an electron in each of the unoccupied p-orbitals. A triplet carbene is generally more stable than a singlet carbene.

Carbene or methylene is formed by the photolysis of either diazomethane (CH_2N_2) or ketene ($\text{CH}_2=\text{C}=\text{O}$).

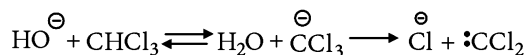


When carbenes are generated in the presence of alkenes, cyclopropane derivatives are obtained by carbene insertion across the double bond. These reactions are known as cycloadditions.



1.48 Basics of Organic Chemistry

Dichlorocarbene is formed by the action of alkali on chloroform.



Carbene is an electron deficient intermediate, having only six electrons around carbon.

Reactions involving carbenes

(i) Reimer-Tiemann reaction

Reimer-Tiemann reaction involves the electrophilic substitution of an activated phenoxide ring by: CCl_2

(ii) Carbylamine reaction

Carbylamine reaction of primary amine with chloroform and strong alkali results in the formation of :CCl_2 as intermediate.

(iii) Cycloaddition

Cycloaddition involves insertion of methylene group (or substituted methylene) across a carbon-carbon double bond to form cyclopropanes

HYDROGEN BONDING

Hydrogen bond may be defined as the weak electrostatic force of attraction which exists between a hydrogen atom bonded to F, O or N and an electronegative atom of the same or neighbouring molecule.

Effect of H – bonding on boiling point

Generally boiling point of an organic compound increases with increase in molecular weight. Compounds with same molecular weight are expected to have same or close boiling points. In associated liquids like alcohols and carboxylic acids greater energy is needed to break the H – bonds (intermolecular) which keeps the molecules together. So they have abnormally high boiling points.

For example,

Consider two isomers, n-butanol and diethyl ether.

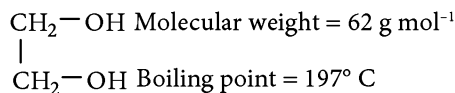
Table 1.9

Compound	1-butanol	diethyl ether
Formula	$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{OH}$	$\text{CH}_3 - \text{CH}_2 - \text{O} - \text{CH}_2 - \text{CH}_3$
Molecular weight	74	74
Boiling point	118°C	35°C

Although butanol and diethyl ether have same molecular weights, butanol has a higher boiling point due to hydrogen bonding.

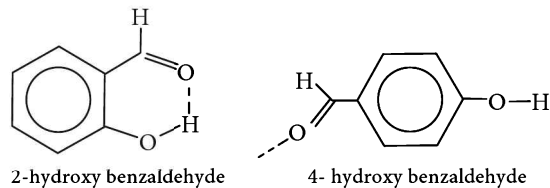
Polyhydroxy alcohols show very high boiling points due to availability of more than one site per molecule for H-bonding.

E.g., Ethylene glycol (or) ethane-1,2-diol



Between 4-hydroxybenzaldehyde and 2-hydroxybenzaldehyde, 4-hydroxybenzaldehyde has a higher boiling point due to intermolecular hydrogen bonding.

In 2-hydroxybenzaldehyde, intramolecular hydrogen bonds are present but in 4-hydroxybenzaldehyde intermolecular hydrogen bonding is present, which requires more energy to separate the molecules.

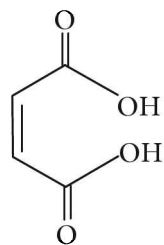


Solubility

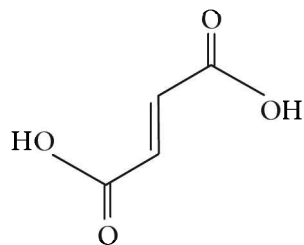
When a substance is dissolved in a solvent, energy must be supplied to separate the molecules by overcoming the intermolecular force of attraction. This energy is obtained by the formation of bonds between solute particles and the solvent molecules.

Lower alcohols like methanol, ethanol, polyhydric alcohols like glycol, glycerol, lower carboxylic acids like acetic acid, propionic acid, dicarboxylic acids like oxalic acid and sugars like glucose are soluble in water, due to their ability to form H – bonds with water molecule.

Effect of hydrogen bonding on acid strength



Maleic acid

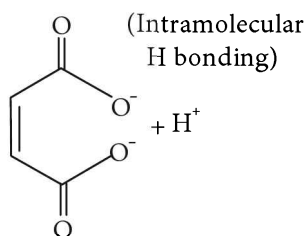
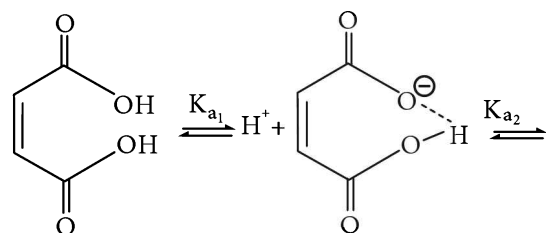


Fumaric acid

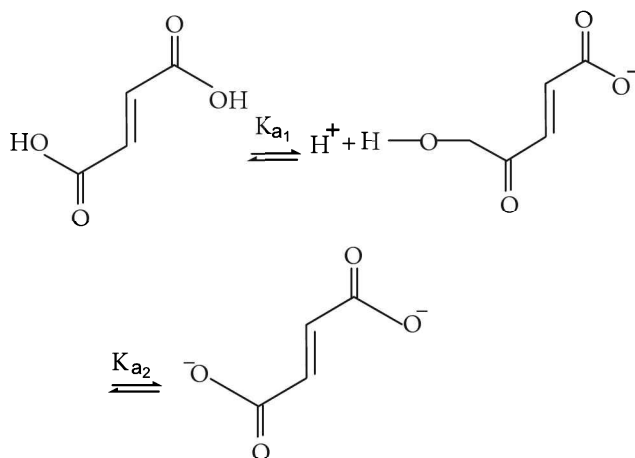
Acids	pK_{a_1}	pK_{a_2}
Maleic acid	1.92	6.23
Fumaric acid	3.02	4.38

Maleic acid is stronger acid than fumaric acid for the first ionization because of the stabilization of the resulting anion by intramolecular hydrogen bonding.

Maleic acid



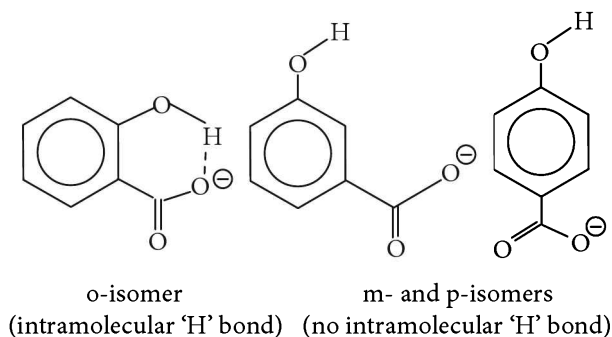
Fumaric acid



Since the maleate anion is stabilised by intramolecular hydrogen bonding, further ionization is very difficult, whereas the fumarate anion is not stabilized by hydrogen bonding and hence readily ionizes to the dianion.

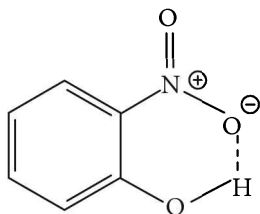
Similarly, ortho hydroxy benzoic acid is a stronger acid than meta and para hydroxy benzoic acid.

o-Hydroxybenzoic acid is a stronger acid because the corresponding (resulting) anion is stabilized by intramolecular hydrogen bonding resulting in a six membered ring (chelation).



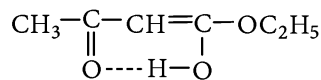
Intermolecular vs intramolecular hydrogen bonding and physical properties

When we compare the properties of ortho and para nitrophenol, one can observe that o-nitrophenol is poorly soluble in water and is volatile in steam. On the other hand p-nitrophenol is slightly more water soluble and non-volatile in steam. These differences can be accounted for by inter and intramolecular hydrogen bonding in these compounds.

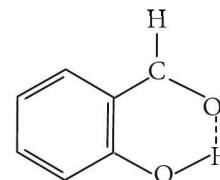
Intramolecular hydrogen bonding in o-nitrophenol

The -NO_2 and -OH groups are located in adjacent positions in o-nitrophenol, which is favourable for the formation of an intramolecular H – bonding. o-Nitrophenol does not have the low volatility of an associated liquid and it does not have the solubility characteristic of a compound that forms hydrogen bonds with water.

Ethylacetoacetate, salicylaldehyde, o-nitrophenol, salicylic acid and acetylacetone are few examples of compounds where intramolecular hydrogen bonding is observed.



Ethyl acetoacetate (enol form)



(salicylaldehyde)

This type of hydrogen bonding prevents the association of such molecules. Low boiling points of salicylaldehyde and o-nitrophenol are explained due to intramolecular hydrogen bonding.

SUMMARY

Nomenclature of organic compounds.	Organic compounds are named by trivial and IUPAC system of nomenclature.
Electron displacement effects	The common electron displacement effects are inductive effect, electromeric effect, resonance effect and hyperconjugative effect.
Inductive effect	Definition Applications in explaining the acidity of substituted carboxylic acids, basic nature of amines, relative stability of carbocations and electrophilic aromatic substitution.
Electromeric effect	Definition and illustration
Resonance	Definition and examples, Resonance energy, Rules of resonance, Resonance or mesomeric effect, Steric inhibition of resonance.
Hyperconjugation	Hyperconjugation in alkenes, carbocations and free radicals, Application of hyperconjugation in explaining relative stability of carbocations, free radicals and alkenes.
Structural isomerism	Definition and examples for chain isomerism, ring-chain isomerism, position isomerism, functional isomerism and metamerism.
Tautomerism	Definition Examples for keto-enol tautomerism, Relative stability of keto and enol forms, other examples of tautomerism.
Projection formulae	Fischer projection formula, Newmann projection formula, Sawhorse projection formula, Wedge and dash formula.
Geometrical isomerism	Geometrical isomerism in alkenes, conditions for geometrical isomerism, E and Z notation of geometrical isomers, Geometrical isomerism in cyclic systems and oximes. Difference in physical properties of geometrical isomers.

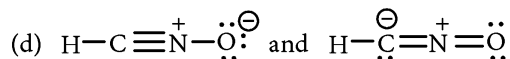
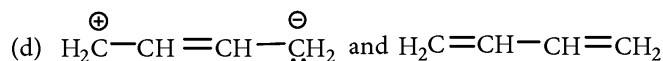
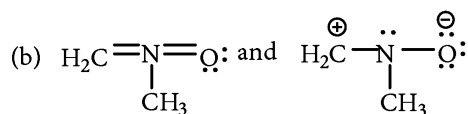
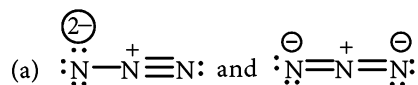
Optical isomerism	Specific rotation, Cause of optical rotation –chirality. Elements of symmetry and chirality, examples of compounds showing optical isomerism. Explanation of enantiomers, racemic mixture and racemisation. Designation of configuration-D, L-system and R, S-system, CIP rules in assigning R and S configuration, optical isomerism of compounds containing more than one chiral centre. Explanation of diastereomers and meso forms.
Conformational isomerism	Definition Conformations of ethane and n-butane and their relative stabilities
Homolytic and heterolytic bond cleavage	Definition Homolytic bond cleavage produces free radicals while heterolytic bond cleavage produces oppositely charged ions.
Nucleophiles and electrophiles	Definition Examples of nucleophiles and electrophiles
Reaction intermediates	Unstable intermediates formed during chemical reactions, e.g., carbocations, carbanions, carbenes etc.
Carbocations	Examples, structure, Relative stability of carbocations, Rearrangement of carbocations, Reactions involving carbocations.
Carbanions	Definition, examples Factors affecting stability, Order of stability of carbanions, Reactions involving carbanions.
Free radicals	Formation of free radicals, stability of free radicals, Reactions involving free radicals.
Carbenes	Definition Explanation of singlet and triplet carbenes, Reactions involving carbenes
Hydrogen bonding	Definition Effect of hydrogen bonding on boiling point, solubility and acid strength, Intramolecular and intermolecular hydrogen bonding.

TOPIC GRIP

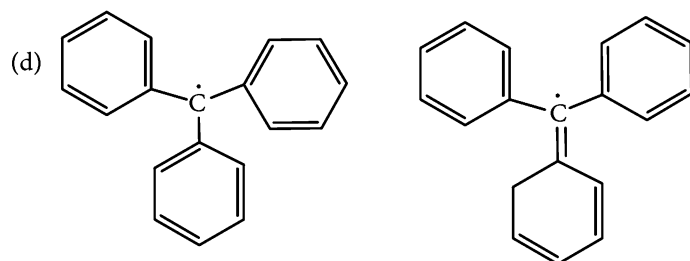
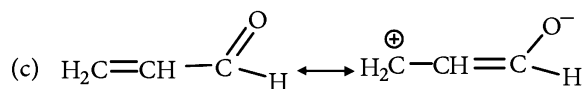
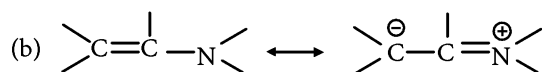
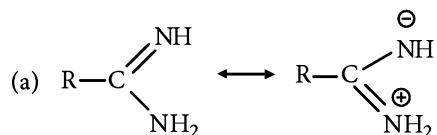


Subjective Questions

1. Give the IUPAC name for $\text{CH}_3 - \text{CH} = \text{CH} - \text{C} \equiv \text{C} - \text{CH}_2 - \text{CH}_3$
2. Four pairs of structures are given below. How many of these pairs are resonance pairs?



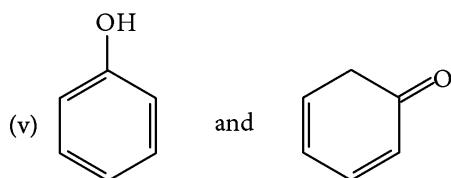
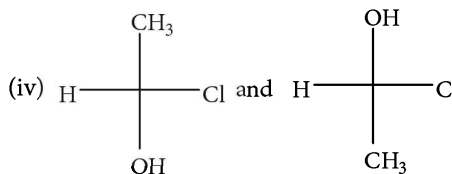
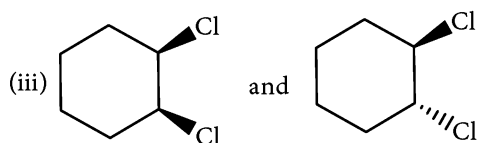
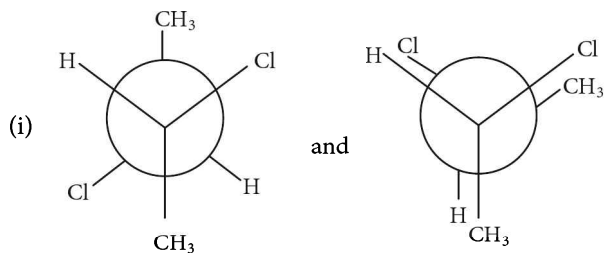
3. Draw curved arrows to convert the first structure in each set to the other.



4. Account for the fact that carboxylic acids are more acidic compared to an alcohol.
5. Account for the indicated order of base strength among the compounds shown. $\text{CH}_3\text{NH}_2 > \text{NH}_3 > \text{NF}_3$
6. Write the enol forms and identify the more stable form in each of the following compounds.
 - (i) 1-phenyl-2-butanone
 - (ii) methyl isopropyl ketone

7. Carbon – oxygen bond lengths in formic acid are $1.23 \text{ \AA}$ and $1.36 \text{ \AA}$ respectively. $\text{H}-\text{C} \begin{matrix} \nearrow \text{O} \\ \searrow \text{O}-\text{H} \end{matrix}$ However, both the carbon –oxygen bonds have the same value in the formate ion $\text{H}-\text{C} \begin{matrix} \nearrow \text{O} \\ \searrow \text{O}^- \end{matrix}$. Rationalize.

8. How are the following compounds related?

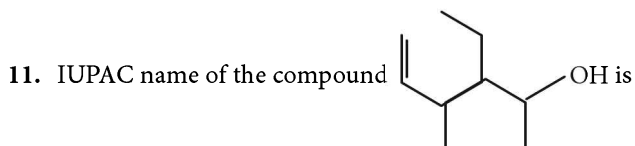


9. Account for the fact that CHCl_3 is more acidic than CHF_3 .
10. Optically active 2-iodobutane on treatment with NaI , loses its optical activity. Explain why.



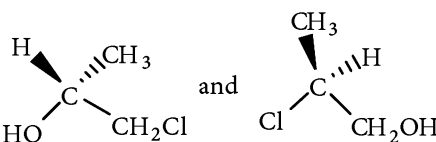
Straight Objective Type Questions

Directions: This section contains multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.



- (a) 4-Ethyl-3-methyl hex-1-en-2-ol
 (b) 3-Ethyl-4-methyl hex-5-en-2-ol
 (c) 3-Methyl-4-ethyl hex-1-en-2-ol
 (d) 3-Ethyl-4-methyl-2-hydroxy hex-5-ene.

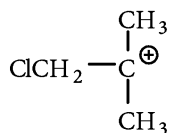
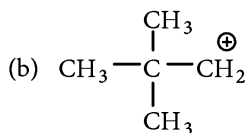
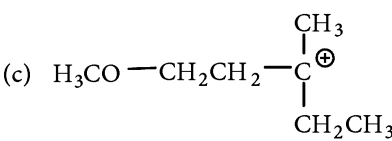
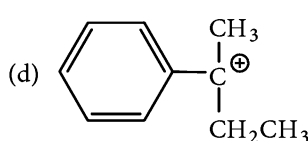
1.54 Basics of Organic Chemistry

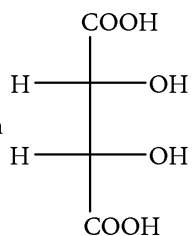
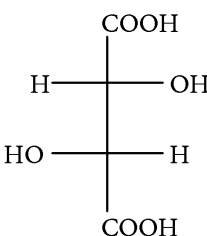
12.  are
- diastereomers
 - constitutional isomers
 - enantiomers
 - two different representations of the same compound

13. Phenol is more acidic than ethyl alcohol because

- phenol is soluble in NaOH
- the phenoxide ion is resonance stabilized
- ethyl alcohol is not soluble in NaOH
- the conjugate base of phenol is strong

14. The most stable carbocation among the following is

- 
- 
- 
- 

15. The relationship between  and  are
- they are enantiomers
 - they are anomers
 - they are meso compounds
 - they are diastereomers



Assertion–Reason Type Questions

Directions: Each question contains Statement-1 and Statement-2 and has the following choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

- Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1
- Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
- Statement-1 is True, Statement-2 is False
- Statement-1 is False, Statement-2 is True

16. Statement 1

If a triple bond is present, along with a double bond and another functional group, the order of priority will be Functional group > double bond > triple bond.

and

Statement 2

$$\begin{array}{c} \text{NO}_2 \\ | \\ \text{ClCH}_2-\text{CH}-\text{CH}_2-\text{CHO} \end{array}$$

The compound $\text{ClCH}_2-\text{CH}-\text{CH}_2-\text{CHO}$ is named as 4-chloro-3-nitrobutanal.

17. Statement 1

Between CCl_3-COOH and oxalic acid, the former is a stronger acid.

and

Statement 2

Electron withdrawing groups decrease the acid strength and increase the base strength.

18. Statement 1

All the carbon atoms are sp^2 hybridized in allene $\text{H}_2\text{C}=\text{C}=\text{CH}_2$.

and

Statement 2

The two H atoms on the first carbon and two hydrogen atoms on the third carbon lie in perpendicular planes in allene.

19. Statement 1

The energy of the resonance hybrid is always lower than that of any of the contributing resonance structures.

and

Statement 2

Greater the number of contributing structures with similar energies greater is the stabilization and lower is the energy of the hybrid.

20. Statement 1

A carbocation can rearrange to form a more stable carbocation or will combine with a nucleophile to form a stable compound or can eliminate a proton to form an olefin.

and

Statement 2

The order of stabilities of carbocation and free radicals is the same.



Linked Comprehension Type Questions

Directions: This section contains 2 paragraphs. Based upon the paragraph, 3 multiple choice questions have to be answered. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

Passage I

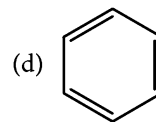
Conformational isomers are structures obtained by rotation around single bonds. Conformational isomers are easily inter-convertible as the energy differences are very small between the various structures.

21. The conformation of cyclohexane which is most stable is

- (a) boat (b) twist boat (c) chair (d) planar

22. The compound which can have conformations among the following is

- (a) CH_3Cl (b) $\text{CH}_2=\text{CH}_2$ (c) $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$

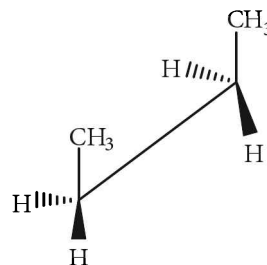


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23. Consider the structure of n-butane given below

Which of the following statements is correct?

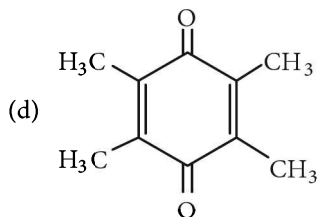
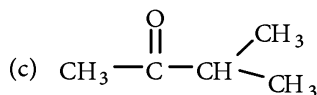
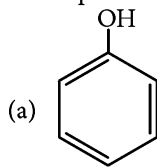
- The structure given above is the Gauche conformation.
- The dihedral angle between the two methyl groups is zero.
- A staggered conformation has a higher energy compared to an eclipsed form.
- The energy difference between the various conformers is so great that the various forms can be isolated easily.



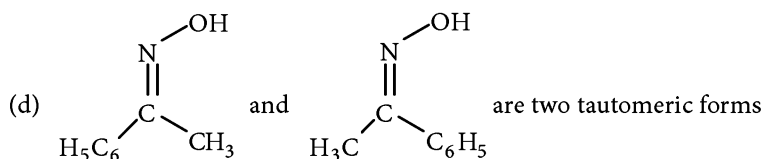
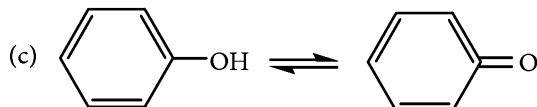
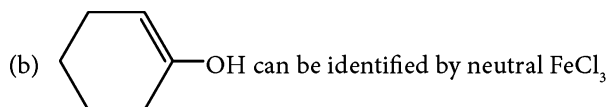
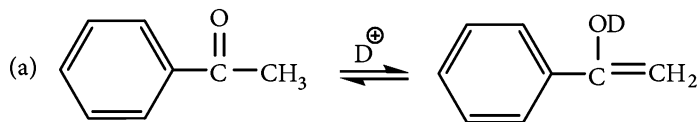
Passage II

Tautomerism is a kind of isomerism where the two isomers are inter convertible by a 1, 3 shift of a proton. The isomers exist as an equilibrium mixture of two forms viz., keto and enol. Generally either a keto or an enol form predominates.

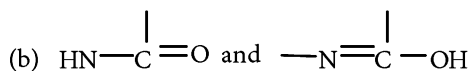
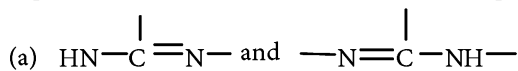
24. A compound that cannot exhibit tautomerism is

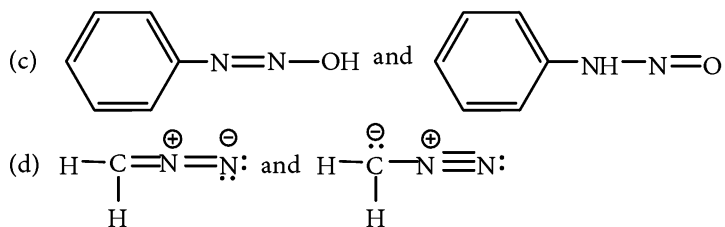


25. Identify the statement/equation which is not correct among the following.



26. A pair of structures which are not tautomeric pairs among the following is





Multiple Correct Objective Type Questions

Directions: Each question in this section has four suggested answers of which ONE OR MORE answers will be correct.

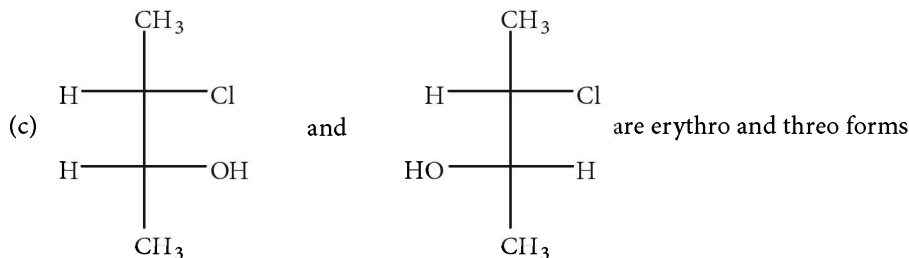
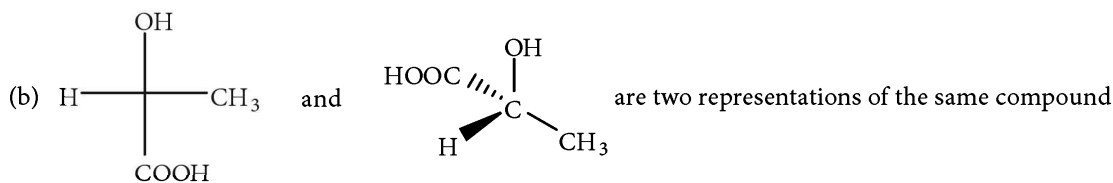
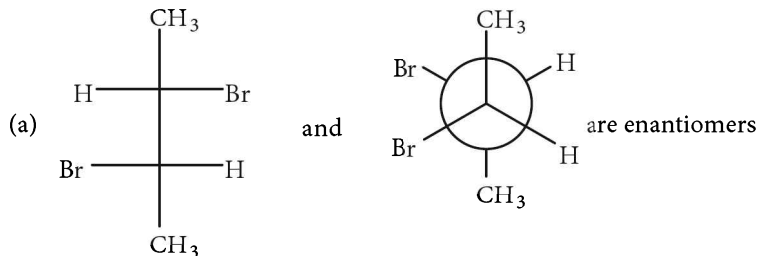
27. The compounds which have only primary and tertiary carbon are

- (a) 2-methylbutane
- (b) 2,3-dimethylbutane
- (c) 2-chloro-2-methylpropane
- (d) 2,2-dimethylpropane

28. Which of the following are correct statements?

- (a) BF_3 and are: CCl_2 electrophiles.
- (b) Dimethylsulphoxide and dimethyl formamide (DMF) are aprotic solvents.
- (c) In butadiene $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$ all the three C-C bond lengths are equal.
- (d) $\text{CH}_2=\text{CH}-\text{Cl}$ has low reactivity because chlorine is attached to an sp^2 carbon.

29. Identify the pair or pairs which are correctly represented.



**Matrix-Match Type Question**

Directions: Match the elements of Column I to elements of Column II. There can be single or multiple matches.

30.

Column I

- (a) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2^+$
- (b) Buta-1,3-diene
- (c) $\text{CH}_3 - \dot{\text{C}}\text{H}_2$
- (d) Benzene

Column II

- (p) Conjugation
- (q) Hyperconjugation
- (r) sp^2 hybridized carbon
- (s) Rearrangement

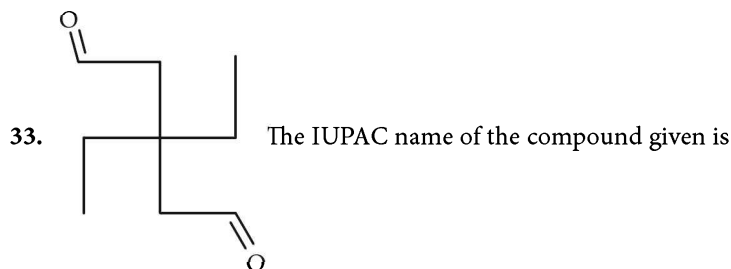
IIT ASSIGNMENT EXERCISE



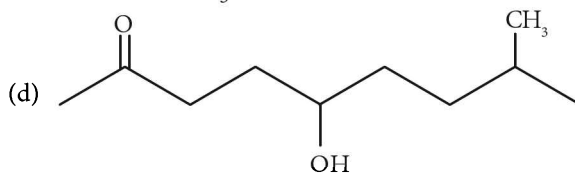
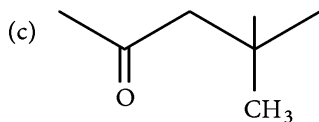
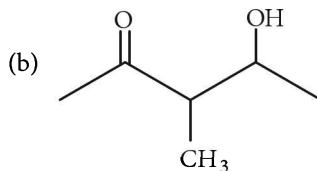
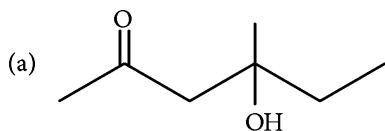
Straight Objective Type Questions

Directions: This section contains multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

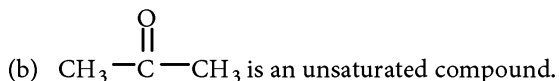
31. The IUPAC name of $\text{CH}_3 - \text{CO} - \text{CHCl} - \text{CH}_2 - \text{COOH}$ is
- 3-Chloro-4-oxopentanoic acid
 - 4-Oxo-3-Chloropentanoic acid
 - 2-Oxo-3-Chloropentanoic acid
 - 1-Carboxy-3-Chloro-4-ketobutane
32. $\text{ClCH}_2 - \text{CHCl} - \text{CH} = \text{CH}_2$ is known by IUPAC nomenclature as
- 1,2-dichloro but-3-ene
 - 3,4-dichloro but-2-ene
 - 3,4-dichloro but-1-ene
 - 1,2-dichloro butene-3



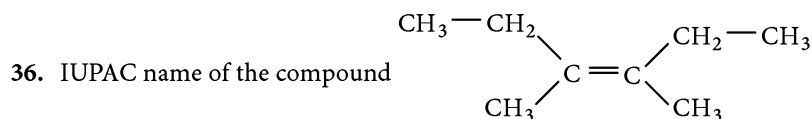
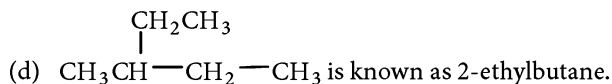
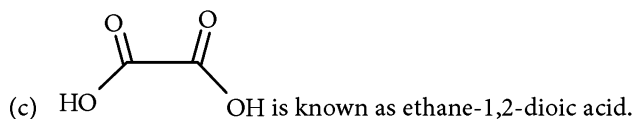
- 2,2-diethyl propane-1,3-dialdehyde
 - 3,3-diethyl pentane-1,5-dial
 - 2,2-diethyl propane-1,3-dial
 - 3,3-dimethyl keto pentane
34. The correct bondline structure of 4-hydroxy-4-methyl pentan-2-one is



35. Identify the correct statement among the following
- The minimum number of Carbon atoms in a branched alkane is three.



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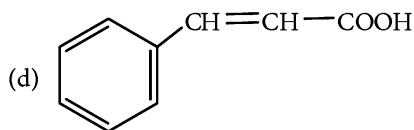
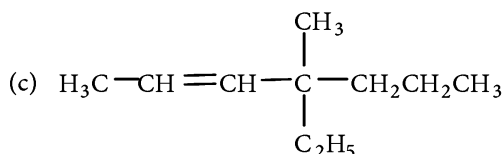
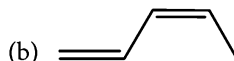
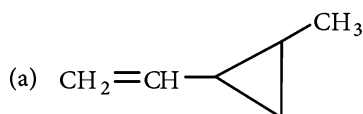
(a) Trans-3,4-dimethylhex-3-ene

(b) Cis-3,4-dimethylhex-3-ene

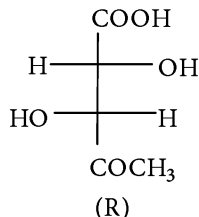
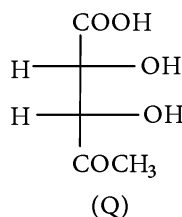
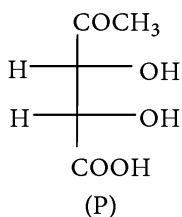
(c) Cis-3,4-dimethylhex-4-ene

(d) Cis-2,3-diethylbut-2-ene

37. A compound which exhibits both geometric and optical isomerism among the following is



38. The correct statement about P, Q and R is



(a) P and Q are enantiomers.

(b) P and Q are diastereomers.

(c) P and R are enantiomers

(d) P and Q are identical.

39. The number of enantiomeric pairs that are possible on monochlorination of isopentane is

(a) 0

(b) 4

(c) 3

(d) 2

40. The wrong statement about resonance is

(a) resonance structures with the greatest number of covalent bonds are most stable.

(b) structures with like formal charges on adjacent atoms have very high energies.

(c) the energy of the resonance hybrid is always higher than the calculated energy of the contributing structure.

(d) resonance with the least number of formal charges are most stable.

41. When (–) 3-Methyl pent–1-ene undergoes catalytic hydrogenation,

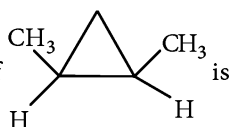
(a) the product obtained has (+) rotation

(b) the product is obtained with retention of configuration

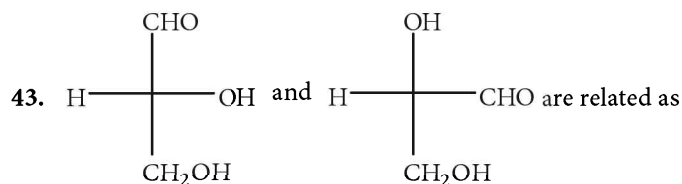
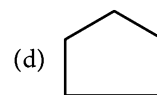
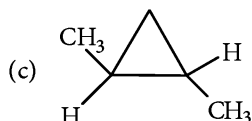
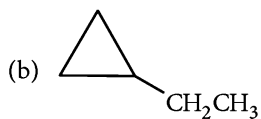
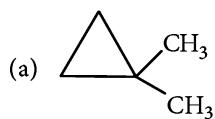
(c) an optically inactive product is obtained

(d) a racemic mixture is obtained

42. A compound which is not a constitutional isomer of



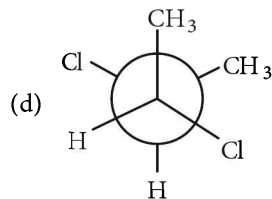
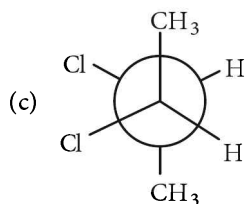
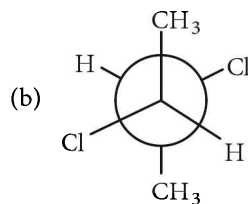
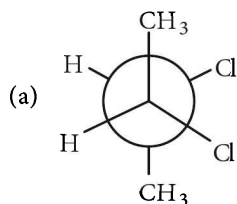
is



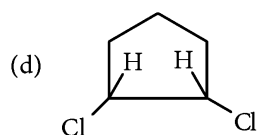
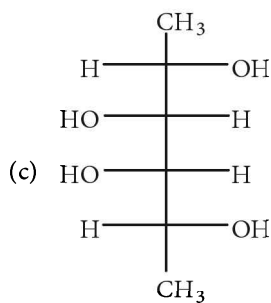
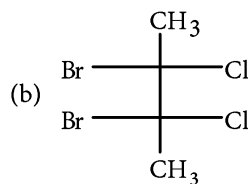
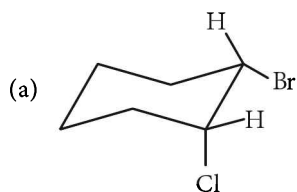
- (a) two representations of the same isomer
(c) constitutional isomers

- (b) enantiomers
(d) epimers

44. The meso form of 2,3 dichloro butane is

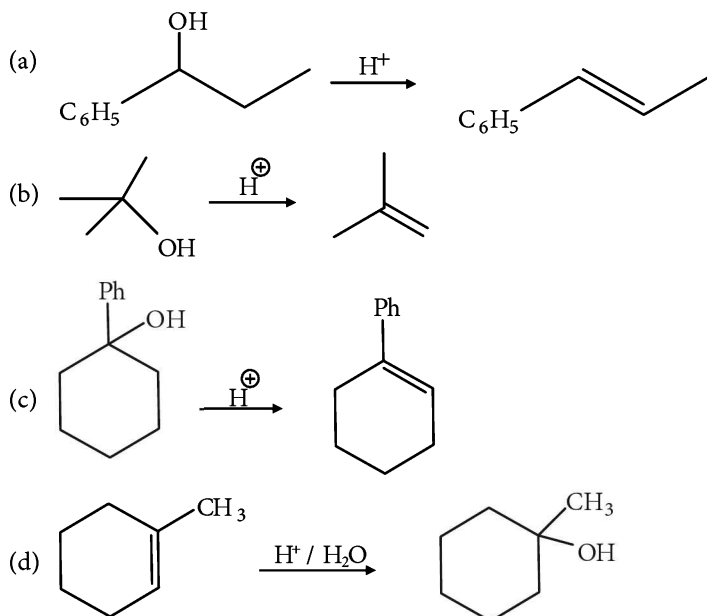


45. A compound among the following which shows optical activity is



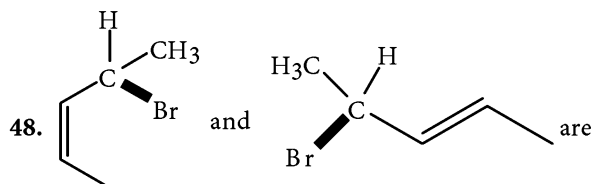
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46. A example of a stereo selective reaction is



47. The correct increasing order of electron donating effect of $(\text{CH}_3)_3\text{C}-$, $(\text{CH}_3)_2\text{CH}-$ and CH_3-CH_2- groups when attached to benzene or unsaturated system is

- (a) $\text{CH}_3-\text{CH}_2- < (\text{CH}_3)_2\text{CH}- < (\text{CH}_3)_3\text{C}-$ (b) $(\text{CH}_3)_3\text{C}- < (\text{CH}_3)_2\text{CH}- < \text{CH}_3-\text{CH}_2-$
 (c) $(\text{CH}_3)_2\text{CH}- < (\text{CH}_3)_3\text{C}- < \text{CH}_3-\text{CH}_2-$ (d) $(\text{CH}_3)_2\text{CH}- < \text{CH}_3-\text{CH}_2- < (\text{CH}_3)_3\text{C}-$



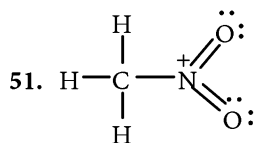
- (a) Structural isomers (b) enantiomers
 (c) diastereomers (d) representation of the same isomer

49. The correct order of stability of conformations of butane is

- (a) anti < gauche < eclipsed (b) eclipsed < anti < gauche
 (c) eclipsed < gauche < anti (d) gauche < anti < eclipsed

50. The specific rotation of a pure optically active compound is $+12^\circ$. The specific rotation of the sample in a reaction with 20% racemization and 80% retention of configuration will be

- (a) $+12^\circ$ (b) -12° (c) $+9.6^\circ$ (d) -2.4°



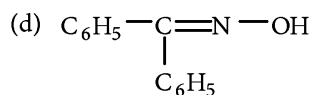
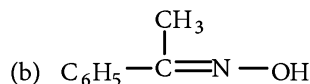
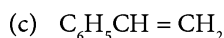
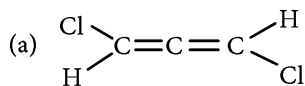
The above structure cannot be a valid resonance structure for nitro methane because

- (a) nitromethane does not show resonance (b) it is a charged structure
 (c) there are ten electrons around nitrogen (d) Oxygen should have a + charge

52. A meso compound

- (a) is an achiral molecule, which contain chiral carbons.
- (b) contains a plane of symmetry or a centre of symmetry.
- (c) is optically inactive due to internal compensation.
- (d) is characterized by all the above.

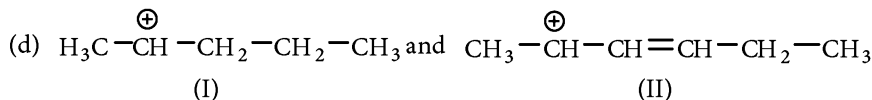
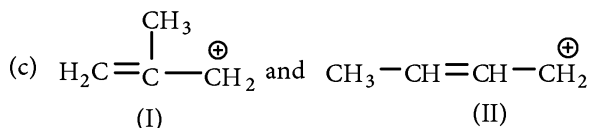
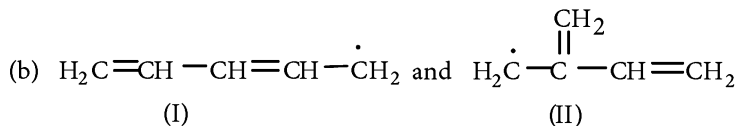
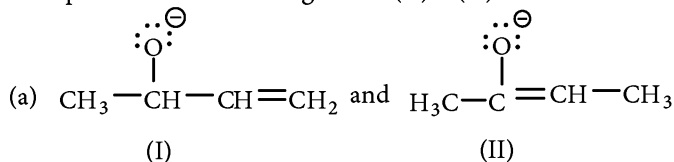
53. Geometrical isomerism is exhibited by



54. Between $\text{CH}_3\text{O}^+\text{CH}_2\text{CH}_2^+$ (I) and $\text{CH}_3\text{CH}_2\text{O}^+\text{CH}_2^+$ (II)

- (a) I is more stable because it is 1° carbocation.
- (b) II is more stable because it is 1° carbocation.
- (c) II is more stable because the cation is stabilized by the lone pair on oxygen.
- (d) Both are equally stable since both the cations are 1° and stabilized by oxygen.

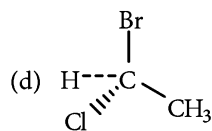
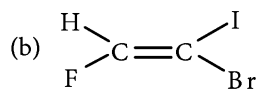
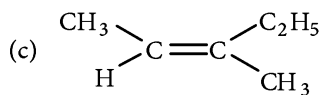
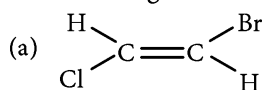
55. Four pairs of structures are given in (A) – (D)



The more stable I or II in each pair will be

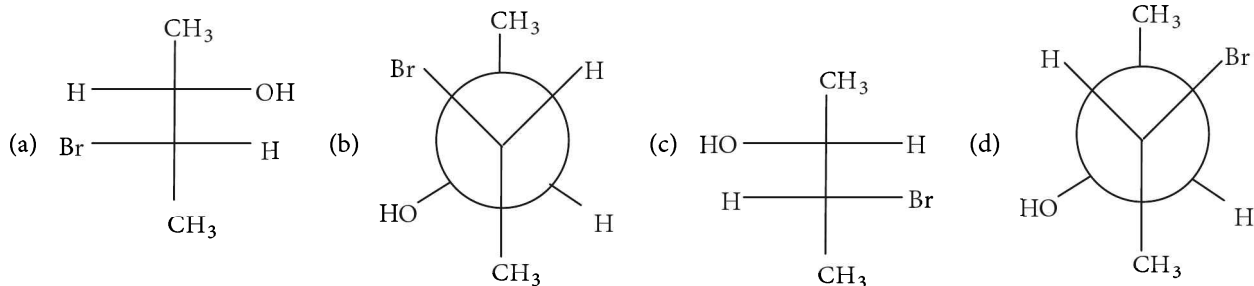
(a) A (I)	B (I)	C (II)	D (II)	(b) A (II)	B (II)	C (I)	D (I)
(c) A (I)	B (II)	C (I)	D (II)	(d) A (II)	B (I)	C (II)	D (II)

56. Which among the following is an 'Z' isomer?



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57. The erythro form of 3-bromo-2-butanol is



58. The incorrect resonance structure of diazomethane is



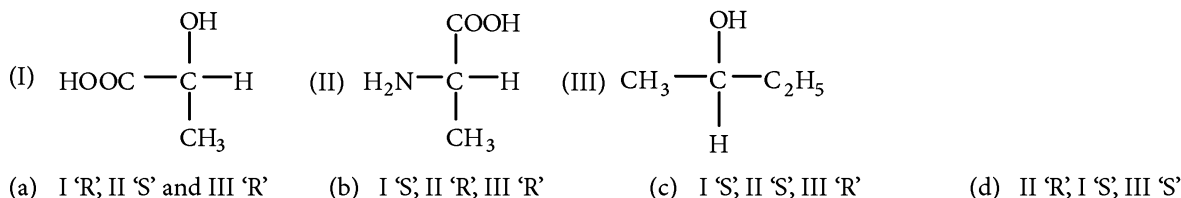
59. A description that does not fit in with the application of resonance among the following is

- Resonance is used to explain the stability of phenoxide ion.
- Resonance is used to explain the poor reactivity of halogen in chlorobenzene.
- Resonance is used to explain the deactivating influence of bromine in bromo benzene.
- Resonance is used explain the neutral behaviour of benzamide.

60. Identify a statement which is not correct among the following

- C_6H_5 group in $\text{C}_6\text{H}_5\text{MgCl}$ acts as an electrophile.
- The two nonbonded electrons of a singlet carbene occupy the same orbital.
- The stability of the alkyl carbocation is influenced by resonance.
- Free radicals are formed in a homolytic bond fission.

61. Assign 'R' and 'S' configuration for the marked I, II and III.



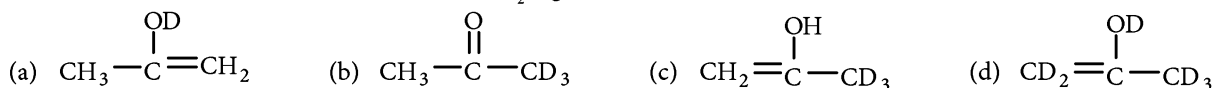
62. In benzene all the C-C bonds are of equal length because of

- resonance
- aromaticity
- hyperconjugation
- tautomerism

63. Which of the following compounds will have a meso isomer also?

- 2-Bromo -3-chlorobutane
- 2, 3-Dichloropentane
- 2-Hydroxy butanoic acid
- 2, 3-Dibromobutane

64. The enol form of acetone after treatment with D_2O gives

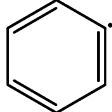
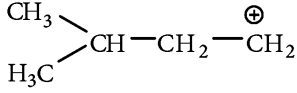


65. The correct decreasing order of nucleophilicity of the following ions for $\text{S}_{\text{N}}2$ reactions in protic solvents is

- $\text{PhS}^- > \text{PhO}^- > \text{OH}^- > \text{C}_2\text{H}_5\text{O}^- > \text{CN}^-$
- $\text{PhS}^- > \text{CN}^- > \text{C}_2\text{H}_5\text{O}^- > \text{OH}^- > \text{PhO}^-$
- $\text{CN}^- > \text{OH}^- > \text{C}_2\text{H}_5\text{O}^- > \text{PhS}^- > \text{PhO}^-$
- $\text{C}_2\text{H}_5\text{O}^- > \text{CN}^- > \text{OH}^- > \text{PhO}^- > \text{PhS}^-$

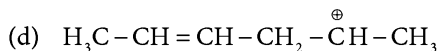
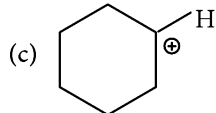
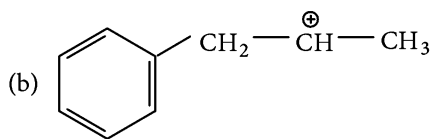
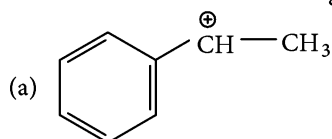
66. The specific arrangement of atoms that characterize a particular stereoisomer is known as

- tautomer
- conformation
- configuration
- geometry

67. A bond that undergoes heterolytic cleavage most readily is
 (a) C – C (b) O – H (c) C – O (d) C – H
68. The hyperconjugative effect of the group R in the compound $R-CH=CH_2$ follows the order.
 (a) $(CH_3)_3C- > CH_3- > CH_3CH_2-$ (b) $CH_3- > CH_3CH_2- > (CH_3)_2CH-$
 (c) $(CH_3)_3C- > CH_3-CH_2- > CH_3-$ (d) $(CH_3)_3C- > CH_3-CH_2- > CH_3-$
69. The isomeric cis-2-butene and trans 2-butene differ in
 (a) the products obtained by addition of HBr (b) their reduction products on hydrogenation
 (c) their products on ozonolysis (d) the products they give on bromine addition
70. Zero inductive effect is shown by
 (a) $-CH_3$ (b) $-H$ (c) $-D$ (d) $-C_6H_5$
71. The least stable carbocation among the following is
 (a) $CH_3-\overset{+}{CH}_2$ (b) $F_3C-\overset{+}{CH}_2$ (c) $F_3\overset{+}{C}$ (d) $CH_3-CH=\overset{+}{CH}$
72. The most stable free radical among the following is
 (a) $H_2C=CH-\overset{\cdot}{C}\begin{matrix} \nearrow CH_3 \\ \searrow CH_3 \end{matrix}$ (b) 
 (c) $(CH_3)_3C\cdot$ (d) $CH_2=CH-CH_2-\dot{C}H_2$
73. The most stable among the isomeric carbocations among $C_5H_{11}^+$ is
 (a) $(CH_3)_2\overset{+}{C}CH_2CH_3$ (b) $(CH_3)C\overset{+}{C}H_2$
 (c) $CH_3\overset{\oplus}{C}H-CH_2CH_2CH_3$ (d) 
74. When $CH_3-\overset{\overset{H}{|}}{\underset{\underset{C_6H_5}{|}}{C}}-\overset{\oplus}{CH}-CH_3$ undergoes rearrangement, the major rearranged ion formed is likely to be
 (a) $CH_3-\overset{\overset{C_6H_5}{|}}{\underset{\underset{\oplus}{|}}{C}}-CH_2-CH_3$ (b) $CH_3-\overset{\overset{H}{|}}{\underset{\underset{\oplus}{|}}{C}}-\overset{\overset{C_6H_5}{|}}{CH}-CH_3$
 (c) $C_6H_5-\overset{\overset{H}{|}}{\underset{\underset{\oplus}{|}}{C}}-\overset{\overset{CH_3}{|}}{CH}-CH_3$ (d) $C_6H_5-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{CH}}-CH_2-\overset{\oplus}{CH}_2$
75. An example of a molecule which shows optical activity but does not contain chiral carbon atom is
 (a) $(CH_3)_2CHCHClCH_3$ (b) 2,3 – Pentadiene
 (c) Mesotartaric acid (d) $CH_3CH_2CHClCH_3$
76. The correct decreasing order of acidity is
 (a) $C_6H_5OH > HC\equiv CH > H_2O > NH_3$ (b) $C_6H_5OH > C_2H_5OH > NH_3 > HC\equiv CH$
 (c) $HC\equiv CH > C_6H_5OH > H_2O > NH_3$ (d) $C_6H_5OH > H_2O > C_2H_5OH > HC\equiv CH$

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77. Most stable carbocation among the following is



78. Choose the correct compound/species from P-S according to the property indicated in each.

(P) The stronger acid of the two $(\text{CH}_3)_2\text{NH}$ (I) or $(\text{CH}_3)_2\text{OH}^+$ (II)

(Q) The stronger base of the two $(\text{CH}_3)_3\ddot{\text{N}}$ (III) or $(\text{CH}_3)_2\ddot{\text{O}}$ (IV)

(R) The stronger acid of the two H_2O (V) or H_2S (VI)

(S) The stronger base of the two OH^- (VII) or SH^- (VIII)

(a) P – II, Q – III, R – VI, S – VII

(b) P – I, Q – III, R – V, S – VIII

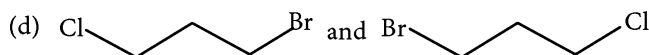
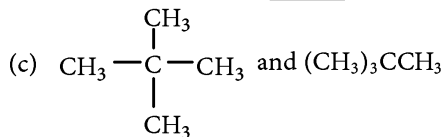
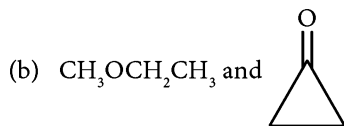
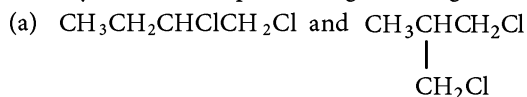
(c) P – II, Q – IV, R – V, S – VIII

(d) P – II, Q – III, R – V, S – VII

79. 4-Nitroaniline is a weaker base compared to 4-cyanoaniline. This is because

- both nitro and cyano are strong electron withdrawing groups.
- the lone pair of nitrogen of the NH_2 group is delocalised in 4-nitro aniline and not in 4-cyanoaniline.
- the negative charge resides on the more electronegative oxygen in nitro aniline in the resonance delocalization.
- cyano group is aligned planar with the ring.

80. Identify the isomeric pair among the sets given below (A) – (D)



81. The correct IUPAC name of is

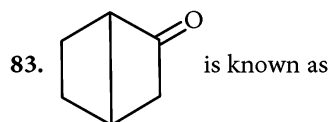
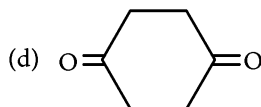
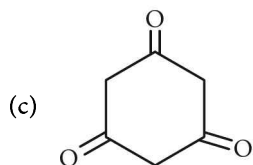
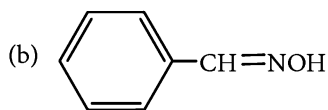
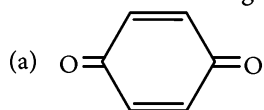
(a) 2-Chloro-5-Cyanophenol

(b) 3-Cyano-6-Chlorophenol

(c) 4-Chloro-3-hydroxybenzene carbonitrile

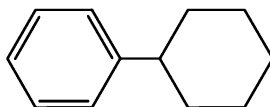
(d) 4-Chloro-1-Cyano-3-hydroxybenzene

82. Which of the following does not exhibit tautomerism?



- (a) Bicyclobutyl ketone
- (b) 1,4, trans annular cyclohexanone
- (c) Bicyclo [2.2.0] hexan-2-one
- (d) Bycyclo [2 . 2. 0] hexan-1-one

84. Which of the following is the correct name for the following compound?

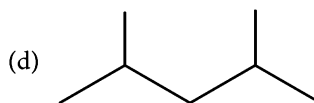
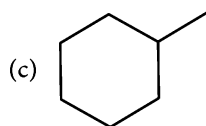
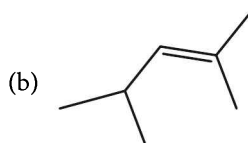
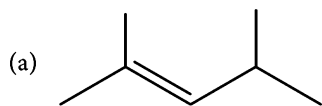
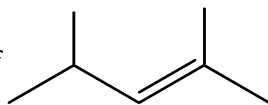


- (a) cyclohexyl benzene
- (b) phenyl cyclohexane
- (c) hexahydro biphenyl
- (d) hexahydrophenyl benzene

85. The IUPAC name of

- (a) 3-Methyl pent-2-en-1-ol
- (b) 2-Ethyl pent-2-en-5-ol
- (c) 3-Ethyl-but-2-en-1-ol
- (d) 3,3-Methyl ethyl prop-2-en-1-ol

86. Which is the structural isomer of

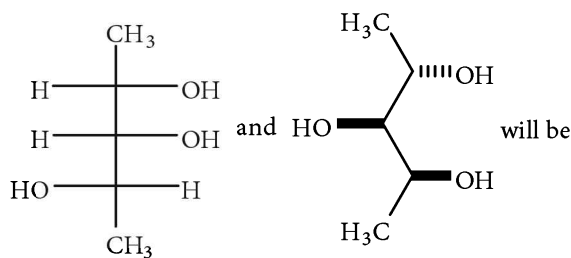


87. A set which contains an electrophile, a Lewis base and a species containing unpaired electrons among the following is

- (a) Cl^- , AlCl_3 and H_2
- (b) SO_3 , $(\text{CH}_3)_2\text{O}$, triplet carbene
- (c) Cl^- , HCl and singlet carbene
- (d) $\text{C}_2\text{H}_5\text{OH}$, NH_3 and Br

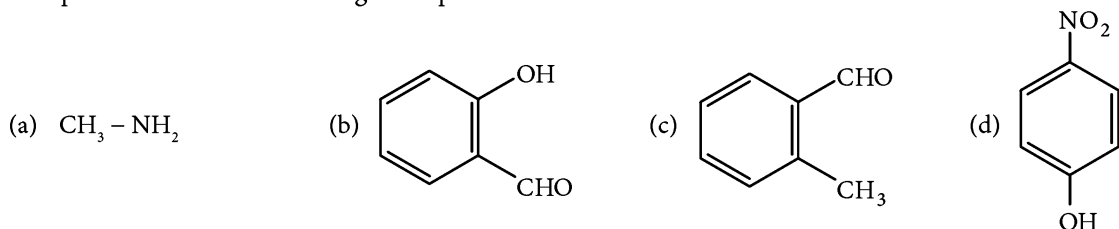
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88. The relationship between



- (a) two representations of the same molecule
(b) diastereomers
(c) enantiomers
(d) anomers

89. Compound in which H-bonding is not possible is



90. A compound can exhibit optical activity even if

- (a) a rotation axis is present
(b) a mirror plane is present
(c) a centre of symmetry is present
(d) an alternating axis of symmetry is present

91. Which of the following is an isomer of 2, 2-dimethyl propane?

- (a) Neopentane (b) 2-Methyl butane (c) Cyclopentane (d) Methyl cyclobutane

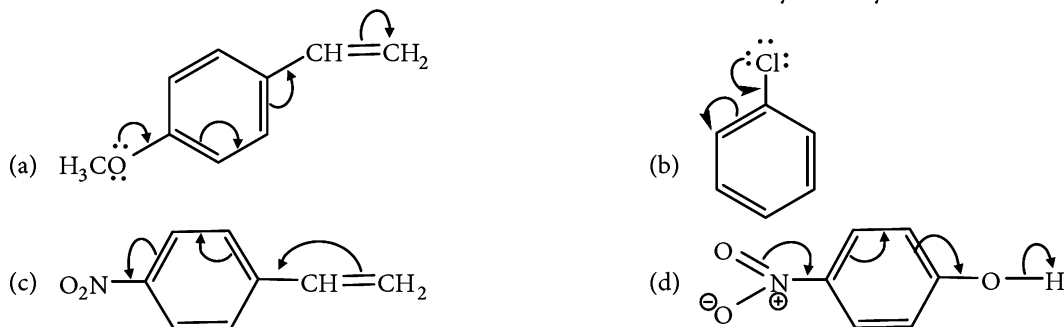
92. Number of structural isomers possible for C_6H_{14} and C_7H_{16} are respectively

- (a) 5 and 7 (b) 5 and 9 (c) 6 and 7 (d) 4 and 8

93. Inductive effect in organic molecule is observed due to

- (a) conjugation
(b) π orbitals
(c) electro negativity difference
(d) electron affinity

94. The movement of electrons in one of the structures is not shown correctly. Identify the structure.



95. Configuration of a chiral molecule can be changed only if

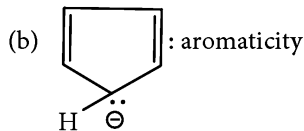
- (a) the compound is rotated out of the plane of paper.
(b) the confirmation is changed by rotation.
(c) the Fischer projection is changed to the Newman projection.
(d) the bond to the chiral carbon is broken.

96. Which of the following carbanions is most stable?

- (a) CH_3CH_2^- (b) $\text{C}_6\text{H}_5-\text{CH}_2^-$ (c) $\text{C}_6\text{H}_5-\text{CH}_2-\text{CH}_2^-$ (d) $\text{CH}_2\text{C}-\text{C}^-(\text{CH}_3)_2$

97. Four sets of carbanions (a – d) with the factors responsible for their stability to a certain extent are given. Identify the carbanion with wrong explanation of stability.

- (a) $\text{Cl}_3\text{C}^\ominus$: p π - d π bond



- (c) $\text{CH}_3\text{C}\equiv\text{C}^\ominus$: sp hybrid orbitals

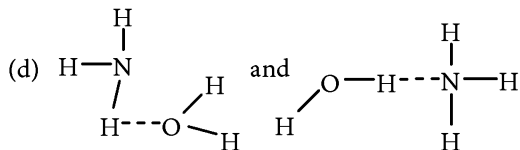
- (d) $\text{H}_2\text{C}-\text{NO}_2^\ominus$: nucleophilic nature of NO_2 group

98. Identify the correct resonance pair among the following.

- (a) $\text{CH}_3-\text{C}(\text{OH})=\text{CH}_2$ and $\text{CH}_3-\text{C}(=\text{O})-\text{CH}_3$

- (b) $\text{H}_2\text{N}-\text{O}-\text{H}$ and $\text{H}_2\text{N}^+=\text{O}^+-\text{H}$

- (c) $\text{H}_2\text{C}=\text{N}^+=\text{N}^\ominus$ and $\text{H}_2\text{C}^\ominus-\text{N}^+=\text{N}$



99. Four pairs of compounds (A) – (D) are given below. Indicate, in each pair, which compound can be more effectively hydrogen bonded.

- (a) $\text{CH}_3\text{CH}_2\text{OH}$ (I) and $\text{CH}_3-\text{O}-\text{CH}_3$ (II)

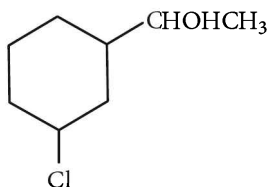
- (b) $(\text{CH}_3)_3\text{N}$ (I) and $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ (II)

- (c) $\text{HOCH}_2-(\text{CH}_2)_4-\text{CH}_2\text{OH}$ (I) and $(\text{CH}_3)_3\text{C}-\text{C}(\text{OH})\text{CH}_3$ (II)

- (d) $\text{CH}_3\text{CH}_2\text{OH}$ (I) and $\text{CH}_3\text{CH}_2\text{SH}$ (II)

- (a) (A) – (I), (B) – (I), (C) – (I), (D) – (I)
 (b) (A) – (I), (B) – (II), (C) – (I), (D) – (II)
 (c) (A) – (I), (B) – (I), (C) – (II), (D) – (II)
 (d) (A) – (I), (B) – (II), (C) – (I), (D) – (I)

100. The number of chiral centres and the stereoisomers possible for the following compound are respectively



- (a) 1 and 2 (b) 3 and 8
 (c) 2 and 4 (d) 4 and 16

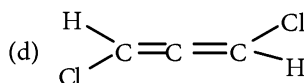
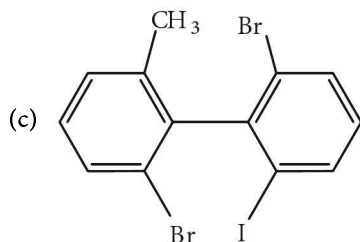
101. The number of stereoisomers possible for 2, 4-hexadiene is

- (a) 4 (b) 2 (c) 3 (d) 6

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102. A molecule which is not chiral among those listed below is

(a) 1-chloro-3-methyl but-1-ene



103. Which of the following is not true about a homolytic fission?

- (a) The products are free radicals.
- (b) The reaction occurs under the influence of heat or light .
- (c) It occurs when the bond breakage is between two atoms of the same electronegativity.
- (d) Intermediates may undergo rearrangement.

104. The weakest acid among those given is

- (a) $\text{Cl}_3\text{C}-\text{COOH}$
- (b) $\text{BrCH}_2\text{CH}_2\text{COOH}$
- (c) $(\text{CH}_3)_3\text{C}-\text{COOH}$
- (d) FCH_2COOH

105. which among the following compounds can exhibit geometrical isomerism?

- (a) 2-phenyl but-1-ene
- (b) 1-phenyl but-2-ene
- (c) 3-phenyl but-1-ene
- (d) 1,1-dichlorobut-1-ene

106. Four pairs of compounds are given below. In each pair, one is chiral while the other is achiral. Identify in each pair which is chiral. Choose from the options given

I $\text{ClCH}_2\text{CHOHCH}_2\text{OH}$ and $\text{HOH}_2\text{C}.\text{CHClCH}_2\text{OH}$

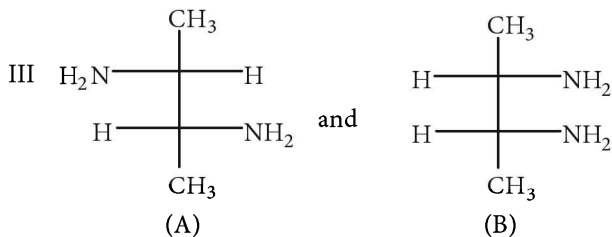
(A)

(B)

II $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Br}$ and $\text{CH}_3\text{CHBrCH}=\text{CH}_2$

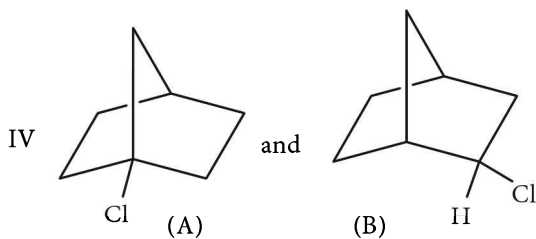
(A)

(B)



(A)

(B)



(A)

(B)

The options are

- (a) I A II B III B IV A
- (c) I A II A III B IV A

- (b) I A II B III A IV B
- (d) I B II B III B IV A

107. Identify the statement which is not correct among the following.
- (a) Acetone exists almost 100% in the keto form. (b) Acetylacetone exists considerably in the enol form.
 (c) Phenol exists almost 100% in the enol form. (d) The enol content of $\text{C}_6\text{H}_5\text{—COCH}_2\text{C}_6\text{H}_5$ is very low.
108. The dipole moment of $\text{C}_2\text{H}_5\text{Cl}$ (2.05 D) is considerably larger than that for vinyl chloride $\text{CH}_2 = \text{CH—Cl}$ (1.44 D) This is because
- (a) of hyperconjugation in ethyl chloride.
 (b) the unshared electron pair in chlorine is in resonance with the olefinic double bond in vinyl chloride.
 (c) Ethane is a saturated molecule.
 (d) of the electromeric effect.
109. Racemic tartaric acid is optically inactive because
- (a) of its meso forms (b) it has a plane of symmetry
 (c) of external compensation (d) symmetrical nature
110. which of the following statements is not correct?
- (a) Resonance and tautomerism describe the same phenomenon.
 (b) A group with a + I effect, attached to a carbocation, increases the stability of the carbocation.
 (c) Weaker the acid, stronger is its conjugate base.
 (d) The —OH and —NH_2 group attached to an aromatic ring exert + M effect.



Assertion–Reason Type Questions

Directions: Each question contains Statement-1 and Statement-2 and has the following 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

111. Statement 1

All olefinic compounds exhibit geometric isomerism.

and

Statement 2

Geometric isomerism in olefins arises due to restricted or hindered rotation between $\text{C} = \text{C}$ bonds.

112. Statement 1

Stereoisomers with D-configuration and L-configuration do not refer to compounds with (+) and (–) rotation respectively.

and

Statement 2

The letters D and L refer to the configuration of atoms or groups at a chiral centre based on D and L glyceraldehydes.

113. Statement 1

Alkyl carbanion such as CH_3^- has pyramidal shape.

and

Statement 2

The carbon atom carrying the negative charge has an octet of electrons.



Linked Comprehension Type Questions

Directions: This section contains 1 paragraph. Based upon the paragraph, 3 multiple choice questions have to be answered. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

Passage I

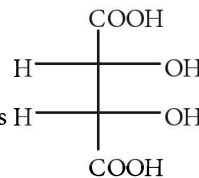
For a compound to exhibit optical activity, it should have a chiral centre or absence of elements of symmetry like plane of symmetry, centre of symmetry and alternating axis of symmetry. Optical activity is also shown by systems like substituted biphenyls and cumulative dienes.

114. Identify the correct statement among the following

(a) Racemic forms are optically inactive but are resolvable.

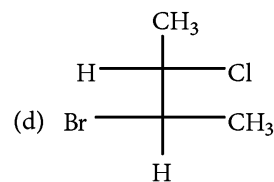
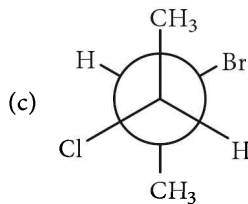
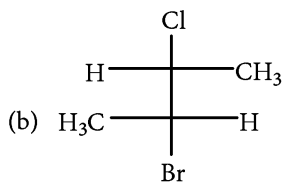
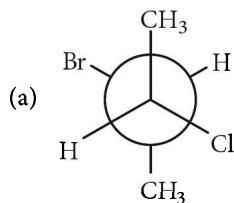
(b) $(\text{CH}_3)_2\text{C}=\text{C}\begin{array}{l} \text{H} \\ \text{CH}-\text{CH}_3 \\ | \\ \text{COOH} \end{array}$ can exhibit both geometric and optical isomerism.

(c) An optically active form of $\text{HOOC}-\text{CHOH}-\text{CHOH}-\text{COOH}$ can be represented as



(d) $\begin{array}{c} \text{CHO} \\ | \\ \text{H} - \text{C} - \text{OH} \\ | \\ \text{H} - \text{C} - \text{OH} \\ | \\ \text{H} - \text{C} - \text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array}$ and $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{HO} - \text{C} - \text{H} \\ | \\ \text{HO} - \text{C} - \text{H} \\ | \\ \text{HO} - \text{C} - \text{H} \\ | \\ \text{CHO} \end{array}$ are enantiomers

115. The enantiomer of $\begin{array}{c} \text{CH}_3 \\ | \\ \text{H} - \text{C} - \text{Cl} \\ | \\ \text{H} - \text{C} - \text{Br} \\ | \\ \text{CH}_3 \end{array}$ is



116. The number of optically active stereoisomers possible for the compound 2,3-dihydroxy butane are

(a) 4

(b) 2

(c) 6

(d) 8



Multiple Correct Objective Type Questions

Directions: Each question in this section has four suggested answers of which ONE OR MORE answers will be correct.

117. The molecules which have dipole moment is/are

(a) CH_2Cl_2	(b) 2, 2-dimethylpropane
(c) Cis-3-hexene	(d) p-chloronitrobenzene

118. A carbocation can

- (a) dimerize
- (b) rearrange to give a more stable carbocation
- (c) eliminate a proton to give an alkene
- (d) add on to a nucleophile to form a stable compound

119. Which of the following statements is/are correct about H-bonding?

- (a) n-Butanol has a higher boiling point than diethylether on account of intramolecular H-bonding.
- (b) Maleic acid is a stronger acid than fumaric acid due to the stabilization of the resulting anion by intramolecular H-bonding.
- (c) p-nitrophenol is steam volatile due to intramolecular hydrogen bonding.
- (d) Hydrogen bond formation intramolecularly involving one molecule only is known as chelation and when formed intermolecularly is known as association.



Matrix-Match Type Question

Directions: Match the elements of Column I to elements of Column II. There can be single or multiple matches.

120.

Column I

- (a) Hydrogen bonding
- (b) van der Waals forces
- (c) Nucleophile
- (d) Resonance stabilization

Column II

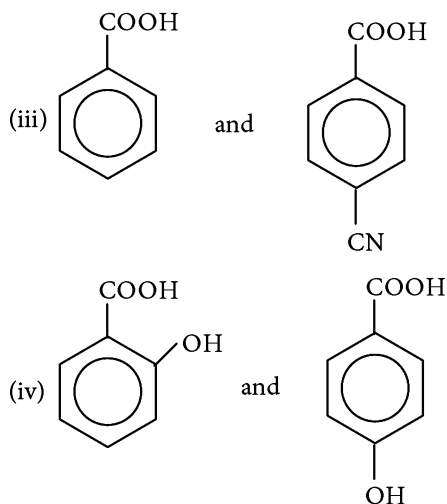
- (p) Conjugate base of phenol
- (q) azide ion
- (r) non covalent interaction
- (s) alcohols

ADDITIONAL PRACTICE EXERCISE

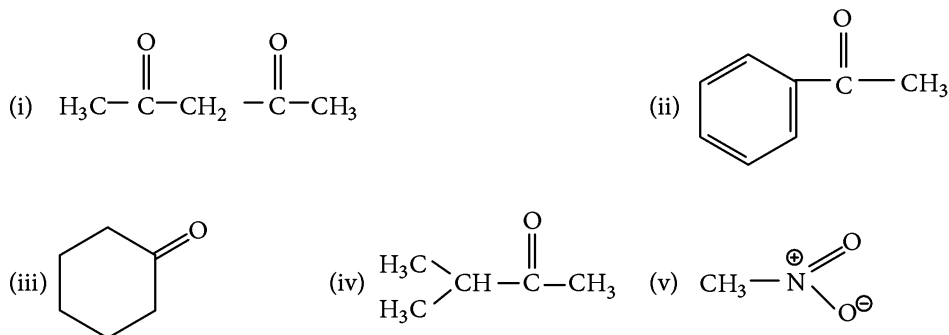


Subjective Questions

121. In $\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ (pentan-2,4-dione) – the hydrogen atoms of the central methylene group $-\text{CH}_2-$ are acidic as a phenolic $-\text{OH}$. Account for this.
122. Arrange the carbocations $(\text{C}_6\text{H}_5)_3\text{C}^\oplus$, $\text{C}^\oplus\text{H}_3$, $(\text{C}_6\text{H}_5)_2\text{C}^\oplus\text{H}$ and $\text{C}_6\text{H}_5\text{C}^\oplus\text{H}_2$ in the increasing order of stability. Justify.
123. Two pairs of compounds are given below, which one in each is more acidic and why?
- (i) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{OH}$ and $\text{H}_3\text{COCH}_2\text{CH}_2\text{CH}_2\text{OH}$
- (ii) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{OH}$ and $\text{CH}_3-\text{CH}_2-\underset{\text{Br}}{\text{CH}}-\text{CH}_2-\text{OH}$



124. Give the enol forms of the following.



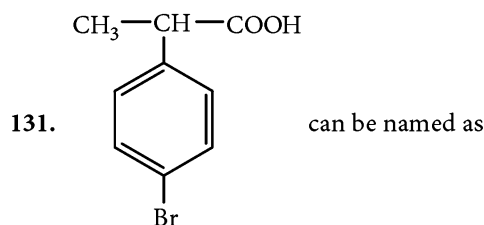
125. The boiling point of CH_3OH is 65°C , while the boiling point of CH_3SH is only 6°C . Explain this difference in boiling point.

126. Draw the Fischer and staggered Newmann projection structures of (+), (–) and meso forms of 2,3-dibromo butane.
127. When (–) lactic acid is treated with methanol under acidic conditions, (+) methyl lactate, an ester, is obtained as the product. Has the configuration at chiral centre changed?
128. Arrange the acids (I–V) listed below in the decreasing order of their acid strength and justify.
- Butanoic acid
 - Trichloro acetic acid
 - Chloroacetic acid
 - Trimethyl acetic acid
 - Bromo acetic acid
129. Account for the fact that when 3,3-dimethyl-2-butanol is treated with HBr, the product formed is 2-bromo-2,3-dimethylbutane and not 3,3-dimethyl-2-bromobutane as expected.
130. Identify the compounds having chiral centres among the following
- 1-Bromopentane
 - 1-Chloro-2-methylpentane
 - 2-Chloro-2-methylpentane
 - Citric acid
 - 1-Chloro-2-bromobutane

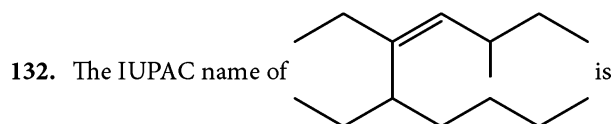


Straight Objective Type Questions

Directions: This section contains multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.



- α -methyl-p-bromophenyl acetic acid
- 2-(4-bromophenyl) propanoic acid
- 2-methyl p-bromophenyl acetic acid
- p-bromophenyl propionic acid



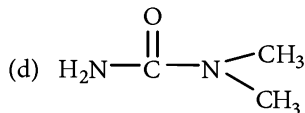
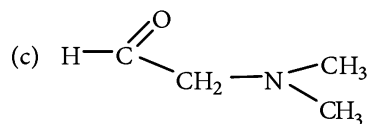
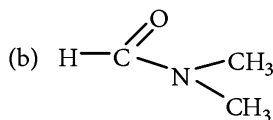
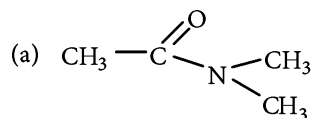
- 5-heptenylheptane
- 3-heptylhept-3-ene
- 3-(3-heptyl) hept-3-ene
- 5,6-Diethyl-3-methyldec-4-ene



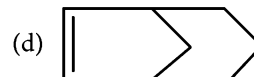
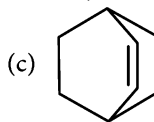
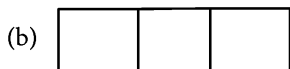
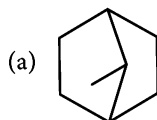
- 90° and 109.5°
- 109.5° and 120°
- 120° and 109.5°
- 120° and 120°

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134. The correct structure of DMF is



135. A compound with M.F C_8H_{14} contains 12 secondary and two tertiary H atoms. The compound is



136. The compound which has only one isopropyl group is

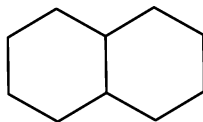
(a) 2,2,2,3-tetramethyl pentane

(b) 2,4-dimethyl pentane

(c) 2,2,3-tri methyl pentane

(d) 2-methyl pentane

137. The IUPAC name of the following is



(a) Decalin

(b) Decahydronaphthalene

(c) Bicyclo[4.4.2]decane

(d) Bicyclo[4.4.0] decane

138. A compound with molecular formula C_7H_{16} exhibits optical isomerism. The compound is

(a) 2,5 dimethylhexane

(b) 2-2-dimethylpentane

(c) 3-methylpentane

(d) 2,3-dimethylpentane

139. (+) Mandelic acid has an optical rotation of $+158^\circ$. What would be the specific rotation of a mixture of 25% (–) and 75% (+) mandelic acid?

(a) $+118.5^\circ$

(b) -118.5°

(c) -79°

(d) $+79^\circ$

140. Identify the statement which is not correct among the following

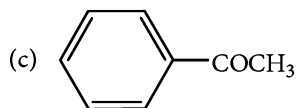
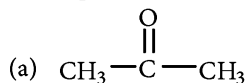
(a) (+) and meso tartaric acids are diastereomers.

(b) The enol percentage of acetyl acetone is more than that of acetone.

(c) Meso butane-2,3-diol can easily be resolved to give (+) and (–) isomers.

(d) $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{CH}_3)_2$ is known as 3-methyl-2-butanol.

141. A compound which can exist in more than one enolic form is

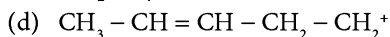


142. An allylic carbocation is less stable than

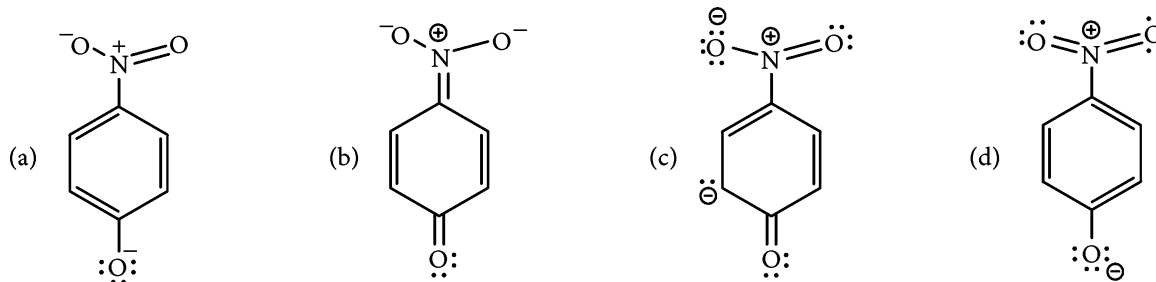
(a) a vinyl cation

(b) neopentyl cation

(c) benzylic cation



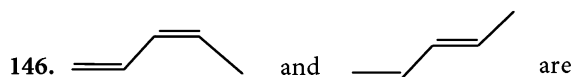
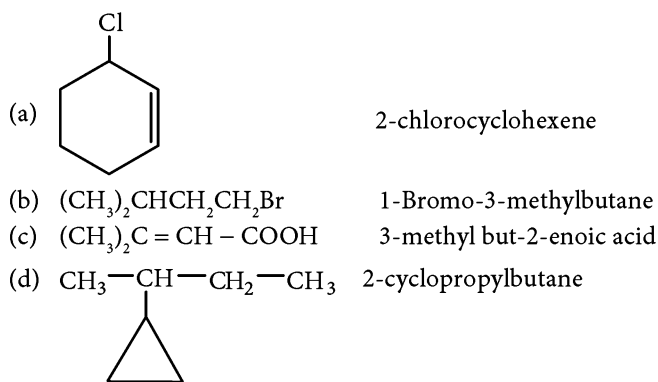
143. A structure which is not permissible for p-nitrophenoxide ion is



144. Which of the following carbocations is most stable?

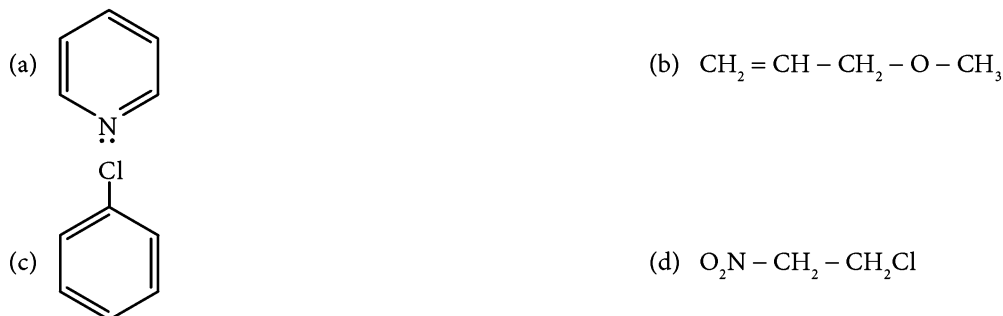
- (a) Trityl (b) benzyl (c) Diphenyl (d) t-butyl

145. Which of the following compounds has been incorrectly named?



- (a) optical isomers
 (b) geometrical isomers
 (c) two different representations of the same compound
 (d) structural isomers

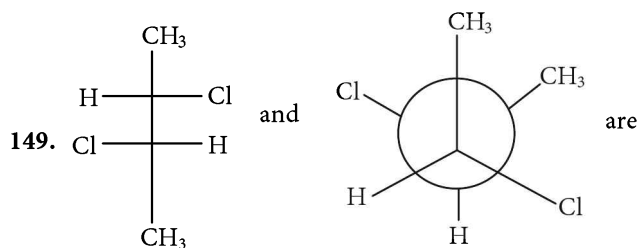
147. An example in which the lone pair of electrons in a heteroatom is used for resonance stabilization among the following is



148. A free radical is

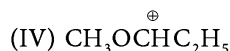
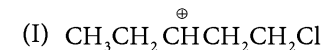
- (a) generated by a heterolytic cleavage (b) paramagnetic
 (c) generally more stable than a carbanion (d) produced in an ionic reaction

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- (a) geometrical isomers
(b) enantiomers
(c) diastereomers
(d) same compound

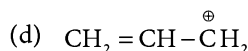
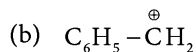
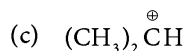
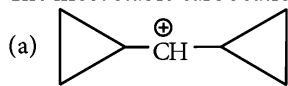
150. Four carbocations (I) – (IV) are given below



The increasing order of stability of the cations will be

- (a) (IV) < (I) < (II) < (III)
(b) (III) < (I) < (II) < (IV)
(c) (IV) < (III) < (I) < (II)
(d) (IV) < (III) < (II) < (I)

151. The most stable carbocation among the following is



152. Identify the correct statements among the following

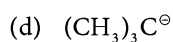
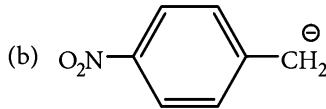
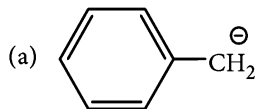
- (I) Removal of a proton from $(\text{H}_3\text{C})_2\text{CH}-\overset{\oplus}{\text{C}}\text{H}-\text{CH}_3$ leads to a more stable carbocation.
(II) The hydrogen bonding is strong in $\text{S}-\text{H} \cdots \text{S}$.
(III) The central carbon atom in a $(\text{CH}_3)_3\text{C}^\bullet$ free radical possesses 5 electrons.
(IV) The number of σ bonds in but-1-en-3-yne is 7.

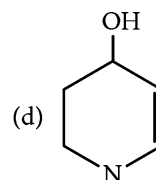
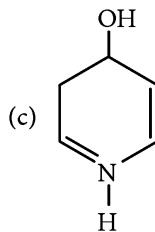
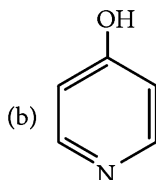
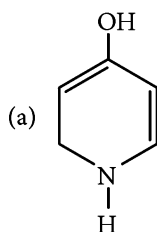
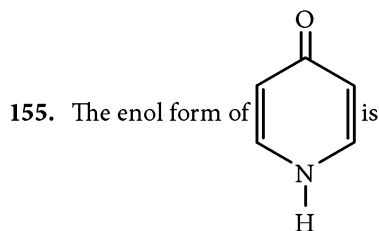
- (a) all are correct
(b) (IV) only
(c) (I) and (IV) only
(d) (I), (III) and (IV)

153. pK_a value is least for

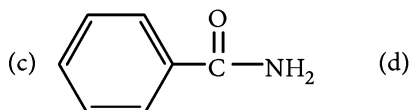
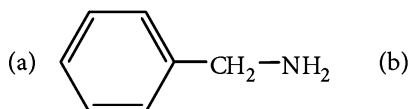
- (a) $(\text{CH}_3)_3\text{C}-\text{COOH}$
(b) $\text{BrCH}_2-\text{CH}_2-\text{CH}_2-\text{COOH}$
(c) $\text{CH}_3-\text{CCl}_2-\text{COOH}$
(d) $\text{CH}_3-\text{CHCl}-\text{COOH}$

154. Least stable among the carbanions given is





156. In which of the following compounds nitrogen is most basic?



157. Homolytic bond fission is observed in

- (a) Syn addition of bromine to ethylene
(c) halogenation of alkanes

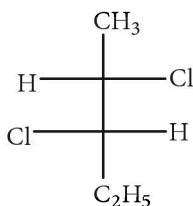
- (b) trans addition of bromine to butene
(d) nitration of benzene

158. The correct IUPAC name of $\text{CH}_3 - \text{O} - \text{CH}_2 - \text{O} - \text{CH}_2 - \text{O} - \text{CH}_3$ is

- (a) 1, 3, 5-Trioxabutane
(c) 2, 4, 6-Trioxaheptane

- (b) 2, 4, 6-Trioxabutane
(d) Dimethoxydimethyl ether

159. The configuration of chiral carbon atoms in the following compound is



- (a) 2(R), 3(S)

- (b) 2(S), 3(R)

- (c) 2(S), 3(S)

- (d) 2(R), 3(R)

160. Strength of a H-bond is

- (a) as good as a covalent bond
(b) between van der Waals forces and covalent bond
(c) equivalent to a dipole-dipole interaction
(d) between an ionic and covalent bond

161. The strongest H-bonding is observed in

- (a) $\text{O} - \text{H} \cdots \text{O}$

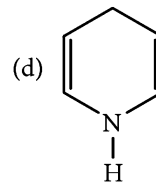
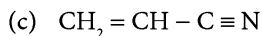
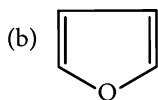
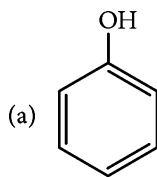
- (b) $\text{N} - \text{H} \cdots \text{N}$

- (c) $\text{F} - \text{H} \cdots \text{O}$

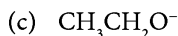
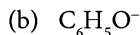
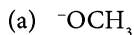
- (d) $\text{F} - \text{H} \cdots \text{F}$

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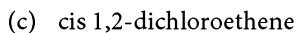
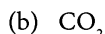
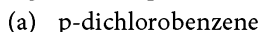
162. In which of the following the lone pair of electrons on the hetero atom do not take part in delocalization?



163. The most reactive among the nucleophiles given is



164. Significant dipole moment is shown by



165. The maximum number of isomers for the compound with molecular formula C_2IBrClF is

(a) 4

(b) 5

(c) 6

(d) 7

166. Identify the statement which is not correct.

(a) Diastereomers are always optically active.

(b) $\text{HC} \equiv \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CHOHCH}_3$ is known by the IUPAC name as hex-5-yn-2-ol.

(c) An achiral molecule is one which has a super imposable mirror image.

(d) Only one monochloro derivative is possible for neopentane.

167. The specific rotation of an isomer of an alkyl halide X containing one chiral carbon atom is $+40^\circ$. During a reaction in solution, it undergoes partial racemization. If the specific rotation of the equilibrium mixture is $+10^\circ$, the ratio of moles of (+) X and (–)X at equilibrium is

(a) 2:3

(b) 5:3

(c) 3:2

(d) 4:3

168. The heat of hydrogenation of cyclohexene is 127 kJ mol^{-1} . When a second double bond is introduced in the molecule, the heat of hydrogenation of the diene is found to be 231 kJ mol^{-1} . The diene is most likely

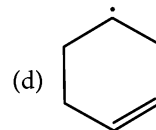
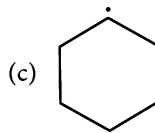
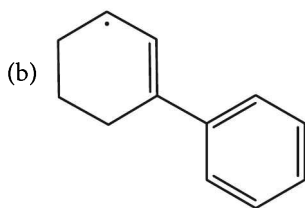
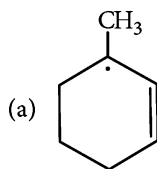
(a) Hexa-1, 4-diene

(b) Hexa-1, 3-diene

(c) Hexa-1, 5-diene

(d) Hexa-1, 2-diene

169. Most stable among the free radicals given is



170. The dipole moment of vinyl chloride is lower than that of ethyl chloride. This is because of

(a) resonance

(b) inductive effect

(c) Hyperconjugation

(d) unstable nature of vinyl chloride



Assertion-Reason Type

Directions: Each question contains Statement-1 and Statement-2 and has the following 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

171. Statement 1

n-propyl free radical is more stable than allyl free radical though both of them contain unpaired electron on a primary carbon.

and

Statement 2

Allyl radical is stabilized by resonance.

172. Statement 1

Stereoisomers which do not have an object and mirror image relationship can be termed as diastereomers.

and

Statement 2

An organic compound having only one chiral centre cannot have diastereoisomers.

173. Statement 1

Two enantiomeric pairs are found among the monobromination products of 2-methylbutane.

and

Statement 2

There is only one chiral centre in the starting material.

174. Statement 1

Heterolytic fission of C – C bond in propane will give mainly ethyl carbocation and methyl carbanion.

and

Statement 2

Ethyl carbocation is stabilized by inductive effect and among unsubstituted carbanions CH_3^- is the most stable one.

175. Statement 1

2,3-pentadiene $\text{CH}_3\text{CH}=\text{C}=\text{CH}-\text{CH}_3$ has no chiral carbons, but it is optically active.

and

Statement 2

The planes of the two double bonds in 2,3-pentadiene are different.

176. Statement 1

All carbon atoms in but-2-ene lie in one plane.

and

Statement 2

All the carbon atoms in but-2-ene are sp^2 hybridized.

1.82 Basics of Organic Chemistry

177. Statement 1

Tropylium cation is more stable than benzyl cation.
and

Statement 2

The tropylium cation is a rearranged and ring expanded form of a benzyl cation.

178. Statement 1

o-Nitrophenol is steam volatile whereas p-nitrophenol is not steam volatile.
and

Statement 2

There is intra molecular hydrogen bonding in o-nitrophenol, whereas there is intermolecular hydrogen bonding in p-nitrophenol.

179. Statement 1

p-Nitrobenzoic acid is more acidic than p-methyl benzoic acid.
and

Statement 2

Substituted benzoic acids are always stronger than benzoic acid.

180. Statement 1

Generally geminal diols (two-OH groups attached to the same carbon) are not stable. However chloral hydrate $\text{Cl}_3\text{C}-\text{CH}(\text{OH})_2$ is stable.
and

Statement 2

Chloral is used in the preparation of DDT.



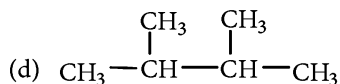
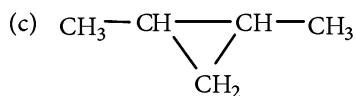
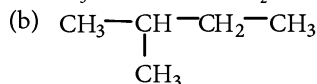
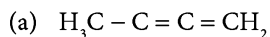
Linked Comprehension Type Questions

Directions: This section contains 3 paragraphs. Based upon the paragraph, 3 multiple choice questions have to be answered. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

Passage I

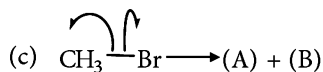
A chemical reaction is one in which old bonds are broken and new bonds are made. During the course of these changes a variety of intermediates are formed before a starting material is converted to final products. Formation of these intermediates depend on several factors like bond energies, kinetics of the reactions etc.

181. When a carbene $:\text{CH}_2$ is formed as an intermediate, the final product formed when one of the substrates is but-2-ene is



182. Identify the correct statement among the following.

- (a) An electrophile has always a positive charge.
 (b) CN^- can act as an ambident nucleophile.



The carbon species A formed is a methyl carbanion.

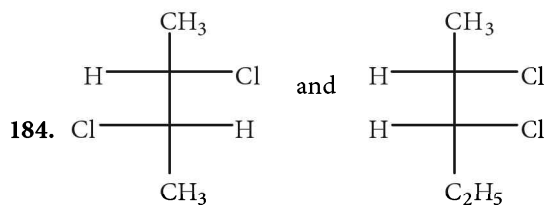
- (d) In CH_3MgBr , the methyl group carries slight positive charge.

183. In which of the following choices, the correct order is not indicated.

- (a) $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$ (the order of base strength)
 (b) $\text{ClCH}_2\text{C}^+(\text{CH}_3)_2 < (\text{CH}_3)_3\text{C}^+ < (\text{CH}_3)_2\text{C}^+\text{COCH}_3$ (stability of carbocation)
 (c) $\text{O}_2\text{N}-\text{CH}_2^- > \text{CH}_3^- > \text{CH}_3\text{CH}_2^-$ (stability of carbanion)
 (d) $\text{H}_2\text{C}=\text{CH}_2 < \text{CH}_3\text{CH}=\text{CHCH}_3 < (\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$ (stability of alkenes)

Passage II

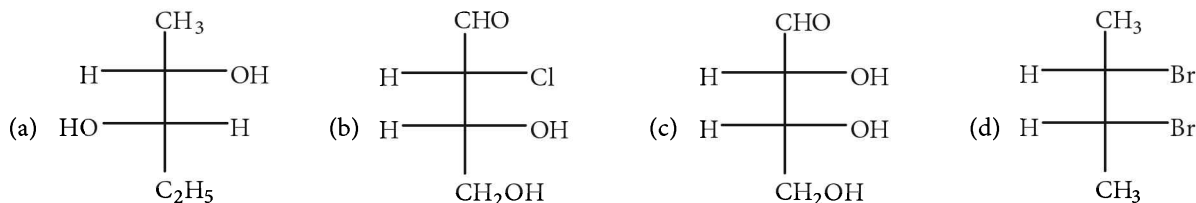
Stereoisomers are different from constitutional isomers in that the former differ from each other in the spatial arrangements while the latter differ on the basis of connectivity of atoms.



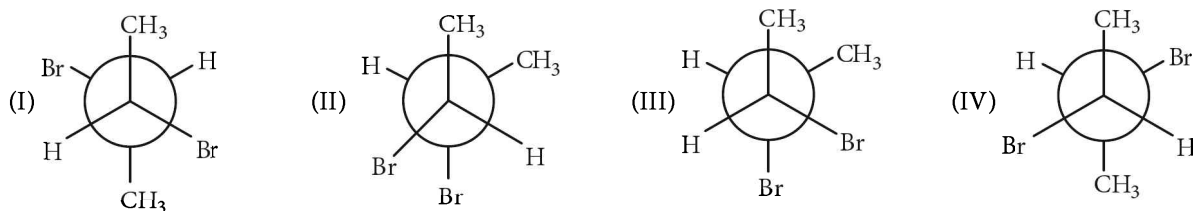
The two compounds are related as

- (a) diastereomers
 (b) enantiomers
 (c) configurational isomers
 (d) two different compounds

185. The threo isomer among the following is



186. Four structures (I) – (IV) are given below



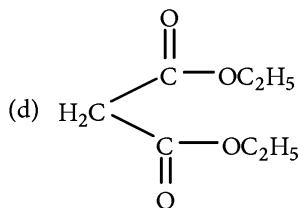
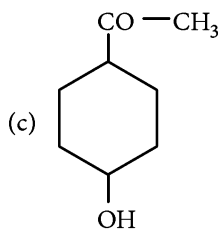
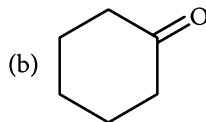
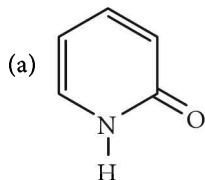
Two diastereomeric structures among those given are

- (a) (I) and (IV)
 (b) (I) and (II)
 (c) (I) and (III)
 (d) (III) and (IV)

Passage III

Keto-enol tautomerism is a special type of isomerism involving the 1,3 shift of a proton. There exists an equilibrium between keto and enol forms. In most cases keto form is more stable while in certain cases enol form is favoured.

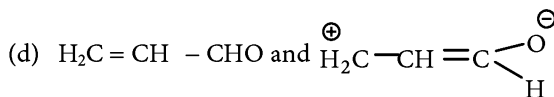
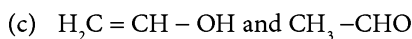
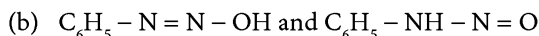
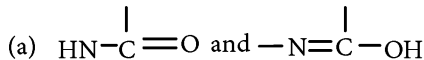
187. In which of the following, enol form dominate over the keto form?



188. The identification of the two enol forms of $\text{CH}_3\text{COCH}_2\text{COCH}_2\text{CH}_3$ (Hexane-2,4-dione) can be established by the study of

- intra molecular H-bonding
- colour reaction of the enol with neutral FeCl_3
- kinetics of the formation of the enol
- ozonolysis

189. One which is not a tautomeric pair among the following is



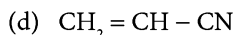
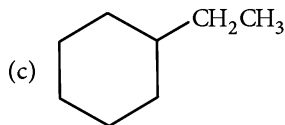
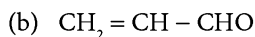
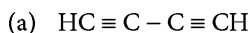
Multiple Correct Objective Type Questions

Directions: Each question in this section has four suggested answers of which ONE OR MORE answers will be correct.

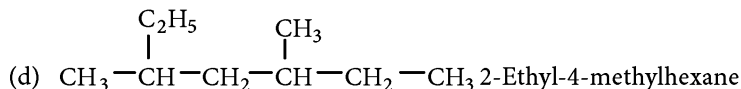
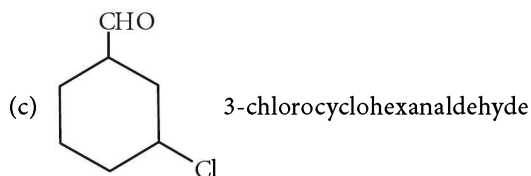
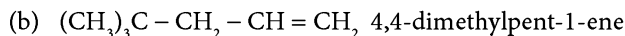
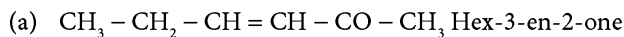
190. Identify the correct statements among the following.

- Acetate ion (CH_3-COO^-) is a weaker base than ethoxide ion ($\text{C}_2\text{H}_5\text{O}^-$).
- HF has higher boiling point than HCl .
- Tartaric acid ($\text{HOOC}-\text{CHOH}-\text{CHOH}-\text{COOH}$) has three optically active isomers.
- $\text{C}_3\text{H}_7\text{CN}$ is known as propyl cyanide as well as butane nitrile.

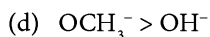
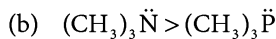
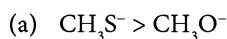
191. Which of the following molecules have only one type of hybridized carbon?



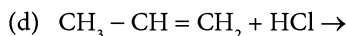
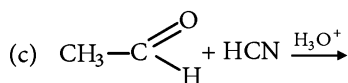
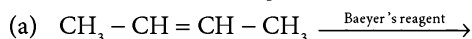
192. Which of the following compounds are named correctly according to the IUPAC rules?



193. Which of the following show the correct order of nucleophilicity?



194. In which of the following reactions, new chiral centre(s) is/are generated.



195. Which of the following statements are correct?

(a) Singlet carbene is paramagnetic.

(b) In the two species CN^- and CO , the common feature is that bond order is three and they are isoelectronic.

(c) Between CH_3Cl and CH_2Cl_2 , the former has a higher dipole moment.

(d) In the species $\text{CH}_3 - \text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{H} \end{array} + \text{HCN} \xrightarrow{\text{H}_3\text{O}^+}$ the order of acidity with respect to the positions indicated is (2) > (1) > (3)

196. Which of the following species is/are stabilized by isovalent hyperconjugation?

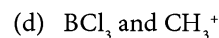
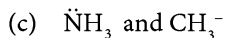
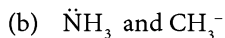
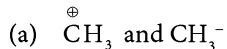
(a) Free radicals

(b) Carbanion

(c) Alkenes

(d) Carbocations

197. Which of the following pairs are isostructural?



Matrix-Match Type Questions

Directions: Match the elements of Column I to elements of Column II. There can be single or multiple matches.

198.

Column I

(a) Carbocation

(b) Free radicals

(c) Singlet carbene

(d) Triplet carbene

Column II

(p) sp^2 hybridization

(q) paramagnetic

(r) diamagnetic

(s) linear

199.

Column I

- (a) Diastereomers
- (b) Chiral centres
- (c) Tautomers
- (d) pent-2-ene

Column II

- (p) spontaneously interconvertible
- (q) cis-trans isomerism
- (r) restricted rotation
- (s) stereoisomerism

200.

Column I

- (a) Free radicals
- (b) Photochemical reaction
- (c) $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_3$
- (d) No bond resonance

Column II

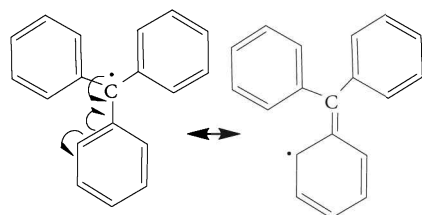
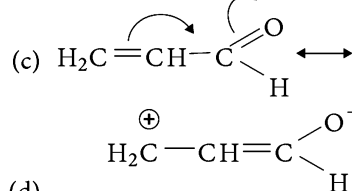
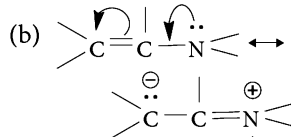
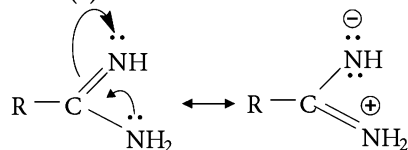
- (p) halogenation of alkanes
- (q) homolytic cleavage
- (r) hyperconjugation
- (s) chain reaction

SOLUTIONS

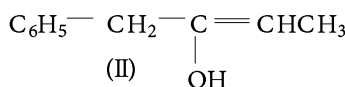
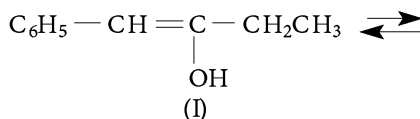
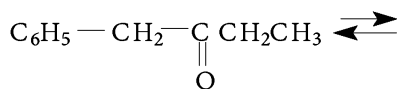
ANSWER KEYS

Topic Grip

1. Hept-2-en-4-yne
2. (a), (c) and (d)
3. (a)



4. Carboxylic acid is acidic because the carboxylate ion formed by ionisation is stabilized by resonance. Such a resonance stabilisation is not possible for alkoxide ion formed from alcohol.
5. CH_3NH_2 is more basic than NH_3 due to the +I effect of methyl group and consequent increase in electron density on nitrogen. NF_3 is less basic than NH_3 due to the -I effect fluorine atoms.
6. (i) 1-Phenyl-2-butanone



The enol (I) is more stable as the double bond is in conjugation with the phenyl ring.

Similarly, write the two enol forms of (ii)

7. Formate ion is a resonance hybrid of two equivalent structures. This makes the carbon-oxygen bonds equivalent.

8. (i) Conformational isomers
(ii) Structural isomers (chain isomers)
(iii) Geometrical isomers
(iv) Enantiomers
(v) Tautomers

9. It is due to the greater stabilization of CCl_3^- compared to CF_3^- .

CCl_3^- is more stable because of the overlap of p-orbital of carbon containing nonbonded electrons with the empty d-orbital of chlorine.

10. Optically active 2-iodobutane undergoes substitution with NaI under $\text{S}_\text{N}2$ conditions to give 2-iodobutane of opposite configuration and rotation. At equilibrium, there will be equal quantities of (+) and (-) 2-iodobutane and a racemic mixture is obtained. This results in the loss of optical activity.

11. (b)
12. (b)
13. (b)
14. (d)
15. (d)
16. (b)
17. (c)
18. (d)
19. (b)

20. (b)
21. (c)
22. (c)
23. (b)
24. (d)
25. (d)
26. (d)
27. (b), (c)
28. (a), (b), (d)
29. (a), (b), (c)
30. (a) $\rightarrow$ (q), (r), (s)
(b) $\rightarrow$ (p), (r)
(c) $\rightarrow$ (q), (r)
(d) $\rightarrow$ (p), (r)

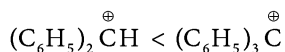
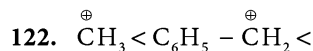
IIT Assignment Exercise

31. (a)
32. (c)
33. (b)
34. (c)
35. (c)
36. (b)
37. (c)
38. (a)
39. (d)
40. (c)
41. (c)
42. (c)
43. (b)
44. (b)
45. (a)
46. (a)
47. (b)
48. (c)
49. (c)
50. (c)
51. (c)
52. (d)
53. (b)
54. (c)
55. (d)
56. (c)
57. (d)
58. (b)
59. (c)
60. (a)
61. (a)
62. (a)
63. (d)
64. (a)
65. (b)
66. (c)
67. (b)
68. (b)
69. (d)
70. (b)
71. (b)
72. (a)
73. (a)
74. (a)
75. (b)
76. (d)
77. (a)
78. (a)
79. (c)
80. (a)
81. (c)
82. (a)
83. (c)
84. (a)
85. (a)
86. (c)
87. (b)
88. (b)
89. (c)
90. (a)
91. (b)
92. (b)
93. (c)
94. (d)
95. (d)
96. (b)
97. (d)
98. (c)
99. (d)
100. (b)
101. (c)
102. (a)
103. (c)
104. (c)
105. (b)
106. (b)
107. (d)
108. (b)
109. (c)
110. (a)
111. (d)
112. (a)
113. (b)
114. (a)
115. (c)
116. (b)

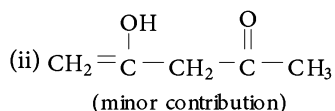
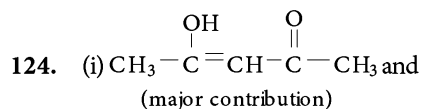
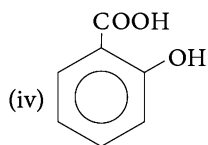
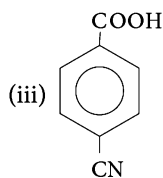
117. (a), (c), (d)
 118. (b), (c), (d)
 119. (b), (d)
 120. (a) → (r), (s)
 (b) → (r)
 (c) → (p), (q), (s)
 (d) → (p), (q)

Additional Practice Exercise

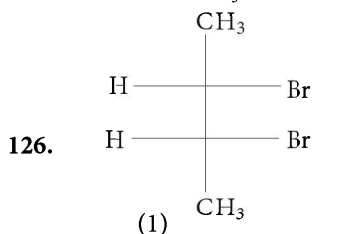
121. The central $-\text{CH}_2$ group is located between two electron withdrawing carbonyl groups. The anion formed by removal of a proton from the central $-\text{CH}_2$ group is stabilized by resonance.



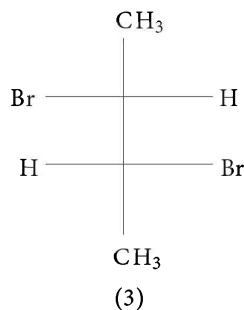
123. (i) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{OH}$
 (ii) $\text{CH}_3-\text{CH}_2-\underset{\text{Br}}{\text{CH}}-\text{CH}_2\text{OH}$



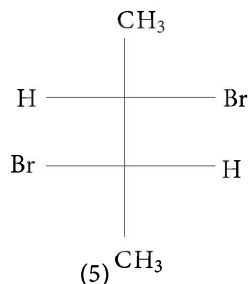
125. Methyl alcohol molecules are associated by intermolecular hydrogen bonding. So larger amount of energy is required to separate the molecules to form vapours. So it has higher boiling point. There is no hydrogen bonding in CH_3SH



meso-2,3-dibromobutane
 (Fischer projection)



(-)-2,3-dibromobutane
 (Fischer projection)



(+)-2,3-dibromobutane
 (Fischer projection)

127. No
 128. $\text{II} > \text{III} > \text{V} > \text{I} > \text{IV}$

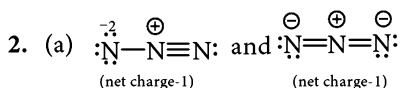
129. It is due to the rearrangement of the intermediate carbocation.

130. (ii) and (v)
 131. (b) 132. (d) 133. (c)
 134. (b) 135. (b) 136. (d)
 137. (d) 138. (d) 139. (d)
 140. (c) 141. (d) 142. (c)
 143. (d) 144. (a) 145. (a)
 146. (b) 147. (c) 148. (b)
 149. (d) 150. (b) 151. (a)
 152. (b) 153. (c) 154. (d)
 155. (b) 156. (a) 157. (c)
 158. (c) 159. (c) 160. (b)
 161. (d) 162. (c) 163. (d)
 164. (c) 165. (c) 166. (a)
 167. (b) 168. (b) 169. (b)
 170. (a) 171. (d) 172. (b)
 173. (c) 174. (a) 175. (a)
 176. (c) 177. (b) 178. (a)
 179. (c) 180. (b) 181. (c)
 182. (b) 183. (a) 184. (d)
 185. (a) 186. (b) 187. (a)
 188. (d)
 189. (d)
 190. (a), (b), (d)
 191. (a), (b), (c)
 192. (a), (b)
 193. (a), (c), (d)
 194. (a), (b), (c)
 195. (b), (c), (d)
 196. (a), (d)
 197. (c), (d)
 198. (a) → (p), (r)
 (b) → (p), (q)
 (c) → (p), (r)
 (d) → (q), (s)
 199. (a) → (q), (s)
 (b) → (s)
 (c) → (p)
 (d) → (q), (r), (s)
 200. (a) → (p), (q), (r), (s)
 (b) → (p), (q), (s)
 (c) → (r)
 (d) → (r)

HINTS AND EXPLANATIONS

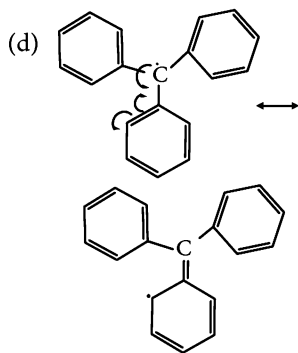
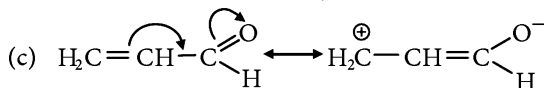
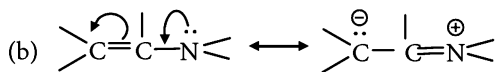
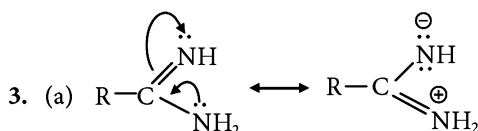
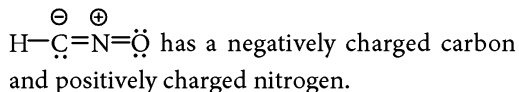
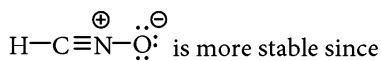
Topic Grip

1. It is hept-2-en-4-yne. The double bond is given priority over the triple bond when both double and triple bonds are present in the same structure. However, the name of the hydrocarbon should end in yne.

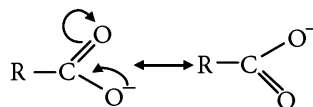


The two structures are resonance structures — they have the same number of electrons and the same net charge (−1).

- (b) Of the two structures, the first one is not a correct structure as it has the central nitrogen with 10 electrons around it. It is not a valid Lewis structure as it violates the octet rule. The other structure is an acceptable Lewis structure.
- (c) The two structures constitute a resonance pair.
- (d) The two structures are permissible resonance structures. Of the two structures,



4. The carboxylate ion formed by loss of a proton from a carboxylic acid is stabilized by resonance as shown below.

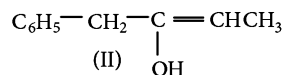
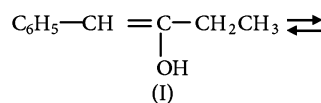
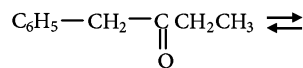


So carboxylic acids readily ionize to form H^+ ions and behave as acids.

On the other hand when a proton is lost from an alcohol an alkoxide ion is formed. For example, ethyl alcohol forms ethoxide ion $\text{CH}_3\text{CH}_2\text{O}^-$. As there are only sigma bonds in an ethoxide ion (or alkoxide ion) there is no resonance stabilization possible. Therefore, the acidity or proton releasing ability of an alcohol is very poor.

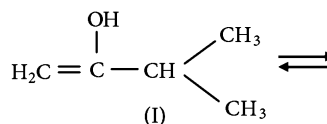
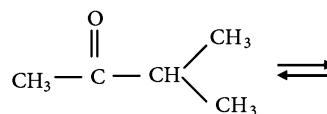
5. NH_3 and its derivatives are Lewis bases due to the presence of lone pair of electrons. In CH_3NH_2 , the methyl group has an electron releasing inductive effect and the amine nitrogen has higher electron density. Hence it is more basic than NH_3 . Fluorine is a strong electron withdrawing group. The cumulative effect of the three fluorine atoms draws the electron density away from nitrogen, thereby making it less basic.

6. (i) 1-Phenyl-2-butanone

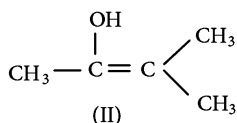


The enol (I) is more stable as the double bond is in conjugation with the phenyl ring.

- (ii) Methyl isopropyl ketone

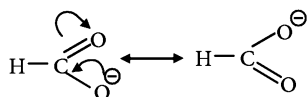


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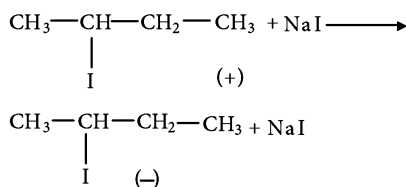
The enol (II) is more stable as the double bond is stabilized by greater substitution by methyl groups.

7. In the formate ion $\text{H}-\text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O}^- \end{array}$, the anion can exist in two resonance forms as shown.



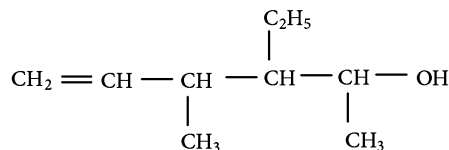
So, a canonical structure can be drawn as, $\text{H}-\text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array}$ where both the C – O bond lengths become equal.

8. (i) Conformational isomers (two different structures for the same compound).
 (ii) Structural isomers (chain isomers)
 (iii) Geometrical isomers
 (iv) Enantiomers (optical isomerism)
 (v) Tautomers (keto-enol tautomerism)
9. CHCl_3 is more acidic than CHF_3 . Since fluorine is more electronegative than chlorine, it is expected that CHF_3 should be more acidic. However, the anion CCl_3^- generated by the loss of a proton from CHCl_3 gets more stabilized than the anion CF_3^- . This is because the unshared electron pair in p-orbital of carbon in CCl_3^- , undergoes extended $p\pi - d\pi$ bonding with the empty d orbital of chlorine. Resonance makes a more contribution than the inductive effect.
10. Optically active 2-iodobutane undergoes substitution with NaI under $\text{S}_\text{N}2$ conditions to give 2-iodobutane of opposite configuration and rotation



At equilibrium, there will be equal quantities of (+) and (–) 2-iodobutane and a racemic mixture is obtained. This results in the loss of optical activity.

11. The IUPAC name of compound



is 3-ethyl-4-methylhex-5-en-2-ol

12. The two compounds are constitutional isomers as the connectivity is different in both the compounds.
13. The phenoxide ion $\text{C}_6\text{H}_5\text{O}^-$ obtained by the loss of a proton from phenol is resonance stabilized. So phenol ionizes to form phenoxide and H^+ .
14. (d) is most stable because it is tertiary benzylic ion.
15. The two structures are diastereomers.
16. Both statements (1) and (2) are correct. However, statement (2) is not a supportive statement for statement (1). Between a double bond and a triple bond, the former is given priority. Hence statement (1) is correct. The aldehyde group is one of the important functional group. Hence it is given a higher priority in statement (2).
17. Statement (1) is correct because three chlorine atoms attached to the α -carbon in trichloro acetic acid increase the acidity of the acid. Though COOH group is an electron withdrawing group, oxalic acid is a weaker acid than $\text{Cl}_3\text{C}-\text{COOH}$.
 Statement (2) is not correct because electron withdrawing groups increase the acidity of acids by electron withdrawal and decrease the base strength.
18. Statement (1) is wrong because the central carbon is sp hybridized. Statement (2) is correct.
19. Both statements (1) and (2) are correct, but statement – 2 is not the real reason for statement – 1
20. Both statements (1) and (2) are correct. However, statement (2) is not supportive of statement of statement (1).

A carbocation is a high energy species with a positive charge on carbon. A carbocation can be 1° , 2° or 3° of which 3° is the most stable.

Rearrangements occur, if the structure permits. Other types of reactions of carbocations are also possible, depending on the availability of reagents. Hence statement (1) is correct.

Free radicals are also similar to carbocations in terms of stability. Hence statement (2) is also correct.

21. Non planar forms of cyclohexane like chair and boat forms are suggested for stability. However, the chair form is the most stable while the boat is less stable because of flagpole interactions.
22. Conformations arise as a result of free rotation about carbon-carbon single bonds.
23. The only correct statement is that the dihedral angle between the two methyl groups is zero.
24. (d)
There is no proton or hydrogen to shift. Hence (d) does not exhibit tautomerism.
25. (d) is not correct. They are not tautomers but geometrical isomers.
26. (d) The two are resonance structures.
27. (b) and (c)

$$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ | \quad | \\ \text{CH}_3 - \text{CH} - \text{CH} - \text{CH}_3 \end{array}$$

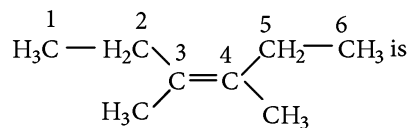
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ | \\ \text{Cl} \end{array}$$

 - (a) contains 1° , 2° and 3° carbons
 - (d) contains 1° and quaternary carbons
28. (a), (b) and (d) are the correct statements.
29. (a), (b) and (c) are correctly represented.
The two structures in (d) are not isomers.

IIT Assignment Exercise

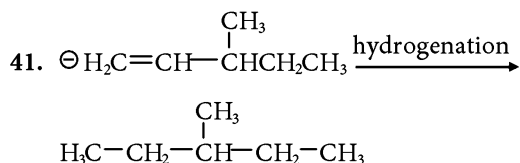
31. -COOH is the principal functional group.
32. The double bond is the main functional group. The two chloro substituents take the 3 and 4 positions in the chain.
33. It is a dialdehyde which is known as dial in IUPAC system.
34. (c) is the correct representation.
35. (c) is the only correct statement.
 - (a) The minimum number of carbon atoms in a branched alkane is 4 and not 3.
 - (d) It is known 3-methylpentane.
 - (b) There is no unsaturation in acetone. It is only a carbonyl group.

36. The IUPAC name of



cis-3,4-dimethyl hex-3-ene.

37. (c) only this compound exhibits both geometric and optical isomerism.
38. P and Q are enantiomers.
39. The mono chloro derivatives which produce chiral centers are $(\text{CH}_3)_2\text{CH}\overset{*}{\text{C}}\text{HClCH}_3$ and $\text{CH}_2\text{Cl}-\overset{*}{\text{C}}\text{H}(\text{CH}_3)\text{C}_2\text{H}_5$. So two pairs of enantiomers are possible.
40. The energy of a resonance hybrid is always less than the energy of any of the contributing structure. The difference in energy between the most contributing structure and the energy of the hybrid is said to be the resonance stabilization energy.
41. $\ominus\text{H}_2\text{C}=\text{CH}-\overset{\text{CH}_3}{\underset{|}{\text{CH}}}\text{CH}_2\text{CH}_3 \xrightarrow{\text{hydrogenation}}$
- $\text{H}_3\text{C}-\text{CH}_2-\overset{\text{CH}_3}{\underset{|}{\text{CH}}}-\text{CH}_2-\text{CH}_3$
- There is no chiral centre in the product and it is optically inactive.

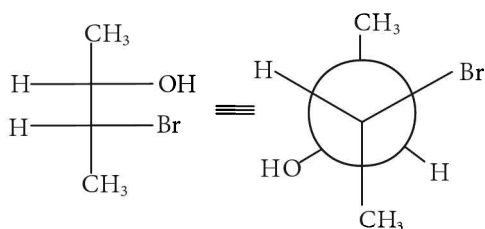


There is no chiral centre in the product and it is optically inactive.

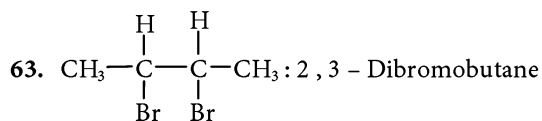
42. (c) It is a stereo isomer.
43. Enantiomers
45. Only the cyclohexane derivative is chiral and is optically active.
46. Any reaction in which only one of a set of stereoisomers is formed exclusively or predominantly is called stereoselective reaction.
47. It is due to hyperconjugation. When attached to benzene or unsaturated system $\text{CH}_3\text{--CH}_2\text{--}$ can have two hyperconjugative structures, $(\text{CH}_3)_2\text{CH--}$ can have only one hyperconjugative structures while $(\text{CH}_3)_3\text{C--}$ cannot have any hyperconjugation.
48. They are cis-trans isomers and hence can be considered as diastereomers.
49. Staggered anti form is the most stable while the eclipsed is the least stable confirmation of n-butane.

1.92 Basics of Organic Chemistry

50. Specific rotation = $12^\circ \times \frac{80}{100} = 9.6^\circ$
51. Second row of elements like N, O, F cannot have more than eight electrons around in the valence shells. This is not a valid Lewis structure. In this structure nitrogen has 10 valence electrons around it
52. A meso compound is an achiral molecule with two or more chiral carbons, contains a plane or centre of symmetry and is optically inactive due to internal compensation.
53. Only the oxime (b) can be represented as geometrical isomers Syn and anti. Other compounds do not exhibit geometrical isomerism.
54. II is more stable because of the lone pair on oxygen as shown.
55. In all the four examples, the ions radicals are stabilized by resonance and extended conjugation.
56. Similar priority groups are on the same side.
57. The erythro form of 3-bromo-2-butanol is represented in the staggered Newman projection as given in (d)

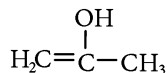


58. There is one hydrogen extra in this structure. Hence it not a correct resonance structure.
59. Bromine in bromobenzene is deactivating by electron withdrawing inductive effect and not by resonance. So statement (c) is not correct.
60. (a) Statement is not correct. The alkyl or aryl group in a Grignard reagent is a nucleophile.
62. Resonance accounts for the same carbon-carbon bond lengths in benzene.

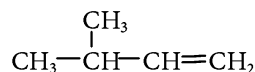


It contains two similar chiral carbon atoms and hence can have the meso form.

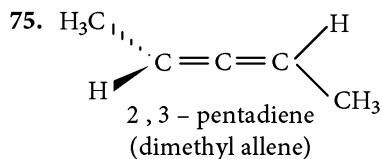
64. (a) only the acidic hydrogen or the hydrogen attached to an electronegative elements gets displaced by deuterium. The enol form of acetone is



65. Nucleophilicity of a group is the ability to form bonds to carbon atoms in nucleophilic substitution reaction. Nucleophilicity depends to some extent on the nature of the solvent.
66. Configuration is the term used to explain the specific or geometric position of the atoms in a particular stereoisomer.
67. An O-H bond is one in which the hydrogen is connected to an electronegative oxygen. Eventhough C-O bond is polar, -O-H bond is more polar and the heterolytic cleavage in -OH is more.
68. Hyperconjugation effect is maximum when the number of hydrogens on the α -carbon to the double bond is maximum. In the alkene specified, when the R group is $-\text{CH}_3$, there are three hydrogens so it can have maximum hyperconjugative structures followed by $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$ which is then followed by



69. Bromine addition to cis 2-butene gives a racemic mixture, while the bromine addition to trans 2-butene gives a meso product.
70. Hydrogen is taken as a reference point for measuring the inductive effect. So the inductive effect hydrogen is assumed to be zero.
71. Presence of groups with -I effect decreases the stability of carbocations. Between (b) and (c), (c) is more stable than (b). In F_3C^+ , the filled 2p orbital of F overlaps partially with the empty 2p orbital on the positively charged carbon. This disperses the positive charge and thus stabilizes CF_3^+ relative to $\text{F}_3\text{C}-\text{CH}_2^+$.
72. (a) is the most stable. The order of stability of free radicals and carbocations is the same. In (a), odd electron is on a tertiary carbon and resonance stabilization is also possible.
73. A tertiary carbocation is most stable.
74. A secondary carbocation rearranges to a 3° carbocation.



It shows optical activity though it does not contain any asymmetric carbon atom.

76. Phenol is the most acidic and acetylene is the least acidic. Lower the pK_a value higher is the acidity. The pK_a values are $C_6H_5OH \approx 10$, $H_2O = 15.74$, $C_2H_5OH = 16$, $C_2H_2 = 25$

77. (a)

It is secondary benzylic carbocation.

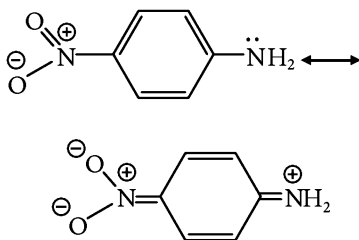
78. (p) Protonated ether is more acidic than amines.

(q) Amine is more basic. Further it is a tertiary amine

(r) H_2S is a stronger acid because the conjugate base ^-SH is weaker than ^-OH the conjugate base of water.

(s) ^-OH is a stronger base compared to ^-SH as a base.

79. The delocalization of lone pair of NH_2 group is more effective in 4-nitroaniline because the negative charge (i.e., electron pair) is on a more electronegative oxygen atom.



80. The only isomeric pair is given is set (a).

81. $-CN$ is the principal functional group.

82. Enolisation is not possible for (a)

83. The ring junction is taken as the starting point for counting and the keto group is given 2-position. Hence the name is bicyclo [2.2.0] hexan-2-one.

84. Cyclohexyl group is the Substituent and the aromatic ring gets priority.

85. The longest straight chain is made up of 5 carbon atoms. It is an alcohol. The double bond is between 2-3 carbon chain.

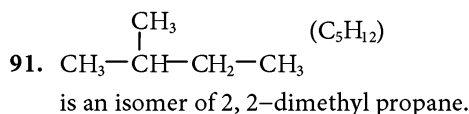
86. Compound in (a) is another representation of the same compound. Compound (b) is the Geometrical isomer while (d) is not an isomer. So only (c) is isomeric with the given compound. They are ring-chain isomers.

87. $(CH_3)_2O$ is a Lewis base, SO_3 is an electrophile involved in sulphonation reactions of aromatic compounds and triplet carbene contains two unpaired electrons.

88. They are stereoisomers, but they do not have an object-mirror image relationship. They are diastereomers.

89. Since there is no hydrogen directly attached to electronegative atom such as oxygen in 2-methyl benzaldehyde, hydrogen bonding is not possible.

90. A molecule can exhibit optical activity even if it has a simple axis of symmetry.

91.  is an isomer of 2,2-dimethyl propane.

92. The IUPAC names of five isomers possible for C_6H_{14} are

(i) hexane

(ii) 2-methylpentane

(iii) 3-methylpentane

(iv) 2,3-dimethyl butane

(v) 2,2-dimethyl butane

The IUPAC names of the nine isomers of C_7H_{16} are

(i) heptane

(ii) 2-methyl hexane

(iii) 3-methylhexane

(iv) 2,2-dimethylpentane

(v) 3,3-dimethylpentane

(vi) 2,3-dimethylpentane

(vii) 2,4-dimethylpentane

(viii) 3-ethylpentane and

(ix) 2,2,3-trimethylbutane

93. The electronegativity of an element causes a partial bond polarization resulting in inductive effect.

94. In p-nitrophenol, nitrogroup is electron withdrawing, but in the structure (d) it is shown as electron releasing.

95. The configuration can be changed only if the bonds are broken and new bonds are made at the chiral centre.

96. Benzylic carbocations, carbanions and free radicals are stabilized by resonance.

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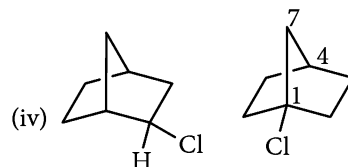
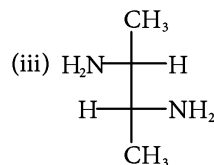
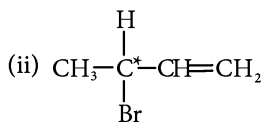
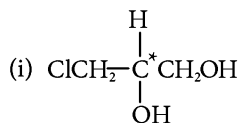
97. $-\text{NO}_2$ group is electron withdrawing and not nucleophilic.
98. Only (c) is the correct resonance structure.
99. (a) Alcohol gets involved in H-bonding than ether because there is no H – attached to an electronegative element in ether.
 (b) A tertiary amine has no hydrogen attached to N, so a 1° amine gets hydrogen bonded.
 (c) There are two OH groups in



- (d) Sulphur is not involved in hydrogen bonding.
100. There are three different chiral centres in the molecule and so 2^3 stereo isomers are possible.
101. (c)
 $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$, It contains two (2,4-hexadiene) double bonds and the two ends are identical. Hence the number of geometrical isomers possible is 3. They are cis – cis, trans – trans and cis – trans isomers. Since the two ends are identical cis – trans and trans – cis isomers are identical.

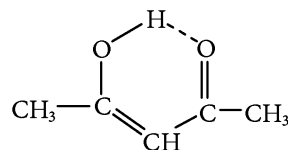
102. $\text{ClCH}=\text{CH}-\overset{\text{CH}_3}{\underset{|}{\text{CH}}}-\text{CH}_3$
 1-chloro-3-methyl-1-butene is not chiral
 All the other molecules are chiral. However, only (b) has a chiral centre, while (c) and (d) are chiral because of non planarity.

103. Homolytic bond fission may occur at the bonds joining two atoms of the same electronegativity or of different electronegativities.
104. Trimethylacetic acid is the weakest acid among those listed, while $\text{Cl}_3\text{C}-\text{COOH}$ is the strongest.
105. 1-phenylbut-2-ene $\text{C}_6\text{H}_5-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_3$ can exist in the form of Cis and trans isomers.
106. The following compounds in each pair are chiral

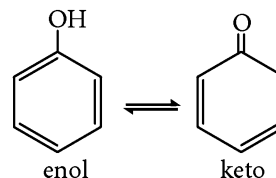


Compound is achiral it has a plane of symmetry; plane of symmetry passes through carbons 1, 4 and 7.

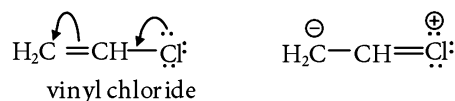
107. The only statement which is not correct is (d)
 The enol content of $\text{C}_6\text{H}_5\text{COCH}_2\text{C}_6\text{H}_5$ (Phenyl benzyl ketone) is quite high. This is because of the extended conjugation and stabilization by resonance.
 All the other statements (a), (b) and (c) are correct.
 In acetone the keto group is thermodynamically more stable than enol form.
 In (b) Acetylacetone exists in the enol form as a major part because in this form it is stabilized by intramolecular H – bonding as shown.



In (c), phenol exists exclusively as the enol form because the ring retains its aromaticity.



108. The resonance interaction tends to oppose the movement of electron towards chlorine in vinyl chloride. In ethyl chloride $\text{C}-\text{Cl}$ single bond is more polar and there is no resonance.



109. Racemic mixture is an equal mixture of (+) and (–) isomers. Mutually the rotation cancels by external compensation.

110. The statement which is not correct is resonance and tautomerism refer to the same phenomenon.

The two are different. In tautomerism, the two structures really exist and they are in equilibrium and can be isolated under suitable conditions.

In resonance, all the structures drawn are not really existing. They are hypothetical.

111. Statement (1) is not correct while statement (2) is correct.

For an olefinic compound to show geometrical isomerism, there should be two different groups attached to the carbon of the double bond. For example, compounds like

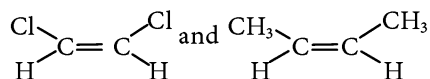
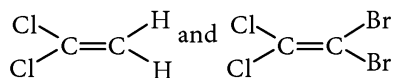


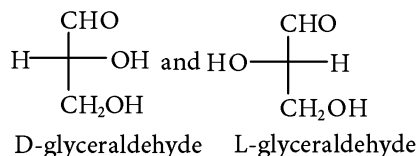
exhibit geometrical isomerism, while compounds like



do not exhibit geometrical isomerism.

112. (a) do not show geometrical isomerism. Both statements (1) and (2) are correct and statement (2) provides an explanation for statement (1)

The classification D and L is based on D – glyceraldehydes and L – glyceraldehydes



113. Both statement –1 and 2 are correct, but statement – 2 is the correct reason for Statement – 1

CH_3^- is pyramidal because the hybridization of C is sp^3 and one of the hybridized orbital contains the non-bonded electron pair. So it contains 3 bond pairs and one lone pair and is pyramidal in shape (similar to NH_3).

114. (a) is the only correct statement.

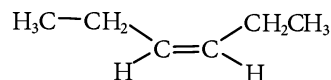
115. (c) is the enantiomer of the molecule given.

116. There are two chiral centres in the molecule and the substituents on each chiral carbon is the same. So there should be $2^n - 1$ ($n = 2$) or 3 stereoisomers. Out of this, one is the meso structure which is optically inactive. So only two optically active isomers are possible.

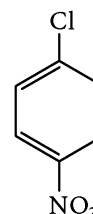
117. (a), (c) and (d) have dipole moment

(a) CH_2Cl_2 has a dipole moment of 1.55 D

(c) cis 3-hexene



(d) p-chloronitrobenzene



Only (b) which is neopentane has no dipole moment.

118. (b), (c) and (d) are correct.

(a) is not correct because carbocations cannot dimerize. But free radicals can dimerize.

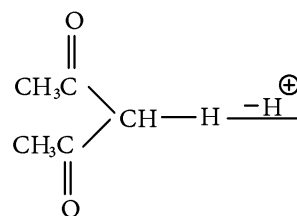
119. (b) and (d) are correct

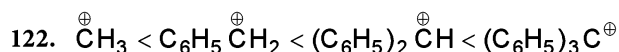
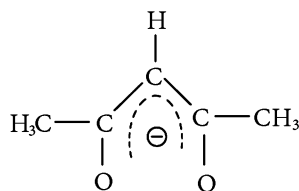
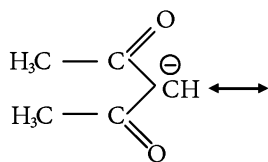
(a) is not correct because the H– bonding formed in n – butanol is intermolecular and not intramolecular.

(c) is not correct because intramolecular hydrogen bonding is not observed in p-nitrophenol

Additional Practice Exercise

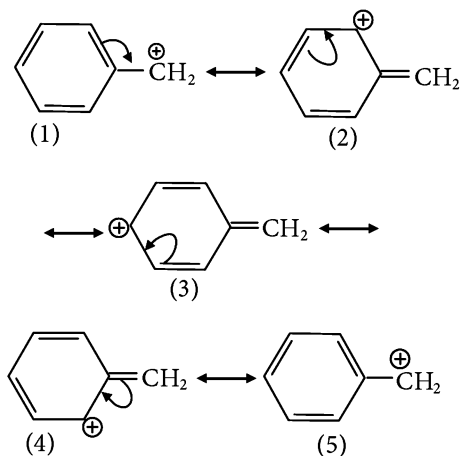
121. Acetyl acetone or (pentane-2,4-dione) is $\text{CH}_3\text{CO}-\text{CH}_2\text{COCH}_3$. The central methylene group $-\text{CH}_2-$ is located between the two carbonyl groups which are strongly electron withdrawing. The resulting anion (I) obtained by the removal of proton from $-\text{CH}_2-$ is very much resonance stabilized.





A methyl or primary carbocation is least stable. With the increase in the number of phenyl groups, the stability increases. In the benzylic cation, the positive charge on $\text{C}_6\text{H}_5\text{CH}_2^{\oplus}$ gets delocalized into the phenyl ring by resonance. In the case of diphenyl carbocation, there is greater delocalization due to two phenyl rings, whereas in the triphenylmethyl cation, there is still further delocalization and maximum stabilization.

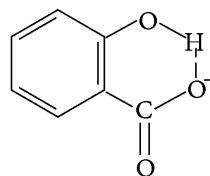
The various resonance structure for benzylic cation can be drawn as follows.



123. (i) Acidity of alcohol is increased by the presence of electron withdrawing groups and decreased by electron releasing groups. Among (i) and (ii), both $-\text{Br}$ and $-\text{OCH}_3$ are $-\text{I}$ groups. But since $-\text{Br}$ is more electron withdrawing than $-\text{OCH}_3$, (i) is more acidic.
- (ii) In $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{OH}$, bromine is on the γ -carbon whereas the bromine is on the β -carbon in $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CH}_2\text{OH}$ making the latter

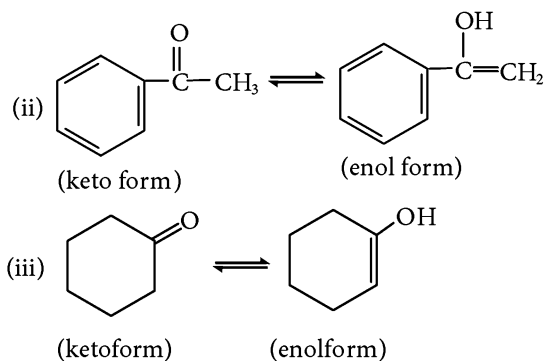
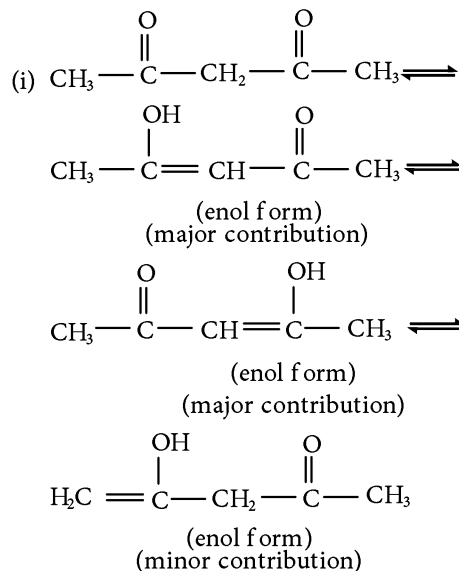
more acidic, since inductive effect decreases with distance.

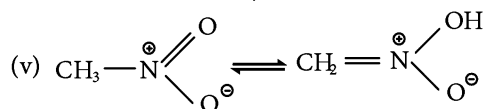
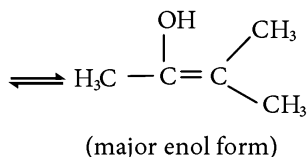
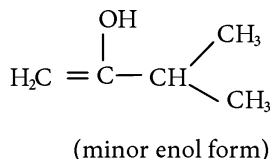
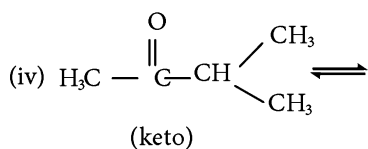
- (iii) Acidity of carboxylic acid depends on the stability of carboxylate ion. In p -cyanobenzoic acid, the carboxylate ion is resonance stabilized to a greater extent due to the presence of $-\text{CN}$ group. But there is no such extra stabilization for benzoic acid.
- (iv) Salicylic acid is more acidic than p -hydroxybenzoic acid because the anion obtained by the removal of H^+ is stabilized by intramolecular hydrogen bonding, which is not possible in the para isomer.



(intramolecular H-bonding in salicylic acid)

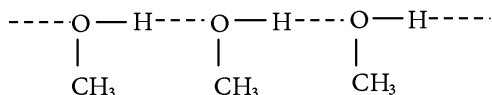
124. The enol forms are given below.



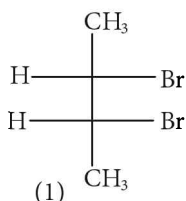


125. Methyl alcohol molecules can form intermolecular hydrogen bonding and get associated. This is due to the high electronegativity of oxygen. An associated molecule has always a higher boiling point.

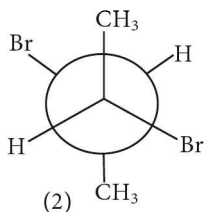
However, in the case of CH_3SH , there is no intermolecular hydrogen bonding involved, because of low electronegativity of sulphur. The molecules are free and independent. They have a lower boiling point. The associated form of methyl alcohol by hydrogen bonding can be represented as shown.



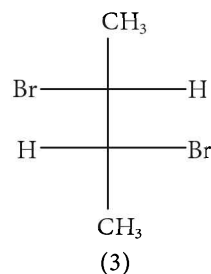
126.



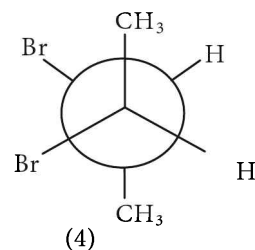
meso-2,3-dibromobutane (Fischer projection)



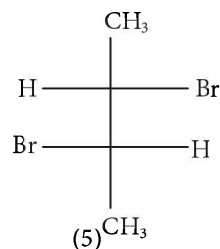
meso-2,3-dibromobutane
(staggered Newmann projection)



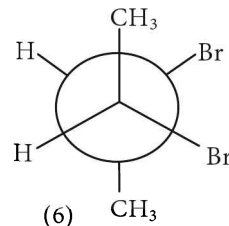
(-)-2,3-dibromobutane
(Fischer projection)



(-)-2,3-dibromobutane



(+)-2,3-dibromobutane
(Fischer projection)



(+)-2,3-dibromobutane
(staggered Newmann projection)

Structures (1), (3) and (5) are Fischer projections.

Structures (2), (4), (6) are staggered Newmann projection

Structures (1) and (2) are meso forms.

Structures (3) and (5) are the D and L forms.

Structures (4) and (6) are Newman projections of the (-) and (+) forms.

Structures (3) and (5) are enantiomers.

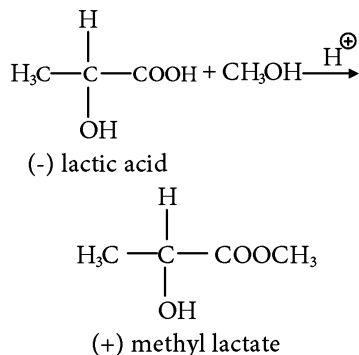
Structures (4) and (6) are enantiomers.

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Structures (1) and (3) are diastereomers.

Meso is optically inactive due to internal compensation.

127. The reaction can be represented as follows

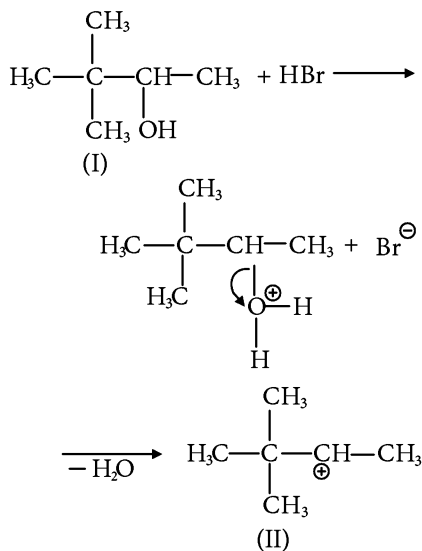


The configuration at the chiral centre is not changed during the esterification reaction. The reaction centre is only the carboxylate group where there is no chirality. The direction of rotation of the product is changed because it is a different molecule.

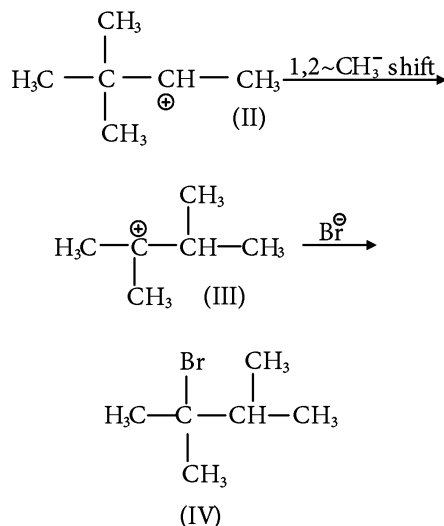
128. $\text{II} > \text{III} > \text{V} > \text{I} > \text{IV}$

Trichloro acetic acid (II) is 10,000 times stronger than acetic acid. This is because of the presence of three chlorine atoms in the α -position to the carboxylic group. The three chlorine atoms have powerful electron withdrawing inductive effects. The exactly opposite effect is shown by the three methyl groups in trimethyl acetic acid (IV), which is the weakest. The three methyl groups are electron releasing and thereby reduce the acidity.

129. The starting material is a secondary alcohol, (I). When (I) reacts with HBr, the first step in the reaction is the formation of a secondary carbocation (II).

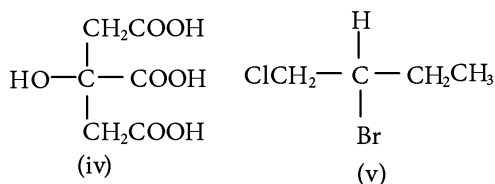
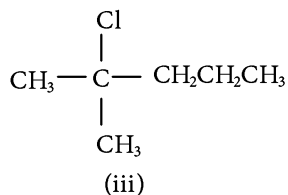
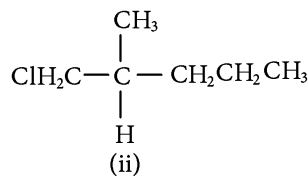
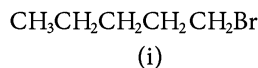


This secondary carbocation (II) rearranges to a more stable tertiary carbocation (III) by the 1,2-shift of a methyl group with a pair of electrons.



Now the bromide ion adds to the tertiary carbocation centre to form the product 2-bromo-2,3-dimethyl butane. The expected product 3,3-dimethyl-2-bromobutane is not formed as the initially formed secondary carbocation is comparatively less stable.

130. Compounds (ii) and (v) have chiral centres.



131. The main functional group is $-\text{COOH}$. Hence it is named as phenyl substituted propanoic acid.

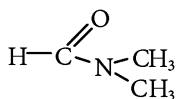
132. Longest carbon chain is chosen.

The substituents are suitably numbered. There are two ethyl substituents in the 5 and 6 position. There is an olefinic double in the long chain. Hence (d) is the correct name.

133. In $\text{Cl}_2\text{C} = \text{CCl}_2$, the hybridization of C is sp^2 while in CCl_4 the hybridization is sp^3 .

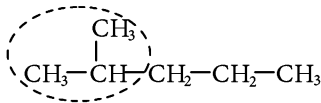
134. Formamide $\text{H}-\text{C}(=\text{O})\text{NH}_2$

N,N-DMF is N,N-Dimethyl formamide which is



135. The only compound that fits in with the description is (b)

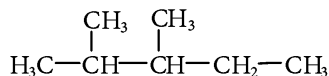
136. 2-Methylpentane is represented by the structure shown below.



This has only one isopropyl group as shown by the dotted circle. All the other compounds have either more than one isopropyl group or none.

137. (d) It is a bicyclic compound. As per IUPAC nomenclature, it is bicyclo[4.4.0]decane. Other common names are decalin and decahydro naphthalene.

138. 2,3-dimethylpentane



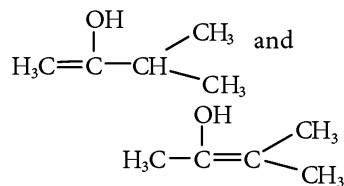
This compound has a chiral centre in carbon-3.

139. A mixture of 75% (+) mandelic acid and 25% (–) mandelic acid means a net 50% of (+) mandelic acid. So rotation is

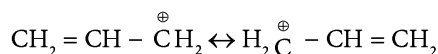
$$\frac{50 \times 158}{100} = +79^\circ$$

140. meso butane 2,3-diol is an internally compensated optically inactive compound. It cannot be resolved into (+) and (–) optically active forms. Hence statement (c) is not correct.

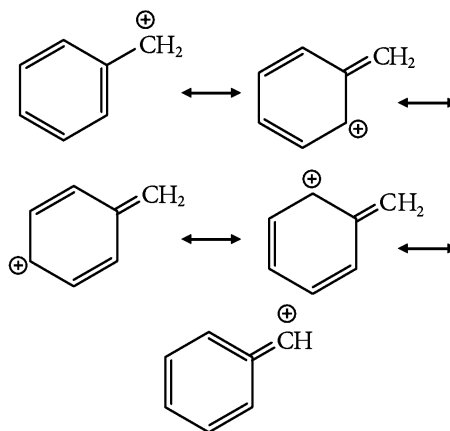
141. Methyl isopropyl ketone is one which can exist in more than one enolic form viz.,



142. Benzylic cation is more stable than an allylic cation because in an allylic carbocation, only two resonance structures are possible

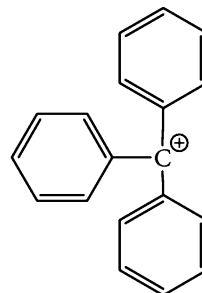


Whereas in a benzylic cation, four resonance structures are possible.



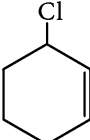
143. This structure is not permissible because it is not a valid Lewis structure, as nitrogen has five bonds around it and a positive charge. Nitrogen has 10 valence electrons around it.

144. Trityl is triphenyl methyl cation

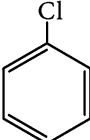


It is the most stable.

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145.  is known as 3-chlorocyclohexene and not as 2-chlorocyclohexene

146. They are geometrical isomers. In one structure, the two smaller groups namely hydrogen atoms are on the same side, while the other structure has the hydrogens located at opposite sides.

147.  In chlorobenzene, the carbon-chlorine bond acquires a partial double bond character by resonance. This is due to the lone pair of electrons from chlorine.

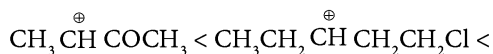
148. A free radical is formed in a homolytic cleavage. It is short lived and is paramagnetic. Free radicals are never found in ionic reaction.

149. They are two representation of the same compound, one is the Fischer projection of the compound, while the other is a Newmann projection in the staggered form.

150. A carbonyl group is an electron withdrawing group and so it destabilizes the cation to the maximum. Hence (III) is least stable.

A methoxy group is electron releasing and stabilizes the carbocation. Hence (IV) is most stable.

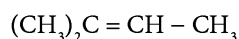
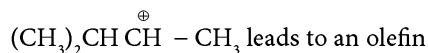
So the order is



151. The special stability of dicyclopropyl methyl carbocation is a result of conjugation between the bent orbitals of cyclopropyl rings and the vacant p-orbital of the cationic carbon.

152. The only correct statement is (iv). Other statements may be corrected as follows.

- (i) Removal of a proton from



- (ii) There is no hydrogen bonding in $\text{S} - \text{H} \cdots \text{S}$

- (iii) In any free radicals the number of electrons around the radical site is 7. (there are three bonds and one odd electrons)

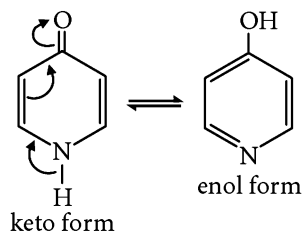
153. The strongest acid will have the lowest pK_a value. Among the acids given $\text{CH}_3\text{CCl}_2\text{COOH}$ is the strongest, hence its pK_a value is least.

154. $(\text{CH}_3)_3\text{C}^-$ is the least stable.

- (a) and (b) are stabilized by resonance

- (c) is stabilized by the electron withdrawing $-\text{NO}_2$ group.

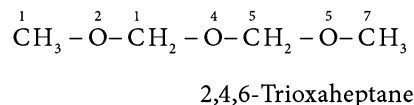
155. There is 1,5-shift of hydrogen due to conjugation and extra stability of the aromatic ring in the enol form of the above ketone. Enolization occurs as follow.



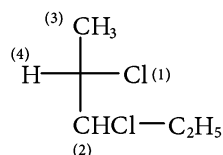
156. In benzylamine, the lone pair on nitrogen is localized. Hence it is most basic. In other structures, the lone pair gets delocalized either by resonance or by the electron withdrawing effect of the $-\text{NO}_2$ group.

157. Halogenation of alkanes is a photo chemical reaction. This involves a homolytic fission leading to free radicals.

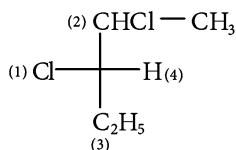
158. Long chain polyethers are named as oxaderivatives of the alkane corresponding to the total number of carbon and oxygen atoms present in the chain



159. Priority of groups at C-2 is



Priority of groups at C-3 carbon is

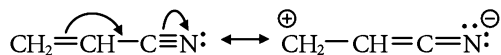


So the correct conjugational designation is 2(S), 3(S)

160. The strength of a hydrogen bond is between a covalent bond and van der Waals attraction. The magnitude of a H-bond is of the order $5 - 10 \text{ kcal mol}^{-1}$ depending on the electronegativity of the elements involved in H-bonding.

161. Fluorine is the most electronegative element and the H-bonding in which the hydrogen is linked to most electronegative atoms will be the strongest.

162. The resonance in (c) does not involve the lone pair on nitrogen



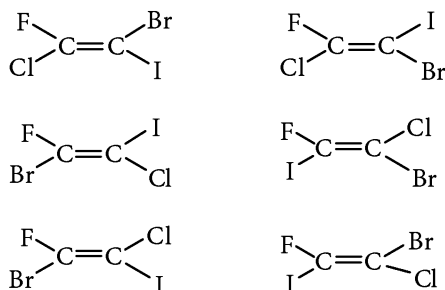
In all other structures, resonance involves the lone pair on nitrogen or oxygen.

163. $(\text{CH}_3)_3\text{CO}^-$ is not only a strong nucleophile, but also a strong base.

164. $\begin{array}{c} \text{Cl} \quad \text{Cl} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{H} \end{array}$ exhibits significant dipole moment

because the two chlorine atoms are on the same side of the double bond.

165. The six isomers are



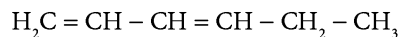
166. The only statement which is not correct is (a). It is not necessary that both the diastereomers have to be optically active. For example, a meso compound is not optically active, whereas its diastereomer is optically active.

Cis-trans geometrical isomers are also diastereomers and they are not optically active unless they have some chiral centres.

167. Specific rotation of the equilibrium mixture if the

$$\text{molar ratio is } 5 : 3 = \frac{5(+40) + 3(-40)}{8} = +10^\circ$$

168. Since the heat of hydrogenation is less than 2×127 , it is clear that the diene has extra stabilization due to resonance. i.e., the diene must be a conjugated diene. So it must be hexa-1,3-diene



169. (b) is most stable as this is resonance stabilized by extended conjugation with the phenyl ring.

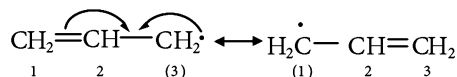
170. Resonance is responsible for the decrease of dipole moment. The C - Cl bond assumes a partial double nature due to delocalization of lone pair of electrons towards carbon of the C = C double bond.

171. Statement (1) is not correct while statement (2) is correct.

$\text{CH}_3\text{CH}_2\text{CH}_2^\bullet$, n-propyl radical is not stabilized by resonance. It can either dimerize or propagate by chain reaction mechanism.

On the other hand, allyl radical,

$\text{CH}_2=\text{CH}-\text{CH}_2^\bullet$, though a primary radical is stabilized by resonance and the radical site can reside on C-3 and C-1 as shown.



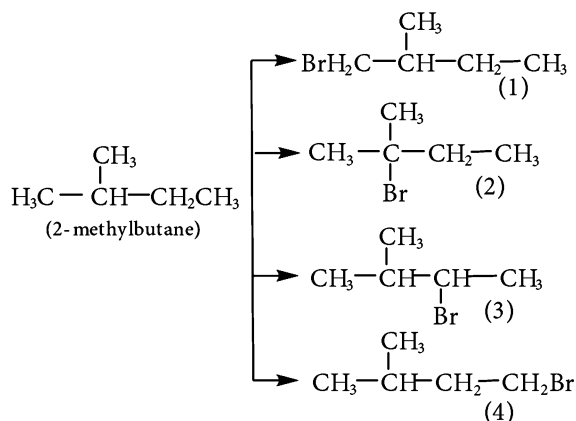
So an allyl radical is more stable, by resonance.

Hence statement (1) is not correct, while statement (2) is correct.

172. Both statements (1) and (2) are correct, but statement (2) is not the explanation of statement (1). Stereoisomers which are not mirror images of each other are called diastereomers. Even geometrical isomers are diastereomers.

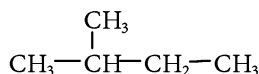
In the case of optically active compound, diastereomers are possible only if the compound contains more than one chiral carbon atoms

173. Statement 1) is correct, while statement (2) is not correct. When 2-methylbutane undergoes monobromination, four monobrominated products are possible as shown (1) - (4)



Out of these (1) and (3) have chiral centres and are optically active. A compound having one chiral centre can produce one enantiomeric pair of *d* and *l* forms. So statement (1) is correct.

The starting material which is 2-methylbutane, has no chiral centre.



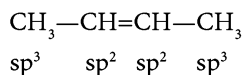
174. Both statements are correct and statement (2) is the reason for the formation of ions mentioned in statement (1).

The other ions that can be formed by the heterolytic fission of C – C bond in propane are $\text{CH}_3-\text{CH}_2^+$ and CH_3^+ . But these ions are less stable compared to $\text{CH}_3-\text{CH}_2^+$ and CH_3^+ .

175. Both statements (1) and (2) are correct and statement (2) provides an explanation for statement (1).

Since the two double bonds are in different planes, the atoms or groups attached to the two sp^2 hybridized carbon atoms are not in the same plane. So the molecule is chiral and shows optical isomerism.

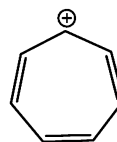
176. Statement (1) is correct, but statement (2) is wrong. The end carbon atoms of but-2-ene are sp^3 hybridized.



Statement (1) is correct because the C – C bonds of the end methyl groups are formed by the sp^2-sp^3 overlap of orbitals. So all the carbon atoms are in the same plane. But the hydrogen atoms of methyl group are not in the same plane.

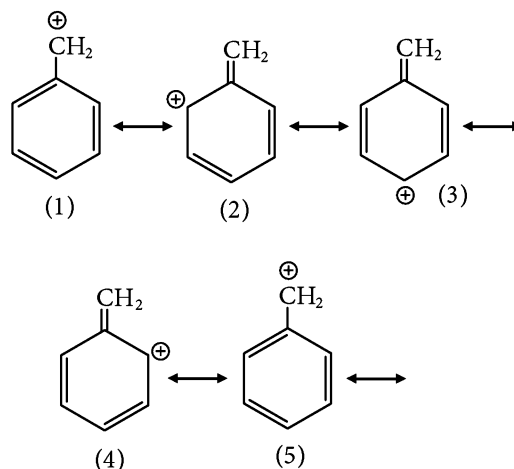
177. Both statements (1) and (2) are correct. However, statement (2) is not the correct explanation for statement (1).

The tropylium ion is C_7H_7^+ is represented as follows



The positive charge on the tropylium ion can get delocalized in the ring and it is aromatic (Huckel's rule).

There is resonance stabilization in the case of benzylic cation also. However, except in two structures which are Kekule structures in the remaining three structures, the aromaticity of the ring is destroyed and consequently the stability is reduced.



Hence statement (1) is correct, but statement (2) is not an explanation for statement (1).

The benzylic cation undergoes ring expansion by rearrangement to give tropylium cation.

178. Both statements (1) and (2) are correct, and statement (2) is supportive of statement (1).

The effect of intramolecular H-bonding in o-nitrophenol is that its boiling point is reduced and steam volatility is increased. So o-nitrophenol is steam volatile.

In the case of p-nitrophenol, intramolecular H-bonding is not possible, but intermolecular H-bonding exists. The molecules are strongly held together by intermolecular H-bonding. Hence it is not steam volatile.

So both the statements (1) and (2) are correct and (2) is supportive of (1).

179. Statement (1) is correct while statement (2) is not correct.

p-nitrobenzoic acid is a stronger acid than benzoic acid. This is because of the strong electron withdrawing nature of the $-\text{NO}_2$ group.

The increase in acidity is due to the combined resonance and inductive effect of the para nitro group which act in the same direction, p-methyl benzoic acid is a weaker acid than benzoic acid because of the electron donating nature of CH_3 group. So statement (1) is correct.

Statement (2) is not correct. The acidity of substituted benzoic acids vary, increases or decreases, depending on the nature of the substituents, whether they are electron releasing or attracting.

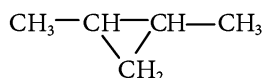
180. Both statements (1) and (2) are correct. However statement (2) does not provide a suitable explanation for statement (1).

Chloral is trichloroacetaldehyde which is Cl_3CCHO . A molecule of water adds readily to give chloral hydrate. Chloral hydrate is a stable crystalline substance. Its stability is due to the electron-withdrawing character of CCl_3 group.

DDT is prepared by heating chlorobenzene and chloral in presence of $\text{con.H}_2\text{SO}_4$.

Hence statement (2) is also correct, although it does not support the statement (1).

181. A carbene inserts across a double bond to produce a three membered ring as shown.



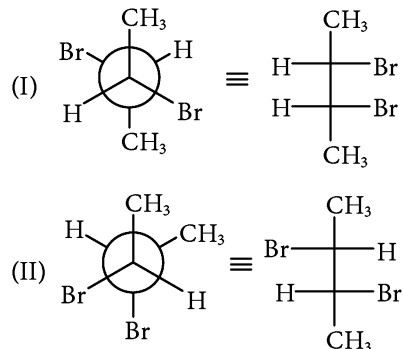
182. The only correct statement is that cyanide ion can behave as an ambident nucleophile. It can get linked either through carbon or through nitrogen.

183. The correct order of base strength is exactly reverse of the order indicated in (a). HI is the strongest acid and hence I^- is the weakest base.

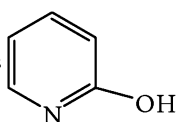
184. They are not related as isomers. They do not have the same molecular formula.

185. A stereoisomer is said to be the threo form when similar groups are anti to each other. An erythro form is one in which two similar groups are on the same side.

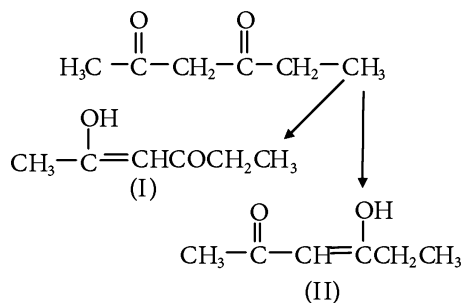
186. When structures (I) and (II) are converted to Fischer forms they appear as follows.



They are diastereomers

187. The enol form is 

188. 2,4 hexanedione gives two enol forms, viz.,



When the two enols (I) and (II) are subjected to ozonolysis, they give different products, namely

- (i) $\text{CH}_3-\text{C}(\text{OH})=\text{CH}-\text{COCH}_2\text{CH}_3$ will give while CH_3COOH and $\text{CH}_3\text{CH}_2\text{COCHO}$
- (ii) $\text{CH}_3-\text{C}(=\text{O})-\text{CH}=\text{C}(\text{OH})\text{CH}_2\text{CH}_3$ will give CH_3COCHO and $\text{CH}_3\text{CH}_2\text{COOH}$ as final products.

189. They are resonance pairs and not tautomeric pairs.

190. Acetic acid is a stronger acid than ethyl alcohol. So the conjugate base of acetic acid namely CH_3COO^- is weaker than the conjugate base of ethyl alcohol namely ethoxide ion ($\text{C}_2\text{H}_5\text{O}^-$).

HF has a higher boiling point because of intermolecular hydrogen bonding.

1.104 Basics of Organic Chemistry

Tartaric acid has three optical isomers; two of which are optically active and the third is optically inactive. So statement (c) is not correct. C_3H_7CN or $CH_3 - CH_2 - CH_2 - CN$ is propyl cyanide. Its IUPAC name is butanenitrile.

191. (a) has sp , (b) has sp^2 and (c) has sp^3 hybridized carbons.

Only (d) has two different types of hybridized carbon atoms sp^2 and sp

192. Only (a) and (b) are named correctly.

For (c) the correct name is 3-chlorocyclohexane carbaldehyde.

For (d), the correct name is 3,5-dimethylheptane.

193. In (a), (c) and (d), the correct order is shown.

In (b) $(CH_3)_3\ddot{P}$ is a better nucleophile compared to $(CH_3)_3\ddot{N}$.

194. In the first three reactions, new chiral centres are generated

195. Singlet carbene does not contain unpaired electron. So it is not paramagnetic.

196. Carbanions are not stabilized by hyperconjugation. Substituted alkenes are stabilized by hyperconjugation, but that is not isovalent hyperconjugation because the total number of bonds are not identical in the Lewis structure and hyperconjugative structures.

197. $\ddot{N}H_3$ and $\overset{\oplus}{C}H_3$ are triangular planar.

CHAPTER

2

ALKANES, ALKENES AND ALKYNES

■■ CHAPTER OUTLINE

Preview

STUDY MATERIAL

Introduction

Preparation of alkanes, alkenes, alkynes

Physical properties of alkanes, alkenes and alkynes

Reactions of alkanes

Reactions of alkenes

Reactions of Alkynes

Estimation of elements

Empirical and molecular formulae of simple compounds

- Concept Strands (1–4)

TOPIC GRIP

- Subjective Questions (10)
- Straight Objective Type Questions (5)
- Assertion–Reason Type Questions (5)
- Linked Comprehension Type Questions (6)

- Multiple Correct Objective Type Questions (3)
- Matrix-Match Type Question (1)

IIT ASSIGNMENT EXERCISE

- Straight Objective Type Questions (20)
- Assertion–Reason Type Questions (31)
- Linked Comprehension Type Questions (31)
- Multiple Correct Objective Type Questions (31)
- Matrix-Match Type Question (1)

ADDITIONAL PRACTICE EXERCISE

- Subjective Questions (10)
- Straight Objective Type Questions (40)
- Assertion–Reason Type Questions (10)
- Linked Comprehension Type Questions (9)
- Multiple Correct Objective Type Questions (8)
- Matrix-Match Type Questions (3)

INTRODUCTION

Hydrocarbons are the simplest organic compounds made up of only two elements, carbon and hydrogen. Open chain or aliphatic hydrocarbons are divided into three classes: alkanes, alkenes and alkynes. The alkanes or the saturated hydrocarbons have the general formula C_nH_{2n+2} .

Alkenes are unsaturated aliphatic hydrocarbons containing a double bond in their structure. They have the general formula C_nH_{2n} . The alkenes are also known as olefins.

The alkynes are also unsaturated hydrocarbons, but they contain a triple bond. The alkynes have the general formula C_nH_{2n-2} .

A series of similarly constituted organic compounds that can be represented by a general formula and in which the neighbouring members differ by $-CH_2$ unit in their molecular formula is known as a homologous series. The hydrocarbons alkanes, alkenes and alkynes form three different homologous series.

Few typical examples of the representatives of each homologous series are given below.

Alkanes (C_nH_{2n+2})

Table 2.1

Name	Molecular	Structural formula
Methane	CH_4	CH_4
Ethane	C_2H_6	CH_3CH_3
Propane	C_3H_8	$CH_3CH_2CH_3$
n - Butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$
Isobutane	C_4H_{10}	$\begin{array}{c} CH_3 \\ \\ CH_3-CH-CH_3 \end{array}$
n - Pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$
Isopentane	C_5H_{12}	$\begin{array}{c} CH_3 \\ \\ CH_3-CH-CH_2-CH_3 \end{array}$
Neopentane	C_5H_{12}	$\begin{array}{c} CH_3 \\ \\ H_3C-C-CH_3 \\ \\ CH_3 \end{array}$

Alkenes (C_nH_{2n})

Table 2.2

Name	Molecular formula	Structural formula
Ethene	C_2H_4	$H_2C=CH_2$
Propene	C_3H_6	$CH_3CH=CH_2$
Butene	C_4H_8	$CH_2=CHCH_2CH_3$ (But-1-ene)
		$\begin{array}{c} CH_3 \quad \quad CH_3 \\ \diagdown \quad \diagup \\ C=C \\ \diagup \quad \diagdown \\ H \quad \quad H \end{array}$ (cis-but-2-ene)
		$\begin{array}{c} CH_3 \quad \quad H \\ \diagdown \quad \diagup \\ C=C \\ \diagup \quad \diagdown \\ H \quad \quad CH_3 \end{array}$ (trans-but-2-ene)

Cis-but-2-ene and trans-but-2-ene are geometrical isomers

Pentene	C_5H_{10}	$CH_2=CHCH_2CH_2CH_3$ (pent-1-ene)
		$\begin{array}{c} CH_3 \quad \quad CH_2CH_3 \\ \diagdown \quad \diagup \\ C=C \\ \diagup \quad \diagdown \\ H \quad \quad H \end{array}$ (cis-pent-2-ene)
		$\begin{array}{c} CH_3 \quad \quad H \\ \diagdown \quad \diagup \\ C=C \\ \diagup \quad \diagdown \\ H \quad \quad CH_2CH_3 \end{array}$ (trans-pent-2-ene)

Alkynes (C_nH_{2n-2})

Table 2.3

Name	Molecular formula	Structural formula
Ethyne	C_2H_2	$HC\equiv CH$
Propyne	C_3H_4	$H_3C-C\equiv CH$
Butyne	C_4H_6	$HC\equiv C-CH_2-CH_3$ (But-1-yne)
		$H_3C-C\equiv C-CH_3$ (But-2-yne)

PREPARATION OF ALKANES, ALKENES, ALKYNES

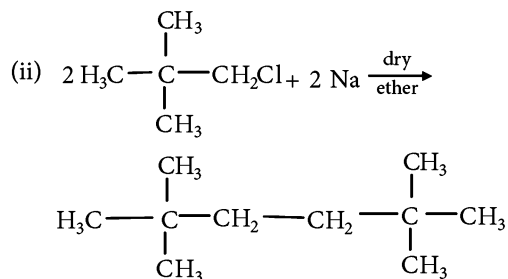
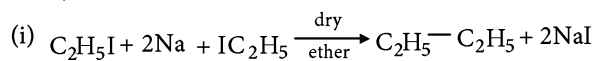
Preparation of alkanes

(1) Wurtz reaction

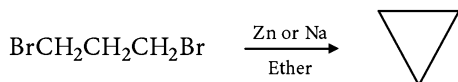
When an alkyl halide (preferably bromide or iodide) is treated with sodium in dry ether, an alkane containing twice the number of carbon atoms present in the alkyl halide is obtained. This is known as Wurtz reaction. Only primary and secondary alkyl halides give good yield of the alkane in Wurtz reaction while the tertiary halides will undergo mainly elimination to give an alkene. Wurtz reaction is suitable only for the preparation of symmetrical alkanes with even number of carbon atoms. The reaction proceeds by a free radical mechanism.

Wurtz reaction is also known as dehalogen coupling. Side reactions like elimination and rearrangement are very common.

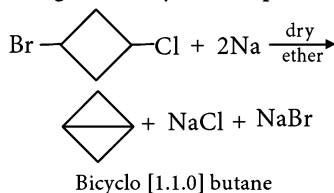
Examples of Wurtz reaction are



(iii) Wurtz reaction is also useful in the closing of small rings. For example, 1,3-dibromopropane, $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{Br}$, can be converted to cyclopropane by treatment with Zn or Na



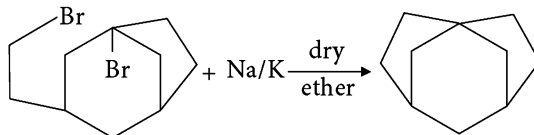
(iv) The reaction of 1-bromo-3-chloro cyclobutane with metallic sodium in the presence of dry ether or dioxane gives a bicyclic compound.



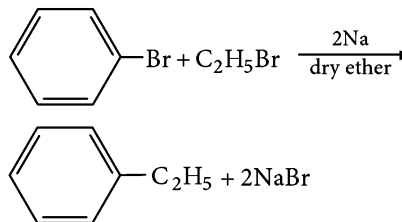
(v) An attempt to synthesize an unsymmetrical molecule like $(\text{CH}_3)_3\text{C—CH}_2\text{CH}_2\text{CH}_3$ by Wurtz synthesis starting

with $(\text{CH}_3)_3\text{C—CH}_2\text{Cl}$ and $\text{CH}_3\text{CH}_2\text{Br}$ in the presence of sodium and dry ether leads to three products, namely, $(\text{H}_3\text{C})_3\text{C—CH}_2\text{CH}_2\text{C}(\text{CH}_3)_3$, $(\text{CH}_3)_3\text{C—CH}_2\text{—CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$.

(vi) The synthesis of a highly strained molecule by Wurtz synthesis has been reported as shown.



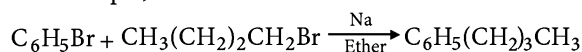
(vii) A useful extension of Wurtz reaction is Wurtz-Fittig reaction. In this process, an alkyl and an aryl halide are treated with sodium to give an alkylbenzene.



Ethylbenzene

The advantage of Wurtz-Fittig reaction is that long n-side chain can be introduced.

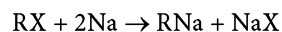
For example,



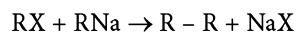
Mechanism of Wurtz reaction

There are two basic steps in the mechanism.

The first step is a halogen-sodium exchange to give an organometallic compound.



In many cases organometallic compound RNa has been isolated. In the second step, the organometallic compound reacts with a second molecule of the alkyl halide to give the alkane.



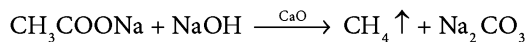
(2) Decarboxylation reactions—Soda lime fusion

The process of eliminating CO_2 from a carboxylic acid is termed as decarboxylation. Normally, a mixture of NaOH and CaO , known as soda lime, is used for decarboxylation of free acids.

2.4 Alkanes, Alkenes and Alkynes

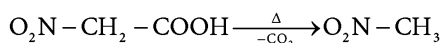
Many carboxylic acids, as a free acid or preferably in the form of a sodium salt, undergo decarboxylation to give hydrocarbons.

For example, sodium acetate CH_3COONa on heating with soda lime gives methane, CH_4 .

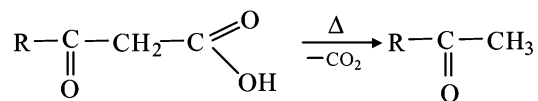


Carboxylic acids having an electron withdrawing substituent like carbonyl group at β -position undergo facile decarboxylation due to the formation of six membered transition state.

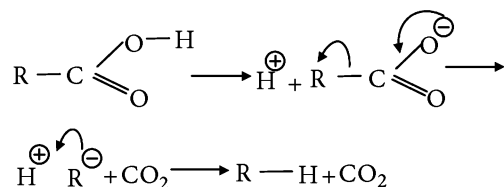
Nitroacetic acid undergoes decarboxylation to give nitromethane.



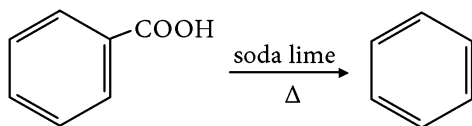
A β -keto acid undergoes facile or easy decarboxylation to give a methyl ketone.



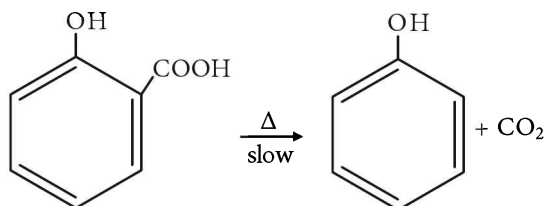
Mechanism of decarboxylation of sodium salts of carboxylic acids and free carboxylic acids to give alkane has been shown as follows.



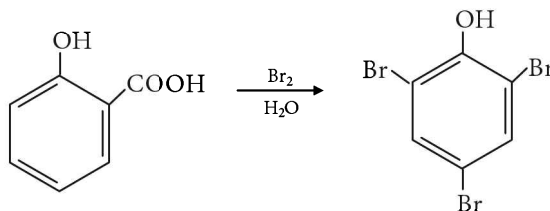
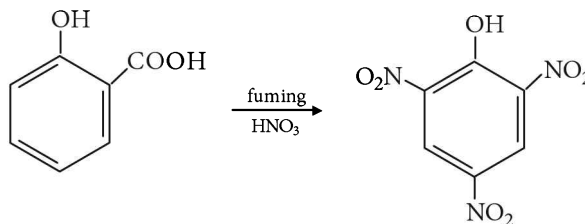
When benzoic acid is heated with soda lime, benzene is obtained.



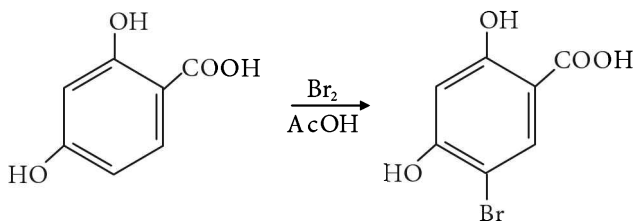
Salicylic acid when heated slowly undergoes decarboxylation to give phenol.



A very interesting instance of decarboxylation has been reported in the case of salicylic acid in the following two examples.

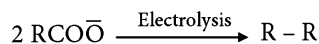


The above decarboxylations occur only in aqueous medium, but when acetic acid is used as solvent, carboxyl group is retained.



(3) Kolbe's electrolytic method

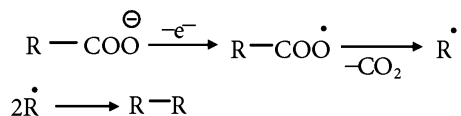
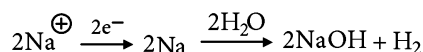
In this method, a concentrated solution of sodium or potassium salt of a carboxylic acid is subjected to electrolysis. Electrolysis results in decarboxylation, followed by a recombination of the radicals to give a hydrocarbon.



The reaction is successful when R is alkyl and not aryl.

A free radical mechanism has been proposed as given below.

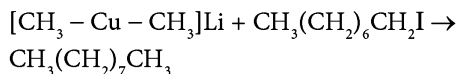
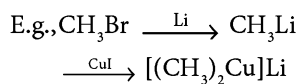
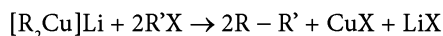
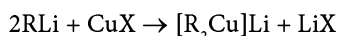
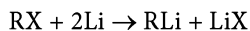
Alkane and CO_2 are liberated at the anode and H_2 is set free at the cathode. Electrolysis of HCOONa does not produce any hydrocarbon but forms only CO_2 and H_2 . Platinum electrodes are used and the yield is increased when DMF (Dimethylformamide) is used as a solvent.

Anode reaction**Cathode reaction**

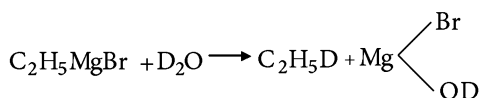
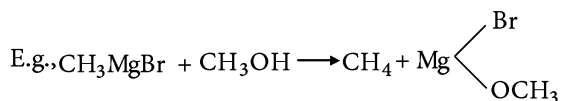
Kolbe's electrolytic decarboxylation is used for the formation of symmetrical dimers. This process is known as electrolytic decarboxylative dimerization.

(4) Corey House synthesis

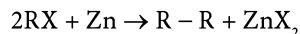
Corey House synthesis can be used for the preparation of alkanes with odd as well as even number of carbon atoms. In this reaction an alkyl halide is first treated with lithium metal in dry ether to form alkyl lithium which is then allowed to react with cuprous iodide to form lithium dialkyl copper. This is then treated with a suitable alkyl halide to get the desired alkane.

**(5) From Grignard reagents**

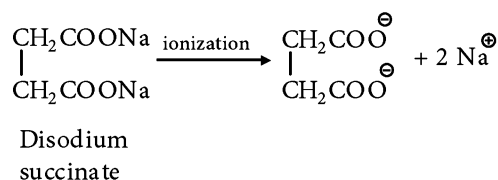
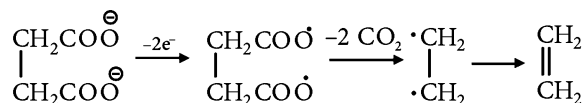
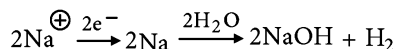
Grignard reagents (alkyl or aryl magnesium halides) react with compounds having active hydrogen like H_2O , alcohols, carboxylic acids, sulphonic acids, amines, ammonia etc., to form the corresponding hydrocarbons.

**(6) Frankland reaction**

Alkyl halides when heated with zinc dust in presence of dry solvent form alkanes with even number of carbon atoms.

**Preparation of alkenes****(1) Kolbe's electrolysis**

When solutions of sodium or potassium salts of a dicarboxylic acid like succinic acid is electrolyzed, ethylene is formed.

**Anode reaction****Cathode reaction****(2) Elimination reactions**

An elimination reaction is the process of removal of atoms or groups from a molecule to form products with multiple bonds. Unsaturated compounds are made by elimination reactions.

Alkenes are prepared by dehydration of alcohols or dehydrohalogenation of alkyl halides by elimination reactions.

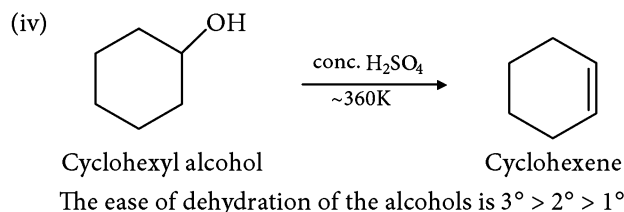
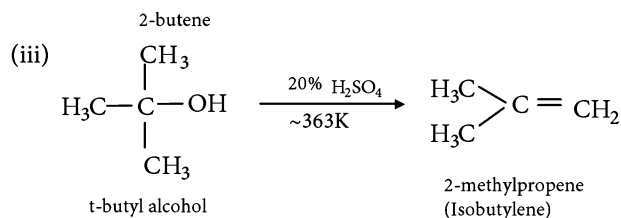
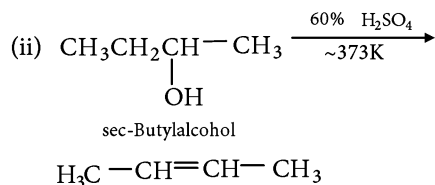
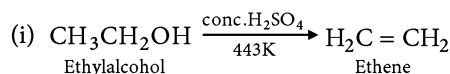
(i) Dehydration of alcohols

An alcohol is converted to an alkene by dehydration. The elimination involves the removal of a molecule of water.

Experimentally the dehydration is carried out either by heating the alcohol with concentrated sulphuric acid or phosphoric acid or by passing the alcohol vapours over a catalyst like Al_2O_3 , ThO_2 at high temperatures.

2.6 Alkanes, Alkenes and Alkynes

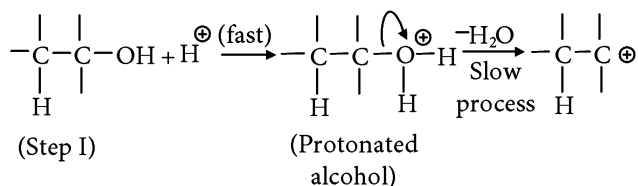
Examples of dehydration of alcohols



Mechanism of dehydration of alcohols

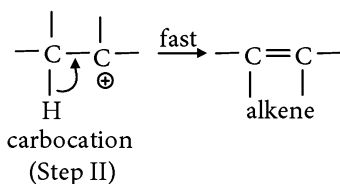
The reaction proceeds by a unimolecular elimination (E1) mechanism. It follows first order kinetics. E1 involves two steps.

In step I, the protonated alcohol undergoes a slow process of heterolysis to give a carbocation.



So, the first step is a fast acid base reaction between the alcohol and the catalyzing acid (mineral acid) to give a protonated alcohol, which is followed by a slow heterolysis to form a carbocation and water.

In step II which is a fast step, there is a rapid elimination of a proton from the carbocation, to form the product alkene.

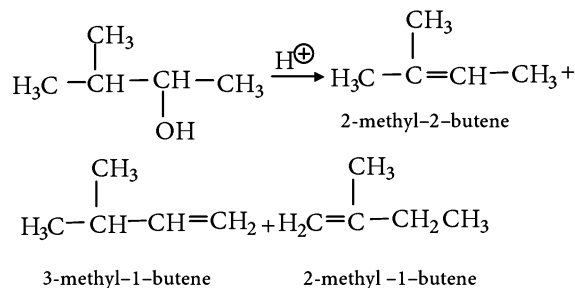


Evidence for unimolecular elimination (E1) mechanism

The reaction follows first order kinetics and there is no primary hydrogen isotope effect. The reaction involves rearrangements.

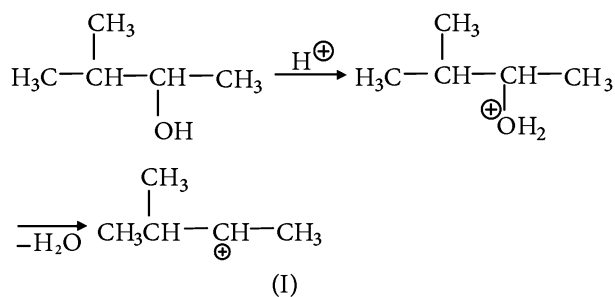
Rearrangements in E1 mechanism

When 3-methyl-2-butanol undergoes elimination, a mixture of three products are obtained. This has been explained due to the occurrence of rearrangements.

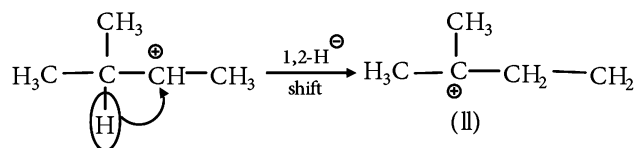


A mechanistic explanation has been given to explain the formation of the three alkenes

The first step yields a carbocation after initial protonation of the alcohol.

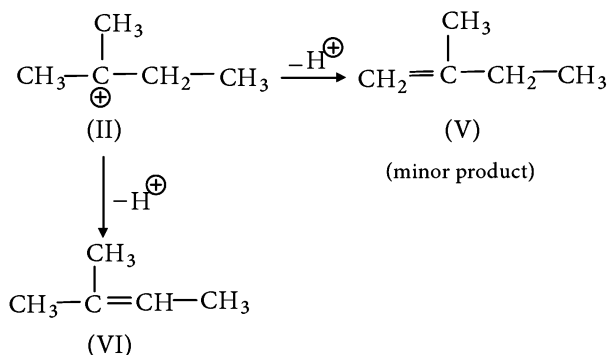
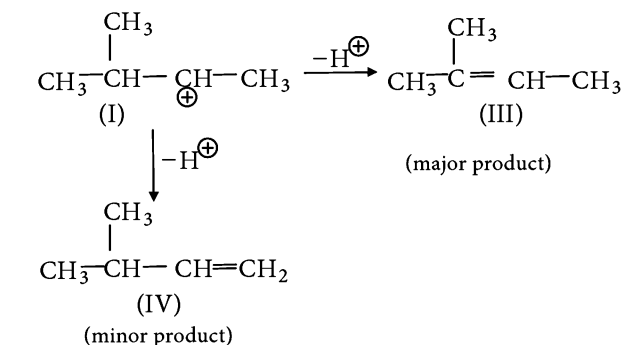


Now the carbocation (I) can undergo a rearrangement to give cation (II).



The rearranged carbocation (II) is formed from (I) by the migration of a hydride ion from the adjacent carbon to form a more stable tertiary cation.

Three different olefins can be obtained by the loss of a proton from cations I and II.



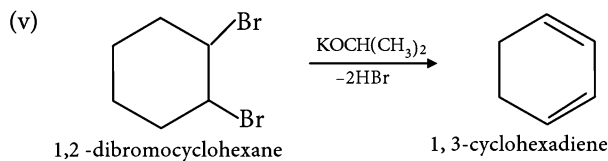
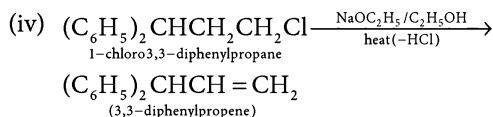
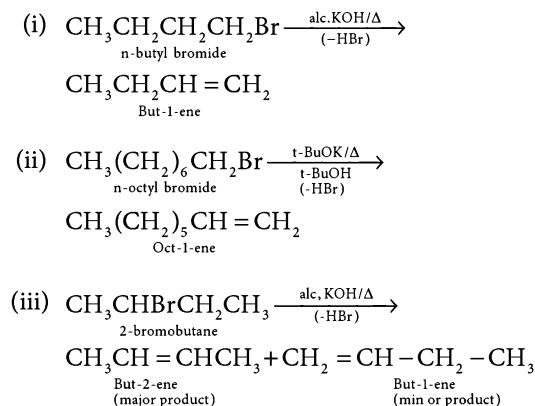
But (III) and (VI) are the same. Hence only three different olefins can be formed effectively in these reactions.

(ii) Dehydrohalogenation of alkyl halides

Alkenes can be prepared by the elimination reactions from alkyl halides by the removal of hydrogen halide.

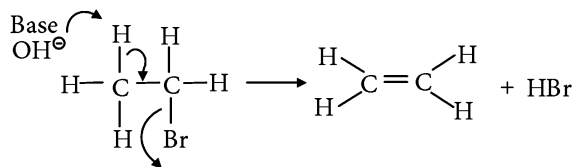
Dehydrohalogenation reactions are usually carried out making use of alkoxides or bases at elevated temperatures. Dehydrohalogenation of 1° and 2° alkyl halides proceed by a bimolecular (E2) mechanism.

Examples of dehydrohalogenation reactions



Mechanism of E2 elimination

Both the substrate and the base participate in a single step of a bimolecular 1,2-elimination. As the base removes a proton from the adjacent carbon atom, the leaving group, namely the halide ion, departs from the first carbon atom.



E2 elimination is a concerted process. A kinetic isotopic effect is observed in the E2 elimination process. Reaction kinetics is typically second order.

Orientation of elimination reaction

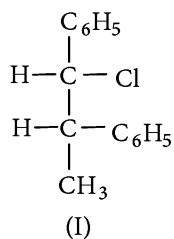
Generally eliminations are 1,2-eliminations (β -eliminations). This means that the hydrogen abstracted by the base is on the β -carbon with respect to the leaving group, which is a halide ion.

It is also observed that in E2 eliminations, the β -hydrogen departs from the opposite side of the molecule with respect to the leaving halide group.

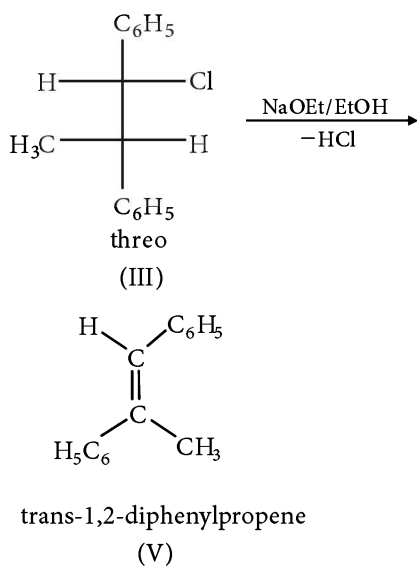
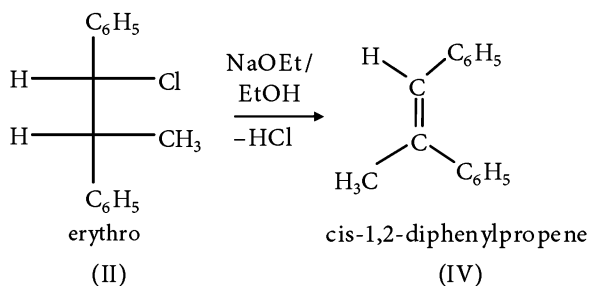
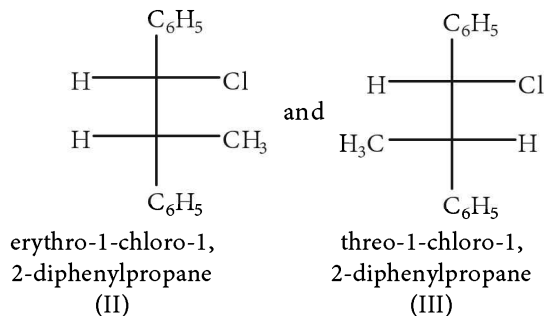
The molecule assumes a conformation in which the two leaving groups are located in the opposite directions but on the same plane. Such a type of spatial arrangement is known as **antiperiplanar**. In other words, bimolecular elimination takes place smoothly from the antiperiplanar conformation. This can be illustrated by means of the following example.

The elimination of HCl from 1-chloro-1,2-diphenylpropane (I) using sodium ethoxide in ethanol leads to two isomers of 1,2-diphenylpropene (IV and V)

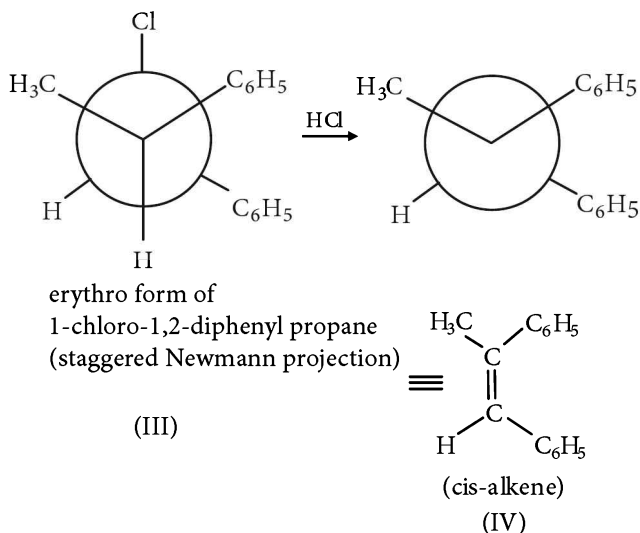
2.8 Alkanes, Alkenes and Alkynes



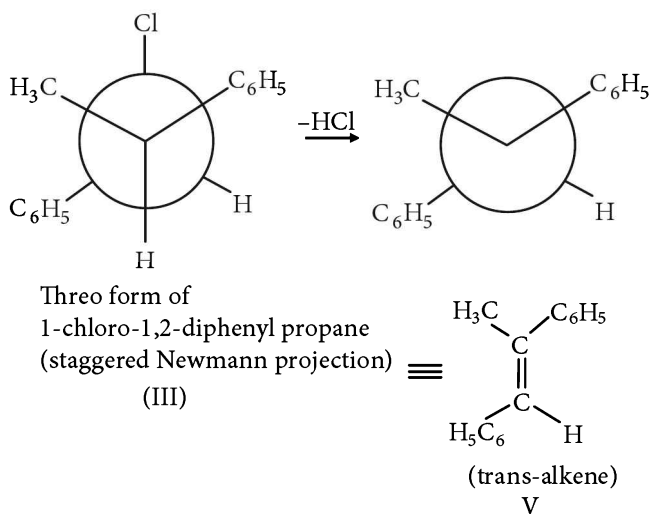
This compound (I) can exist in two stereochemical forms namely erythro and threo (II) and (III).



This can be illustrated by their respective Newmann projections. They assume the conformation in which H and Cl to be eliminated are anti to each other



Thus erythro isomer on dehydrohalogenation gives cis-1,2-diphenylpropene (IV)



Threo isomer on dehydrohalogenation gives trans-1,2-diphenylpropene (V)

Rules of elimination (Direction of elimination)

There are two rules of elimination.

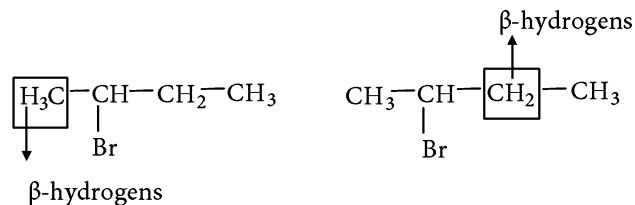
- Saytzeff rule
- Hofmann rule

(i) Saytzeff rule

Whenever an alcohol undergoes dehydration or an alkyl halide undergoes dehydrohalogenation, the most substituted alkene is obtained as the major product.

Many compounds may have more than one β -type hydrogen, which can be lost in an elimination.

For example, in 2-bromobutane, there are two types of β -hydrogens available.

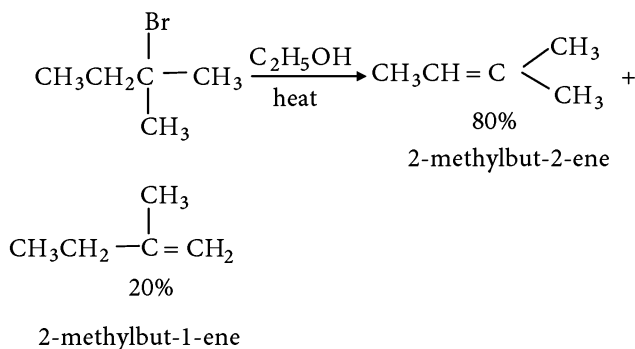


If one β -hydrogen of the end methyl group is lost, then the product formed will be but-1-ene, $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_3$ (less substituted olefin).

If one of the β -hydrogens of the $-\text{CH}_2-$ group is lost, an internal alkene is formed, namely, but-2-ene, $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$ (more substituted alkene).

According to Saytzeff rule, the more substituted olefin is the major product. In the above example, but-2-ene is formed as the major product.

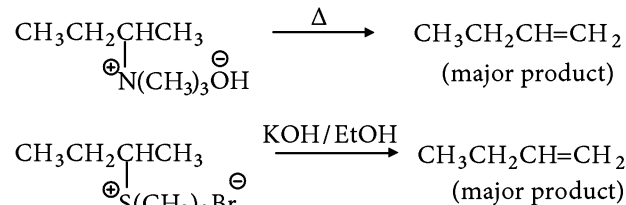
Similarly, 2-Bromo-2-methylbutane on dehydrohalogenation gives 2-methylbut-2-ene as the major product and 2-methylbut-1-ene as the minor product.



(ii) Hofmann elimination (Hofmann's rule)

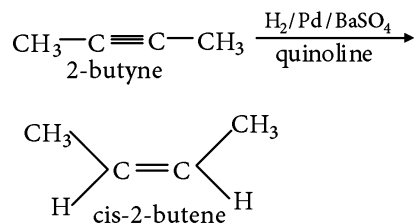
When salts like quaternary ammonium hydroxide or sulphonium halides undergo elimination, a less substituted olefin is obtained as the major product. This is known as Hoffmann's rule of elimination.

Examples:

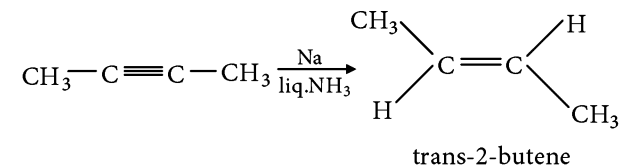


(iii) Reduction of alkynes

Alkynes can be partially reduced to cis alkene by using Lindlar's catalyst (which is H_2 and Pd on solid CaCO_3 or BaSO_4 , deactivated or poisoned with sulphur or quinoline or palladized charcoal partially deactivated with sulphur or quinoline). The addition of hydrogen to alkyne is syn addition.



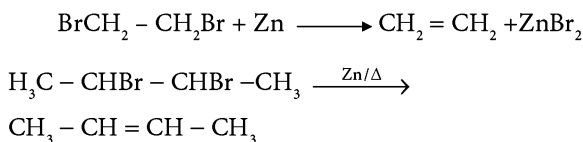
Alkynes can also be reduced partially to trans alkene by reducing with sodium and liquid ammonia. LiAlH_4 also reduces alkynes to trans alkenes.



(3) Reaction with zinc dust

1,2-dihalo compounds form alkenes when heated with zinc dust and methanol

For example

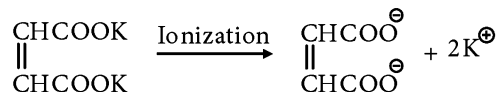


2.10 Alkanes, Alkenes and Alkynes

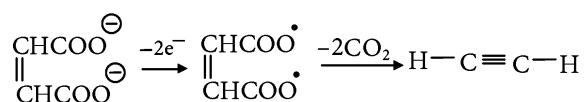
Preparation of alkynes

(1) Kolbe's electrolysis

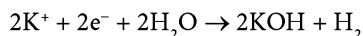
Electrolysis of potassium or sodium salt of an unsaturated acid like maleic or fumaric acid produces acetylene.



Anode reaction

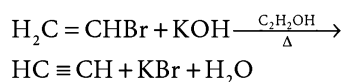
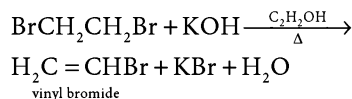


Cathode reaction



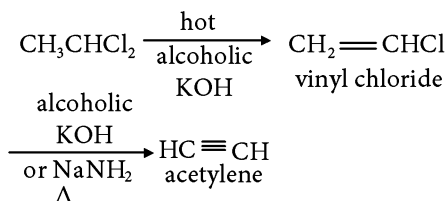
(2) Elimination reactions

- (i) Ethylene dibromide on reaction with ethanolic NaOH or KOH gives acetylene. The reaction proceeds in two steps, giving vinyl bromide in the first step, which then undergoes further elimination to give acetylene.

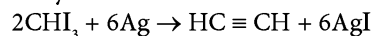


NaNH₂ in liquid NH₃ can also be used in place of alcoholic KOH solution to give a better yield of the product.

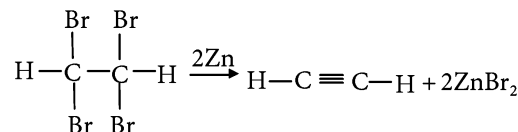
- (ii) Ethylidene chloride CH₃CHCl₂ on reaction with hot alcoholic KOH leads to acetylene.



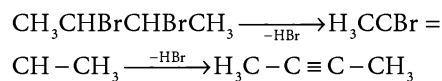
- (iii) Iodoform (CHI₃) on heating with Ag powder gives acetylene.



- (iv) α, α, β, β-tetrahalo alkanes form alkynes when treated with zinc dust and methanol

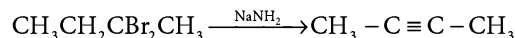


- (v) Alkynes of the type H₃CC≡CCH₃ can be prepared from vicinal dibromides.

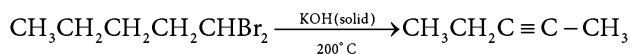


The double dehydrohalogenation can occur either by means of NaNH₂ or hot alcoholic KOH.

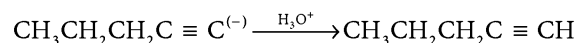
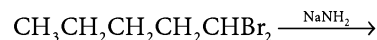
- (vi) A gem dihalide like CH₃CH₂CB₂CH₃ can undergo a double dehydrohalogenation to give an alkyne.



- (vii) 1,1-Dibromopentane can be treated with hot solid KOH to give 2-pentyne, an internal alkyne.



The initially formed terminal alkyne rearranges to give an internal alkyne. 1,1-dibromopentane can also be treated with NaNH₂ to give a terminal alkyne as shown.



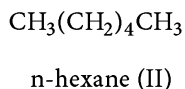
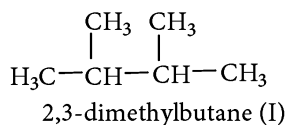
PHYSICAL PROPERTIES OF ALKANES, ALKENES AND ALKYNES

Melting point and boiling point

Alkanes are non polar and insoluble in water because they do not possess polar groups which can participate either in hydrogen bonding or in dipole-dipole interactions with water.

The boiling points of straight chain alkanes increase with increase in molecular mass. Among isomeric alkanes, the branched chain isomer has lower boiling point than the corresponding straight chain alkane

For example, 2,3-dimethylbutane (I) has a lower boiling point than n-hexane (II).



This is because (I) has a more compact structure and less surface area and as a result has weaker intermolecular van der Waals forces. The boiling point of n-hexane is 69°C and 2,3-dimethylbutane is 58°C.

The first four alkanes are colourless gases (C_1 to C_4), and the next thirteen (C_5 – C_{17}) are liquids and the higher members are solids. The only attractive forces observed in alkanes are the weak van der Waals forces.

The variation of boiling point for alkenes and alkynes is similar to that of alkanes.

Dipole moments

Dipole moment of methane is zero. The dipole moments of all alkanes, whether straight chain or branched, will be negligibly small. Dipole moment forces operate in polar molecules. The positive end of one polar molecule is drawn towards the negative end of another polar molecule. These types of interactions are called dipole-dipole interactions. On account of these interactions, the polar molecules are held together by stronger forces than non polar molecules having higher molecular weights.

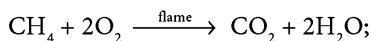
The polarity of a molecule not only depends on the polarity of the individual bonds, but also depends on the way by which the bonds are directed. Effectively the polarity depends on the shape of the molecule.

REACTIONS OF ALKANES

Combustion

Combustion of alkanes is the process by which the hydrocarbons are completely oxidised to CO_2 and H_2O by burning in an atmosphere of oxygen. The combustion is initiated by a flame or spark. Once started, the combustion process gives off heat (exothermic), which is sufficient to maintain the high temperature and permit the burning to continue. *The quantity of heat evolved when one mole of a hydrocarbon is burnt to carbon dioxide and water is known as heat of combustion.*

Combustion of methane

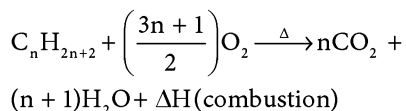


Enthalpy of combustion, $\Delta H = -890 \text{ k cal mol}^{-1}$

Burning of methane, under the influence of a catalyst, under regulated conditions, results in hydrogen.

Although the reactions are exothermic, initiation of the reaction requires a fairly high temperature. This means that combustion reactions of hydrocarbons need high energy of activation.

Other examples of combustion of alkanes follow the same pattern.

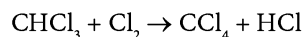
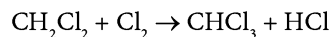
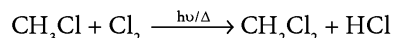
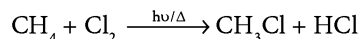


Heat of combustion values increase with increase in molecular weight of the hydrocarbon.

Halogenation

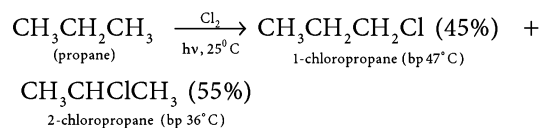
The reaction of alkanes with halogen is a substitution reaction. In general they are known as halogenations. In these substitution reactions, a halogen like fluorine, chlorine, bromine or iodine replaces a hydrogen of the hydrocarbon.

When methane is treated with chlorine in the presence of diffused sunlight or UV light or heated to high temperature (573 – 773K), a reaction occurs and all the four hydrogen atoms of methane are successively and rapidly replaced.

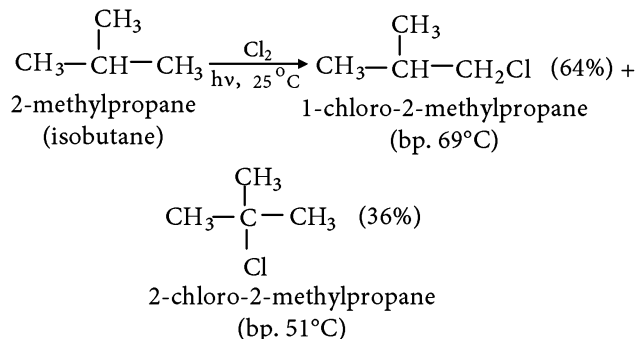
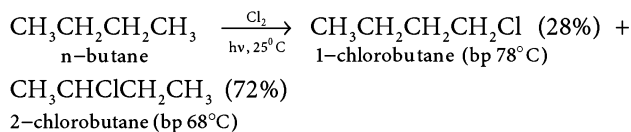


With rare exceptions, direct halogenation of alkanes is not a suitable method for the preparation of alkyl halides because a mixture of different alkyl halides are generally obtained.

From a simple alkane, depending on which hydrogen is replaced, a number of isomeric halogenated products can be formed. For a monochlorination reaction, for example,



2.12 Alkanes, Alkenes and Alkynes



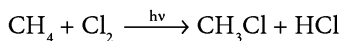
Bromination of alkanes occurs in the presence of light at a slightly higher temperature to give predominantly one monobrominated isomer. This is in contrast to chlorination, where the distribution of monochlorinated products is in random. So bromination is a selective process.

For example, propane on monobromination gives 97% of 2-bromopropane and butane gives 98% of 2-bromobutane, while isobutane gives almost exclusively 2-bromo-2-methylpropane and trace amount of 1-bromo-2-methylpropane.

Mechanism of reaction

The halogenation of alkanes occurs by radical mechanism. The reaction is promoted by heat or light.

In order to illustrate the mechanism of halogenation, the chlorination of methane to give methyl chloride is taken as an example.

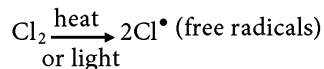


The reaction is initiated by a homolytic cleavage of a chlorine molecule to give chlorine free radicals, which are very reactive species. This chlorine free radical abstracts rapidly a hydrogen atom from methane. This in turn results in another active free radical, which is a methyl radical, which combines with chlorine molecule to form methyl chloride and chlorine radical. Another reaction sequence is initiated by this new chlorine radical in a repeating process known as chain reaction. A stepwise mechanism in which each step generates reactive free radical intermediate which causes the next series of reactions to occur is called a chain reaction.

There are three important steps in the above chain reaction.

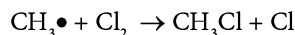
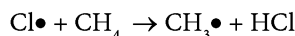
Step I-Chain initiation step

In this step free radicals are generated by a homolytic cleavage.



Sometimes, free radicals are initiated by the presence of radical initiators. For example, $\text{C}_6\text{H}_5\text{COOOCOC}_6\text{H}_5$ (dibenzoylperoxide), $(\text{CH}_3)_3\text{COOC}(\text{CH}_3)_3$ (ditertiarybutyl peroxide) are used as radical initiators.

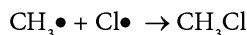
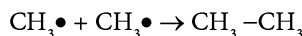
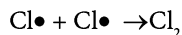
Step II-Chain propagation step



In each chain propagating step, one radical that is formed already, generates another radical.

Step III-Chain termination step

In this step, the following reaction could occur to terminate the chain reaction.



All the reactive particles generated are consumed. No fresh radicals are generated in these steps. The above mechanism explains the formation of small quantity of ethane in the halogenation of methane.

Under a given set of conditions, large numbers of molecules of methyl chloride are formed for every photon (quantum) of light absorbed.

Relative reactivities of halogens with methane

The order of reactivity of halogens with alkanes is $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$.

Among the halogens, fluorine is too reactive and iodine is too slow to react. The two remaining halogens left are chlorine and bromine. Chlorine is more reactive than bromine. Chlorination produces a random mixture of monochlorinated products. On the other hand bromine is bit slow to react, but is more selective. A specific monobrominated product is formed predominantly.

Free radical initiators and inhibitors

Formation of free radicals are initiated or accelerated by some typical free radicals initiators like H_2O_2 , benzoyl peroxide, *t*-butyl peroxide and some hydroperoxides.

The free radicals formed are suppressed by some substances which act as scavengers. e.g., nitric oxide, molecular oxygen, and benzoquinone. These are referred to as inhibitors.

Relative percentage of halogenated products

Relative reactivity of primary, secondary and tertiary hydrogens in alkanes with respect to halogenation has been studied in detail. The relative reactivities are 1 : 3.8 : 5 for 1°, 2° and 3° hydrogens in the case of chlorination.

When *n*-butane reacts with Cl_2 , two monochlorinated butanes are formed, namely 1-chlorobutane $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ and 2-chlorobutane $\text{CH}_3\text{CHClCH}_2\text{CH}_3$.

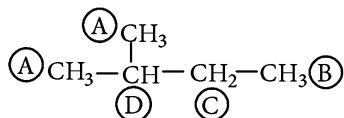
There are six equivalent primary hydrogens which lead to 1-chlorobutane and four equivalent secondary hydrogens, which lead to 2-chlorobutane. The ratio of 1° : 2° is 3 : 2. The relative amount of 1-chlorobutane obtained is $3 \times 1 = 3$ and 2-chlorobutane is $2 \times 3.8 = 7.6$. The percentage of 1-chlorobutane can be obtained by adding the relative amounts, viz., 3 and 7.6 and arriving at the percentage,

$$\frac{3}{(3 + 7.6)} \times 100 = 28\%.$$

The percentage of 2-chlorobutane can be similarly obtained by adding the relative amount and arriving at the percentage,

$$\frac{7.6}{(3 + 7.6)} \times 100 = 72\%.$$

Four different monochlorinated products can be formed from 2-methylbutane.



In the structure, there are

6 primary hydrogens (A) of relative reactivity 1

3 primary hydrogens (B) of relative reactivity 1

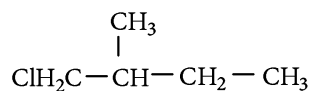
2 secondary hydrogens (C) of relative reactivity 3.8

1 tertiary hydrogen (D) of relative reactivity 5

$$(6 \times 1 = 6) + (3 \times 1 = 3) + (2 \times 3.8 = 7.6) +$$

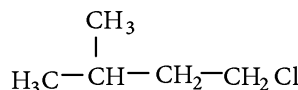
$$(1 \times 5 = 5) = 21.6$$

So the percentage distribution of monochlorinated products will be,



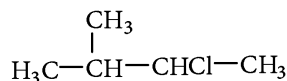
$$6 \times 1 = 6$$

$$\frac{6}{21.6} \times 100 = 28\%$$

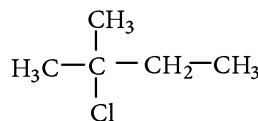


$$3 \times 1 = 3$$

$$\frac{3}{21.6} \times 100 = 14\%$$



$$\frac{7.6}{21.6} \times 100 = 35\%$$



$$\frac{5}{21.6} \times 100 = 23\%$$

The relative reactivity of primary, secondary and tertiary hydrogens for a replacement by bromine has been evaluated to be 1 : 82 : 1600.

In propane $\text{CH}_3\text{CH}_2\text{CH}_3$, there are $(3 + 3) = 6$ primary hydrogens and $(1 \times 2) = 2$ secondary hydrogens. So the ratio of 1° : 2° hydrogens in propane is 6 : 2 or 3 : 1. The percentage of 1-bromopropane that can be formed is,

$$(3 \times 1 = 3) + (1 \times 82 = 82) = 85.$$

$$\frac{3}{85} \times 100 = 3.5\%.$$

The percentage of 2-bromopropane which can be

$$\text{formed is } \frac{82}{85} \times 100 = 96.5\%.$$

In 2-methylpropane or isobutane $\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_3\text{C} - \text{CH} - \text{CH}_3 \end{array}$,

the percentage of $\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_3\text{C} - \text{C} - \text{CH}_3 \\ | \\ \text{Br} \end{array}$ formed on bromination

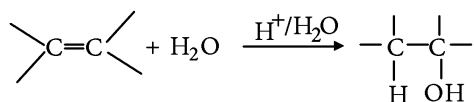
$$\text{will be } \frac{1600}{1609} \times 100 = 99.4\%$$

Almost exclusively tertiary butyl bromide is formed by the monobromination of isobutane.

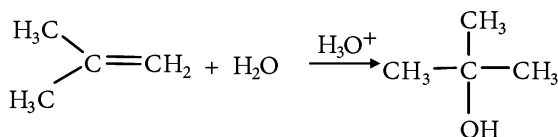
REACTION OF ALKENES

Acid catalysed hydration

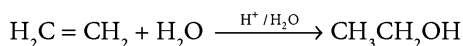
Addition of water to alkenes occurs in the presence of an acid catalyst. The acid catalyzed addition of water to alkenes follows the Markovnikov's rule. The reaction is reversible and the mechanism of hydration of an alkene is the reverse of the dehydration of an alcohol catalyzed by acids. The product obtained in the hydration of an alkene is an alcohol.



The acid often used to catalyze the hydration of an alkene is dilute H_2SO_4 , dilute HCl or phosphoric acid (H_3PO_4). The reactions are usually regioselective. A typical example of such a reaction is

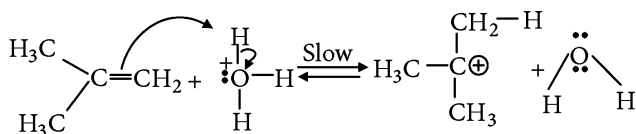


A very simple example of hydration of an alkene is the formation of ethylalcohol from ethene.

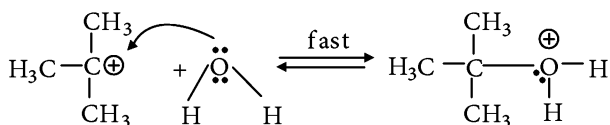


The **mechanism** of hydration of an alkene takes place as follows.

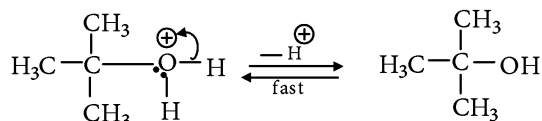
- (i) The alkene accepts a proton from the acid to form a carbocation.



- (ii) In the next step, the intermediate carbocation formed reacts with a molecule of water to form a protonated alcohol.



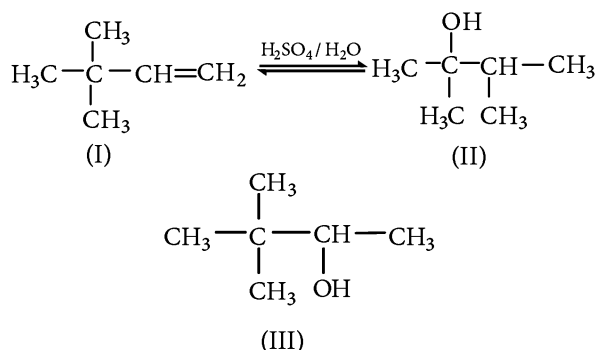
- (iii) In the last step, a proton is lost to form the final product—alcohol.



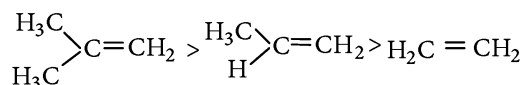
The rate determining step in the hydration of alkene is the first step in which the carbocation is formed. In the hydration of an alkene, it is preferable to use a dilute acid so that the quantity of water is high.

Whenever carbocations are involved, rearrangements will occur if the initial carbocation formed can be converted to a more stable one. In such cases, the expected products of hydration are not formed.

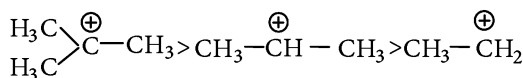
For example, the hydration of 3,3-dimethylbut-1-ene (I) leads to 2,3-dimethylbutan-2-ol (II) instead of the expected 3,3-dimethylbutan-2-ol (III).



The following order of reactivity is observed, when the degree of substitution around a double bond increases.



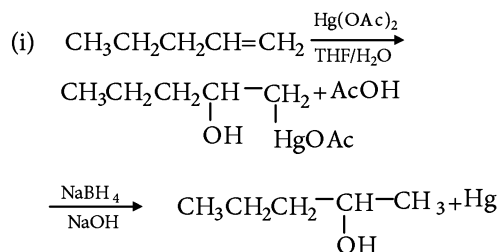
This is due to the stability and ease of formation of the carbocation formed as intermediates during the hydration of the olefin.



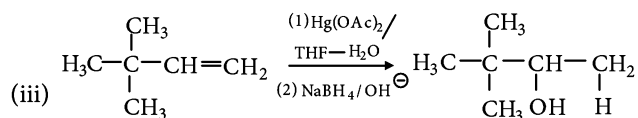
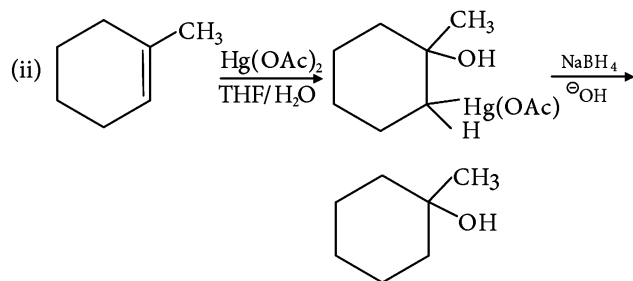
Oxymercuration–Demercuration

This is a highly regioselective reaction. The groups constituting water, namely H and OH are added to the two carbons of the double bond in accordance with Markovnikov's rule.

There are two steps in the overall reaction, namely oxymercuration and demercuration. The first step is brought about by means of mercuric acetate $\text{Hg}(\text{OAc})_2$ in H_2O –THF medium while the second step makes use of NaBH_4 in the presence of a base. The following examples illustrate the reaction



In the reaction, Markovnikov's addition of water to double bond occurs. Since carbocations are not involved no rearrangements are observed in the reaction.

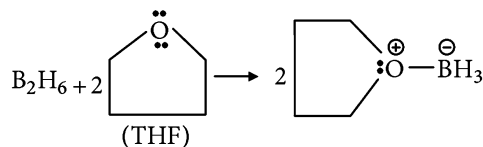


Example (iii) given above is an illustration of the fact that no rearrangement has occurred during the addition of water to double bond.

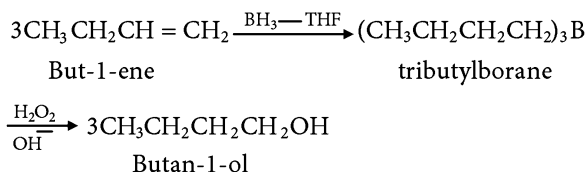
Hydroboration–oxidation

This reaction involves the addition of water to an unsymmetrical double bond against Markovnikov's rule. This reaction is also a highly regioselective addition.

Hydroboration can be carried out making use of diborane (B_2H_6). Boronhydride BH_3 usually exists as a dimer – diborane (B_2H_6). Diborane is dissolved in THF (Tetrahydrofuran – solvent) to give a complex.

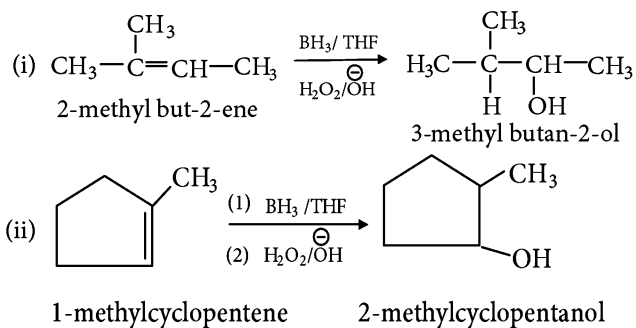


BH_3 is an electron deficient compound and it is a Lewis acid. BH_3 accepts a pair of electrons from oxygen of THF to form a complex.



So hydroboration reaction also occurs in two steps, the first step being the addition of diborane in THF to the double bond and the second step being the oxidation of the borane formed to give the alcohol.

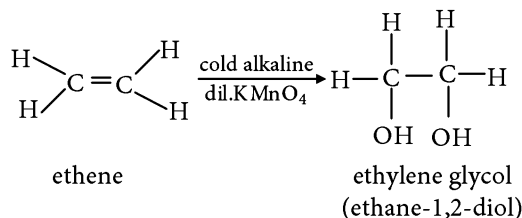
Two other examples of hydroboration are given below



Hydroboration–oxidation method provides a route in the synthesis of alcohols which cannot be obtained through acid catalysed hydration of olefins or by oxymercuration–demercuration method.

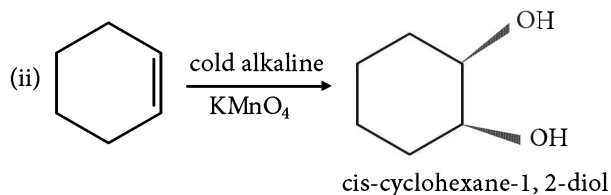
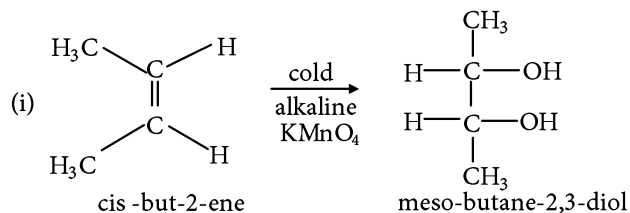
Reactions with KMnO_4

Cold dilute alkaline KMnO_4 solution (Baeyer's reagent) oxidises the olefinic double bonds to give 1,2-diols known as glycols.



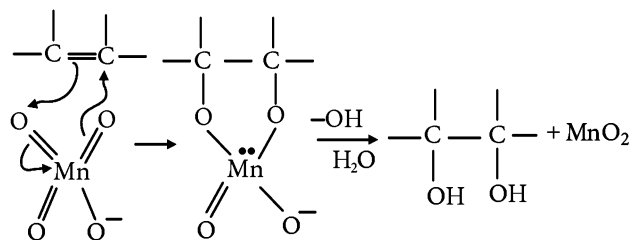
2.16 Alkanes, Alkenes and Alkynes

Conversion of a double bond to give a dihydroxy compound is known as hydroxylation. A *cis*-1, 2-diol is formed when an olefin is treated with cold dilute alkaline KMnO_4 solution.



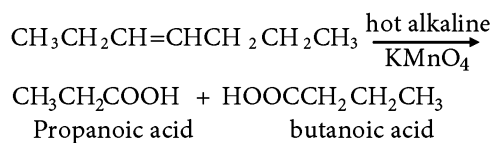
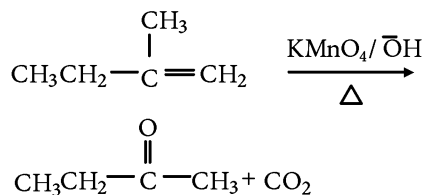
Alkaline KMnO_4 is a mixture of MnO_4^- and OH^- ions. The pink colour of the alkaline permanganate fades on reaction with unsaturated hydrocarbons and hence this reaction used as a test for unsaturation (Baeyer's test).

Mechanism

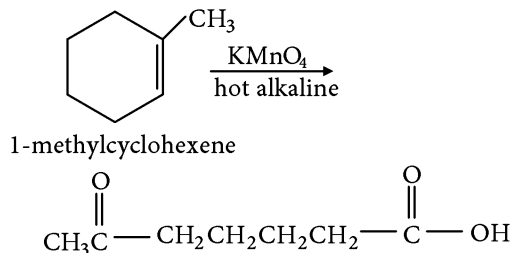


If an olefin is oxidized with hot concentrated alkaline KMnO_4 (or acid KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$) the products obtained could be a ketone or a carboxylic acid or CO_2 depending on the structure of alkene. The $\text{C}=\text{C}$ gets cleaved under these conditions.

For example,

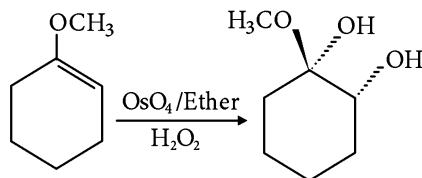
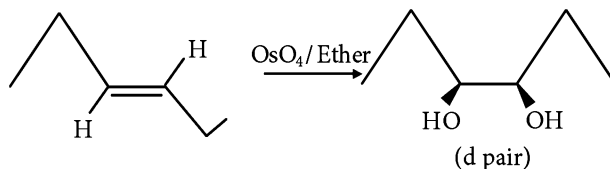
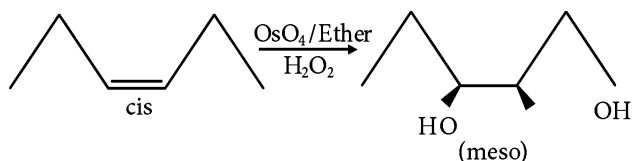


The cyclic alkene shown below, on oxidation with hot KMnO_4 solution gives a ketoacid.

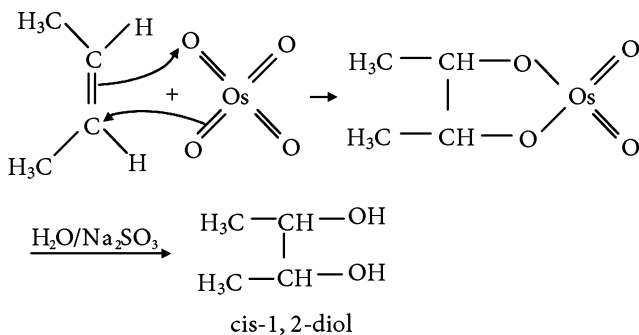


Cis hydroxylation with OsO_4 (Osmium tetroxide)

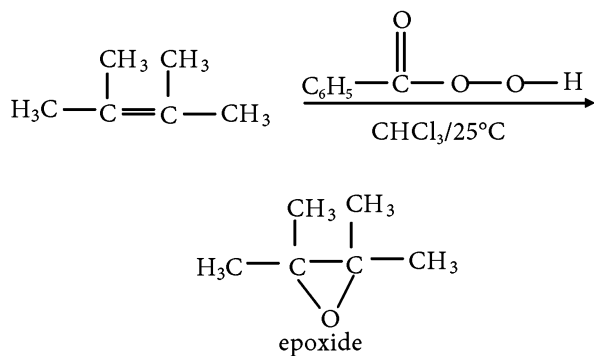
Alkenes can be hydroxylated in the *cis* position making use of OsO_4 in ether medium, followed by oxidation.



Mechanism



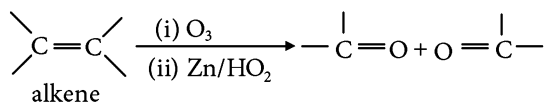
Epoxidation using a peracid



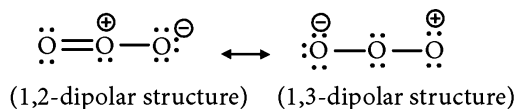
Epoxides are formed when olefins are treated with peracids.

Ozonolysis

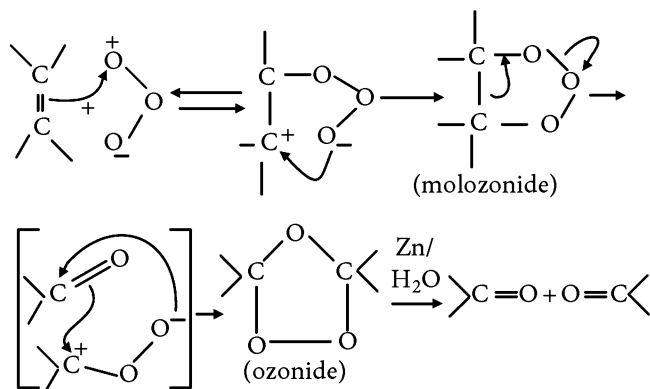
Alkenes react with ozone to form ozonides. Ozonides on reduction with Zn dust and water give aldehydes and ketones depending upon the structure of the alkene. The process of formation of an ozonide and its subsequent decomposition together is known as ozonolysis. Ozonolysis can be represented in a general way as shown.



Ozone can be represented as a resonance hybrid.

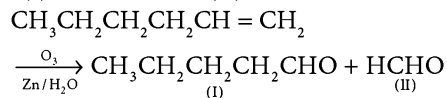


Mechanism of ozonolysis

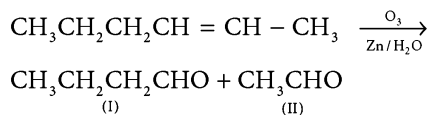


Ozonide formation is by a 1,3-dipolar cycloaddition. Reductions of the ozonide with Zn/H₂O, and acid, H₂ and Raney nickel, Ph₃P etc., gives aldehydes or ketones.

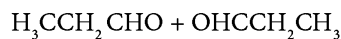
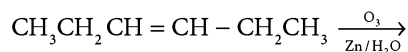
1-Hexene on ozonolysis with O₃/Zn/H₂O gives pentanal (I) and methanal (II)



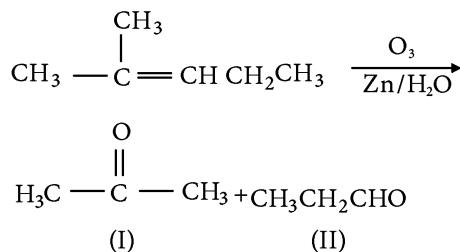
2-Hexene on ozonolysis gives two aldehydes namely butanal (I) and ethanal (II).



3-Hexene gives two molecules of propanal.

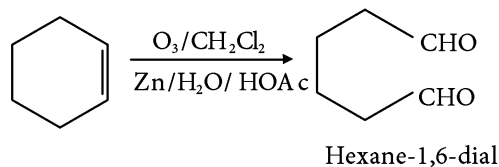


2-Methyl-2-pentene gives one molecule of acetone (I) and one of propanal (II).

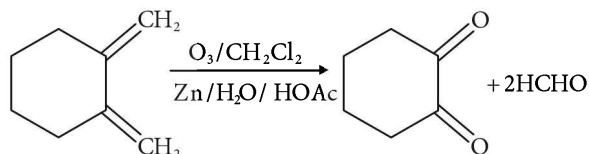


From the structure of the aldehydes or ketones formed by ozonolysis, the exact structure of the alkene can be arrived at.

Cyclohexene on ozonolysis gives hexane-1,6-dial.

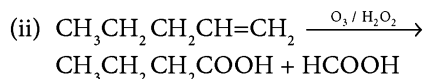
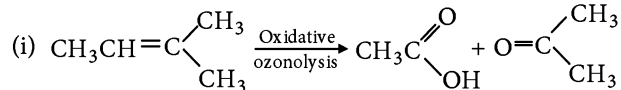


1, 2-dimethylenecyclohexane gives cyclohexane-1,2-dione and two molecules of HCHO on ozonolysis.

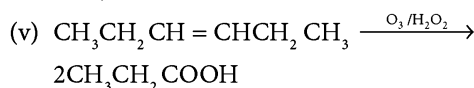
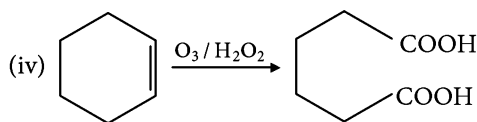
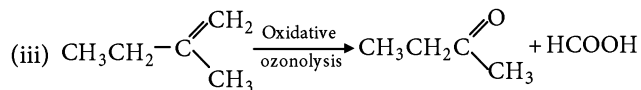


2.18 Alkanes, Alkenes and Alkynes

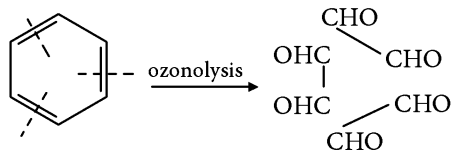
Oxidative cleavage of olefins by ozonolysis results in ketones and carboxylic acids. Oxidative ozonolysis is usually carried out by means of H_2O_2



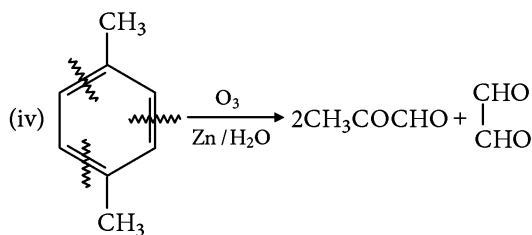
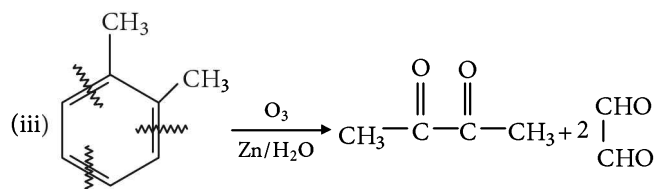
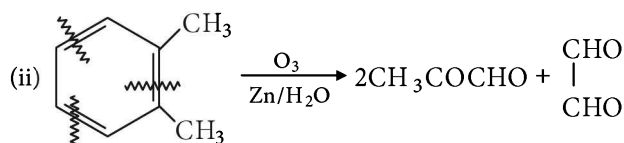
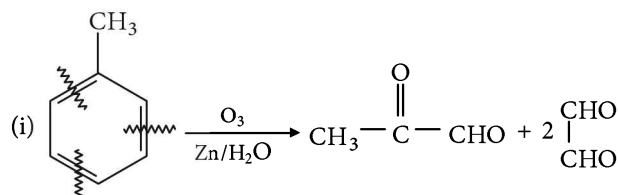
On strong heating, formic acid decomposes to form CO_2



Benzene on ozonolysis gives three molecules of ethane-1,2-dial (glyoxal).



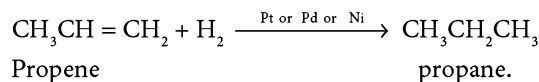
Alkyl substituted aromatic compounds undergo ozonolysis to give various products depending on the position of substituents. For example



Reduction

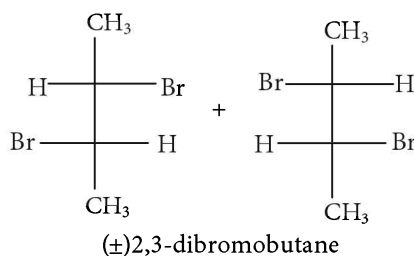
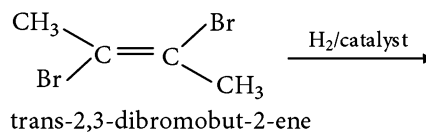
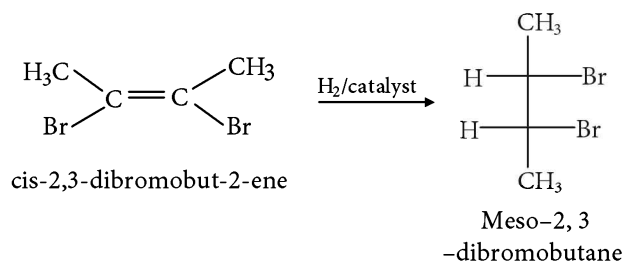
Carbon-carbon double bonded compounds or alkenes can be reduced by hydrogen in the presence of catalysts to give saturated compounds. The process is generally known as catalytic hydrogenation. Hydrogenation occurs with olefinic compounds, irrespective of the type of substituents, whether electron withdrawing or electron releasing nature.

When propene undergoes hydrogenation in the presence of finely divided Pt, Pd or Ni, the product obtained is propane.

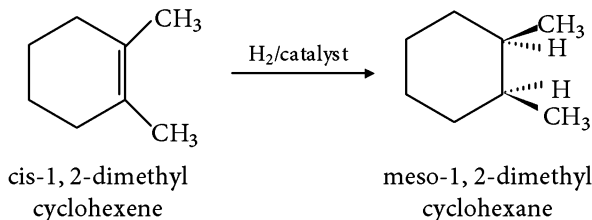


The catalysts used are said to be heterogeneous catalysts because the catalysts and the reactants are in different phases—catalysts are solids and the reacting substances are gases.

Cis-2,3-dibromobut-2-ene on catalytic hydrogenation gives meso-2,3-dibromobutane, whereas trans-2,3-dibromobut-2-ene gives a racemic mixture of 2,3-dibromobutane.



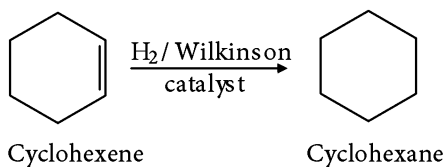
Cis-1,2-dimethylcyclohexene gives meso 1,2-dimethylcyclohexane.



Heat of hydrogenation values ΔH are very useful in deciding the stabilities of alkenes. Heat of hydrogenation values show that pent-2-ene is more stable than pent-1-ene.

Between cis and trans pent-2-ene, trans is more stable than cis isomer. All the three pentenes namely pent-1-ene, cis-pent-2-ene and trans-pent-2-ene give the same product on hydrogenation, namely n-pentane. The enthalpy of hydrogenation of pent-1-ene, cis-pent-1-ene and trans-pent-2-ene are -125 kJ mol^{-1} , -119 kJ mol^{-1} and -115 kJ mol^{-1} respectively. The heat evolved on hydrogenation per mole will be less for more stable alkene.

Homogeneous catalytic hydrogenation of alkenes can also be carried out by making use of certain specific catalysts. e.g., Wilkinson's catalyst. The homogenous catalyst used here is chlorotris (triphenyl phosphine) rhodium (I), $[\text{RhCl}(\text{PPh}_3)_3]$.



Electrophilic addition reactions

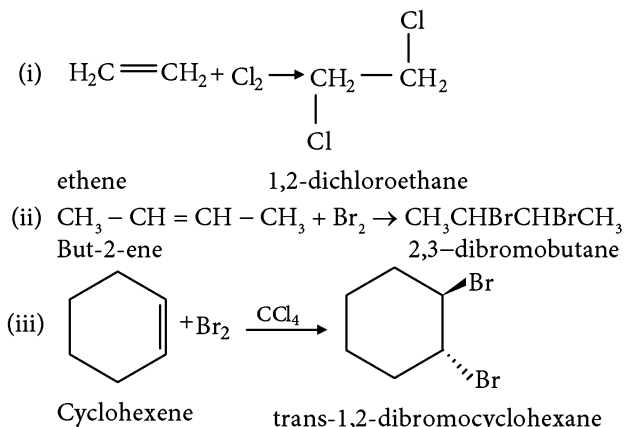
One of the important reactions of an alkene is the addition to the double bond.

In an alkene, the electrons involved in the π -bond are loosely held compared to the electrons involved in the σ -bond. So in alkenes, the π -electrons serve as a source of electrons. These π -electrons are donated for bond formation with groups or reagents which are electron deficient or electrophilic in nature. So this type of addition is termed as *electrophilic addition to the double bond*.

There are a number of reagents that can undergo electrophilic addition to the double bond. They are halogens (particularly chlorine and bromine), hydrogen halides (HCl, HBr, HI), sulphuric acid, water, hypohalous acid (HOCl, HOBr), and so on.

(1) Addition of chlorine and bromine

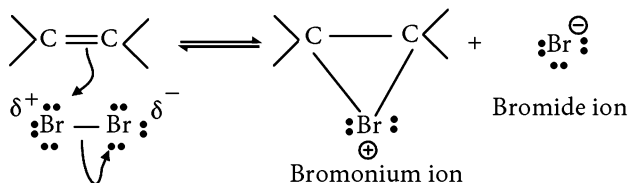
Alkenes react rapidly with chlorine or bromine in suitable solvents (non-nucleophilic solvents) to form vicinal dihalides, namely 1,2-dichloroalkane or 1,2-dibromoalkane.



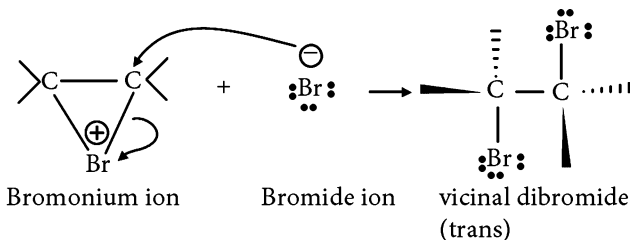
Addition of bromine to a double bond, resulting in the rapid decolourization of bromine water or bromine dissolved in CCl_4 , is taken as a test for unsaturation. (Baeyer's test)

Mechanism of halogen addition to alkenes

The bromine molecule gets polarized as Br^+ and Br^- , as it approaches the alkene. The polarized bromine molecule transfers Br^+ with six electrons in its valence shell to the alkene resulting in the formation of a cyclic bromonium ion. A free bromide ion with eight electrons around it is set free.

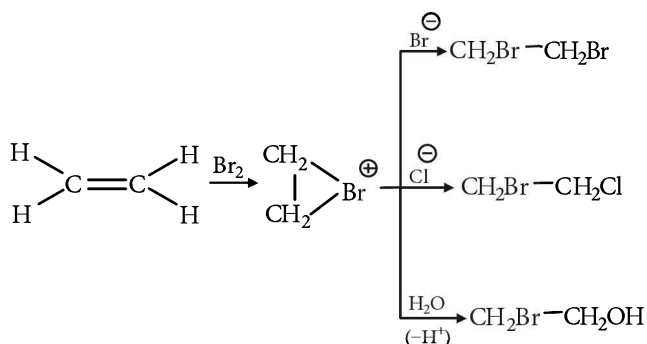


In the second step, the free bromide ion attacks any one of the two carbon atoms from the rear side of the bromonium ion. This results in the opening of the highly strained three membered ring to form the vicinal dibromide. The two bromine atoms of the bromine molecule get attached to the two carbon atoms of alkene to give a dibromide with the two bromine atoms in the trans orientation. Hence a trans 1,2-dibromide is obtained by the addition of bromine to the double bond.



2.20 Alkanes, Alkenes and Alkynes

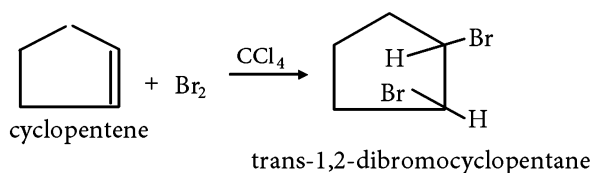
When ethylene is bubbled into an aqueous solution of bromine containing NaCl, three different products are formed. Once the bromonium ion intermediate is formed after the initial addition of bromine to olefin, it can react with other nucleophiles to give different products.



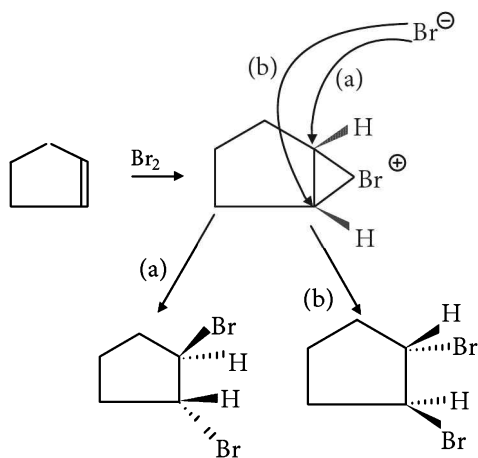
The exact nature of the product formed depends on the additional nucleophile available in the medium. Aqueous solution of NaCl is inert towards ethylene.

Stereochemistry of addition of halogen to alkenes

When bromine adds to cyclopentene, an anti-addition occurs to give trans-1,2-dibromocyclopentane.



In the first step, a bromonium ion is formed by the initial attack of the bromine molecule on the double bond. In the second step, nucleophilic attack by the bromide ion



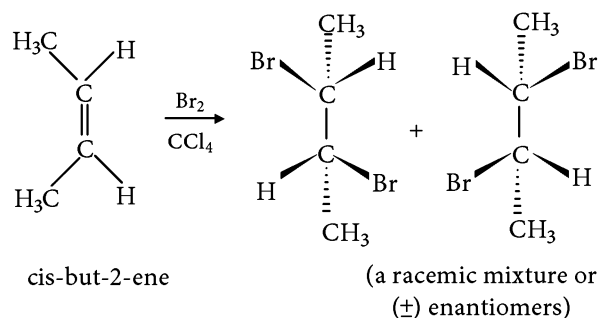
causes inversion of configuration. The inversion of configuration at one carbon atom of the cyclopentane ring leads to the formation of trans-1, 2-dibromide enantiomer. The other enantiomer results from the attack of the bromide ion on the other carbon atom.

So one gets a racemic mixture ($\pm$) of two trans isomers (enantiomers) of 1,2-dibromocyclopentane. The product is optically inactive — a racemic mixture.

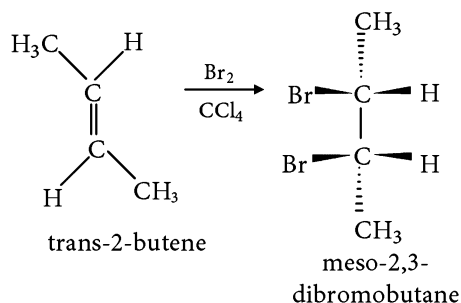
Stereospecific reaction

A reaction is said to be stereospecific when a particular stereoisomer of a starting compound (for example, cis-but-2-ene or trans-but-2-ene) reacts with a reagent to give a specific stereoisomer of the product. The other stereoisomer of the same starting material will give another stereoisomer of the product with the same reagent.

For example, when cis-but-2-ene is treated with bromine the product formed is a racemic mixture of enantiomers, i.e., ($\pm$) 2,3-dibromobutane.



When trans-but-2-ene reacts with bromine, the product obtained is meso-2,3-dibromobutane.

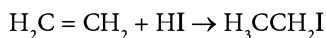


(ii) Addition of hydrogen halides

An alkene is converted by hydrogen chloride, hydrogen bromide or hydrogen iodide to the corresponding alkyl

halide. The order of reactivity of hydrogen halide is $\text{HI} > \text{HBr} > \text{HCl}$.

Ethene is converted to ethyl iodide by HI.

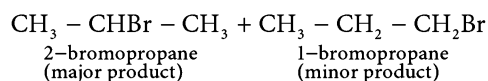
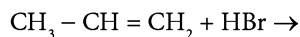


But-2-ene is converted to 2-bromobutane by the addition of HBr.



Markovnikov's rule

When an unsymmetrical reagent like hydrogen halide is added to an unsymmetrical alkene, two products may be formed. But the two products are not formed in equal amounts. One will predominate. For example, when propene is treated with HBr, both 2-bromopropane and 1-bromopropane are formed as products. But experimentally it has been found that the major product is 2-bromopropane.

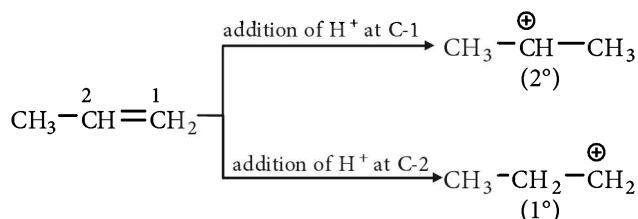


2-bromopropane
(major product)

1-bromopropane
(minor product)

The Russian chemist Markovnikov studied many reactions of this type and suggested a rule to predict the major product in such reactions. The rule is known as Markovnikov's rule and it states that *when an unsymmetrical reagent adds across an unsymmetrical double bond, the negative part of the attacking reagent joins with the carbon atom which carries smaller number of hydrogen atoms.*

The reason for addition according to Markovnikov's rule can be understood from the mechanism of addition of hydrogen halide to alkenes. The first step involves the addition of H^+ to alkene to form a carbocation. The two carbocations that can be formed from propene are shown below.

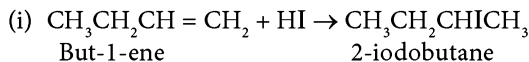


Since 2° carbocation is more stable, it is formed predominantly. This carbocation then rapidly combines with Br^- to form 2-bromopropane as the major product.

Thus, Markovnikov's addition occurs through the formation of more stable carbocation intermediate.

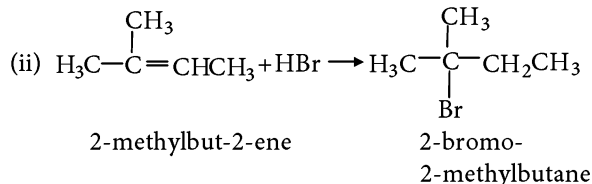
This type of addition which gives predominantly one possible isomeric product is known as regioselective addition.

Some more examples of regioselective additions are given below.



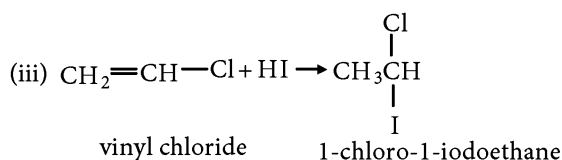
But-1-ene

2-iodobutane



2-methylbut-2-ene

2-bromo-
2-methylbutane



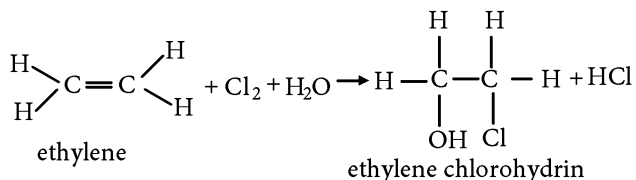
vinyl chloride

1
1-chloro-1-iodoethane

Addition of HOX (HOCl, HOBr, HOI)

If the halogenation of an alkene is carried out in an aqueous solution (instead of a solvent like CCl_4), the product obtained is a halohydrin.

For example, ethene reacts with chlorine in aqueous medium to give ethylene chlorohydrin.

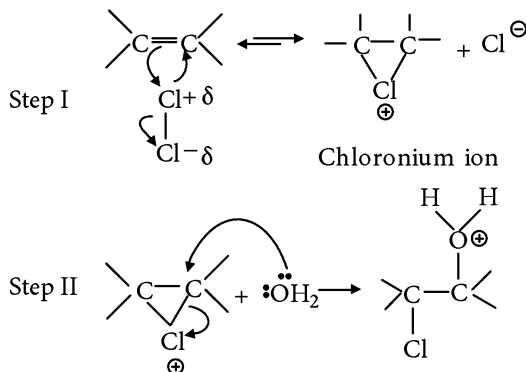


ethylene

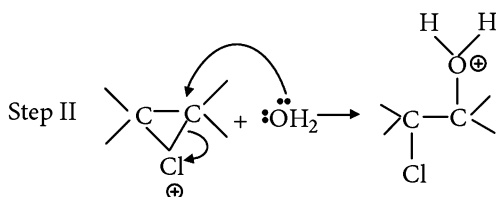
ethylene chlorohydrin

Mechanism for halohydrin formation

There are three steps:

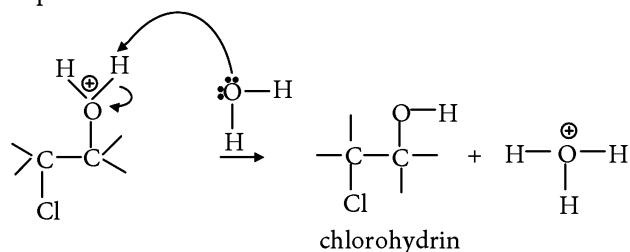


Chloronium ion



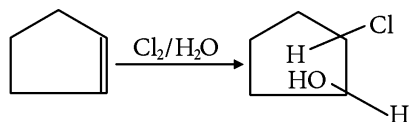
2.22 Alkanes, Alkenes and Alkynes

Step III

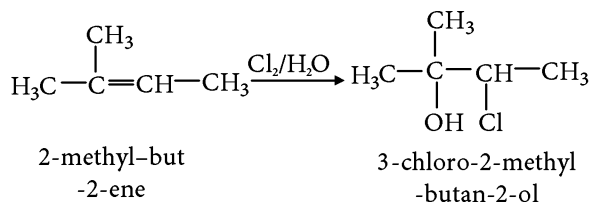


In the first step, a chlorine atom adds on to the double bond resulting in the formation of a chloronium ion. In contrast to the addition of a halogen in a non aqueous medium, in the chlorohydrin formation, a water molecule acts as a nucleophile and breaks the three membered chloronium ion ring. This results in a protonated chlorohydrin. The last step consists of the loss of a proton from the protonated chlorohydrin to give chlorohydrin. This is an anti-addition, which results in trans-chlorohydrin according to Markovnikov's rule.

Cyclopentene reacts with $\text{Cl}_2/\text{H}_2\text{O}$ to give a trans-chlorohydrin.



Addition of halohydrin to an unsymmetrical olefin follows Markovnikov's rule.



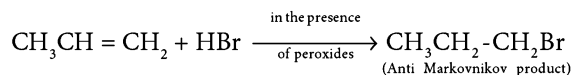
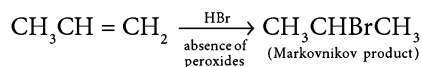
When Cl_2 reacts in aqueous medium, HOCl (hypochlorous acid) is formed. The more negative part of HOCl is $-\text{OH}$ and the less negative part Cl takes the role of Cl^+ . According to Markovnikov rule, the more negative part, OH^- adds to the carbon with less number of hydrogens. The chlorine attaches itself to the other carbon.

Anti Markovnikov addition (Kharasch effect or peroxide effect)

It has been found that when HBr is added to an unsymmetrical alkene, Markovnikov's product is obtained as the

major product. But when HBr is treated with unsymmetrical alkenes in the presence of peroxide, addition takes place against Markovnikov's rule.

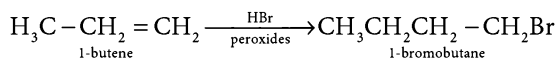
For example,



This difference in the formation of two regiospecific products with the same substrates under different experimental conditions was explained by Kharasch and Mayo (1933).

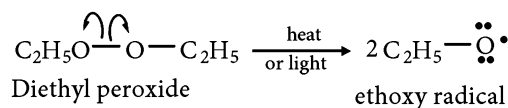
Peroxides like H_2O_2 (hydrogen peroxide), hydroperoxides like $\text{C}_6\text{H}_5\text{COOOH}$ (benzoyl hydroperoxide), dialkylperoxides like $\text{C}_2\text{H}_5\text{OOC}_2\text{H}_5$ etc., initiate a chain radical reaction under the influence of free radicals formed by these peroxides.

But-1-ene, for example, reacts with HBr to form 1-bromobutane, in the presence of peroxides.



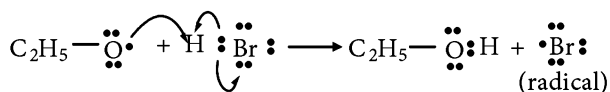
The reaction proceeds by a radical mechanism

In the first step, chain is initiated by the formation of radicals.

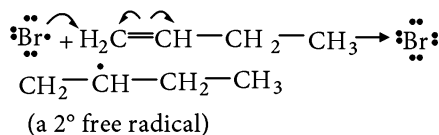


This happens because the $-\text{O}-\text{O}-$ bond in diethyl peroxide is very weak and gets cleaved easily to give $\text{C}_2\text{H}_5\text{O}^\bullet$ (ethoxy free radical).

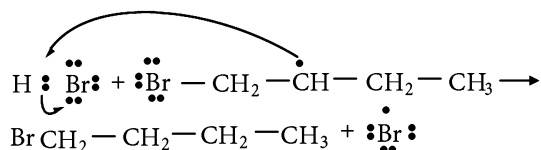
The ethoxy radical formed abstracts a hydrogen radical from HBr to form a bromine radical.



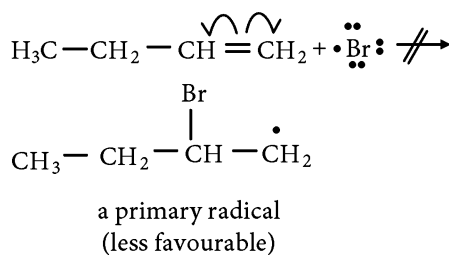
In the next step, the bromine radical attacks the alkene, but-1-ene, to produce a more stable secondary radical.



In the last step, the secondary radical abstracts a hydrogen from HBr. This leads to the final product namely 1-bromobutane and at the same time a bromine radical is set free. The chain gets terminated by two bromine radicals getting linked to give a bromine molecule.



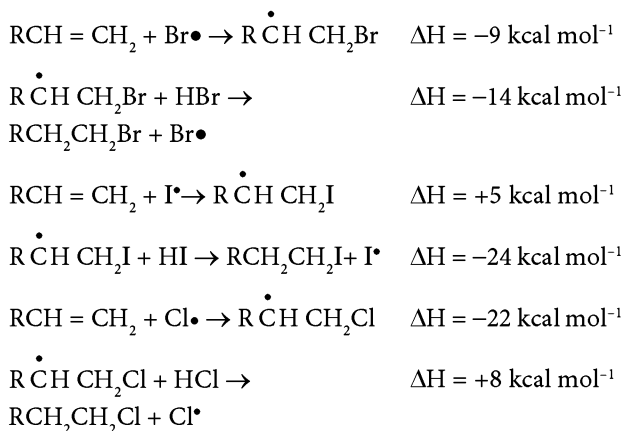
If the bromine radical had attacked the secondary carbon atom, a less stable, primary radical would have resulted.



This abnormal addition of HBr to alkene in presence of peroxides is known as *Kharasch effect or peroxide effect*. Other hydrogen halides do not show the peroxide effect. This is not significant with HF and HCl because

both HF and HCl do not form free radicals easily due to their large bond energies, which are 136 kcal mol⁻¹ and 104 kcal mol⁻¹ respectively, whereas H-Br bond energy is 88 kcal/mol.

In the case of HI, the bond energy is comparatively low (71 kcal mol⁻¹), and the iodine radicals are easily formed. But iodine free radicals prefer to recombine to form I₂ molecule rather than to add to the double bond and hence radical mechanism is not observed. Free radical reactions work well when both the propagation steps are exothermic. In the case of HBr both the propagation steps are exothermic, but in the case of HCl and HI one of the steps is endothermic. An endothermic step corresponds to a slow reaction that breaks the chain.

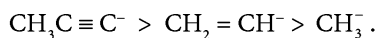


REACTIONS OF ALKYNES

(1) Acidity

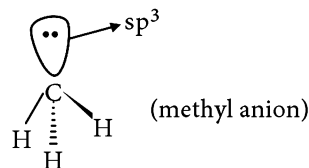
The hydrogen attached to an acetylenic carbon is fairly acidic. In unsubstituted acetylene ($\text{HC} \equiv \text{CH}$), the acidity of hydrogen has a pK_a value of 25. However, the acidity of acetylenic hydrogen is weaker than the acidity of the hydrogen of water (pK_a of hydrogen of water = 15.7). The hydrogen of alcohols R-OH also have a higher acidity ($\text{pK}_a = 16 - 19$). The acidity of the hydrogen of ammonia NH_3 is weaker compared to acetylenic hydrogen (pK_a of hydrogen of NH_3 is 34).

On the basis of the acidities of the hydrogens, in acetylene, ethylene and methane there is a vast difference in the stability of the corresponding carbanions.



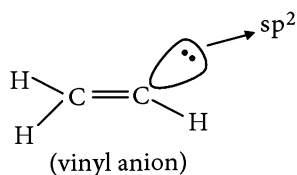
This difference in stability may be explained in terms of the character of the orbital occupied by the lone pair of electrons in the three anions.

Methyl anion has a pyramidal structure with a lone pair of electrons in one of the four sp^3 hybridized orbitals

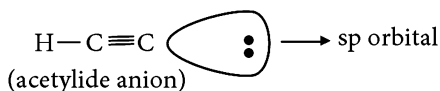


The lone pair of electrons in the vinyl anion is in an sp^2 orbital.

2.24 Alkanes, Alkenes and Alkynes



In the acetylide anion, the lone pair of electrons is in an sp orbital.



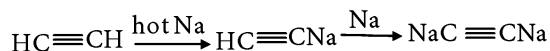
Electrons in an s -orbital are held closer to the nucleus than when compared to the electrons in p orbitals. Closer to the nucleus means greater electrostatic attraction by the nucleus, lower energy for s -electron and greater stability compared to p -electrons. Greater the value of s -character in a hybrid orbital containing a pair of electrons, more acidic is the hydrogen.

Metal acetylides

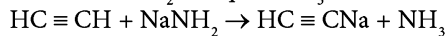
The hydrogen attached to an acetylenic carbon is acidic and this hydrogen can be replaced by metals like Na, Cu, Ag to form metal acetylides.

(i) Formation of acetylides of alkali metal

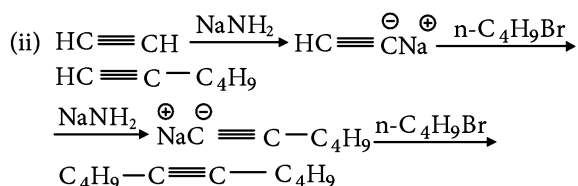
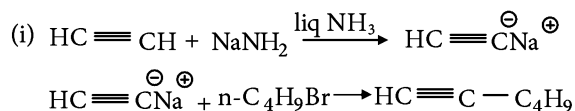
When acetylene is passed over heated sodium, monosodium acetylide is formed first followed by disodium acetylide.



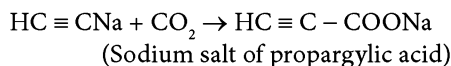
Terminal alkynes also form sodium alkynide when treated with NaNH_2 in liquid NH_3



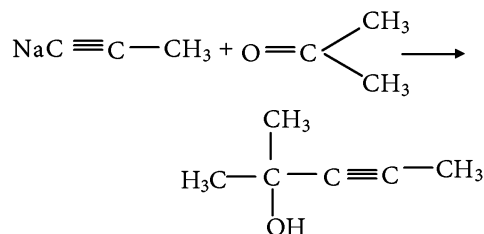
In view of the acidity of the acetylenic hydrogen, alkynes can be further alkylated.



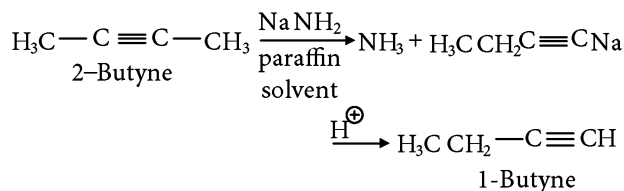
The monosodium derivative of acetylene absorbs dry CO_2 to form the sodium derivative of propargylic acid.



The monosodium derivative of acetylenic compounds react with carbonyl compounds to give acetylenic alcohol.

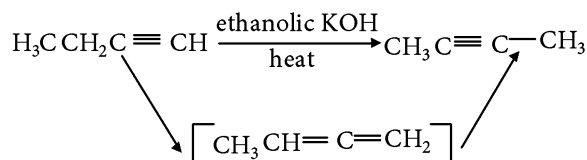


When an alkyne like 2-butyne is heated with sodamide in an inert solvent like paraffin, the acetylenic bond moves towards the end of the chain.

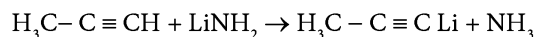


This is an example of isomerisation of butyne, i.e., alkynes.

Similarly, a terminal alkyne can also isomerize to give an internal alkyne under suitable conditions.

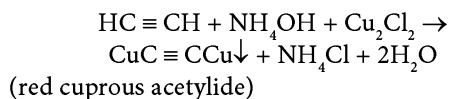


Lithium derivative of acetylenes can be prepared by the action of alkynes on lithium amide in dioxane medium.

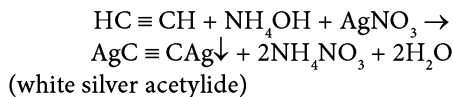


(ii) Formation of copper and silver acetylides

When acetylene is passed through an ammoniacal cuprous chloride solution, a red precipitate of cuprous acetylide is obtained.



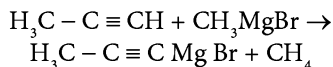
Similarly, when acetylene is passed through a solution of ammoniacal silver nitrate solution, a white precipitate of silver acetylide is obtained.



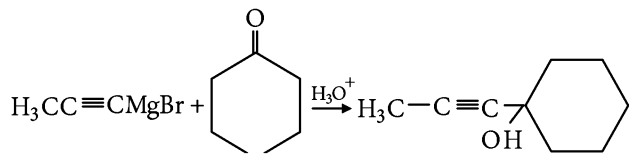
The same observation is given by all terminal alkynes.

The reaction of an alkyne with ammoniacal silver nitrate solution is used as a test for distinguishing the terminal alkynes from internal alkynes. These tests are not answered by the internal alkynes because of the absence of replaceable terminal acidic hydrogens in internal alkynes.

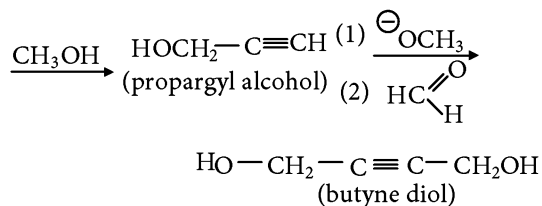
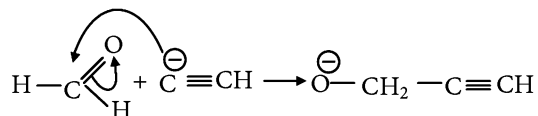
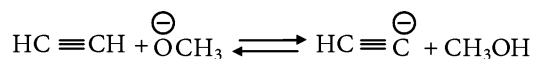
Grignard reagents react with acetylenic hydrogen to form suitable derivatives. For example.,



The hydrogen of the terminal acetylenic group is sufficiently acidic to react with Grignard reagent to form acetylenic Grignard complex and a hydrocarbon corresponding to the initial Grignard reagent. The acetylenic Grignard complex can be suitably reacted with other carbonyl compounds to give alcohols. For example,

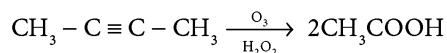
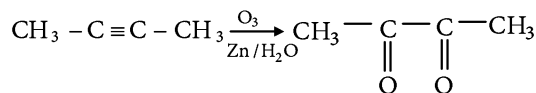


Reaction of acetylene with HCHO in the presence of sodium methoxide as a catalyst results in butyne diol with small quantities of propargyl alcohol.



Ozonolysis

Alkynes are oxidized to vicinal diketones by ozonolysis with $\text{O}_3/\text{Zn}/\text{H}_2\text{O}$ or to carboxylic acids by oxidative ozonolysis with $\text{O}_3/\text{H}_2\text{O}_2$.

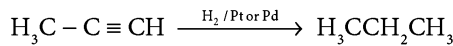


The analysis of the products formed would help to identify the position of the triple bond.

Addition reactions

(i) Reduction

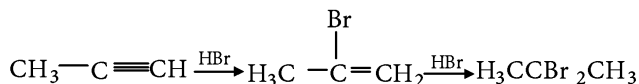
Alkynes can be completely reduced to alkanes by hydrogenation using Pt or Pd as catalysts.



Alkynes can be partially reduced to cis alkenes by reduction with Lindlar's catalyst and to trans alkene by sodium in liquid NH_3 (as discussed earlier in the preparation of alkenes).

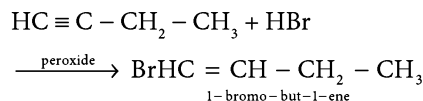
(ii) Addition of HBr

When HBr is added to unsymmetrical alkyne like prop-1-yne, the reaction proceeds in accordance with Markovnikov's rule.



(iii) Addition of HBr in the presence of peroxides

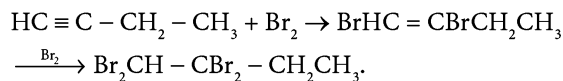
When 1-butyne reacts with HBr in the presence of peroxides, 1-bromo-1-butene is formed.



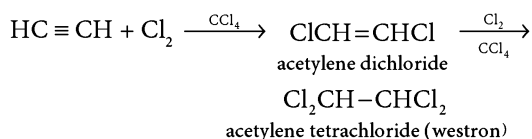
The product is obtained by an anti Markovnikov addition. The reaction proceeds by a radical mechanism.

(iv) Addition of Bromine

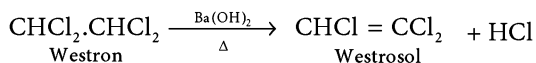
When bromine adds on to but-1-yne, the product obtained is 1,2-dibromobut-1-ene. Further, addition of bromine leads to a tetrabromide.



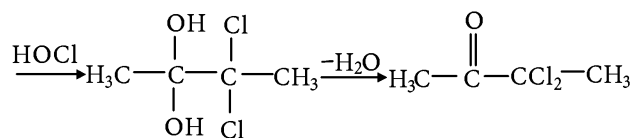
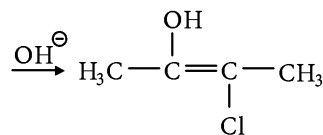
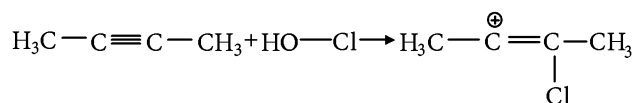
The reactivity order of addition of halogens is $\text{Cl}_2 > \text{Br}_2 > \text{I}_2$.



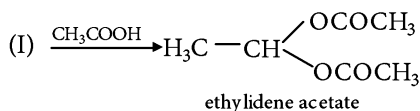
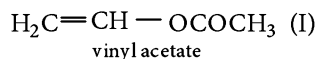
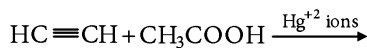
When Westron is passed over heated $\text{Ba}(\text{OH})_2$ or $\text{Ca}(\text{OH})_2$, westrosol is obtained. It is used as a solvent for oils, fats, waxes, as a refrigerant and as an anaesthetic.

**(v) Addition of hypohalous acid**

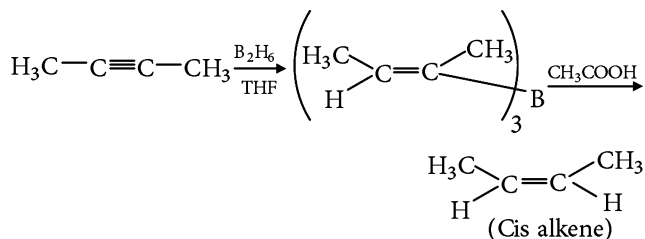
The addition of hypohalous acid to alkynes occurs in two steps forming α, α -dichloro carbonyl compound.

**(vi) Addition of acetic acid**

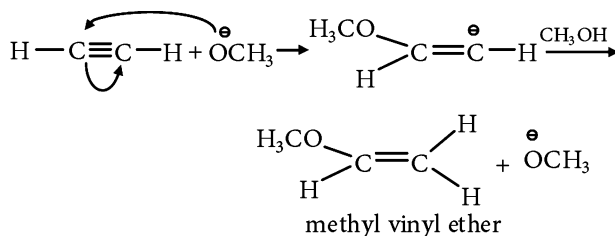
In the presence of mercuric ions, acetic acid adds to alkynes forming vinyl acetate followed by the addition of one more molecule of acetic acid to form ethylidene acetate.

**(vii) Hydroboration**

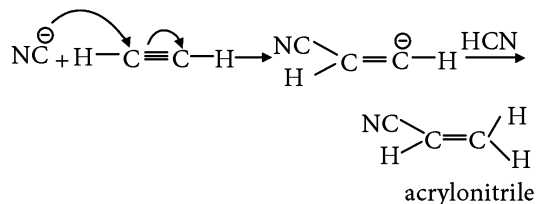
Addition of diborane to acetylene produces vinyl borane, which on treatment with acetic acid gives cis-alkene. This has been one of the methods of converting an alkyne to a cis-alkene.

**(viii) Addition of methanol**

When methanol reacts with acetylene, methyl vinyl ether is formed. A small catalytic quantity of sodium methoxide is also used. The reaction is initiated by the nucleophilic attack by the methoxide ion on acetylene.

**(ix) Addition of hydrogen cyanide**

Addition of HCN to acetylene in the presence of cyanide ions as a catalyst results in vinyl cyanide or acrylonitrile.

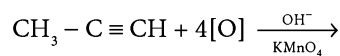
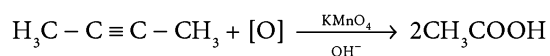


Acrylonitrile is an essential constituent for the preparation of synthetic rubber, buna-N-rubber, which is a copolymer of vinyl cyanide and butadiene.

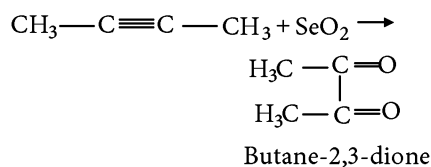
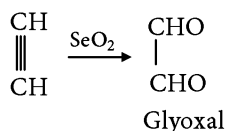


2.28 Alkanes, Alkenes and Alkynes

Substituted acetylenes on oxidation with alkaline KMnO_4 undergo cleavage at the triple bond to give carboxylic acids with lesser number of carbon atoms.

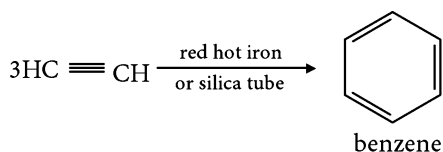


Oxidation of acetylene can be effected with SeO_2 to give glyoxal.

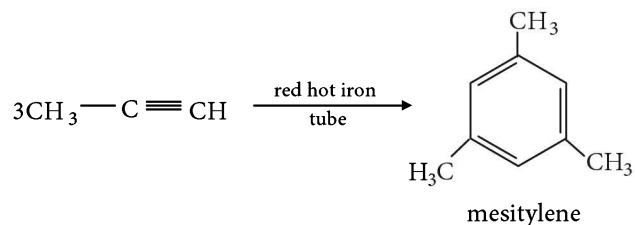


Polymerization

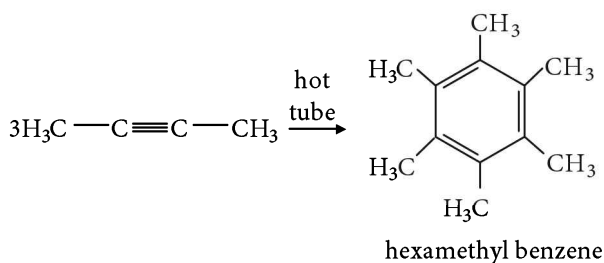
When acetylene is passed through a red hot tube, it undergoes polymerization to give benzene.



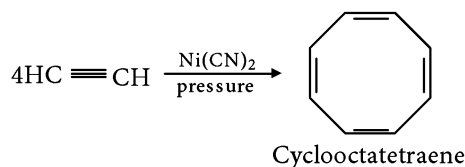
Propyne, $\text{CH}_3\text{C}\equiv\text{CH}$, polymerizes to give mesitylene, when passed over red hot iron tube.



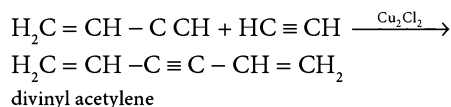
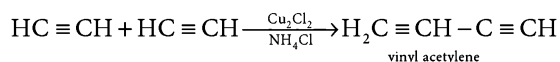
2-Butyne polymerizes to give hexamethyl benzene.



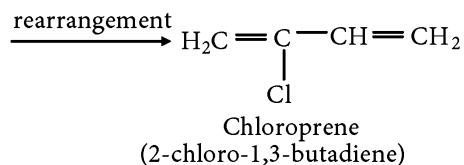
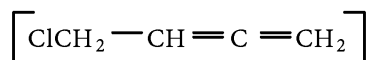
Acetylene polymerizes to cyclooctatetraene in presence of $\text{Ni}(\text{CN})_2$



When acetylene is treated with a solution of cuprous chloride in ammonium chloride, it undergoes polymerization to give a dimer (vinylacetylene) and a trimer (divinylacetylene).



When vinyl acetylene is treated with conc. HCl in the presence of cuprous chloride and ammonium chloride chloroprene is obtained.



Chloroprene readily polymerizes to give a type of rubber known as neoprene.

ESTIMATION OF ELEMENTS

In order to arrive at the correct structure of an organic compound, it is necessary to know the empirical and molecular formulae of the compound.

The presence of various elements in an organic compound can be detected by some tests in qualitative analysis. An organic compound necessarily contains carbon and

hydrogen. The other elements that are likely to be found in a compound are oxygen, nitrogen, halogen, sulphur and phosphorus.

The exact quantities of carbon and hydrogen in an organic compound are estimated by quantitative analysis using Liebig Combustion method.

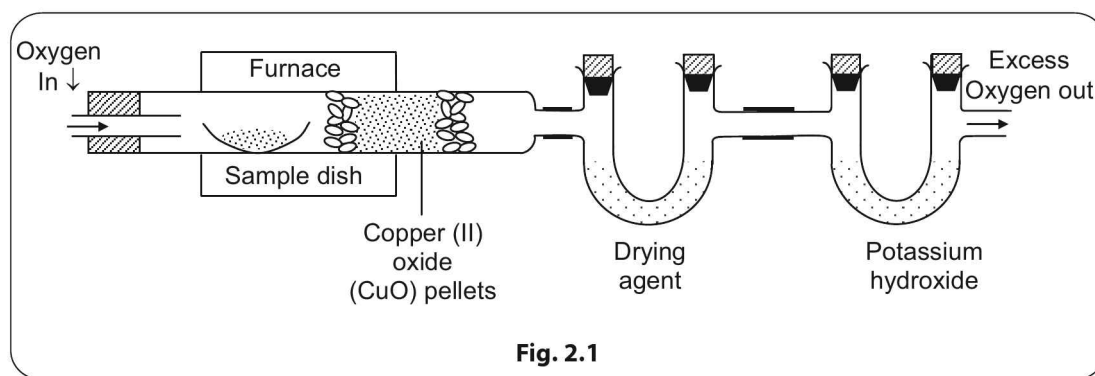
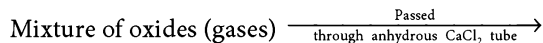
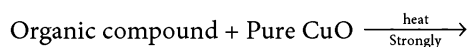
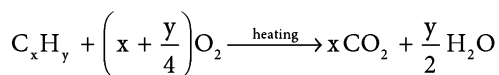


Fig. 2.1



Increase in weight of CaCl_2 tube gives the weight of H_2O $\xrightarrow[\text{passed through dry KOH tubes}]{\text{Gases are further}}$ Increase in weight of KOH tubes gives the weight of CO_2

A small quantity of the organic compound (say about 100 mg) is weighed accurately in a clean dry platinum boat and mixed with two or three times its weight of pure dry copper oxide and heated strongly in a long pyrex hard glass combustion tube. The material is heated in a current of oxygen. The gases released are passed through a series of U-shaped absorption tubes which are filled with anhydrous CaCl_2 , dry KOH solid (pellets) respectively. These U-tubes are previously weighed accurately and their initial weights are known, after sometime, the tubes are weighed again and repeatedly until there is no further increase in weights of the absorption tubes are noticed.



(i) Estimation of Carbon

Let us assume that the increase in weight of KOH absorption tube is 'a' g. Let the initial weight of the organic substance taken be 'x' g.

If 44 g of CO_2 is produced, the weight of carbon is 12 g.

If 'a' g of CO_2 is produced, the weight of carbon is

$$\frac{12}{44} \times a \text{ g}$$

$$\frac{12}{44} \times a \text{ g of carbon is present in 'x' g of the substance.}$$

$$100 \text{ g of the substance contains } \frac{12}{44} \times \frac{a}{x} \times 100 = \% \text{ carbon}$$

(ii) Estimation of Hydrogen

Let us assume that the increase in weight of CaCl_2 absorption tube is 'b' g. The initial weight of the organic substance taken be 'x' g. If 18 g of water is produced, the weight of hydrogen is 2g. If 'b' g of water is produced, the weight of

$$\text{hydrogen is } \frac{2}{18} \times b = \frac{2b}{18} \text{ g}$$

$$\frac{2b}{18} \text{ g of hydrogen is present in x g of the organic substance. 100 g of the substance contains}$$

$$\frac{2}{18} \times b \times \frac{100}{x} = \% \text{ Hydrogen}$$

The quantities of other elements present like nitrogen, halogen, sulphur, phosphorus are estimated by various

2.30 Alkanes, Alkenes and Alkynes

methods. Quantitative analysis is used to determine the percentage composition of a compound. There are standard

methods available for analyzing the compound to find out the percentages of the elements present.

EMPIRICAL AND MOLECULAR FORMULAE OF SIMPLE COMPOUNDS

After the completion of the percentage composition of elements, the empirical formula of the compound is found out. Empirical formula is the simplest formula that shows the ratio of the various elements in the formula of the compound. When the empirical formula is multiplied by a small whole number, molecular formula is obtained.

Molecular formula = (Empirical formula) $\times$ n

where n is a small whole number

$$n = \frac{\text{Molecular formula weight}}{\text{Empirical formula weight}} \quad (\text{or})$$

$$n = \frac{2 \times \text{vapour density}}{\text{Empirical formula weight}}$$

CONCEPT STRANDS

Concept Strand 1

An organic compound containing C, H and O weighing 0.1435 g gave on combustion 0.3253 g of CO_2 and 0.1339 g of water. Calculate the percentages of C, H and O in the compound.

Solution

Weight of organic compound = 0.1435 g

Weight of CO_2 formed = 0.3253 g

Weight of H_2O formed = 0.1339 g

$$\begin{aligned} \text{Percentage of carbon} &= \frac{12}{44} \times 100 \times \frac{0.3253}{0.1435} \\ &= 61.83 \end{aligned}$$

$$\begin{aligned} \text{Percentage of hydrogen} &= \frac{2}{18} \times \frac{0.1339}{0.1435} \times 100 \\ &= 10.37 \end{aligned}$$

The percentage of oxygen is found out by difference

$$100 - (61.83 + 10.37) = 100 - 72.20 = 27.80\%$$

Percentage of oxygen = 27.80

Concept Strand 2

An organic compound containing C, H and O, has 52.2% carbon, 13% hydrogen and rest of oxygen. Calculate the empirical formula of the compound?

Solution

Percentage of carbon = 52.2

$$\text{C} : \text{H} : \text{O} = \frac{52.2}{12} : \frac{13.0}{1} : \frac{34.8}{16} = 4.35 : 13.0 : 2.17$$

Dividing these numbers by the smallest number, we get the atomic ratio.

$$\text{C} : \text{H} : \text{O} = \frac{4.35}{2.17} : \frac{13.0}{2.17} : \frac{2.17}{2.17} = 2 : 6 : 1$$

The empirical formula = $\text{C}_2\text{H}_6\text{O}$

Concept Strand 3

A hydrocarbon contains 88.88% of carbon and its molecular weight is 54 g mol^{-1} . Arrive at the molecular formula of hydrocarbon and propose three structures for the isomeric compounds.

Solution

Percentage of carbon = 88.88

Percentage of hydrogen = 11.12

$$\text{C} : \text{H} = \frac{88.88}{12} : \frac{11.12}{1} = 7.4 : 11.12$$

Dividing by the smallest number, we get

$$\text{C} : \text{H} = \frac{7.4}{7.4} : \frac{11.12}{7.4} = 1 : 1.5 = 2 : 3$$

$\therefore$ Empirical formula = C_2H_3

Empirical formula weight = $12 \times 2 + 3 \times 1 = 27$

Mol Weight = 54

$$\therefore n = \frac{54}{27} = 2$$

Molecular formula = Empirical formula $\times 2 = \text{C}_4\text{H}_6$

Four possible isomeric structures could be

1. 1-Butyne	$\text{HC} \equiv \text{C} - \text{CH}_2 - \text{CH}_3$
2. 2-Butyne	$\text{H}_3\text{C} - \text{C} \equiv \text{C} - \text{CH}_3$
3. 1,3-Butadiene	$\text{H}_2\text{C} = \text{CH} - \text{CH} = \text{CH}_2$
4. 1,2-Butadiene	$\text{CH}_3 - \text{CH} = \text{C} = \text{CH}_2$

Concept Strand 4

An organic compound accounted for 40% carbon and 6.7% hydrogen. 0.010 g of the compound in the gaseous form occupied a volume of 8.15 mL at 25°C and 1 atm pressure (760 mm). Arrive at the molecular formula of the compound. Propose a possible structure for the compound.

Solution

Percentage of carbon = 40.0

$$\text{Relative number of atoms} = \frac{40.0}{12} = 3.33$$

Percentage of hydrogen = 6.7

$$\text{Relative number of atoms} = \frac{6.7}{1} = 6.7$$

Percentage of oxygen = 53.30

$$\text{Relative number of atoms} = \frac{53.30}{16} = 3.33$$

Dividing by the smallest number, empirical formula of the compound = CH_2O

8.15 mL of the compound weighs 0.010 g at 25°C and 760 mm pressure

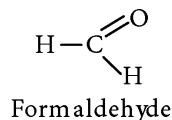
Molecular weight

$$= \frac{\text{WRT}}{\text{PV}} = \frac{0.010 \times 0.0821 \times 298}{1 \times 0.00815} = 30.02 \text{ g mol}^{-1}$$

Empirical formula weight = 30

Molecular formula is the same as the empirical formula which is CH_2O

Possible structure of the compound is



SUMMARY

Introduction

General formulae of alkanes, alkenes and alkynes,

Examples

Preparation of alkanes

Wurtz reaction.

Decarboxylation of sodium salts of carboxylic acids with soda lime.

Kolbe's electrolytic synthesis.

Corey-House synthesis.

Preparation using Grignard reagent

Frankland reaction.

Preparation of alkenes

Kolbe's electrolytic method.

Dehydration of alcohols and its mechanism

Dehydrohalogenation of alkyl halides

Orientation of elimination reactions-Saytzeff's rule and Hofmann's rule. Reduction of alkynes-reduction using Lindlar's catalyst gives cis alkenes while reduction using Na/liq.NH_3 gives trans alkene.

Preparation of alkynes

Kolbe's electrolysis

Preparation by elimination of dihalides

2.32 Alkanes, Alkenes and Alkynes

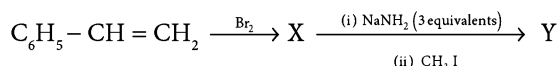
Physical properties of alkanes, alkenes and alkynes	Variation of melting and boiling point among isomeric compounds and also with increase in molecular mass.
Reactions of alkanes	Combustion reaction, Halogenation of alkanes-takes place by free radical mechanism. The relative reactivity of 1°, 2° and 3° hydrogen in alkanes for chlorination is 1 : 3.8 : 5 and that for bromination is 1 : 82 : 1600
Reactions of alkenes	Acid catalysed hydration gives alcohol-Markovnikov's addition of water takes place. Oxymercuration- reduction also gives alcohol and net effect involves addition of water in accordance with Markovnikov's rule. Hydroboration-oxidation involves addition of water against Markovnikov's rule. Cold dilute alkaline KMnO_4 and OsO_4 produce cis diols with alkenes. Peracids give epoxides. Ozonolysis gives a mixture of aldehydes and ketones depending upon the structure of the alkene. Alkenes undergo electrophilic addition reactions with halogens, hydrogen halides, hypohalous acids etc. Explanation of Markovnikov's rule and peroxide effect. Stereochemistry of addition of halogen to alkenes. Regioselective and stereospecific reactions.
Reactions of alkynes	Acidity of alkynes-terminal alkynes are acidic due to the presence of hydrogen on sp hybridized carbon. Ozonolysis of alkynes gives dicarbonyl compounds. Electrophilic addition reactions with halogens, hydrogen halide and hypohalous acids. Hydroboration-oxidation reaction. Addition of HCN Hydration of alkynes : acetylene gives acetaldehyde while other alkynes give ketones. Polymerization reactions.
Estimation of elements	Experimental method of determination of carbon and hydrogen in an organic compound.
Empirical and molecular formula	Definition Calculation of empirical and molecular formula of a compound from its percentage composition.

TOPIC GRIP

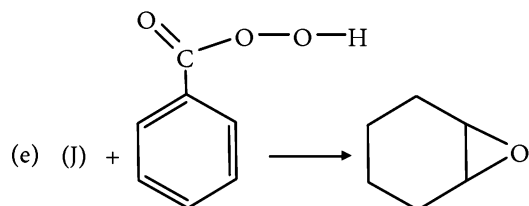
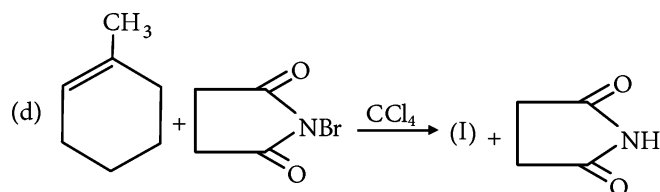
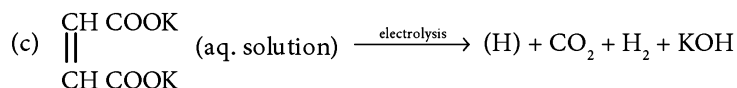
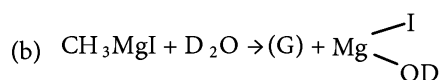
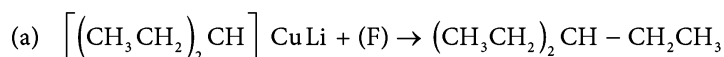


Subjective Questions

1. Identify the products X and Y in the following reaction



2. Identify the compounds marked by letters (F), (G), (H), (I), and (J) in the following reactions.



3. Write the structural formula of a hydrocarbon of molecular formula

- C_6H_{12} having only secondary hydrogens
- C_5H_{12} having only primary hydrogens
- C_6H_{14} having only primary and tertiary hydrogens

4. Rationalize the following statements/observations

- Alkanes are unreactive when compared with alkenes.
- In the case of isomeric alkanes, the boiling points decrease with increase in branching of the chain.
- Normal alkanes with even number of carbon atoms melt at a higher temperature than the adjacent alkane having odd number of carbon atoms.

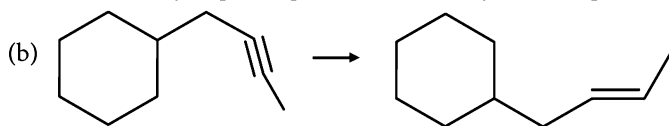
5. (a) Write the structure of organic product formed by heating $\text{C}(\text{CH}_2\text{I})_4$ with zinc dust.

- (b) How is buta-1, 3-diene prepared from but-1-ene

- (c) What are the products expected when ethylene is passed into an aqueous solution of bromine containing dissolved sodium chloride?

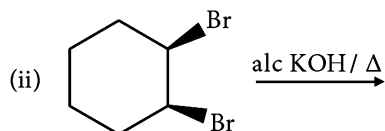
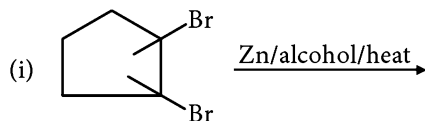
2.34 Alkanes, Alkenes and Alkynes

6. (a) How is $\text{CH}_3\text{CH}_2\text{CHBr}_2$ converted to $\text{CH}_3\text{CHBrCH}_2\text{Br}$



Indicate the reagent used for the above conversion

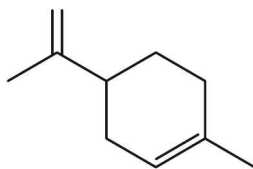
(c) Identify the products formed in the following reactions.



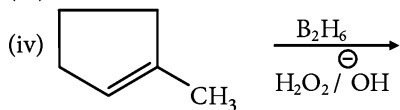
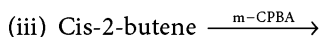
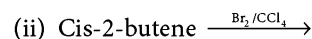
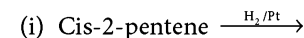
7. What are the products formed when buta-1, 3-diene is treated with HBr in 1:1 molar proportion? Explain the formation of the products.

8. (a) Identify the products of reductive ozonolysis of the monomer of natural rubber.

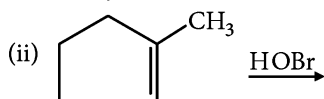
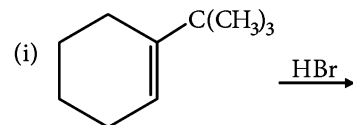
(b) What are the products of reductive ozonolysis of limonene whose structure is given below



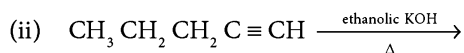
9. Complete the following equations showing the stereo chemistry of the product wherever applicable.



10. (a) Identify the products expected in the following reactions



(b) Identify the products (if there are two products, the major product) in the following reactions.



- (c) (i) Why a Grignard reagent cannot be prepared from $\text{HC} \equiv \text{C} - \text{CH}_2\text{Br}$?
 (ii) How is $\text{HC} \equiv \text{CH}$ converted to $\text{DC} \equiv \text{CD}$?



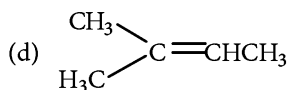
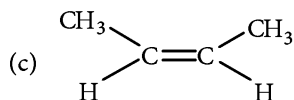
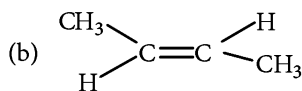
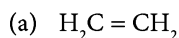
Straight Objective Type Questions

Directions: This section contains multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

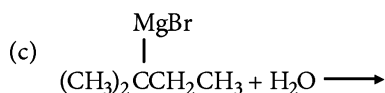
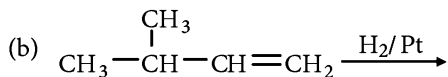
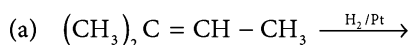
11. The best method of preparation of an alkane with odd number of carbons from two alkylhalides is

- (a) Wurtz reaction (b) Kolbe's electrolysis
 (c) Corey-House synthesis (d) Ullmann reaction

12. The most stable alkene among the following is



13. A reaction that will lead to 2-methylbutane is

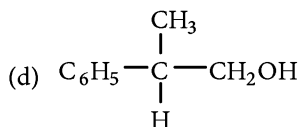
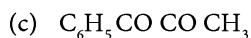
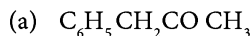


- (d) all the reactions given (a) - (c)

14. When propyne is treated with excess chlorine water, the final product obtained is

- (a) 1, 1-dichloro propanone (b) 2, 3 dichloro dihydroxy propane
 (c) 2, 2-dichloropropanal (d) 1-hydroxy-3-chloro propanone

15. $\text{C}_6\text{H}_5\text{C} \equiv \text{C} - \text{CH}_3 \xrightarrow[85^\circ\text{C}]{\text{H}_2\text{SO}_4/\text{HgSO}_4}$ product The product formed is



Assertion-Reason Type Questions

Directions: Each question contains Statement-1 and Statement-2 and has the following 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

2.36 Alkanes, Alkenes and Alkynes

16. Statement 1

Markovnikov rule is based on the relative stability of carbocations.

and

Statement 2

Markovnikov rule is applicable for electrophilic addition of unsymmetrical reagents to unsymmetrical alkenes.

17. Statement 1

Alkynes are more reactive than alkenes in electrophilic addition reactions.

and

Statement 2

Electrophilic addition to both alkenes and alkynes involve a three membered cyclic intermediate and the bromonium ion type intermediate is less stable for an alkyne than for an alkene.

18. Statement 1

Among the alkenes, 1-pentene (I), cis 2-pentene (II) and trans 2-pentene (III), the decreasing order of stability is III > II > I.

and

Statement 2

The relative stability of alkenes is explained by hyperconjugation and steric effect.

19. Statement 1

$\text{CH}_3 - \overset{\text{CH}_3}{\underset{|}{\text{CH}}} - \text{CH} = \text{CH}_2$ on reaction with mercuric acetate followed by treatment with NaBH_4 and a base gives $\text{CH}_3\text{CH}(\text{CH}_3)\text{CHOHCH}_3$.

and

Statement 2

Oxymercuration reactions proceed by a radical mechanism.

20. Statement 1

$\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$ is more reactive towards HBr compared to ethylene.

and

Statement 2

The carbocation formed in $\text{CH}_3\text{CH} = \text{CH} - \text{CH}_3$ during the addition of HBr is more stabilized compared to the cation formed from ethylene.



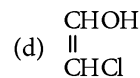
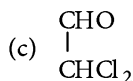
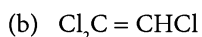
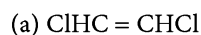
Linked Comprehension Type Questions

Directions: This section contains 2 paragraphs. Based upon the paragraph, 3 multiple choice questions have to be answered. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

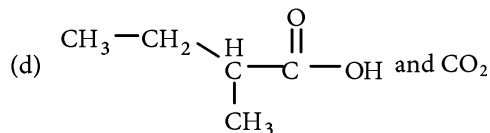
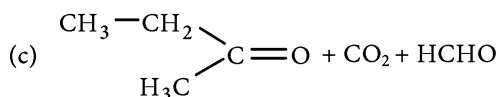
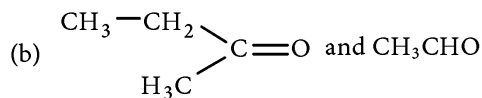
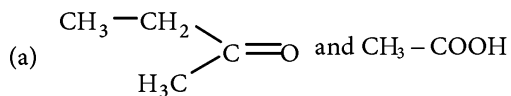
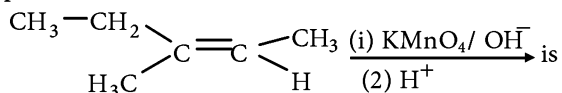
Passage I

Alkenes and alkynes act as nucleophiles and react with electrophiles by a reaction known as electrophilic addition. The π electrons of the multiple bonds are areas of high electron density.

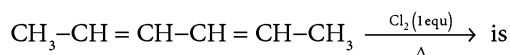
21. Addition of Cl_2 water to ethyne gives



22. The product obtained in the reaction



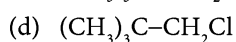
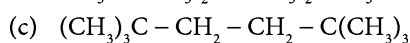
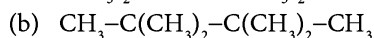
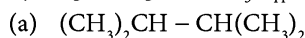
23. The major product in the following reaction is



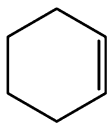
Passage II

The relative reactivity of 1°, 2° and 3° hydrogens for chlorination is 1 : 3.8 : 5 while for bromination it is 1 : 82 : 1600. Allylic, vinylic and aliphatic hydrogens also vary in their reactivity.

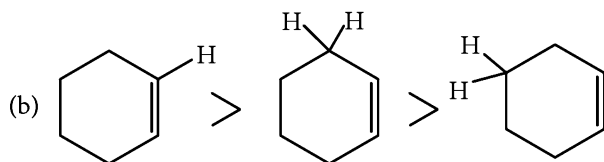
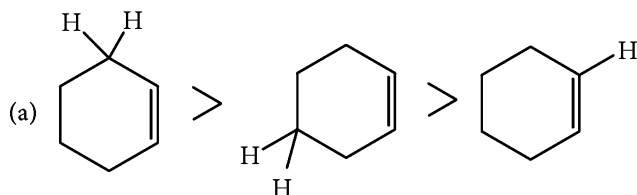
24. A hydrocarbon C_5H_{12} (A) on treatment with chlorine undergoes monochlorination by the replacement of the only 1° hydrogen to give (B) $\text{C}_5\text{H}_{11}\text{Cl}$. When (B) is treated with Na metal in ether, the product obtained could be



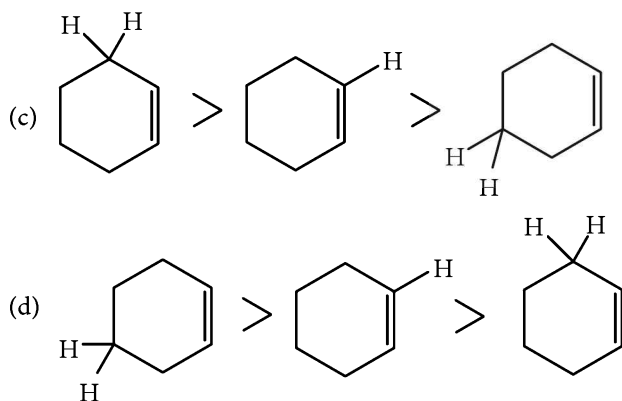
25. Consider the following structure



The reactivity sequence of the hydrogens towards substitution will be



2.38 Alkanes, Alkenes and Alkynes



26. A hydrocarbon having only primary hydrogens is

- (a) Cyclohexane (b) 2-methylpropane
(c) 2,3 dimethyl but-2-ene (d) n-butane



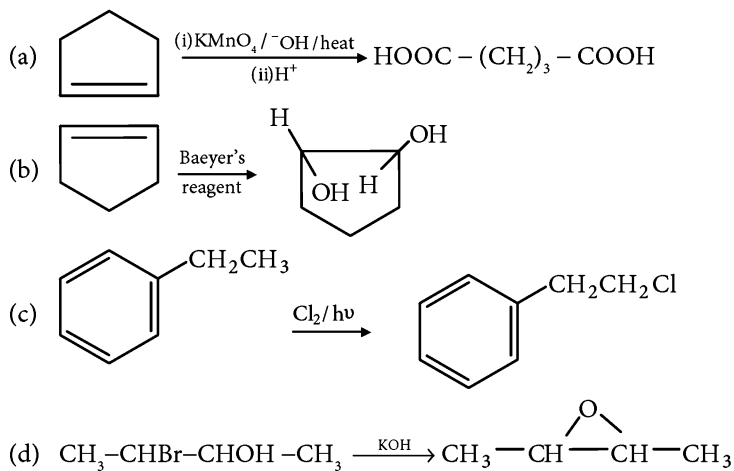
Multiple Correct Objective Type Questions

Directions: Each question in this section has four suggested answers of which ONE OR MORE answers will be correct.

27. Which of the following compounds can exhibit geometrical isomerism?

- (a) $\text{IBrC} = \text{CFCI}$ (b) Cinnamic acid
(c) Benzophenone oxime (d)

28. Which of the following reactions are correctly represented?



29. Identify the correct statements among the following

- (a) Chlorination of n-butane involves the attack by a free radical.
(b) 2,3-Dimethylbutane can form only two monochloro derivatives

- (c) Between $\text{CH}_3\text{--C}\equiv\text{C--CH}_2\text{--CH}_3$ (I) and $\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--C}\equiv\text{CH}$ (II), only (II) will react with CH_3MgI .
- (d) When a mixture of ethane, ethylene and ethyne is passed into a solution of ammoniacal AgNO_3 , the gases bubbling out will be a mixture of ethane and ethylene



Matrix-Match Type Question

Directions: Match the elements of Column I to elements of Column II. There can be single or multiple matches.

30.

Column I

- (a) Neopentane
- (b) Cyclohexane
- (c) 2, 2-dimethyl butane
- (d) 2, 2, 3, 3 – tetramethyl butane

Column II

- (p) equatorial hydrogens
- (q) Secondary hydrogens
- (r) Quaternary carbon
- (s) Only one monochloro derivative

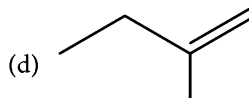
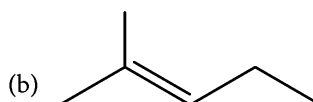
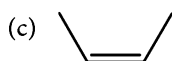
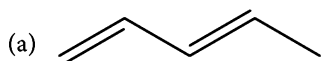
IIT ASSIGNMENT EXERCISE



Straight Objective Type Questions

Directions: This section contains multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

31. Which of the following alkene is most stable?



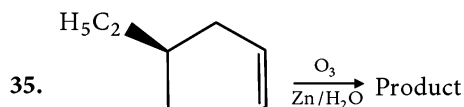
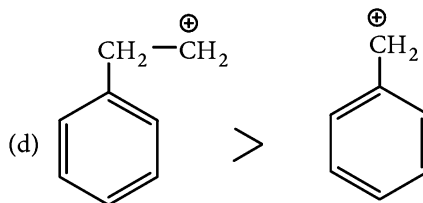
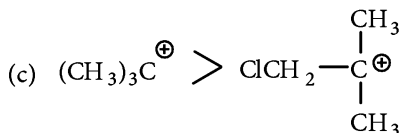
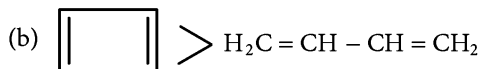
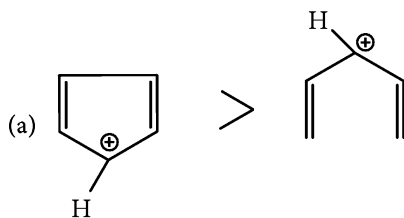
32. Four reagents and specific reactions in which they are involved are given. Identify the wrongly matched option among the following

(a) Hot alcoholic KOH	– dehydrohalogenation
(b) $\text{H}^+/\text{H}_2\text{O}$	– hydration
(c) H^+/Δ	– dehydration
(d) Unsymmetrical alkene $\xrightarrow[\text{peroxide}]{\text{HCl}}$	– anti Markovnikov addition

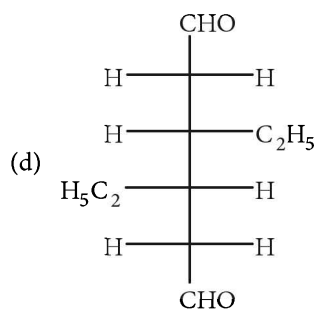
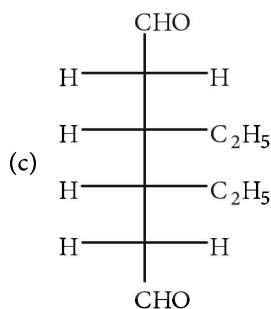
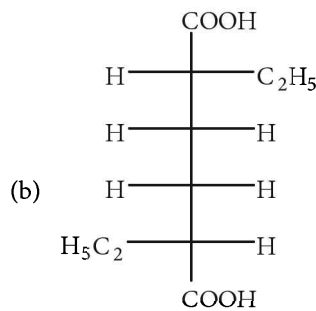
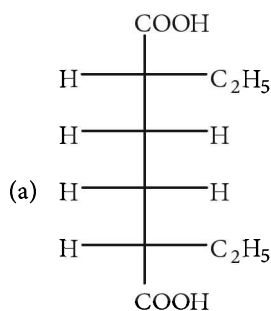
33. A reagent that can form a hydrocarbon with a Grignard reagent is

(a) HCOOC_2H_5	(b) $\text{C}_6\text{H}_5\text{NH}_2$
(c) CH_3COCH_3	(d) $\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$

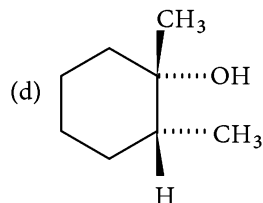
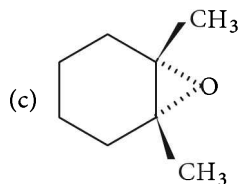
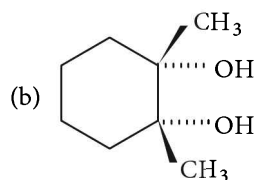
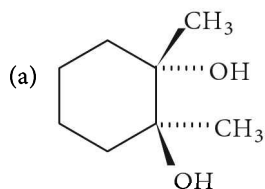
34. In which of the following the correct comparison of stability is represented?



The structure of the product is



36. When is treated with Baeyer's reagent, the major product obtained is



37. In the photochemical chlorination of ethane, the presence of oxygen in the reaction mixture

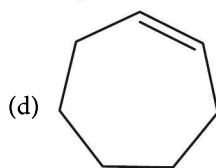
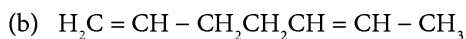
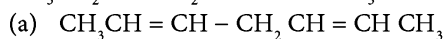
- accelerates the rate of formation of the halogenated product.
- does not have any effect in the reaction.
- makes the reaction explosive.
- retards the halogenation process.

38. The major product obtained when 2-phenylpropene is treated with water containing acid is

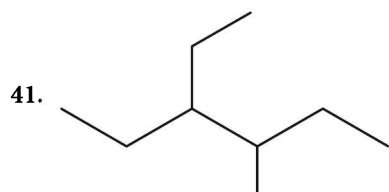
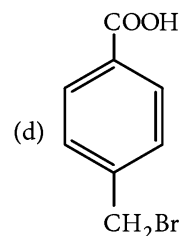
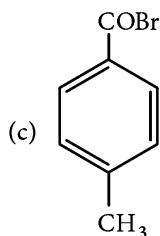
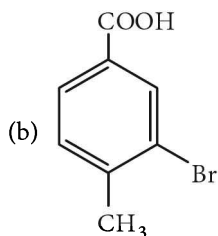
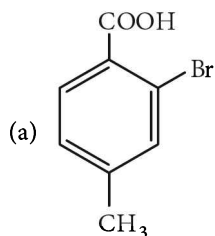
- $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$
- $\text{C}_6\text{H}_5\text{CH}_2\text{CHOHCH}_3$
- $\text{C}_6\text{H}_5\text{CHOHCH}_2\text{CH}_3$
- $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{OH}$

2.42 Alkanes, Alkenes and Alkynes

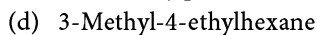
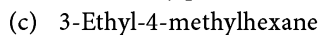
39. $\text{CH}_3\text{CH}_2\text{CHI} \text{CH}_2\text{CH}=\text{CH}-\text{CH}_3 \xrightarrow{\text{alc. KOH}/\Delta}$ (A). The product (A) is



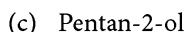
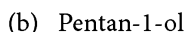
40. The product formed when p-toluic acid reacts with N-bromosuccinimide in CCl_4 medium is



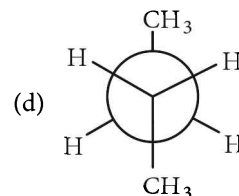
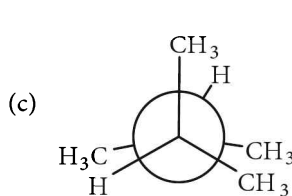
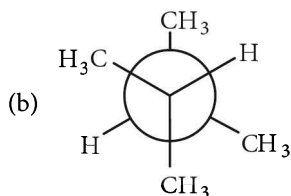
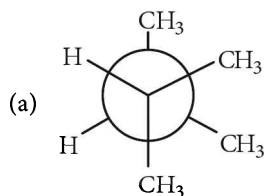
The IUPAC name of the hydrocarbon given above is



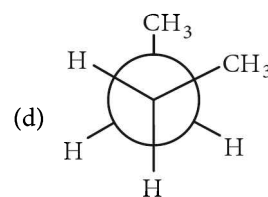
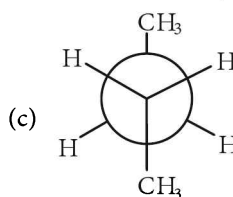
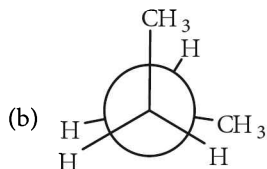
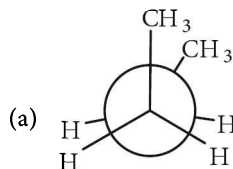
42. 1-Pentyne reacts with 40% H_2SO_4 in the presence of 1% HgSO_4 to give



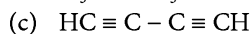
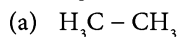
43. The conformation of 2, 3-dimethylbutane of least energy is



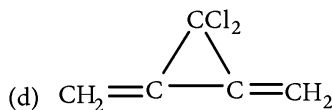
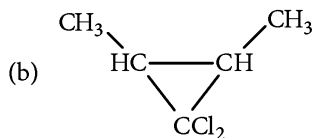
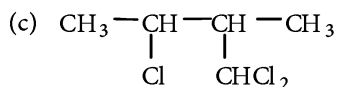
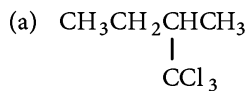
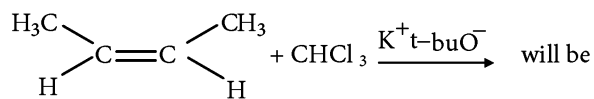
44. The structure of n-butane having maximum dihedral angle between the two CH_3 groups will be



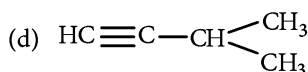
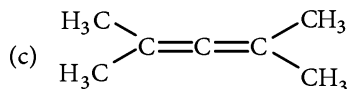
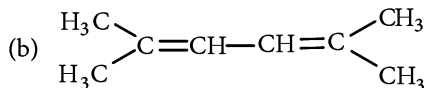
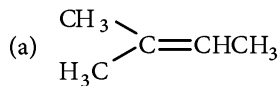
45. Among the following which has the shortest C-C single bond length?



46. The product obtained in the reaction



47. Ozonolysis of a compound gives acetone and CO_2 . The compound could be



48. Which of the following will have zero dipole moment?

(a) Cis 1, 2 dichloroethene

(b) 1, 1 dichloroethene

(c) Cis-2-butene

(d) trans-1, 2 dichloroethene

49. Alkanes and alkenes can be prepared by

(a) Wurtz reaction

(b) Williamson synthesis

(c) Dehydrohalogenation

(d) Kolbe's electrolysis

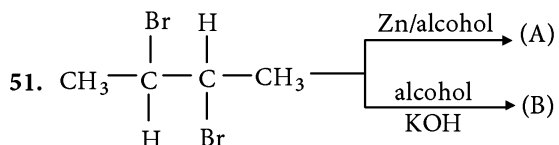
50. HI does not exhibit peroxide effect because

(a) HI is a reducing agent.

(b) the iodine free radicals formed recombine readily to form the iodine molecule.

(c) the bond energy of HI is very high that it does not undergo homolytic fission to give iodine radicals.

(d) Free radical reactions work well when both the propagation steps are endothermic.



(A) and (B) are respectively

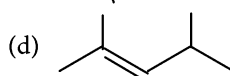
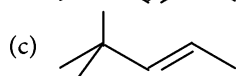
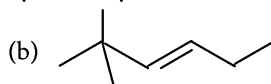
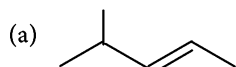
(a) But-2-yne and but-2-ene

(b) But-2-ene and but-2-yne

(c) Butane and but-2-ene

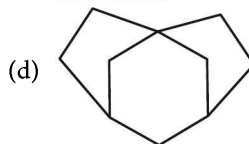
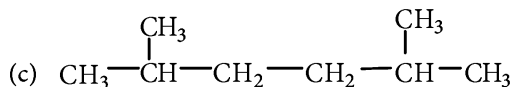
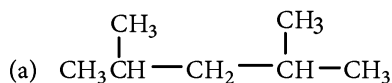
(d) But-2-ene and butane

52. Treatment of an alkene with hot alkaline KMnO_4 gives t-butyl carboxylic acid and acetic acid. The alkene is



2.44 Alkanes, Alkenes and Alkynes

53. Which of the following compounds cannot be synthesized by Wurtz reaction.



54. When n-hexane is passed over heated alumina or chromic oxide catalyst under pressure, the product formed is

- (a) Iso hexane (b) cyclohexane (c) butane and ethane (d) Benzene

55. Simplest alkane which can exhibit optical activity is

- (a) 3-methyl hexane (b) 3-methyl heptane (c) 2-methyl butane (d) neopentane

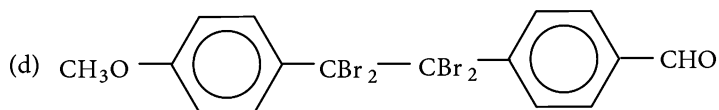
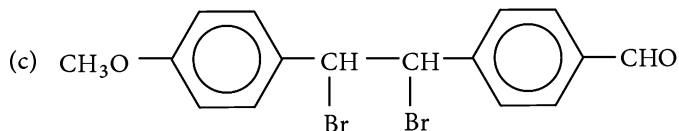
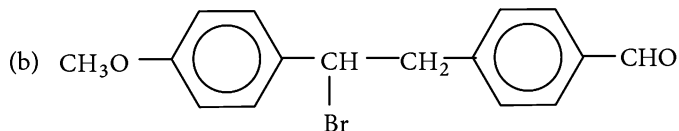
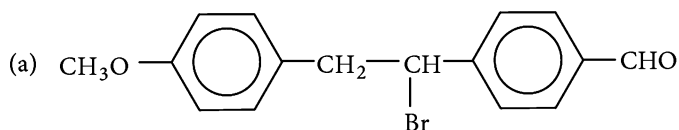
56. $\text{CH}_3\text{COCH}_2\text{CH}_3$ can be reduced to n-butane when the reducing agent is

- (a) NaBH_4 (b) LiAlH_4 (c) Zn(Hg)/HCl (d) H_2S

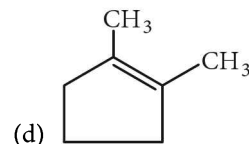
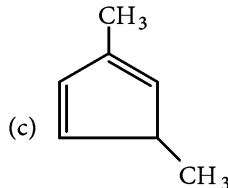
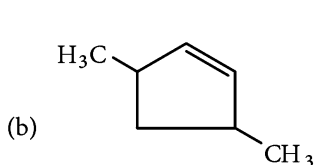
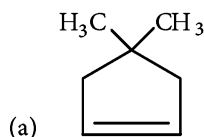
57. 1, 6 Dibromohexane can be converted to cyclohexane, when treated with Na or Zn, in the presence of a catalyst. This reaction is known as

- (a) Wurtz coupling (b) Dieckmann cyclization (c) Freund's method (d) Diels Alder reaction

58. When $\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{CHO}$ is treated with HBr in CCl_4 , the major product obtained is



59. The unsaturated compound which gives $\text{OHC}-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CHO}$ as the product of reductive ozonolysis is



60. Which of the following is not a β elimination?

- (a) dehydration of alcohols
- (b) dehydrohalogenation of alkyl halides
- (c) dehalogenation of vicinal dibromides
- (d) dehydrohalogenation of chloroform

61. The reactions of alkenes are mainly

- (a) nucleophilic additions
- (b) nucleophilic substitutions
- (c) free radical reactions
- (d) electrophilic additions

62. The conversion $\text{CH}_3 \overset{\text{CH}_3}{\underset{|}{\text{CH}}} - \text{CH} = \text{CH}_2 \longrightarrow \text{H}_3\text{C} - \overset{\text{CH}_3}{\underset{|}{\text{CH}}} - \text{CHOH} - \text{CH}_3$ can be successfully carried out by

- (a) $\text{H}^+/\text{H}_2\text{O}$
- (b) Hydroboration-oxidation
- (c) HBr addition in the presence of peroxides followed by hydrolysis with aqueous KOH
- (d) Oxymercuration-reduction

63. $\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_3 \xrightarrow[\text{quinoline}]{\text{H}_2 / \text{Pd} - \text{BaSO}_4} (\text{A}) \xrightarrow[\text{CCl}_4]{\text{Br}_2} (\text{B})$. The product (B) is

- (a) meso - 2, 3 - dibromo butane
- (b) racemic - 2, 3 - dibromo butane
- (c) 2, 2, 3, 3 - tetra bromo butane
- (d) 1, 4 - dibromo butane

64. $\text{H}_3\text{C} - \text{C} \equiv \text{CH} + \text{CH}_3\text{MgI} \longrightarrow (\text{A}) + \text{CH}_4$

$(\text{A}) + \text{CH}_3\text{I} \longrightarrow (\text{B}) + \text{MgI}_2$

(A) and (B) are

- (a) $\text{H} - \text{C} \equiv \text{C} - \text{MgI}$ and CH_4
- (b) $\text{H}_3\text{C} - \text{C} \equiv \text{C} - \text{CH}_3$ and CH_4
- (c) $\text{CH}_3 - \text{C} \equiv \text{C} - \text{MgI}$ and $\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_3$
- (d) $\text{H}_3\text{C} - \text{C} \equiv \text{C} - \text{I}$ and $\text{Mg} \begin{array}{c} \diagup \text{I} \\ \diagdown \text{I} \end{array}$

65. One of the following synthetic procedures will not be successful with Corey-House synthesis. Identify the reactions

(a) $\text{CH}_3\text{CH}_2\text{Cl} \xrightarrow[\text{(ii) CuI}]{\text{(i) Li/ether}} (\text{CH}_3\text{CH}_2)_2\text{CuLi} \xrightarrow{\text{CH}_3\text{CH}_2\text{Cl}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

(b) $(\text{CH}_3\text{CH}_2)_2\text{CuLi} \xrightarrow{\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{Br}} \text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_3$

(c) $\left[(\text{CH}_3)_2\text{CH} \right]_2\text{CuLi} \xrightarrow{(\text{CH}_3)_2\text{CHCH}_2\text{Br}} (\text{CH}_3)_2\text{CH} - \text{CH}_2\text{CH}(\text{CH}_3)_2$

(d) $\left[(\text{CH}_3)_3\text{C} - \text{CH}_2 \right]_2\text{CuLi} \xrightarrow{\text{CH}_3\text{CH}_2\text{Br}} (\text{CH}_3)_3\text{CCH}_2\text{CH}_2\text{CH}_3$

66. Identify the product in the given reaction.

$\text{CH}_3\text{CH} = \text{CH}_2 + \text{NOCl} \rightarrow (\text{A})$

(a) $\text{CH}_3 - \text{CHCl} - \text{CH}_2\text{NO}$

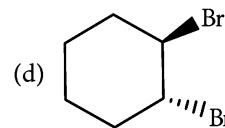
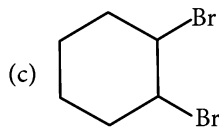
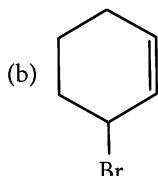
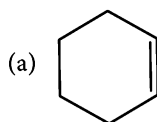
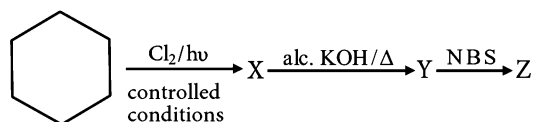
(b) $\text{CH}_3 - \underset{\text{NO}}{\underset{|}{\text{CH}}} - \text{CH}_2\text{Cl}$

(c) $\text{CH}_3\text{CH}_2\text{CHClNO}$

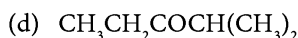
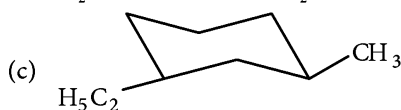
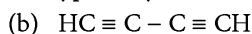
(d) $\text{CH}_3\text{NOCH}_2\text{CH}_2\text{Cl}$

2.46 Alkanes, Alkenes and Alkynes

67. Identify the compound Z in the following sequence of reactions



68. Among the following compounds which one has more than one type of hybridization of carbon



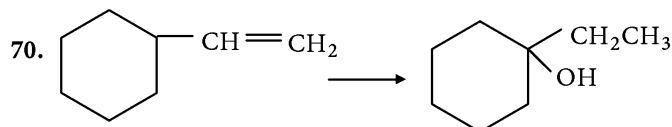
69. $\text{HC}\equiv\text{N}$ is more acidic than $\text{HC}\equiv\text{CH}$ because

(a) HCN is an acid whereas, $\text{HC}\equiv\text{CH}$ is a hydrocarbon.

(b) HCN has a pK_a of 9.2.

(c) In addition to greater s character of the hybrid orbitals, the presence of more electronegative nitrogen further stabilizes the anion ^-CN .

(d) of the triple bond nature of the $^-\text{C}\equiv\text{N}$ bond.



The sequence of reactions to be followed for the above conversion are

(a) hydrogenation and hydration

(b) hydrogenation, halogenation and hydration

(c) oxymercuration, dehydration and hydration

(d) hydroboration, dehydration and hydration

71. A reaction in which an alkene is formed is

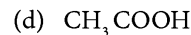
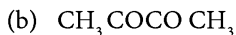
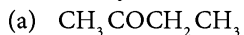
(a) 1-bromo-1-methylcyclohexane is treated with NaOH in the presence of acetone.

(b) 1-bromo-1-methylcyclohexane is treated with $(\text{C}_2\text{H}_5)_3\text{N}$.

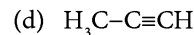
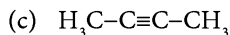
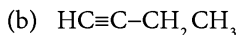
(c) Chlorocyclohexane is heated with $(\text{CH}_3)_3\text{CONa}$ in t-butanol

(d) 1-bromo-1-phenylbutane is treated with aqueous NaOH

72. When $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$ is treated with ozone by reductive ozonolysis procedure the product(s) obtained is/are



73. The silver salt of a mono acidic alkyne contains 67% Ag. The structure of the alkyne is



74. The correct decreasing order of the acidity of hydrogen in acetylene, phenol, alcohol, ethylene and acetic acid is

(a) Acetic acid > Phenol > alcohol > acetylene > ethylene

(b) Phenol > acetic acid > alcohol > acetylene > ethylene

(c) Acetic acid > alcohol > phenol > acetylene > ethylene

(d) Acetic acid > acetylene > phenol > alcohol > ethylene

75. An ester on hydrolysis gave an acid which on Kolbe's electrolysis gave ethane. The ester is

- (a) $\text{CH}_3\text{CH}_2\text{COOCH}_3$ (b) $\text{H}_2\text{C} \begin{array}{l} \nearrow \text{COOC}_2\text{H}_5 \\ \searrow \text{COOC}_2\text{H}_5 \end{array}$ (c) $\text{CH}_3\text{COOC}_2\text{H}_5$ (d) $\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5$

76. Acetylene reacts with chlorine water to give

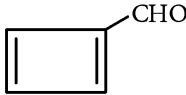
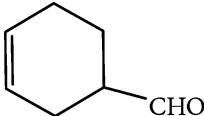
- (a) $\text{Cl}_2\text{CH}-\text{CHCl}_2$ (b) $\begin{array}{c} \text{CHO} \\ | \\ \text{CHCl}_2 \end{array}$
(c) $\text{CH}_3-\text{CO}-\text{CH}_2-\text{CH}_2-\text{COCH}_3$ (d) $\begin{array}{c} \text{CHOH} \\ || \\ \text{CHCl} \end{array}$

77. An alkene on mild oxidation with dil. aqueous KMnO_4 gave a product which on further treatment with HIO_4 gave hexane-2, 5-dione. The alkene is

- (a) $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$ (b) $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$
(c) Cyclohexane (d) 1, 2 dimethyl cyclobutene

78. $\text{HOH}_2\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{OH} \xrightarrow{\text{H}_3\text{PO}_4/\Delta} \text{A} \xrightarrow{\text{CH}_2=\text{CH}-\text{CHO}} \text{B}$

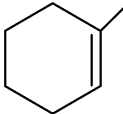
The structure of (B) is

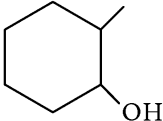
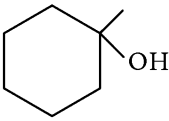
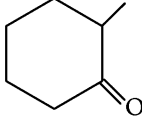
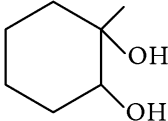
- (a) $\text{H}_3\text{C}-\text{CH}=\text{CH}-\text{CH}_2-\text{CHO}$ (b) 
(c)  (d) $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}-\text{CHO}$

79. $\text{CH}_3\text{CH}_2\text{CH}_3 \xrightarrow{\text{Br}_2/h\nu} (\text{A}) \xrightarrow{\text{Mg/Ether}} (\text{B}) \xrightarrow{\text{D}_2\text{O}} (\text{C})$

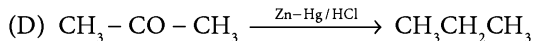
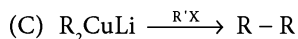
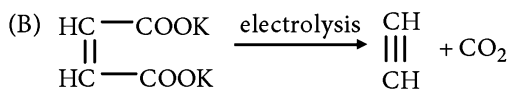
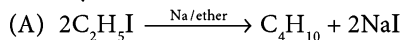
The major product C formed is

- (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{D}$ (b) $\text{CH}_3\text{CH}_2\text{CH}_3$ (c) $\text{CH}_3\text{CHDCH}_3$ (d) $\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_3 \\ | \\ \text{OD} \end{array}$

80. When  is treated with diborane in dry ether followed by oxidation with alkaline hydrogen peroxide, the major product obtained is

- (a)  (b) 
(c)  (d) 

81. Identify the name of reactions (A) – (D) given below



- (a) (A) Ulmann reaction (B) Electrolytic cleavage (C) Grignard reaction (D) Wolff-kishner reduction
(b) (A) Wurtz reaction (B) Kolbe's electrolysis (C) Corey-House synthesis (D) Clemmensen reaction

2.48 Alkanes, Alkenes and Alkynes

- (c) (A) Wurtz reaction (B) Decarboxylation (C) Frankland reaction (D) Clemmensen reduction
 (d) (A) Wurtz-Fittig reaction (B) Decarboxylative coupling (C) Corey-House synthesis (D) Clemmensen reduction

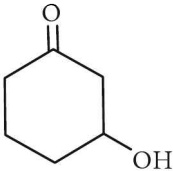
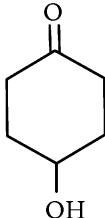
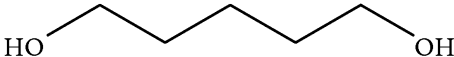
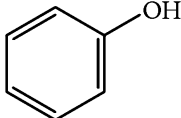
82. An oxidizing agent such as HNO_3 is also added in the iodination of n-butane. This is to

- (a) make the reaction less violent (b) prevent the formation of poly iodinated product
 (c) prevent the reducing action of HI (d) increase the yield of the desired isomer

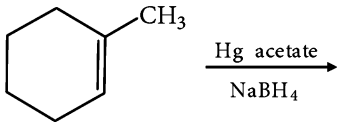
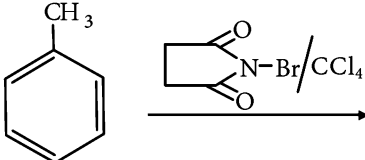
83. The major product formed in the reaction of HBr with $(\text{CH}_3)_2\text{CH}-\text{CH}=\text{CH}_2$ is

- (a) $\text{CH}_3-\overset{\text{Br}}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\text{CH}_3$ (b) $(\text{CH}_3)_2\text{CH}-\text{CH}_2-\text{CH}_2\text{Br}$
 (c) $(\text{CH}_3)_2\text{CH}-\text{CHBr}-\text{CH}_3$ (d) $\text{CH}_3-\underset{\text{CH}_2\text{Br}}{\text{CH}}-\text{CH}_2-\text{CH}_3$

84. Among the following, dehydration is easiest with

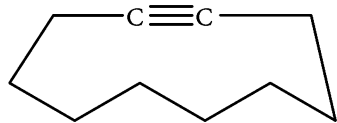
- (a)  (b) 
 (c)  (d) 

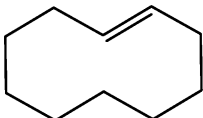
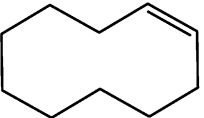
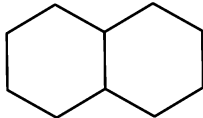
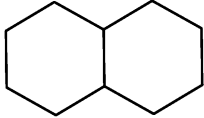
85. In which of the following reactions, carbocation intermediates are involved

- (a) $\text{CH}_3\overset{\text{CH}_3}{\text{CH}}-\text{CH}=\text{CH}_2 \xrightarrow{\text{H}^+/\text{H}_2\text{O}}$ (b) 
 (c)  (d) $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}(\text{CH}_3)_2 \xrightarrow[\text{H}_2\text{O}/\text{OH}^-]{\text{BH}_3/\text{THF}}$

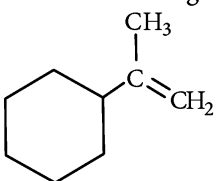
86. The total number of chlorinated products given by ethane is

- (a) 6 (b) 7 (c) 8 (d) 9

87.  $\xrightarrow{\text{Na/liq NH}_3}$ Product. The product is

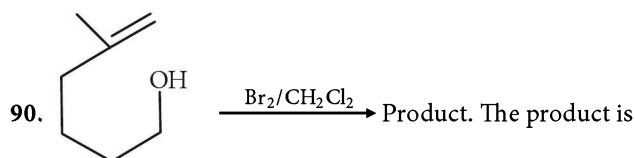
- (a)  (b) 
 (c)  (d) 

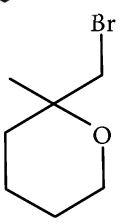
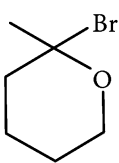
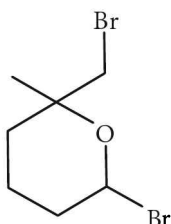
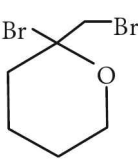
88. Which of the following alkenes will undergo acid catalysed hydration most readily?

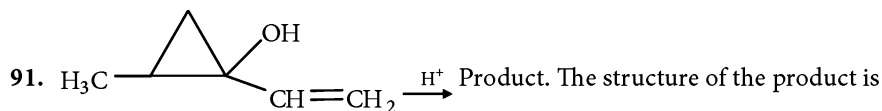
- (a)  (b) Cis-2-butene (c) trans-2-butene (d) 1-butene

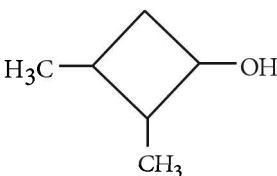
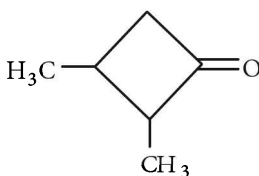
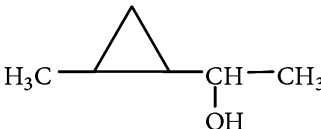
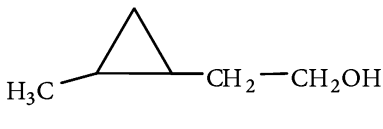
89. Choose the correct statement with regard to 3-methyl but-1-ene

- (a) A tertiary alcohol is formed by hydration in the presence of an acid.
 (b) a primary alcohol is formed by oxymercuration reaction.
 (c) An optically active secondary alcohol is formed by hydroboration-oxidation.
 (d) The alkene is less reactive than ethene towards hydration under acid catalyzed conditions.

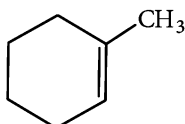


- (a)  (b)  (c)  (d) 



- (a)  (b) 
 (c)  (d) 

92. In which of the following reactions, addition does not occur in accordance with Markovnikov rule?

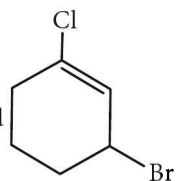
- (a) $\text{CH}_3 - \text{CH} = \text{CH}_2 + \text{HCl} \xrightarrow{\text{H}_2\text{O}_2}$ (b)  $\xrightarrow{\text{HBr}/\text{H}_2\text{O}_2}$
 (c) $\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH}_2 \xrightarrow{\text{HI}/\text{H}_2\text{O}_2}$ (d) $\text{CH}_3 - \text{CH} = \text{CH}_2 \xrightarrow{\text{HOCl}}$

93. Which of the following is the correct statement?

- (a) Acetylene is less reactive than ethylene in electrophilic addition reaction.
 (b) The hydrolysis of Mg_2C_3 (Magnesium carbide) produces acetylene.
 (c) Ozonolysis of acetylene produces CO_2 and H_2O .
 (d) Reduction of dialkyl acetylene using Lindlar's catalyst gives a trans olefin.

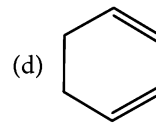
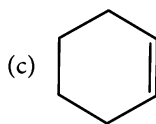
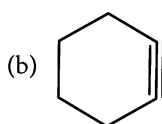
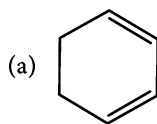
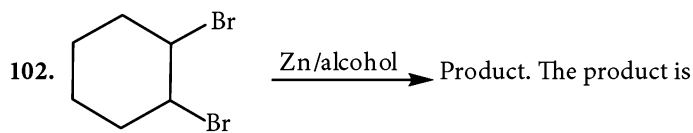
2.50 Alkanes, Alkenes and Alkynes

94. A compound that decolourizes alkaline KMnO_4 and gives a red precipitate with ammoniacal cuprous chloride is
 (a) 1-butyne (b) 1-pentene (c) 2-butyne (d) 2-pentyne
95. Which of the following on hydration will give an aldehyde?
 (a) $\text{HC} \equiv \text{C} - \text{CH}_3$ (b) $\text{CH}_3\text{CH}_2 - \text{C} \equiv \text{C} - \text{CH}_3$
 (c) $\text{HC} \equiv \text{CH}$ (d) $\text{C}_6\text{H}_5\text{C} \equiv \text{CH}$
96. An alkene on reductive as well as oxidative ozonolysis gave only one product. The alkene is
 (a) propene (b) 2,3-dimethyl-2-butene (c) pent-2-ene (d) 2-methyl propene
97. Only glyoxal $\text{CHO} - \text{CHO}$ is obtained by the ozonolysis of
 (a) Cyclobutene (b) 1,3-butadiene (c) ethyne (d) 2-butene



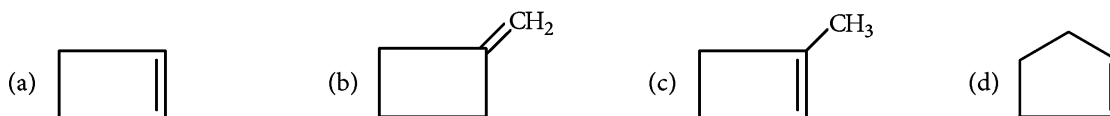
98. The IUPAC name of the compound is

- (a) 6-bromo-2-chlorocyclohexene (b) 3-bromo-1-chlorocyclohexene
 (c) 1-bromo-3-chlorocyclohexene (d) 2-bromo-6-chlorocyclohexene
99. HBr reacts with $\text{CH}_2 = \text{CH} - \text{OCH}_3$ in the absence of peroxides to give mainly
 (a) BrCH_2CHO and CH_3OH (b) $\text{BrCH}_2 - \text{CH}_2 - \text{OCH}_3$
 (c) $\text{H}_3\text{C} - \text{CHBr} - \text{OCH}_3$ (d) CH_3CHO and CH_3Br
100. Reaction of trans-2-phenyl-1-bromocyclohexane with hot alcoholic NaOH gives
 (a) 3-phenylcyclohexene (b) 1-phenylcyclohexene
 (c) 2-bromophenyl cyclohexane (d) 2-phenyl cyclohexanol
101. An alkene which is least reactive towards electrophilic addition, among the following is
 (a) $\text{H}_2\text{C} = \text{CH} - \text{Cl}$ (b) $(\text{CH}_3)_2\text{C} = \text{CH}_2$ (c) $(\text{CH}_3)_2\text{C} = \text{C}(\text{CH}_3)_2$ (d) $\text{ClCH}_2\text{CH} = \text{CH}_2$

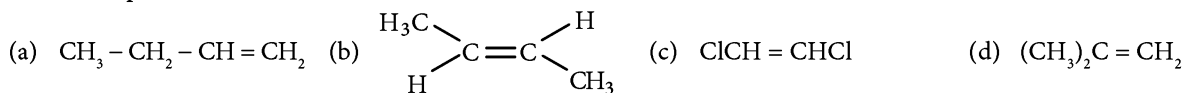


103. $\text{CH}_3 - \text{CH} = \text{CH}_2 + \text{Br}_2 \rightarrow (\text{A}) \xrightarrow{\text{NaNH}_2} (\text{B}) \xrightarrow{\text{H}^+} (\text{C})$. The structure of (C) is
 (a) $\text{CH}_3\text{C} \equiv \text{CH}$ (b) $\text{H}_3\text{C} - \text{C} \equiv \text{C} - \text{CH}_3$ (c) $\text{BrCH}_2 - \text{CH}_2 - \text{CH}_2\text{Br}$ (d) $\text{H}_2\text{C} = \text{C} = \text{CH}_2$
104. A reaction that does not lead to an alkene is
 (a) Kolbe's electrolysis (b) α -elimination (c) Wittig reaction (d) dehalogenation
105. The number of structural and stereoisomers of a bromo compound $\text{C}_5\text{H}_9\text{Br}$ formed by the addition of HBr to pent-2-yne are respectively
 (a) 4 and 2 (b) 1 and 2 (c) 2 and 4 (d) 2 and 1
106. 2-methylpropane on oxidation with KMnO_4 gives
 (a) acetone (b) t-butyl alcohol (c) isobutylene (d) t-butylperoxide

107. The major product obtained in the acid catalyzed dehydration of cyclobutyl methanol is



108. The electrophilic addition reaction of HBr will be fastest in



109. An organic compound (A) C_5H_8 does not react with Tollens reagent but reacts with H_2 in the presence of Lindlar catalyst to give (B). Aqueous chlorine water reacts with (B) to give (C) which when reacted with hot alcoholic KOH gives (D). The compound (D) is



110. The reagent that does not react with ethyne is



Assertion-Reason Type Questions

Directions: Each question contains Statement-1 and Statement-2 and has the following 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

111. Statement 1

Ethyne reacts with sodamide to evolve H_2 gas.

and

Statement 2

Ethyne is less acidic than water.

112. Statement 1

When $\text{CH}_3\text{CH}_2 - \text{CH} = \text{CH}_2$ undergoes allylic bromination with NBS, the product formed is exclusively $\text{CH}_3\text{CHBrCH} = \text{CH}_2$.

and

Statement 2

Allylic radical site undergoes rearrangement by resonance stabilization.

113. Statement 1

When cis-2-butene reacts with Baeyer's reagent, the product obtained is optically inactive.

and

Statement 2

Dilute KMnO_4 brings anti hydroxylation.



Linked Comprehension Type Questions

Directions: This section contains 1 paragraph. Based upon the paragraph, 3 multiple choice questions have to be answered. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

Passage I

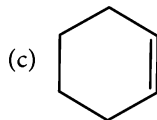
Alkenes undergo a variety of reactions like hydrogenation, halogenation, oxidation, epoxidation and so on. The double bond of the alkenes acts as electron donor.

114. Alkenes can be converted to carbonyl compounds by

- (a) ozonolysis
- (b) Oxymercuration
- (c) Hydroboration
- (d) treatment with peracid

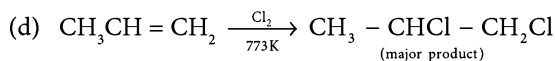
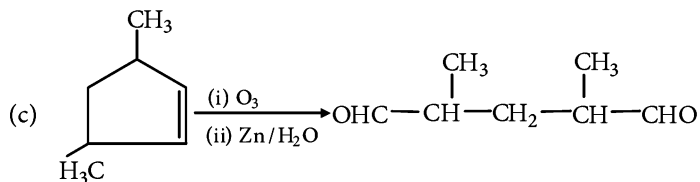
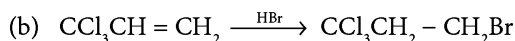
115. An unsaturated hydrocarbon gave, on treatment with alkaline KMnO_4 under hot conditions, one mole of adipic acid. The unsaturated hydrocarbon could be

- (a) $\text{H}_3\text{C} - \text{C} \equiv \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$
- (b) $\text{H}_3\text{C} - \text{CH}_2 - \text{C} \equiv \text{C} - \text{CH}_2 - \text{CH}_3$



- (d)

116. In which of the following cases the product is not shown correctly?



Multiple Correct Objective Type Questions

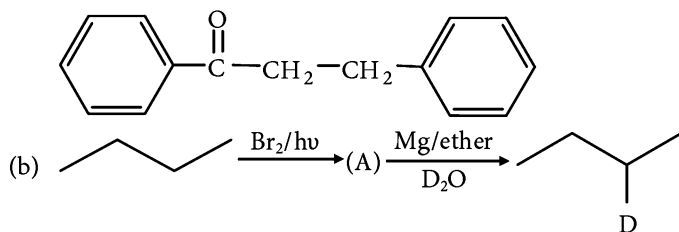
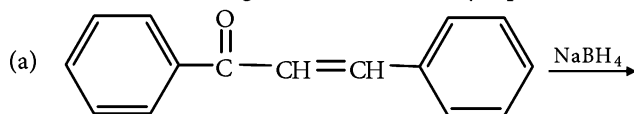
Directions: Each question in this section has four suggested answers out of which ONE OR MORE answers will be correct.

117. Which of the following statements is correct?

- (a) Cyclopropane will react with chlorine or bromine at room temperature, in diffused light to give a dihalogen derivative.

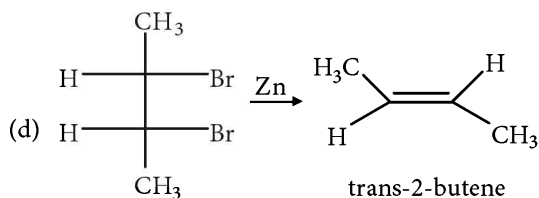
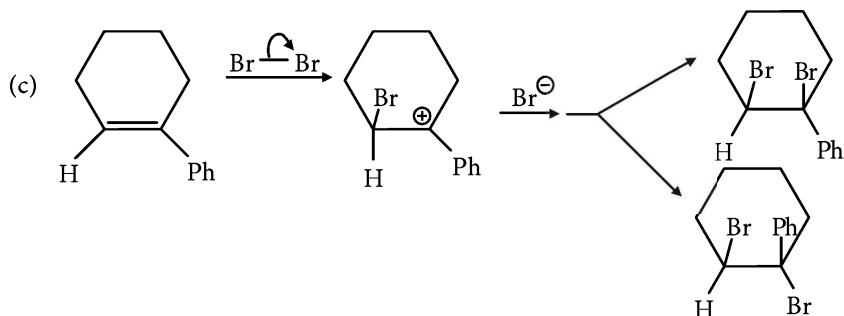
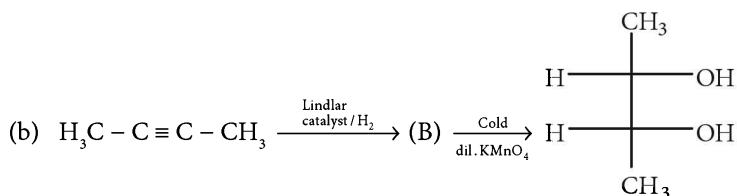
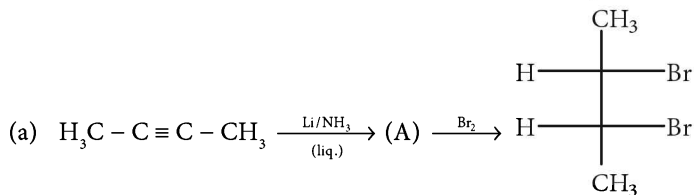
- (b) A hydrocarbon of molecular formula C_4H_6 should contain always a triple bond.
 (c) The trans isomer of an alkene is generally less polar than the cis isomer.
 (d) $H_2C = CH - CH_2 - CH = CH_2$ is an example of cumulated diene.

118. Which of the following reactions is correctly represented?



- (c) When n-butane is monochlorinated the major product formed is a racemic mixture.
 (d) When buta-1,3-diene is treated with HBr in 1 : 1 molar proportion at $-40^\circ C$, the major product obtained is the 1,2-addition product $CH_3 - CHBr - CH = CH_2$.

119. In which of the following reactions, the stereochemistry is correctly represented in the products?



**Matrix-Match Type Question**

Directions: Match the elements of Column I to elements of Column II. There can be single or multiple matches.

120.

Column I

- (a) Markovnikov addition
- (b) anti Markovnikov hydration
- (c) OsO_4 and an alkene
- (d) Catalytic hydrogenation

Column II

- (p) 1-Butyne and HOCl
- (q) syn addition
- (r) Hydroboration-oxidation
- (s) Addition of HI to but-1-ene in the presence of $(\text{C}_6\text{H}_5\text{COO})_2$

ADDITIONAL PRACTICE EXERCISE

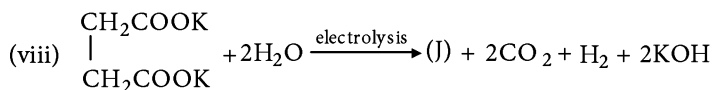
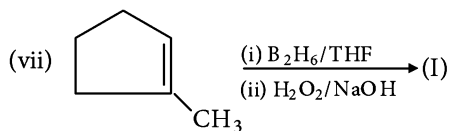
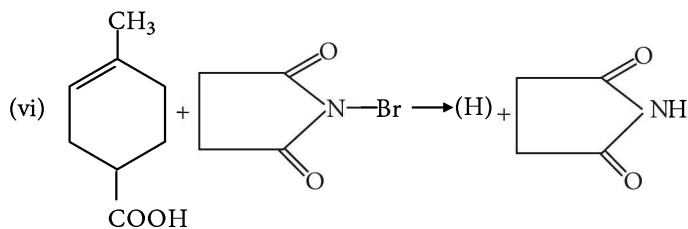
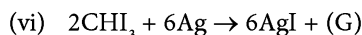
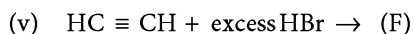
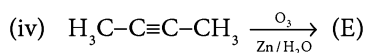
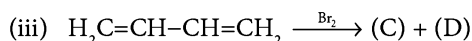
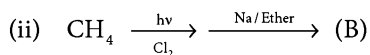
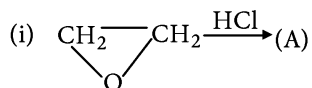


Subjective Questions

121. When 3-methyl-2-butanol reacts with HBr, the expected product is 2-bromo-3-methyl-butane. But the actual product formed is 2-bromo-2-methylbutane. Account for this.
122. An organic compound (3.0 g) gave on complete combustion, 3.476 g of CO_2 and 1.422 g of water. The molecular weight of the compound is 228. Give molecular formula of the compound.
123. Both benzene (C_6H_6) and ethene (C_2H_4) contain olefinic double bonds. But benzene often undergoes aromatic electrophilic substitution and not addition, while ethylene often undergoes electrophilic addition and not substitution. Why?

124. How do the products obtained by the reaction of maleic acid and fumaric acid with bromine differ?

125. Complete the following equations by identifying (A)–(J).

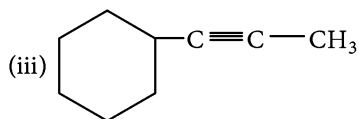
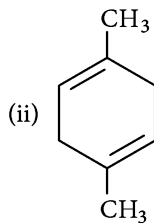
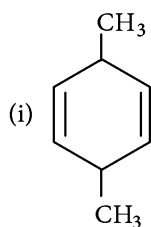


126. How is 1, 3-butadiene made from

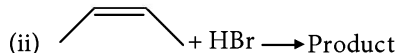
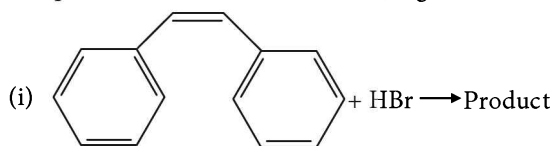
- 1-butene
- acetylene

2.56 Alkanes, Alkenes and Alkynes

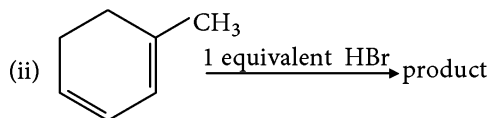
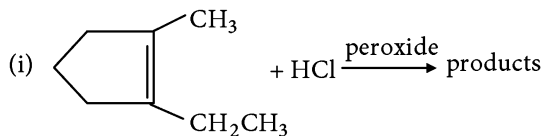
127. What are the products obtained when the following compounds are treated with O_3 followed by Zn and H_2O ?



128. Compare the two reactions (A) and (B) given below. Which of the two would be faster and why? Identify the products.



129. Identify the products in the reactions given below.



130. When ethylene gas is passed into a mixture of an aqueous solution of bromine and sodium chloride, the products formed are $BrCH_2CH_2Br$, $BrCH_2CH_2OH$ and $BrCH_2CH_2Cl$. Justify the formation of these products by giving a suitable mechanism.



Straight Objective Type Questions

Directions: This section contains multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

131. Alkanes are chemically unreactive. However they undergo the type of reactions except

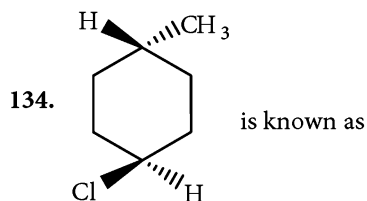
- (a) Halogenation (b) oxidation (c) addition (d) Nitration

132. When N-bromosuccinimide reacts with $H_3\overset{*}{C}CH=CH_2$ the product(s) is/are

- (a) $\overset{*}{CH}_3-\overset{Br}{\underset{|}{CH}}-CH_3$ only
 (b) a mixture of $BrCH_2-\overset{*}{CH}=CH_2$ and $BrCH_2-\overset{*}{CH}=CH_2$
 (c) $H_2\overset{*}{C}=CH-CH_2Br$ only
 (d) $CH_2=\overset{*}{CH}-CH_2Br$ only

133. A compound with the molecular formula, C_4H_6 , does not exist in cis or trans form. It does not produce a precipitate with ammoniacal $AgNO_3$ solution. The compound as such is optically inactive but a monohalogen derivative can be optically active. The compound is

- (a) $CH_3C \equiv C - CH_3$ (b) $CH_3 - CH = C = CH_2$ (c) $CH_3 - CH_2 - C \equiv C - H$ (d) 



- (a) 4-chloro-1-methylcyclohexane (b) trans 4-chloro-1-methylcyclohexane
(c) trans 1-chloro-4-methylcyclohexane (d) trans 1-methyl-4-chlorocyclohexane

135. Which of the following compounds on reductive ozonolysis will give two molecules of $CH_2(CHO)_2$?

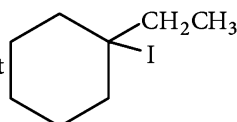
- (a) 1,3-cyclohexadiene (b) 2,4-hexadiene
(c) 1,4-cyclohexadiene (d) 1-Methyl-1,3-cyclopentadiene

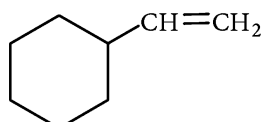
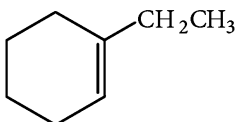
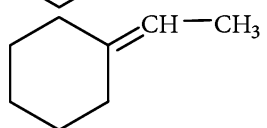
136. Which group or atom in each of the following pairs gets priority according to CIP rules used for assigning R and S configuration for chiral molecules?

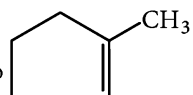
- (a) $-CH_2OH$ or $-CH_2Cl$ (b) $-CH = CH_2$ or $-CH_2CH_3$ (c) $-NH_2$ or $-OH$ (d) $-CH_2OH$ or $-CHO$

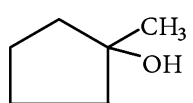
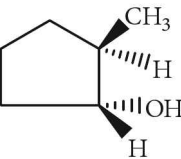
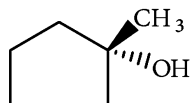
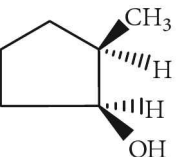
Choose from the options given below

- (a) A : $-CH_2OH$, B : $-CH = CH_2$, C : $-NH_2$, D : $-CHO$
(b) A : $-CH_2Cl$, B : $-CH = CH_2$, C : $-OH$, D : $-CHO$
(c) A : $-CH_2OH$, B : $-CH_2CH_3$, C : $-NH_2$, D : $-CHO$
(d) A : $-CH_2Cl$, B : $-CH_2 - CH_3$, C : $-OH$, D : $-CH_2OH$

137. In order to get  as the major product, which alkene among the following is to be treated with HI?

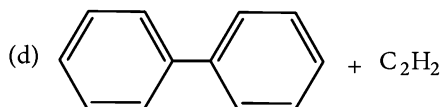
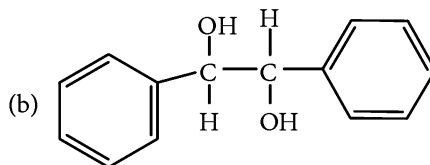
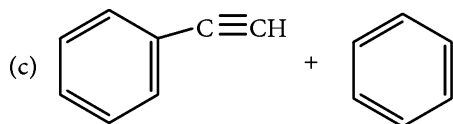
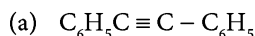
- (a)  (b) 
(c)  (d) either (b) or (c)

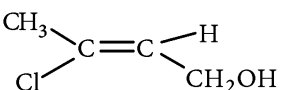
138. Addition of diborane in THF followed by treatment with H_2O_2 in the presence of OH^- to  gives

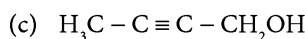
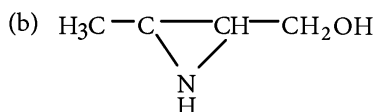
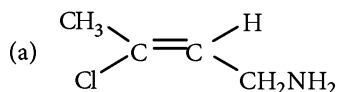
- (a)  (b) 
(c)  (d) 

2.58 Alkanes, Alkenes and Alkynes

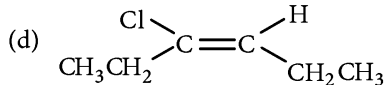
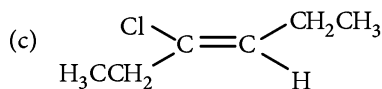
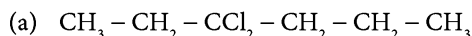
139. $\text{C}_6\text{H}_5 - \text{CH} = \text{CH} - \text{C}_6\text{H}_5 \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{Br}_2} (\text{A}) \xrightarrow[\Delta]{2\text{NaNH}_2} (\text{B})$. The structure of (B) is



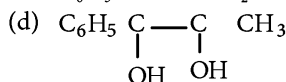
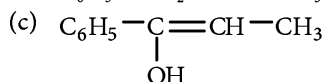
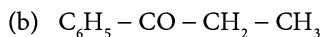
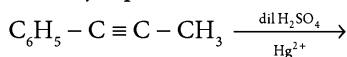
140.  $\xrightarrow[\text{H}_3\text{O}^+]{\text{NaNH}_2}$ product. The structure of the product is



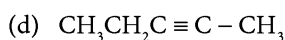
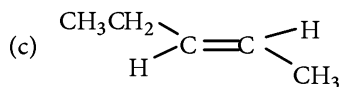
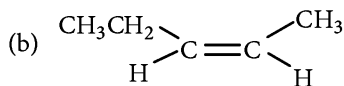
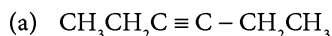
141. $\text{CH}_3\text{CH}_2\text{C} \equiv \text{CCH}_2\text{CH}_3 \xrightarrow[\text{Solvent}]{\text{HCl}} (\text{A}) \xrightarrow[\text{Solvent}]{\text{HCl}} (\text{B})$. The structure of (B) is



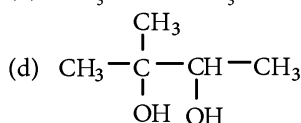
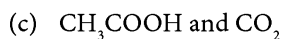
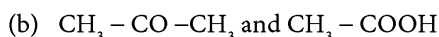
142. The major product formed in the following reaction is



143. $\text{CH}_3\text{CH}_2\text{C} \equiv \text{CH} \xrightarrow[\text{CH}_3\text{I}]{\text{NaNH}_2} (\text{A}) \xrightarrow[\text{Lindlar's catalyst}]{\text{H}_2} (\text{B})$. The structure of the major product (B) is



144. The compound $\text{CH}_3 - \overset{\text{CH}_3}{\underset{|}{\text{C}}} = \text{CH}_2 - \text{CH}_3$ when treated with NaIO_4 in presence of KMnO_4 gives

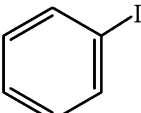


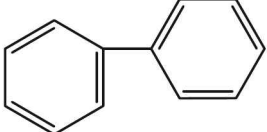
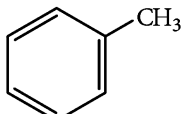
145. trans-2-butene (C) is the final product in the reaction

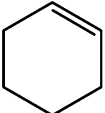
- (a) $\text{H}_3\text{C}-\text{C}\equiv\text{CH} \xrightarrow{\text{NaOH}} (\text{A}) \xrightarrow{\text{CH}_3\text{I}} (\text{B}) \xrightarrow{\text{Na/liq NH}_3} (\text{C})$
 (b) Propyne $\xrightarrow{\text{NaNH}_2} (\text{A}) \xrightarrow{\text{CH}_3\text{Br}} (\text{B}) \xrightarrow{\text{H}_2/\text{Lindlar's catalyst}} (\text{C})$
 (c) $\text{CH}_3\text{C}\equiv\text{CH} \xrightarrow{\text{KNH}_2} (\text{A}) \xrightarrow{\text{CH}_3\text{Br}} (\text{B}) \xrightarrow{\text{Li/liq NH}_3} (\text{C})$
 (d) $\text{H}_3\text{C}-\text{C}\equiv\text{C}-\text{CH}_3 \xrightarrow{\text{NaNH}_2} (\text{A}) \xrightarrow{\text{CH}_3\text{I}} (\text{B}) \xrightarrow{\text{Na/liq NH}_3} (\text{C})$

146. $(\text{CH}_3)_2\text{CuLi}$ is known as

- (a) Corey-House reagent (b) Gilman reagent (c) Grignard reagent (d) Ullmann reagent

147.  + $(\text{CH}_3)_2\text{CuLi} \rightarrow (\text{A})$. (A) is

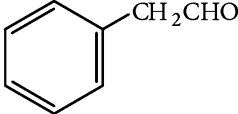
- (a) CH_3I (b)  (c)  (d) CH_3-CH_3

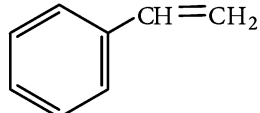
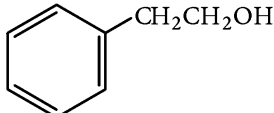
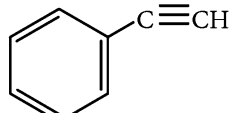
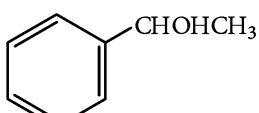
148.  $\xrightarrow{\text{X}} (\text{A}) \xrightarrow{\text{Y}} \text{Cyclohexene-C}_2\text{H}_5$ The reagents X and Y that could be used in the above conversion would be

- (a) NBS, $(\text{C}_2\text{H}_5)_2\text{CuLi}$ (b) Li, CuI, $\text{C}_2\text{H}_5\text{I}$ (c) $(\text{C}_2\text{H}_5)_2\text{CuLi}$, NBS (d) NaNH_2 , $\text{C}_2\text{H}_5\text{I}$

149. The product formed when ethene and air under pressure is passed over silver catalyst heated to 500K is

- (a) Epoxy ethane (b) Ethanal (c) Ethanoic acid (d) Methanal

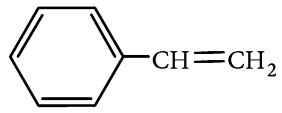
150. The starting material to prepare  by hydroboration using a hindered borane such as disiamyl borane followed by oxidation is

- (a)  (b) 
 (c)  (d) 

151. The addition of Br_2 to maleic acid results in

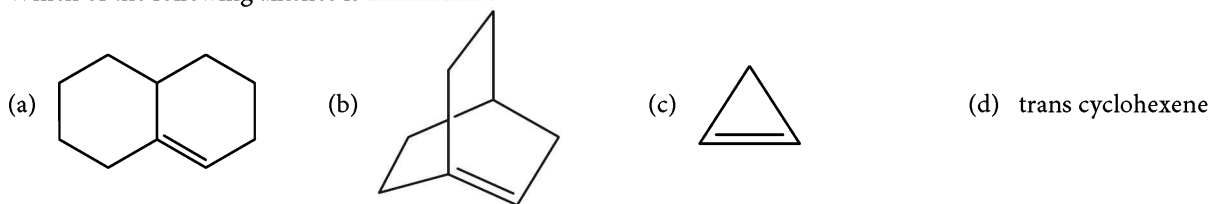
- (a) dl-1,2-dibromosuccinic acid (b) maleic acid dibromide
 (c) meso-1,2-dibromo succinic acid (d) dibromo tartaric acid

152. Addition of bromine to the double bond would be least favourable in the compound

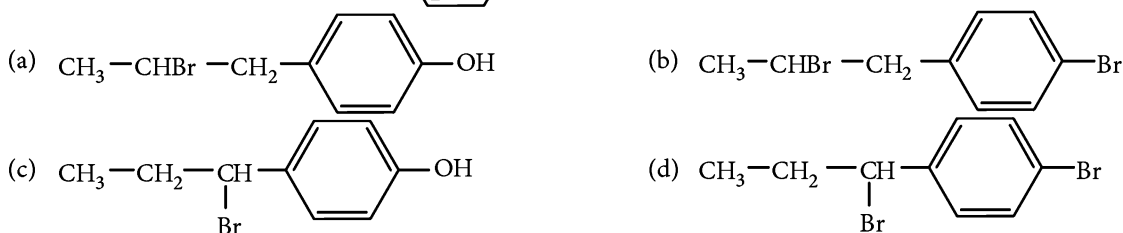
- (a)  (b) $\text{CH}_2=\text{CH}-\text{COOH}$
 (c) $\text{H}_2\text{C}=\text{CH}_2$ (d) $\text{CH}_3-\text{CH}=\text{CH}_2$

2.60 Alkanes, Alkenes and Alkynes

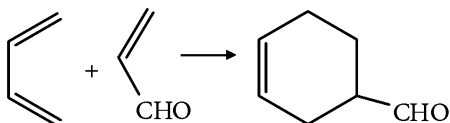
153. Which of the following alkenes is most stable?



154. The reaction of $\text{CH}_3-\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{OH}$ with HBr gives mainly



155. The following reaction is known as

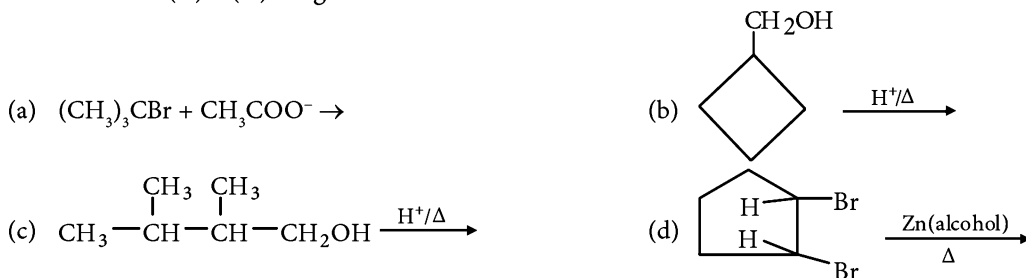


(a) Friedel-Crafts reaction (b) Diels-Alder reaction (c) Corey-House reaction (d) Frankland reaction

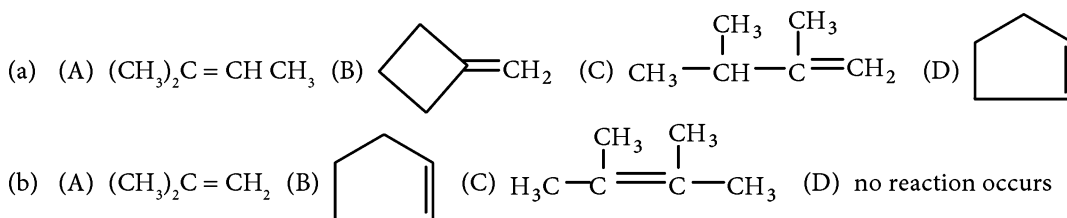
156. Identify the incorrect statement among the following

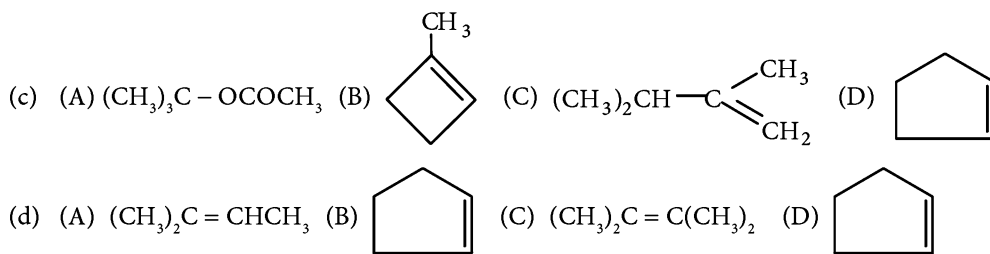
- (a) The molecule $\begin{array}{c} \text{BrCH}_2 \\ \diagup \\ \text{C}=\text{C} \\ \diagdown \\ \text{ICH}_2 \end{array} \begin{array}{c} \diagup \\ \text{CH}_2\text{I} \\ \diagdown \\ \text{CH}_2\text{Br} \end{array}$ can exhibit cis-trans isomerism
 (b) The dipole moment of CH_2Cl_2 is greater than that of CH_3Cl .
 (c) The cis isomers become increasingly less stable as the size of the R groups increase.
 (d) Alkenes with two identical groups on the same doubly bonded carbon have no geometrical isomers.

157. Four reactions (A) – (D) are given below



Identify the major products in each and choose from the options given below.

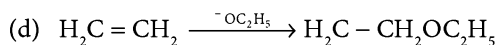
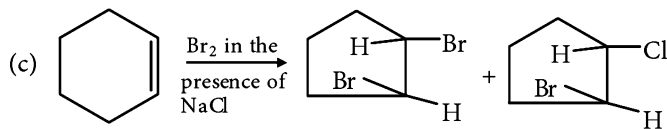
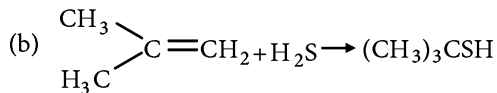
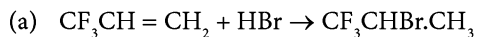


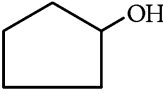


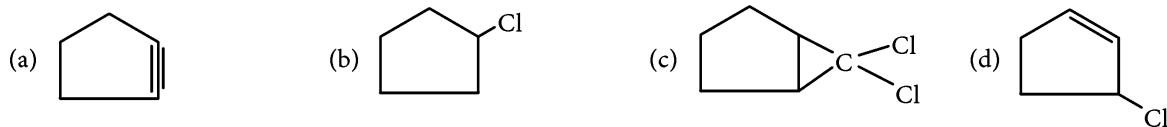
158. $(\text{CH}_3)_2\text{C} = \text{CH}_2 + \text{ICl} \rightarrow (\text{CH}_3)_2\text{CClCH}_2\text{I}$ is an example of

- (a) anti Markovnikov addition to the double bond (b) a regioselective reaction
(c) an electrophilic substitution reaction (d) a stereospecific reaction

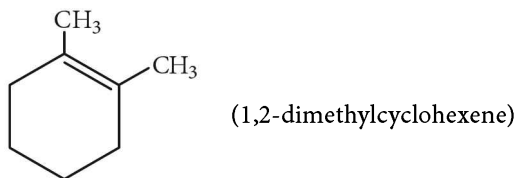
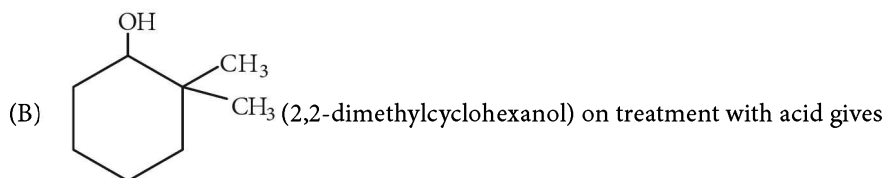
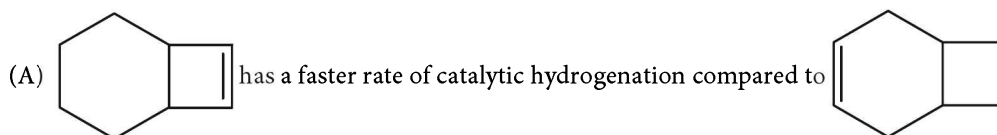
159. Identify the reaction in which the equation is represented correctly



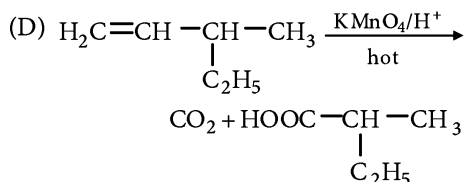
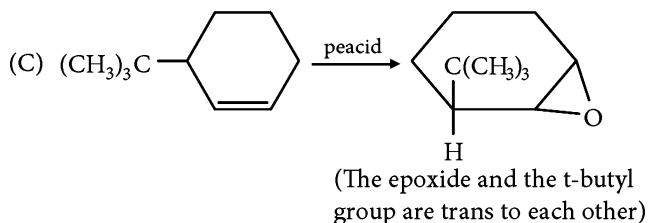
160.  $\xrightarrow{\text{con. H}_2\text{SO}_4 / \Delta}$ (A) $\xrightarrow{\text{CHCl}_3 / \text{KOH}}$ (B). The structure of (B) is



161. Four statements/reactions are given below (A) – (D). Classify them as correct (T) or false (F). Choose from the options given.



2.62 Alkanes, Alkenes and Alkynes



Choose from the options given

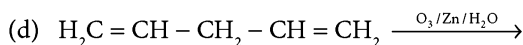
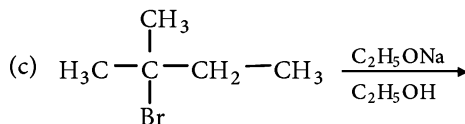
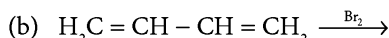
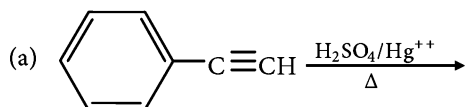
(a) (A) = T, (B) = T, (C) = T, (D) = T

(b) (A) = T, (B) = F, (C) = T, (D) = F

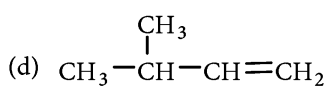
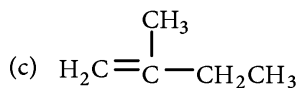
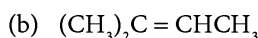
(c) (A) = F, (B) = F, (C) = T, (D) = F

(d) (A) = F, (B) = F, (C) = F, (D) = F

162. Which of the following reactions give mainly a single product?



163. The alkene which will have the lowest heat of hydrogenation value will be



164. When propyne reacts with excess of chlorine water, the product obtained is

(a) 1,1-dichloro propan-2-one

(b) 1,1-dichloropropan-2-ol

(c) 2,2-dichloropropan-1-ol

(d) 1,2-dichloropropane

165. Which of the following statements is correct?

(a) Ethylene show conformational isomerism.

(b) Hex-3-ene does not show peroxide effect on treatment with HBr in presence of peroxides.

(c) When but-1-ene is treated with excess of bromine, the product obtained is 2-bromobutane.

(d) Reactivity order of the hydrocarbons is alkane < alkenes < alkynes.

166. Which of the following alkenes exhibit geometrical isomerism?

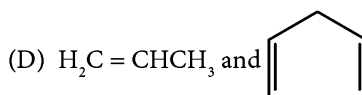
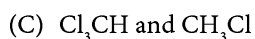
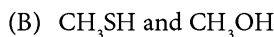
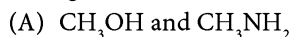
(a) 2,4-hexadiene

(b) 2-methyl-1-butene

(c) 1-methylcyclopentene

(d) 1,3-butadiene

167. Four pairs of compounds are given below. Which of the compound in each pair is more acidic? Choose from the options given



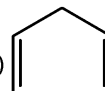
The options are

(a) (A) CH_3OH , (B) CH_3OH , (C) CHCl_3 , (D) $\text{CH}_2 = \text{CH} - \text{CH}_3$

(b) (A) CH_3OH , (B) CH_3SH , (C) Cl_3CH , (D)

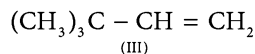
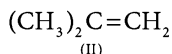
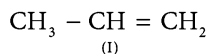


(c) (A) CH_3NH_2 , (B) CH_3SH , (C) CH_3Cl , (D)



(d) (A) CH_3OH , (B) CH_3SH , (C) CH_3Cl (D) $\text{CH}_2 = \text{CH} - \text{CH}_3$

168. The reactivity of the following alkenes towards hydrogen (hydrogenation) is



(a) (III) > (I) > (II)

(b) (III) > (II) > (I)

(c) (I) > (II) > (III)

(d) (II) > (III) > (I)

169. The maximum number of optical isomers produced on monochlorination of 2-methylbutane will be

(a) 2

(b) 3

(c) 4

(d) 1

170. The compound which gives methanal, ethanal and glyoxal on ozonolysis is

(a) Hexa-1,3-diene

(b) Penta-1,3-diene

(c) Penta-1,4-diene

(d) Penta-1,2-diene



Assertion–Reason Type Questions

Directions: Each question contains Statement-1 and Statement-2 and has the following 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

171. **Statement 1**

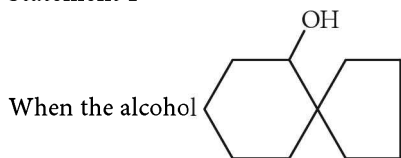
Ethyne is less reactive than ethene towards electrophilic reagents such as Br_2 .

and

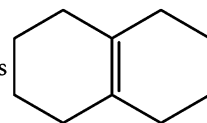
Statement 2

Ethyne is more acidic than ethene.

172. **Statement 1**



undergoes dehydration, the major product formed is



and

Statement 2

Saytzeff rule is followed in the dehydration of alcohols and dehydrohalogenation of alkyl halides.

2.64 Alkanes, Alkenes and Alkynes

173. Statement 1

Erythro-2,3-dibromobutane on reaction with zinc and alcohol gives trans 2-butene.

and

Statement 2

Elimination requires trans periplanar geometry.

174. Statement 1

In the halogenation of alkanes under photochemical conditions, the reaction proceeds faster in an atmosphere of oxygen.

and

Statement 2

Halogenation of alkanes takes place by radical mechanism.

175. Statement 1

Boiling point of n-pentane is higher than that of neopentane while the melting point of n-pentane is lower than that of neopentane.

and

Statement 2

Boiling point of alkanes depend upon the surface area while melting point depends upon the packing of molecules in the solid state. Neopentane fits into the crystal lattice more readily and it has minimum surface area compared to n-pentane.

176. Statement 1

Addition of HBr to vinyl chloride gives 1-Bromo-1-chloroethane.

and

Statement 2

HBr adds to vinyl chloride against Markovnikov's rule.

177. Statement 1

Oxymercuration reduction of an alkene gives an alcohol in which the –OH group is added to a more branched carbon of the double bond, while hydroboration–oxidation of an alkene gives an alcohol in which the –OH group is added to a less branched carbon of the alkene.

and

Statement 2

Hydration of an alkene in the presence of an acid is one of the standard methods of preparation of an alcohol from alkenes.

178. Statement 1

If the structures of the ozonolysis products are known, the structure of an unknown alkene can be deduced.

and

Statement 2

The reaction of an alkene with ozone and its subsequent decomposition to yield products of double bond cleavage is known as ozonolysis.

179. Statement 1

The addition of acetylide ion to cyclohexanone can be used in the synthesis of a tertiary alcohol.

and

Statement 2

The acetylide ion is a strong base and nucleophile as it is the conjugate base of weakly acidic acetylene ($pK_a = 25$).

180. Statement 1

Reaction of 2-Methylbut-2-ene with NOBr gives $(\text{CH}_3)_2\text{C}(\text{Br})\text{CH}(\text{NO})\text{CH}_3$ as the major product.

and

Statement 2

Addition of NOBr to alkene takes place contrary to Markovnikov's rule.



Linked Comprehension Type Questions

Directions: This section contains 3 paragraphs. Based upon the paragraph, 3 multiple choice questions have to be answered. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

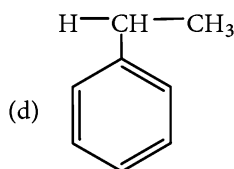
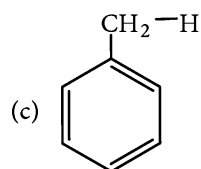
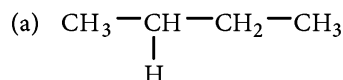
Passage I

The three main classes of hydrocarbons are alkanes, alkenes and alkynes. Alkanes having cyclic structure are called cycloalkanes. They exhibit chain and ring chain isomerism. Alkenes and alkynes are more reactive than alkanes.

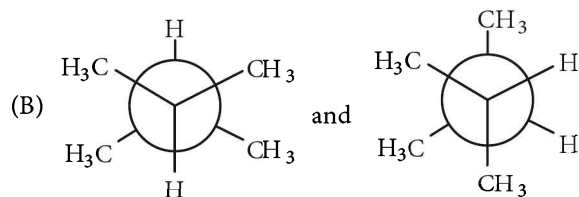
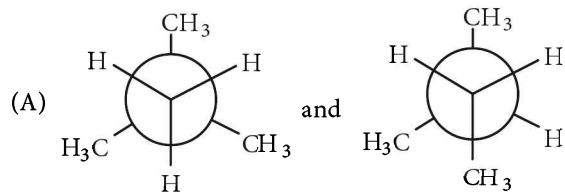
181. A certain hydrocarbon has the molecular formula C_5H_8 . Which of the following is not a structural possibility for this hydrocarbon?

- (a) a cycloalkane (b) contains a ring and a double bond
(c) contains two double bond and no ring (d) an alkyne

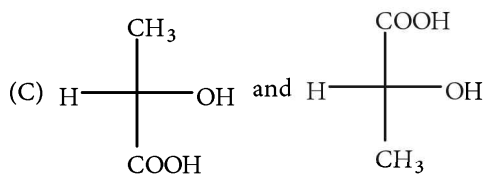
182. In each of the following options, one hydrogen atom is shown prominently than others. Identify the most reactive hydrogen among these towards halogenation in presence of light.



183. Four pairs of structures (A) – (D) are given. Determine whether the two structures represent constitutional isomer, conformations of the same compound or stereoisomers which cannot be interconverted by rotation about single bonds.



2.66 Alkanes, Alkenes and Alkynes



(D) Cis 1,2-dimethylcyclopentane and trans 1,3-dimethylcyclopentane

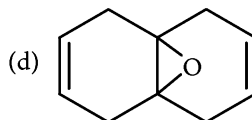
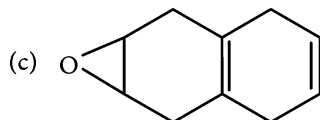
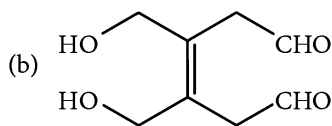
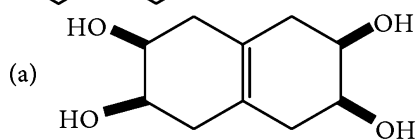
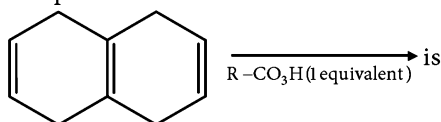
Choose from the options given below

- (a) (A) enantiomers (B) constitutional (C) conformational (D) same compound
 (b) (A) constitutional (B) enantiomers (C) enantiomers (D) conformational
 (c) (A) constitutional (B) constitutional (C) enantiomers (D) diastereomers
 (d) (A) constitutional (B) same compound (C) enantiomers (D) constitutional

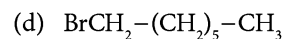
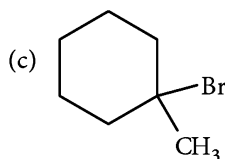
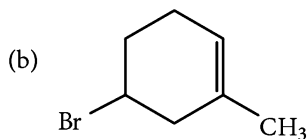
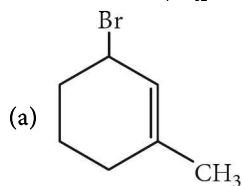
Passage II

Alkenes are a highly reactive group of compounds as they undergo a wide variety of reactions like hydrogenation, ozonolysis, halogenation, epoxidation and halohydrin formation. Many of the reactions are regioselective or stereoselective reactions.

184. The product formed in the reaction



185. An organic compound (A) has the M.F. $\text{C}_7\text{H}_{13}\text{Br}$. On treatment with NaOC_2H_5 in ethanol under hot conditions (A) is converted to C_7H_{12} (B). Ozonolysis of (B) gave only 6-oxoheptanal. Compound (A) could be



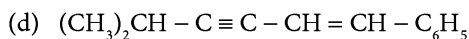
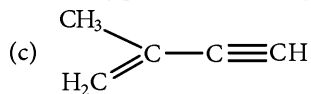
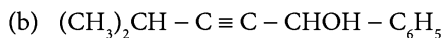
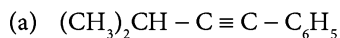
186. When bromine is added to a solution of 1-hexene in methanol, the product formed is

- (a) $\text{BrCH}_2 - \text{CHBr} - \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
 (b) $\text{H}_3\text{C} - \text{CHBr} - \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
 (c) a mixture of $\text{BrCH}_2\text{CHBrCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{BrCH}_2 - \text{CH}(\text{OCH}_3) - \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
 (d) $\text{H}_3\text{COCH}_2 - \text{CH}_2 - \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

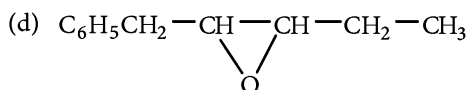
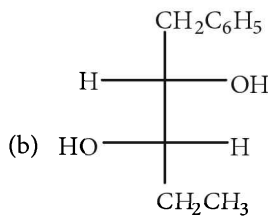
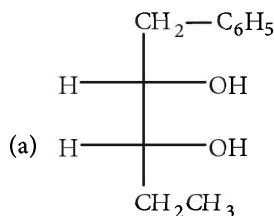
Passage III

Alkynes are less reactive than alkenes towards electrophilic reagents. But the alkyne chemistry is useful for organic synthesis, in the form of hydration of the triple bond, formation of metalacetylides, selective reduction of alkynes and few other related reactions.

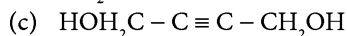
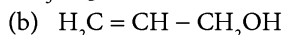
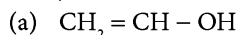
187. $(\text{CH}_3)_2\text{CH} - \text{C} \equiv \text{CH} \xrightarrow[\text{(3)H}_3\text{O}^+]{\text{(1)NaNH}_2, \text{(2)C}_6\text{H}_5\text{CHO}}$ Product. The product is



188. $\text{CH}_3\text{CH}_2\text{C} \equiv \text{CH} \xrightarrow[\text{C}_6\text{H}_5\text{CH}_2\text{Br}]{\text{NaNH}_2} \text{(A)} \xrightarrow{\text{Lindlar catalyst / H}_2} \text{(B)} \xrightarrow{\text{dil alk KMnO}_4} \text{(C)}$ The structure of (C) is



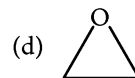
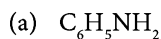
189. Acetylene and HCHO react together in the presence of NaOCH_3 to give



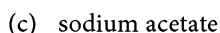
Multiple Correct Objective Type Questions

Directions: Each question in this section has four suggested answers out of which ONE OR MORE answers will be correct.

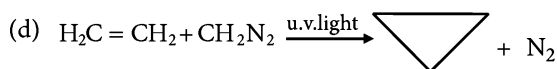
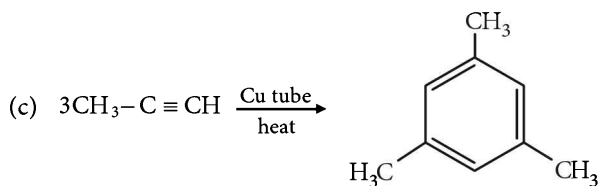
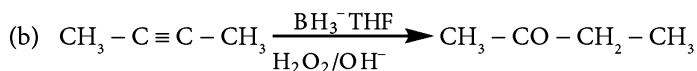
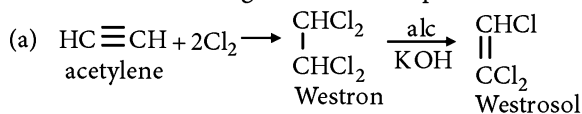
190. Grignard reagents give alkanes when reacted with



191. Kolbe's electrolytic synthesis gives hydrocarbons with



192. Which of the following reactions are represented correctly?



2.68 Alkanes, Alkenes and Alkynes

193. Identify the correct statement among the following.

- (a) A hydrocarbon of M.F. C_6H_{12} on reductive ozonolysis gave only one product which fails to react with Tollens reagent. The hydrocarbon could be 2,3 dimethyl but-2-ene.
- (b) Addition of bromine to trans-2-butene gives a racemic mixture of two optically active enantiomers.
- (c) But-1-yne and but-2-yne can be distinguished using ammoniacal cuprous chloride.
- (d) Ozonolysis of acetylene gives glyoxal.

194. Which of the following reactions will result in 2,2-dibromopropane?

- (a) $CH_3C \equiv CH + 2HBr \rightarrow$
- (b) $CH_3 - CBr = CH_2 + HBr \rightarrow$
- (c) $CH_3 - CH = CH_2 + Br_2 \rightarrow$
- (d) $CH_3CH = CHBr + HBr \rightarrow$

195. Identify the correct statement(s), regarding the chlorination of alkanes.

- (a) The relative rates of abstraction of tertiary, secondary and primary hydrogen atoms are in the ratio 5.0 : 3.8 : 1 respectively.
- (b) The more reactive chlorine radical is less selective.
- (c) The reaction proceeds through homolytic cleavage.
- (d) When n-butane is chlorinated, the product formed is $CH_3CHClCH_2CH_3$ exclusively as the secondary hydrogen is more readily displaced.

196. The cis hydroxylation of alkenes can be effected by

- (a) reaction with OsO_4
- (b) addition of Baeyer's reagent
- (c) reaction with H_2O_2 and formic acid
- (d) reaction with an acid in the presence of water.

197. Which of the following reactions give an alkyne?

- (a) sodium fumarate $\xrightarrow[\text{electrolysis}]{\text{Kolbe's}}$
- (b) $CH_3CBr_2CHBr_2 \xrightarrow{Zn / \text{alcohol} / \Delta}$
- (c) $CH_3CH_2CHBr_2 \xrightarrow{NaNH_2 / \Delta}$
- (d) $CH_3CHBr - CH_2Br \xrightarrow{NaNH_2}$



Matrix-Match Type Questions

Directions: Match the elements of Column I to elements of Column II. There can be single or multiple matches.

198.

Column I

- (a) Corey House synthesis
- (b) $(CH_3)_2CH - CH_2CH_3$
- (c) $(CH_3)_2CH - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} - CH_3$
- (d) Organometallic compound

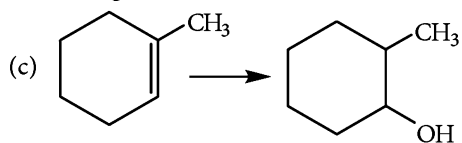
Column II

- (p) One isopropyl unit
- (q) Grignard reagent
- (r) Lithium dialkyl copper
- (s) unsymmetrical alkane

199.

Column I

- (a) Anti Markovnikov addition
 (b) Halogenation of alkanes



- (d) Ozonolysis

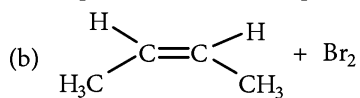
Column II

- (p) Hydration by hydroboration-oxidation
 (q) syn addition
 (r) radical mechanism
 (s) Locating the position of double bond

200.

Column I

- (a) $\text{H}_2\text{C} = \text{CH} - \text{CH} = \text{CH}_2 + \text{HBr}$



- (c) $\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_3 \xrightarrow{\text{Li/liq. NH}_3}$

- (d) $\text{CH}_3 - \text{CH} = \text{CH}_2 + \text{HBr}$

Column II

- (p) trans-alkene
 (q) stereoselective
 (r) conjugate addition
 (s) Electrophilic addition

Additional Practice Exercise

121. It is due to the rearrangement of the intermediate carbocation

122. $C_6H_{12}O_9$

123. The double bonds in benzene are delocalised due to resonance. Hence benzene does not undergo addition reactions.

124. Maleic acid gives racemic mixture of dibromide while fumaric acid gives the meso dibromide

125. A: $HO-CH_2-CH_2Cl$

B: CH_3-CH_3

C: $H_2C=CH-CH(Br)-CH_2Br$

D: $BrCH_2-CH=CH-CH_2Br$

E: $CH_3-C(=O)-C(=O)-CH_3$

F: $H_3C-CHBr_2$

G: $HC\equiv CH$

H:

I:

J: $CH_2=CH_2$

126. (i) By treating with NBS followed by dehydrohalogenation using alcoholic KOH.

(ii) $2CH\equiv CH \xrightarrow[N_4C]{CuCl} H_2C=$

$CH-C\equiv CH$

$\xrightarrow[\text{Catalyst}/H_2]{\text{Lindlar's}} 1,3\text{-butadiene}$

127. Carbonyl compounds are formed by ozonolysis

128. (i) reacts faster because the intermediate carbocation formed is more stable.

129. (i)

(ii)

130. Cyclic bromonium ion formed by initial attack of Br^+ will react with Br^- , Cl^- and H_2O to form the three products.

131. (c) 132. (b) 133. (b)

134. (c) 135. (c) 136. (b)

137. (d) 138. (b) 139. (a)

140. (c) 141. (a) 142. (b)

143. (b) 144. (b) 145. (c)

146. (b) 147. (c) 148. (a)

149. (a) 150. (c) 151. (a)

152. (b) 153. (a) 154. (c)

155. (b) 156. (b) 157. (b)

158. (b) 159. (c) 160. (c)

161. (a) 162. (a) 163. (b)

164. (a) 165. (b) 166. (a)

167. (b) 168. (a) 169. (c)

170. (b) 171. (b) 172. (b)

173. (a) 174. (d) 175. (a)

176. (c) 177. (b) 178. (a)

179. (a) 180. (c) 181. (a)

182. (d) 183. (d) 184. (d)

185. (c) 186. (c) 187. (b)

188. (a)

189. (c)

190. (a), (c)

191. (a), (b), (c)

192. (a), (b), (c), (d)

193. (a), (c), (d)

194. (a), (b)

195. (a), (b), (c)

196. (a), (b)

197. (a), (b), (c), (d)

198. (a) $\rightarrow$ (r), (s)

(b) $\rightarrow$ (p), (s)

(c) $\rightarrow$ (p), (s)

(d) $\rightarrow$ (q), (r)

199. (a) $\rightarrow$ (p), (r)

(b) $\rightarrow$ (r)

(c) $\rightarrow$ (p), (q)

(d) $\rightarrow$ (q), (s)

200. (a) $\rightarrow$ (r), (s)

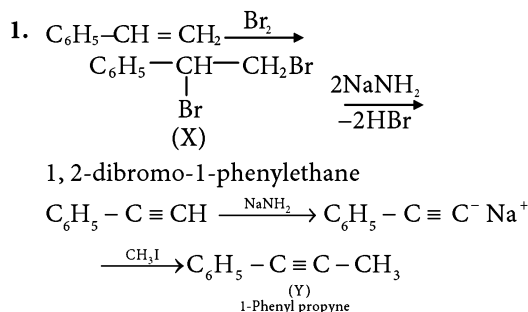
(b) $\rightarrow$ (q), (s)

(c) $\rightarrow$ (p), (q)

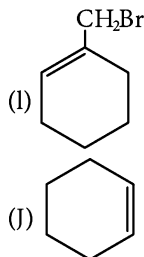
(d) $\rightarrow$ (s)

HINTS AND EXPLANATIONS

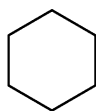
Topic Grip



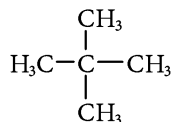
2. (F) = $\text{CH}_3\text{CH}_2\text{Br}$
 (G) = CH_3D
 (H) $\text{HC}\equiv\text{CH}$



3. (a) C_6H_{12} only secondary hydrogen cyclohexane

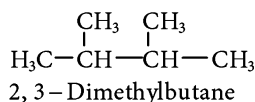


- (b) C_5H_{12} – only primary hydrogens



2, 2-Dimethylpropane or neopentane

- (c) C_6H_{14} only primary and tertiary hydrogens



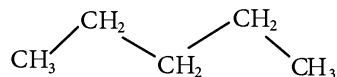
4. (a) Alkanes have only C–C and C–H sigma bonds. These bonds are nonpolar and there are no specific reaction sites where reagents can attack. Hence they are inert. In the case of alkenes, the pi bond

between the carbon atoms act as a source of extra electrons which can be donated for participation in a variety of reactions. Hence alkenes are more reactive than alkanes.

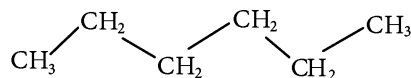
- (b) Let us take for example, three isomeric pentanes, viz., n-pentane (309K), isopentane (301K) and neopentane (282.5K).

This is due to the fact that with increase in branching the shape of the molecule tends to approach that of a sphere. As a result, the surface area of the branched isomer decreases. Due to reduction in surface area, the van der Waals forces operating between the molecules decreases and hence the boiling point decreases with increase in branching.

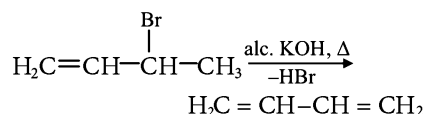
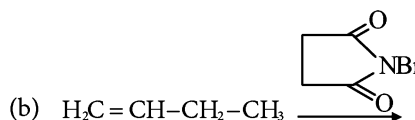
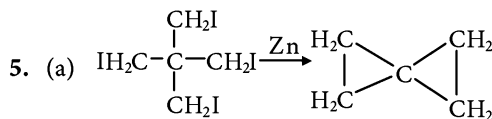
- (c) Because of the zig-zag shape of the chains the terminal methyl groups of the alkane with odd number of carbon atoms will lie on the same side



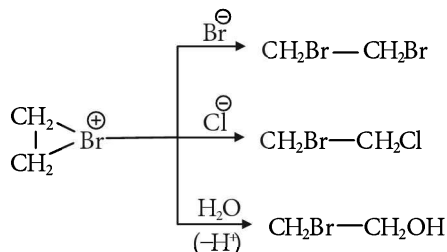
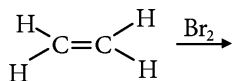
In the case of alkane with even number of carbon atoms the terminal methyl groups will be on the opposite side.



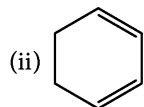
Hence n-alkanes with even number of carbon atoms are packed more closely in the crystal lattice. This increases the intermolecular forces of interaction. So n-alkanes with even number of carbon atoms have higher melting point than adjacent alkane with odd number of carbon atoms.



- (c) The three products formed in the reaction are
1,2-Dibromoethane,
1-Bromo-2-chloroethane and
2-Chloroethanol.

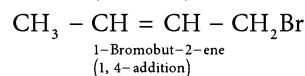
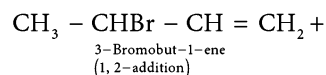
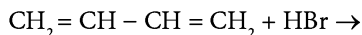


6. (a) $\text{CH}_3 - \text{CH}_2 - \text{CHBr}_2 \xrightarrow{\text{alc. KOH}} \text{CH}_3 - \text{C} \equiv \text{CH}$
 $\text{CH}_3 - \text{CHBr} - \text{CH}_2\text{Br}_2 \xrightarrow{\text{Lindkr's at.}} \text{CH}_3 - \text{CH} = \text{CH}_2$
 (b) Na and liquid NH_3 .
 (c) (i) no product is formed as both bromine atoms are cis oriented.



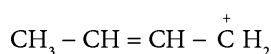
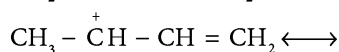
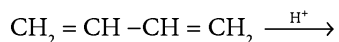
- (ii) A conjugated diene is the preferred product.

7. Two addition products are formed when buta-1,3-diene is treated with HBr in 1 : 1 molar ratio.



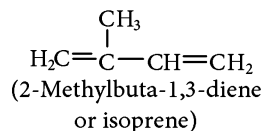
The proportion of the two products obtained depends on the temperature. 1,2-addition product is the kinetically controlled product while 1,4-product is the thermodynamically controlled product. At 40°C , 80% of the product is the 1,4-addition product.

The formation of the two products is due to two resonance structures possible for the carbocation intermediate formed by the addition of H^+ to butadiene

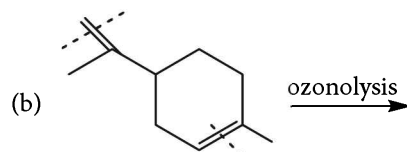
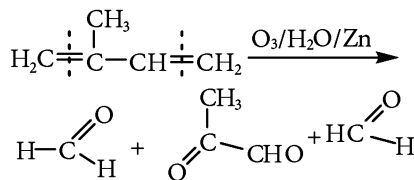


In the resonance hybrid, there will be partial positive charge on C-2 and C-4. Hence Br^- can attack these two carbon atoms giving 1, 2 and 1, 4-addition products.

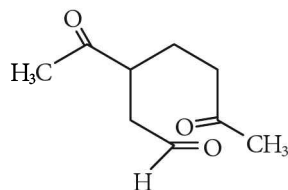
8. (a) The monomer of natural rubber is



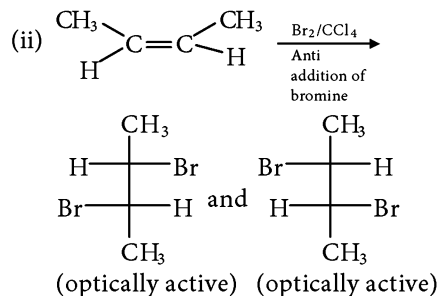
When this undergoes ozonolysis the following products are obtained.



HCHO and

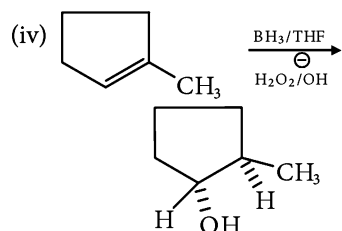
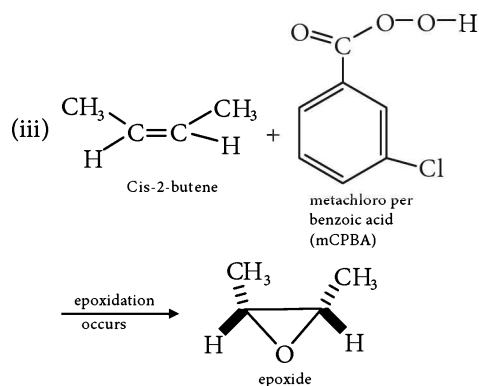


9. (i) $\begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{CH}_3 & & \text{CH}_2\text{CH}_3 \end{array} \xrightarrow{\text{H}_2/\text{Pt}}$
 Cis-2-pentene
 $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$
 n-pentane
 (no stereo chemistry)

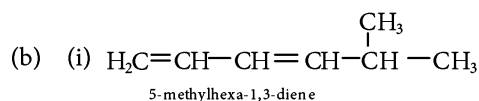
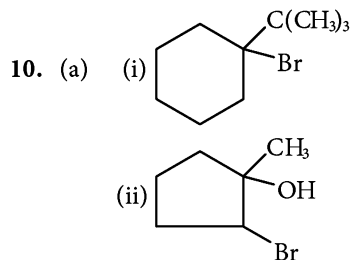


Anti addition of bromine to cis-2-butene gives racemic mixture of two optically active products (2,3-dibromobutane)

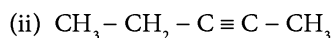
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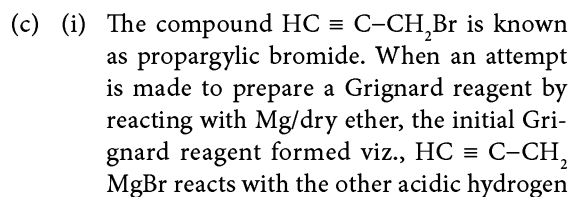
Anti Markovnikov addition of water occurs. The orientation of H and OH is cis.



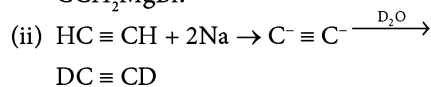
The above product is obtained as the major product because a conjugated diene is more stable than a non conjugated product. So in this dehydrohalogenation, Saytzeff's rule is violated.



Alkynes are known to undergo rearrangement when heated with ethanolic KOH. The triple bond migrates from the terminal position to an internal carbon.



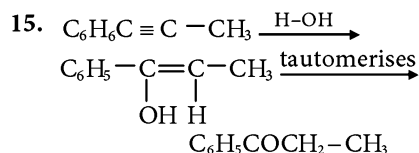
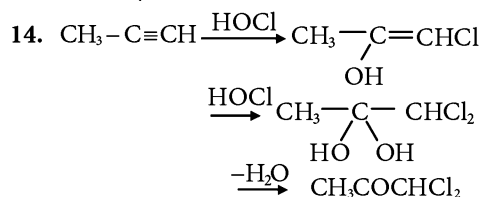
of the terminal acetylene to form $\text{BrMgC}\equiv\text{CCH}_2\text{MgBr}$.



11. Corey-House synthesis is the best method of preparing an alkane with odd number of carbons.

12. Greater the substitution around the double bonded carbons, greater will be the stability. Hence trimethyl substituted ethylene is the most stable alkene among those given.

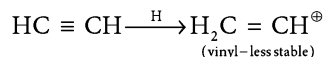
13. All the reactions listed in (a) – (c) will result in 2-methylbutane.



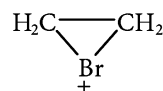
16. Both Statements (1) and (2) are correct. However statement (2) is not an explanation for statement (1) Markovnikov rule states that when an unsymmetrical reagent such as hydrogen halide adds on to an unsymmetrical alkene, the negative part of the addendum adds to the carbon of the alkene with the least number of hydrogens.

17. Statement (1) is not correct while statement (2) is correct.

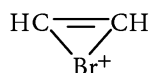
Alkenes are more reactive than alkynes in electrophilic additions reactions. When an electrophile like HX adds to a double bond, this leads to the formation of a carbocation in the first step. The carbocation may be 1°, 2° or 3° depending on the nature of the alkene. In the case of an alkyne-vinyl cation which is less stable is formed



Further addition of bromine to double bond leads to a more stable bromonium ion intermediate

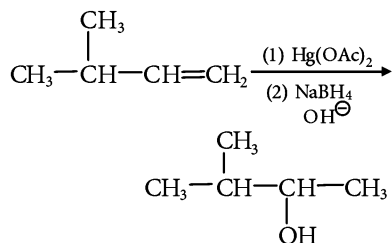


While the addition of bromine to an acetylene leads to a less stable cyclic three membered intermediate



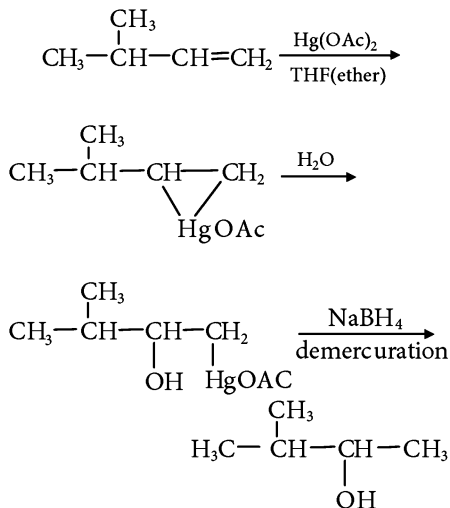
So statement (1) is not correct, while statement (2) is correct.

18. Both statements (1) and (2) are correct and statement (2) is an explanation for statement (1)
19. Statement (1) is correct while statement (2) is wrong. The oxymercuration of an olefin leads to the hydration of the olefin without a carbocation rearrangement. So the reaction gives as follows



So statement (1) is correct.

On the other hand the statement (2) is not correct oxymercuration reactions do not proceed via radical mechanism. The reaction proceeds via a three membered mercurium ion intermediate.

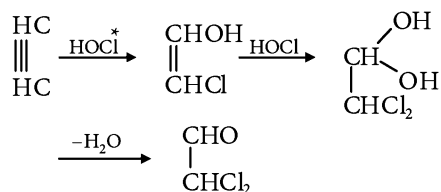


So, statement (1) is correct while statement (2) is not correct.

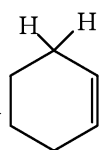
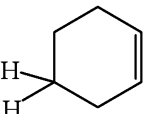
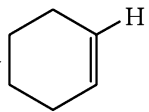
20. Both statement (1) and (2) are correct and statement (2) is an explanation for statement (1). A carbocation intermediate is formed in both the cases. The cation $\text{CH}-\overset{\oplus}{\text{CH}}-\text{CH}_2-\text{CH}_3$ formed is more stable than $\text{CH}_3-\overset{\oplus}{\text{CH}}_2$

21. CHO is the product.
 CHCl_2

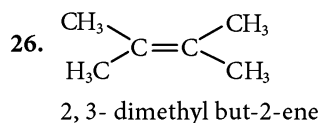
The reaction proceeds like this



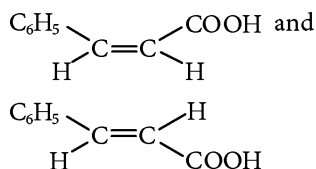
* Cl_2 water contains HOCl

22. Alkanes can be oxidatively cleaved with hot alkaline permanganate solution to give carboxylic acid and ketone depending on substitution. In this case the double bond gets cleaved to give a ketone and acetic acid.
23. It is 1, 4 addition of Cl_2 to a conjugated diene.
 1, 4-addition product predominates at higher temperature. The double bond gets shifted to 2, 3 positions of the starting diene.
24. (A) is neopentane
 $\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_3\text{C}-\text{C}-\text{CH}_2\text{Cl} \\ | \\ \text{CH}_3 \end{array}$ The product of Wurtz reaction
 is $\begin{array}{c} \text{CH}_3 \quad \quad \text{CH}_3 \\ | \quad \quad | \\ \text{H}_3\text{C}-\text{C}-\text{CH}_2-\text{CH}_2-\text{C}-\text{CH}_3 \\ | \quad \quad | \\ \text{CH}_3 \quad \quad \text{CH}_3 \end{array}$
25. Allylic hydrogen  will be most reactive than an aliphatic hydrogen  which is more reactive than a vinylic hydrogen 

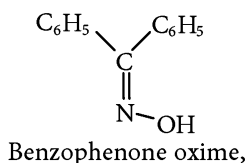
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27. (a), (b) and (d) can exhibit geometric isomerism. Cinnamic acid can exist as

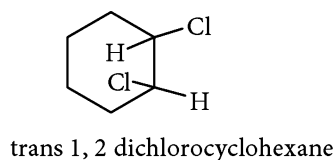
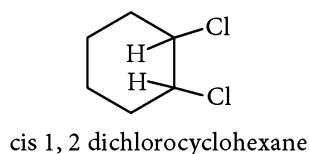


Benzophenone oxime does not exhibit syn and anti isomerism because, the two groups attached to carbon of the C = N bond are similar as shown.



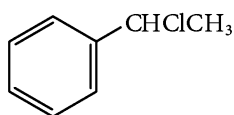
Only unsymmetrical oximes exhibit geometrical isomerism.

1,2 dichlorocyclohexane can exist as cis and trans isomers due to the rigidity of the cyclic structure.



28. (a) and (d) are correctly represented  on treat-

ment with Baeyer's reagent will give a Cis 1,2 diol
on halogenation under photochemical conditions will give a benzylic halide



29. (a) – (d) All the four Statements are correct.

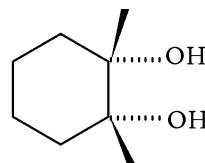
30. (a) → (r), (s)
(b) → (p), (q), (s)

- (c) → (q), (r)
(d) → (r), (s)

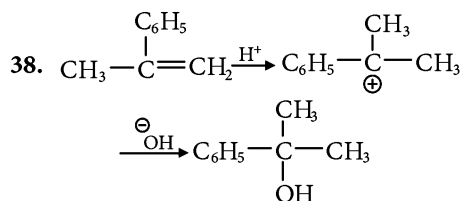
IIT Assignment Exercise

31. A conjugated diene is more stable. This is because of additional resonance stabilization.
32. Anti Markovnikov rule is applicable only for HBr addition to an unsymmetrical alkene. Hence (d) is not correctly represented.
33. Aniline is a compound which contains an active hydrogen. All compounds having an active hydrogen (hydrogen attached directly to an electronegative atom is known as active hydrogen) react with Grignard reagent to produce a hydrocarbon.
34. A tert-butyl cation is more stable than a 3° cation with an electron withdrawing halogen attached to one of the substituents. In all the other pairs, the stability is not correctly indicated.

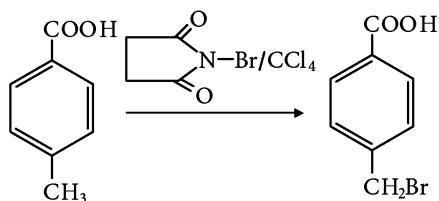
36. Cis-hydroxylation occurs to give



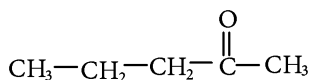
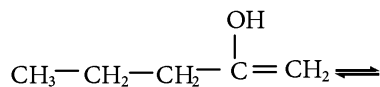
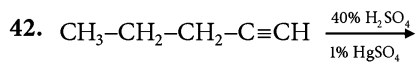
37. The presence of oxygen in a free radical induced reaction acts as a radical inhibitor and therefore retards the reaction.



39. There are two β-hydrogens available. However the diene $\text{CH}_3\text{CH}_2\text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{CH}_3$ is preferentially formed because it is a conjugated diene and is more stable than an isolated diene.
40. The reaction is an example of benzylic bromination. So the product formed is



41. The substituents of same priority are listed in the alphabetical order. So ethyl takes precedence over the methyl.



43. This is one of the staggered conformations of 2, 3 dimethyl butane. The other staggered Newman projection given in (a) has all the four —CH_3 groups close by and hence has higher energy. The structure (c) is eclipsed which is more strained. The structure (d) corresponds to the staggered conformation of n-butane.

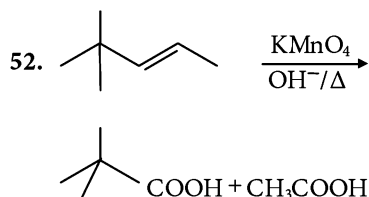
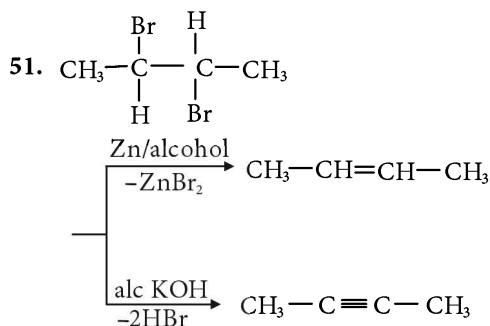
44. In the Saw horse projection given, the two methyl groups are in an antiperiplanar orientation – where the dihedral angle will be 180° which is maximum.

45. The C–C bond in (c) is formed by the overlap of sp hybridized orbitals. So it is shorter than other C–C bonds among the options given.

46. CCl_2 is generated by the reaction of CHCl_3 with a strong base like potassium tert-butoxide. This electrophilic species $\ddot{\text{C}}\text{Cl}_2$ inserts across the double bond to give a three membered ring structure.

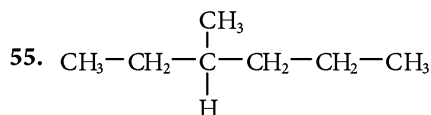
49. Kolbe's electrolysis can be utilized for the synthesis of alkanes, alkenes and alkynes.

50. Peroxide effect does not work well for HI addition to unsymmetrical alkene because the reaction will proceed by radical mechanism only when both the propagation steps are exothermic.



53. This cannot be synthesized by wurtz reaction as it contains an odd number of carbon atoms though the molecule appears to be symmetrical.

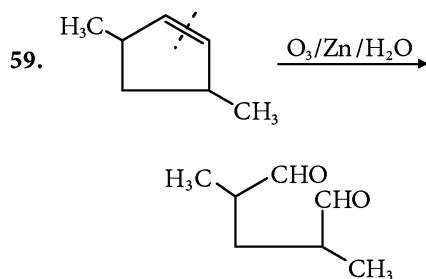
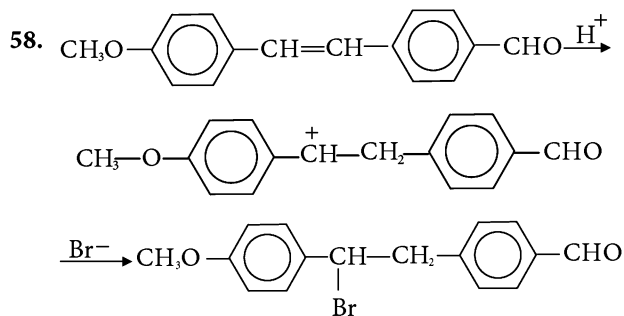
54. Alkanes containing six carbon atoms when heated in the presence of Cr_2O_3 or V_2O_5 or MoO_3 (molybdenum oxide) supported over alumina, it undergoes aromatization to give benzene. Aromatization can also be effected by catalysts such as Pt, Pd and Ni at high temperature (873K)



This is the simplest hydrocarbon that can show optical isomerism.

56. Zn (Hg)/HCl is known as Clemmenson reagent. This is used for the reduction of a carbonyl group to a methylene group or a hydrocarbon.

57. This is an extension of wurtz reaction and this is known as Freund's synthesis. Cyclization is difficult if the number of carbon atoms is more than six.



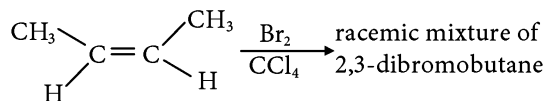
2.78 Alkanes, Alkenes and Alkynes

60. Generally eliminations are 1,2 eliminations or β -eliminations as the groups that are lost, are eliminated from 1, 2 positions. However, as there is only one carbon in chloroform, there cannot be any β -elimination, and both the groups are lost from one and the same carbon which is known as α -elimination or 1, 1 elimination.

61. Since alkenes are a source of electrons, electrophilic reagents attack them. So the reactions of alkenes are mainly electrophilic additions.

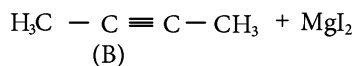
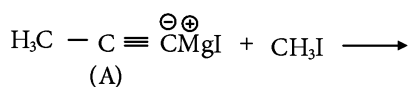
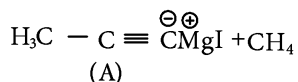
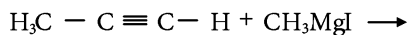
62. Oxymercuration is the process by which H-OH can be added across a double bond following Markovnikov rule, without any rearrangements of carbocations.

63. $\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_3 \xrightarrow[\text{reagent}]{\text{Lindlar's}}$



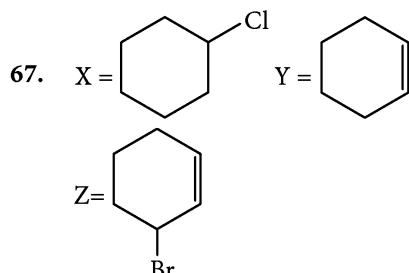
Cis alkenes on anti addition give a racemic mixture of the products.

64. The reaction is



65. The alkyl halide which reacts with the lithium dialkylcopper should be either a primary or a secondary halide. A tertiary halide does not participate in Corey-House synthesis.

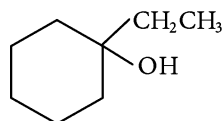
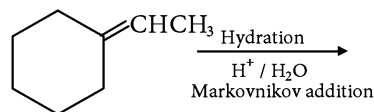
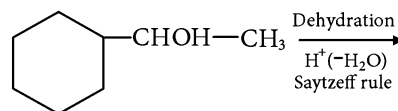
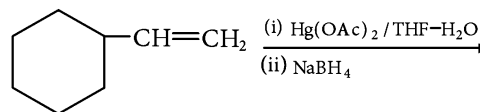
66. It is a Markovnikov addition. The more negative Cl^- attaches to the carbon containing least number of hydrogen. So the product is $\text{CH}_3\text{CHCl} - \text{CH}_2\text{NO}$.



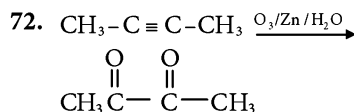
68. There are two types of carbons, one set with sp^3 hybridization while the carbonyl carbon is of sp^2 hybridization

69. Cyanide ion is stabilized by the electronegative nitrogen. This is in addition to the triple bond nature which is due to sp hybridization.

70. The sequence of reactions will be



An alkene is formed in this reaction by elimination. All the other reactions are substitution reactions.



73. The alkyne is monoacidic. One hydrogen is replaced by a silver atom. So the mass of silver salt containing 108 g of Ag is

$$\frac{100}{67} \times 108 = 161\text{g}$$

This is the molecular weight of the silver salt of alkyne.

$\therefore$ Molecular weight of alkyne = $161 - 108 + 1 = 54$

Probable structure is $\text{HC} \equiv \text{C} - \text{CH}_2\text{CH}_3$ which is (b)

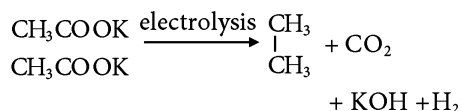
74. This is based on the pK_a values of these compounds.

The pK_a values are

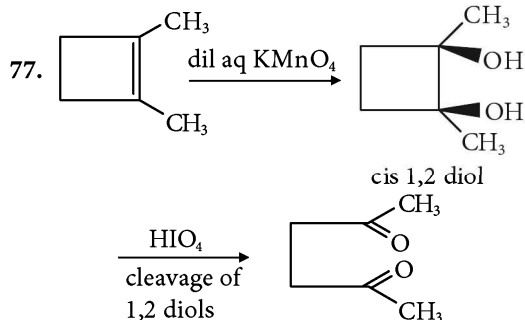
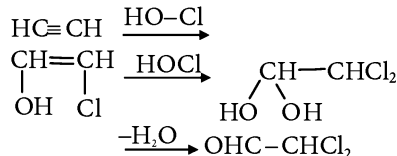
Acetic acid	—	4.5
Phenol	—	10
Alcohol	—	16
Acetylene	—	25
Ethylene	—	40

Increase in pK_a values means decreasing acidity.

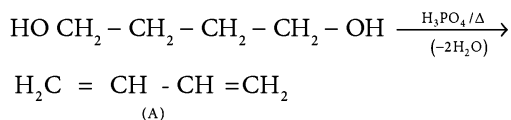
75. $\text{CH}_3\text{COOC}_2\text{H}_5$ on hydrolysis gives CH_3COOH and $\text{C}_2\text{H}_5\text{OH}$. Acetic acid CH_3COOH when subjected to Kolbe's electrolysis gives ethane



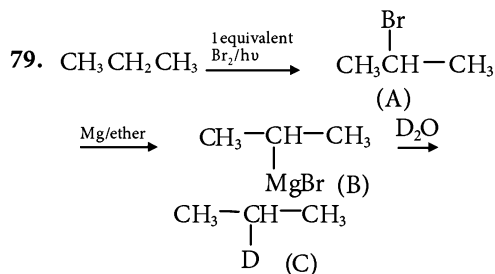
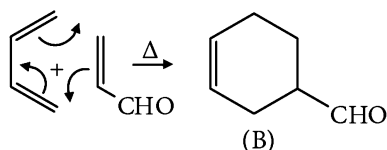
76. Chlorine water is HOCl



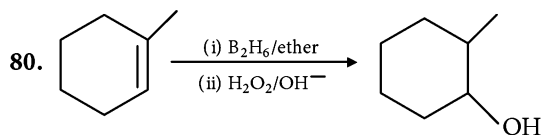
78. The first product (A) is formed by dehydration



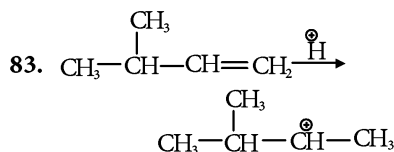
(A) is a 1, 3 conjugated butadiene, This undergoes a thermal (4 + 2) cyclo addition with acrolein. The conversion of (A) to (B) is known as Diels-Alder reaction.



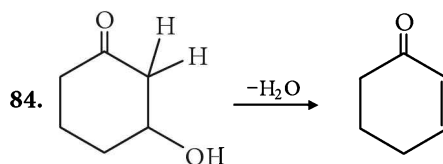
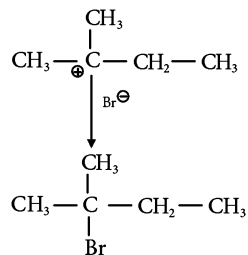
Bromination is highly selective and the major mono-brominated product is $\text{CH}_3\text{CHBrCH}_3$.



82. Iodine is very slow to react in halogenation of alkanes. Further the HI which is also formed as a side product reduces the main product, viz., $\text{C}_4\text{H}_9\text{I}$ back to butane C_4H_{10} . So an oxidizing agent is used to oxidize HI to I_2



This rearranges to a more stable tertiary carbocation by a 1,2 hydride shift followed by addition of Br^- ion to give the major product.



An α, β unsaturated ketone is obtained as a product which is very stable.

2.80 Alkanes, Alkenes and Alkynes

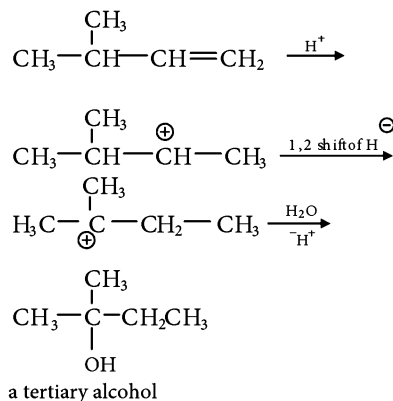
85. Only in the hydration reaction of an olefin, in the presence of a mineral acid, a carbocation intermediate is observed. All the other reactions proceed without the formation of carbocations.

86. $\text{CH}_3\text{CH}_2\text{Cl}$, CH_3CHCl_2 , $\text{CH}_2\text{ClCH}_2\text{Cl}$, CH_3CCl_3 , $\text{ClCH}_2\text{CHCl}_2$, ClCHCCl_3 , $\text{CHCl}_2\text{CHCl}_2$, $\text{CHCl}_2\text{CCl}_3$ and CCl_3CCl_3

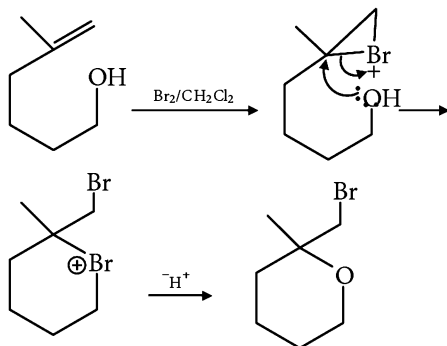
87. The reduction of the triple bond by Na/liquid NH_3 gives trans alkene.

88. During the hydration, a carbocation is formed as an intermediate. A tertiary carbocation is most favourable. So (a) gets hydrated most readily.

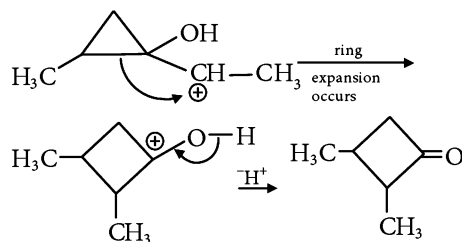
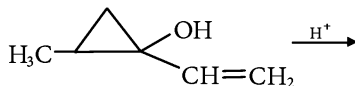
89. When hydrated under acid conditions, the alkene undergoes rearrangement to a more stable tertiary carbocation to which the nucleophile adds. So a tertiary alcohol is formed.



90. The reaction proceeds as follows



91. The reaction proceeds as follows.

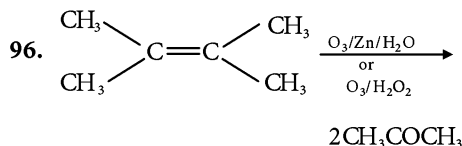


92. Only the addition of HBr in the presence of H_2O_2 or any other peroxide occurs against Markovnikov rule. All the other reactions follow Markovnikov rule whether peroxides are present or absent.

93. The only correct statement is the reactivity of acetylene and ethylene, where the latter is more reactive than acetylene in electrophilic additions.

94. 1-butyne contains an acidic hydrogen and it gives a red precipitate with ammoniacal cuprous chloride.

95. Acetylene or C_2H_2 is the only alkyne which can give an aldehyde on hydration in the presence of mercuric sulphate and H_2SO_4 . All the other alkynes will give only ketones.

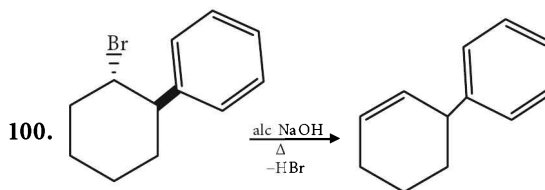


Ketones cannot be further oxidized easily to acids.

97. Ethyne on ozonolysis gives glyoxal.

98. Chlorine gets priority over bromine as it is attached to one of the carbons of the double bond of the cyclohexene ring.

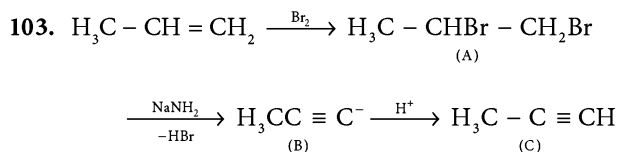
99. It is normal Markovnikov addition and bromine adds to the carbon having the least number of hydrogen atoms. Further the presence of the $-\text{OCH}_3$ group stabilizes the intermediate carbocation produced.



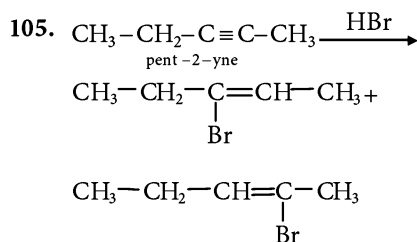
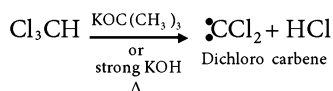
A hydrogen which is antiperiplanar to the bromine is needed for elimination. Hence 3-phenylcyclohexene is the product obtained.

101. A halogen is attached to an olefinic carbon in $\text{CH}_2 = \text{CH} - \text{Cl}$, hence it is least reactive.

102. This is an example of dehalogenation. So only bromine is removed. Dehydrohalogenation does not occur.

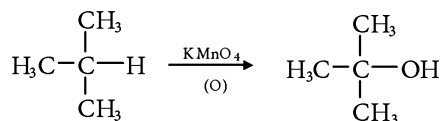


104. An α elimination generally does not lead to an alkene as the two groups are eliminated from one and the same carbon. For example formation of dichloro carbene is an example of α -elimination

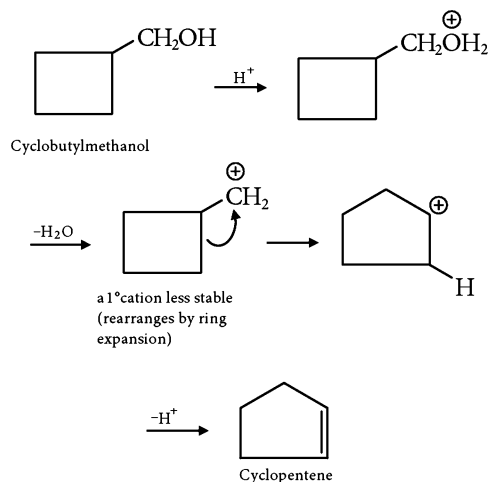


The above two products are the structural isomers of the bromo compound. Each of these structural isomers can exist as a pair of cis-trans isomers. So total number of stereoisomers = 4.

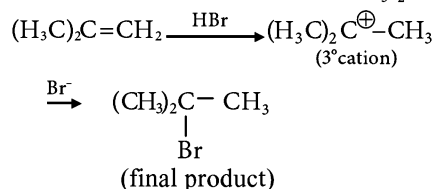
106. t-butyl alcohol is the oxidation product of 2-methylpropane. For the oxidation to occur the alkane should contain a tertiary hydrogen.



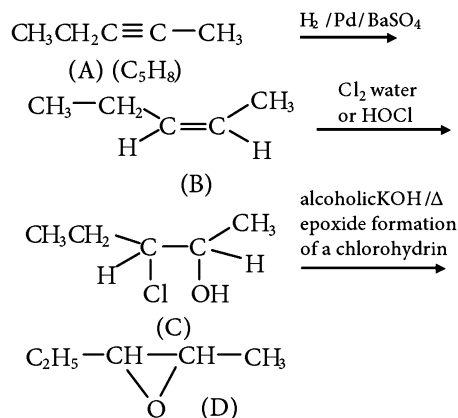
107. A ring expansion occurs followed by elimination. The reactions can be represented as shown



108. The addition of HBr to the olefin depends on the ease of formation of the carbocation as an intermediate. A tertiary carbocation is most favourable and one such 3° carbocation is formed with $(\text{CH}_3)_2\text{C} = \text{CH}_2$

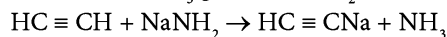


109. The sequence of reactions can be represented as follows



110. Only NaOH will not react with acetylene, as the acidity of hydrogen is not high enough to react with NaOH. In other words, a base stronger than NaOH is required to abstract an acetylene hydrogen.

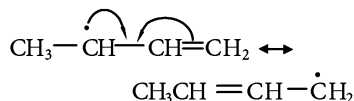
111. Statement (1) is wrong because ethyne reacts with sodamide to form NH_3 gas and not H_2 .



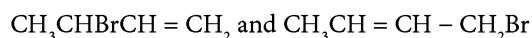
Statement (2) is correct.

2.82 Alkanes, Alkenes and Alkynes

112. Statement (1) is wrong while statement (2) is correct. Reaction of $\text{CH}_3\text{CH}_2 - \text{CH} = \text{CH}_2$ with NBS proceeds by a radical mechanism. There is resonance stabilization of the allylic radicals as shown.

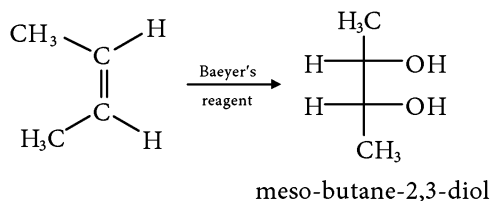


So bromine radical can attack either carbon (3) or carbon (1) viz., give two products



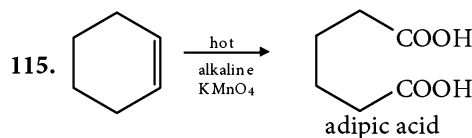
Hence statement (1) is not correct. Statement (2) is correct because the allyl radical gets stabilized by resonance.

113. Statement (1) is correct while statement (2) is not correct. Baeyer's reagent is dilute alkaline permanganate. It reacts with alkene to produce cis-1,2 diols. When cis-2-butene reacts with Baeyer's reagent, it forms meso butane-2,3-diol which is optically inactive.

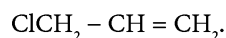


Hence statement (1) is correct. Statement (2) is not correct because antihydroxylation does not occur with dil alkaline KMnO_4 .

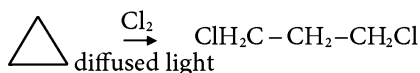
114. Ozonolysis cleaves the alkene to either aldehydes or ketones.



116. Propene undergoes preferential substitution at allylic position at high temperature of 750-773K. Hence the main product will be



117. (a) and (c) is correct as the highly strained cyclopropane reacts with the halogen in diffused light to give a dihalo-dibromo or dichloro-derivative by ring opening



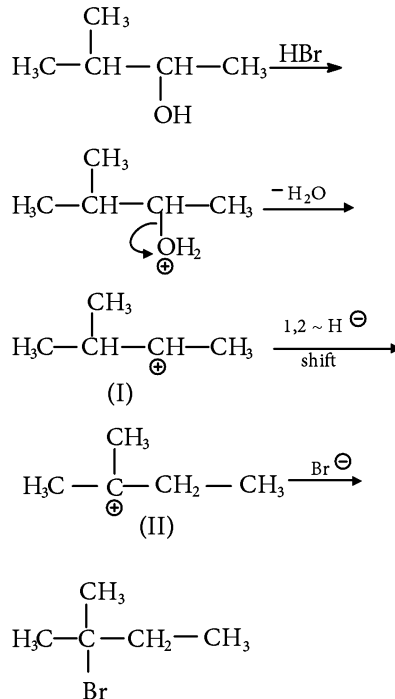
The other statements (b) and (d) are not correct. Statement (c) also correct.

118. NaBH_4 does not reduce the double bond but it reduces $>\text{C}=\text{O}$ to $>\text{CHOH}$. So statement (a) is not correct. Buta-1,3-diene when treated with HBr at very low temperature, the kinetically controlled 1,2-addition product predominates.

119. All the four reactions stereochemistry is correctly represented.
120. (a) $\rightarrow$ (p), (s)
(b) $\rightarrow$ (q), (r)
(c) $\rightarrow$ (q)
(d) $\rightarrow$ (q)

Additional Practice Exercise

121. When 3-methyl-2-butanol reacts with HBr, the first step in the reaction is the formation of the carbocation (I) by initial protonation and elimination of a molecule of water. This carbocation (I) rearranges to a more stable carbocation (II) by 1,2-hydride shift. The driving force for the rearrangement is the formation of more stable carbocation from the less stable one. Now the nucleophile Br^- attacks the new carbocation (II) to give the product.



122. 44 g of CO_2 contains 12 g of carbon and 18 g of H_2O contains 2 g of hydrogen.

Percentage of carbon in the compound

$$= \frac{12}{44} \times \frac{3.476 \times 100}{3.0} = 31.6 \%$$

The percentage of hydrogen in the compound

$$= \frac{2}{18} \times \frac{1.422 \times 100}{3.0} = 5.26\%$$

Oxygen is found out by difference

$$= 100 - (31.6 + 5.26) = 63.14\%$$

$$\text{Carbon} = \frac{31.6}{12} = 2.63$$

$$\text{Hydrogen} = \frac{5.26}{1} = 5.26$$

$$\text{Oxygen} = \frac{63.14}{16} = 3.9$$

Dividing by the smallest number,

$$\text{C} = \frac{2.63}{2.63} = 1$$

$$\text{H} = \frac{5.3}{2.63} = 2$$

$$\text{O} = \frac{3.9}{2.63} = 1.5$$

$$\text{Empirical formula} = \text{C}_2\text{H}_4\text{O}_3$$

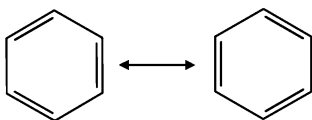
$$\text{Empirical formula weight} = 76$$

$$n = \frac{228}{76} = 3; \text{Molecular formula}$$

$$= (\text{empirical formula}) \times n$$

$$\text{Molecular formula} = \text{C}_6\text{H}_{12}\text{O}_9$$

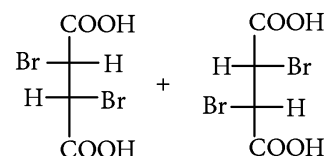
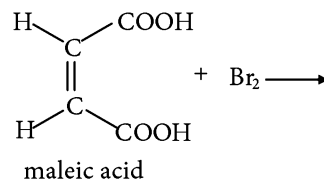
123. Benzene possesses a conjugated system of double bonds participating in resonance. Resonance involves aromatic stabilization with the delocalization of π -electrons, which imparts extra stability.



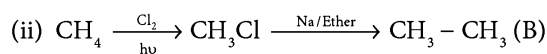
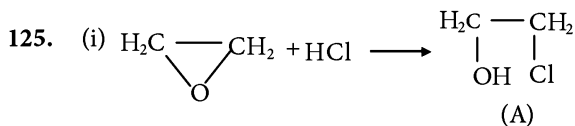
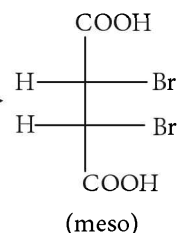
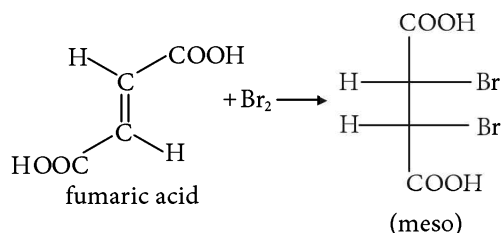
During an electrophilic addition, benzene will lose its aromaticity. So this reaction actually does not occur. On the other hand, during an aromatic electrophilic substitution, the aromatic nature of benzene with the double bonds in the ring are retained.

In contrast, in the case of olefins, electrophilic addition across a double bond, results in saturated compounds, which are energetically favourable and more stable than double bonded compounds. Hence addition is preferred over substitution.

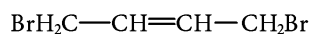
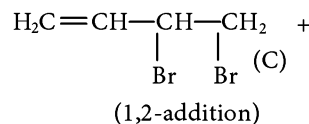
124. Addition of bromine (trans addition) to maleic acid (cis alkene) results in a racemic mixture, while the addition of bromine to fumaric acid (trans alkene) results in a meso compound as shown.



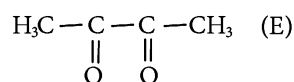
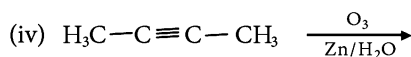
racemic mixture

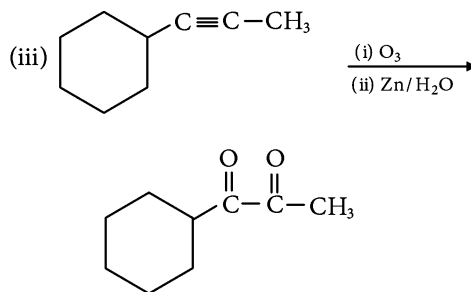
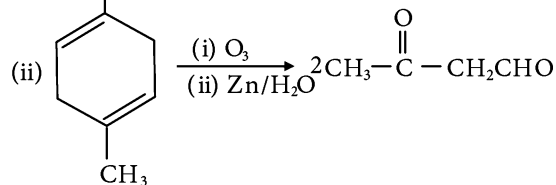
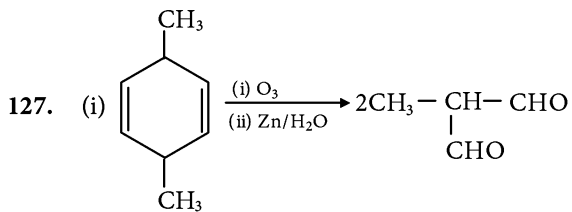
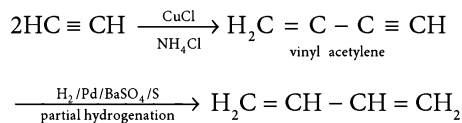
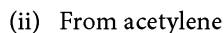
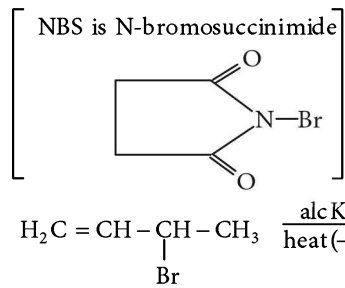
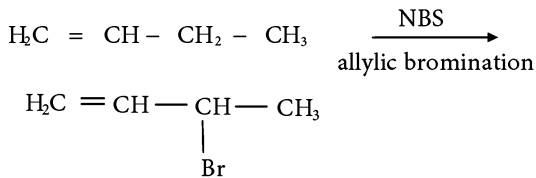
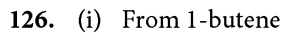
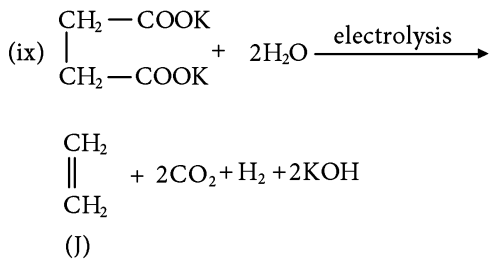
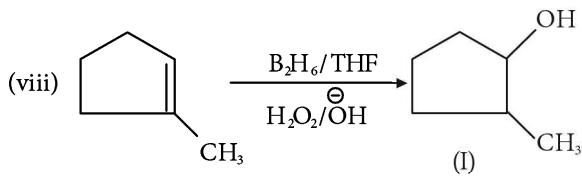
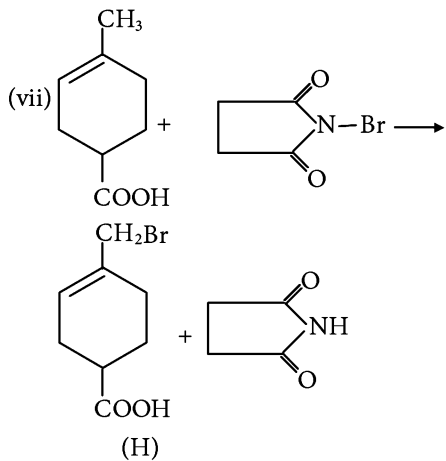
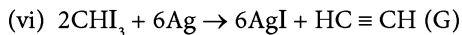
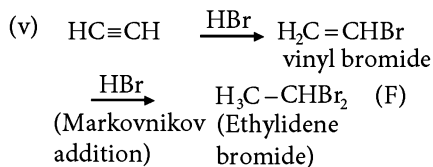


[Note: Here it is assumed that only mono chloro product is formed as the major product.]

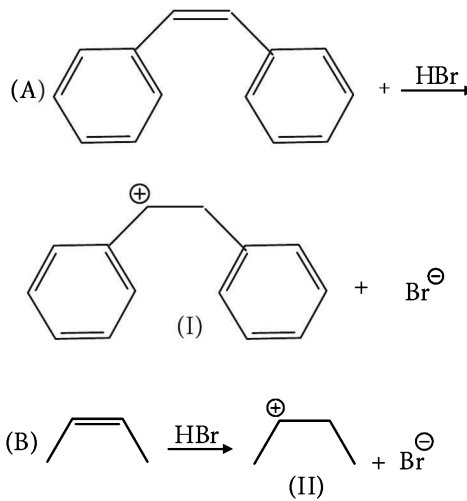


(1,4-addition) (D)



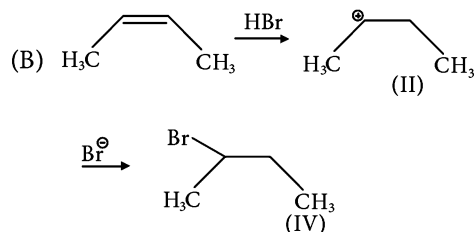
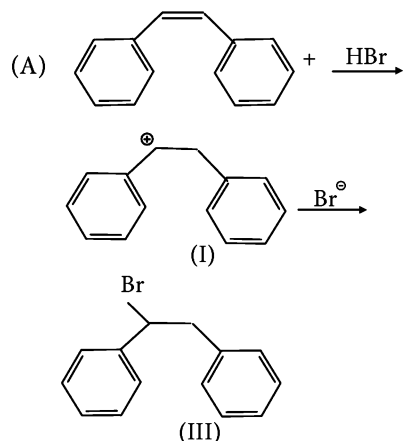


128. Both the reactions (A) and (B) involve the addition of HBr to a double bond, they depend on the formation of a stable carbocations (I) and (II) by initial protonation.

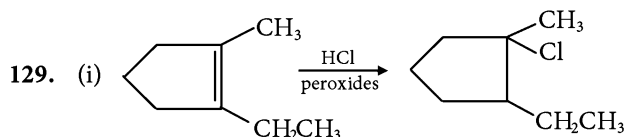


(I) is a more stable carbocation because of the extra stabilization given by the phenyl group by resonance, while the cation in (II) is stabilized by the electron releasing inductive effect hyperconjugative of the $-CH_3$ group which is weak.

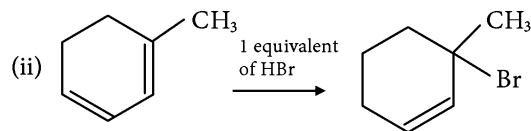
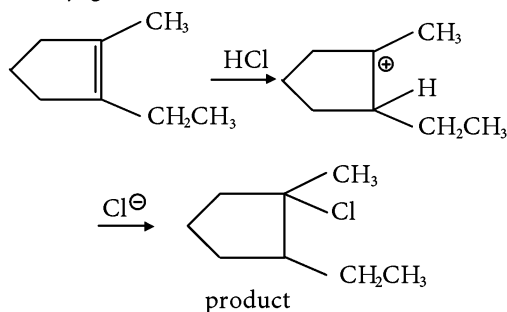
Both the cations react further with the nucleophile $Br^\ominus$ to give the final products (III) and (IV).



Since the intermediate of reaction (A) is stable than that of (B), reaction (A) will proceed faster.

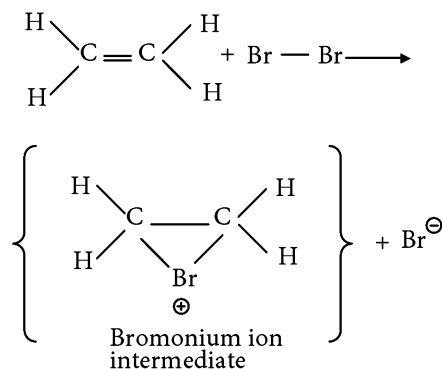


There is no peroxide effect in the addition of HCl to an unsymmetrical double bond. The reaction of HCl proceeds by an ionic mechanism. A carbocation is better stabilized by an adjacent methyl group than by an ethyl group by hyperconjugation.



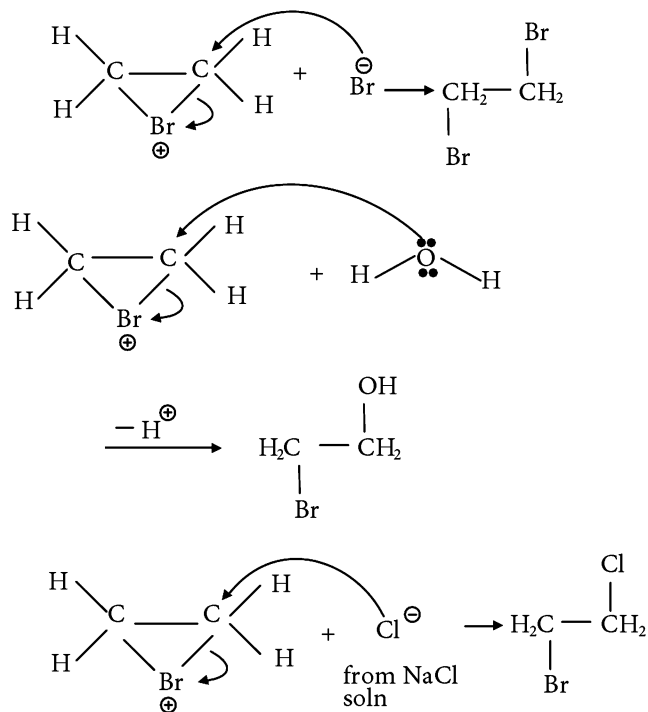
It is a conjugate or 1,4-addition product.

130. When ethylene reacts with a molecule of bromine, the first intermediate formed is a bromonium ion.



The reactive intermediate bromonium ion is free to react with three different nucleophilic species, namely a bromide ion (Br^-), a molecule of water ($H-\ddot{O}-H$) and a chloride ion (Cl^-) from NaCl solution.

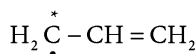
The three reactions occur as follows



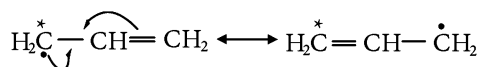
2.86 Alkanes, Alkenes and Alkynes

131. Alkanes do not undergo addition reactions. They mainly undergo substitution reactions.

132. The reaction is an example of an allylic bromination. The reaction proceeds by radical mechanism. As a key intermediate an allylic radical is formed.



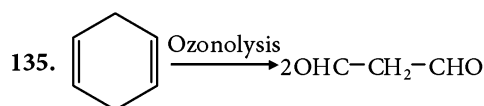
This can stabilize by an allylic rearrangement to give



Hence a mixture of two bromides are possible.

133. $\text{CH}_3-\text{CH}=\text{C}=\text{CH}-\text{X}$ is a substituted allene; it can show optical activity.

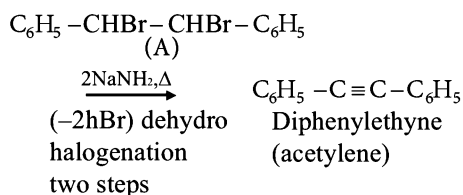
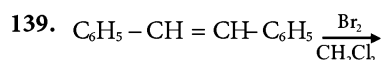
134. Between a methyl group and a chloro substituent, the chloro group has a priority. So the compound is 1-chloro-4-methylcyclohexane. Since both $-\text{Cl}$ and $-\text{CH}_3$ groups are trans to each other, the compound is known as trans-1-chloro-4-methylcyclohexane.



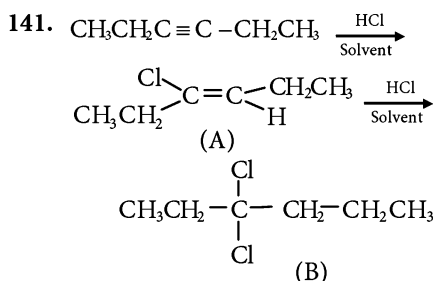
136. (b)

137. Both (b) and (c) can be used. Any one of them would give the same halide,

138. It is a hydroboration reaction of an unsymmetrical alkene. It is the addition of water by anti Markonikov route. However, hydration of the double bond occurs by the syn addition. Hence product (b) is the right choice.

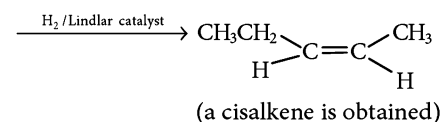
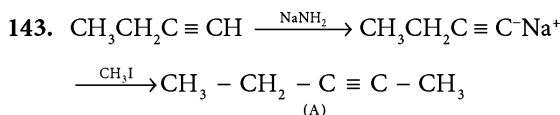
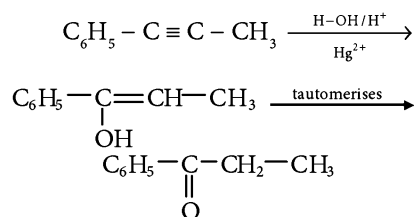


140. Vinylic halides undergo dehydrohalogenation when treated with strong base like NaNH_2 . so the product obtained is but-2-yn-1-ol.

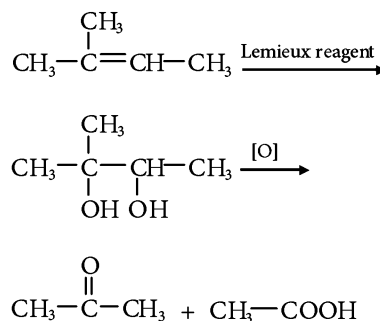


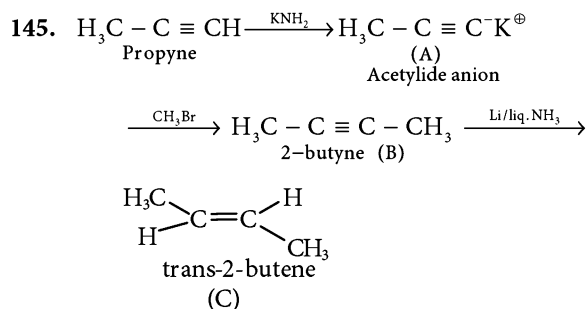
Electrophiles like HCl undergo addition reactions with alkynes as they do with alkenes. When excess HCl is used, the reaction proceeds in two stages to give dichlorohexane.

142. It is hydration of alkynes



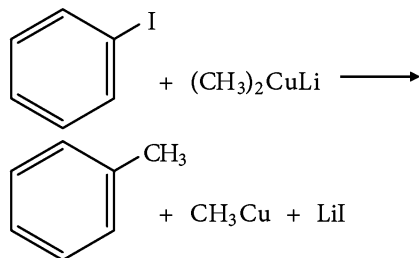
144. An aqueous solution of sodium periodate (NaIO_4) containing small quantity KMnO_4 is known as Lemieux reagent. The reagent oxidizes alkene first to cis-diol, which is then cleaved by the periodate first to aldehydes and ketones. Aldehydes are further oxidized to acids. The reaction takes place even at room temperature



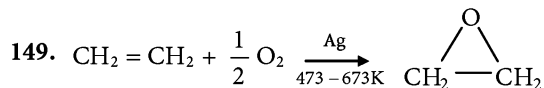
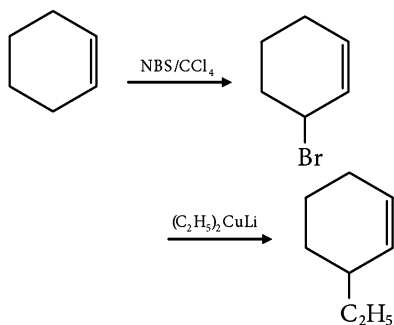


The last step is a stereoselective reaction-from (B) to (C)

146. Lithium dialkyl copper is called Gilman reagent, and it is useful for coupling reactions with organic chlorides, bromides and iodides, but not with organic fluorides. This is useful in making new C – C bonds. The reaction is known as Corey-House synthesis.
147. Toluene is obtained in 93% yield by reacting iodo-benzene with lithium dimethyl copper reagent. The complete equation can be represented as



148. First a halogen is introduced in the allylic position by the use of N-bromosuccinimide. Then by Corey-House synthesis an ethyl group replaces the bromine in the ring.



Epoxyethane (ethylene oxide) is manufactured by this method.

150. A terminal alkyne by hydroboration using disiamylborane followed by oxidation gives an aldehyde.

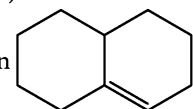


This is a cis dicarboxylic acid, containing a C = C double bond. When anti addition of bromine occurs a racemic mixture is obtained to give dl or (±) 2,3-dibromo succinic acid.

This is an example of stereo selective addition. It is also stereospecific because cis acid gives a racemic mixture, while the trans acid (fumaric acid) gives a meso compound.

152. The addition would be facilitated by an electron donating group while an electron withdrawing group like –COOH would be retarding the rate considerably. Hence $\text{H}_2\text{C}=\text{CH}-\text{COOH}$ would be slow to react. The presence of a benzene ring speeds up the reaction due to the formation of a benzylic carbonium ion intermediate.

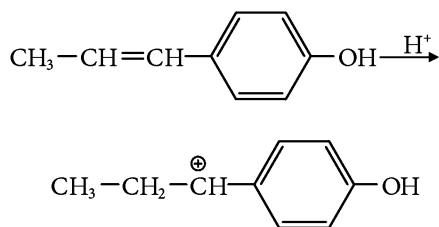
153. (a) is most stable.

In  the double bond is at a ring junction. However, it is not bridge head bicyclic system. Further, it is a trans double bond in a ten membered ring. The other double bonded compounds are not stable.

Compound (b), violates Bredt's rules: a double bond cannot be there in a bridge head of a bicyclic system. Compound (c) is a highly strained ring.

Compound (d) is trans cyclohexene which is too strained to be stable.

154. The major product formed is (c) because of the stabilization of the intermediate carbocation by resonance



The positive charge is delocalized into the benzene ring. So it is more stable than the other carbocation that can be formed from the unsaturated compound. This carbocation combines with Br^- to form product (c).

2.88 Alkanes, Alkenes and Alkynes

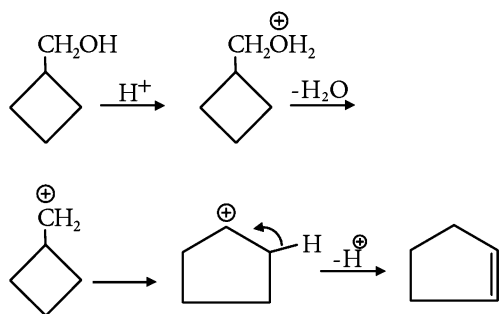
Phenolic -OH group cannot be easily replaced by treatment with HBr under ordinary conditions.

155. In Diels-Alder reaction an alkene containing an electron withdrawing group (called dienophile) is added 1,4 to a conjugated diene to form a six membered ring compound. It is a (4 + 2) cyclo addition reaction.

156. Dipole moment of CH_2Cl_2 is less than that of CH_3Cl . Among the chloroderivatives of methane, CH_3Cl has the highest dipole moment.

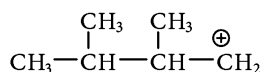
157. $\text{A} = (\text{CH}_3)_2\text{C} = \text{CH}_2$

Since $(\text{CH}_3)_3\text{CBr}$ is a tertiary halide, elimination occurs.

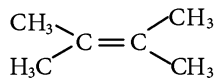
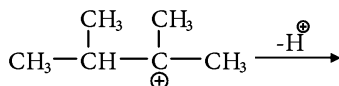
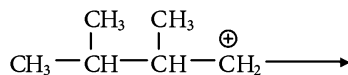


A ring expansion to a larger (five membered ring) is energetically a favourable process. This is followed by deprotonation to give cyclopentene as the final product.

C = A carbocation intermediate



is formed which rearranges by a 1,2 hydride shift to form a more stable carbocation, which loses a proton to form the olefin.



(d) Since both bromine atoms are cis to each other, no elimination occurs, as antiperiplanar orientation is necessary for elimination. So no reaction occurs.

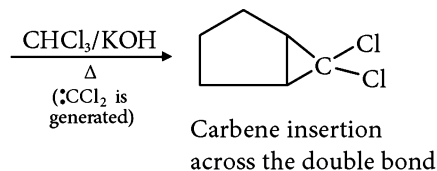
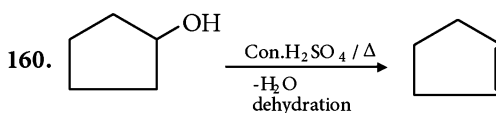
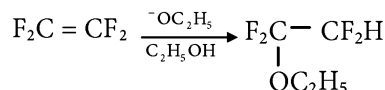
158. In this reaction which is an electrophilic addition to the double bond, the negative part of the addendum adds to the carbon containing least number of hydrogen in accordance with the Markovnikov rule. So this is an example of regioselective reaction.

159. The only reaction which is correctly represented is the bromine addition in the presence of NaCl to cyclohexene. The product formed is a mixture of 1,2-dibromocyclohexane and 1-bromo-2-chlorocyclohexane.

The remaining reactions viz., (a), (b) and (d) are not presented correctly. In (a) because of the presence of an electron withdrawing group an anti Markovnikov product $\text{CF}_3\text{CH}_2 - \text{CH}_2\text{Br}$ will be obtained.

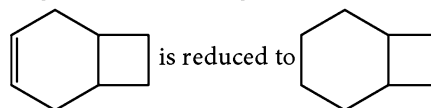
In (b), the reaction does not proceed to give the product shown, viz., $(\text{CH}_3)_3\text{CSH}$. This because H_2S is a very weak acid and the nucleophile ^-SH is not produced by ionization. In order to generate an appreciable concentration of ^-SH , a trace of con. H_2SO_4 has to be used.

(d) is not correctly represented. Ethylene by itself does not react with nucleophiles or bases like $^-\text{OC}_2\text{H}_5$ to form an addition compound. However if electron withdrawing groups are present in the olefin like $\text{F}_2\text{C} = \text{CF}_2$, then addition of $^-\text{OC}_2\text{H}_5$ readily takes place to give



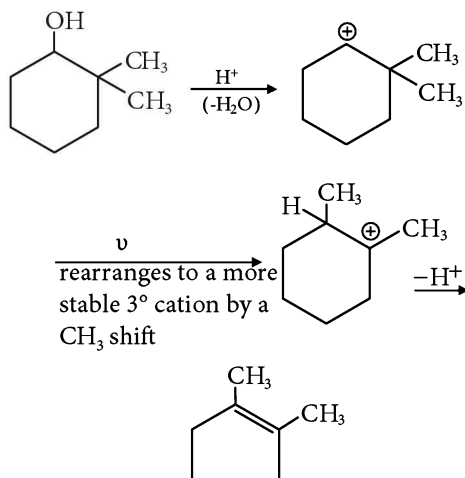
161. All the four statements/equations are correct

(a) when reduced, the more strained cyclobutene is converted to cyclobutane. There is great relief of ring strain. Whereas, when



there is only a small change in ring strain. Hence reduction of cyclobutene ring is faster. Statement is true.

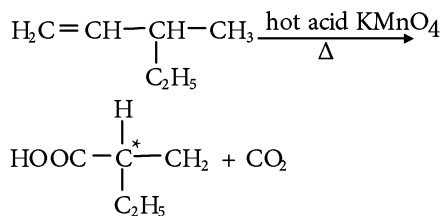
(b) true



(c) true

Since, t-butyl group is a bulky group, the epoxide ring is formed trans to t-butyl group

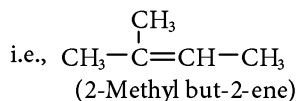
(d) True



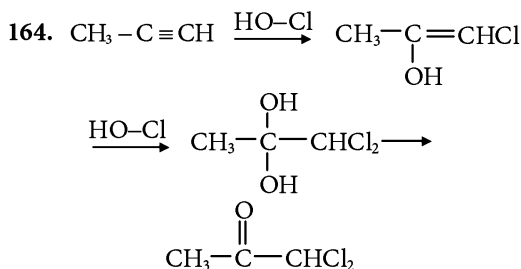
The double bond gets cleaved to give CO₂ and a chiral acid.

162. Only the reaction of hydration of phenyl acetylene with H₂SO₄/Hg⁺⁺ ions gives a single product viz., C₆H₅COCH₃. In all the other cases, more than one product is formed.

163. Heat of hydrogenation is a measure of the stability of the alkene. Greater the number of alkyl groups attached to the double bonded carbon, more stable is the alkene. So the alkene with maximum substitution will have the lowest value of heat of hydrogenation.



will liberate minimum heat per mole in hydrogenation.



165. (b) is the only statement which is correct.

Alkenes do not show rotational or conformational isomerism as the rotation is restricted between two carbon atoms connected by a multiple bond.

(b) is correct. 3-Hexene is a symmetrical alkene H₃C-CH₂-CH=CH-CH₂-CH₃

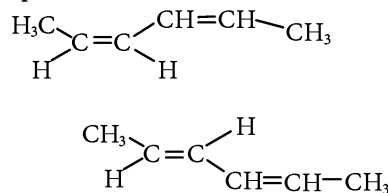
So there is no observation of peroxide effect.

(c) is not correct because a dibromide BrH₂C-CHBr-CH₂-CH₃ is the product.

(d) is not correct because alkynes are comparatively less reactive than alkenes. So the correct order is alkane < alkynes < alkenes.

166. 2,4-hexadiene only can exhibit geometrical isomerism among the compounds listed.

For example



167. The acidity of hydrogen is decided by two factors – (i) the electronegativity of the element to which the hydrogen is attached and (ii) the stability of the anion formed after the proton (hydrogen) has been removed.

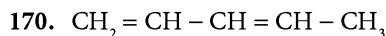
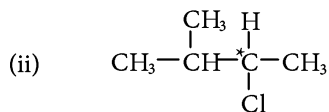
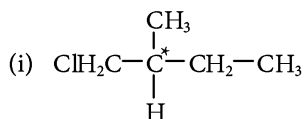
In the case of D, is a stronger acid because the anion formed is stabilized by resonance and it is aromatic.

168. The reactivity of alkenes towards hydrogen depends on the hyperconjugative effect and consequent stability of alkene. The reactivity decreases with increase in stability. Since maximum hyperconjugative structures are possible for II, it is the most stable alkene and hence the least reactive one towards hydrogenation. Since no hyperconjugation is possible in III, it is the least stable and most reactive one towards hydrogenation. Hence the order of reactivity towards hydrogen is III > I > II

2.90 Alkanes, Alkenes and Alkynes

(Note: The reactivity towards hydrogen halides is determined by the relative stability of the carbocation intermediate)

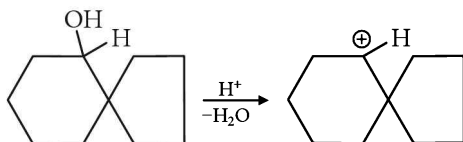
169. Two enantiomeric pairs and hence four optical isomers are possible because of the formation of products with chiral carbon atoms as shown below



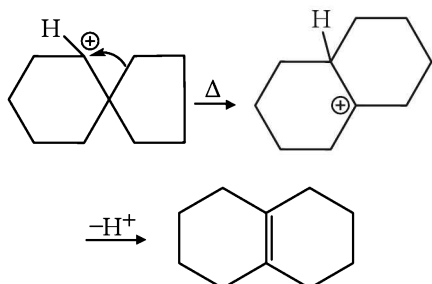
171. Both statements are correct, but statement (2) is not the explanation of statement (1)

A possible contributing factor for the decreased reactivity of a triple bond to electrophiles may be the fact that bridged bromonium ion formed as intermediate is more strained than the bridged bromonium formed from ethene.

172. Both statements (1) and (2) are correct, but statement (2) does not provide an explanation for statement (1). This is an alcohol dehydration accompanied by a rearrangement.



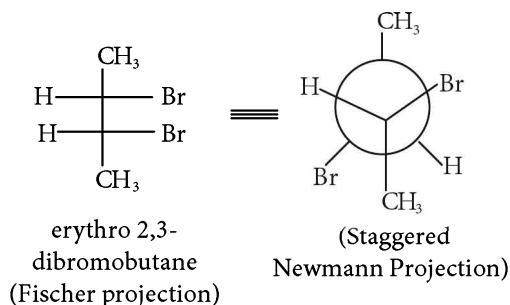
The initially formed carbocation intermediate in a 2° cation. This rearranges to a tertiary carbocation by ring enlargement.



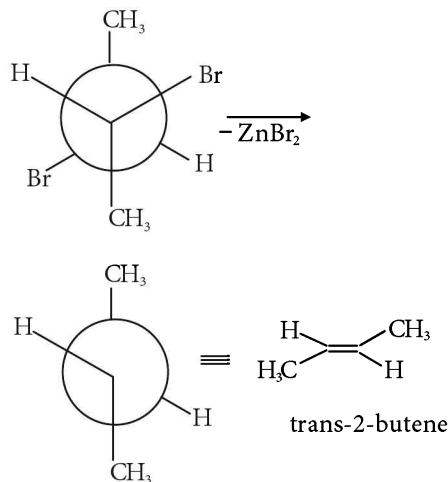
So statement (1) is correct.

Statement (2) is also correct because when alcohols and alkylhalides undergo elimination, Saytzeff rule is followed to give a more substituted olefin. However, statement (2) does not provide an explanation for statement (1).

173. Both Statement-1 and Statement-2 are correct and the Statement-2 is the correct explanation for the Statement-1 made. Erythro-2,3-dibromobutane is represented in the Newmann projection formula as shown



Anti periplanar configuration is an essential structural requirement for E2 elimination.



174. Statement (1) is not correct while statement (2) is correct.

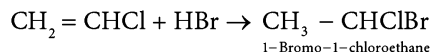
Oxygen acts as a radical inhibitor and slows down the photochemical free radical process. Hence statement (1) is not correct. Statement (2) is correct.

175. Both statements (1) and (2) are correct and statement (2) is the correct explanation of statement (1)

Boiling point of isomeric alkanes decreases with increase in branching because of the reduction in surface area and consequent decrease in van der Waals

attraction. There is no such regular trend for melting point. It depends on the effectiveness of packing in the solid state.

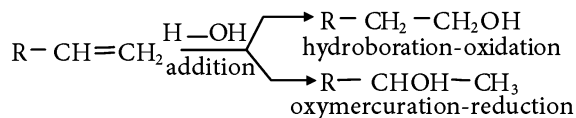
176. Statement (1) is correct while statement (2) is wrong.



The addition follows Markovnikov's rule. Hence statement (2) is not correct.

177. Both the statements are correct. However, statement (2) is of a general nature and does not fully support the statement (1).

Both oxymercuration and hydroboration methods involve the net addition of $\text{H}-\text{OH}$ to the double bond. This can be illustrated by the following general example.

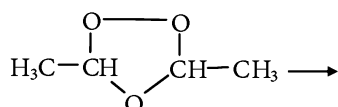
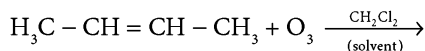


The advantage of these two methods are, both the methods are highly regioselective and both occur without rearrangements. The alcohol is the final product. Hence statement (1) is correct.

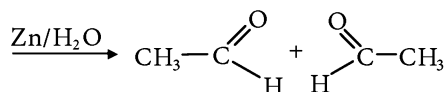
Statement (2) is also correct as the hydration of an alkene by water in the presence of acid also leads to an alcohol. However, the regioselectivity is not certain. The reaction is accompanied by rearrangement and carbocations are formed as intermediates. So statement (2) does not support statement (1).

178. Both statements (1) and (2) are correct and statement (2) is supportive of statement (1).

Ozonolysis means cleavage by ozone, i.e., bond breaking by ozone. The carbon-carbon double bonds are broken in the formation of an ozonide.



Ozonide C - C double bond is broken

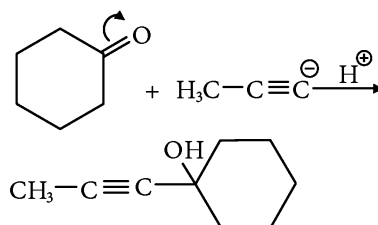


This results in two units of CH_3CHO

Hence both the statements are correct.

179. Both statements (1) and (2) are correct and statement (2) supports statement (1).

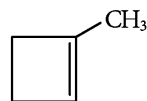
An acetylide ion is produced from a terminal alkyne like $\text{H}_3\text{C}-\text{C}\equiv\text{CH}$ by treating with a strong base like NaNH_2 , and the resulting anion $\text{CH}_3\text{C}\equiv\text{C}^-$ is a powerful nucleophile. A ketone like cyclohexanone can react with the base to produce a 3° alcohol



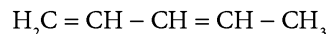
Hence both the statements are correct and supportive of each other.

180. Statement (1) is correct while statement (2) is wrong. NOBr adds as NO^+ and Br^- to the double bond. Addition follows Markovnikov's rule.

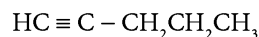
181. (a) This cannot be a cycloalkane because the general formula of cycloalkane is C_nH_{2n} . All the others are possible. For example
(b) It contains one ring and one double bond



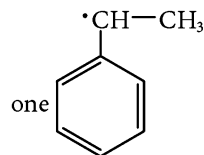
- (c) Contains two double bonds and no ring



- (d) It can also be alkyne



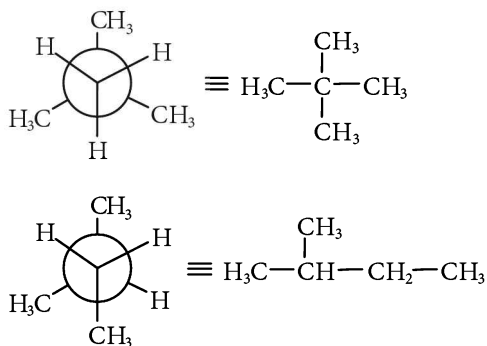
182. Halogenation in presence of light takes place by free radical mechanism. The free radical produced after the removal of hydrogen as $\text{H}^\cdot$ from (d) is the most stable



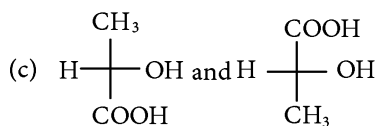
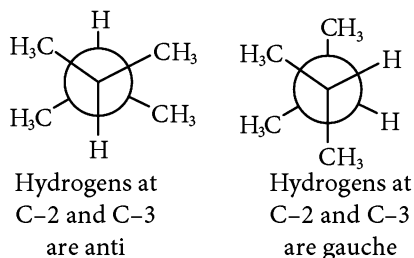
Hence (d) is the most reactive.

2.92 Alkanes, Alkenes and Alkynes

183. (a) They are constitutional isomers

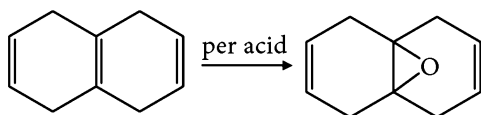


- (b) The two are the two different conformations of the same compound. Both are $(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)_2$. Two different staggered conformations are given.



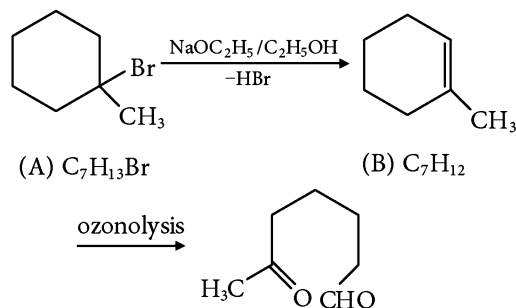
- (d) They are two different isomeric compounds and not stereoisomers. One compound is cis 1,2-dimethyl cyclopentane whereas the other compound is trans 1,3-dimethyl cyclopentane. They are only constitutional and not stereoisomers as the connectivity is different.

184. Peroxid reaction with an alkene is epoxidation

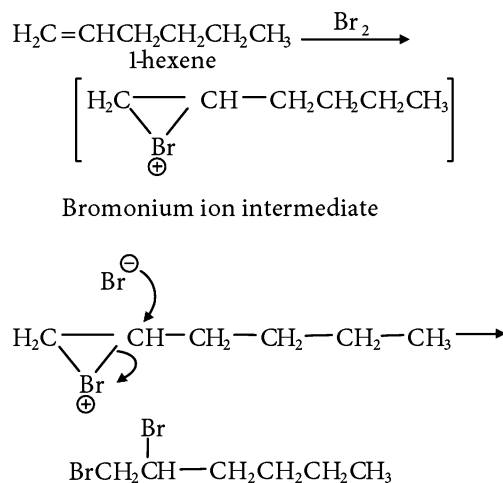


Epoxidation is an electrophilic addition. Oxygen gets inserted in the double bond which is more electron rich—which is more highly substituted. So, the product epoxide is formed at the ring junction.

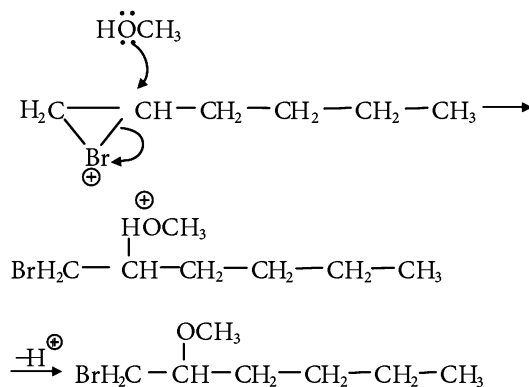
185. The compound (A) is a tertiary halide.



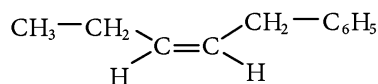
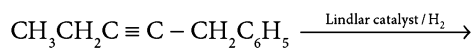
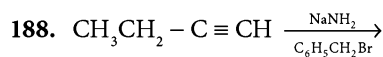
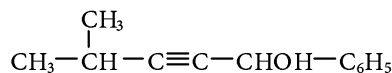
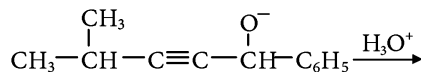
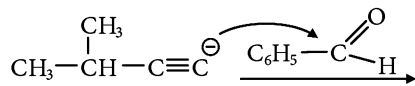
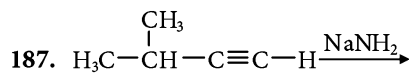
186. The first step in the reaction of the alkene with bromine is the formation of the bromonium ion intermediate.



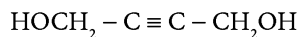
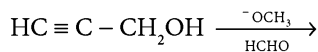
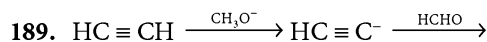
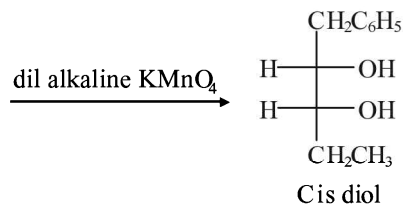
The bromonium ion can react with bromide ion to form the 1,2-dibromide. It is also possible that the nucleophile $\text{CH}_3\ddot{\text{O}}\text{H}$ (methanol) also can attack the intermediate to form 1-bromo-2-methoxyhexane



So a mixture of products are formed.



cis alkene



190. Active hydrogen compounds give alkane with Grignard reagent.

HCOOC_2H_5 gives an aldehyde, while  gives a primary alcohol.

191. (a), (b) and (c)

192. (a) – (d)

All the four reactions are represented correctly.

193. (a), (c) and (d) are correct.

194. (a) and (b) will lead to 2,2-dibromopropane. Explanation to be given.

195. All the statements except (d) are correct. Chlorination is random. Two mono chlorinated products viz., $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ and $\text{CH}_3\text{CHClCH}_2\text{CH}_3$ are obtained. On the other hand bromination is more selective.

196. Only (a) and (b) are correct. Reaction with H_2O_2 and formic acid brings about antihydroxylation.

197. (a) – (d) all the four reactions give alkyne

(a) $\text{HC}\equiv\text{CH}$

(b), (c) and (d) give $\text{H}_3\text{C}-\text{C}\equiv\text{CH}$

198. (a) $\rightarrow$ (r), (s)

(b) $\rightarrow$ (p), (s)

(c) $\rightarrow$ (p), (s)

(d) $\rightarrow$ (q), (r)

199. (a) $\rightarrow$ (p), (r)

(b) $\rightarrow$ (r)

(c) $\rightarrow$ (p), (q)

(d) $\rightarrow$ (q), (s)

200. (a) $\rightarrow$ (r), (s)

(b) $\rightarrow$ (q), (s)

(c) $\rightarrow$ (p), (q)

(d) $\rightarrow$ (s)

CHAPTER

3

BENZENE AND PHENOLS

■■ CHAPTER OUTLINE

Preview

STUDY MATERIAL

BENZENE

Structure of Benzene

Properties of Aromatic Compounds

Hückel's Rule of Aromaticity

Methods of Preparation of Benzene

Aromatic Electrophilic Substitution

Effect of Substituents in Aromatic Electrophilic Substitution

Addition Reactions of Benzene

- Concept Strands (1-8)

PHENOLS

General Methods of Preparation of Phenols

Acidity of Phenols

Reactions of Phenol

Electrophilic Substitution Reactions of Phenol

Hydrogen Bonding in Phenols

- Concept Strands (9-11)

TOPIC GRIP

- Subjective Questions (10)
- Straight Objective Type Questions (5)
- Assertion-Reason Type Questions (5)
- Linked Comprehension Type Questions (6)
- Multiple Correct Objective Type Questions (3)
- Matrix-Match Type Question (1)

IIT ASSIGNMENT EXERCISE

- Straight Objective Type Questions (80)
- Assertion-Reason Type Questions (3)
- Linked Comprehension Type Questions (3)
- Multiple Correct Objective Type Questions (3)
- Matrix-Match Type Question (1)

ADDITIONAL PRACTICE EXERCISE

- Subjective Questions (10)
- Straight Objective Type Questions (40)
- Assertion-Reason Type Questions (10)
- Linked Comprehension Type Questions (9)
- Multiple Correct Objective Type Questions (8)
- Matrix-Match Type Questions (3)

BENZENE

Benzene was first isolated by Michael Faraday in 1825. It was found in coal tar by Hofmann in 1845 and this is still a very good source of benzene and its derivatives. Benzene

was first synthesized by Berthelot in 1870 by passing acetylene through a red hot tube.

STRUCTURE OF BENZENE

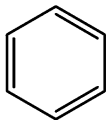
Analysis and molecular mass determination show that the molecular formula of benzene is C_6H_6 . Since it has eight hydrogen atoms less than the corresponding saturated alkane (i.e., hexane C_6H_{14}), a high degree of unsaturation is expected for benzene.

Under suitable conditions, benzene undergoes addition reactions with H_2 , Cl_2 and O_3 . In all these reactions, three molecules of the reagent are added on to benzene. This shows the presence of three double bonds in benzene.

Eventhough benzene contains three double bonds, it does not answer the usual tests for unsaturation. For example, it does not decolourize bromine dissolved in CCl_4 . Instead, under ordinary conditions benzene undergoes substitution reactions like saturated compounds. This shows that the double bonds in benzene are different from ordinary double bonds of aliphatic compounds.

Kekulé structure

In 1865, August Kekulé (a German scientist) suggested a cyclic structure for benzene. It consists of a hexagonal ring of six carbon atoms joined together with alternate single and double bonds.

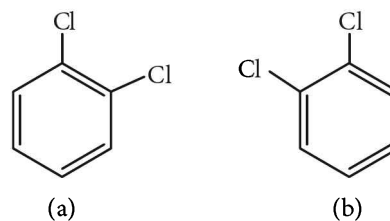


Limitations of Kekulé structure

- (i) The presence of three double bonds should make the molecule highly reactive towards addition reactions. But benzene behaves as a saturated compound. Kekulé structure could not explain the peculiar behaviour of double bonds in benzene and also its unusual stability.
- (ii) The Kekulé structure contains three carbon-carbon double bonds and three carbon-carbon single bonds. The normal bond length of carbon-carbon single

bond is $1.54 \text{ \AA}$ (or 154 pm) and that of $C = C$ is $1.34 \text{ \AA}$ (or 134 pm). But experimentally it is found that all the carbon-carbon bonds in benzene are of equal length. The value is found to be $1.39 \text{ \AA}$ (139 pm) which is in between that of single bond and double bond.

- (iii) According to Kekulé structure, we expect two isomers of 1,2-disubstituted benzene as shown below.

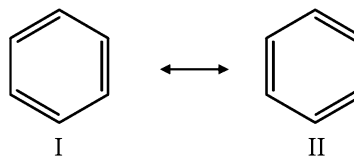


In structure (a), there is a double bond between the two carbon atoms containing chlorine, but in structure (b) there is only a single bond. But actually only one o-dichlorobenzene (or 1,2-disubstituted benzene) is known.

The structure of benzene is best described by (1) resonance theory and (2) molecular orbital theory.

Resonance theory

According to resonance theory, benzene is a resonance hybrid of two Kekulé structures I and II shown below.



These two structures I and II are known as the canonical structures of benzene. The actual structure of benzene is a resonance hybrid of these two structures. As a result of

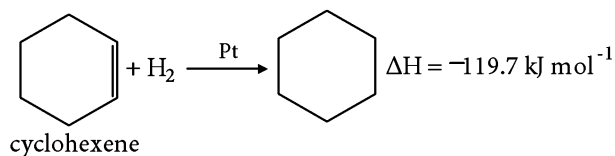
resonance, all the carbon-carbon bond lengths in benzene become equal and lie in between $C = C$ and $C - C$ bond lengths.

Further, a resonance hybrid will always be more stable than any of the canonical structures. Thus the actual molecule of benzene is more stable than either of the two Kekulé structures. The difference between the energy of the most stable contributing structure and the energy of resonance hybrid is known as resonance energy. Resonance energy is a measure of stabilization due to resonance. Resonance energy of benzene has been found to be about $150.6 \text{ kJ mol}^{-1}$.

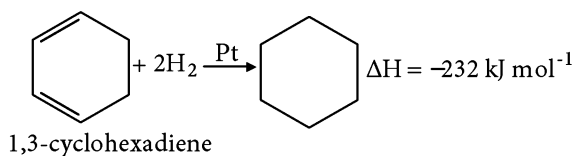
Calculation of resonance energy

The resonance energy of benzene can be calculated from the heat of hydrogenation data.

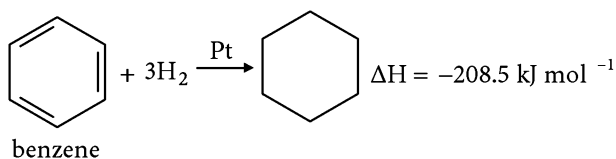
When cyclohexene, which contains one double bond, is hydrogenated to give cyclohexane, the heat of the reaction was found to be $-119.7 \text{ kJ mol}^{-1}$.



This value is just similar to any similarly substituted alkene. When 1,3-cyclohexadiene is hydrogenated to give cyclohexane, the value of ΔH expected is $-239.4 \text{ kJ mol}^{-1}$ and the actual value obtained was also nearly the same (-232 kJ mol^{-1}).



Extending this analogy, if benzene which is 1,3,5-cyclohexatriene is hydrogenated under similar conditions, approximately $359.1 \text{ kJ mol}^{-1}$ of heat is expected to be liberated. The observed enthalpy of hydrogenation of benzene is $-208.5 \text{ kJ mol}^{-1}$.



$$\text{Calculated } \Delta H = 3 \times -119.7 = -359.1 \text{ kJ mol}^{-1}$$

$$\text{Observed } \Delta H = -208.5 \text{ kJ mol}^{-1}$$

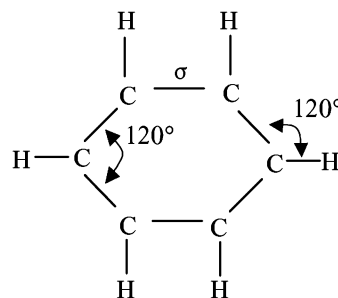
$$\text{Difference} = 150.6 \text{ kJ mol}^{-1}$$

These experimental results indicate that benzene is more stable than the hypothetical 1,3,5-cyclohexatriene by $150.6 \text{ kJ mol}^{-1}$. This difference between the quantity of heat actually released and the value expected by calculation on the basis of Kekulé structure is called the resonance energy of benzene.

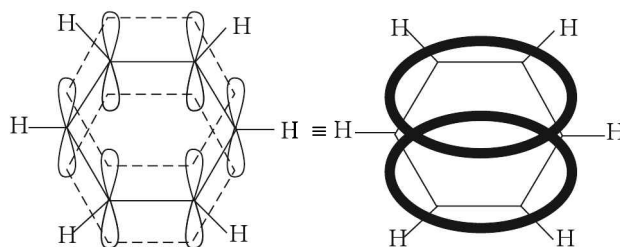
Molecular orbital structure of benzene

The structure of benzene is best explained in terms of the modern molecular orbital theory. All six carbon atoms in benzene are sp^2 hybridized. The sp^2 hybrid orbitals overlap with each other and with s orbitals of the 6 hydrogen atoms forming $C - C$ and $C - H$ σ bonds, respectively.

Since the bonds result from the overlap of planar sp^2 orbitals, all carbon and hydrogen atoms in benzene lie in the same plane. All σ bonds in benzene lie in one plane and all bond angles are 120° .



Each carbon atom in benzene possesses an unhybridised p-orbital containing one electron. These p-orbitals are perpendicular to the plane of σ bonds. The lateral overlap of these p-orbitals produce π bonds. Since the system is completely symmetric, the $2p_z$ orbital of any one carbon atom can overlap equally well with the $2p_z$ orbital on the carbon atoms at its left or right. This results in the continuous overlapping and the resultant π electron cloud is shown in the figure. The net result is that there are two continuous rings of π electron cloud, one above and the other below the plane of the hexagonal ring.



3.4 Benzene and Phenols

Aromatic character (aromaticity)

Aromatic compounds are cyclic compounds having characteristic stability in spite of having double bonds in their structures. Simple aromatic compounds contain one or more benzene rings. They are known as *benzenoid aromatic compounds*. There is yet another series of compounds which exhibit aromatic properties but lack benzene like

structures. They are called *non-benzenoid aromatic compounds*. Heterocyclic compounds such as pyrrole, thiophene, etc., are simple examples of non-benzenoid aromatic compounds.

The term aromaticity is used to signify the characteristic physical and chemical behaviour of aromatic compounds.

PROPERTIES OF AROMATIC COMPOUNDS

- (i) Aromatic compounds are unusually stable. They have low heats of hydrogenation and combustion.
- (ii) They fail to undergo addition reactions, though they contain double bonds. They readily undergo substitution reactions like nitration, halogenation, sulphonation, Friedel-Crafts alkylation and acylation.
- (iii) Aromatic compounds are planar molecules.
- (iv) Aromatic compounds are generally resistant to oxidation reactions under ordinary conditions.
- (v) Aromatic compounds have cyclic structures with delocalized π bonds.
- (vi) Due to the presence of π electron clouds above and below the plane, the aromatic ring serves as a source of electrons and is easily attacked by electrophiles. In aromatic systems, the electrophilic substitution does not destroy the aromaticity of the ring. Therefore, electrophilic aromatic substitution is quite typical and a characteristic reaction of an aromatic ring system like benzene.

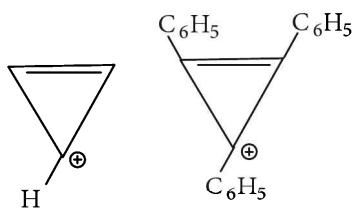
HÜCKEL'S RULE OF AROMATICITY

Eventhough most of the aromatic compounds are derivatives of benzene, presence of a benzene ring is not essential for a compound to show aromatic character. The modern theory of aromaticity was advanced by Hückel on the basis of molecular orbital calculations.

Hückel's rule states that a conjugated, planar, cyclic system will be aromatic if it contains $(4n + 2)$ delocalized π electrons, where n is zero or integers like 1, 2, 3.....

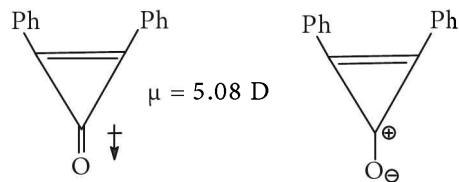
Thus, to be aromatic, a conjugated cyclic planar system must have $2(n = 0)$, $6(n = 1)$, $10(n = 2)$ delocalized π -electrons.

Two electron systems



Cyclopropenyl cation is a cyclic π system with two electrons. Many cyclopropenium salts have actually been prepared. Triphenylcyclopropenyl cation is such a stable carbocation that many of its salts can be isolated and stored.

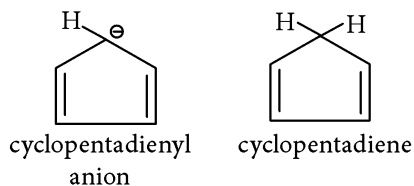
Diphenyl cyclopropenyl ketone has an unusually high dipole moment. This has been explained on the basis that the dipolar resonance structure contributes more to the resonance hybrid as it involves the stable aromatic cyclopropenyl cation.



Six electron systems

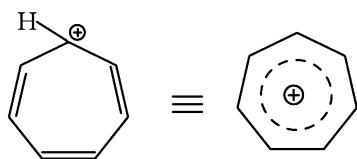
The most important cyclic system satisfying Hückel's rule with $n = 1$ is benzene. Cyclopentadienyl anion is a fairly

stable carbanion. The conjugate acid of this anion is a hydrocarbon with acidic hydrogen of $pK_a = 16$.

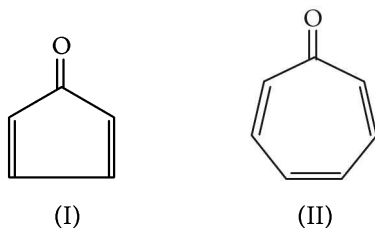


The acidity of methylene hydrogen of cyclopentadiene is as strong as that of an alcohol or water.

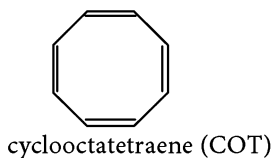
Cycloheptatrienyl cation having six π electrons is remarkably stable and is aromatic and is known as tropylium ion.



On account of this reason, between the two ketones cyclopentadienone (I) and cycloheptatrienone or tropone (II), the latter is unusually stable and the former is highly reactive.

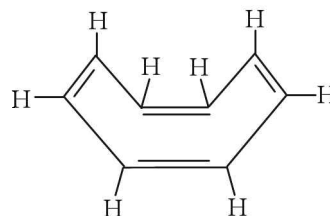


Eight and ten electron systems



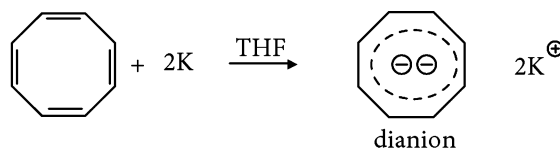
Cyclooctatetraene is a cyclic hydrocarbon having 8π electrons. It is a conjugated polyene. COT is not planar molecule, but a tub shaped molecule. The π electrons of the conjugated double bonds are twisted with respect to one another and overlap is very much reduced.

Cyclooctatetraene (COT) is a very reactive compound like olefins and answers tests for unsaturation.



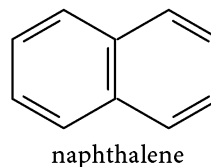
Systems which are cyclic, non-planar and have $4n\pi$ electrons (where $n = 2, 3$ etc.) in conjugation are considered to be non-aromatic.

Cyclooctatetraene readily reacts with alkali metals like Na or K in ether medium to form salts of a dianion.

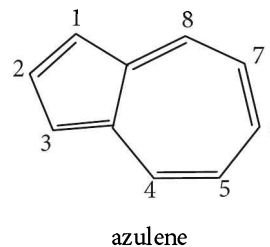


The dianion has a planar structure and has 10π electrons. Therefore, cyclooctatetraenyl dianion is a planar aromatic system.

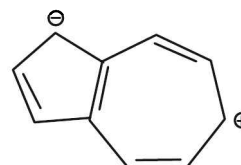
Naphthalene is 10π electron aromatic system.



Azulene is an isomer of naphthalene and is also an example of a nonbenzenoid aromatic compound.



Azulene has a resonance energy of 205 kJ mol^{-1} . There is substantial separation of charge between the rings in azulene.



3.6 Benzene and Phenols

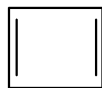
There are two rings which are aromatic, a five membered and the other a seven membered.

Four electron systems: Antiaromaticity

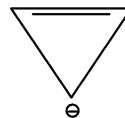
Cyclic compounds which have a planar structure and containing $4n$ π electrons (where $n = 0, 1, 2$ etc) in conjugation are said to be antiaromatic.

Cyclobutadiene, cyclopropenyl anion and cyclopentadienyl cation are a few species which have $4n$ π electrons in

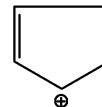
the ring and are antiaromatic. Such species are not formed easily.



cyclobutadiene



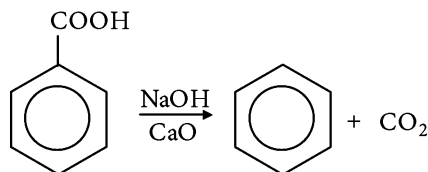
cyclopropenyl
anion



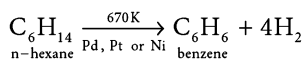
cyclopentadienyl
cation

METHODS OF PREPARATION OF BENZENE

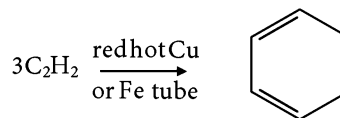
- (i) Benzene is prepared by the decarboxylation of benzoic acid using sodalime.



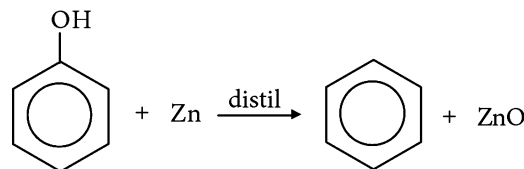
- (ii) Benzene could be obtained by the cyclisation of n-hexane at about 670K in presence Pd, Pt or Ni as catalyst.



- (iii) Benzene is synthesized by the polymerization of acetylene.



- (iv) Phenol when distilled with zinc dust gives benzene.



Benzene is mainly obtained from coal tar.

AROMATIC ELECTROPHILIC SUBSTITUTION

One of the important characteristic reactions of an aromatic ring system is the electrophilic substitution. There is a cloud of π electrons, above and below the plane of the ring. In comparison with the electrons forming the σ bond, the π electrons are loosely held and are available to any reagent seeking the electrons. Benzene ring serves as a source of electrons in aromatic electrophilic substitution reactions.

The compounds or species that get attached or substituted are electron deficient in nature and therefore these reactions are generally known as aromatic electrophilic substitution.

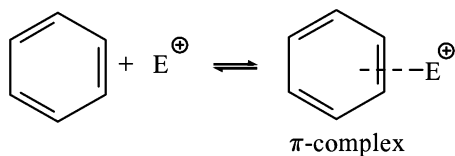
Electrophilic substitution reactions include a wide range of reactions like nitration, halogenation, sulphonation, Friedel-Crafts alkylation, Friedel Crafts acylation and related reactions.

Mechanism of electrophilic substitution (Arenium ion mechanism)

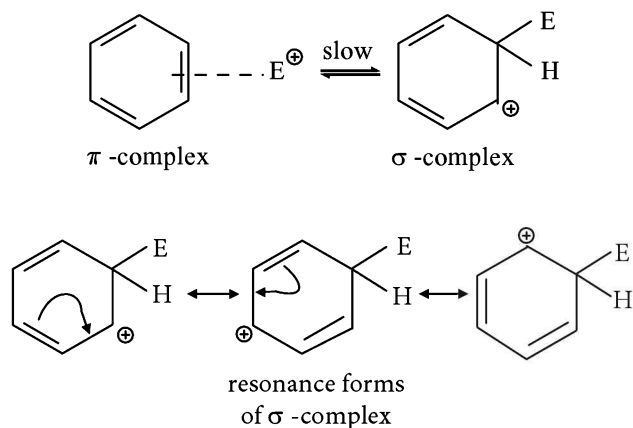
Aromatic electrophilic substitution involves the following steps.

A complex between the π electrons of the aromatic ring and an electron acceptor (electrophile) known as the

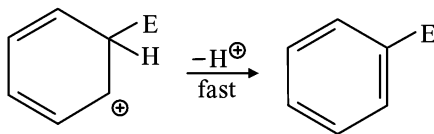
π -complex is formed initially in some electrophilic aromatic substitution. It is often referred to as a charge transfer complex, since some part of electron density is transferred from the aromatic ring to the electrophile.



The π -complex initially formed leads further to a cyclohexadienyl cation known as a Wheland intermediate or arenium ion or sigma complex, which is stabilized by resonance.



The sigma complex formed then loses a proton in a fast step to form the final product.

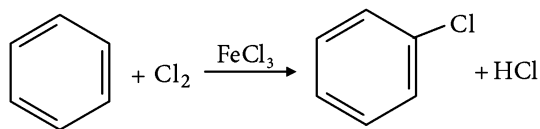


Since no C – H bond is broken in the rate determining step, generally no isotope effect is seen in aromatic electrophilic substitutions.

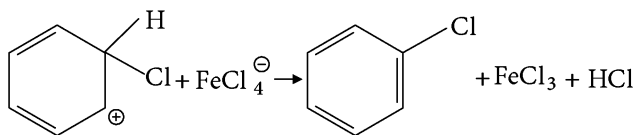
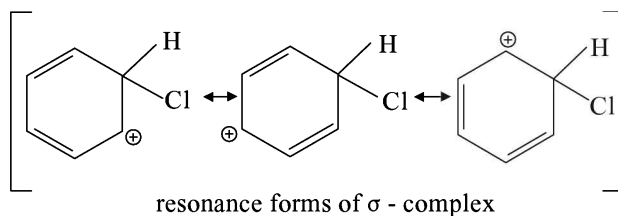
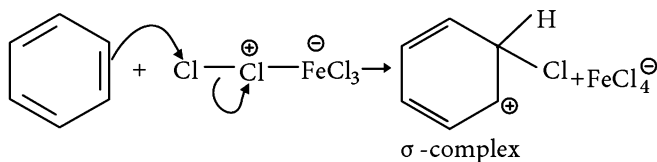
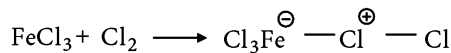
(i) Halogenation

Halogenation in an aromatic system involves the introduction, by substitution, of a halogen atom in the ring.

For example,



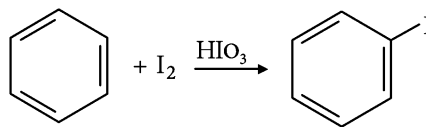
The following steps are involved in a halogenation. FeCl_3 or Fe metal is used as a catalyst or a halogen carrier.



The key step in the halogenation is the attachment of the chloronium ion ($\text{Cl}^\oplus$) or positively charged chlorine to the aromatic ring. A free chloronium ion is generally not formed, but FeCl_3 combines with Cl_2 molecule to form a complex, $\text{Cl}_3\text{Fe}^\ominus - \text{Cl}^\oplus - \text{Cl}$, from which the chloronium ion ($\text{Cl}^\oplus$) is transferred.

The reagents used most often for aromatic halogenation are Cl_2 or Br_2 .

Iodination is a very slow process and is reversible. The HI produced in the reaction reduces iodobenzene to benzene. For iodination, the reaction has to be carried out in the presence of oxidizing agents such as HNO_3 , HIO_3 , etc which will oxidize HI produced in the reaction to iodine.



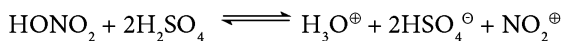
In contrast, fluorination is highly exothermic and hence direct fluorination is not employed to prepare fluorobenzene.

(ii) Nitration

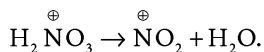
Nitration is the process by which a nitro group, $-\text{NO}_2$, is introduced in the aromatic ring by substitution. Benzene

3.8 Benzene and Phenols

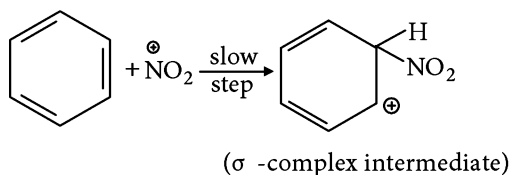
undergoes nitration to form nitrobenzene, when treated with a 1 : 1 mixture of conc. H_2SO_4 and conc. HNO_3 (known as nitrating mixture). The mechanism is given below.



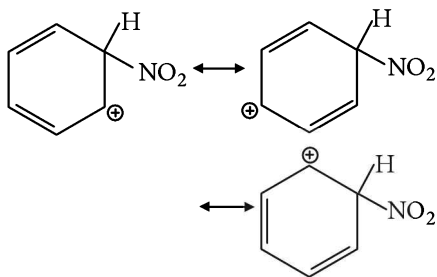
NO_2^+ formed is known as nitronium ion which is known as the nitrating species. Protonated nitric acid H_2NO_3^+ dissociates to give the nitronium ion, losing a molecule of water.



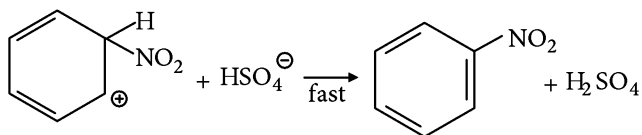
The next step is the slow rate determining step in which nitronium ion attacks the benzene ring to form the σ complex,



The intermediate σ complex formed in the nitration process can be stabilized by resonance.



The next step is a fast step which involves the removal of a proton.



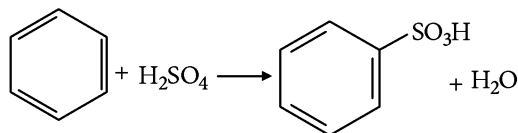
The formation of the nitronium ion (NO_2^+) is an acid base reaction between nitric acid and sulphuric acid. H_2SO_4 , which is stronger acid serves as a proton donor and HNO_3 , which is the weaker acid acts as a proton acceptor.

Since the nitro group, which enters first, is a ring deactivating group, entry of additional nitro groups becomes difficult.

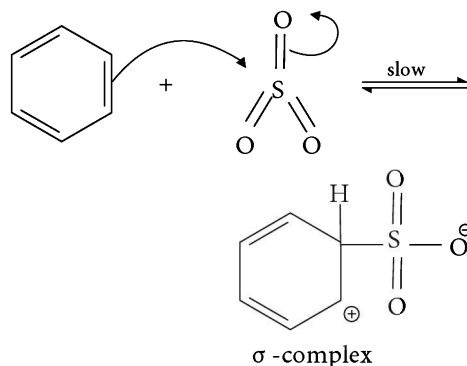
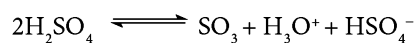
(iii) Sulphonation

Sulphonation is one of the very important industrial reactions of aromatic compounds. It is an important reaction in the production of detergents, which are linear alkyl benzene sulphonates.

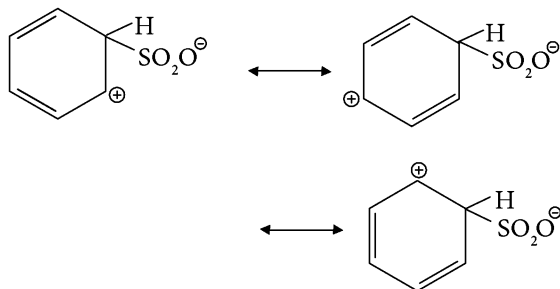
The electrophile in the sulphonation process of an aromatic ring is sulphur trioxide, SO_3 . Fuming sulphuric acid ($\text{H}_2\text{S}_2\text{O}_7$) or conc. H_2SO_4 is the most common source of SO_3 . Benzene reacts with fuming H_2SO_4 at room temperature to produce benzene sulphonic acid.



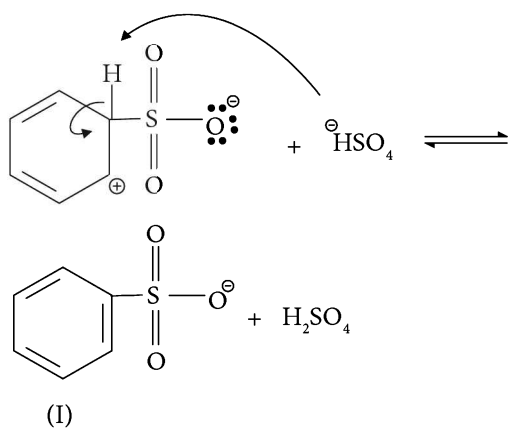
The mechanism of sulphonation is given below



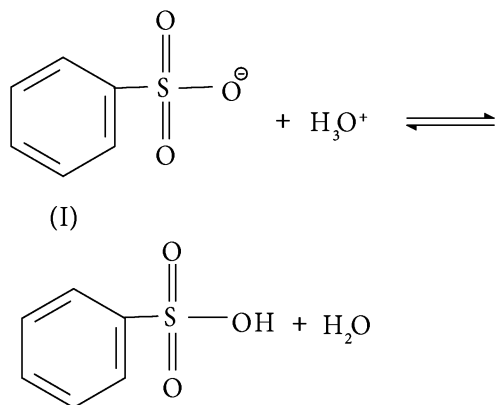
σ -complex can be stabilized by resonance



In the next step, a proton is removed from the arenium ion (σ -complex) to form benzene sulphonate ion.



The benzene sulphonate ion (I) formed accepts a proton to form the final product benzene sulphonic acid.

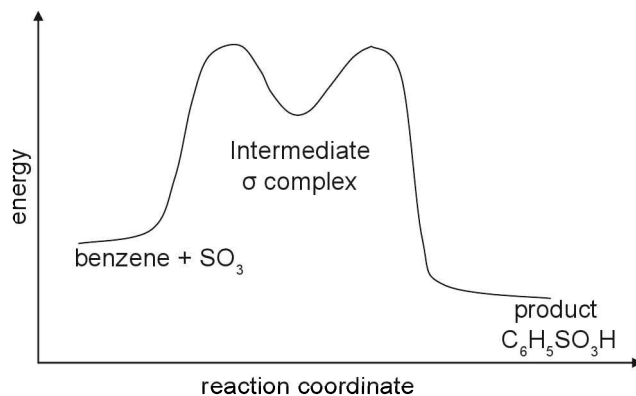


All the steps are in equilibrium and therefore the position of equilibrium can be suitably altered by the conditions that are employed.

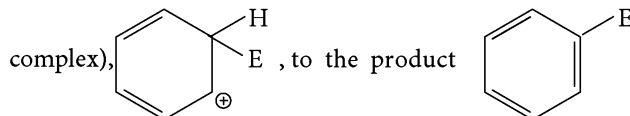
Sulphonation and desulphonation processes are often used in synthetic work. If a benzene ring is to be sulphonated, either conc. H_2SO_4 or fuming H_2SO_4 can be used. On the other hand, if a sulphonic acid group is to be removed from benzene ring, dil. H_2SO_4 can be employed using steam with the mixture. The equilibrium is shifted to the left.

Thus, *sulphonation differs from other aromatic substitution reactions. The reaction is reversible and shows a moderate isotope effect.*

The activation energy profile for aromatic sulphonation is given below. From the figure, it is clear that the activation energies for the conversion of the intermediate to the reactant and product are same.



With the exception of sulphonation, most aromatic electrophilic substitutions are irreversible. This is because, the energy barrier for the conversion of the arenium ion (sigma complex),



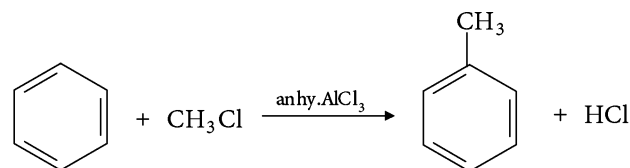
, is less than the energy required for the reverse reaction, namely the elimination of the E^+ (electrophile) from the intermediate to form the parent compound.

(iv) Friedel-Crafts reaction

Formation of a carbon-carbon bond between an aromatic ring and an aliphatic carbon is of particular value in organic reactions. The Friedel-Crafts reaction and related reactions are important ways to introduce a carbon side-chain to the aromatic ring system.

(a) Friedel - Crafts alkylation

A typical example for an alkylation under Friedel-Crafts conditions is given below.



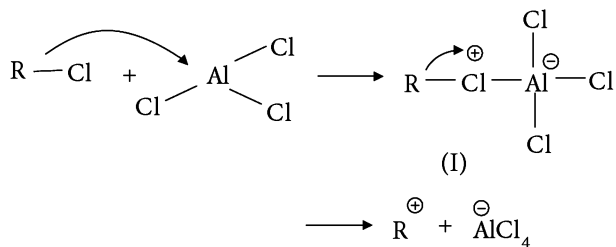
The electrophile or the carbocations required for the alkylation is usually generated from alkyl halides.

Anhydrous aluminium chloride is the most common catalyst used for the reaction. Other Lewis acids like FeCl_3 , BF_3 or, sometimes, acids like HF , H_3PO_4 , H_2SO_4 are also used as catalysts depending on the reagents and conditions.

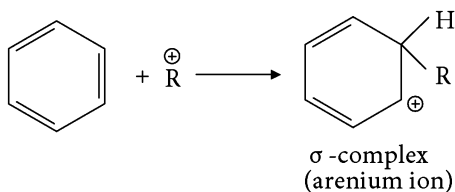
3.10 Benzene and Phenols

The mechanism of the reaction starts with the formation of the carbocation in the first step. The electrophile (carbocation) generated attacks the benzene ring to form the arenium ion intermediate which is stabilized by resonance. This ion, then loses a proton to form alkyl benzene.

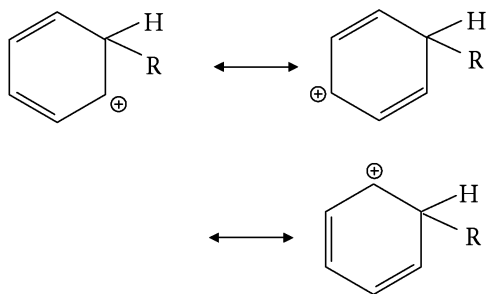
Mechanism of Friedel—Crafts alkylation



Initially, a complex (I) is formed, which dissociates to form R^+ and AlCl_4^- .

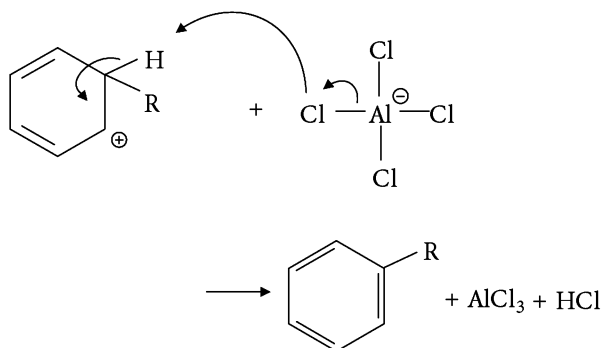


The arenium ion stabilizes by resonance.



A proton is removed from the arenium ion (carbocation) intermediate to form the alkyl benzene, which is the final product. AlCl_3 used as catalyst is liberated along with the evolution of HCl .

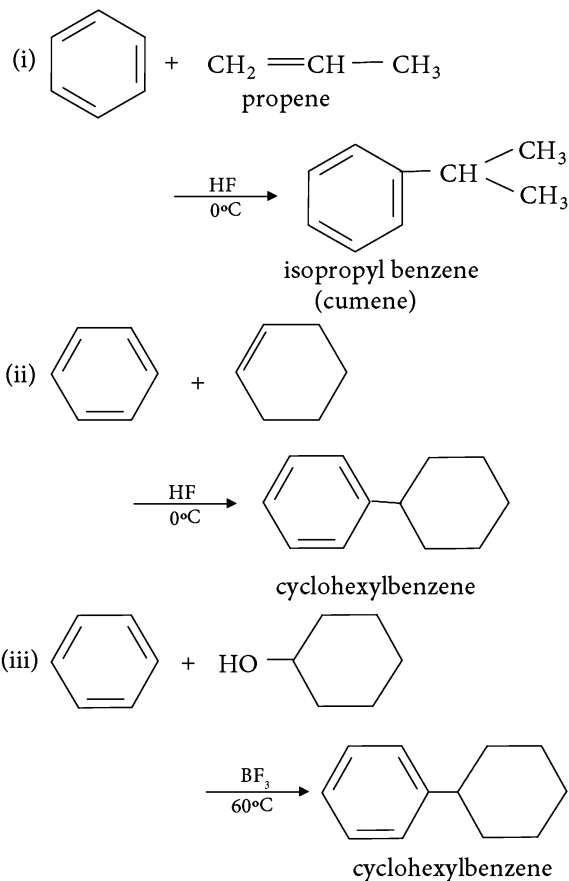
When $\text{R}-\text{X}$ is a primary halide, for example CH_3-Cl , a simple carbocation like CH_3^+ is not formed directly. Instead, AlCl_3 forms a complex with an alkyl halide and this complex as a whole acts as the electrophile. In the complex, for example $\text{H}_3\text{C}-\overset{\delta+}{\text{---}}-\overset{\delta-}{\text{Cl}}:\text{AlCl}_3$, the carbon-halogen



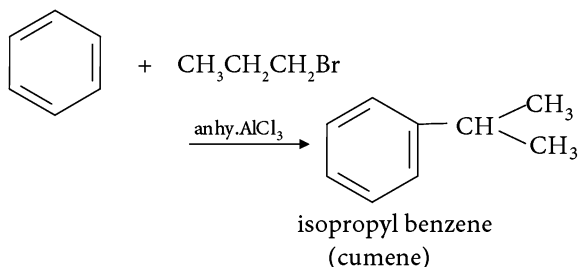
bond is nearly broken (dotted lines) and the carbon of the alkyl group has a considerable positive charge. Eventhough this complex is not a carbocation by itself, it acts as if it were a carbocation and transfers a positive alkyl (methyl) group to the aromatic ring.

Generally, Friedel-Crafts alkylations are effected by making use of alkyl halides and anhydrous AlCl_3 . There are also a few other reagents, which can be used for the alkylation of the benzene nucleus, making use of Lewis acids other than AlCl_3 .

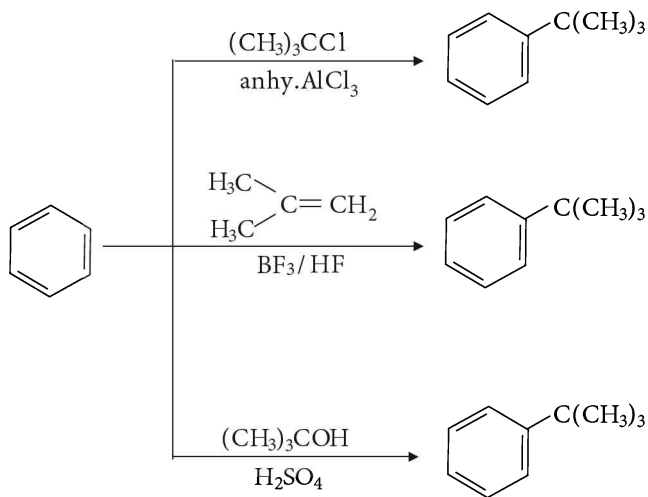
For example,



Involvement of carbocations as reactive intermediates imposes a limitation to alkylations by Friedel-Crafts reactions. Even when 1-bromopropane, a primary alkyl halide is used with benzene in the presence of AlCl_3 , the major product obtained is isopropyl benzene.



The intermediate primary carbocation $\text{CH}_3\text{CH}_2\text{CH}_2^\oplus$ formed rearranges to a more stable secondary carbocation $\text{CH}_3-\text{CH}^\oplus-\text{CH}_3$ before reacting with the aromatic ring. *t*-butyl benzene is the major product formed in all the following reactions even though three different reagents have been used with benzene in the presence of a Lewis acid catalyst



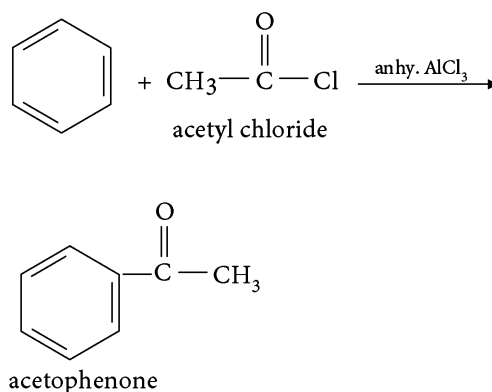
(b) Friedel-Crafts acylation

In contrast to alkylation, Friedel-Crafts acylation is a very good method to introduce a carbon side-chain to an aromatic ring like benzene nucleus. The product obtained on acylation is an aromatic ketone which can be directly used or can be reduced by suitable reagents to an alkyl benzene.

The reaction whereby an acyl group, $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-$, is introduced in the compound is called an acylation reaction. The

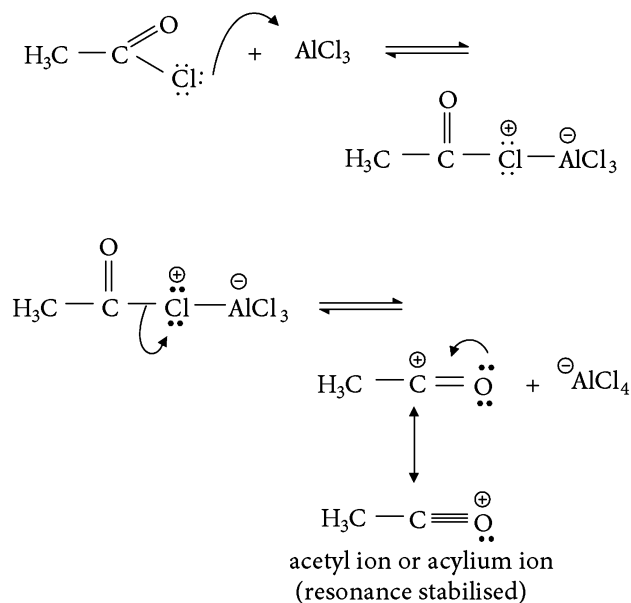
two common acyl groups are $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-$ (acetyl group) and $\text{C}_6\text{H}_5-\overset{\text{O}}{\parallel}{\text{C}}-$ (benzoyl group).

For example,



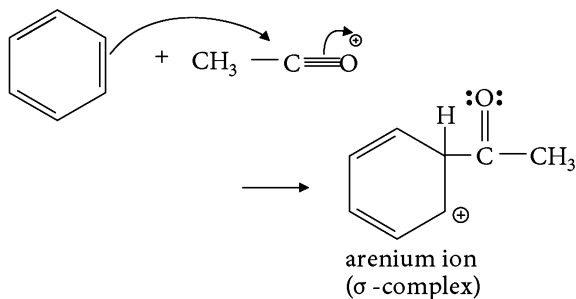
Mechanism of Friedel-Crafts acylation

The electrophile in this reaction is the acylium ion.

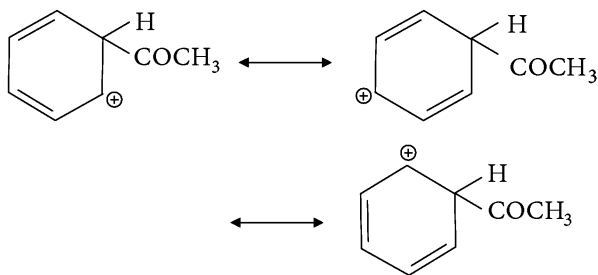


3.12 Benzene and Phenols

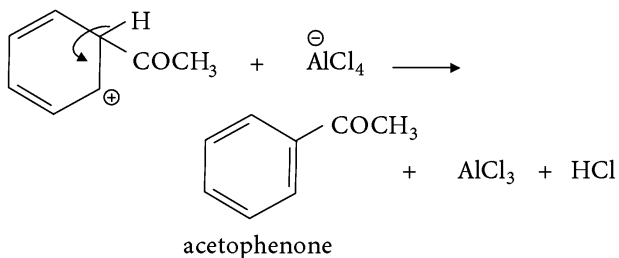
In the first step, acylium ion attacks benzene to form arenium ion.



Arenium ion is stabilized by resonance as shown below.



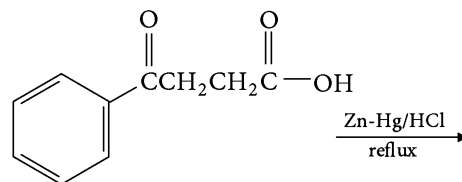
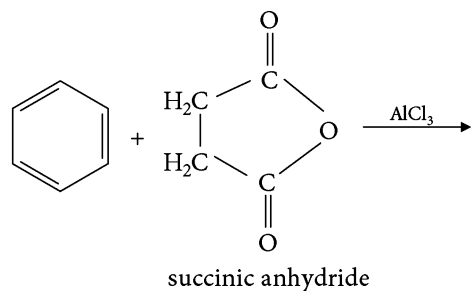
In the next step, arenium ion loses a proton to form acetophenone.



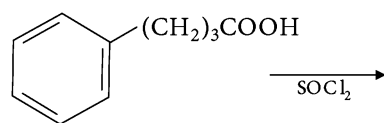
AlCl_3 (a Lewis acid) forms a complex with the ketone (acetophenone) formed. This complex is then treated with water to liberate the free ketone.

A few of the several *important applications of Friedel-Crafts acylation reactions* are given below.

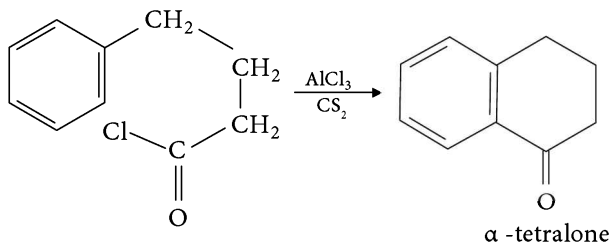
- (i) When cyclic anhydrides are used, Friedel-Crafts acylation provides a means of introducing an additional ring to an aromatic compound.



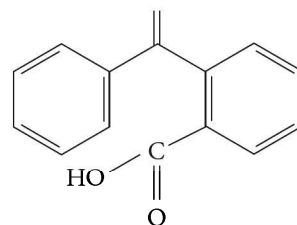
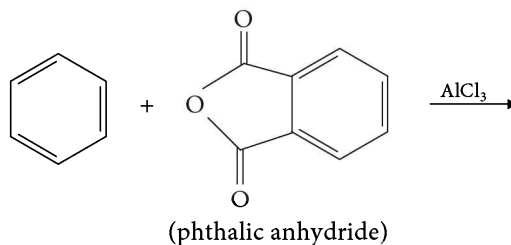
3-benzoylpropanoic acid

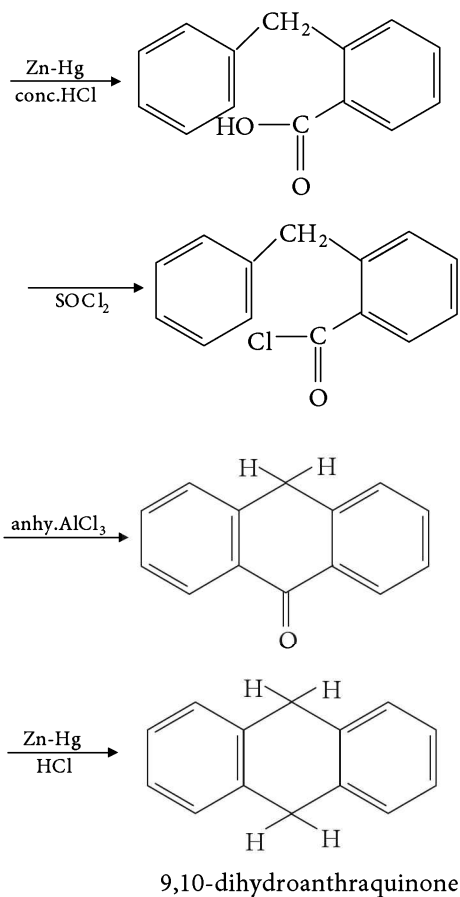


4-phenylbutanoic acid



- (ii) 9,10-dihydroanthraquinone can be synthesized from benzene by the Friedel-Crafts acylation.



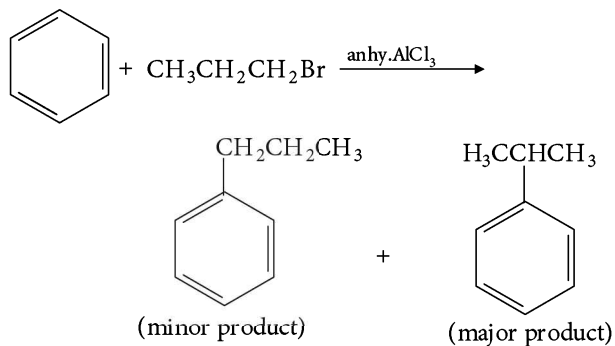


Limitations of Friedel-Crafts reactions

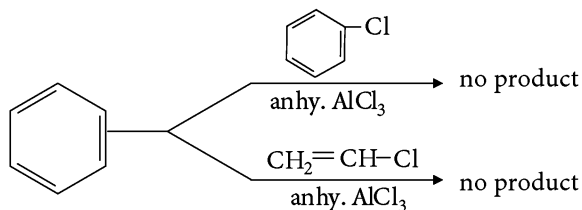
A number of restrictions on the application of Friedel-Crafts reactions limit the usefulness. They are

- (i) The carbocation formed from an alkyl halide or an alkene or an alcohol, rearranges to a more stable carbocation. The major product formed by electrophilic substitution is usually the one which is formed by the attack of the more stable carbocation.

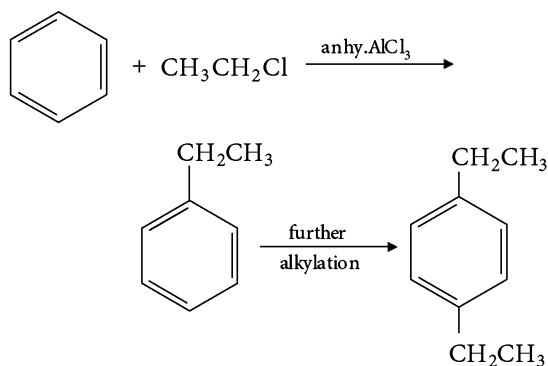
For example,



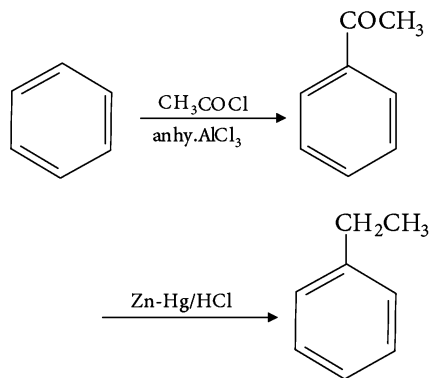
- (ii) Aryl and vinyl halides cannot be used in Friedel-Crafts reactions, because they do not form a carbocation readily.



- (iii) Polyalkylations often occur. Once an alkylation occurs on a benzene ring, the ring gets activated by the electron releasing inductive effect of the introduced alkyl group. So, further alkylation is favoured. Under such circumstances, it is difficult to control the reaction at the monoalkylated state.



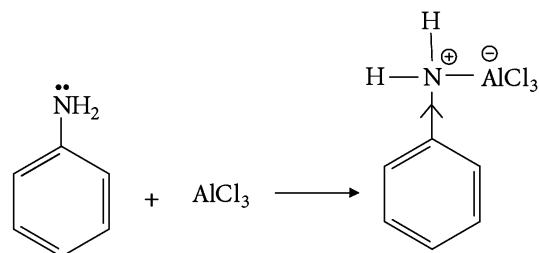
For example, if monoethylbenzene is to be synthesized, the best route is to synthesize acetophenone, and then reducing it by Clemmensen's reduction with zinc amalgam and conc. HCl.



- (iv) Friedel-Crafts reactions usually give poor yields when powerful electron withdrawing groups like $-\text{NO}_2$, $-\text{COOH}$, $-\text{CF}_3$, $-\text{COCH}_3$, $-\text{SO}_3\text{H}$, etc., are present

3.14 Benzene and Phenols

on the aromatic ring. Presence of electron releasing groups like $-\text{NH}_2$, $-\text{N}(\text{CH}_3)_2$, $-\text{NHCH}_3$, etc, in the aromatic ring also gives poor yields because these electron releasing groups are converted to powerful electron withdrawing groups by the Lewis acid which are used to catalyze the Friedel-Crafts reactions. Any meta directing group makes an aromatic ring electron deficient and makes it difficult to undergo an alkylation or acylation under Friedel-Crafts conditions.

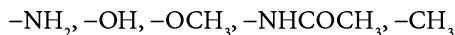


Polyacylation does not occur in benzene ring because the acyl group is an electron withdrawing group and deactivates the ring for further acylation process.

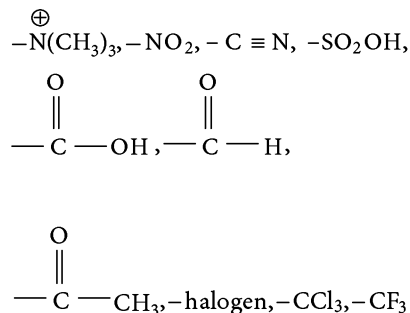
EFFECT OF SUBSTITUENTS IN AROMATIC ELECTROPHILIC SUBSTITUTION

Reactivity in aromatic electrophilic substitution depends on the tendency of the substituent group already present in the benzene ring. *A substituent group which releases electrons activates the ring. A substituent group which withdraws electrons deactivates the ring.*

Electron releasing (activating) groups in benzene ring



Electron withdrawing (deactivating) groups in benzene ring

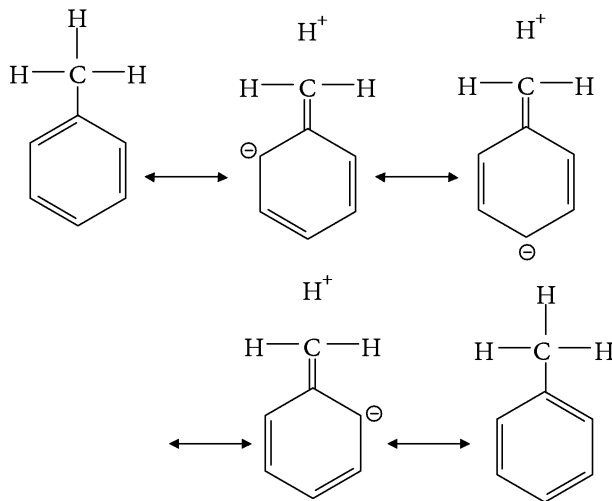


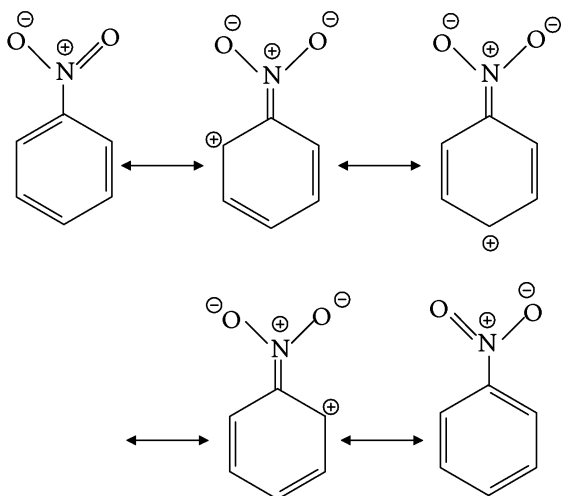
An activating group activates all positions of the benzene ring, but ortho and para positions are activated much more than the meta. That is why an activating group is said to be ortho-para directing towards electrophilic substitution reactions.

Similarly, a deactivating group deactivates all positions in the ring, but the ortho and para positions are more deactivated and meta is comparatively less deactivated. Hence a deactivating group is meta directing, towards electrophilic substitution (except halogens).

For example, it is seen that an alkyl substituent like $-\text{CH}_3$, increases the electron density at ortho and para positions by hyperconjugation and an electron withdrawing group such as $-\text{NO}_2$ decreases the electron density at ortho and para position by mesomeric effect.

In the case of ring activating groups like $-\text{CH}_3$, since there is greater electron density at ortho and para position, electrophilic substitution takes place at ortho and/or para position with respect to $-\text{CH}_3$ group. Similarly, since there is lesser electron density at ortho and para position when an electron withdrawing group such as $-\text{NO}_2$ is attached,

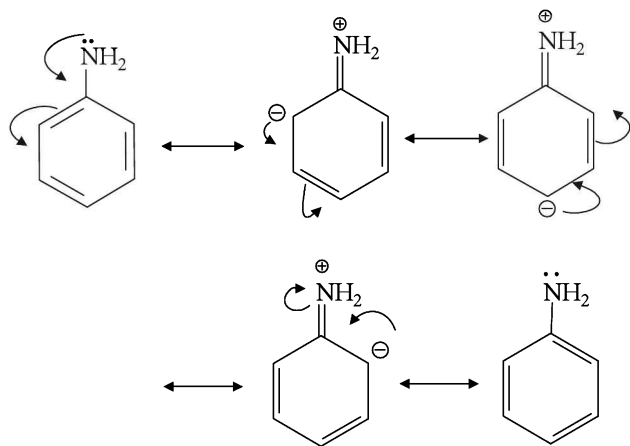




electrophilic substitution takes place at meta position which is relatively more electron rich than ortho and para carbons.

Groups like $-\text{OH}$, $-\text{NH}_2$, etc. when attached directly to the benzene nucleus act as powerful activators towards electrophilic substitution by electron release. They do so mainly by resonance effect.

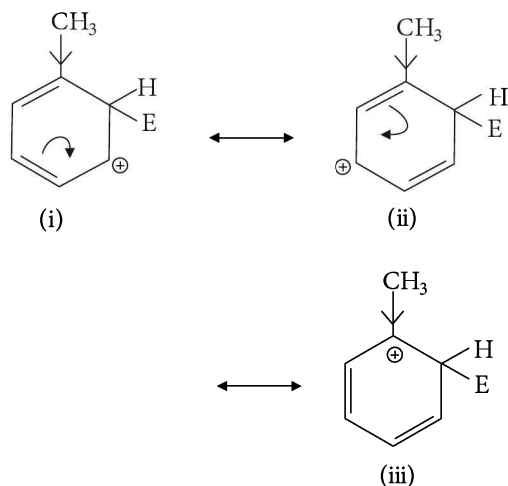
Resonance structures of aniline



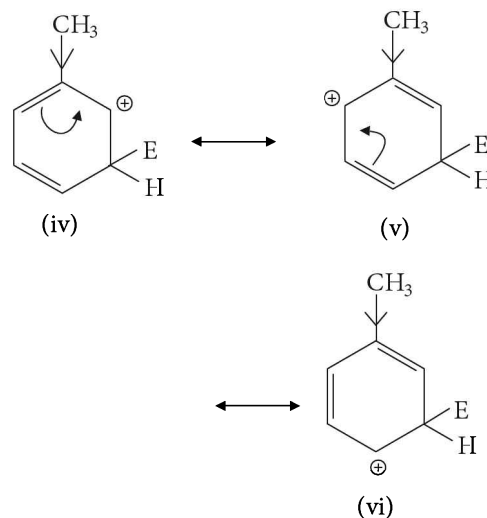
Two ortho positions and para position in aniline become electron rich by delocalization of electrons by electron release due to resonance.

The directive influence of substituents can be better understood if we consider the relative stability of the arenium ion intermediate.

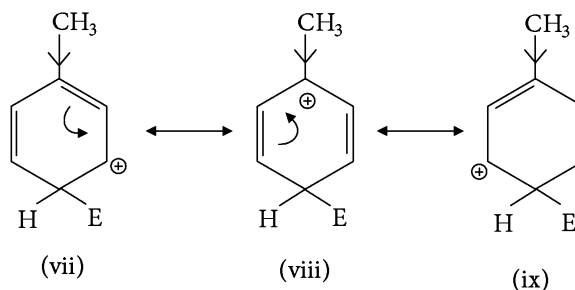
For example, the various resonance structures for an ortho attack for toluene are



The various resonance structures for a meta attack for toluene are



The various resonance structures for a para attack for toluene are

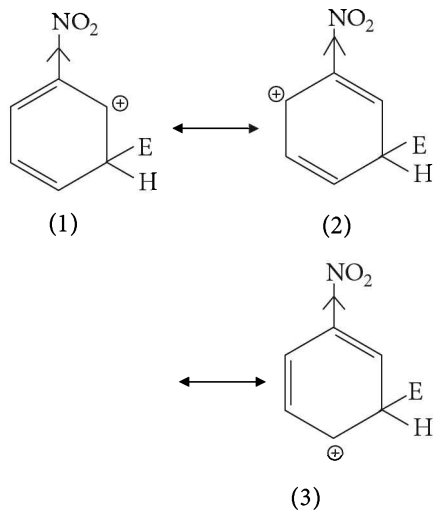


Due to the +I effect of $-\text{CH}_3$ group, structures (iii) and (viii) for ortho and para attack are very much stabilized.

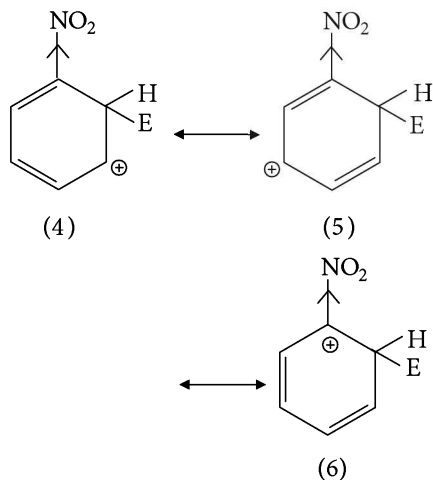
3.16 Benzene and Phenols

There is no such stabilization for the arenium ion formed for meta attack. Hence $-\text{CH}_3$ group is ortho, para directing.

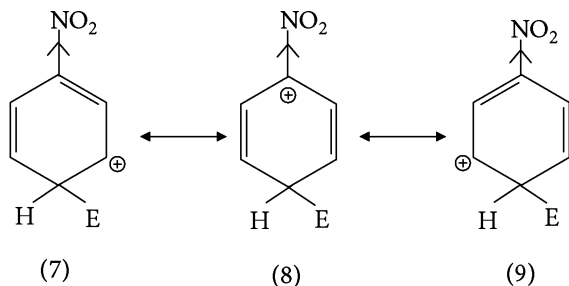
Similarly, the various resonance structures for a meta attack for nitrobenzene are



The various resonance structures for an ortho attack for nitrobenzene are



The various resonance structures for a para attack for nitrobenzene are

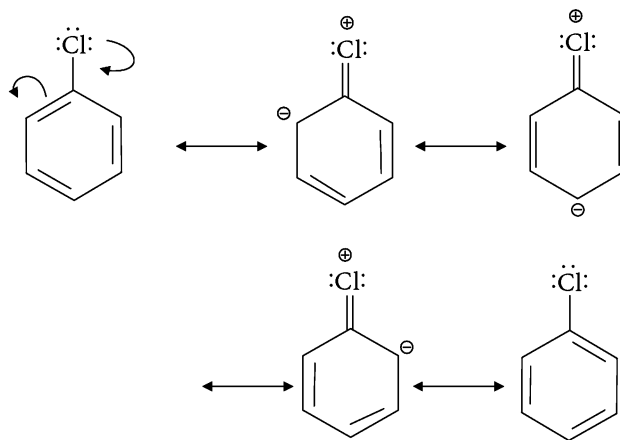


Due to the electron withdrawing nature of $-\text{NO}_2$ group, structures (6) and (8) for ortho and para attack are considerably destabilized. There is no such destabilization for meta attack. Hence $-\text{NO}_2$ group is meta directing.

Halogens are unusual in their role on electrophilic substitution. They are deactivating, but ortho, para directing. Deactivation is characteristic of electron withdrawing groups whereas ortho, para orientation is a characteristic of electron releasing groups.

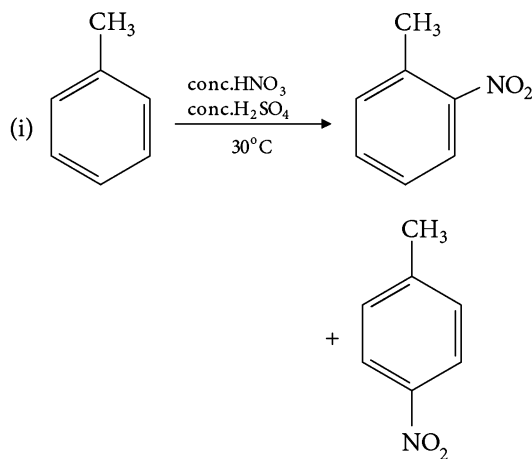
In the case of halogens, both electron release and withdrawal are observed. Halogens withdraw electrons by inductive effect and release electrons by resonance effect.

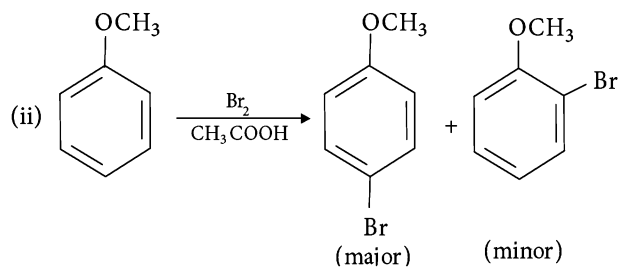
In chlorobenzene, chlorine releases a pair of electrons and accommodates a positive charge.



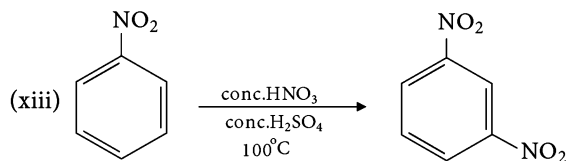
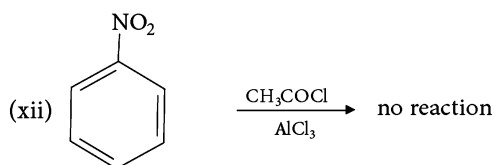
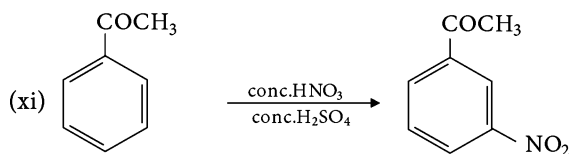
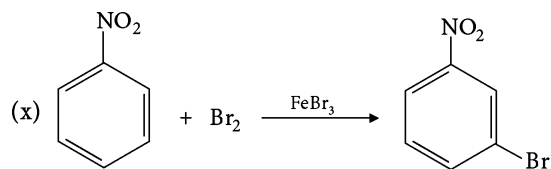
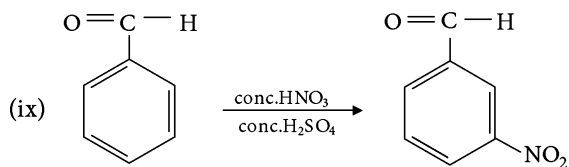
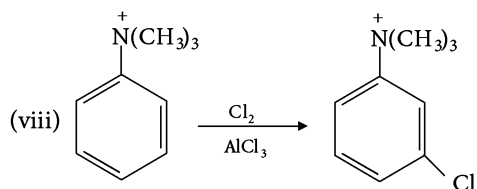
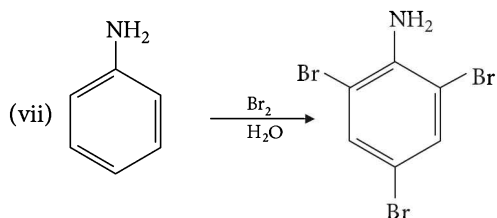
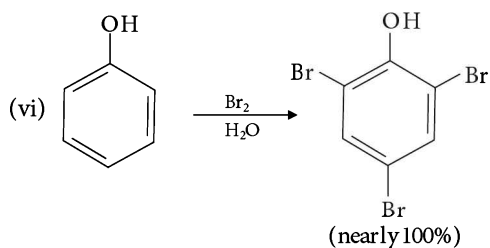
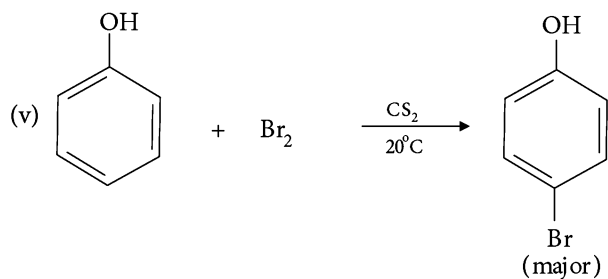
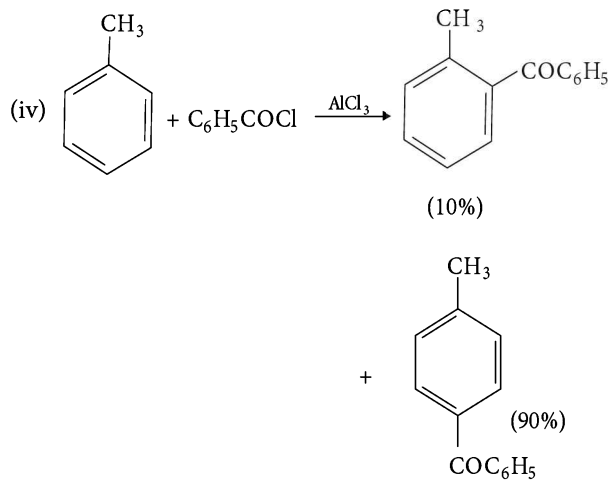
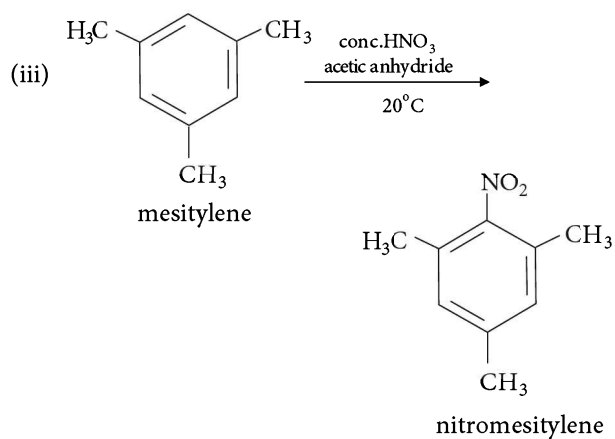
Reactivity of halogens is controlled by the strong inductive effect and orientation is controlled by the resonance effect.

Examples of electrophilic aromatic substitution reactions

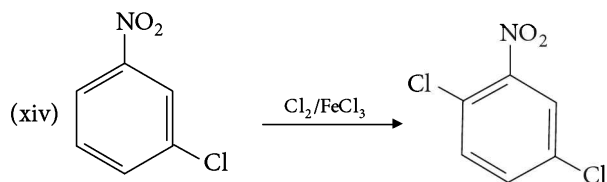




Br_2 in CH_3COOH is a mild brominating agent and only monobromination takes place.

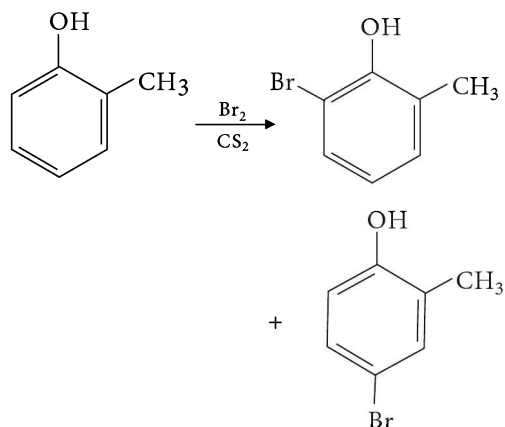


3.18 Benzene and Phenols



If a meta directing group is located in a meta position to an ortho, para directing group, the entering electrophile (the third substituent) enters a position ortho to the meta directing group.

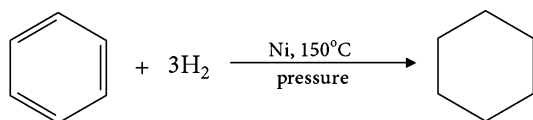
(xvi) If a strong activating group competes with a weaker one or with a deactivating group, the former controls the reaction. Thus



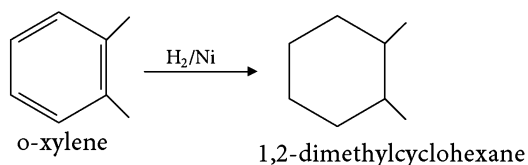
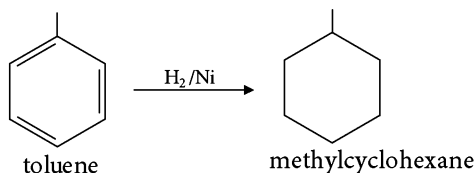
ADDITION REACTIONS OF BENZENE

(i) Catalytic hydrogenation

Benzene reacts with hydrogen in the presence of nickel (or platinum) catalyst at 150°C under pressure to form cyclohexane

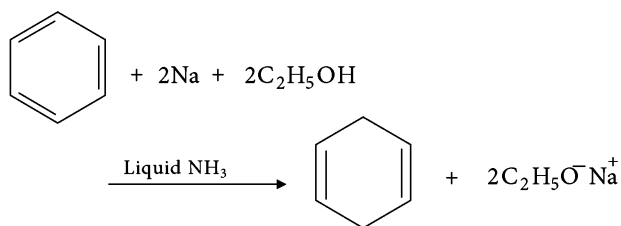


Under similar conditions, toluene gives methyl cyclohexane and xylenes give dimethyl cyclohexane



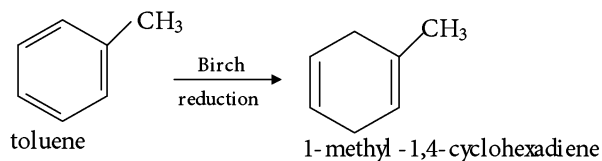
(ii) Birch reduction

When benzene is reduced with Li or Na in liquid ammonia and ethanol, the product obtained is 1,4-cyclohexadiene.

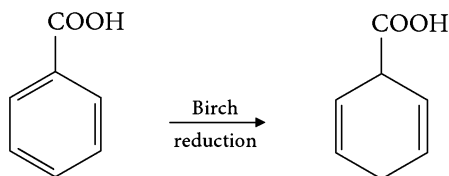


An alkali metal like Li or Na in liquid NH_3 is a source of solvated electrons. The reaction proceeds by anionic radical mechanism.

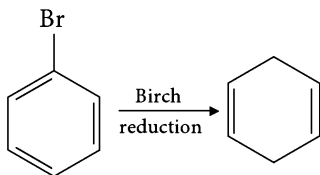
When electron releasing groups like CH_3 are present in the benzene nucleus, the product obtained is exclusively 1-methyl-1,4-cyclohexadiene and not the isomeric product viz, 3-methyl-1,4-cyclohexadiene.



When electron withdrawing groups like $-\text{COOH}$ are present in the benzene nucleus, the product obtained is 2,5-cyclohexadiene-1-carboxylic acid.



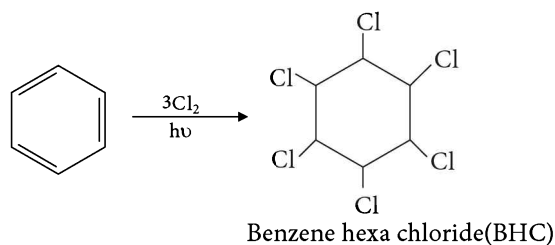
A very interesting reaction occurs when bromobenzene is subjected to Birch reduction.



The expected product (3-bromo-1,4-cyclohexadiene) is not formed as the final product. This is because of the fact that 3-bromo-1,4 cyclohexadiene is an allylic bromide and it results in an organometallic compound with Li or Na as $R-Li^+$ or $R-Na^+$. This strongly basic anion abstracts H^+ from ethanol to form the 1,4-diene.

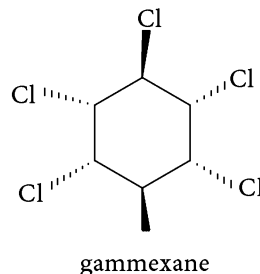
(iii) Addition of halogen

Benzene reacts with chlorine and bromine in presence of sunlight or ultraviolet light to produce ben-



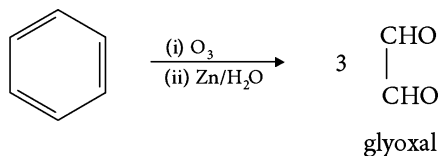
zene hexachloride ($C_6H_6Cl_6$) and benzene hexabromide ($C_6H_6Br_6$), respectively. The reaction proceeds via free radical addition of chlorine (or bromine) on benzene.

Out of the nine isomers possible theoretically for benzene hexachloride, the γ -isomer is the most important one and is used as a powerful insecticide under the name of 'gammexane' or '666' or 'lindane'.



(iv) Ozonolysis

When treated with ozone, benzene triozone is formed which on hydrolysis yields gloyal.

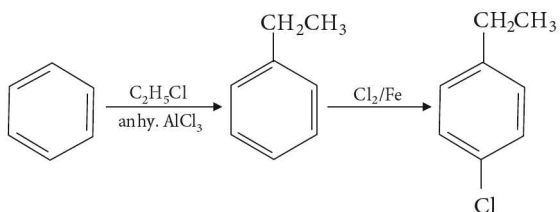


CONCEPT STRANDS

Concept Strand 1

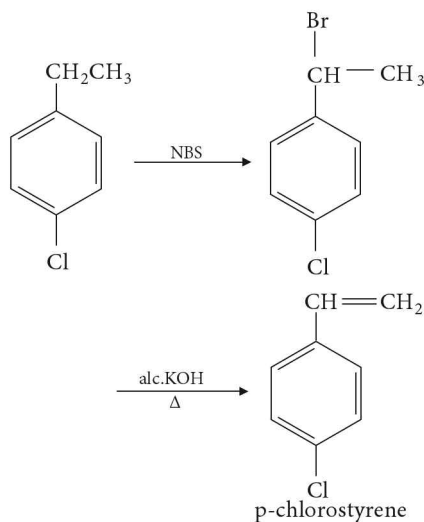
How is benzene converted to p-chlorostyrene?

Solution



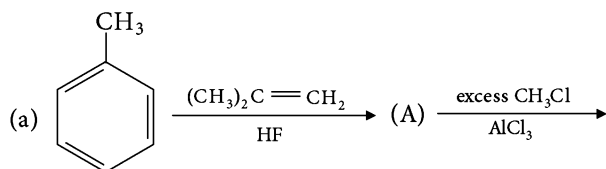
(this gives rise to polyalkylation as given on p. 3.213) Hence Friedel-Crafts acylation is to be done with CH_3COCl and followed by Clemmensen reduction.

A small quantity of o-chloroethyl benzene is also produced, which is separated from p-chloroethyl benzene.



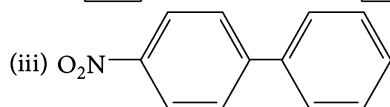
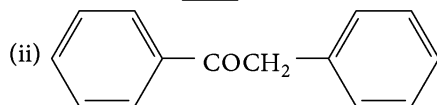
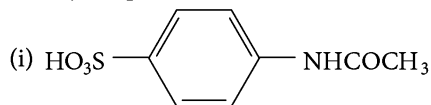
3.20 Benzene and Phenols

Concept Strand 2

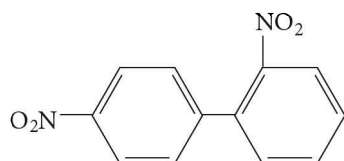
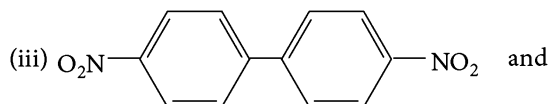
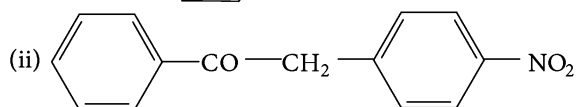
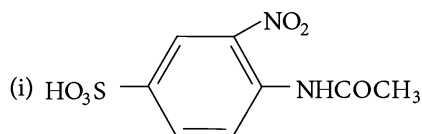
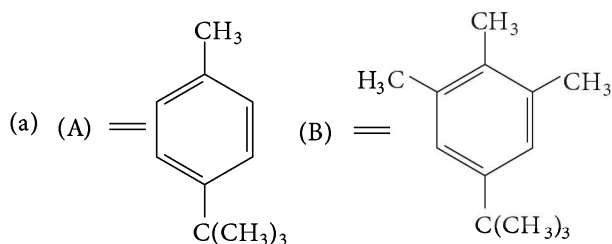


(B). Identify (A) and (B).

(b) Identify the product of mononitration of



Solution



Concept Strand 3

Give reasons for the following observations

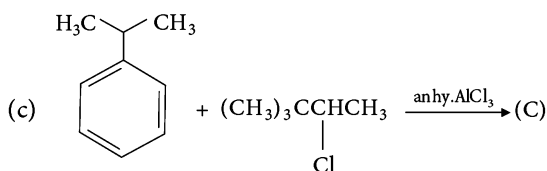
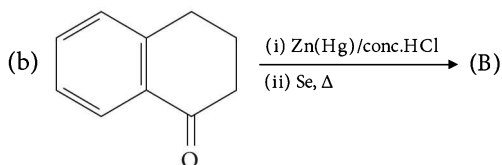
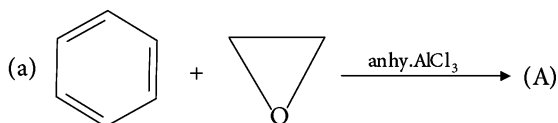
- Nitration of benzene gives only mononitrobenzene.
- Carbon-carbon bond length in benzene is 1.40 Å.

Solution

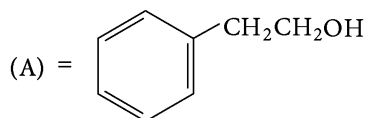
- Benzene on nitration gives nitrobenzene. Once mononitrobenzene is formed, the benzene ring gets deactivated by the electron withdrawing influence of nitro group and the ring fails to undergo further nitration unless very strong and drastic conditions are followed.
- Carbon-carbon bond length in benzene is 1.40 Å. The carbon-carbon single bond length is 1.53 Å, while the carbon-carbon double bond length is 1.32 Å. The value 1.40 Å is about midway between the values for a singly bonded carbon atoms and doubly bonded carbon atoms. This is due to resonance. All the six carbon-carbon bonds in benzene become identical due to resonance.

Concept Strand 4

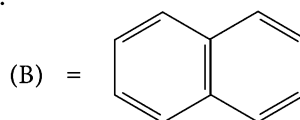
Identify the lettered compounds (A)-(C) in the following reactions.



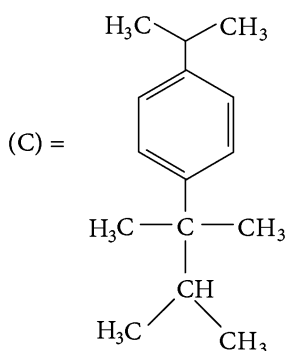
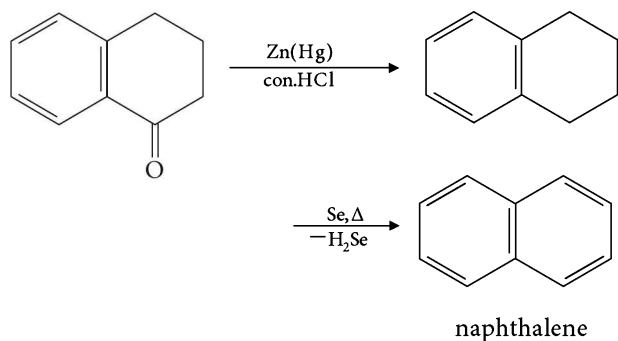
Solution



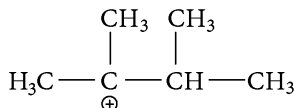
A Friedel-Crafts reaction in which 'O' donates its lone pair to the Lewis acid AlCl_3 , followed by C-O bond cleavage gives a carbocation which then takes the benzene ring to give (A).



First the ketone gets reduced to 1,2,3,4-tetrahydronaphthalene, which undergoes dehydrogenation by selenium under hot conditions to give naphthalene.

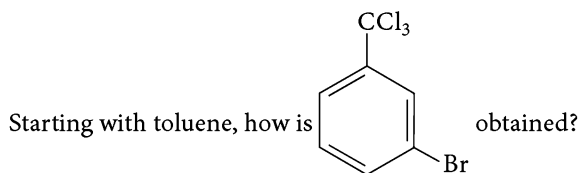


A more stable carbocation (a 3° cation) is formed by a 1,2-shift of a methyl group.

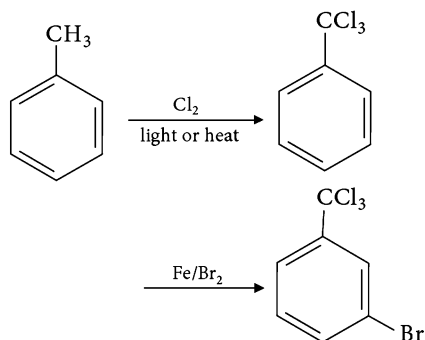


This cation gets attached to the activated para position to give the para derivative as the major product.

Concept Strand 5

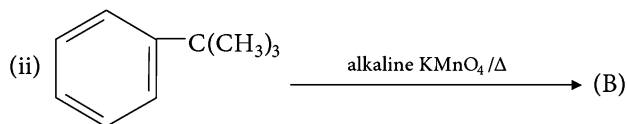
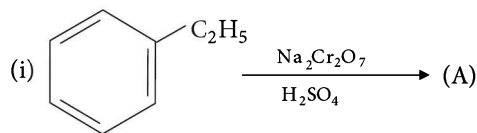


Solution



Concept Strand 6

Identify the major products (A) and (B) in the following reactions.



Solution

(i) The side chain has an α -hydrogen; so irrespective of the length of the side chain, the product formed is $\text{C}_6\text{H}_5\text{COOH}$.

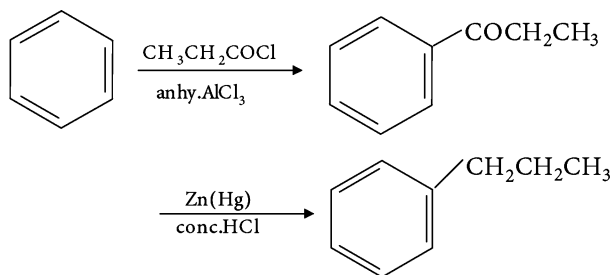
(ii) The side chain has no α -hydrogen. So extensive cleavage of ring takes place and the ultimate product is CH_3COOH .

Concept Strand 7

How is n-propylbenzene prepared from benzene?

Solution

n-propyl benzene can be prepared in two stages. In the first step, benzene is converted to a ketone by Friedel-Crafts acylation process. Now, the ketone is reduced by Clemmensen reduction ($\text{Zn(Hg)} / \text{conc.HCl}$) to give n-propylbenzene.



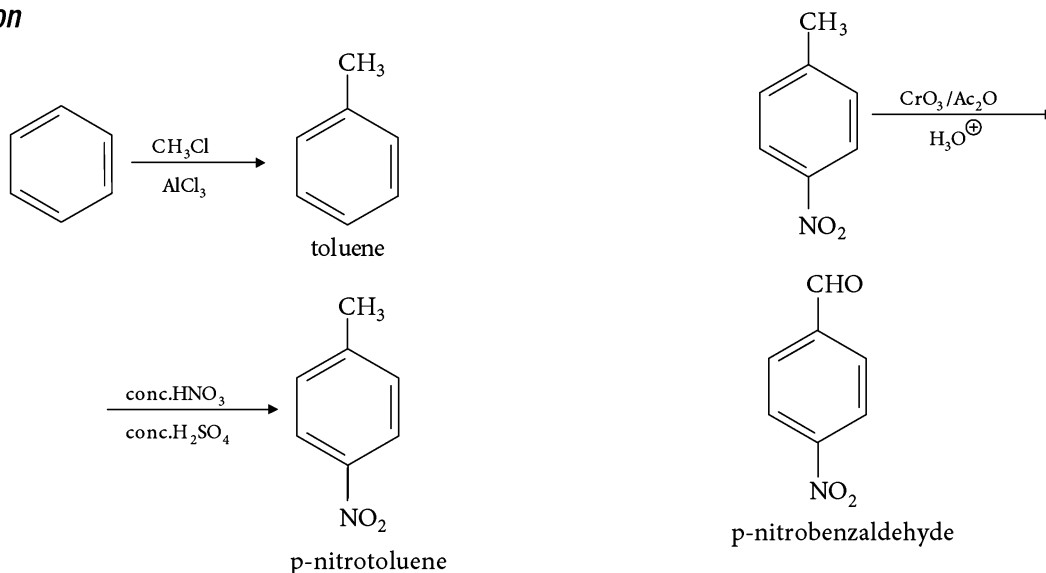
Another convenient method of preparing n-propyl benzene is to treat benzene with cyclopropane in presence of AlCl_3 .

3.22 Benzene and Phenols

Concept Strand 8

How is benzene converted to p-nitrobenzaldehyde?

Solution

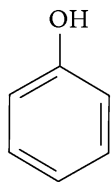


A small quantity of o-nitrotoluene is also formed which is separated from the mixture to get pure p-nitrotoluene.

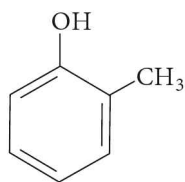
PHENOLS

Phenols are aromatic compounds containing hydroxyl groups directly attached to the benzene nucleus. The simplest member of the family is $\text{C}_6\text{H}_5\text{OH}$ known as phenol

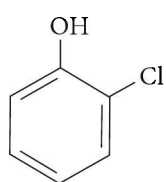
or carbolic acid. Phenols differ from alcohols in having the $-\text{OH}$ group directly attached to the aromatic ring. Some important phenols are given below.



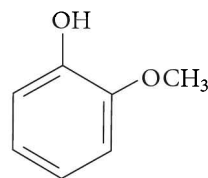
phenol



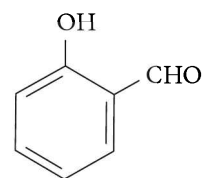
o-cresol



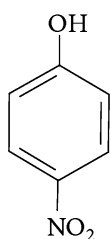
o-chlorophenol



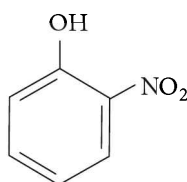
o-methoxyphenol



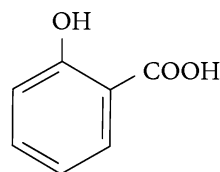
salicylaldehyde



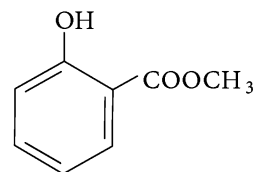
p-nitrophenol



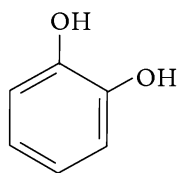
o-nitrophenol



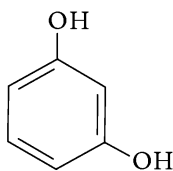
salicylic acid



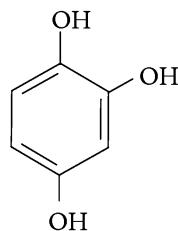
methyl salicylate
(oil of wintergreen)



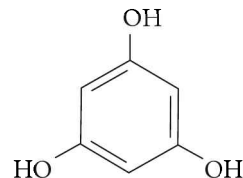
catechol



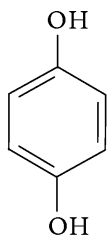
resorcinol



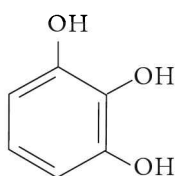
hydroxyquinol



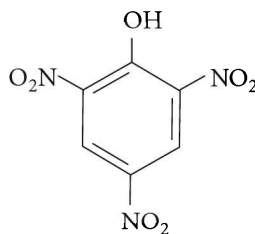
phloroglucinol



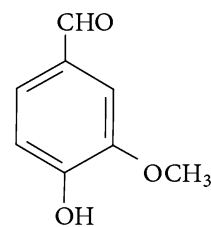
quinol



pyrogallol



picric acid



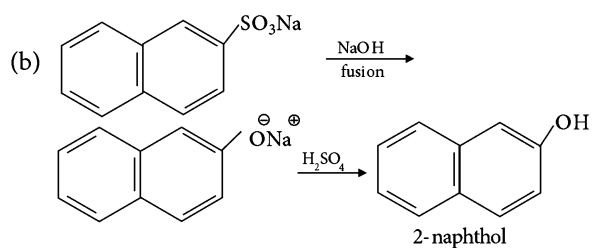
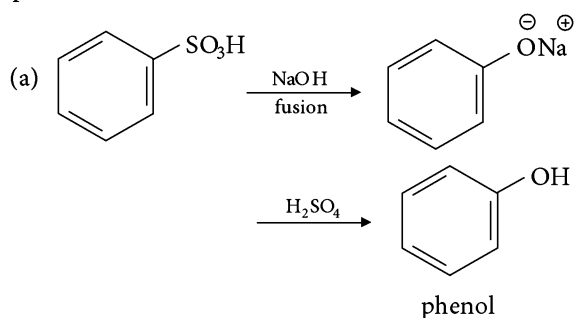
vanillin

Being hydroxy compounds, their chemical properties are similar to alcohols in some respects. For example, phenols can be converted to esters and ethers on reaction with suitable reagents and conditions. However, phenols differ

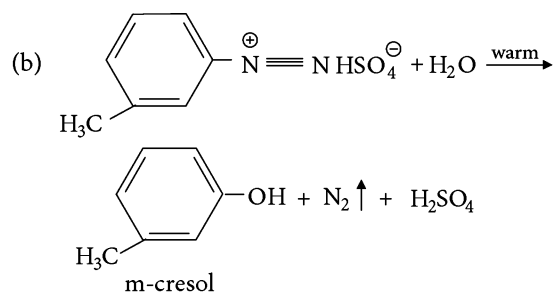
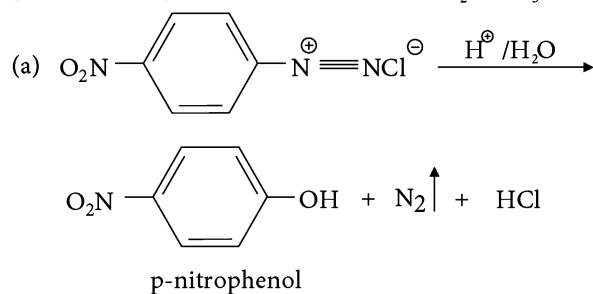
significantly in most of their properties and methods of preparation.

GENERAL METHODS OF PREPARATION OF PHENOLS

- (i) Sodium salts of sulphonic acids on fusion with alkali (NaOH) followed by treatment with dilute acid give phenols.

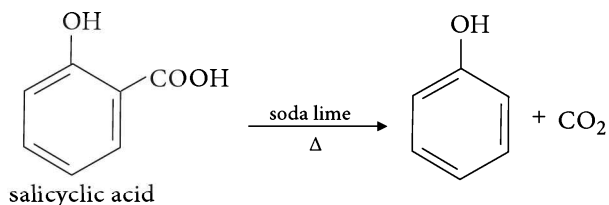


- (ii) When diazonium salts are warmed in dilute acid solutions, phenols are produced. As the conditions are mild, this method is very useful for the preparation of phenols having substituents like $-\text{Cl}$, $-\text{NO}_2$, $-\text{CH}_3$, etc.



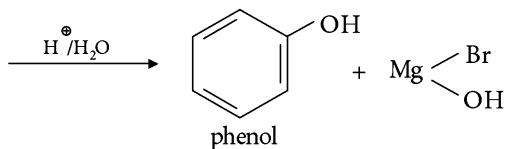
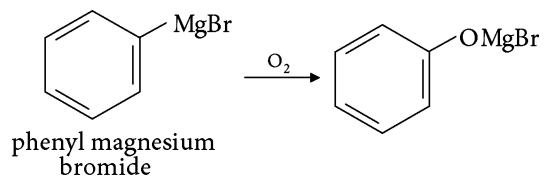
3.24 Benzene and Phenols

- (iii) Phenolic acids like salicylic acid when distilled with soda lime undergoes decarboxylation to give phenols.

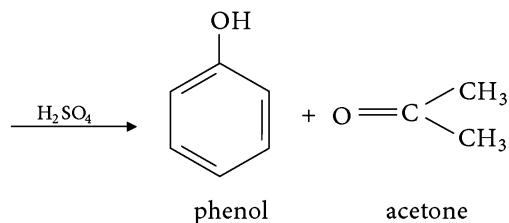
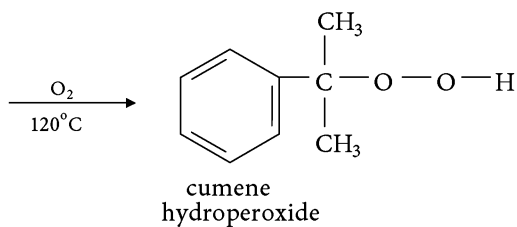
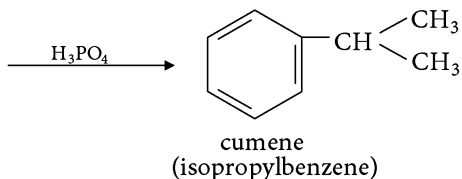
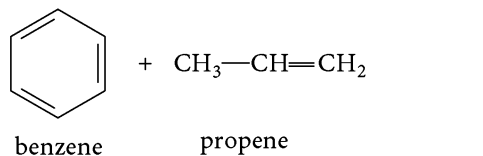


Soda lime is a mixture of CaO and NaOH and is a decarboxylating agent.

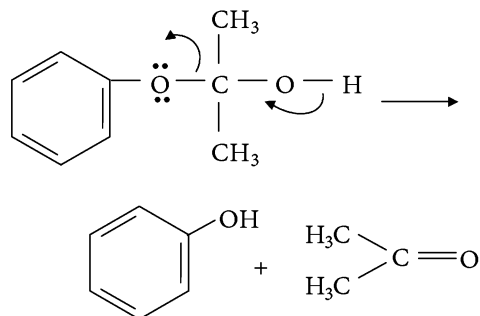
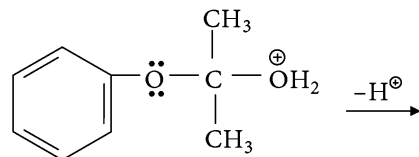
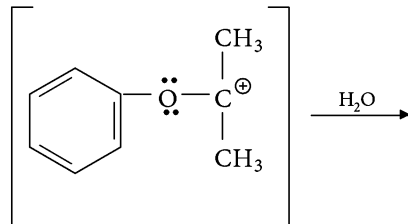
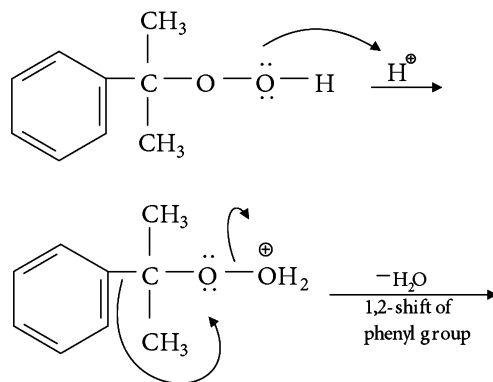
- (iv) Grignard reagents like $\text{C}_6\text{H}_5\text{MgBr}$ in the presence of oxygen give oxygenated derivatives, which on hydrolysis under acidic conditions give phenols.



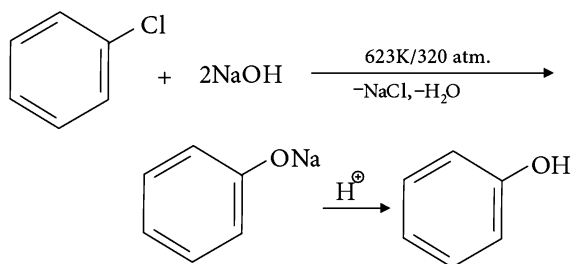
- (v) Phenols can be prepared from cumene hydroperoxide, as shown.



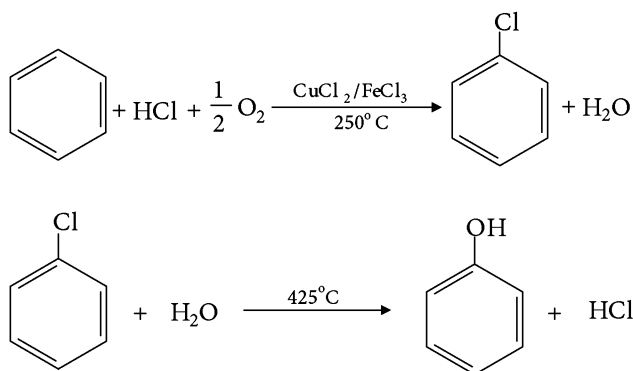
Mechanism



- (vi) Dow's process: Phenols can be prepared from aryl halides like chlorobenzene by heating with caustic soda at high temperature and pressure in an autoclave.

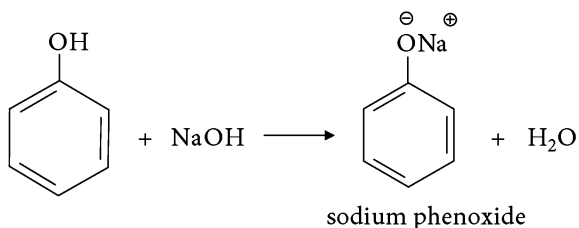


(VII) Raschig's process: A mixture of benzene vapour, air and HCl is passed over CuCl_2 and FeCl_3 as catalyst at 250°C to give chlorobenzene, which is then hydrolysed with superheated steam at 425°C to form phenol.



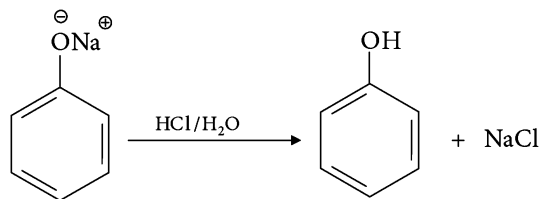
ACIDITY OF PHENOLS

Phenols are acidic in nature and they form sodium phenoxides on reaction with aqueous NaOH solution.



Bases like NaHCO_3 and Na_2CO_3 solutions are not strong enough to form a sodium salt with phenol.

Free phenol can be regenerated from sodium phenoxide by the action of dilute mineral acids.



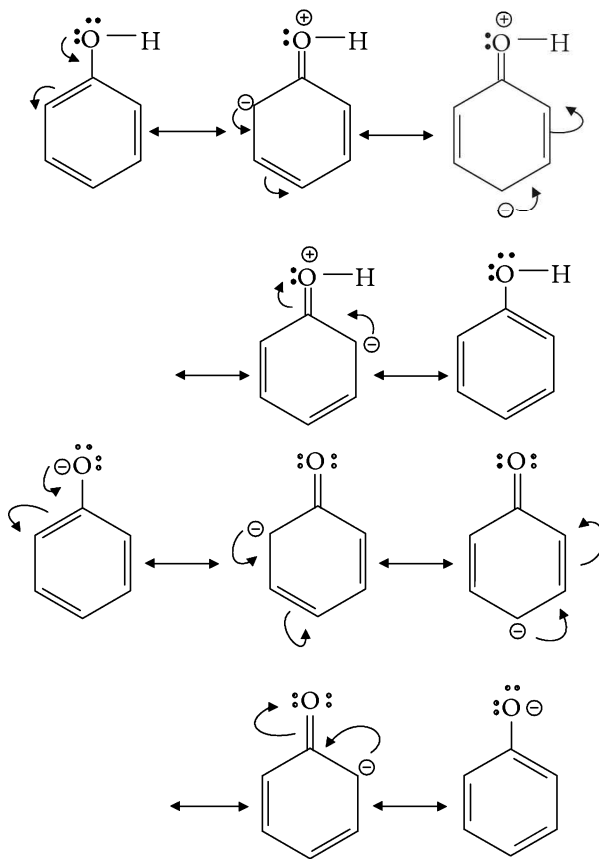
Simple phenol has a pK_a value of 9.9. *Electron withdrawing substituents like $-\text{NO}_2$, $-\text{Cl}$, $-\text{CN}$, etc. enhance the acidity and electron releasing substituents like alkyl, $-\text{OCH}_3$, etc. decrease the acidity of phenols.*

Comparison of acidities of phenols with alcohols

Phenols are much more acidic than alcohols. The acidic character of phenol is due to the greater resonance stabilization of phenoxide ion. Both phenol and phenoxide ion

are stabilized by resonance. But phenoxide ion is more stabilized by resonance than phenol. Hence phenol ionizes and behaves as an acid.

Resonance structures of phenol and phenoxide ion are given below.

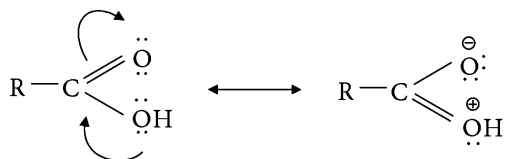


3.26 Benzene and Phenols

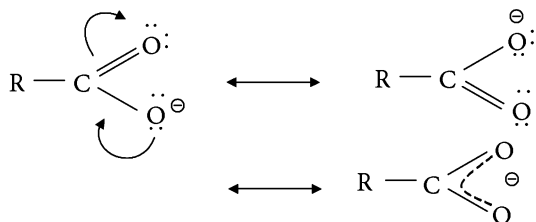
In the case of alcohol, the alkoxide ion (RO^-) formed by ionization is less stable due to the +I effect of alkyl group. Resonance is not possible for alkoxide ion. Hence alcohols have negligible tendency to ionize and they are much less acidic than phenols.

Comparison of acidities of phenols with carboxylic acids

A carboxylic acid can be represented by resonance structures and is stabilized.



A carboxylate anion is more stabilized by resonance.



Though phenoxide ion is resonance stabilized, its stability is less when compared to a carboxylate ion. This is because a carboxylate ion has two equivalent structures, which are equally favoured when compared to the five resonance structures of phenoxide ion, all of which are not equivalent.

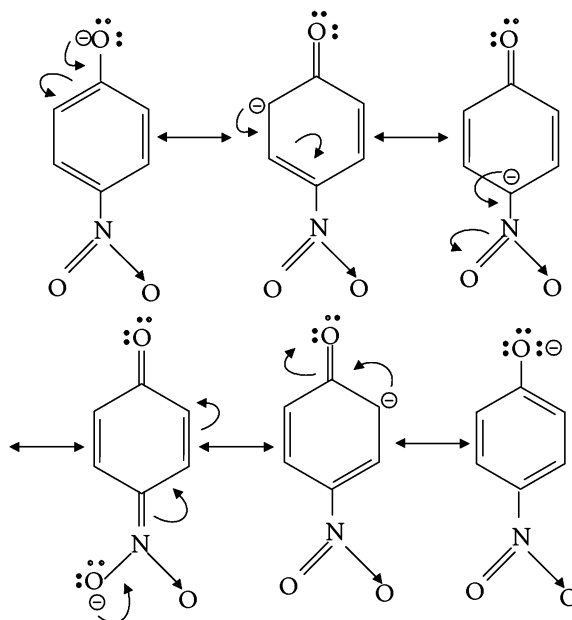
The pK_a of a carboxylic acid, for example acetic acid, is 4.5 whereas, phenol has a pK_a of 9.9, which shows that a carboxylic acid is stronger than phenol. Comparing the acidities of carbonic acid (H_2CO_3) and phenol, we find that the former is a stronger acid than the latter. The pK_a of carbonic acid is 6.35. Hence phenol is regenerated from aqueous solution of sodium phenoxide by passing CO_2 gas through it.

The fact that phenols are not soluble in aqueous NaHCO_3 whereas carboxylic acids are soluble is used to distinguish phenols from carboxylic acid and also to separate a mixture of the two.

Effect of substituents on the acidity of phenols

Consider the case of p-nitrophenol. p-Nitrophenoxide ion can be represented by a number of resonance structures.

Nitro group in the ortho position or a para position in the benzene ring of nitrophenols stabilizes the phenoxide ion by electron withdrawal.



So electron withdrawing substituents like $-\text{NO}_2$, $-\text{CN}$ or $-\text{Cl}$ would make the phenols more acidic than the unsubstituted phenol.

Similarly, if electron releasing groups like methyl or methoxy are present as substituents in phenol, the acidity of phenol is decreased. The negative charge on phenoxide ion is intensified by electron release either by inductive effect or resonance effect and hence the phenoxide ion is destabilized.

Relative acid strength of substituted phenols

(i) Nitrophenols

p-nitrophenol > o-nitrophenol > m-nitrophenol > phenol
o-nitrophenol is slightly less acidic than p-nitrophenol due to intramolecular hydrogen bonding which makes loss of proton little more difficult in o-nitrophenol.

(ii) Cresols

Phenol > m-cresol > p-cresol > o-cresol

(iii) Halophenols

In general halophenols are more acidic than phenol. This shows that $-\text{I}$ effect of halogen dominates over the $+\text{R}$ effect in deciding the acid character. Since $-\text{I}$ effect decreases with distance, the acid strength follows the order.

o-halophenol > m-halophenol > p-halophenol

Because of almost identical size of 2p orbitals of C and F, the $-I$ effect and $+R$ effect almost balance each other in the case of p-fluorophenol and hence its acidic strength is almost the same as that of phenol

Among o-halophenols, o-fluorophenol is the weakest acid due to strong intramolecular hydrogen bonding. For

other o-halophenols, the acidity is decided by the $-I$ effect of halogen. Thus ,

o-chlorophenol > o-bromophenol > o-iodophenol > o-fluorophenol.

REACTIONS OF PHENOL

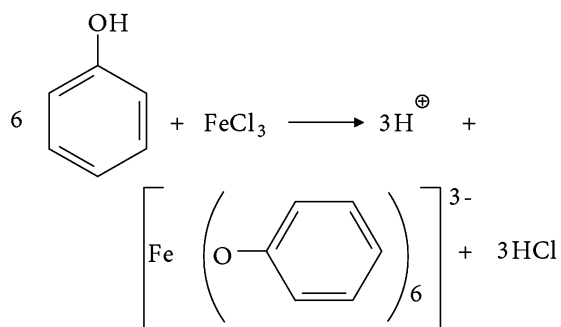
(i) Reaction with neutral $FeCl_3$ Solution:

Many phenols (though not all) react with dilute neutral $FeCl_3$ solution to give water soluble coloured complexes. They behave as enols —C=C—OH .

The colours produced by various phenols are given below.

Violet colour	- phenol, salicylic acid, resorcinol, p-hydroxybenzoic acid
Green colour	- catechol, o-cresol
Blue or bluish violet	- m-cresol, p-cresol
Red colour	- pyrogallol, quinol
Dark violet	- phloroglucinol

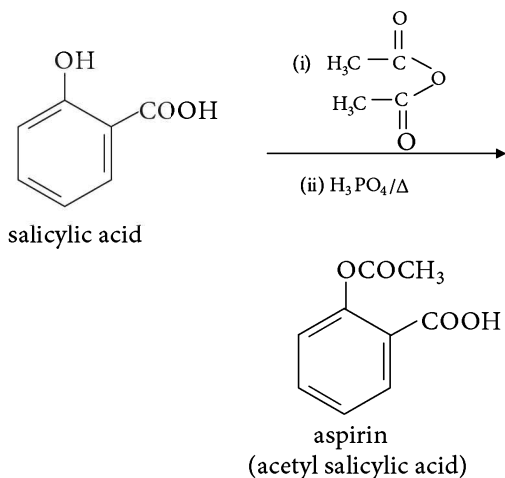
These coloured complexes are coordination compounds in which iron is hexa-coordinated.



(ii) Ester formation

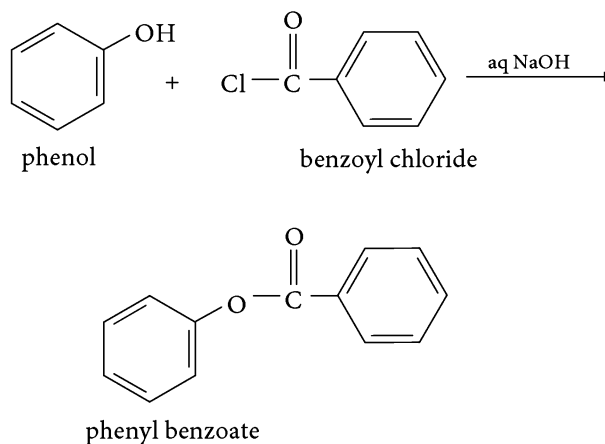
Phenols can be converted to the phenolic ester by the action of acid chlorides, acid anhydrides under the catalytic influence of mineral acids or bases.

(a) Acetyl salicylic acid or aspirin can be prepared from salicylic acid by the action of acetic anhydride in presence of a small amount of con. H_2SO_4 or H_3PO_4 .



(b) Schotten-Baumann reaction

Benzoyl derivatives or esters of phenol can be made by reaction of a phenol with benzoyl chloride in the presence of 10% NaOH solution. This reaction is known as Schotten-Baumann reaction.

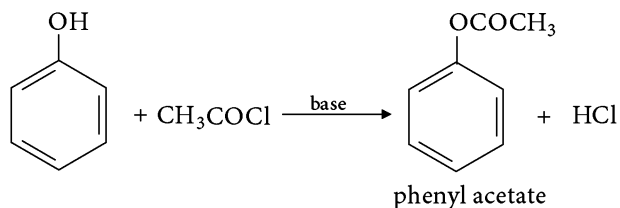


Conversion of a phenol to an ester is not generally effected by a direct reaction of phenol with carboxylic acid.

3.28 Benzene and Phenols

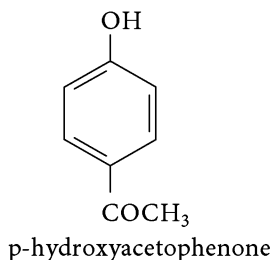
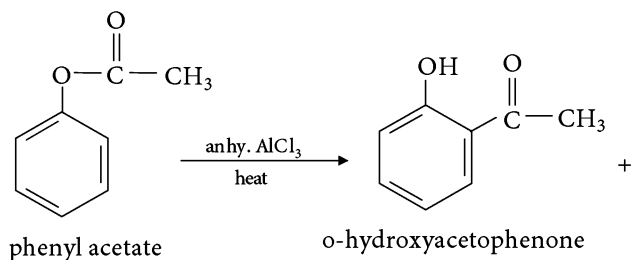
The reaction is reversible and also slightly endothermic for phenol.

(c) Phenol reacts with acetyl chloride CH_3COCl in the presence of a base to give the acetyl derivative.



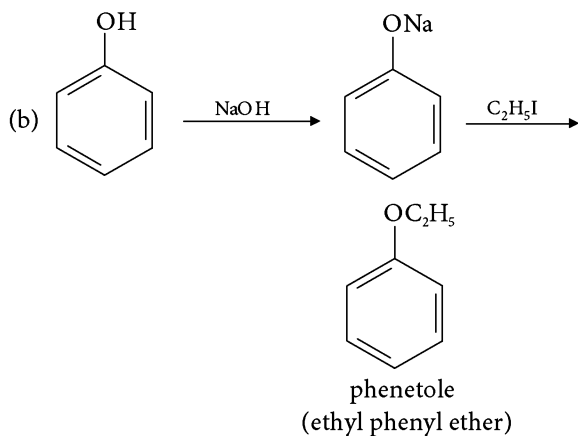
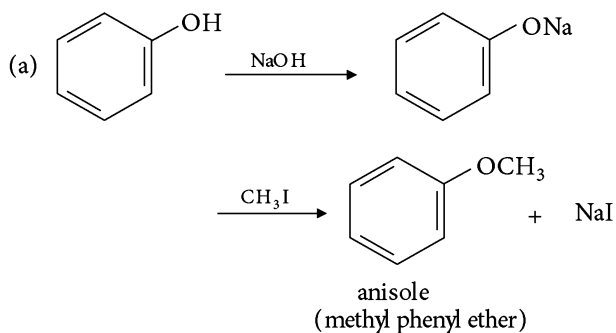
(iii) Fries rearrangement

Esters of phenol, such as phenyl acetate, on heating with a Lewis acid catalyst like anhydrous aluminium chloride, undergo a rearrangement known as Fries rearrangement to give a phenolic ketone.

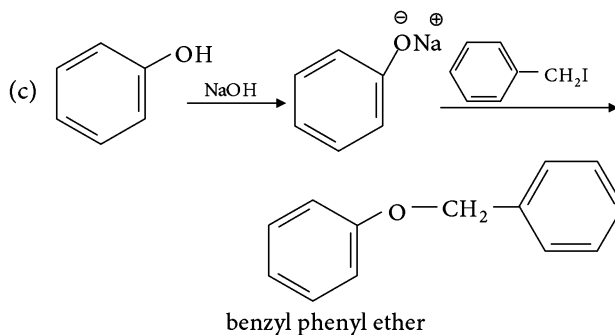


(iv) Formation of aryl – alkyl ethers

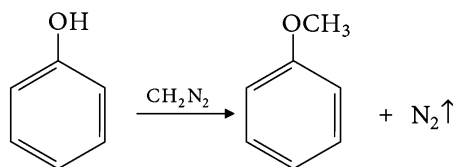
When phenol is heated with an alkyl halide like CH_3I or $\text{C}_2\text{H}_5\text{I}$ in the presence of NaOH , methyl phenyl ether or ethyl phenyl ether is formed, respectively.



with benzyl iodide, phenol gives benzyl phenyl ether.

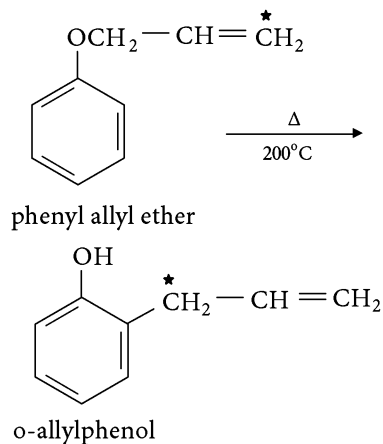


(d) Phenol when treated with diazomethane gives anisole.

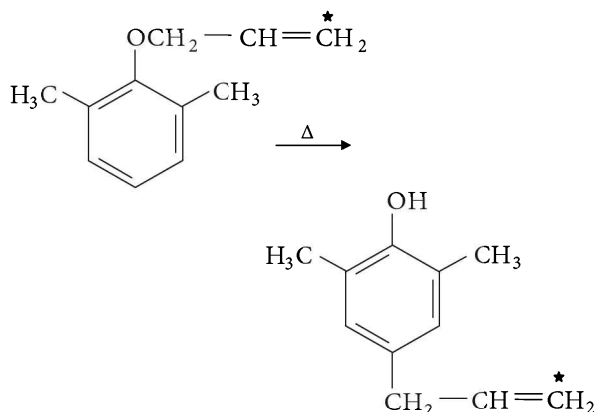


(v) Claisen rearrangement

When allyl ether of phenol is heated to about 200°C , in the absence of any catalyst, it rearranges to o-allylphenol. This thermal rearrangement is known as Claisen rearrangement.



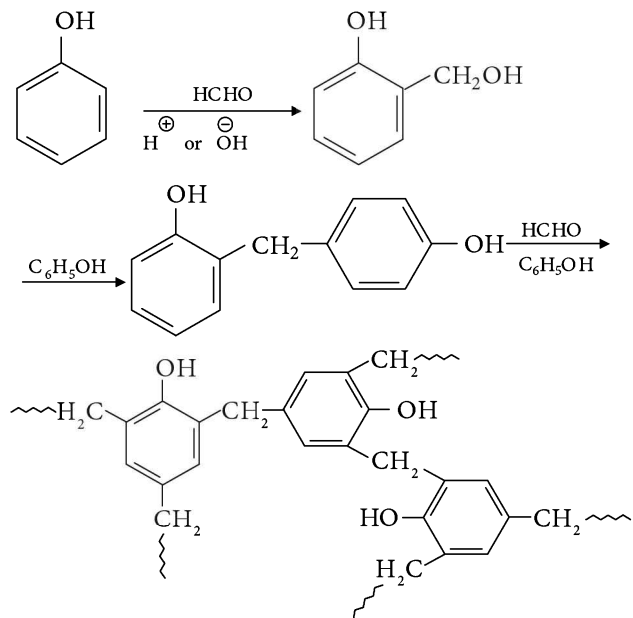
If both the ortho positions are blocked, the migration occurs to the para position. Migration to meta position has not been observed.



There is no reaction when the para and both the ortho position are blocked.

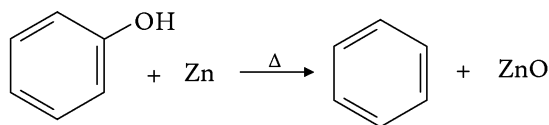
(vi) Reaction with HCHO

When phenol reacts with HCHO in the presence of an acid or alkali, polymers like bakelite are obtained. The reaction is also known as Lederer – Manasse reaction.



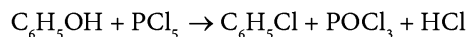
(vii) Reaction with zinc dust

When phenol is distilled with zinc dust, benzene is obtained.



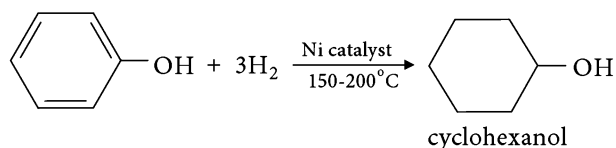
(viii) Reaction with phosphorous (V) chloride

With phosphorus pentachloride, chlorobenzene is obtained. The yields are very poor.



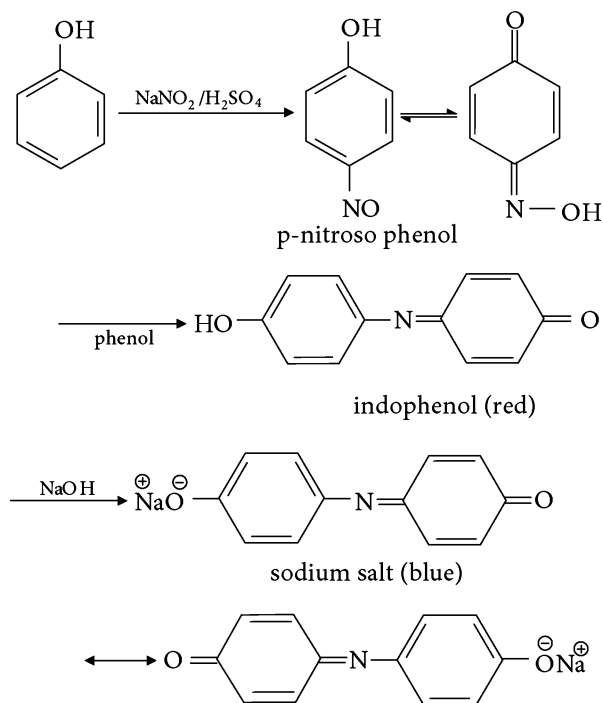
(ix) Hydrogenation

Hydrogenation of phenol in the presence of nickel as catalyst at a higher temperature results in cyclohexanol.



(x) Liebermann's nitroso reaction

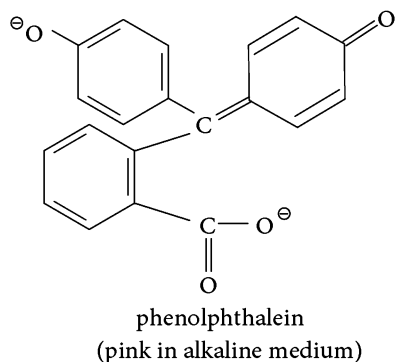
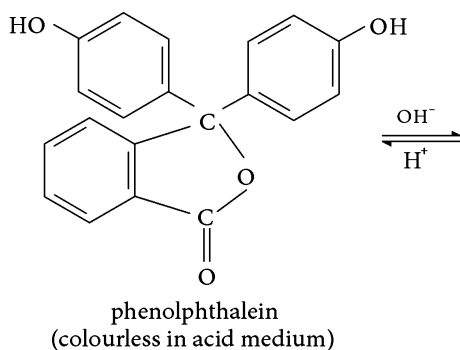
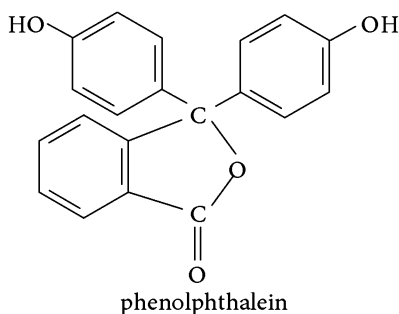
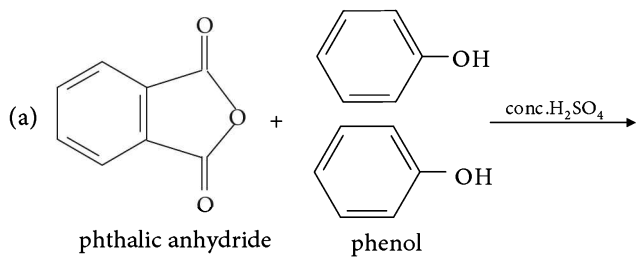
Phenol on warming with sodium nitrite in the presence of conc. H_2SO_4 , gives a deep green or blue coloured product which changes to red when diluted. When made alkaline with NaOH solution, blue colour is obtained.



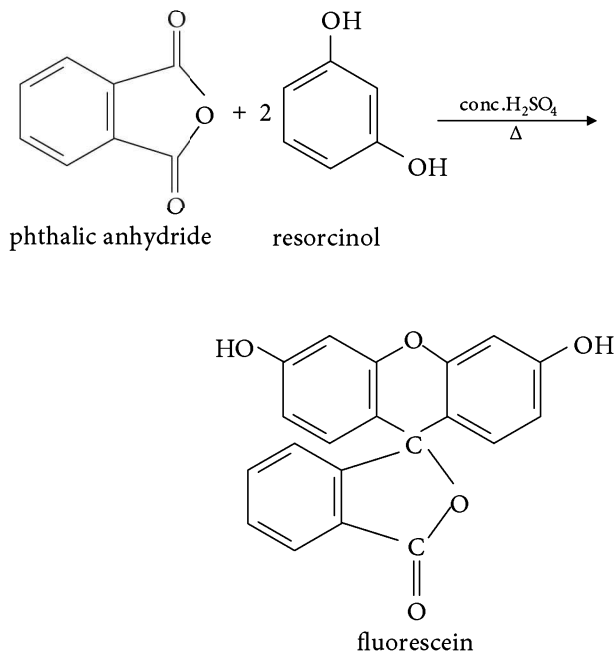
3.30 Benzene and Phenols

(xi) Phthalein fusion reaction

Phenol, when mixed with phthalic anhydride in the presence of $\text{conc. H}_2\text{SO}_4$ or anhydrous ZnCl_2 and heated, gives phenolphthalein. In dilute alkaline medium, it is pink in colour and is colourless in acid medium.

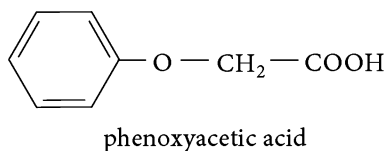
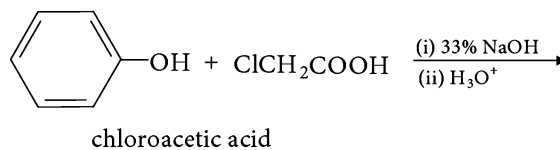


(b) Similarly, when phthalic anhydride and resorcinol are heated in the presence of $\text{conc. H}_2\text{SO}_4$, fluorescein is formed.



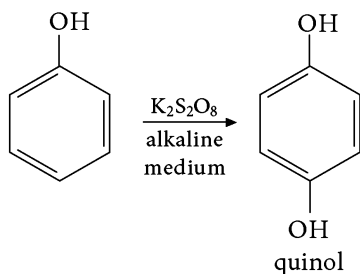
(xii) Formation of phenoxyacetic acid

When phenol reacts with chloroacetic acid in strongly alkaline medium, phenoxyacetic acid separates out.



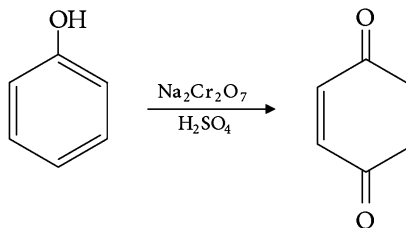
(xiii) Oxidation of phenol

Phenol when treated with potassium persulphate in alkaline solution undergoes oxidation to give quinol.



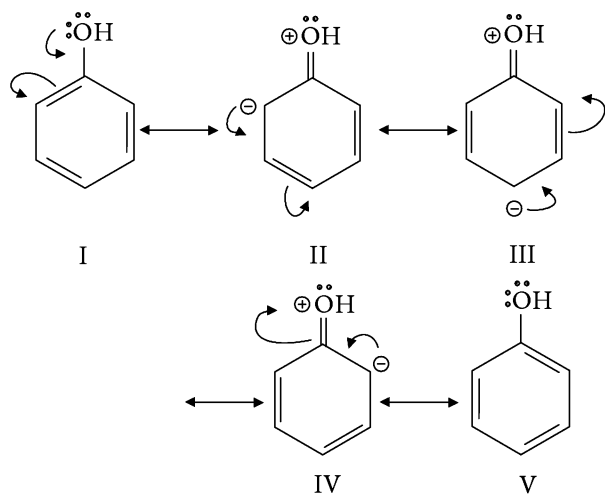
This reaction is known as Elbs persulphate oxidation.

Oxidation of phenol with chromic acid produces benzoquinone.

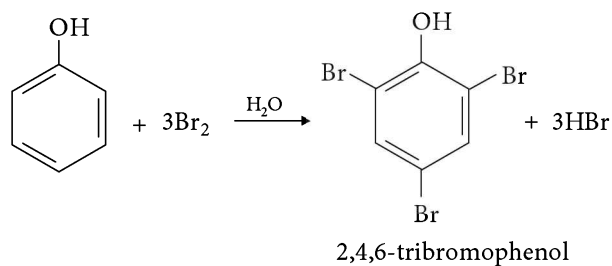


ELECTROPHILIC SUBSTITUTION REACTIONS OF PHENOL

As a typical aromatic compound, phenols undergo aromatic electrophilic substitution. The $-\text{OH}$ group in phenol highly activates the benzene ring by resonance. Compared to an unsubstituted benzene ring, phenol is much more active towards electrophilic substitution. The $-\text{OH}$ group in phenol is activating and ortho, para directing.

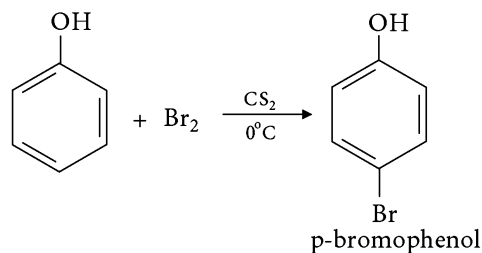


(i) Bromination

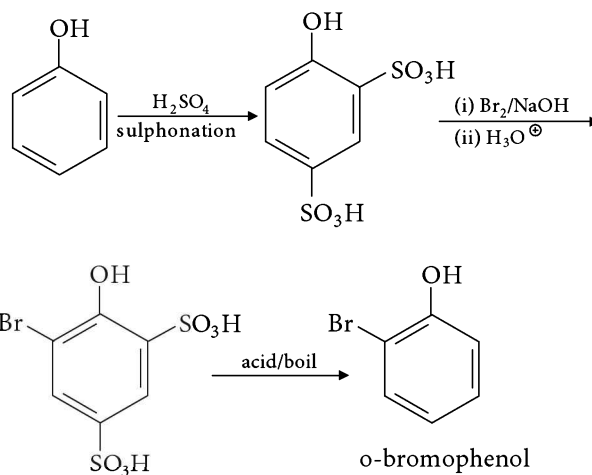


The $-\text{OH}$ group in phenol is so activating that an electrophile, $\text{Br}^\oplus$, from bromine water attacks all the three available electron rich positions. So, on bromination of phenol, 2,4,6-tribromophenol is obtained with the evolution of HBr .

If bromination is to be restricted to one position, i.e., p-bromophenol is required, then phenol is treated with Br_2 in CS_2 or CCl_4 at a low temperature.



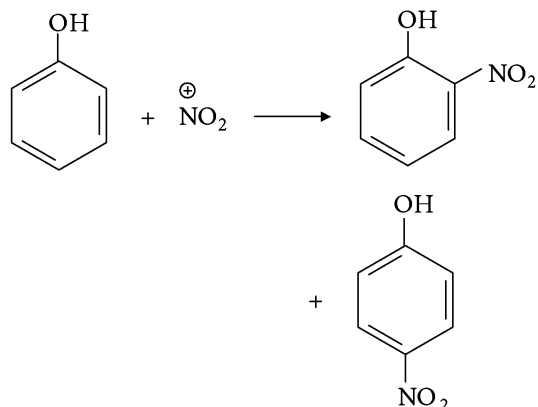
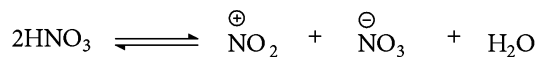
o-bromophenol can be obtained from phenol by the following route.



3.32 Benzene and Phenols

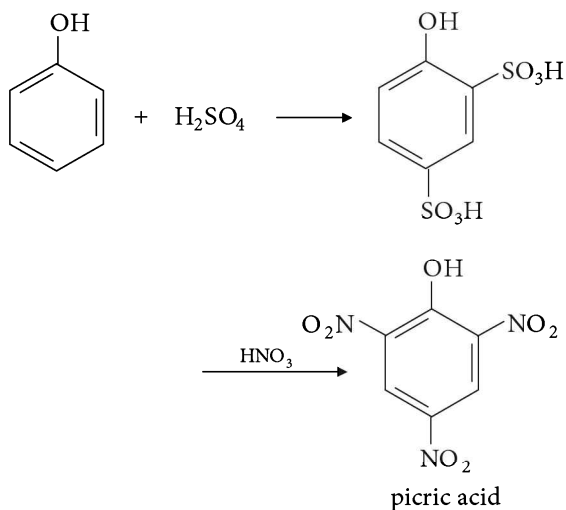
(ii) Nitration

–OH is a highly activating group. Nitration is possible even with dil. HNO_3 .

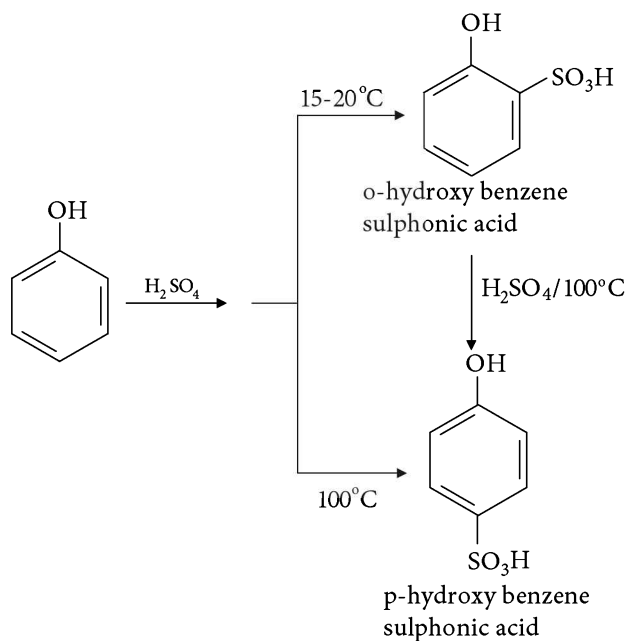
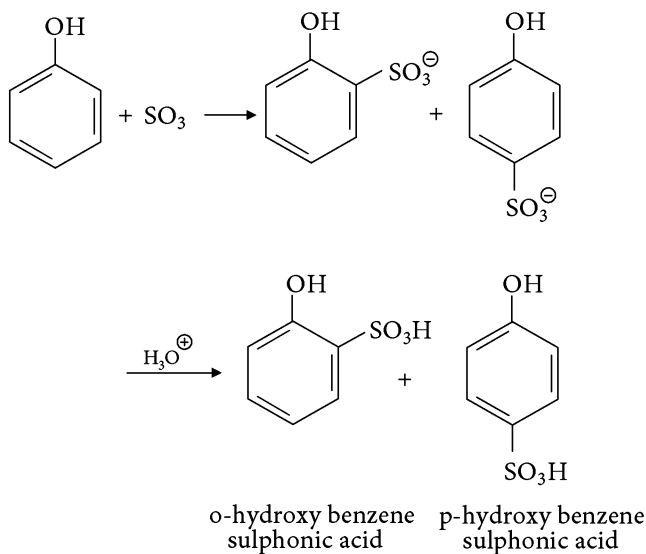
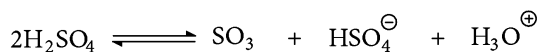


A mixture of o- and p-nitrophenols are obtained.

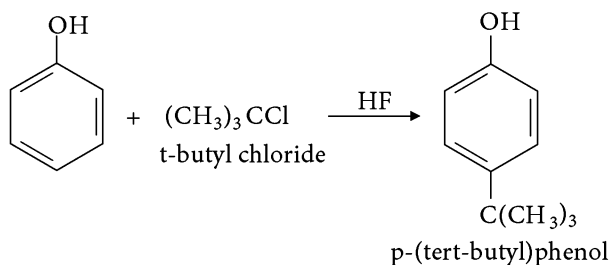
HNO_3 is a strong oxidizing agent, and when further nitration is attempted, benzene ring is likely to be affected. In such a case, ring can be first deactivated by sulphonations then can be nitrated to give picric acid.



(iii) Sulphonation

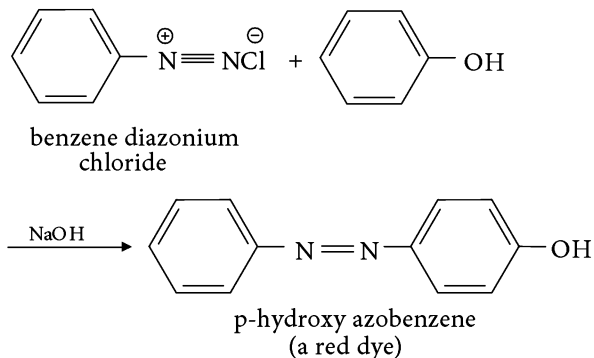


(iv) Friedel – Crafts alkylation and acylation



(v) Coupling with diazonium salts

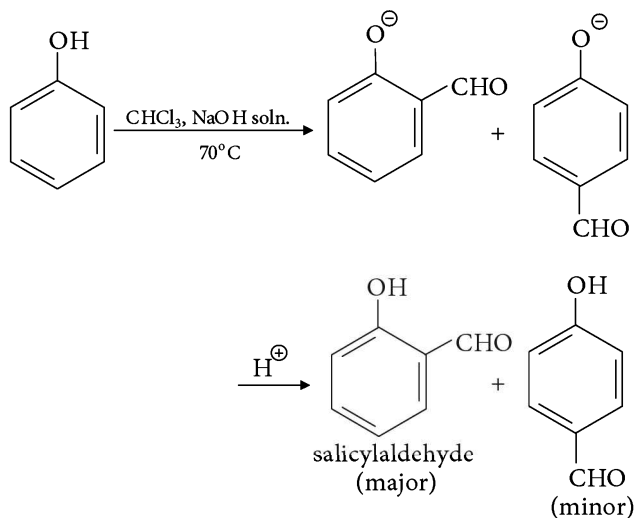
Phenols couple with diazonium salts in alkaline medium to form p-hydroxy azobenzene.



This reaction is referred to as coupling reaction.

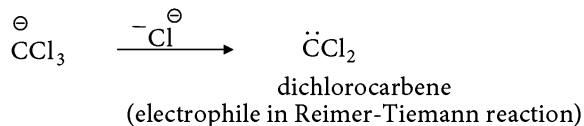
(vi) Reimer–tiemann reaction

When phenol is treated with chloroform in the presence of alkali, a formyl group ($-\text{CHO}$ group) is introduced in the benzene ring in the ortho or para position to give a mixture o-hydroxybenzaldehyde (or salicylaldehyde) and p-hydroxybenzaldehyde. This reaction is known as Reimer-Tiemann reaction. This is one of the examples of formylation reaction. A benzal chloride derivative is initially formed as an intermediate which is hydrolyzed to the aldehyde in alkaline medium.

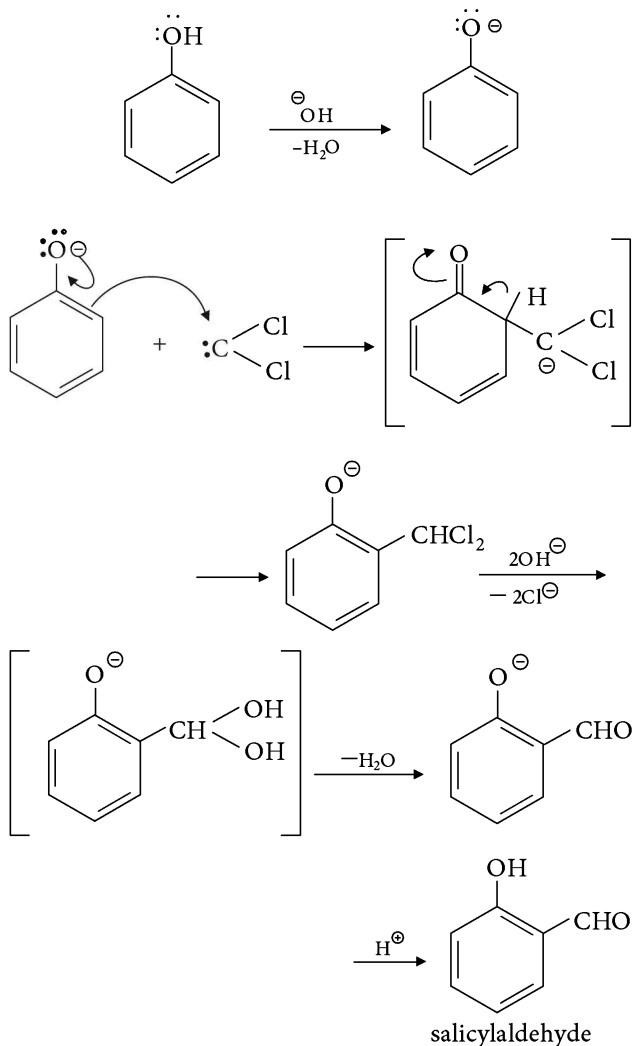
**Mechanism of Reimer–Tiemann reaction**

The reaction involves electrophilic substitution in an activated benzene nucleus. The activation is effected by the phenoxide ion.

The first step in the reaction is the formation of the electrophilic reagent $:\text{CCl}_2$, dichlorocarbene, resulting by the action of strong alkali on CHCl_3 (one of the very few examples of α - elimination). Although electrically neutral, dichlorocarbene is an electron deficient species.

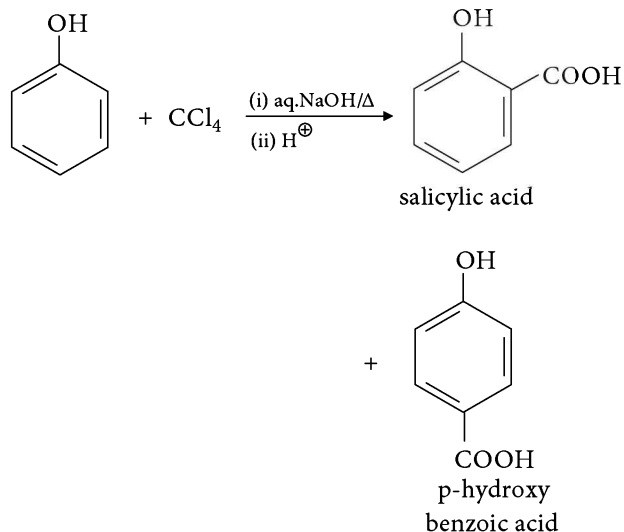


The next step is the attack by the activated aromatic substrate on the electrophilic reagent to give the benzal derivative of the phenoxide ion.



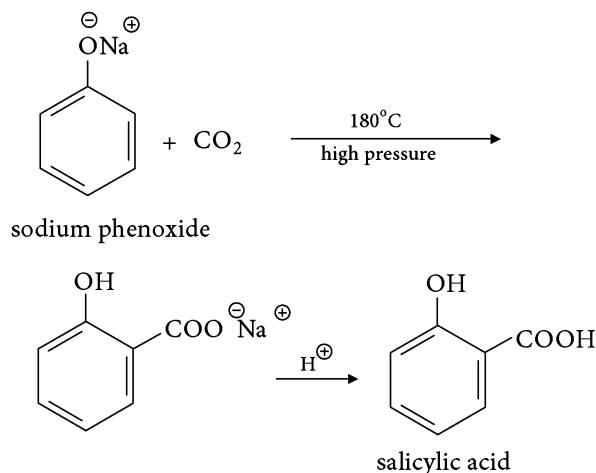
Modification of Reimer-Tiemann reaction

In the place of CHCl_3 , carbon tetrachloride has been used to produce a mixture of ortho and para hydroxybenzoic acids from phenol.

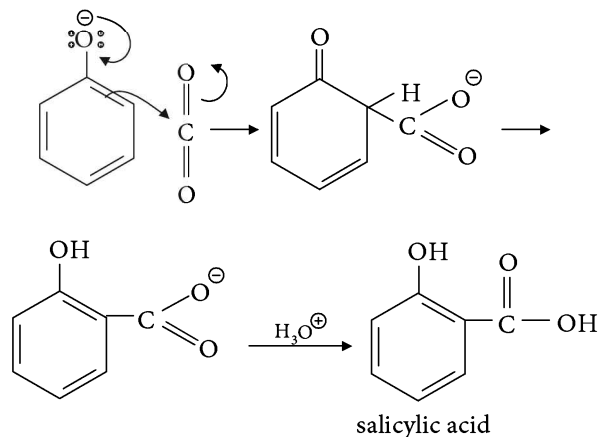
**(vii) Kolbe's reaction**

When phenol (preferably sodium phenoxide) is heated with CO_2 under pressure at 180°C , a carboxylic group is introduced in the benzene ring resulting in the sodium salt of salicylic acid which on treatment with a mineral acid produces salicylic acid.

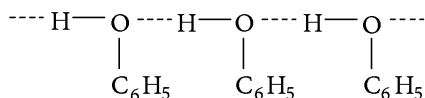
A small percentage of p-hydroxybenzoic acid is also obtained as a byproduct.

**Mechanism of Kolbe's reaction**

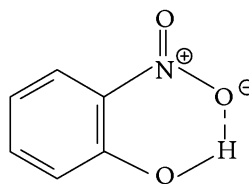
Phenoxide is more active than phenol itself towards aromatic electrophilic substitution. In Kolbe's reaction, carbon dioxide acts as an electrophile.

**HYDROGEN BONDING IN PHENOLS**

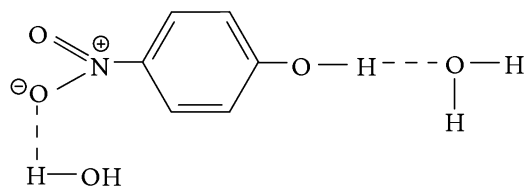
Phenol is soluble in water because of hydrogen bonding. Two or more units of phenol will get linked by hydrogen bonding. Hydrogen of the phenol gets attached to electronegative atoms such as oxygen to form hydrogen bonding. Intermolecular hydrogen bonding occurs in phenols.



When the physical properties of isomeric nitrophenols (o-, m- and p-nitrophenols) are compared, it can be seen that o-nitrophenol has a lower boiling point than its isomers, and is also steam volatile.



This is an instance of intramolecular H-bonding. The solubility of o-nitrophenol in water is very poor (0.2 g in 100 mL). When we consider p-nitrophenol, the hydrogen bonding observed is intermolecular. This can form hydrogen bonds with water molecules as well as with another molecule of p-nitrophenol.



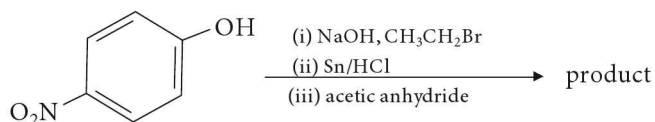
This results in higher solubility of para nitrophenol in water and it is non-volatile in steam. Steam distillation depends on a substance having an appreciable vapour pressure at the boiling point of water; by lowering the vapour pressure, intermolecular hydrogen bonding inhibits steam distillation of the para isomer.

Other phenols that exhibit intramolecular hydrogen bonding are salicylaldehyde, salicylic acid and the ones that exhibit intermolecular hydrogen bonding are p-hydroxybenzaldehyde, p-hydroxybenzoic acid, etc.

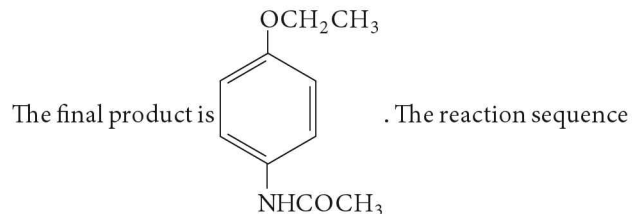
CONCEPT STRANDS

Concept Strand 9

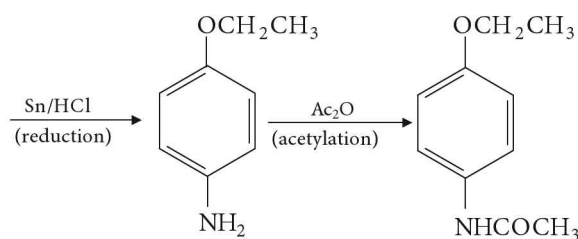
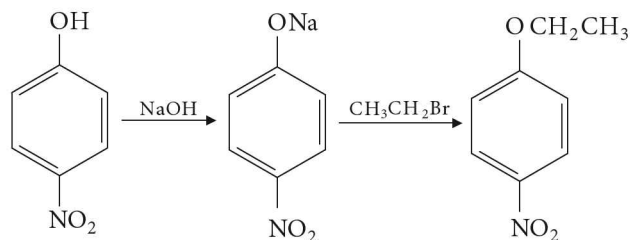
Identify the end product of the reaction,



Solution

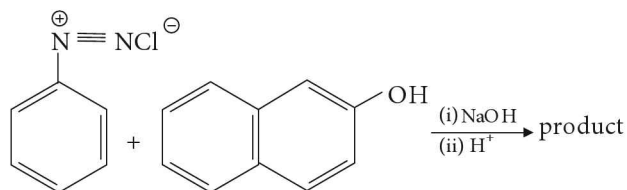


is as follows.

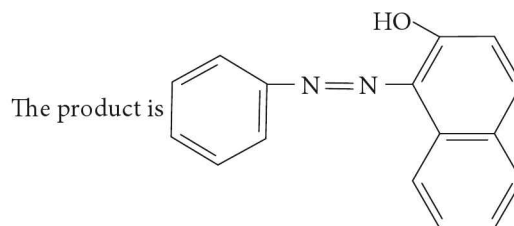


Concept Strand 10

Identify the product in the following reaction.



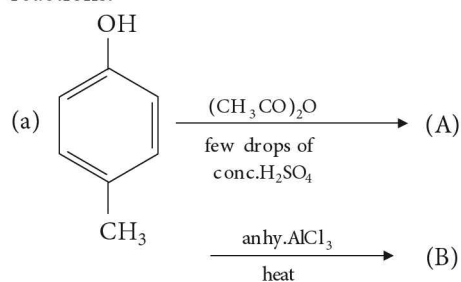
Solution



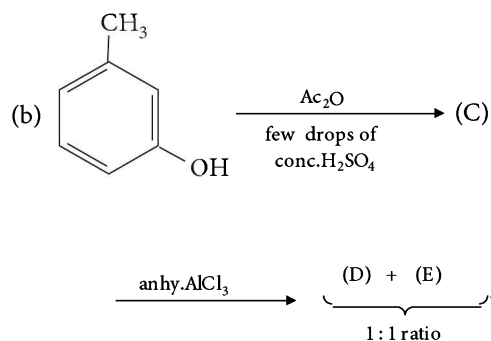
This is an example of a coupling reaction, resulting in a red orange coloured dye, the most activated site in 2-naphthol is the 1-position to which the diazonium group gets attached.

Concept Strand 11

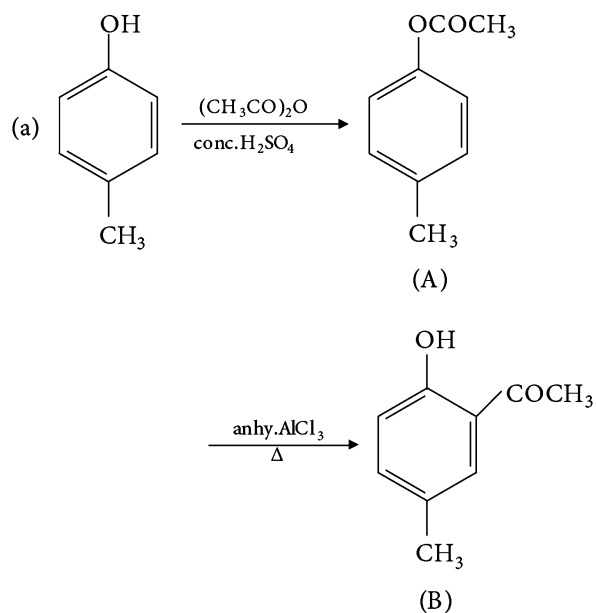
Identify the lettered products in the following sequence of reactions.



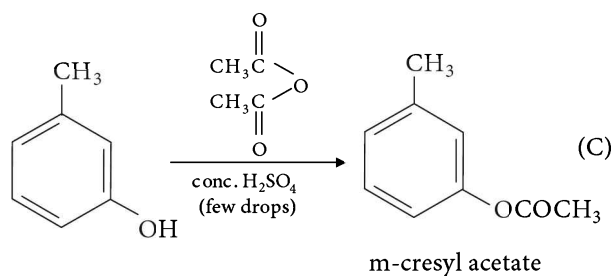
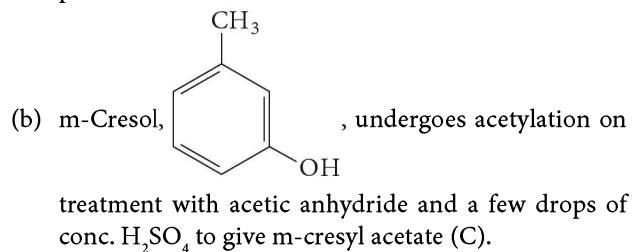
3.36 Benzene and Phenols



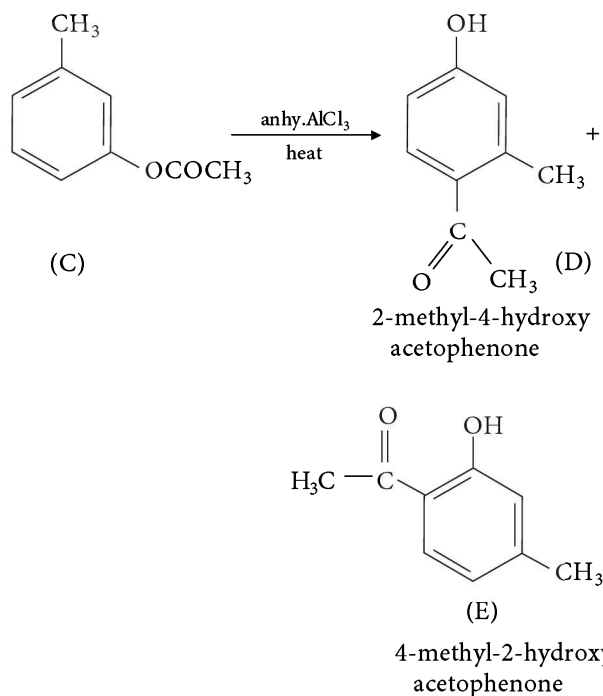
Solution:



p-cresol undergoes acetylation by means of acetic anhydride in the presence of conc. H_2SO_4 to give p-cresyl acetate (A). On treatment with anhydrous AlCl_3 , under hot conditions, (A) undergoes a thermal rearrangement known as Fries rearrangement to give 5-methyl-2-hydroxy acetophenone (B) as the major product.



(c) undergoes Fries rearrangement under hot conditions in the presence of anhydrous AlCl_3 to give a mixture of (D) and (E).



SUMMARY

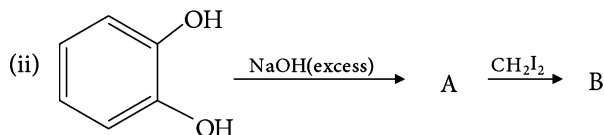
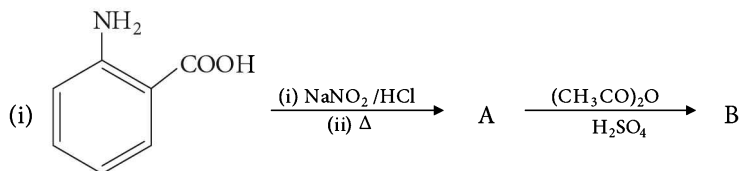
Structure of benzene	Kekulé structure, Resonance theory, Molecular orbital structure of benzene
Aromaticity	Characteristic properties of aromatic compounds. Hückel's rule of aromaticity, Examples for two electron and six electron systems. Antiaromaticity—definition and examples
Preparation of benzene	Preparation from benzoic acid, n-hexane, acetylene and phenol
Aromatic electrophilic substitution	General mechanism. Mechanism of halogenation, nitration, sulphonation and Friedel-Crafts reaction. Limitations of Friedel-Crafts reaction.
Effect of substituents in aromatic electrophilic substitution	Examples for activating and deactivating groups. Ortho-para directing groups and meta directing groups. Examples of electrophilic aromatic substitution reactions.
Addition reactions of benzene	Catalytic hydrogenation, Birch reduction, addition of halogen, Ozonolysis of benzene.
Preparation of phenols	Preparation from sulphonic acids and diazonium salts. Preparation of phenol by nucleophilic substitution of aryl halides and by using Grignard reagent. Manufacture of phenol from cumene. Dow's process and Raschig's process.
Acidity of phenols	Phenols are acidic because of the resonance stabilization of phenoxide ion. Presence of electron withdrawing groups such as $-\text{NO}_2$, $-\text{CN}$ etc increase the acidity of phenols. Presence of electron donating groups decrease the acidity.
Reactions of phenols	Reaction with ferric chloride solution, ester formation, Schotten-Baumann reaction, Fries rearrangement, Claisen rearrangement. Reaction with HCHO , zinc dust and hydrogen in presence of catalyst. Liebermann's nitroso reaction, phthalein fusion reaction, oxidation of phenol.
Electrophilic substitution reactions of phenol	Bromination, nitration, nitrosation, sulphonation, Friedel-Crafts reaction, coupling reaction to form azo dyes, Reimer-Tiemann reaction, Kolbe's reaction. Preparation of picric acid, salicylaldehyde, salicylic acid and azo dyes.

TOPIC GRIP



Subjective Questions

1. Benzene undergoes electrophilic substitution more readily than nucleophilic substitution. Why?
2. How can benzene be converted to m-dibromobenzene?
3. Nitrobenzene does not undergo Friedel-Crafts alkylation reaction. Why?
4. (i) How many isomers of the mono substitution product(s) are possible for
 - (a) benzene
 - (b) naphthalene
 - (c) anthracene
 (ii) Write the structure of all the isomers of the tribromo derivatives of benzene.
5. How is m-dinitrobenzene converted to m-nitrophenol?
6. Phenol is an acid but does not react with saturated NaHCO_3 solution. Why is it so?
7. Explain the reason for the following observations.
 - (i) Phenol does not readily react with PCl_5 to form chlorobenzene but alcohols readily form alkyl chloride.
 - (ii) o-nitrophenol is steam volatile and its solubility in water is less than that of p-nitrophenol.
8. Identify the products A and B in each of the following reaction.



9. A variety of substituent groups are listed. Indicate the effect of these groups on electrophilic aromatic substitution. Classify them as activating or deactivating and also mention their directing influence.

$-\text{C}_6\text{H}_5$, $-\text{NH}_2$, $-\text{Cl}$, $-\text{N}(\text{CH}_3)_2$, $-\text{OH}$, $-\text{CN}$, $-\text{NHCOCH}_3$, $-\text{NHCH}_3$, $-\text{OC}_2\text{H}_5$, $-\text{CH}_3$, $-\text{SO}_3\text{H}$, $-\text{F}$, $-\text{I}$, $-\text{OCH}_3$, $-\text{C}_2\text{H}_5$, $-\text{N}(\text{CH}_3)_3^+$, $-\text{COOH}$, $-\text{COOR}$, $-\text{CHO}$, $-\text{CO}-$, $-\text{Br}$.

10. Explain the following:

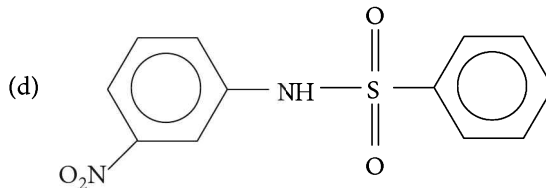
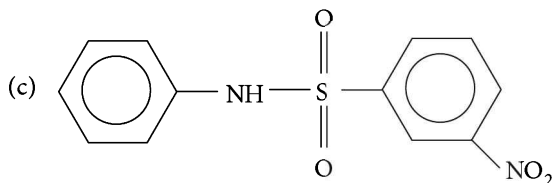
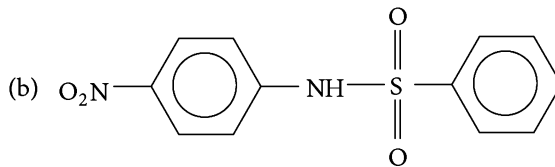
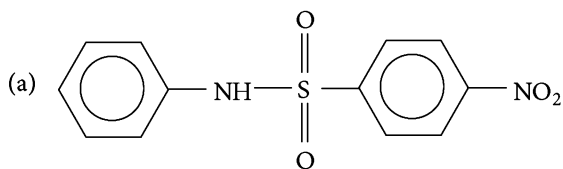
- (a) The pK_a for cyclopentadiene is 16 but 1,4-pentadiene has $\text{pK}_a = 45$
- (b) Pyridine is basic but pyrrole is not basic.



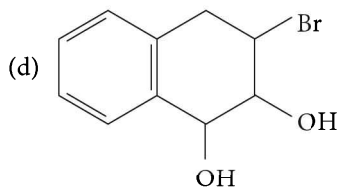
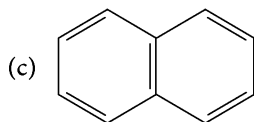
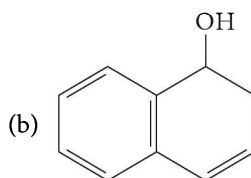
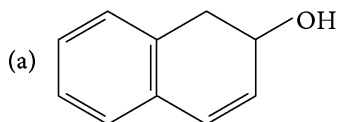
Straight Objective Type Questions

Directions: This section contains multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

11. The major product obtained by the mononitration of $\text{C}_6\text{H}_5 - \text{NH} - \text{SO}_2 - \text{C}_6\text{H}_5$ is



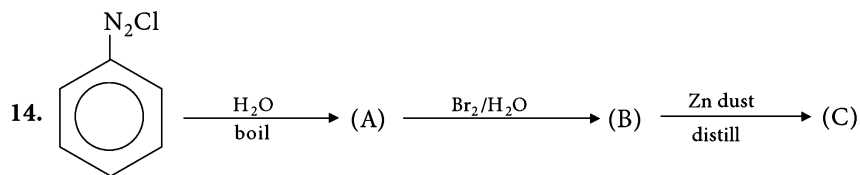
12. $\xrightarrow[\text{(ii) alc.KOH}]{\text{(i) NBS}}$ The major product obtained is



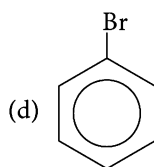
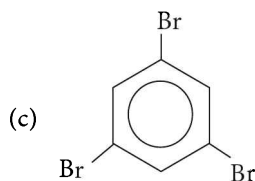
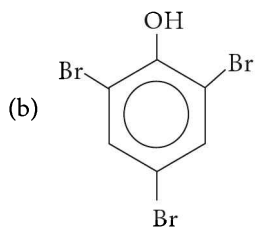
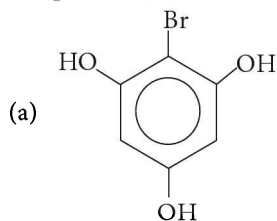
13. The IUPAC name of is

- (a) 4-chloro-3-cyanophenol
- (b) 3-Hydroxy-6-chlorobenzenecarbonitrile
- (c) 2-chloro-5-hydroxybenzene carbonitrile
- (d) 4-chloro-5-cyanophenol

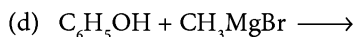
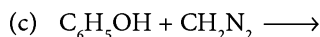
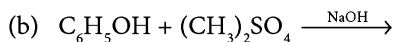
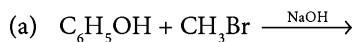
3.40 Benzene and Phenols



The product (C) is



15. Which of the following reactions will not give $\text{C}_6\text{H}_5\text{OCH}_3$ as the product?



Assertion–Reason Type Questions

Directions: Each question contains Statement-1 and Statement-2 and has the following 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

16. Statement 1

Friedel-Crafts acylation reaction of benzene with acetyl chloride in presence of anhydrous AlCl_3 gives only acetophenone and not polysubstituted product.

and

Statement 2

Friedel-Crafts acylation is an electrophilic substitution reaction.

17. Statement 1

p-Nitrophenol is a stronger acid than o-Nitrophenol.

and

Statement 2

Steric effect due to the presence of $-\text{NO}_2$ group at ortho position of $-\text{OH}$ group decreases the acidic strength of o-Nitrophenol.

18. Statement 1

Rates of nitration of benzene (C_6H_6) and hexadeuterobenzene (C_6D_6) are identical if the same nitrating mixture is used at the same temperature.

and

Statement 2

C – D bond is stronger than C – H bond.

19. Statement 1

Benzene is reduced to 1, 4-cyclohexadiene by reaction with sodium in liquid ammonia in the presence of ethanol.

and

Statement 2

The reaction involves the formation of benzene anion radical which takes up proton from ethanol to give finally the reduction product.

20. Statement 1

o-Hydroxy benzene sulphonic acid on heating to 373K changes to p-Hydroxybenzene sulphonic acid.

and

Statement 2

Sulphonation of phenol is a reversible process.



Linked Comprehension Type Questions

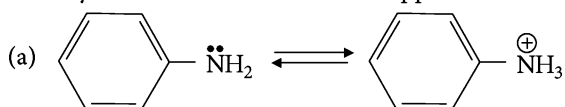
Directions: This section contains 2 paragraphs. Based upon the paragraph, 3 multiple choice questions have to be answered. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

Passage I

Aromatic electrophilic substitution reactions of benzene

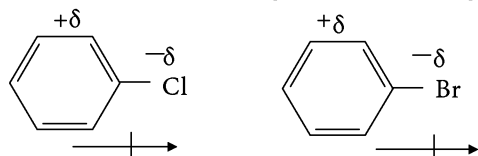
Aromatic electrophilic substitutions are characteristic reactions of a benzene ring. The most common examples of aromatic substitution reactions are nitration, halogenation and acylation. The use of an acid catalyst is characteristic of these reactions. The reactions proceed by an addition—elimination mechanism. A substituent group already present in the benzene ring has a marked directing influence on further substitution by an electrophile.

21. Identify the statement, which is not applicable in terms of an aromatic electrophilic substitution.



If the amino group is protonated, it changes from ortho and para directing to meta directing.

(b) The electron withdrawing effect of the halogen deactivates an aromatic ring towards electrophilic substitution.

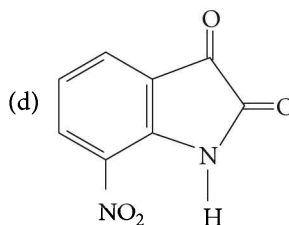
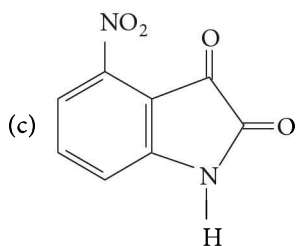
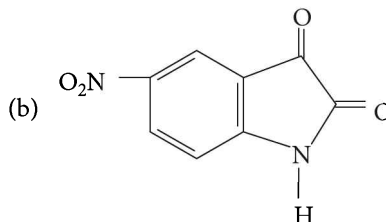
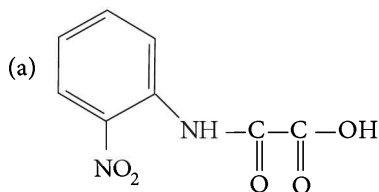
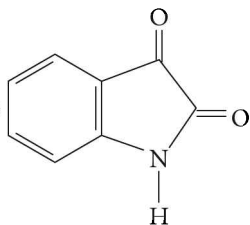


(c) The halogen atoms provide an interesting duality in their effect on electrophilic aromatic substitution.

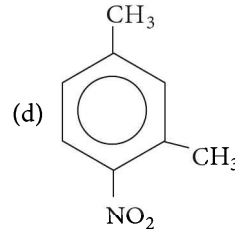
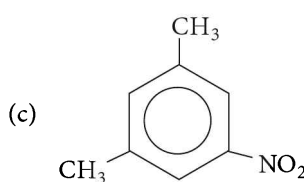
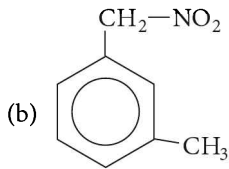
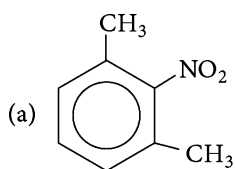
(d) In the aromatic electrophilic substitution reaction, the loss of a proton occurs to form the final product in the rate determining step.

3.42 Benzene and Phenols

22. The major product of mono nitration of is



23. When meta xylene is subjected to nitration, the major mononitrated product obtained is



Passage II

Phenols are useful organic compounds that can be used for the preparation of a wide variety of organic compounds such as salicylaldehyde, salicylic acid, picric acid, phenolphthalein, bakelite etc. Phenols are acidic due to the greater stability of phenoxide ion by resonance. Since -OH group is a highly activating group, phenols undergo electrophilic substitution reaction much more readily than benzene.

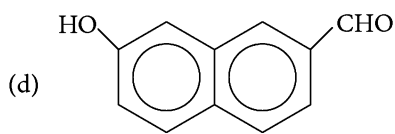
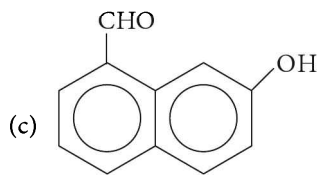
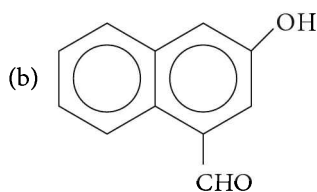
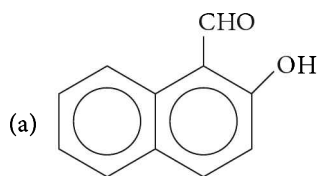
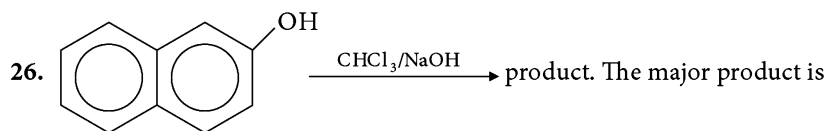
24. The product formed when phenol is heated with salicylic acid in the presence of phosphoryl chloride is

- (a) aspirin
(c) anisole

- (b) salol
(d) gallic acid

25. Which of the following statements is not correct?

- (a) Picric acid forms charge transfer complexes known as picrates with polynuclear aromatic hydrocarbons.
(b) o-Fluorophenol is a weaker acid than o-chlorophenol.
(c) p-cresol when treated with bromine water gives a dibromide derivative.
(d) 1-Naphthol when treated with benzene diazonium chloride in alkaline medium undergoes coupling at 2-position.



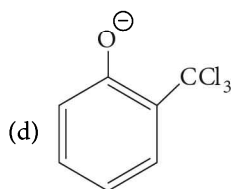
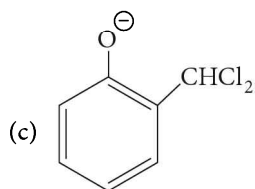
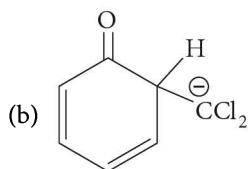
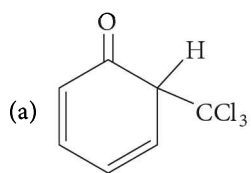
Multiple Correct Objective Type Questions

Directions: Each question in this section has four suggested answers of which ONE OR MORE answers will be correct.

27. Which of the following statement(s) regarding ortho and para nitrophenol is/are correct?

- (a) o-Nitrophenol is less soluble in water than p-nitrophenol.
- (b) o-Nitrophenol is more acidic than p-nitrophenol.
- (c) o-Nitrophenol is steam volatile while p-nitrophenol is not.
- (d) o-Nitrophenol has higher melting point than p-nitrophenol.

28 Which of the following species are involved in the reaction of phenol with chloroform and alkali to form salicylaldehyde?



29. The deactivating as well as meta directing group(s) among the following is/are

- (a) $-\text{CH}_2\text{Cl}$
- (b) $-\text{CCl}_3$
- (c) $-\text{NR}_3^+$
- (d) $-\text{C}_6\text{H}_5$

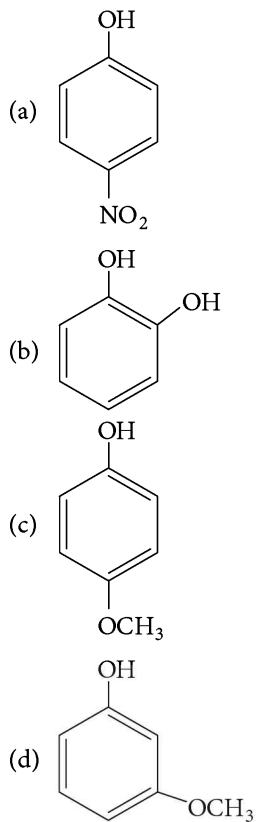


Matrix-Match Type Question

Directions: Match the elements of Column I to elements of Column II. There can be single or multiple matches.

30.

Column I



Column II

(p) More acidic than phenol

(q) Less acidic than phenol

(r) +R effect

(s) -I effect

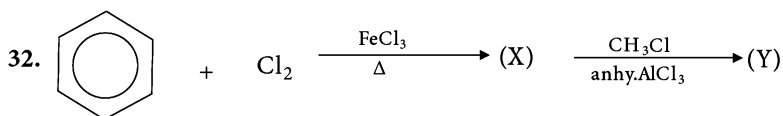
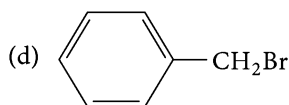
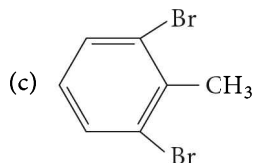
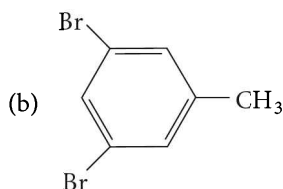
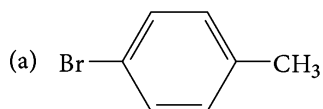
IIT ASSIGNMENT EXERCISE



Straight Objective Type qUESTIONS

Directions: This section contains multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

31. Toluene on bromination in presence of light yields



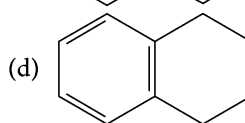
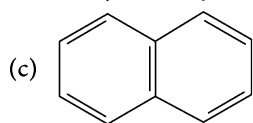
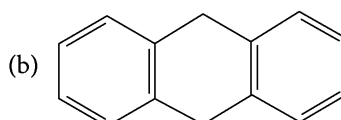
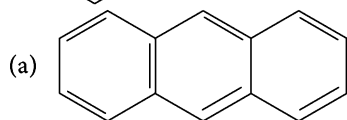
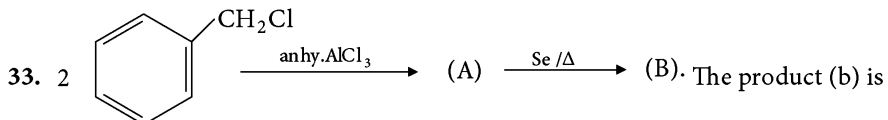
(Y) is

(a) a mixture of ortho and para dichlorobenzenes.

(b) a mixture of ortho, meta and para dichlorobenzenes.

(c) a mixture of ortho and para chlorotoluenes.

(d) a mixture of ortho, meta and para chlorotoluenes.



34. The most strongly deactivating substituent in electrophilic aromatic substitution is

(a) -F

(b) -C≡N

(c) $-\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{OH} \end{array}$

(d) -CF₃

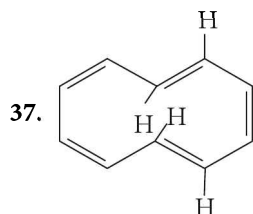
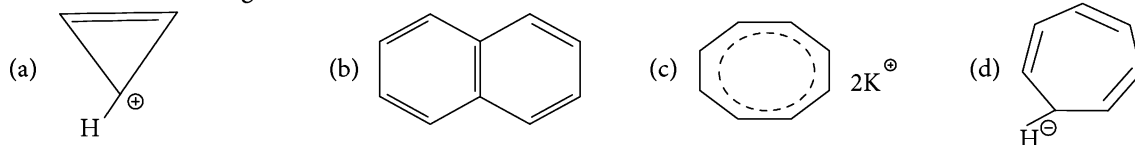
35. The wrong statement relating to the influence of substituents on aromatic electrophilic substitution reactions is

(a) The rate determining step in an electrophilic substitution is the one which leads to the formation of an arenium ion.

3.46 Benzene and Phenols

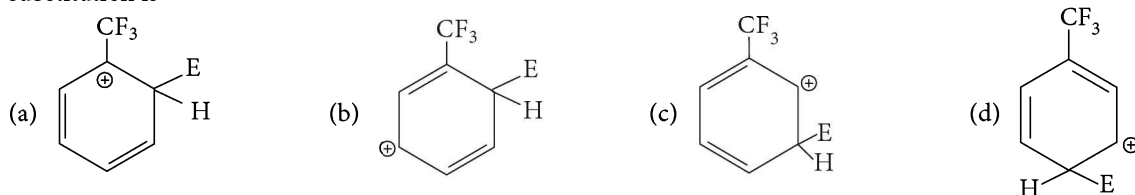
- (b) Electron releasing groups make the transition state more stable and the transition state resembles the arenium ion.
- (c) The arenium ion is a highly energetic intermediate and the step that leads to it is a highly exothermic step.
- (d) An electron withdrawing substituent makes the arenium ion less stable and the transition state leading to such an arenium ion is less stable.

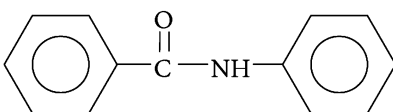
36. Which of the following structures is not aromatic?

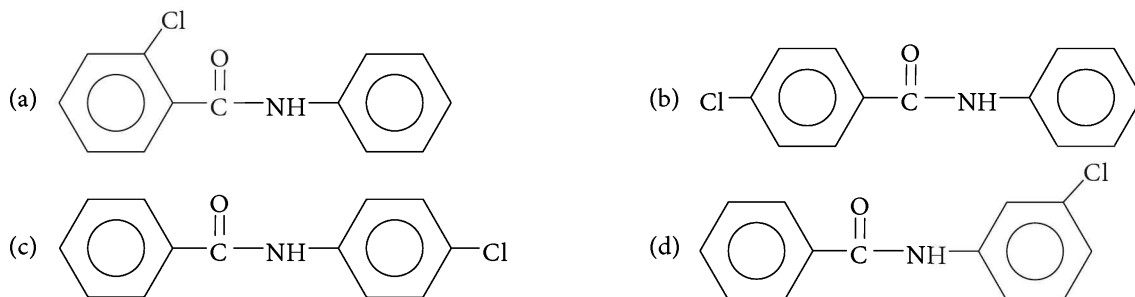


The molecule given above is

- (a) aromatic
 - (b) non-aromatic because it does not satisfy Huckel rule of aromaticity.
 - (c) non-aromatic because its electron distribution is not uniform.
 - (d) non-aromatic because there are two trans double bonds which force the molecule out of planarity.
38. A highly unstable contributor to the resonance structure when trifluoromethyl benzene undergoes electrophilic substitution is

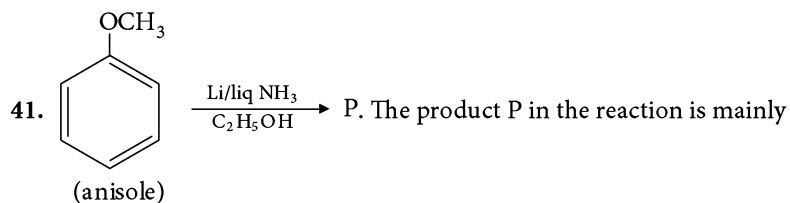


39. The major monochloro derivative formed by the reaction of  with $\text{Cl}_2/\text{AlCl}_3$ is

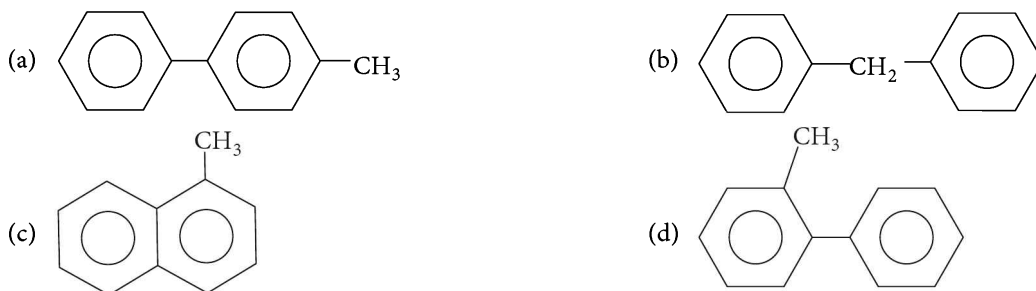
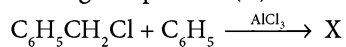


40. The products formed when toluene is treated with ozone and the product is subjected to reduction with zinc dust and water are

- (a) Glyoxal and acetaldehyde
- (b) Glyoxal and acetone
- (c) Formaldehyde and acetaldehyde
- (d) Glyoxal and methyl glyoxal



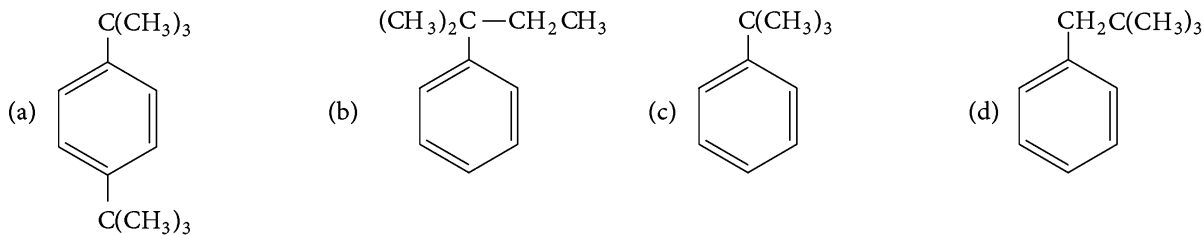
42. The organic product (X) formed in the following reaction is



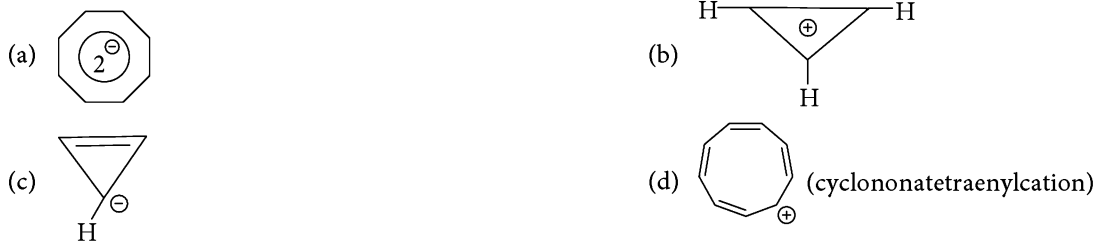
43. Electrophilic substitution such as halogenation takes place most readily in the case of



44. Neopentyl bromide reacts with benzene under Friedel-Crafts conditions to give mainly

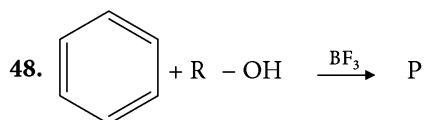
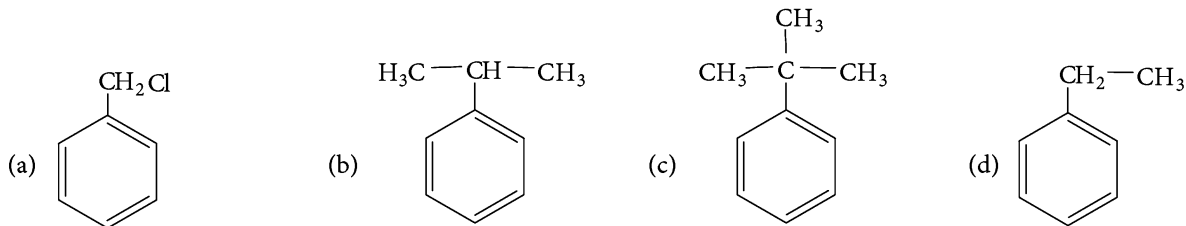


45. Which of the following species/molecule is antiaromatic

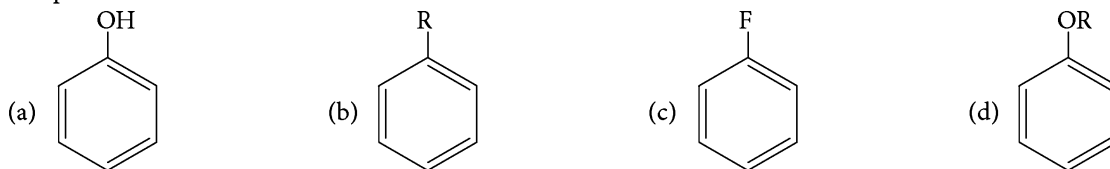


3.48 Benzene and Phenols

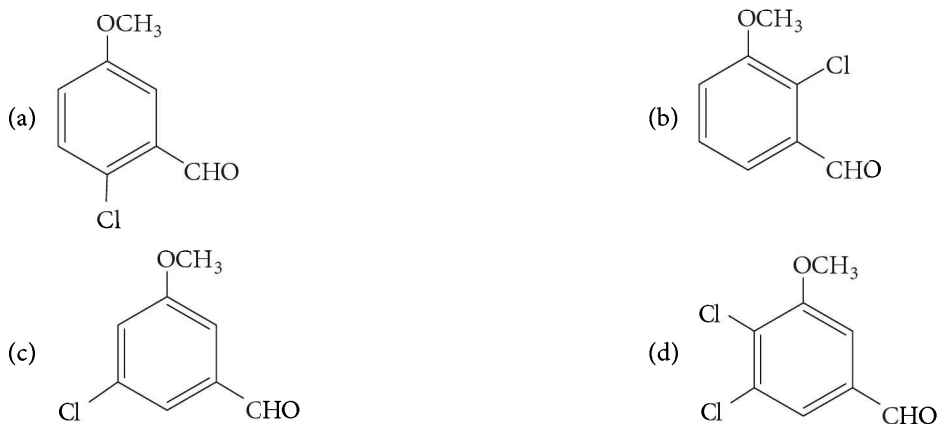
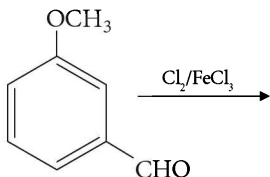
46. Nitrobenzene is prepared by treating benzene with a mixture of con. HNO_3 and $\text{con. H}_2\text{SO}_4$ (nitrating mixture). In the nitrating mixture, HNO_3 acts as a/an
 (a) base (b) acid (c) catalyst (d) oxidizing agent
47. Which of the following compound will not give benzoic acid on refluxing with alkaline KMnO_4 followed by acidification?



The product P in the above reaction is



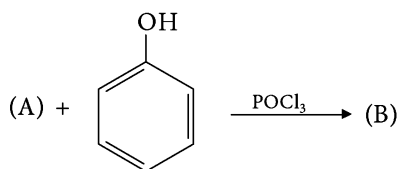
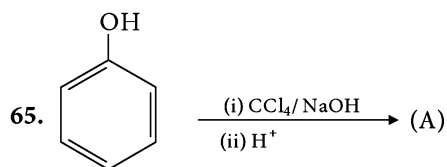
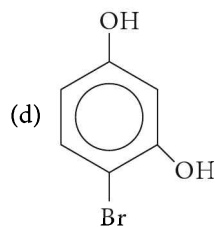
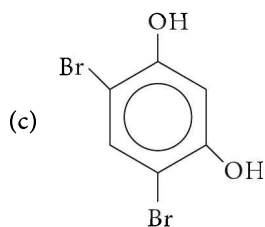
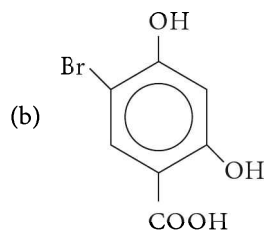
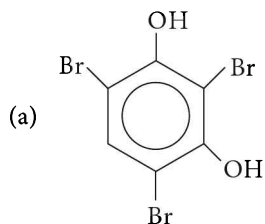
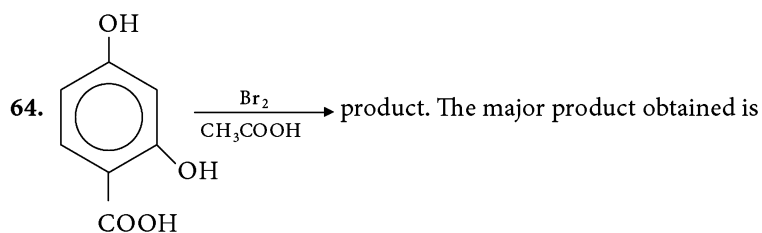
49. The major chlorination product of the following reaction is



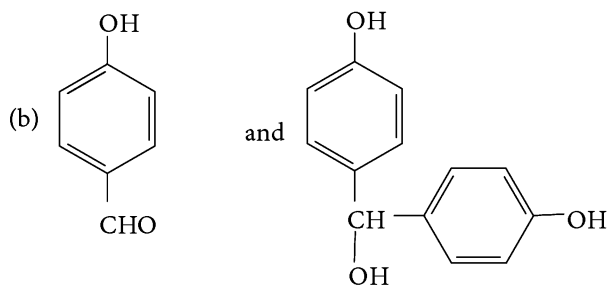
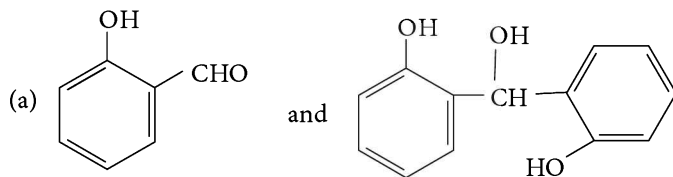
50. When benzene is treated with chlorine under the influence of ultra violet light
 (a) chlorobenzene is obtained (b) benzyl chloride is obtained
 (c) 1,4-dichlorobenzene is obtained (d) benzene loses its aromaticity
51. Phenol is more acidic than ethanol because
 (a) greater resonance stabilization of phenoxide ion (b) phenol has greater H-bonding than ethanol
 (c) phenol has larger molar mass (d) phenol has higher boiling point than ethanol

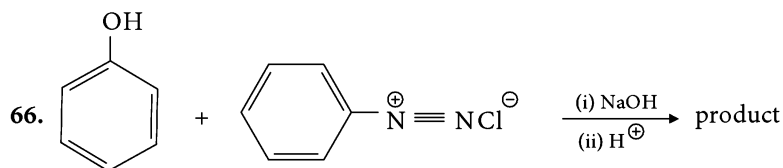
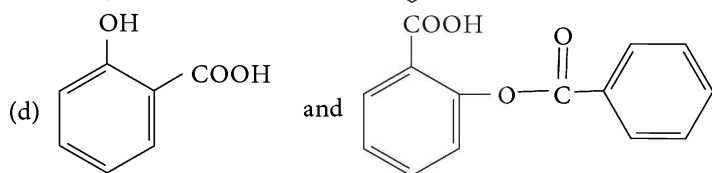
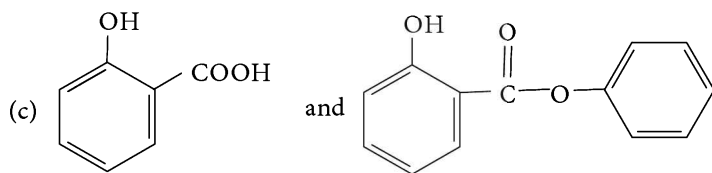
52. Phenol can be distinguished from ethanol by all reagents except
 (a) NaOH (b) neutral FeCl_3 (c) Na (d) bromine water
53. Phenol + phthalic anhydride $\xrightarrow[\text{heat}]{\text{conc. H}_2\text{SO}_4}$ (X). The product (X) is used as
 (a) an antipyretic (b) a catalyst
 (c) an indicator (d) a laboratory reagent
54. The product(s) formed when phenol is heated above 150°C with CH_3COCl and anhydrous aluminium chloride is/are
 (a) a mixture of o- and p-cresol (b) acetophenone
 (c) a mixture of o- and p-hydroxy acetophenone (d) o-hydroxy benzoyl chloride
55. Phenol on warming with conc. H_2SO_4 and NaNO_2 gives brown colour. On adding NaOH solution, the colour changes to green or blue. This test is called
 (a) Victor Meyer's test (b) Libermann's test
 (c) Lucas test (d) Baeyer's test
56. When phenol is exposed to air for a long period or treated with chromic acid, it is oxidized to
 (a) p-benzoquinone (b) glyoxal (c) CO_2 (d) oxalic acid
57. The increasing order of acidic strength among p-methoxyphenol, p-cresol and p-nitrophenol is
 (a) p-cresol < p-methoxyphenol < p-nitrophenol
 (b) p-methoxyphenol < p-cresol < p-nitrophenol
 (c) p-cresol < p-nitrophenol < p-methoxyphenol
 (d) p-methoxyphenol < p-nitrophenol < p-cresol
58. Sodium phenoxide when heated with CO_2 under pressure gives sodium salicylate. This reaction is known as
 (a) Reimer-Tiemann reaction
 (b) Schotten-Baumann reaction
 (c) Williamson's synthesis
 (d) Kolbe's reaction
59. The compound (A) when treated with methanol and few drops of conc. H_2SO_4 gives the smell of oil of winter green. The compound (A) is
 (a) phenol (b) benzene
 (c) p-cresol (d) salicylic acid
60. $\text{C}_6\text{H}_6 + \text{CH}_3 - \text{CH} = \text{CH}_2 \xrightarrow[523\text{K}]{\text{H}_3\text{PO}_4} (\text{X}) \xrightarrow[403\text{K}]{\text{O}_2/\text{OH}^-} (\text{Y}) \xrightarrow{\text{H}^+/\text{H}_2\text{O}} (\text{Z})$. (Z) contains
 (a) cumene (b) acetone
 (c) both phenol and acetone (d) cinnamaldehyde
61. Which of the following statements is correct about phenols?
 (a) Electron releasing groups increases acidic character
 (b) Electron withdrawing substituents decreases acidic character
 (c) Phenol is less resonance stabilized than phenoxide ion.
 (d) Phenol turns red litmus blue
62. $\text{C}_6\text{H}_5\text{OH} + \text{C}_6\text{H}_5\text{COCl} \rightarrow \text{C}_6\text{H}_5\text{OCOC}_6\text{H}_5 + \text{HCl}$. This reaction is called
 (a) Schotten-Baumann reaction (b) Perkin reaction
 (c) Schmidt reaction (d) Claisen reaction
63. Phenol + bromine water $\rightarrow$ white precipitate. The product is
 (a) o-bromophenol (b) p-bromophenol
 (c) a mixture of (a) and (b) (d) 2,4,6-tribromophenol

3.50 Benzene and Phenols

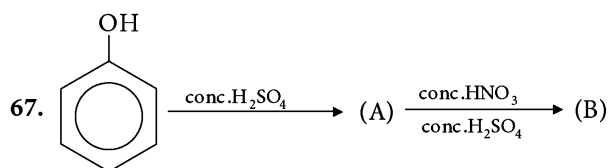
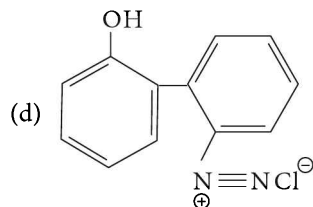
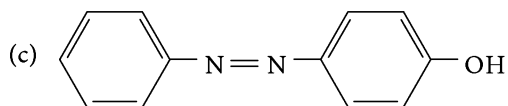
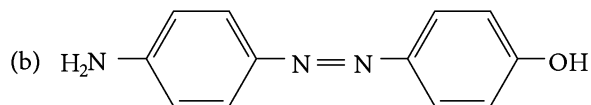
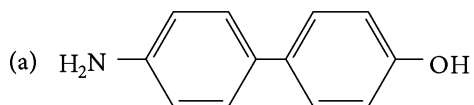


(a) and (b) respectively are

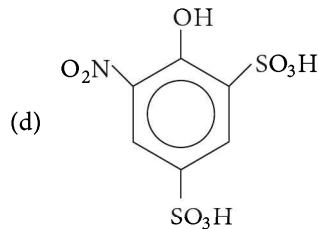
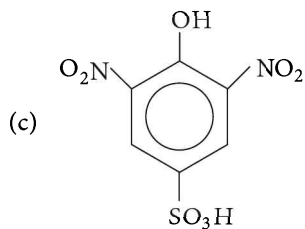
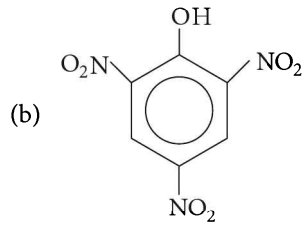
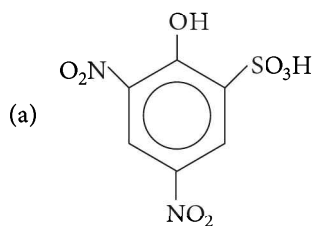




The structure of the product is

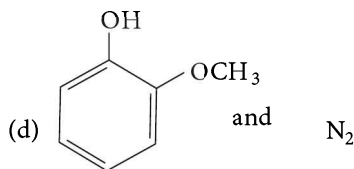
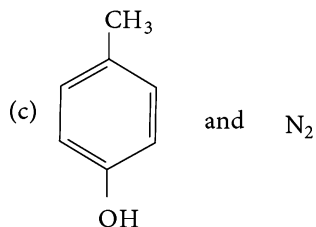
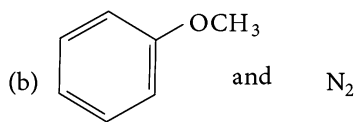
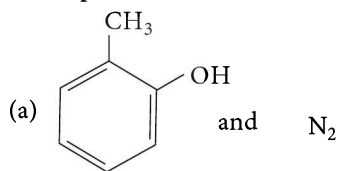


The product (b) is

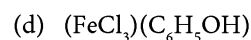
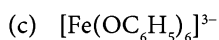
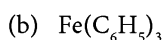
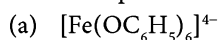


3.52 Benzene and Phenols

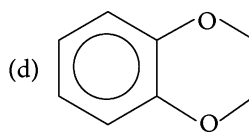
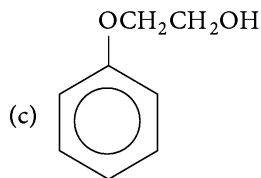
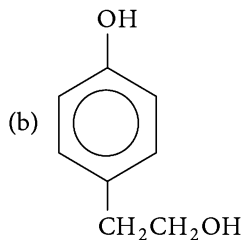
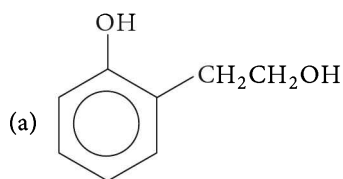
68. When phenol reacts with diazomethane (CH_2N_2), the products formed are



69. When phenol reacts with dilute neutral FeCl_3 solution, a violet colouration is produced. The structure of the violet coloured species is



70. When phenol is treated with ethylene oxide in presence of acid the major product is



71. The maximum number of benzenoid aromatic isomeric compounds having the molecular formula $\text{C}_7\text{H}_8\text{O}$ are

(a) 6

(b) 5

(c) 4

(d) 3

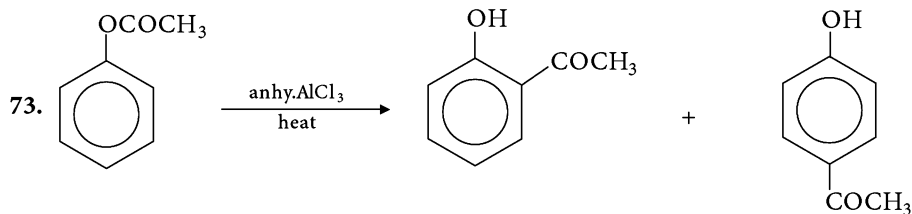
72. When phenol is treated with benzoyl chloride in the presence of aqueous NaOH solution, an ester of phenol is formed. The reaction is known as

(a) Fischer's esterification

(b) Kolbe's reaction

(c) Coupling reaction

(d) Schotten-Baumann reaction



The reaction is called

(a) Fries rearrangement

(b) Beckmann rearrangement

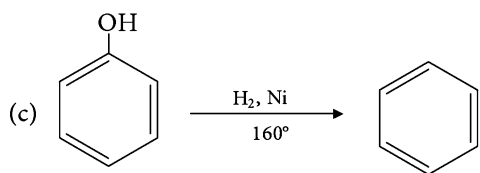
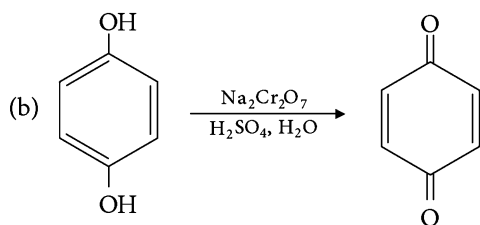
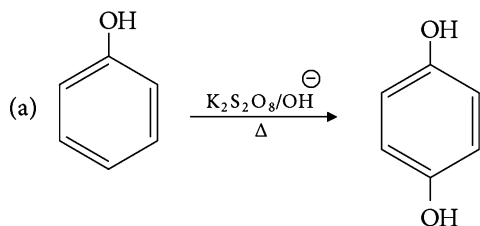
(c) Hoffmann's rearrangement

(d) pinacol-pinacolone rearrangement

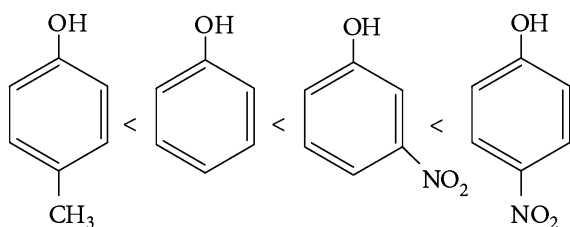
74. Phenol reacts with dilute HNO_3 at 40°C to give a mixture of ortho and para nitro phenols. They are readily separated by

- filtration
- solvent extraction
- steam distillation
- fractional crystallization

75. Identify the reaction/statement which is not correctly represented



(d) The order of acidity of phenols can be represented as



76. Identify the wrong statement among the following related to phenol.

- Phenol is a weaker acid than carbonic acid.
- When distilled with zinc, phenol gives benzene.
- Among the three isomers of nitrophenol, the one that is least soluble in water is p-nitrophenol.
- Formation of phenol from chlorobenzene is an example of nucleophilic aromatic substitution.

77. Which of the following reagents cannot be used to distinguish between benzyl alcohol and phenol?

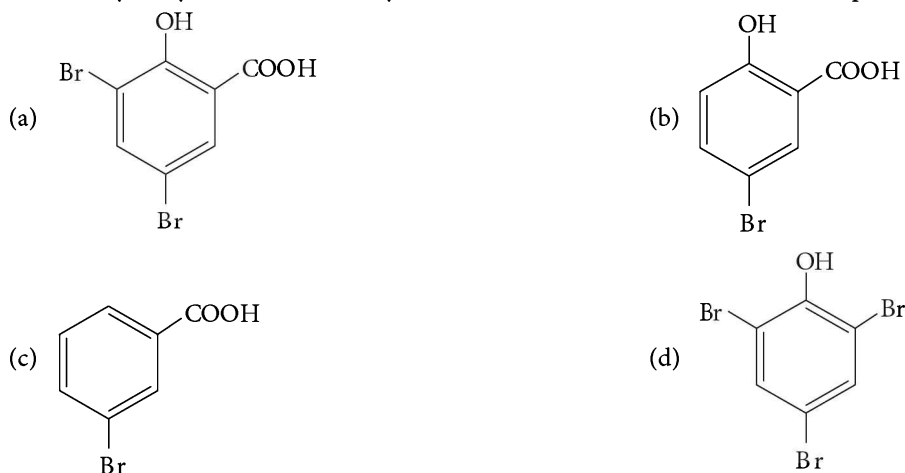
- FeCl_3
- NaOH (aqueous)
- Br_2/CCl_4
- NaHCO_3 solution

78. The reaction of phenol with $(\text{CH}_3)_2\text{SO}_4$ (dimethyl sulphate) in alkaline solution gives

- o-cresol
- p-cresol
- a mixture of o and p-cresol
- anisole

3.54 Benzene and Phenols

79. When 2-hydroxybenzoic acid (salicylic acid) is treated with bromine water, the product formed is



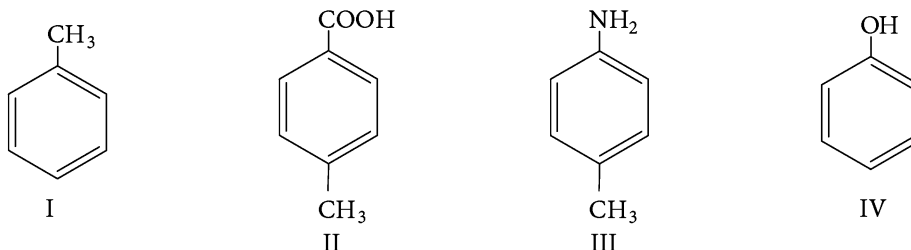
80. An organic compound having the molecular formula C_7H_8O is insoluble in $NaHCO_3$ solution but dissolves in aqueous $NaOH$. When treated with bromine water the compound rapidly forms a precipitate having the molecular formula $C_7H_5OBr_3$. The organic compound is

- (a) o-cresol (b) m-cresol
(c) p-cresol (d) anisole

81. The compound which gives phthalic acid on vigorous oxidation with alkaline $KMnO_4$ is



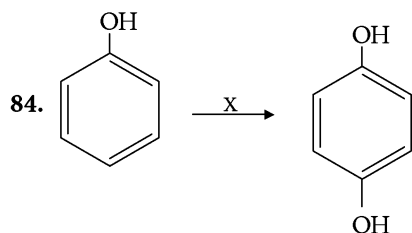
82. The correct order of decreasing reactivity towards chlorination among the following compounds is



- (a) $IV > I > III > II$ (b) $IV > III > I > II$ (c) $III > IV > I > II$ (d) $III > IV > II > I$

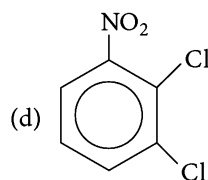
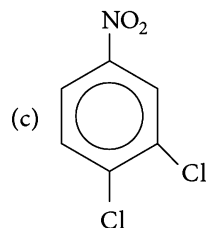
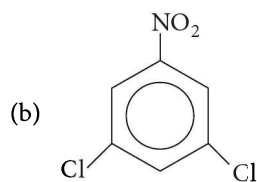
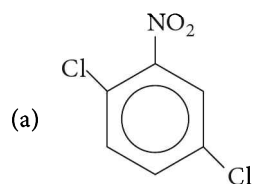
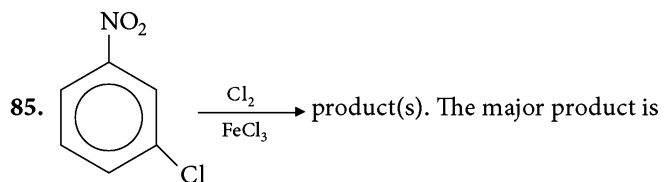
83. A compound having the molecular formula $C_6H_4Br_2$ when heated with nitrating mixture gave two isomers of the mononitro derivative. The compound is

- (a) 1,2-Dibromobenzene (b) 1,3-Dibromobenzene
(c) 1,4-Dibromobenzene (d) either 1,3 or 1,4-dibromobenzene



The reagent used for the above conversion is

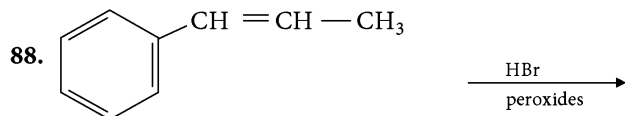
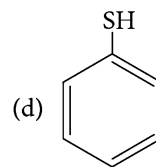
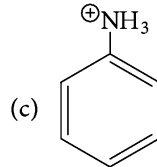
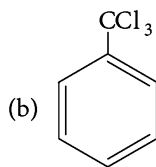
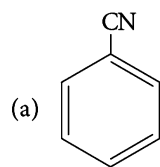
- (a) $\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ (b) Aqueous KOH (c) $\text{K}_2\text{S}_2\text{O}_8/\text{OH}^-$ (d) HCHO/OH^-



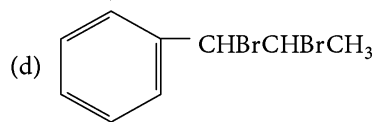
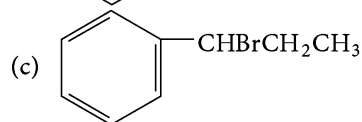
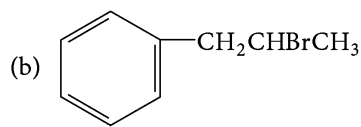
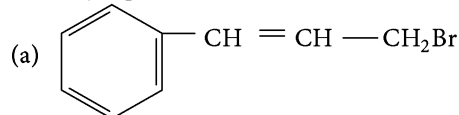
86. The carboxyl group is displaced when salicylic acid undergoes

- (a) bromination (b) nitration (c) either (a) or (b) (d) dehydration

87. Which of the following compound gives mainly ortho and para nitro derivatives when treated with nitrating mixture?

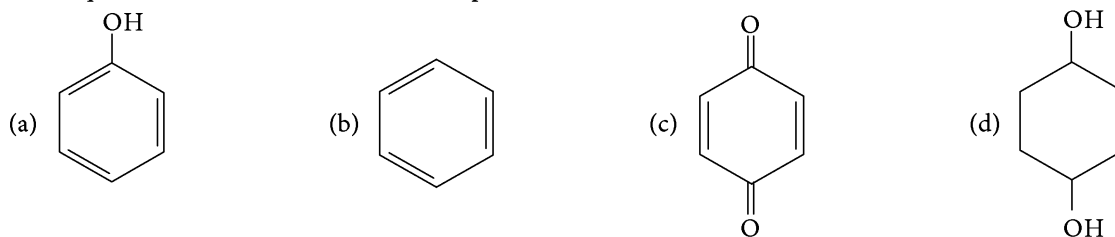


The major product formed is



3.56 Benzene and Phenols

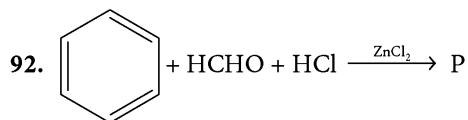
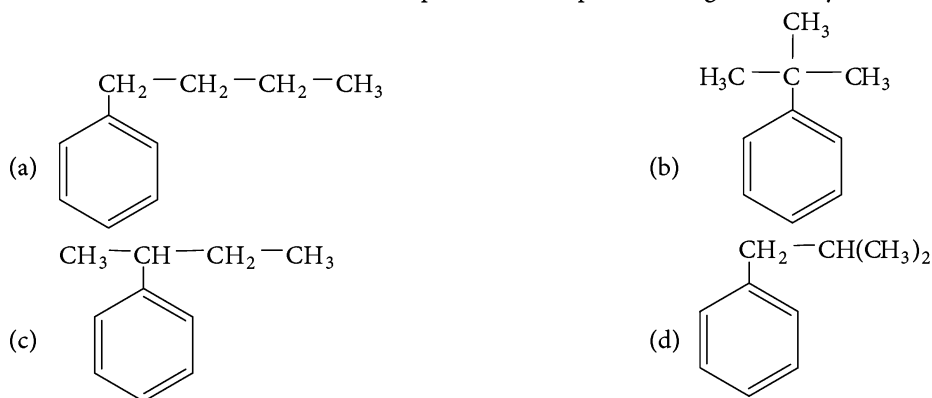
89. When quinol is distilled with zinc dust, the product formed is



90. The conversion of cumene hydroperoxide to phenol and acetone involves

- (a) an oxidative process (b) a 1,2-phenyl migration
(c) Friedel-Crafts alkylation (d) keto-enol tautomerism

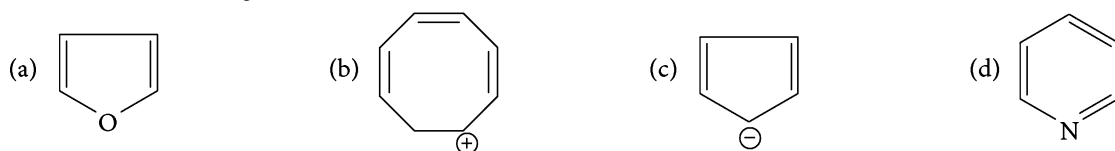
91. Reaction of benzene with isobutene in presence of sulphuric acid gives mainly



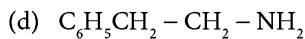
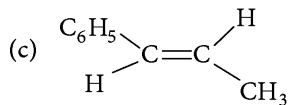
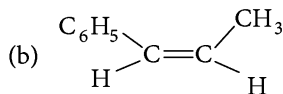
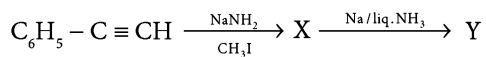
The organic compound P formed in the above reaction is



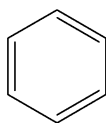
93. Which of the following does not exhibit aromatic character?



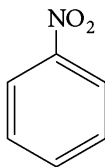
94. The product Y in the following sequence of reaction is



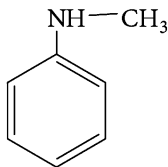
95. The correct decreasing order of reactivity towards electrophilic substitution reaction of the following compounds is



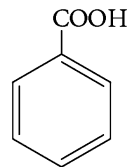
I



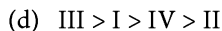
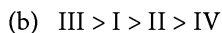
II



III

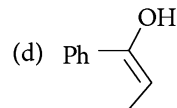
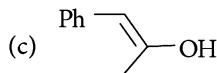
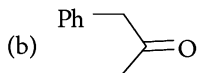
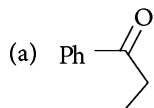


IV

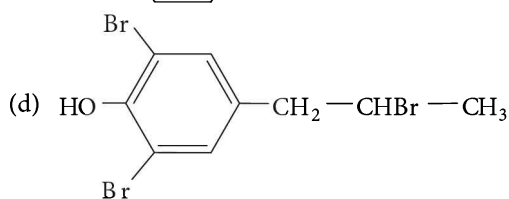
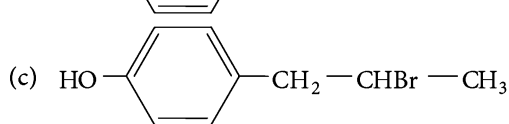
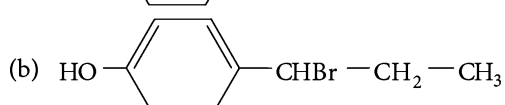
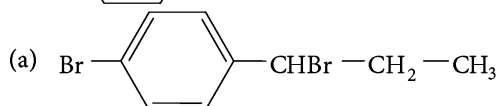
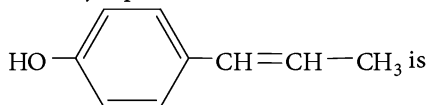


96. $\text{Ph} - \text{C} \equiv \text{C} - \text{Me} \xrightarrow{\text{Hg}^{2+}/\text{H}_3\text{O}^+}$ product

The major product formed in the above reaction is

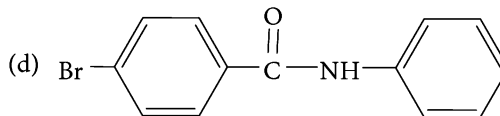
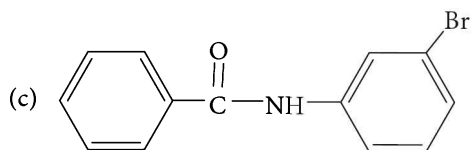
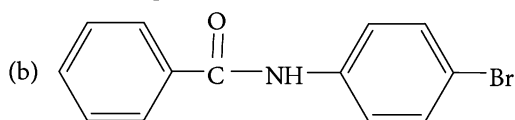
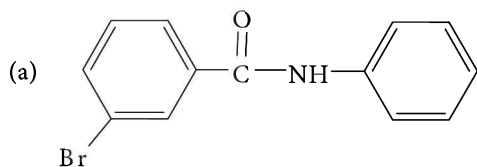


97. The major product formed when HBr reacts with



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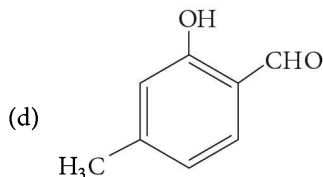
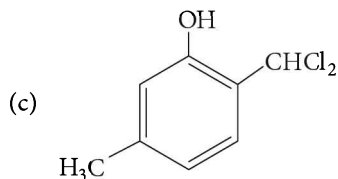
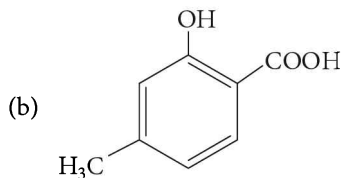
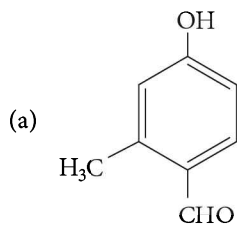
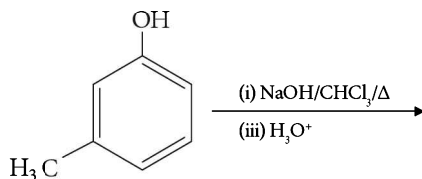
98. The major product formed by the reaction of N-phenylbenzamide with Br_2/Fe is



99. An organic compound X having the molecular formula $\text{C}_7\text{H}_8\text{O}$ is soluble in NaOH . When treated with bromine water, X gives a compound Y having the molecular formula $\text{C}_7\text{H}_6\text{OBr}_2$. The oxidation of compound X with alkaline KMnO_4 followed by acidification gives Z (MF: $\text{C}_7\text{H}_6\text{O}_3$) which is steam volatile. The compound X is

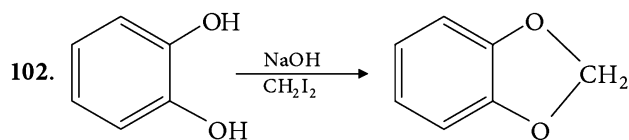
- (a) anisole (b) benzyl alcohol (c) o-cresol (d) p-cresol

100. The major product formed in the following reaction is



101. The maximum number of structural isomers possible when one hydrogen atom in diphenyl methane is substituted by a chlorine atom is

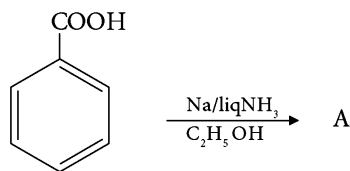
- (a) 8 (b) 4 (c) 6 (d) 3



The above reaction can be considered as an example of

- (a) Wittig reaction (b) Ullmann reaction
(c) Williamson's reaction (d) Kolbe-Schmidt reaction

103. The major product A in the following reaction is



- (a)
- (b)
- (c)
- (d)

104. The product formed when phenol is treated with H_2/Ni at 475°C is

- (a) Cyclohexanol (b) Toluene
(c) Cyclohexane (d) Cyclopentane

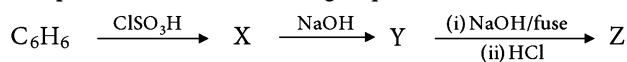
105. Which of the following reactions of phenol is used for its quantitative estimation?

- (a) Reaction with bromine (b) Reaction with con. HNO_3
(c) Reaction with FeCl_3 solution (d) Reaction with CO_2

106. The reaction of 4-hydroxybenzene sulphonic acid with excess bromine water gives

- (a) 3-Bromo-4-hydroxybenzenesulphonic acid
(b) 3,5-Dibromo-4-hydroxybenzenesulphonic acid
(c) 2,4,6-Tribromophenol
(d) 4-Bromobenzenesulphonic acid

107. The product Z in the following sequence of reaction is



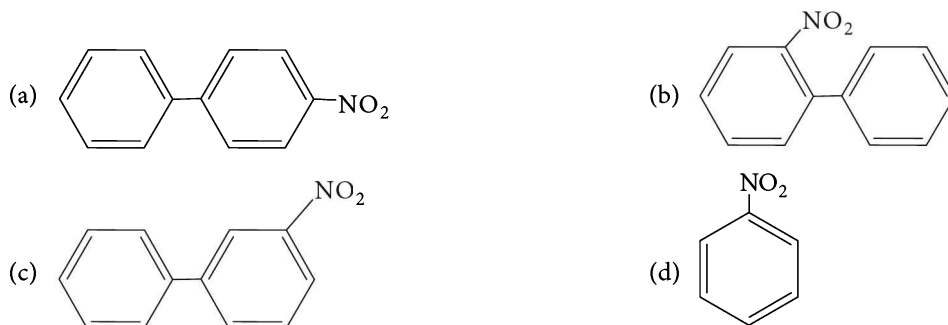
- (a)
- (b)
- (c)
- (d)

108. Reaction of benzene with 1,2-dichloroethane in presence of anhydrous aluminium chloride will give

- (a)
- (b)
- (c)
- (d)

3.60 Benzene and Phenols

109. Mononitration of biphenyl by treating with nitrating mixture gives mainly



110. $\text{C}_6\text{H}_5\text{C} \equiv \text{CH} \xrightarrow[\text{(3) Na/liq. NH}_3]{\text{(1) CH}_3\text{MgBr, (2) C}_6\text{H}_5\text{CH}_2\text{Cl}}$ (A). The product (A) is



Assertion-Reason Type Questions

Directions: Each question contains Statement-1 and Statement-2 and has the following 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

111. Statement 1

Nitrobenzene and aniline do not undergo Friedel-Crafts reaction with $\text{CH}_3\text{CH}_2\text{Cl} / \text{AlCl}_3$
and

Statement 2

$-\text{NO}_2$ and $-\text{NH}_2$ groups combine with AlCl_3 to form adducts.

112. Statement 1

$\text{C}_6\text{H}_5 - \text{CH}_2 - \text{CH}_3$ (ethyl benzene) on reaction with NBS gives mainly $\text{C}_6\text{H}_5 - \text{CHBr} - \text{CH}_3$.
and

Statement 2

The reaction with NBS proceeds by free radical mechanism.

113. Statement 1

Salicylic acid may be prepared from sodium phenoxide by Kolbe-Schmidt reaction using carbon dioxide.
and

Statement 2

Kolbe-Schmidt reaction is a nucleophilic substitution reaction.

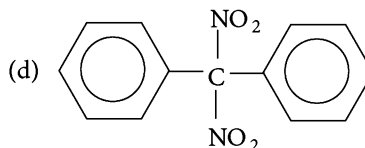
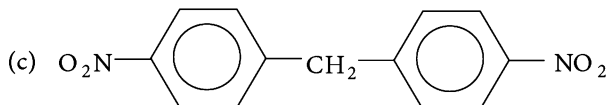
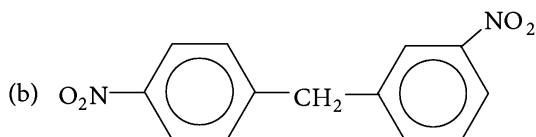
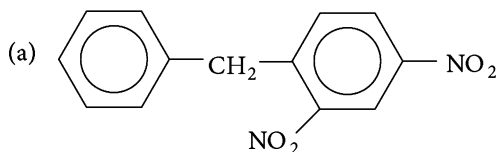
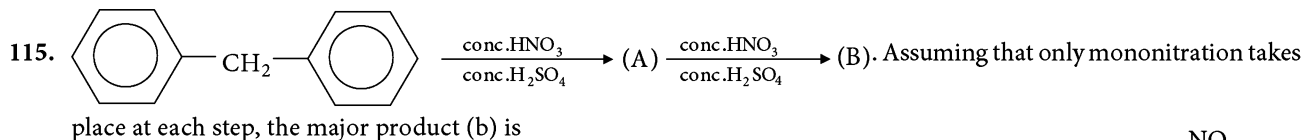
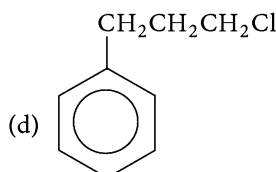
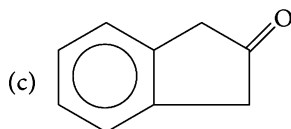
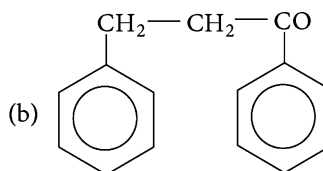
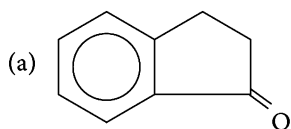
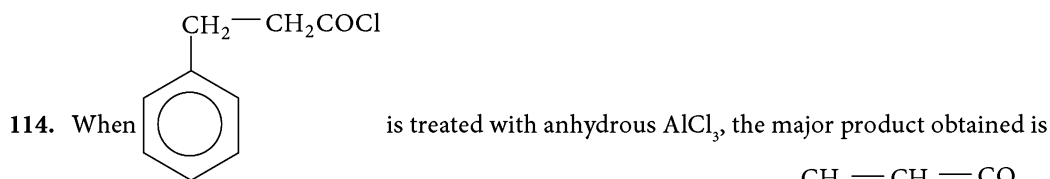


Linked Comprehension Type Questions

Directions: This section contains 1 paragraph. Based upon the paragraph, 3 multiple choice questions have to be answered. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

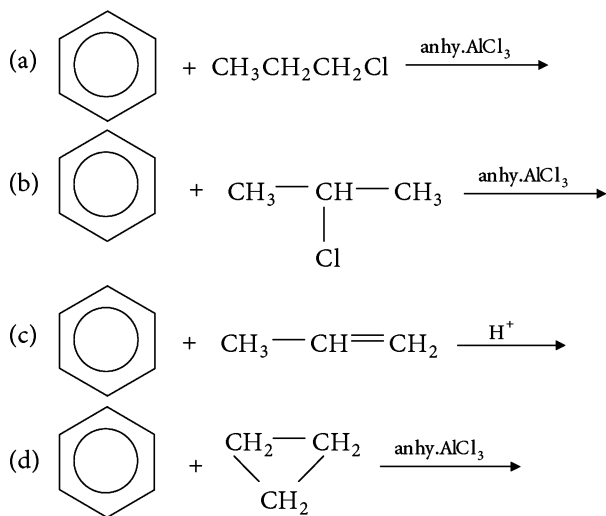
Passage I

Benzene and its derivatives undergo a variety of electrophilic substitution reactions like halogenation, nitration, sulphonation, Friedel-Crafts alkylation, Friedel-Crafts acylation etc. The substituents on the ring determine the reactivity of the reaction and the orientation of the entering electrophile. The substituents can be electron donating and electron withdrawing and could orient the entering electrophile to ortho, meta or para positions.



3.62 Benzene and Phenols

116. Which of the following reactions will give n-propyl benzene as the major product?



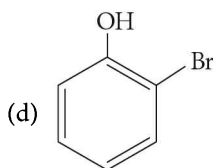
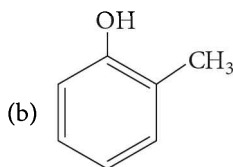
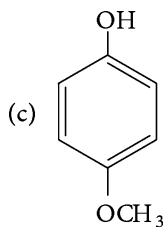
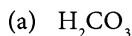
Multiple Correct Objective Type

Directions: Each question in this section has four suggested answers of which ONE OR MORE answers will be correct.

117. Reaction of nitrobenzene with chlorine in presence of FeCl_3 gives m-chloronitrobenzene as the major product. Which of the following statement(s) is/are correct regarding the formation of the meta isomer?

- (a) Nitro group increases the electron density at the meta position of the benzene ring.
- (b) Nitro group withdraws electron mainly from ortho and para position by resonance and hence meta position becomes position of comparatively higher electron density
- (c) The intermediate arenium ion formed by the initial attack of Cl^+ at the meta position is more stable compared to that formed by attack at ortho and para positions.
- (d) Loss of aromaticity occurs when Cl^+ attacks at the ortho and para positions and not at the meta position.

118. Which of the following is/are more acidic than phenol?



119. Which of the following will give 2,4,6-tribromophenol when treated with bromine water?

- (a) Salicylic acid
- (c) p-Chlorophenol

- (b) 4-Hydroxybenzenesulphonic acid
- (d) Catechol



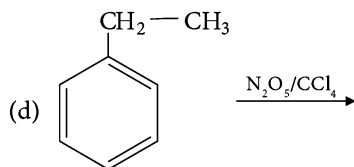
Matrix-Match Type Question

Directions: Match the elements of Column I to elements of Column II. There can be single or multiple matches.

120.

Column I

- (a) Friedel-Crafts acylation
 (b) Reimer-Tiemann reaction
 (c) $\text{C}_6\text{H}_6 \xrightarrow{\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}/\text{AlCl}_3}$



Column II

- (p) Electrophilic substitution
 (q) Cumene
 (r) Nitronium ion
 (s) Dichlorocarbene
 (t) Rearrangement of carbocation

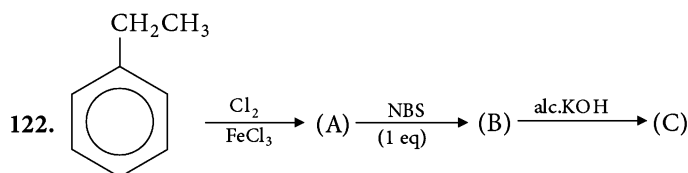
ADDITIONAL PRACTICE EXERCISE



Subjective Questions

121. Give, in the form of simple equations, the method of generation of electrophiles in the following aromatic electrophilic substitutions.

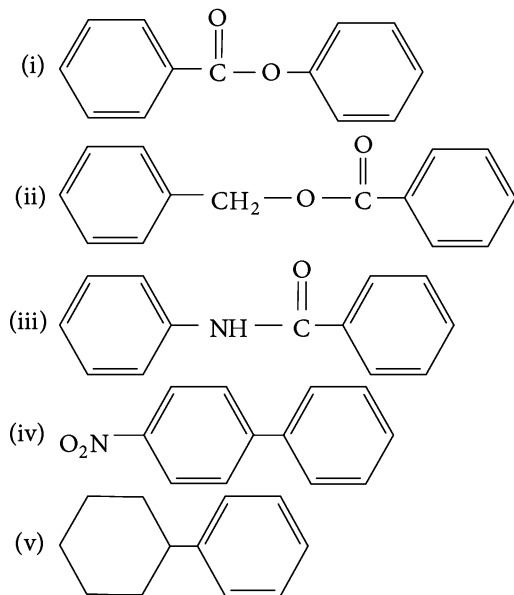
- (i) Sulphonation
- (ii) Friedel-Crafts alkylation
- (iii) Friedel-Crafts acylation



Identify the major products (a), (b) and (c).

123. Define and explain the term isotope effect. Does isotope effect have any influence on electrophilic aromatic substitution?

124. Give the major product of mono nitration of the following compounds. Justify each case.



125. Explain the following observation.

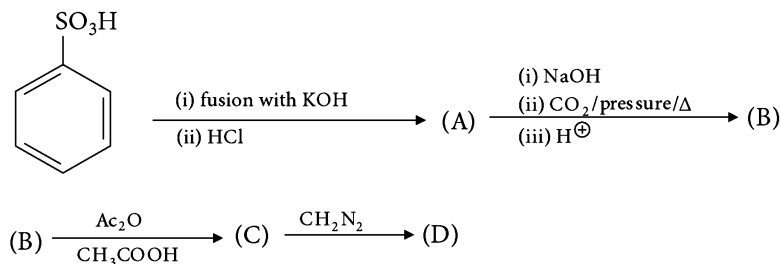
- (a) Cyclooctatetraene is not stable but when potassium is dissolved in cyclooctatetraene the dianion formed is very stable.
- (b) Cycloheptatrienone is stable, but cyclopentadienone is unstable and undergoes Diels-Alder reaction with itself.

126. Starting from benzene how will you prepare m-nitrobenzoic acid?

127. Write equations for the preparation of the following compounds from benzene.

- (a) ortho-nitrobenzoic acid or o-nitrobenzoic
- (b) 1-bromo-4-trichloromethyl benzene

128. Identify the lettered compounds (a)-(d).



129. Why is pyrrole a much weaker base than pyridine?

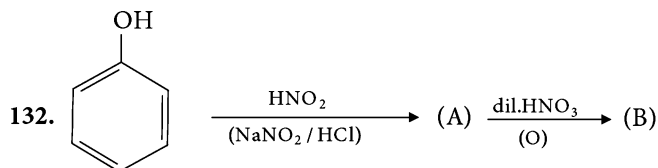
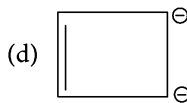
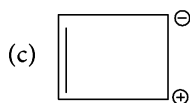
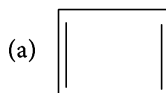
130. Why is ortho fluoro phenol a weaker acid than ortho chlorophenol?



Straight Objective Type Questions

Directions: This section contains multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

131. A four membered ring which is aromatic is



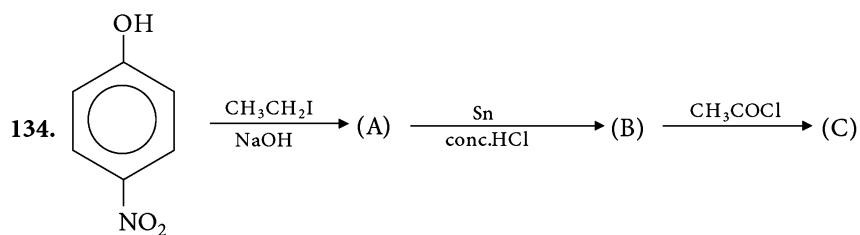
(A) and (b) are respectively

- (a) o-nitrophenol and o-nitrobenzoic acid.
- (b) p-nitrosophenol and p-nitrophenol
- (c) m-nitrosophenol and m-nitrophenol
- (d) p-nitrosophenol and p-aminophenol

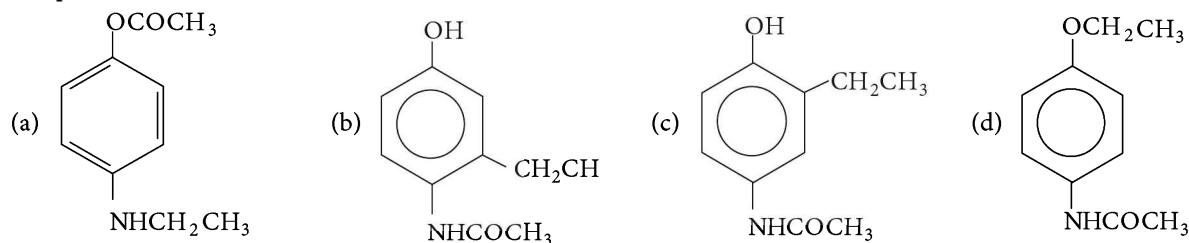
133. Identify the wrong statement.

- (a) Phenols are stronger acids than alcohols, but weaker than carboxylic acids
- (b) Phenols, being stronger acids, are soluble in aqueous NaOH solution and in saturated NaHCO_3 solution.
- (c) Phenols are acidic because of resonance stabilization of the phenoxide ion formed by ionization.
- (d) The pK_a of phenol is about 10.

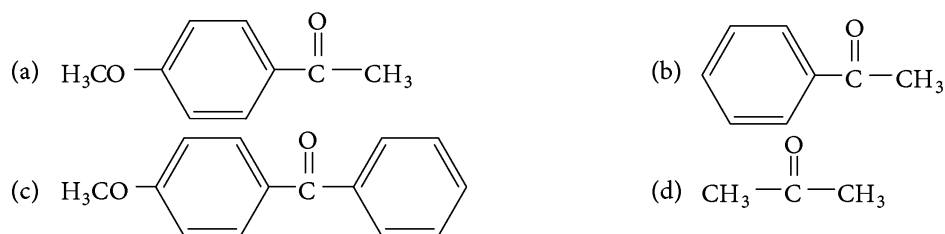
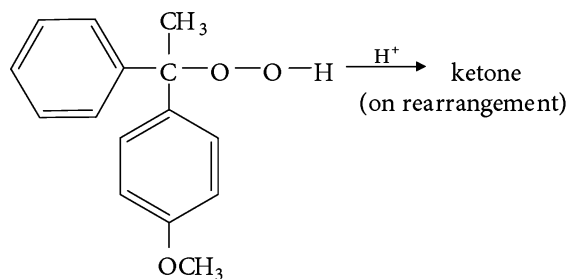
3.66 Benzene and Phenols



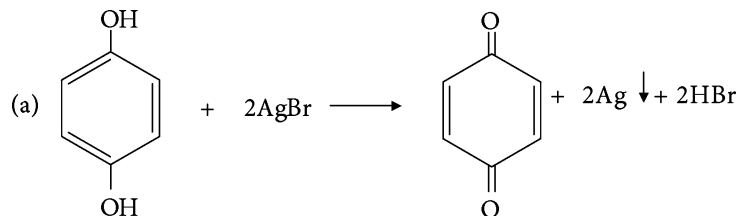
The product (c) is



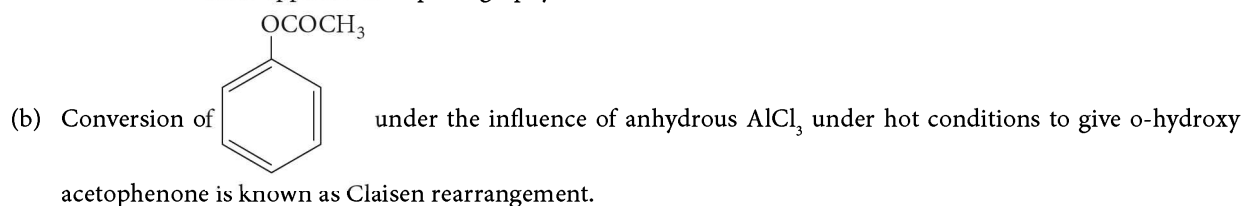
135. When the hydroperoxide shown below rearranges under acid conditions, the ketone obtained is mainly



136. Identify the statement or reaction which is correctly represented.



This reaction finds application in photography.



- (c) In the azodye test when phenyl diazonium chloride is reacted with phenol, the phenolic $-\text{OH}$ is replaced by the diazonium group.
 (d) Between phenol and cyclohexanol, the latter has a lower pK_a value.

137. Reimer-Tiemann reaction involves

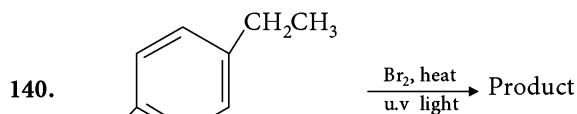
- (a) an aromatic nucleophilic substitution (b) a carbocation intermediate
 (c) a nucleophilic addition (d) a carbene intermediate

138. Phenol is less acidic than

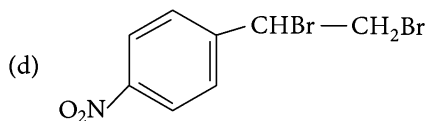
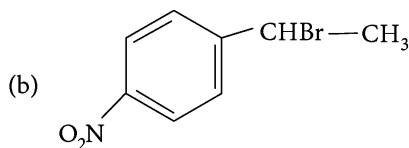
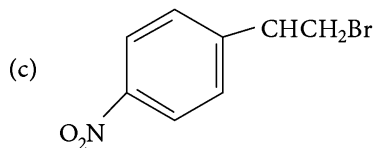
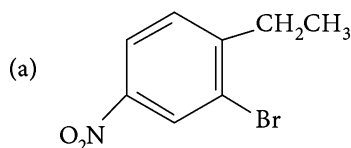
- (a) water (b) ethanol (c) p-nitrophenol (d) p-methoxyphenol

139. Naphthalene $\xrightarrow[\text{V}_2\text{O}_5, 773 \text{ K}]{\text{air}}$ (A) $\xrightarrow[\text{Con. H}_2\text{SO}_4]{\text{phenol}}$ (B) The product (b) in the above reaction is

- (a) phenyl benzoate (b) phenolphthalein (c) Fluorescein (d) p-hydroxyazobenzene



The structure of the product is



141. The increasing order of acid strength of 4-Methoxyphenol (I), 4-Nitrophenol (II) and 4-Methylphenol (III) is

- (a) $\text{III} < \text{I} < \text{II}$ (b) $\text{I} < \text{II} < \text{III}$ (c) $\text{I} < \text{III} < \text{II}$ (d) $\text{III} < \text{II} < \text{I}$

142. The correct order of activating influence of the following groups when attached to benzene ring is

- (a) $-\text{O}^- > -\text{OCOCH}_3 > -\text{OH} > -\text{COCH}_3$ (b) $-\text{O}^- > -\text{OH} > -\text{OCOCH}_3 > -\text{COCH}_3$
 (c) $-\text{OH} > -\text{O}^- > -\text{OCOCH}_3 > -\text{COCH}_3$ (d) $-\text{OH} > -\text{OCOCH}_3 > -\text{O}^- > -\text{COCH}_3$

143. The reagent used to convert phenol to quinol is

- (a) $\text{KMnO}_4/\text{H}_2\text{SO}_4$ (b) KOH followed by acidification
 (c) $\text{K}_2\text{S}_2\text{O}_8$ followed by acidification (d) Moist silver oxide

144. Ozonolysis of o-xylene gives

- (a) glyoxal and methyl glyoxal only (b) glyoxal and dimethyl glyoxal only
 (c) methyl glyoxal and dimethyl glyoxal only (d) glyoxal, methyl glyoxal and dimethyl glyoxal

145. When benzene vapours are passed through a red hot tube at $973\text{K} - 1073\text{K}$, it forms

- (a) acetylene (b) maleic anhydride (c) biphenyl (d) naphthalene

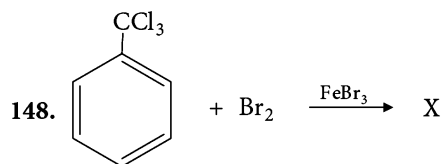
146. Reaction of excess of benzene with chloroform in presence of anhydrous chloride gives

- (a) biphenyl (b) triphenyl methane (c) anthracene (d) diphenyl methane

147. Ethyl benzene $\xrightarrow{\text{NBS}}$ A $\xrightarrow{\text{alc. KOH}}$ B. The product B in the above reaction sequence is

- (a) styrene (b) 1-phenyl ethanol (c) 2-phenyl ethanol (d) p-ethylphenol

3.68 Benzene and Phenols



The major product X in the above reaction is

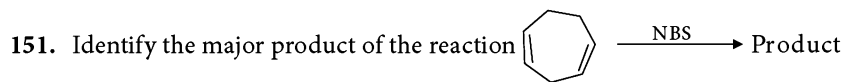
- (a) o-bromo benzotrichloride (b) p-bromobenzotrichloride
(c) m-bromo benzotrichloride (d) a mixture of o-bromo and p-bromobenzotrichloride

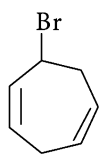
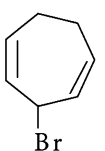
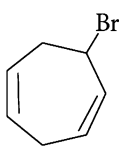
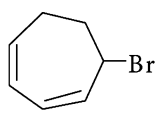
149. Which among the following is more acidic than phenol?

- (a) o-methoxy phenol (b) m-methoxy phenol
(c) p-methoxyphenol (d) none of these

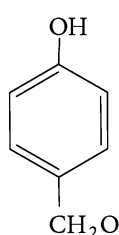
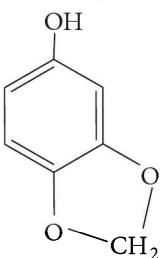
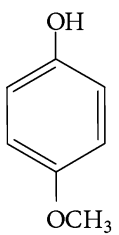
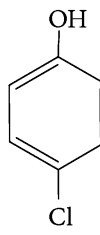
150. Which of the following will decompose NaHCO_3 solution with the liberation of CO_2 gas?

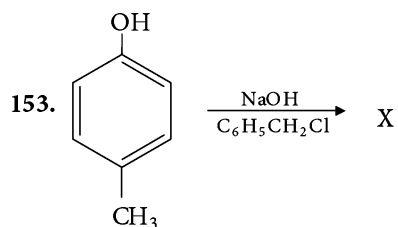
- (a) phenol (b) p-nitrophenol (c) p-cresol (d) 2,4,6-trinitrophenol



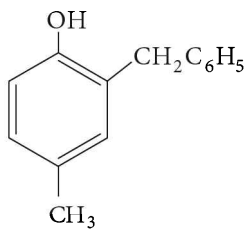
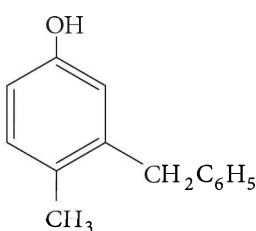
- (a)  (b)  (c)  (d) 

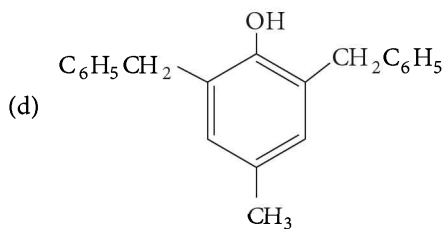
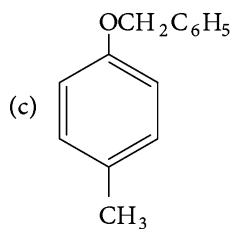
152. The most acidic phenol among the following is

- (a)  (b)  (c)  (d) 

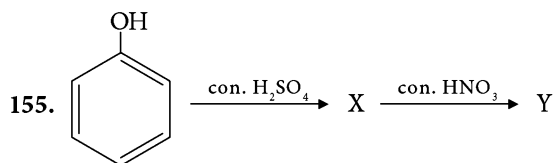
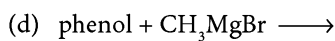
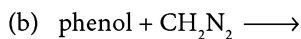
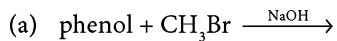


The major product X in the above reaction is

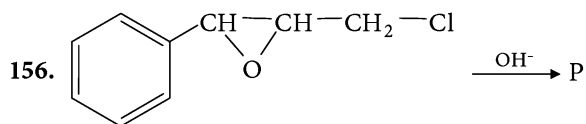
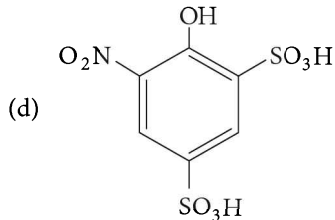
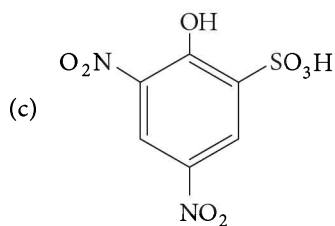
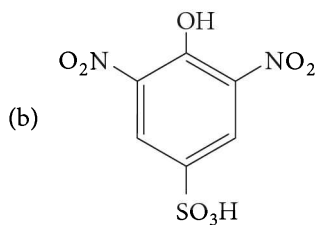
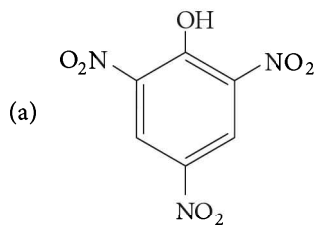
- (a)  (b) 



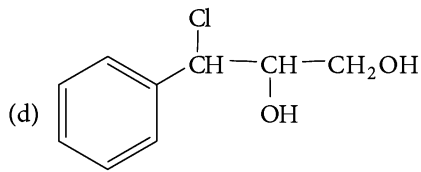
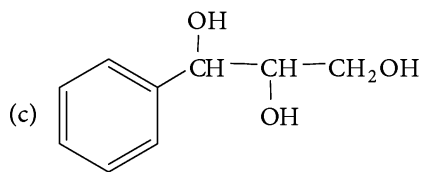
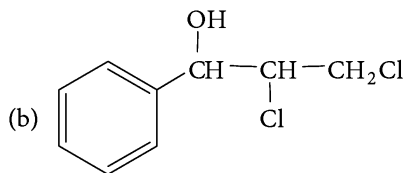
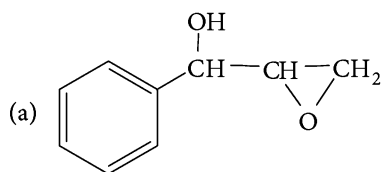
154. Anisole is not formed in the reaction



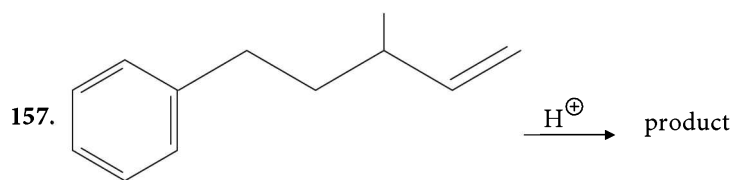
The product Y in the above sequence of reaction is



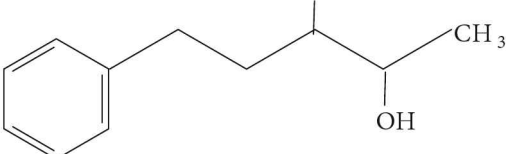
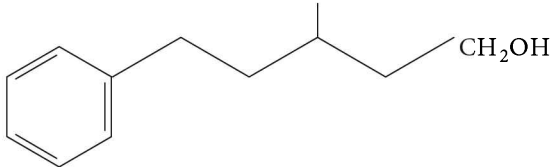
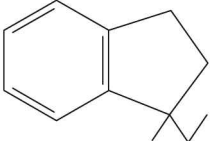
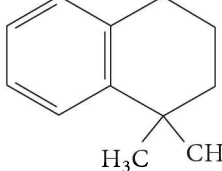
The product P in the above reaction is

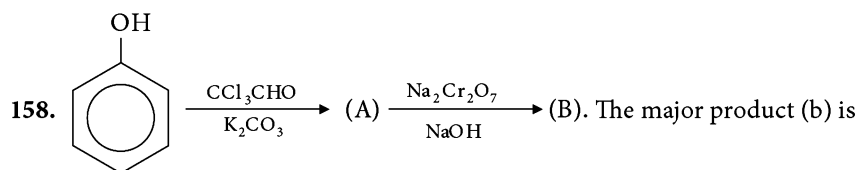


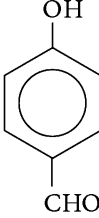
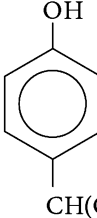
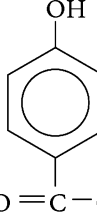
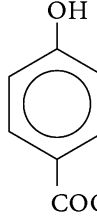
3.70 Benzene and Phenols

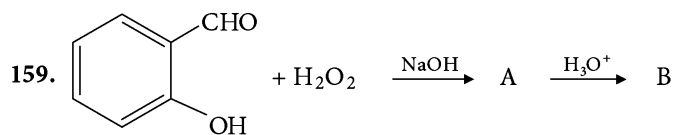


The likely structure of the product is

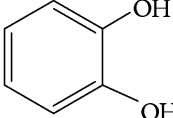
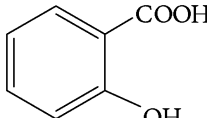
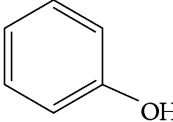
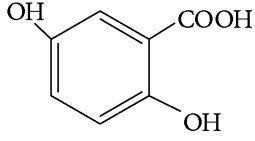
- (a)  (b) 
- (c)  (d) 

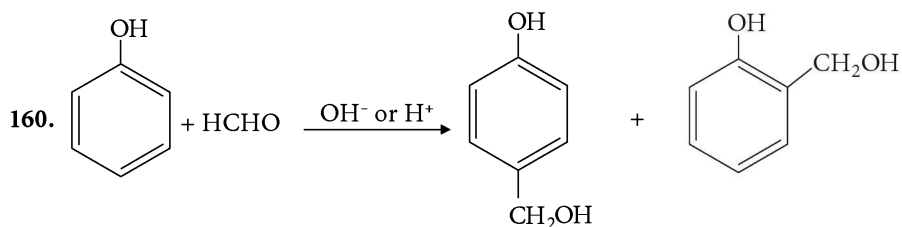


- (a)  (b) 
- (c)  (d) 



The major product B formed in the above reaction is

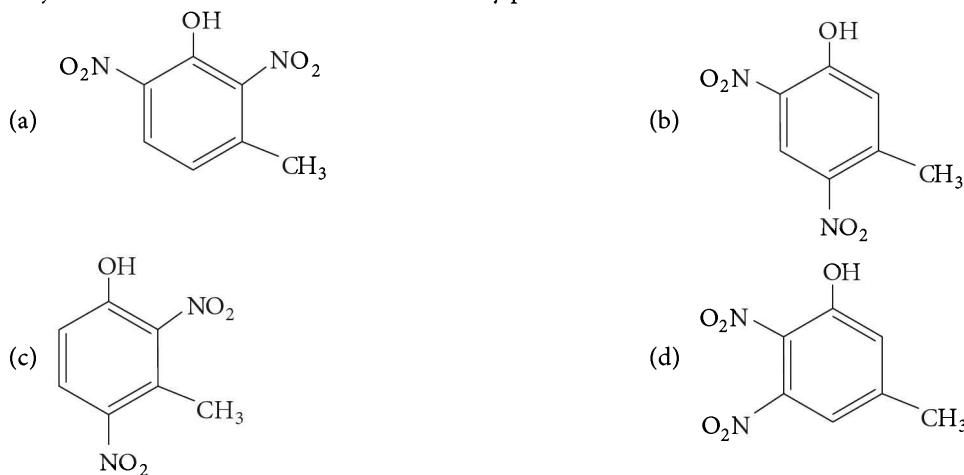
- (a)  (b) 
- (c)  (d) 



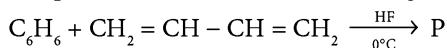
The above reaction is known as

- (a) Friedel-Crafts reaction
 (b) Lederer-Manasse reaction
 (c) Knoevenagel reaction
 (d) Kolbe-Schmidt reaction

161. Major dinitro derivative formed from 3-Methylphenol is



162. The product P formed in the following reaction is



- (a) $\text{C}_6\text{H}_5 - \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_3$
 (b) $\text{C}_6\text{H}_5 - \text{CH} = \text{CH}_2$
 (c) $\text{C}_6\text{H}_5 - \text{C}(\text{CH}_3) = \text{CH} - \text{CH}_3$
 (d) $\text{C}_6\text{H}_5 - \text{CH}_2 - \text{CH}_2 - \text{CH} = \text{CH}_2$

163. In which of the following reactions, Ethylbenzene is not formed as the final product?



The major product formed in the above reaction is

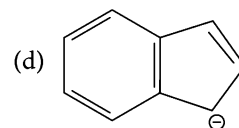
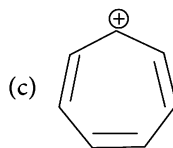
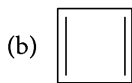
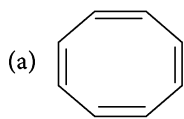
- (a) $\text{C}_6\text{H}_5 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$
 (b) $\text{C}_6\text{H}_5 - \text{CH}(\text{CH}_3) - \text{CH}_3$
 (c) $\text{C}_6\text{H}_5 - \text{CH} = \text{CH} - \text{CH}_3$
 (d) $\text{C}_6\text{H}_5 - \text{CH}_2 - \text{CH} = \text{CH}_2$

165. p-cresol on heating with zinc dust gives

- (a) benzene
 (b) toluene
 (c) p-xylene
 (d) benzaldehyde

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166. The compound or species, which is antiaromatic among the following, is



167. (Resorcinol) when heated with phthalic anhydride to about 473K, the product formed is

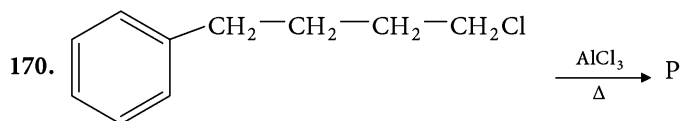
- (a) Fluorescein (b) phenolphthalein (c) Eosin (d) methyl orange

168. Which of the following reagents can effect hydroxylation at an aromatic carbon?

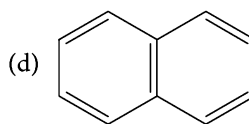
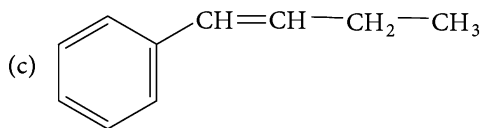
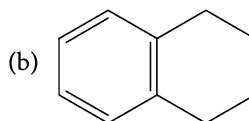
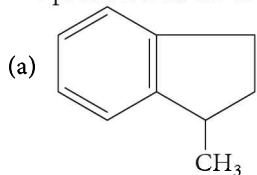
- (a) aqueous KOH (b) alcoholic KOH (c) alkaline KMnO_4 (d) Fenton's reagent

169. An aromatic compound having the molecular formula C_8H_{10} gave only one mono nitro derivative on nitration. The compound is

- (a) ethyl benzene (b) o-xylene (c) m-xylene (d) p-xylene



The product P in the above reaction is



Assertion-Reason Type Questions

Directions: Each question contains Statement-1 and Statement-2 and has the following 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

171. **Statement 1**

Phenol gives p-bromophenol as the major product when treated Br_2 dissolved in carbon disulphide at low temperature.
and

Statement 2

p-Bromophenol has lower pK_a value than phenol.

172. Statement 1

Pure phenol is a colourless solid but turns reddish brown on keeping.
and

Statement 2

Phenol is slowly oxidized by air to quinone.

173. Statement 1

Phenol reacts with PCl_5 to give only a small amount of chlorobenzene, the main product is triphenyl phosphate $(\text{C}_6\text{H}_5\text{O})_3\text{P}=\text{O}$ or $(\text{C}_6\text{H}_5)_3\text{PO}_4$.
and

Statement 2

C – O bond in phenol has partial double bond character.

174. Statement 1

Phenol is more reactive than benzene in electrophilic substitution reactions.
and

Statement 2

The higher reactivity of phenol is due to the higher acidity of phenol.

175. Statement 1

The preference for O–acylation of phenols arises because the acylations are kinetically controlled and O–acylations are faster than C–acylations.
and

Statement 2

The isomerization from aryl esters to aryl ketones under the influence of aluminium chloride is called Fries rearrangement.

176. Statement 1

$\text{C}_6\text{H}_5 - \overset{+}{\text{N}}(\text{CH}_3)_3$ gives meta nitro derivative on nitration almost exclusively.
and

Statement 2

All deactivating groups are meta directing groups.

177. Statement 1

Fluorine deactivates benzene ring more than other halogens when attached to the benzene ring.
and

Statement 2

Fluorine in fluorobenzene is an ortho, para directing group.

178. Statement 1

Phenoxide ion is more reactive than phenol towards electrophiles.
and

Statement 2

Phenoxide ion is stabilized more by resonance than phenol.

179. Statement 1

On heating with $\text{con. H}_2\text{SO}_4$, benzene gives benzene sulphonic acid which when heated with superheated steam under pressure gives back benzene.

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and

Statement 2

Kinetic isotope effect is not observed in sulphonation reaction of benzene.

180. Statement 1

Phenol undergoes Kolbe's reaction whereas ethanol does not.

and

Statement 2

Phenoxide ion is more basic than ethoxide ion.

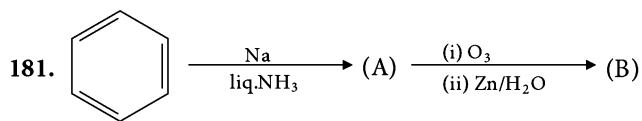


Linked Comprehension Type Questions

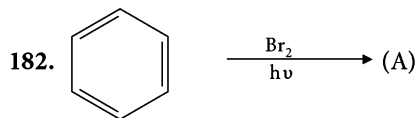
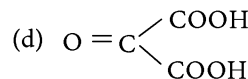
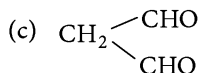
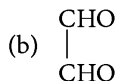
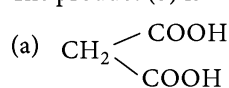
Directions: This section contains 3 paragraphs. Based upon the paragraph, 3 multiple choice questions have to be answered. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

Passage I

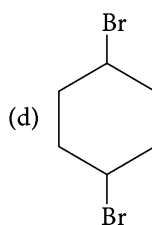
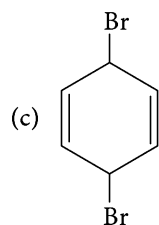
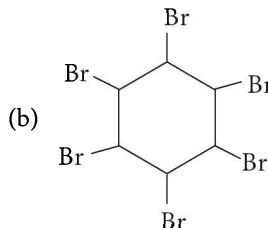
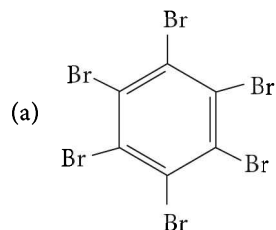
Though benzene has three double bonds, it does not answer tests for unsaturation like discharging the colour of bromine water or colour of cold dilute alkaline KMnO_4 . It behaves like a saturated hydrocarbon and gives substitution reactions. However it does give a few addition reactions of the double bond like Birch reduction, addition of halogen, ozonolysis etc., where it behaves like an unsaturated compound.



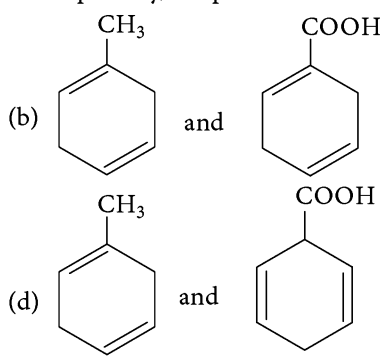
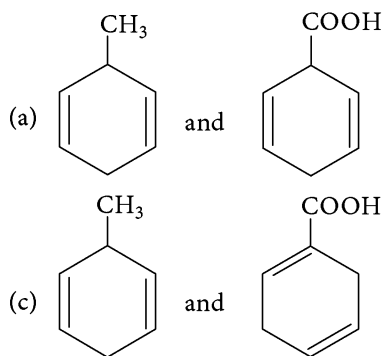
The product (b) is



The major product is



183. When toluene and benzoic acid are subjected to Birch reduction separately, the products obtained, respectively, are

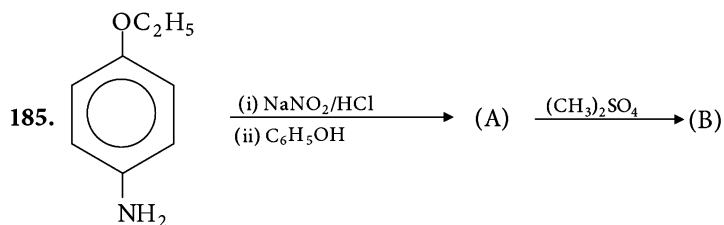
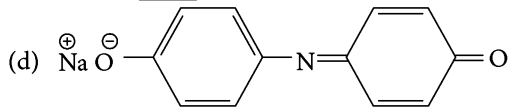
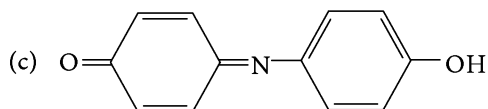
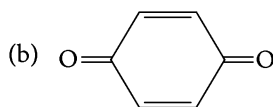
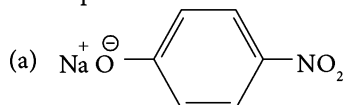


Passage II

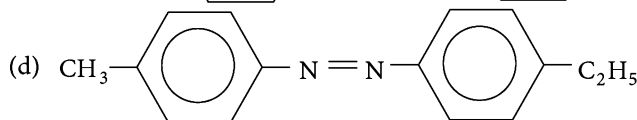
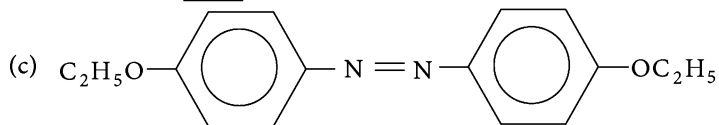
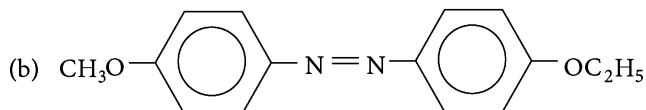
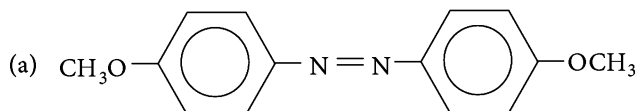
Name reactions of phenols

Phenols undergo a variety of name reactions such as Reimer–Tiemann reaction, Schotten–Baumann reaction, Liebermann's nitroso reaction, Williamson's synthesis and so on. The activating influence of the phenolic group plays a dominant role in such reactions. In addition, phenols undergo phthalein fusion, diazocoupling and other reactions like Fries rearrangement.

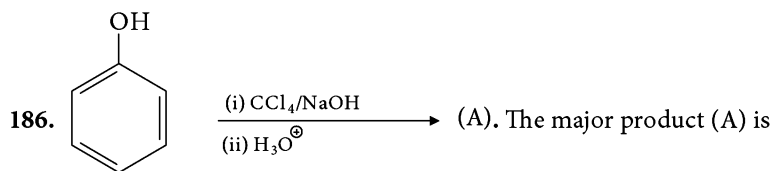
184. When phenol is treated with NaNO_2 and H_2SO_4 , the product obtained is



The major product (B) is



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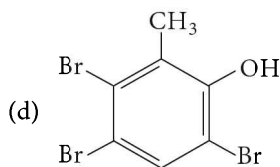
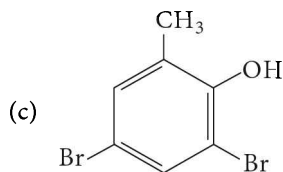
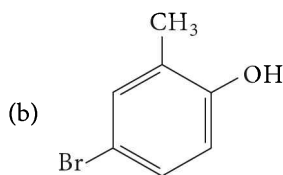
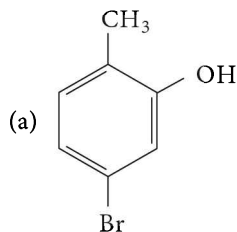
- (a) salicylic acid (b) benzoic acid
(c) salicylaldehyde (d) benzene

Passage III

Properties of phenols

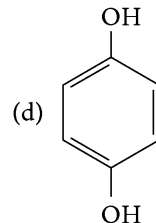
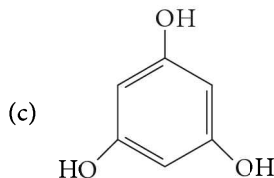
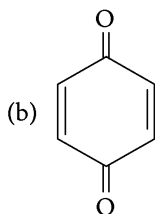
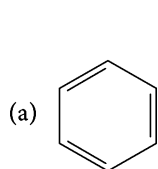
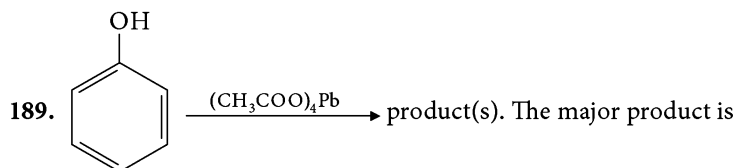
Phenols are a group of compounds with $-\text{OH}$ group directly attached to the aromatic ring. Phenols have higher boiling points than the corresponding compounds of similar molecular weight due to hydrogen bonding. Phenols are acidic in nature. The presence of substituents such as $-\text{NO}_2$ group imparts greater acidity to phenols. Phenols undergo a variety of reactions like aromatic electrophilic substitution, rearrangement reactions, polymerization, reduction and coupling reactions.

187. The major product formed when o-cresol is treated with Br_2 in CS_2 at ice cold conditions is



188. The $\text{C}-\text{O}$ bond length in phenol is shorter compared to $\text{C}-\text{O}$ bond length in alcohols. This is due to

- (a) the sp^2 nature of the carbon of the phenol.
(b) the delocalization of the electron density from the ring to the more electronegative oxygen.
(c) the dipole distribution of the $\text{C}-\text{O}$ bond in phenol with the oxygen at the negative end of the dipole.
(d) the acidic nature of the phenolic hydrogen.

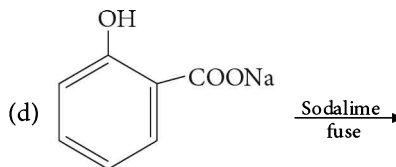
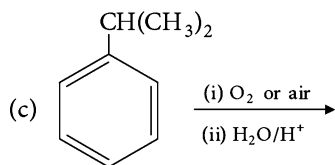
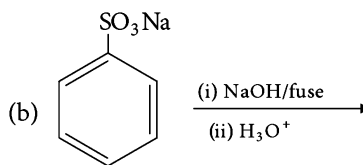
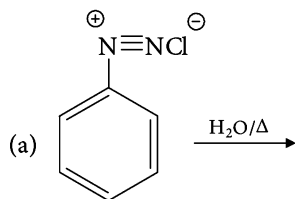




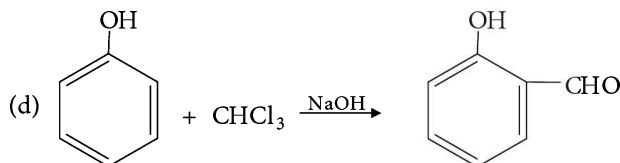
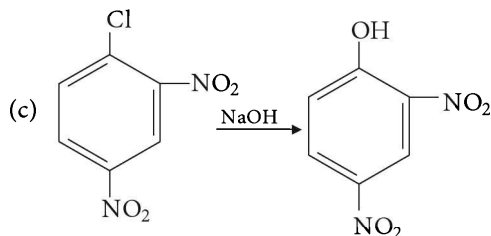
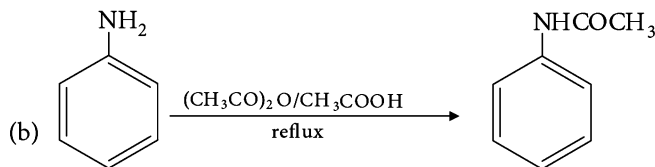
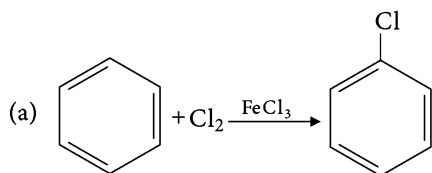
Multiple Correct Objective Type Questions

Directions: Each question in this section has four suggested answers of which ONE OR MORE answers will be correct.

190. The method(s) by which phenol can be synthesized is/are



191. Which of the following are aromatic electrophilic substitution reactions?

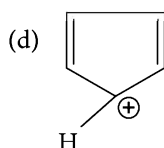
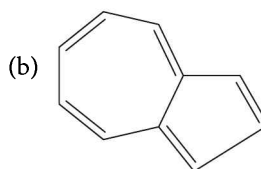
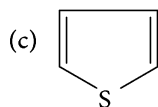
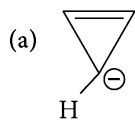


192. Which of the following statement(s) is/are correct?

- (a) Benzene on heating with air in presence of vanadium pentoxide at 700K gives maleic anhydride
- (b) There is no kinetic isotope effect for nitration of benzene.
- (c) Benzene hexachloride is an unsaturated compound.
- (d) Distillation of o-cresol and p-cresol with zinc dust gives the same product.

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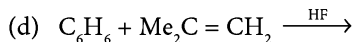
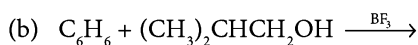
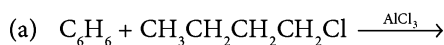
193. The aromatic species among the following is/are



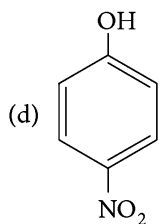
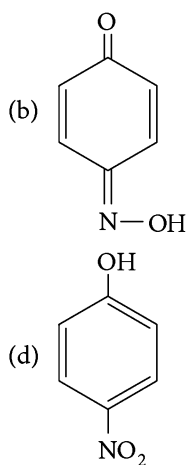
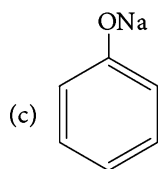
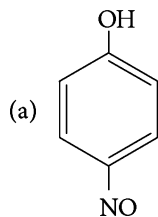
194. Which of the following undergo electrophilic substitution reaction faster than benzene?

- (a) Ethyl benzene (b) Bromobenzene (c) Anisole (d) Naphthalene

195. The reaction (s) which give tert-butyl benzene among the following is/are



196. Phenol reacts with HNO_2 to form



197. o-Nitrophenol has lower pK_a than

- (a) p-nitrophenol (b) o-cresol (c) o-fluorophenol (d) p-methoxyphenol



Matrix-Match Type Questions

Directions: Match the elements of Column I to elements of Column II. There can be single or multiple matches.

198.

Column I

- (a) Salicylic acid
(b) p-Hydroxy acetophenone
(c) Quinol
(d) picric acid

Column II

- (p) characteristic colour with neutral FeCl_3 solution
(q) Kolbe's reaction
(r) Fries rearrangement
(s) Elbs persulphate oxidation
(t) Decomposes NaHCO_3 solution

199.

Column I

- (a) $\text{C}_6\text{H}_6 + \text{CH}_3 - \text{CH} = \text{CH}_2 \xrightarrow{\text{H}_2\text{SO}_4}$
 (b) $\text{C}_6\text{H}_5\text{OH} + \text{C}_6\text{H}_5\text{COCl} \xrightarrow{\text{NaOH}}$
 (c) $\text{C}_6\text{H}_6 + \xrightarrow{\text{AlCl}_3}$
 (d) $\text{C}_6\text{H}_5\text{OH} \xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) CCl}_4 / \text{NaOH}}$

Column II

- (p) Schotten-Baumann reaction
 (q) Friedel-Crafts reaction
 (r) Reimer-Tiemann reaction
 (s) Isopropyl benzene
 (t) Electrophilic substitution

200.

Column I

- (a) Electrophilic substitution
 (b) Nucleophilic substitution
 (c) Free radical substitution
 (d) Coupling reaction

Column II

- (p) $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{C}_6\text{H}_5\text{OH} \xrightarrow{\text{NaOH}}$
 (q) Toluene + NBS $\longrightarrow$
 (r) Dow's process
 (s) Phenol $\longrightarrow$ picric acid
 (t) $\text{C}_6\text{H}_5\text{ONa} + \text{CH}_3\text{Br} \longrightarrow$

SOLUTIONS

ANSWER KEYS

Topic Grip

- It is due to the presence of an electron cloud containing six π electrons in benzene ring
- Benzene is first nitrated and then brominated
- Nitro group is a deactivating group.
- (i) (a) 1 (b) 2 (c) 3
(ii) 1, (2, (3-tribromobenzene), 1, (2, (4-tribromobenzene and) 1, (3, (5-tribromobenzene
- m-Dinitrobenzene is first reduced with ammonium sulphide to form m-nitroaniline. It is then diazotised and warmed with water.
- Phenol is a weaker acid than carbonic acid
- (i) The C–O bond in phenol has partial double bond character due to resonance and hence not easily cleaved by PCl_5
(ii) There is intramolecular hydrogen bonding in o-nitrophenol
- (i) A: Salicylic acid
B: aspirin
(ii) A:
B:
- Meta directing groups: $-\text{NO}_2$, $-\text{N}^+(\text{CH}_3)_3$, $-\text{CN}$, $-\text{COOH}$, $-\text{COOR}$, $-\text{SO}_3\text{H}$, $-\text{CHO}$, $-\text{CO}-$
- (a) Cyclopentadiene ionises to form stable cyclopentadienyl anion and H^+ and hence it is acidic.
(b) The lone pair of electrons on nitrogen in pyrrole is in-

cluded for aromatic stability. So it is not readily available for protonation

11. (b)	12. (c)	13. (c)
14. (c)	15. (d)	16. (b)
17. (c)	18. (b)	19. (a)
20. (b)	21. (d)	22. (b)
23. (d)	24. (b)	25. (d)
26. (a)		
27. (a), (c)		
28. (b), (c)		
29. (b), (c)		
30. (a) $\rightarrow$ (p), (s)		
(b) $\rightarrow$ (p), (r), (s)		
(c) $\rightarrow$ (q), (r), (s)		
(d) $\rightarrow$ (p), (s)		

97. (b)	98. (b)	99. (c)
100. (d)	101. (b)	102. (c)
103. (a)	104. (a)	105. (a)
106. (c)	107. (b)	108. (d)
109. (a)	110. (d)	111. (c)
112. (b)	113. (c)	114. (a)
115. (c)		
116. (d)		
117. (b), (c)		
118. (a), (d)		
119. (a), (b)		
120. (a) $\rightarrow$ (p)		
(b) $\rightarrow$ (p), (s)		
(c) $\rightarrow$ (p), (q), (t)		
(d) $\rightarrow$ (p), (r)		

IIT Assignment

31. (d)	32. (c)	33. (a)
34. (d)	35. (c)	36. (d)
37. (d)	38. (a)	39. (c)
40. (d)	41. (a)	42. (b)
43. (d)	44. (b)	45. (c)
46. (a)	47. (c)	48. (b)
49. (a)	50. (d)	51. (a)
52. (c)	53. (c)	54. (c)
55. (b)	56. (a)	57. (b)
58. (d)	59. (d)	60. (c)
61. (c)	62. (a)	63. (d)
64. (b)	65. (c)	66. (c)
67. (b)	68. (b)	69. (c)
70. (c)	71. (b)	72. (d)
73. (a)	74. (c)	75. (c)
76. (c)	77. (d)	78. (d)
79. (d)	80. (b)	81. (d)
82. (c)	83. (a)	84. (c)
85. (a)	86. (c)	87. (d)
88. (b)	89. (b)	90. (b)
91. (b)	92. (a)	93. (b)
94. (c)	95. (d)	96. (a)

Additional Practice

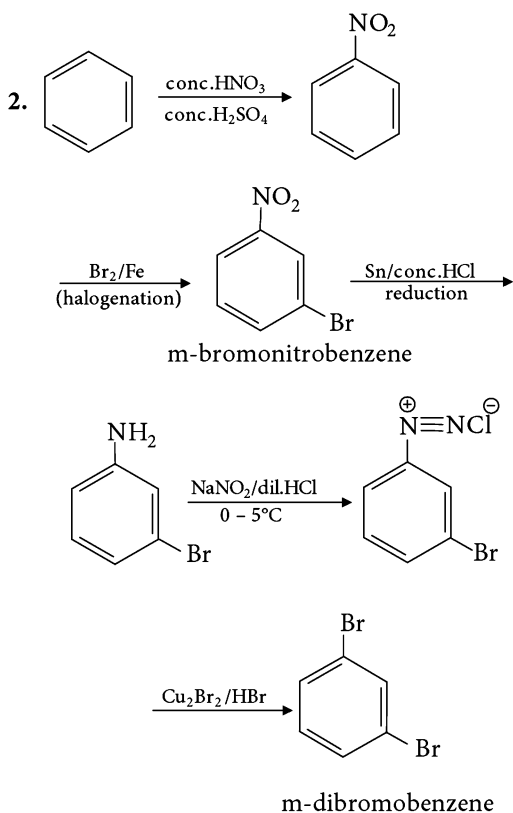
- (i) $2\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_3\text{O}^+ + \text{HSO}_4^- + \text{SO}_3$
(ii) $\text{RCl} + \text{AlCl}_3 \rightleftharpoons \text{R}^+ + \text{AlCl}_4^-$
(iii) $\text{RCOCl} + \text{AlCl}_3 \rightleftharpoons \text{RCO}^+ + \text{AlCl}_4^-$
- C: p-chlorostyrene
- No kinetic isotope effect is observed for nitration and halogenation. Due to the reversible nature, (sulphonation shows small kinetic isotope effect.
- Nitration preferentially takes place on the activated benzene ring.
- (a) The dianion of cyclooctatetraene satisfies Huckel's rule and is aromatic
(b) Cycloheptatrienone is polarised and the carbon gets positive charge and the cation is aromatic (Huckel's rule)

126. Convert first benzene to toluene by Friedel-Crafts reaction. Side chain oxidation of toluene gives benzoic acid which on nitration gives m-nitrobenzoic acid.
127. (a) Benzene $\xrightarrow[\text{AlCl}_3]{\text{CH}_3\text{Cl}}$ toluene
 $\xrightarrow{\text{nitration}}$ o-nitrotoluene
 $\xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) alk KMnO}_4}$ o-nitrobenzoic acid
- (b) Benzene $\xrightarrow[\text{AlCl}_3]{\text{CH}_3\text{Cl}}$ toluene
 $\xrightarrow[\text{Fe}]{\text{(i) Br}_2}$ p-bromotoluene
 $\xrightarrow{\text{Cl}_2/h\nu}$ product
128. A: Phenol B: Salicylic acid
 C : aspirin D : Methyl ester formation occurs at the acid group of aspirin.
129. The lone pair on nitrogen in pyrrole is involved in giving it aromatic stability
130. There is intramolecular hydrogen bonding in ortho fluorophenol.
131. (d) 132. (b) 133. (b)
 134. (d) 135. (b) 136. (a)
 137. (d) 138. (c) 139. (b)
 140. (b) 141. (c) 142. (b)
 143. (c) 144. (d) 145. (c)
 146. (b) 147. (a) 148. (c)
 149. (b) 150. (d) 151. (b)
 152. (d) 153. (c) 154. (d)
 155. (a) 156. (a) 157. (c)
 158. (a) 159. (a) 160. (b)
 161. (b) 162. (a) 163. (c)
 164. (a) 165. (b) 166. (b)
 167. (a) 168. (d) 169. (d)
 170. (b) 171. (b) 172. (a)
 173. (a) 174. (c) 175. (b)
 176. (c) 177. (d) 178. (b)
 179. (c) 180. (c) 181. (b)
 182. (b) 183. (d) 184. (c)
 185. (b) 186. (a) 187. (b)
 188. (a)
189. (b)
 190. (a), (b), (c), (d)
 191. (a), (d)
 192. (a), (b), (d)
 193. (b), (c)
 194. (a), (c), (d)
 195. (b), (d)
 196. (a), (b)
 197. (b), (c), (d)
 198. (a) $\rightarrow$ (p), (q), (t)
 (b) $\rightarrow$ (p), (r)
 (c) $\rightarrow$ (p), (s)
 (d) $\rightarrow$ (p), (t)
 199. (a) $\rightarrow$ (q), (s), (t)
 (b) $\rightarrow$ (p)
 (c) $\rightarrow$ (q), (t)
 (d) $\rightarrow$ (r), (t)
 200. (a) $\rightarrow$ (p), (s)
 (b) $\rightarrow$ (r), (t)
 (c) $\rightarrow$ (q)
 (d) $\rightarrow$ (p)

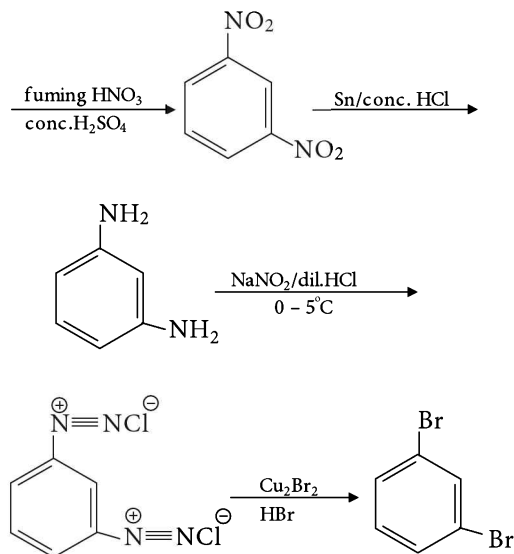
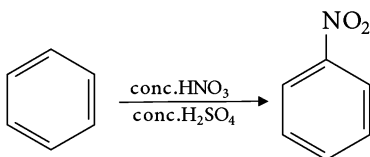
HINTS AND EXPLANATIONS

Topic Grip

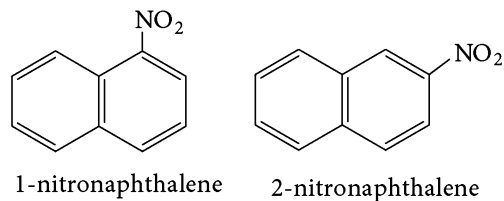
1. Due to the presence of an electron cloud containing six π electrons, benzene is a rich source of electrons. Hence, it attracts electrophilic reagents and repels nucleophiles. So benzene undergoes electrophilic substitution easily and nucleophilic substitution with difficulty.



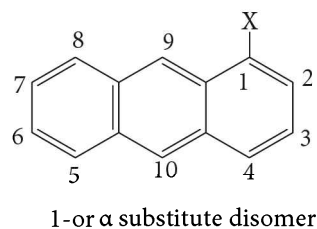
Benzene has to be nitrated first and then brominated. Bromination of benzene in the first step should be avoided, as bromine in bromobenzene so formed, not only deactivates but it is also ortho and para directing. Alternatively,

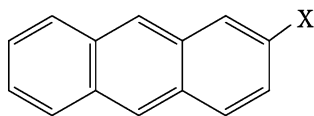
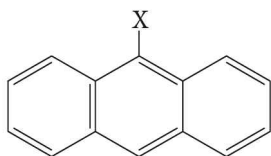


3. Nitrobenzene does not undergo Friedel-Crafts alkylation reaction because the electron density of the benzene ring (which is the source for electrons) is decreased by the electron withdrawing nature of the nitro group attached to it.
4. (i) (a) Since all the hydrogen atoms of benzene are equivalent, only one monosubstitution product is possible for benzene.
- (b) Two monosubstitution products are possible for naphthalene. For example,

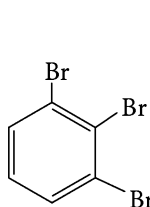


- (c) There are three possible mono substitution products for anthracene. For example

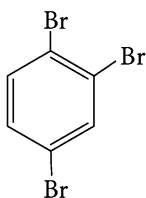


2-or β isomer9-or γ isomer

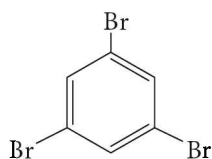
(ii) Three isomers are possible



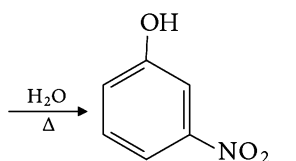
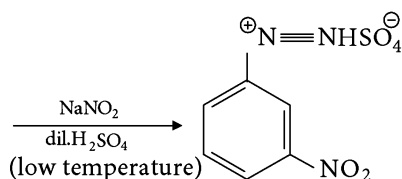
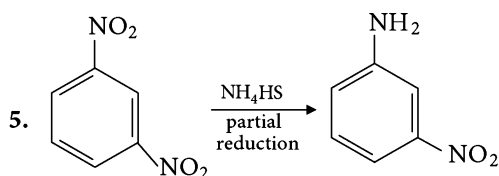
1,2,3-tribromobenzene



1,2,4-tribromobenzene



1,3,5-tribromobenzene

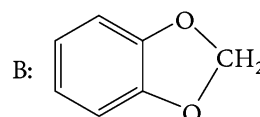
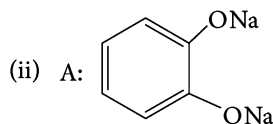
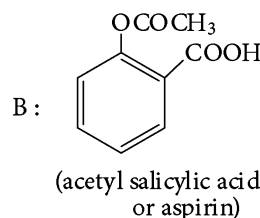
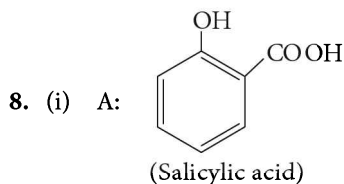


m-nitrophenol

6. Phenol is a weak acid because, the $\text{C}_6\text{H}_5\text{OH}$ group loses a proton to form a phenoxide ion ($\text{C}_6\text{H}_5\text{O}^\ominus$) which is stabilized by resonance. Phenol is a weaker acid than carbonic acid and so phenol cannot produce CO_2 from NaHCO_3 solution.

7. (i) The $\text{C}-\text{O}$ bond in phenol has partial double bond character and hence strong due to resonance. So it cannot be easily cleaved by PCl_5 to form chlorobenzene. But the $\text{C}-\text{O}$ bond in alcohols is pure single bond and can be readily cleaved by PCl_5 to form alkyl chloride.

(ii) There is intramolecular hydrogen bonding in o-nitrophenol and so it exists as discrete molecules. Thus its boiling point is lower and is steam volatile. Further it does not form hydrogen bonds with water. So it is less soluble in water. In p-nitrophenol there is intermolecular hydrogen bonding and exist as associated molecules. So it has higher boiling point and is not steam volatile. Again, it can form hydrogen bonds with water and hence is more soluble in water.



9. Groups can be classified as activating and deactivating groups. Groups activate by increasing the electron density of the ring and deactivate by decreasing the electron density of the ring.

Electron releasing groups, which activate the electrophilic substitution process are ortho and para

3.84 Benzene and Phenols

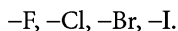
directing, while electron withdrawing groups which deactivate the aromatic substitution process are meta orienting (except halogens).

Activating, electron releasing and ortho para directing groups are $-\text{NH}_2$ (strongly activating), $-\text{NHCH}_3$ (strongly activating), $-\text{N}(\text{CH}_3)_2$ (strongly activating), $-\text{OCH}_3$ (moderately activating), $-\text{OC}_2\text{H}_5$ (moderately activating), $-\text{NHCOCH}_3$ (moderately activating), $-\text{C}_6\text{H}_5$ (weakly activating), $-\text{CH}_3$ (weakly activating) and $-\text{C}_2\text{H}_5$ (weakly activating).

Deactivating, electron withdrawing and meta orienting groups are $-\text{NO}_2$, $-\text{N}^+(\text{CH}_3)_3$, $-\text{CN}$, $-\text{C}(=\text{O})\text{OH}$, $-\text{C}(=\text{O})\text{OR}$, $-\text{SO}_3\text{H}$, $-\text{C}(=\text{O})\text{H}$ and



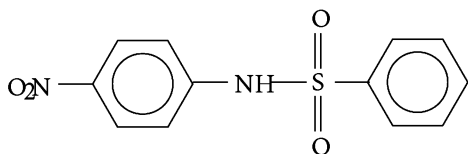
Groups, which are deactivating by inductive effect, and ortho-para orienting are



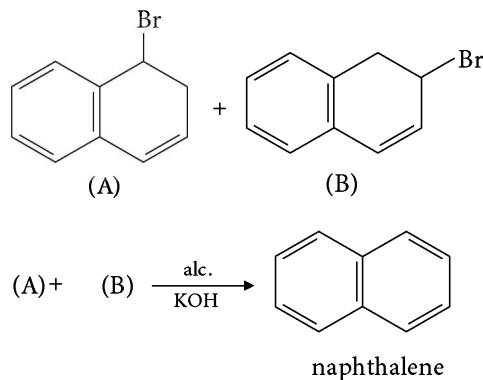
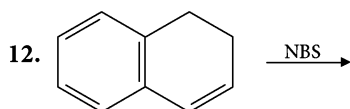
10. When cyclopentadiene ionizes, it gives the anion which has 6 pi electrons and is stable according Huckel rule. But 1, 4-pentadiene anion is not stable. Hence cyclopentadiene is more acidic.

(b) In pyridine the lone pair electrons are not used for pi bonding since there are already 6 pi electrons. But in pyrrole there are two double bonds and the lone pair on nitrogen is included for aromatic stability. Hence the lone pair is not available for protonation. Hence pyrrole is not basic.

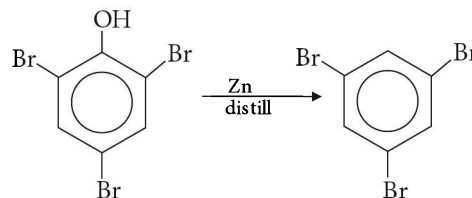
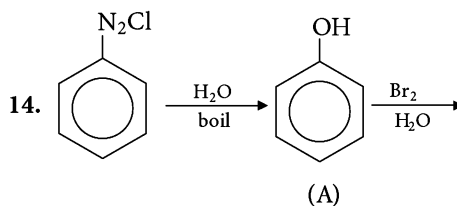
11. $-\text{NH}-$ group is ring activating and ortho-para directing $-\text{SO}_2-$ group is ring deactivating and meta directing. Substitution takes place at the more activated ring to get



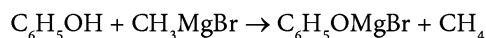
as the major product.



13. $-\text{CN}$ group gets preference over $-\text{OH}$ group in a polyfunctional compound.



15. Grignard reagents react with compounds having acidic hydrogen to give the corresponding hydrocarbon.



16. Both statements are correct but statement 2 is not the reason for statement 1.

Polysubstitution does not take place in Friedel-Crafts acylation because the group introduced in the aromatic ring is a deactivating group.

17. Statement 1 is true but statement 2 is false.

The formation of intramolecular hydrogen bonding between $-\text{OH}$ and $-\text{NO}_2$ group makes o-nitrophenol slightly less acidic than p-nitrophenol.

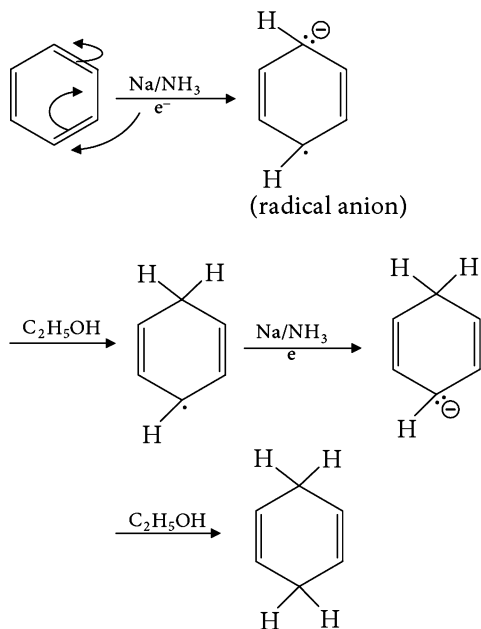
18. Both statements are true but statement 2 is not the reason for statement 1

Nitration is an electrophilic substitution reaction. The rate determining step in nitration of an aromatic compound is the formation of the σ -complex (arenium ion intermediate). Since $\text{C}-\text{H}$ or $\text{C}-\text{D}$

bond cleavage is not involved in the formation of the σ -complex, benzene and hexadeutero benzene undergo nitration with the same rate. Cleavage of C-H or C-D occurs only in the next fast step of the reaction.

19. Both statements are correct and statement 2 is the correct explanation for statement 1

The reduction of benzene with Na(Li or K) in liquid NH_3 in presence of an alcohol such as ethanol is known as Birch reduction. The reaction involves the transfer of solvated electrons to the benzene ring to form radical anion. The radical anion accepts a proton from the alcohol to give a radical, which is reduced to a carbanion by another sodium atom. Finally, the carbanion accepts another proton from alcohol to form 1,4-cyclohexadiene.



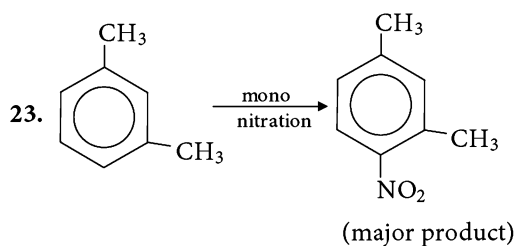
20. Both statements are correct, but statement 2 is not the main reason for statement 1

p-Hydroxybenzene sulphonic acid is more stable than the ortho isomer, but the energy of activation for its formation is higher. So when temperature is increased, o-hydroxybenzene sulphonic acid is converted to the more stable p-isomer.

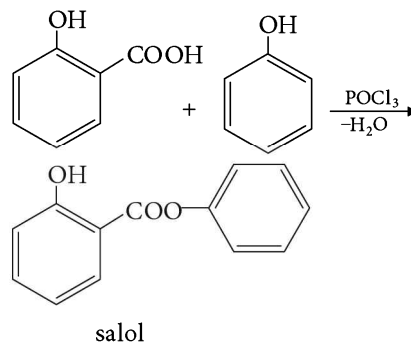
In the sulphonation of phenol, o-hydroxybenzene sulphonic acid is the kinetically controlled product and p-hydroxybenzene sulphonic acid is the thermodynamically controlled product.

21. The statement (d) is not correct. The loss of a proton does occur in the final step, but it is a fast step and not the rate determining step. This has been proved in the isotope effect studies. So statement (d) is wrong.

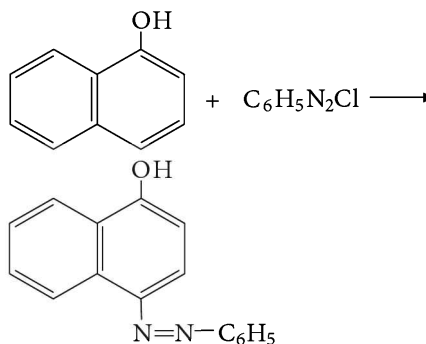
22. There are two carbonyl groups which are deactivating and an amino group which is activating. The nitro group enters the para position to the $-\text{NH}_2$ group to give (b).



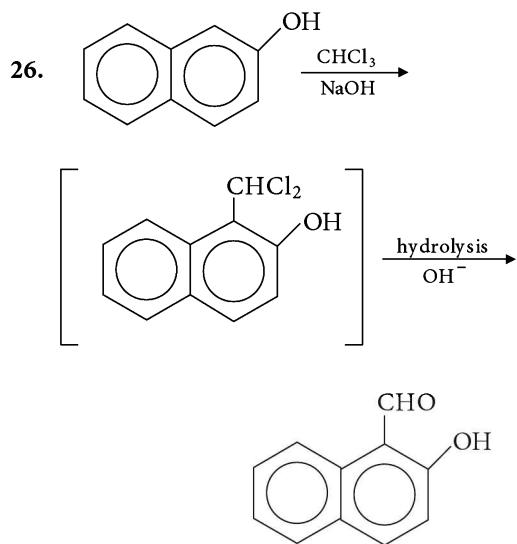
24. Phenol reacts with salicylic acid in presence of POCl_3 to form phenyl salicylate known as salol. It is used as an antiseptic.



25. 1-Naphthol undergoes coupling with diazonium chloride at position 4



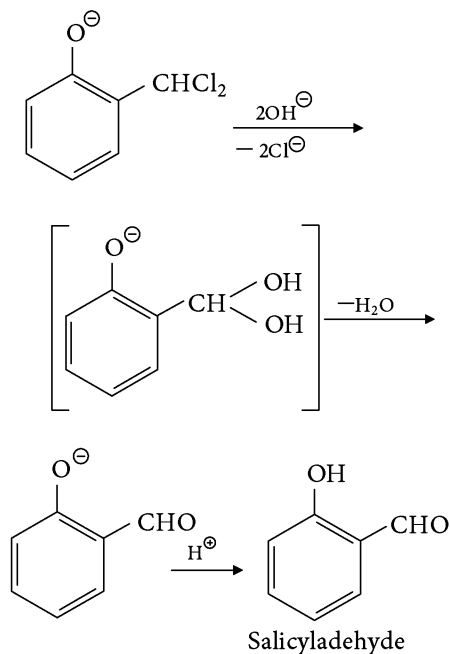
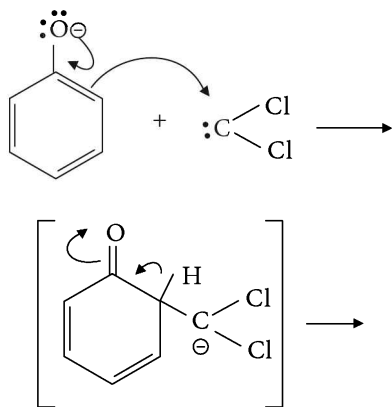
3.86 Benzene and Phenols



This is an example of Reimer Tiemann reaction

27. There is intramolecular hydrogen bonding in o-nitrophenol. So there is less interaction between different molecules in o-nitrophenol compared to p-nitrophenol where the molecules are associated by intermolecular hydrogen bonding. Hence o-nitrophenol has lower melting point, less solubility in water and is more volatile compared to p-nitrophenol.

28. The reaction of phenol with chloroform and alkali to form salicylaldehyde is known as Reimer-Tiemann reaction. Dichlorocarbene ($\ddot{\text{C}}\text{Cl}_2$) formed by the reaction of chloroform with alkali is the electrophile involved in the reaction. The electrophile attacks the phenoxide ion formed by the reaction of phenol with NaOH and the reaction proceeds as shown below.



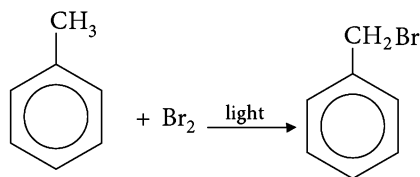
29. $-\text{CCl}_3$ and $-\text{NR}_3^+$ are electron withdrawing and deactivating groups and they are meta directing when present in the benzene ring. $-\text{CH}_2\text{Cl}$ and $-\text{C}_6\text{H}_5$ groups are ortho, para directing.

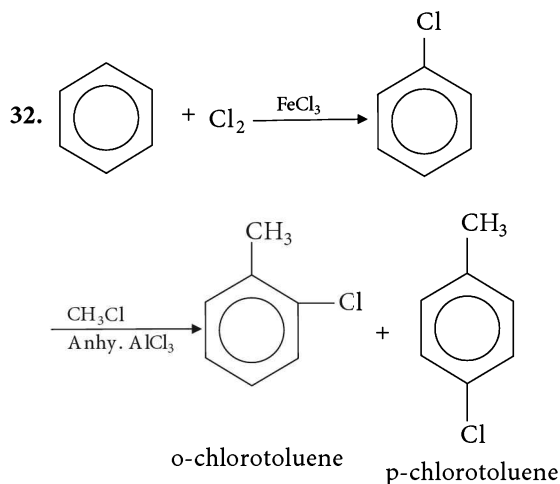
30. (a) $\rightarrow$ (p), (s)
 (b) $\rightarrow$ (p), (r), (s)
 (c) $\rightarrow$ (q), (r), (s)
 (d) $\rightarrow$ (p), (s)

p-Nitrophenol is more acidic than phenol due to $-\text{R}$ and $-\text{I}$ effect of nitro group. Catechol ($\text{pK}_a = 9.85$) is slightly more acidic than phenol ($\text{pK}_a = 10$). p-Methoxyphenol is less acidic than phenol because the $+\text{R}$ effect dominates $-\text{I}$ effect. m-Methoxyphenol is more acidic than phenol due to $-\text{I}$ effect. Resonance effect is not possible since $-\text{OCH}_3$ group is in the meta position.

IIT Assignment Exercise

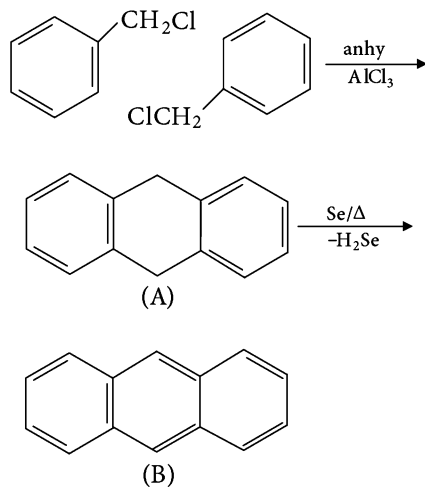
31. In the presence of light, side-chain gets substituted by halogens.





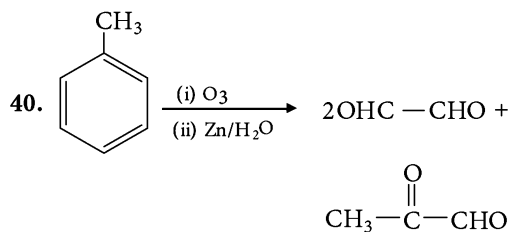
Halogens are ortho, para directing groups.

33. Benzyl chloride undergoes intermolecular Friedel-Crafts alkylation in presence of anhydrous aluminium chloride to give 9,10-dihydroanthracene (A). Se acts as a dehydrogenating agent and converts (A) to anthracene (B).



34. Eventhough all the four groups listed are deactivating groups in an aromatic electrophilic substitution reaction, the most deactivating is $-\text{CF}_3$ group. In the $-\text{CF}_3$ group, the three fluorine atoms are attached to a carbon, and they have a cumulative electron withdrawing influence. Hence $-\text{CF}_3$ is most deactivating.
35. An arenium ion is a highly energetic intermediate, but the step that leads to its formation should be endothermic and not exothermic, hence part of the statement (c) is not correct.

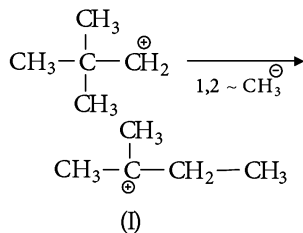
36. For a structure to be aromatic, it should be cyclic planar conjugated system of double bonds, obeying Huckel's $(4n + 2)$ rule of aromaticity. Cyclopropenyl cation (a) and naphthalene (b) are aromatic. Cyclooctatetradienyl dianion (c) is also aromatic as the structure has 10 electrons as required by Huckel's rule. Cycloheptatrienyl anion is not aromatic because there are 8π electrons in the system.
37. Although the molecule has 10 π electrons, required for Huckel's $(4n + 2)$ rule of aromaticity the molecule is non-aromatic because two of the double bonds are in trans orientation. This forces the molecule out of plane.
38. Among the resonance structures for the sigma complex arising from an ortho attack, the contributing structure (a) is highly unstable relative to the other three, because in that structure (a) the positive charge is located on the ring carbon atom that bears the electron withdrawing group namely the trifluoromethyl group ($-\text{CF}_3$). If we consider the resonance structures for the σ complex for meta attack, we find that no such structure bearing a positive charge on carbon to which the $-\text{CF}_3$ group is attached will be found. Hence meta attack is more preferred compared to ortho or para attacks.
39. Due to the presence of lone pair on nitrogen, $-\ddot{\text{N}}\text{H}-$ group activates the benzene ring to which it is attached and preferential electrophilic attack occurs on that ring. $-\ddot{\text{N}}\text{H}-$ group is ortho, para directing group.



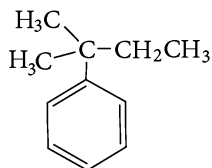
41. The reduction of aromatic rings with Li(or Na or K) in liquid NH_3 in presence of alcohol is known as Birch reduction. In Birch reduction, 1,4-addition of hydrogen takes place and nonconjugated cyclohexadiene is formed. When substituted aromatic compounds are subjected to Birch reduction, electron donating groups such as methoxy group is generally found at the nonreduced position of the product.
42. It is Friedel-Crafts reaction and is used for the preparation of diphenylmethane.

3.88 Benzene and Phenols

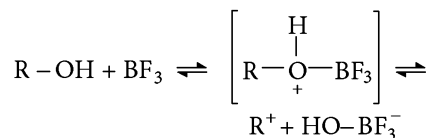
43. Methoxy group ($-\text{OCH}_3$) is a more powerful activating group than $-\text{CH}_3$ group. Hence electrophilic substitution is easiest with methoxybenzene (d) among the given compounds. Br and CHO groups are deactivating groups.
44. In the presence of a Lewis acid like anhydrous AlCl_3 , a neopentyl cation rearranges to a more stable tertiary cation (I)



Now (I) attacks the benzene ring to give

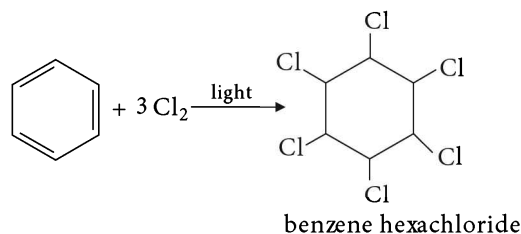


45. The only antiaromatic structure among those given is cyclopropenyl anion.
A cyclic conjugated system which is destabilized in the ring system compared to the same number of double bonds in an open chain structure are called antiaromatic. Cyclopropenyl anion is a cyclic 4π electron system and it is antiaromatic.
46. The electrophile $-\text{NO}_2^+$ involved in nitration is produced by an acid-base reaction between H_2SO_4 and HNO_3 . Since HNO_3 accepts proton from H_2SO_4 , HNO_3 acts as a base.
- $$\text{HO} - \text{NO}_2 + \text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_2\text{O}^+ - \text{NO}_2 + \text{HSO}_4^-$$
- $$\text{H}_2\text{O}^+ - \text{NO}_2 + \text{H}_2\text{SO}_4 \rightleftharpoons \text{NO}_2^+ + \text{H}_3\text{O}^+ + \text{HSO}_4^-$$
47. When benzene homologues are oxidized, the side chain gets oxidized to carboxylic acid group. Whatever be the length of the side chain, the ultimate oxidation product is benzoic acid. The carbon directly bonded to benzene should have at least one hydrogen atom for it to be oxidized.
48. It is Friedel-Crafts alkylation reaction. Alkyl carbocation is formed from alcohol as follow.



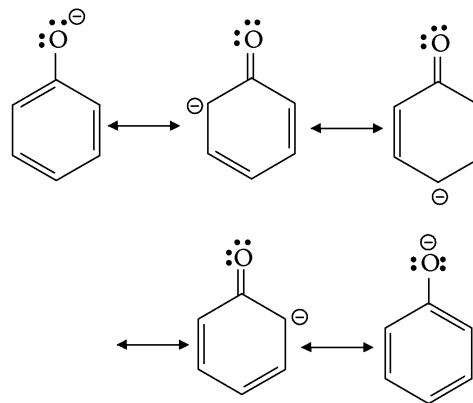
The carbocation R^+ (electrophile) attacks the benzene ring giving finally alkyl substituted aromatic hydrocarbon.

49. $-\text{OCH}_3$ group is activating and $-\text{CHO}$ group is deactivating. In such cases the activating group controls the orientation of the product. When a meta directing group is meta to an ortho, para directing group, the incoming group mainly goes ortho to the meta directing group.
50. An addition reaction occurs. Three molecules of chlorine are added to one molecule of benzene to produce hexachlorocyclohexane or BHC.

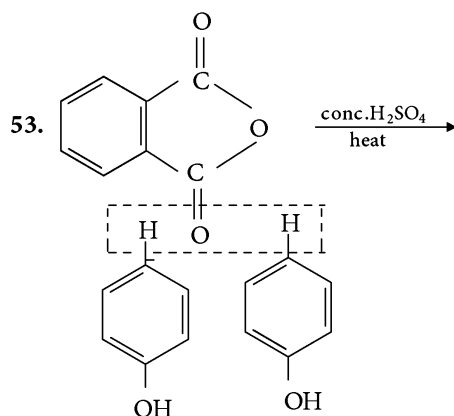


In this process, benzene loses its aromaticity. BHC exists in a number of stereochemical forms, one such isomer is γ -isomer known as gammexene, which is used as an insecticide.

51. Phenoxide ion is stabilized by resonance while alkoxide ion is not.

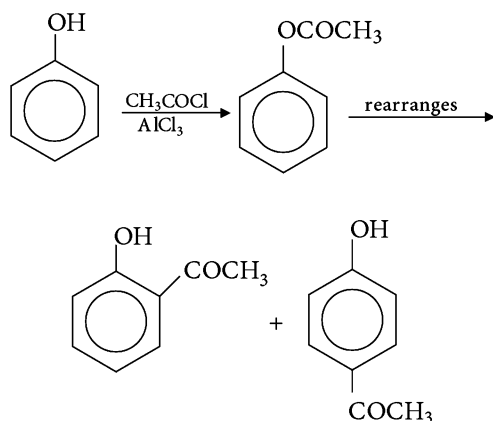


52. Phenol and ethanol will form soluble sodium phenoxide and sodium ethoxide respectively, with sodium. Only phenol will react with NaOH , neutral FeCl_3 and bromine water.

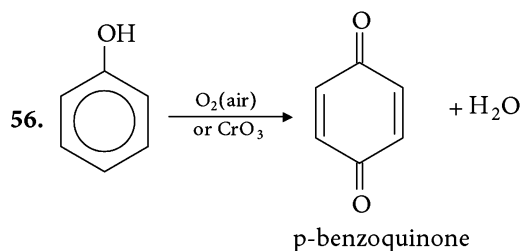


Phenolphthalein is used as an indicator in acid-base titrations.

54. The phenyl acetate formed undergoes Fries rearrangement to give the final product

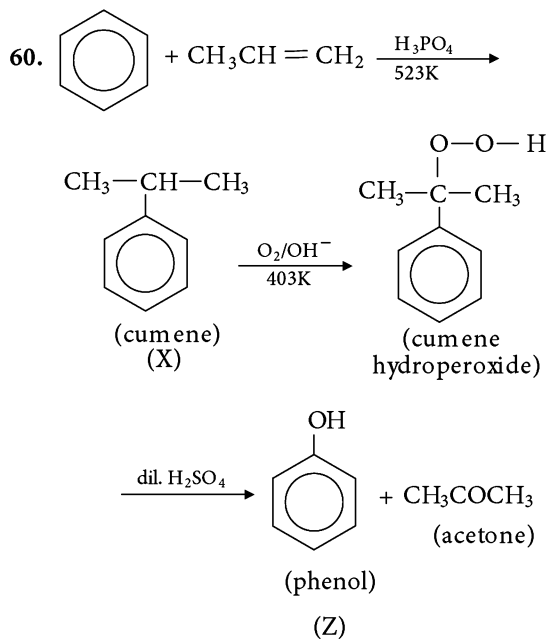


55. Phenol undergoes nitrosation to form p-nitrosophenol. Its enol form reacts with another molecule of phenol to form indophenol (brown solid). Indophenol forms a blue colour in alkali.

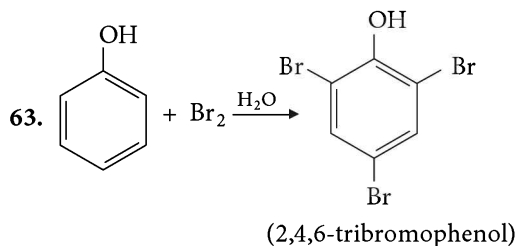


57. Electron withdrawing groups increase acidity while electron donating groups decrease the acidity. $-\text{OCH}_3$ is more electron donating (due to resonance effect) than $-\text{CH}_3$ (inductive effect).

58. Kolbe's reaction is the conversion of sodium phenoxide to salicylic acid by heating with CO_2 under pressure.
59. Salicylic acid when treated with methanol and few drops of $\text{conc. H}_2\text{SO}_4$ gives methyl salicylate (oil of wintergreen).

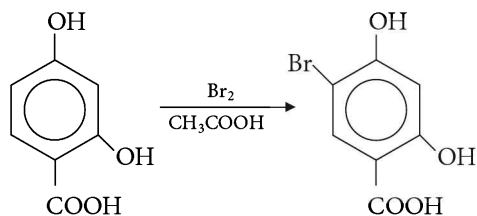


61. In the case of phenol, electron withdrawing groups increase the acidity by resonance stabilization of the phenoxide ion formed whereas, electron releasing group destabilizes the phenoxide ion and thus decreases the acidity. Phenol is acidic and hence turns blue litmus to red. Phenoxide ion is more resonance stabilised than phenol.
62. Schotten-Baumann reaction involves benzoylation of the compounds containing active hydrogen such as phenols, primary or secondary amines and alcohols with benzoyl chloride in aqueous NaOH or pyridine.

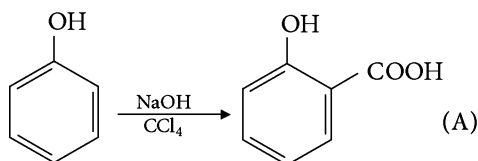


64. If bromine in acetic acid is used, bromination takes place without decarboxylation.

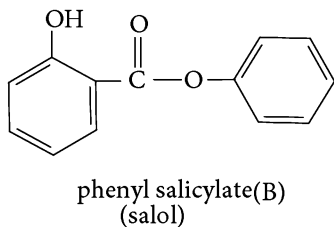
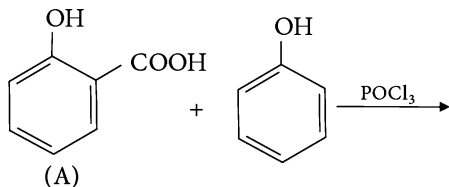
3.90 Benzene and Phenols



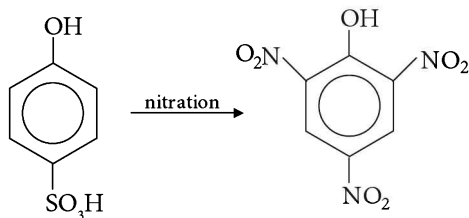
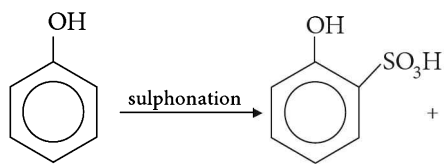
65. Reimer-Tiemann reaction can be applied for the synthesis of salicylic acid from phenol by using an alkaline solution of phenol and carbon tetrachloride. So (A) is salicylic acid. A small amount of p-hydroxy benzoic acid is also obtained which is separated.



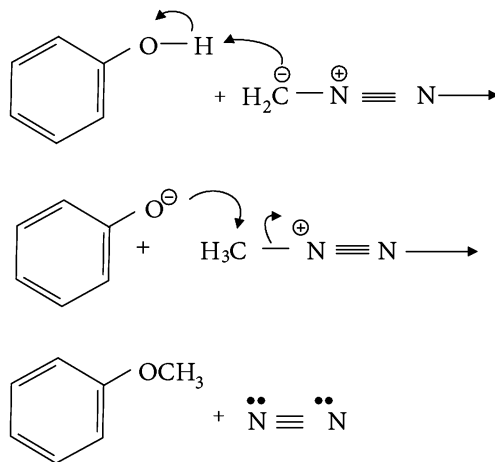
When salicylic acid is treated with phenol in the presence of phosphoryl chloride (POCl_3), the phenyl ester of salicylic acid or salol (B) is obtained.



66. The reaction is known as coupling reaction. Benzene diazonium chloride reacts with phenol to give an azo dye, parahydroxyazobenzene by coupling reaction.
67. Phenol on sulphonation gives a mixture of ortho and para hydroxybenzene sulphonic acid, both of which on nitration gives picric acid (2,4,6-trinitro phenol) by loss of $-\text{SO}_3\text{H}$ group.

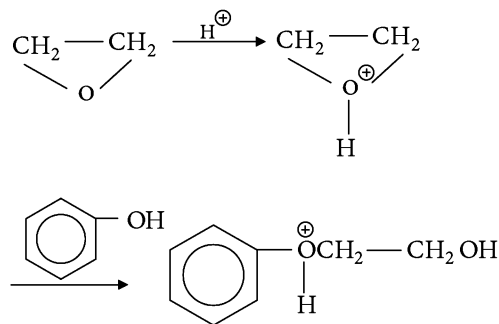


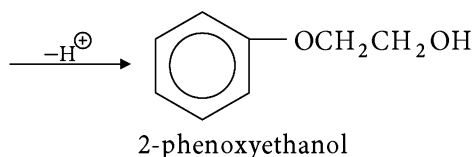
68. The use of diazomethane to convert a phenol to a methyl ether or a carboxylic acid to a methyl ester is a standard procedure. The mechanism of the formation of phenyl methyl ether from phenol by the use of diazomethane can be shown as follows.



69. Phenols give colour reactions with dilute neutral FeCl_3 solution. Simple phenol gives a violet or purple colour with dil. FeCl_3 solution. The composition of the coloured compound is $[\text{Fe}(\text{OC}_6\text{H}_5)_6]^{3-}$.
- $$6\text{C}_6\text{H}_5\text{OH} + \text{FeCl}_3 \rightarrow 3\text{H}^+ + [\text{Fe}(\text{OC}_6\text{H}_5)_6]^{3-} + 3\text{HCl}$$

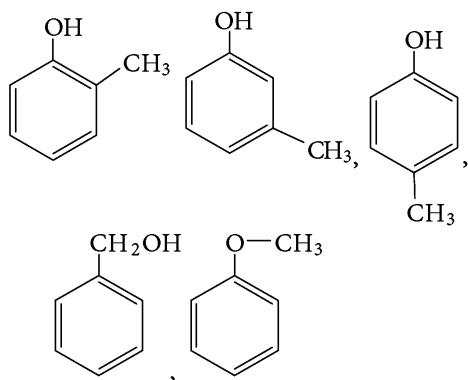
70. 2-phenoxyethanol is formed.



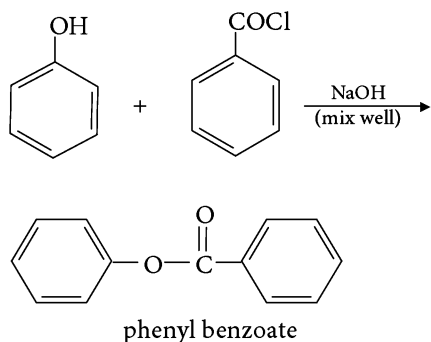


71. (b)

Structures of isomers are



72. This reaction is generally known as benzoylation reaction and commonly called as Schotten-Baumann reaction. This reaction occurs under alkaline conditions. The two components namely phenol and benzoyl chloride are mixed together in the presence of aqueous NaOH solution and shaken well so that the product (phenyl benzoate) separates out as an oil.

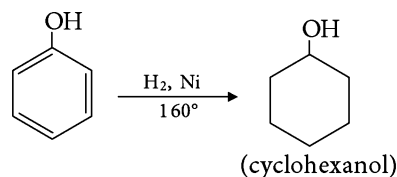


73. Fries rearrangement is shown by esters of phenol. Esters of phenol yield ortho or para hydroxy ketones or a mixture of both on treatment with anhydrous $AlCl_3$. For example, phenyl ethanoate yields a mixture of ortho and para hydroxy acetophenones. It involves migration of an acyl group from phenolic oxygen to ortho and para positions of the aromatic ring.

74. o-nitrophenol is steam volatile due to intramolecular hydrogen bonding.

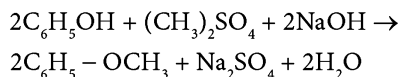
75. The only reaction which is not correctly represented is (c)

The correct answer is

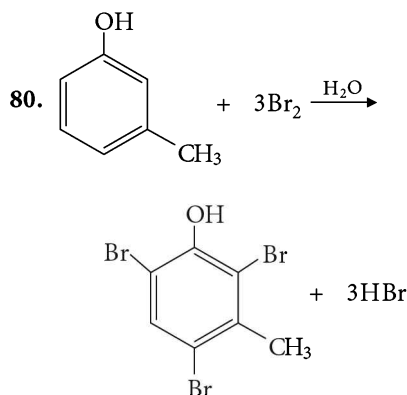


Only the double bonds get reduced, while the $-OH$ group remains intact.

76. The only wrong statement is about the solubility of nitrophenol in water. Ortho nitrophenol is involved in intramolecular hydrogen bonding and therefore less soluble in water compared to its isomers.
77. $NaHCO_3$ solution will not react either with phenol or benzyl alcohol and hence cannot be used to distinguish between them
78. Sodium phenoxide reacts with dimethyl sulphate to form anisole



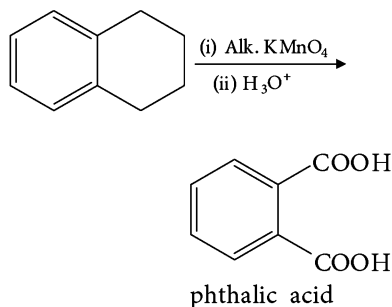
79. Salicylic acid undergoes decarboxylation with the formation of 2,4,6-tribromophenol when treated with bromine water. The displacement of carboxyl group occurs only when the reaction is carried out in aqueous solution.



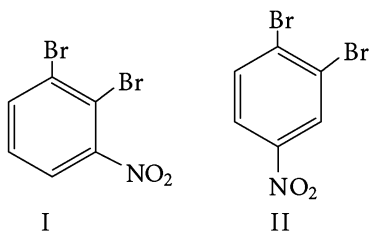
81. When oxidized with hot alkaline $KMnO_4$, the side chain attached to benzene ring gets oxidized to

3.92 Benzene and Phenols

–COOH. The carbon directly bonded to benzene should have at least one hydrogen atom for it to be oxidized to –COOH.

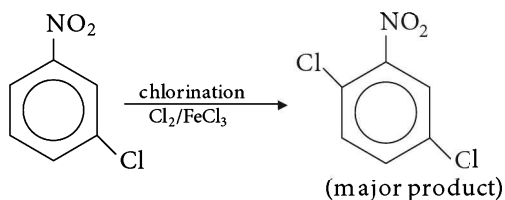


82. p-toluidine (III) is the most reactive compound towards electrophilic substitution because of the activating effects of both -NH_2 and CH_3 . Since nitrogen is less electronegative than oxygen, the lone pair is less firmly held by nitrogen and hence -NH_2 group is more activating than -OH group. 4-Methylbenzoic acid (II) is least reactive because of the deactivating influence of -COOH group.
83. 1,2-Dibromobenzene can give two mononitroderivatives I and II

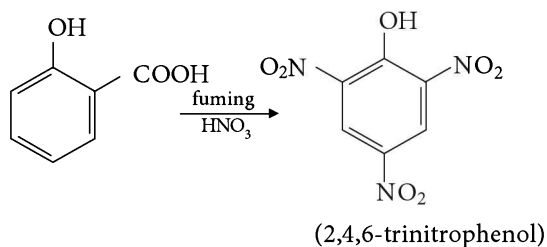
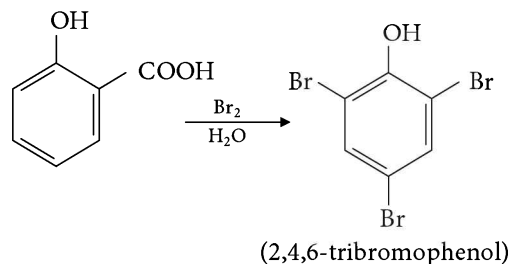


1,3-Dibromobenzene will give three and 1,4-dibromobenzene will give only one mononitro derivative.

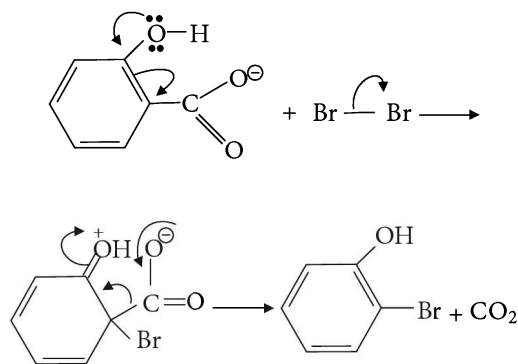
84. Phenol is oxidized to quinol by alkaline potassium persulphate. Hydroxylation occurs normally in the para position, but if this is blocked o-substitution occurs. This is known as Elbs persulphate oxidation.
85. When a meta directing group is present meta to an ortho, para directing group, then the incoming electrophile goes to the ortho position with respect to the meta directing group (rather than para).



86. Both bromination (with bromine water) and nitration (with fuming nitric acid and sulphuric acid) cause displacement of the carboxyl group of salicylic acid, resulting in the formation of 2,4,6-tribromophenol on bromination and 2,4,6-trinitrophenol (picric acid) on nitration.

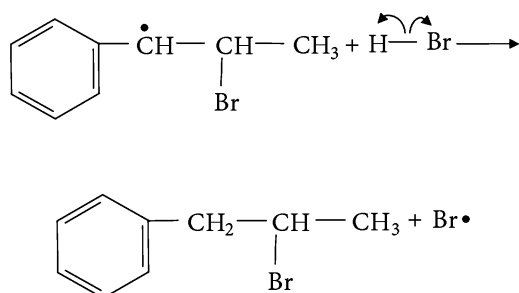
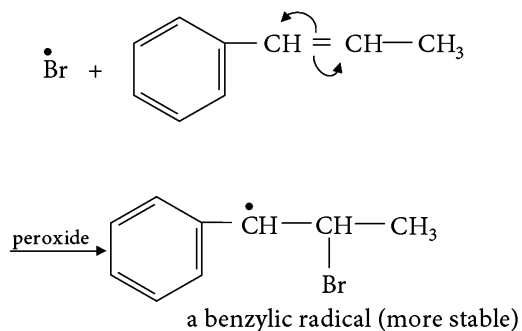


The following mechanism has been proposed for bromination

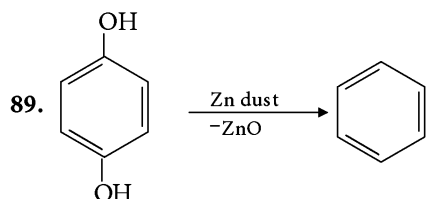


The displacement of carboxyl group was observed in the case of bromination in aqueous medium, but not in acetic acid medium.

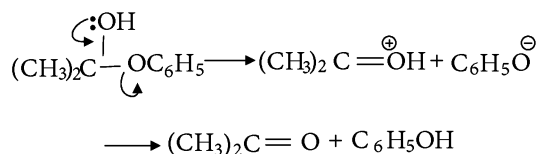
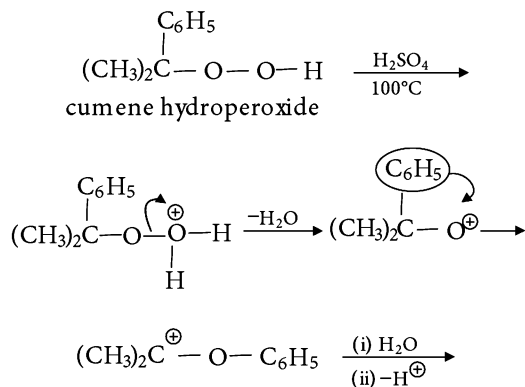
87. $-\text{SH}$ group is ortho, para directing while $-\text{CN}$, $-\text{CCl}_3$ and $-\text{NH}_3^+$ are meta directing groups.
88. HBr addition to olefins in the presence of peroxides proceed by the free radical mechanism. Bromine radical ($\dot{\text{Br}}$), generated by the peroxides adds on to the olefin in the chain initiation step as follows.



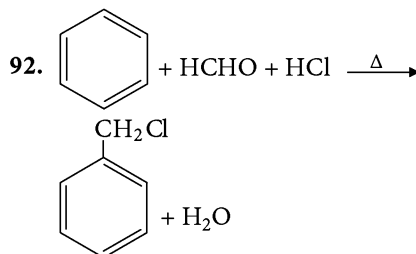
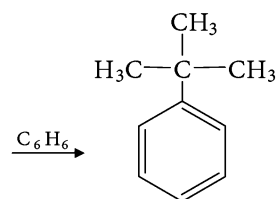
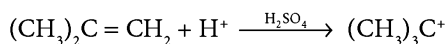
When HBr addition to 1-phenylpropene in the presence of peroxide occurs, the step that determines the orientation of the reaction is the chain propagation step. Bromine radical attacks the carbon of the side chain so as to form a more stable secondary benzylic radical, which then gives the final product.



90. The mechanism of conversion of cumene hydroperoxide to phenol and acetone involves the 1,2-shift of a phenyl group. The mechanism is depicted as follows.



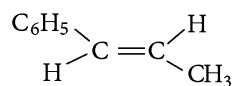
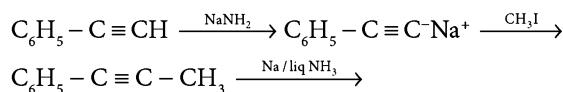
91. It is Friedel-Crafts alkylation reaction. The major product formed is tert-butylbenzene.



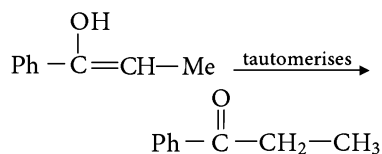
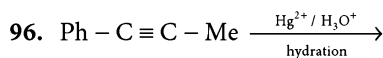
The reaction is known as chloromethylation

93. The cation represented in (b) is not fully conjugated as it contains sp^3 hybridized carbon atom in the ring.

94. The various steps may be represented as



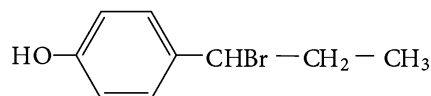
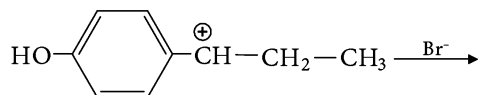
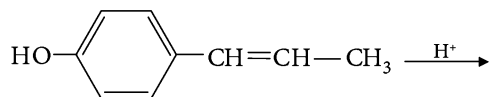
95. $-\text{NH}-\text{CH}_3$ group activates the benzene ring by +R (or +M) effect. $-\text{NO}_2$ and $-\text{COOH}$ group are deactivating groups. $-\text{NO}_2$ group deactivates benzene ring more than $-\text{COOH}$ group.



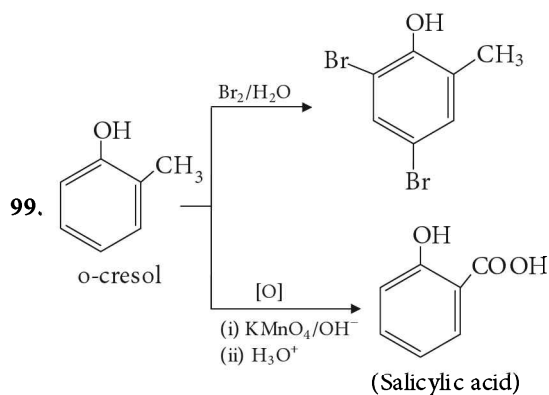
3.94 Benzene and Phenols

–OH group is mainly added to the carbon attached to benzene ring because the resulting ketone is more stable due to extended conjugation.

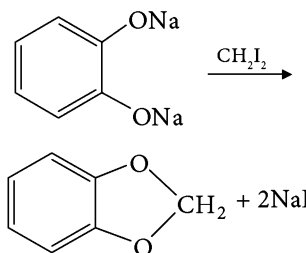
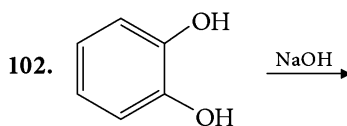
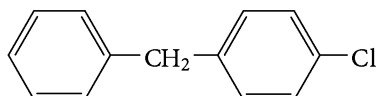
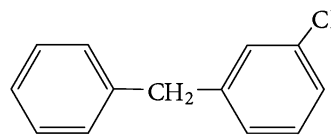
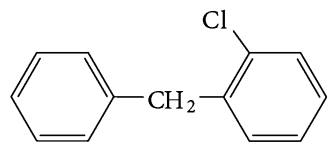
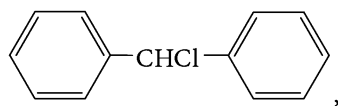
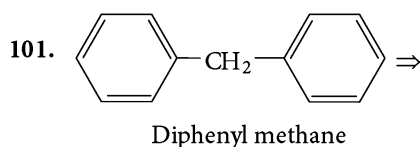
97. First step in the addition of HBr to $C = C$ is the formation of a carbocation by addition of H^+ . The more stable benzylic carbocation is formed preferentially in the given reaction. It then combines with Br^- to form the product



98. Bromine preferentially enters the para position of the benzene ring activated by the lone pair of –NH– group in N-phenyl benzamide.

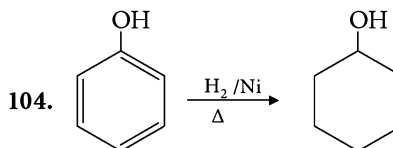


100. The major product formed in the reaction is 2-Hydroxy-4-methylbenzaldehyde. It is Reimer-Tiemann reaction.



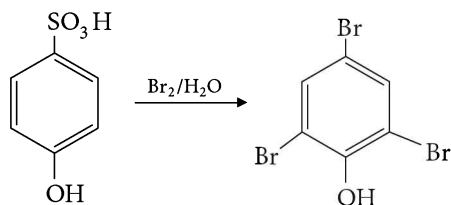
This reaction can be considered as an example Williamson's synthesis.

103. It is Birch reduction. In Birch reduction, 1,4-addition of hydrogen takes place and nonconjugated cyclohexadiene is formed. Electron withdrawing groups present in the benzene ring are usually found in the reduced position in the product.

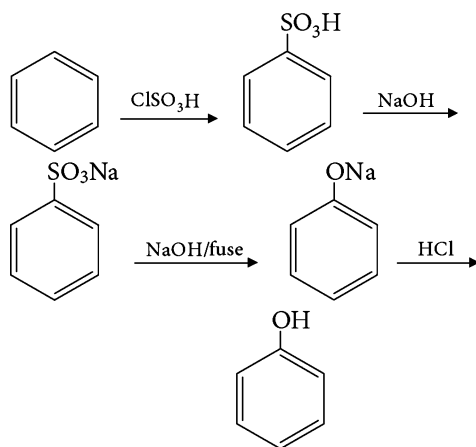


105. Reaction of phenol with bromine in aqueous medium to form tribromophenol is used for the volumetric (quantitative) estimation of phenol.

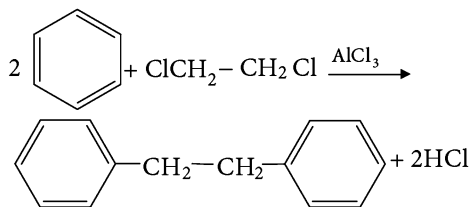
106. Bromine will replace –SO₃H group also when 4-hydroxybenzene sulphonic acid is treated with excess bromine water to give 2,4,6-tribromophenol as the final product.



107. The reaction of benzene with chlorosulphonic acid (ClSO_3H) first gives benzene sulphonc acid. This on reaction with NaOH gives sodium benzene sulphonate which will give phenol on fusing with NaOH followed by acidification.

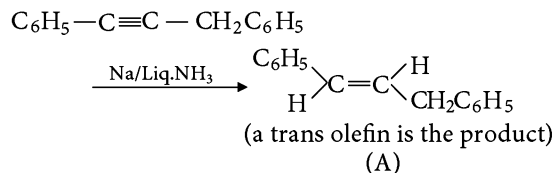
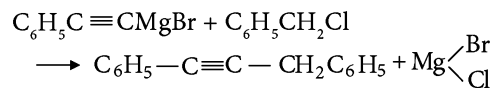
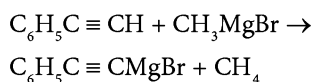


108. Bibenzyl (or 1,2-diphenyl ethane) is formed when benzene is treated with $\text{CH}_2\text{Cl} - \text{CH}_2\text{Cl}$ in presence of anhydrous AlCl_3 . It is Friedel-Crafts reaction.

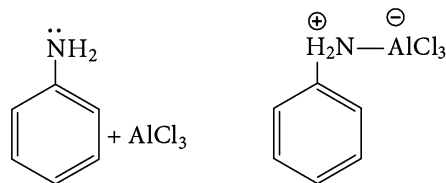


109. Biphenyl undergoes the usual electrophilic substitution reactions and in this phenyl group acts as ortho-para orienting group. On nitration, the main product is 4-nitrobiphenyl together with small amount of 1-nitrobiphenyl.

110. The sequence of reactions are

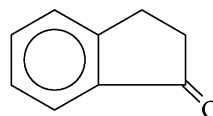
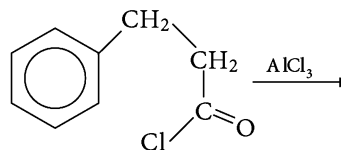
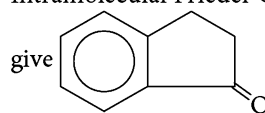


111. Statement 1 is correct but statement 2 is wrong. Nitrobenzene does not undergo Friedel-Crafts reaction because of the strong deactivating effect of $-\text{NO}_2$ group. In the case of aniline, Friedel-Crafts reaction does not take place because it forms an adduct with the Lewis acid AlCl_3 and the functional group is converted to a powerful electron withdrawing group.

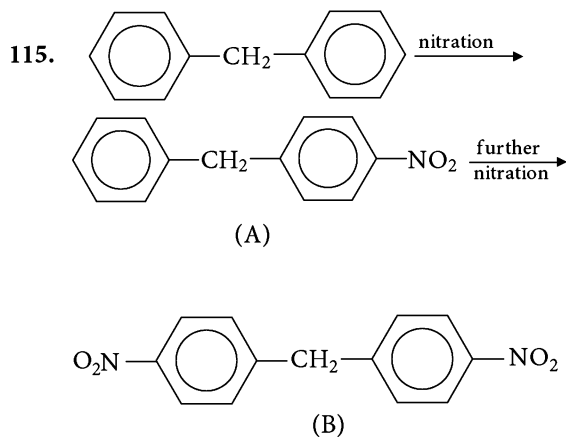


So statement 2 is not completely correct

112. Both statement 1 and 2 are correct. But statement 2 does not clearly explain the reason for the formation of $\text{C}_6\text{H}_5 - \text{CHBr} - \text{CH}_3$ as the major product.
113. Statement 1 is correct but statement 2 is false. Kolbe-Schmitt reaction is an example of aromatic electrophilic substitution reaction.
114. Intramolecular Friedel-Crafts acylation takes place to

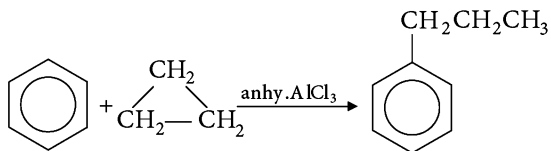


3.96 Benzene and Phenols

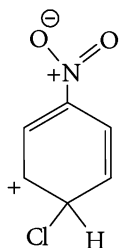
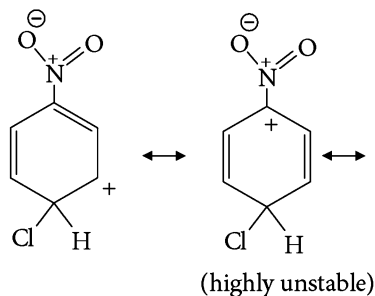


In (A), one ring has an electron withdrawing and ring deactivating $-\text{NO}_2$ group. So the second $^\oplus\text{NO}_2$ goes to the other ring, which is relatively more reactive.

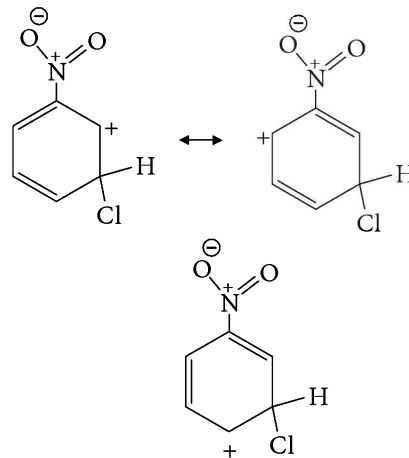
116. A good means of introducing n-propyl group is to use cyclopropane as the alkylating agent in presence of anhydrous AlCl_3 .



117. The intermediate arenium ion formed by initial attack at ortho and para positions is less stable because it contains canonical structures having positive charge on carbon containing electron withdrawing $-\text{NO}_2$ group.

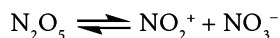


But the arenium ion formed by meta attack does not have such an unstable canonical structure



118. Phenol ($\text{pK}_a \approx 10$) is less acidic than carbonic acid (H_2CO_3 , $\text{pK}_a \approx 6.3$). Presence of electron withdrawing groups increase the acidity of phenol.
119. $-\text{COOH}$ group and $-\text{SO}_3\text{H}$ groups are displaced in bromination of salicylic acid and 4-hydroxy benzene sulphonic acid giving 2,4,6-tribromophenol as the final product.
120. (a) $\rightarrow$ (p)
 (b) $\rightarrow$ (p), (s)
 (c) $\rightarrow$ (p), (q), (t)
 (d) $\rightarrow$ (p), (r)

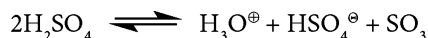
Nitration of aromatic compound can also be carried out using $\text{N}_2\text{O}_5/\text{CCl}_4$. N_2O_5 dissociates spontaneously in CCl_4 medium as



Additional Practice Exercise

121. (i) Sulphonation

The reagent used is conc. H_2SO_4 .

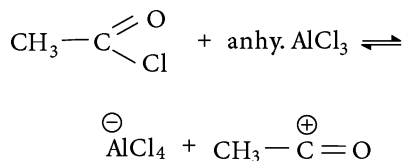


The electrophile is SO_3 .

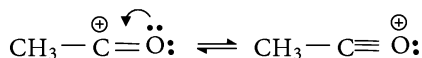
- (ii) Friedel-Crafts alkylation

$\text{CH}_3^\oplus$ or alkyl carbocation is the electrophile generated.

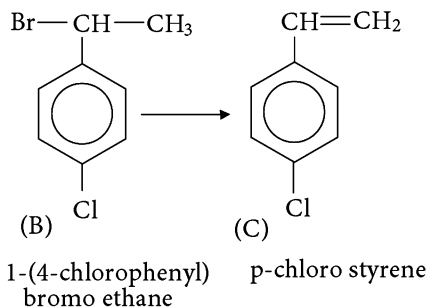
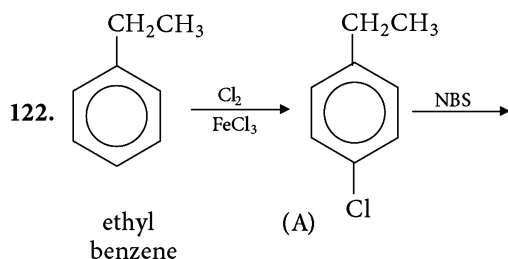
(iii) Friedel – Crafts acylation



The acylium ion is stabilized by resonance as follows.



Acyl cation is the electrophile involved.

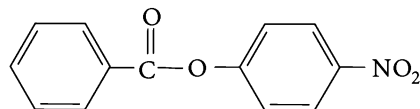


A small amount of 2-chloroethylbenzene is also formed along with (A) which is separated by suitable means.

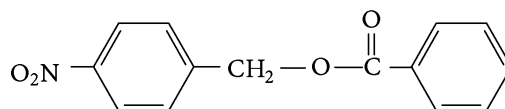
123. A difference in the rate of a reaction due to a difference in the isotope present (for example, deuterium instead of hydrogen) in a reaction is called an isotope effect. Isotope effect is used to find out whether cleavage of a particular bond in the substrate takes place in the rate determining step or not. For example, in aromatic electrophilic substitution, C – H bond of benzene is broken and a new C – electrophile bond is formed. To find out whether C – H bond cleavage occurs in the rate determining step, hexadeuterobenzene (C_6D_6) containing C – D bond is prepared. Benzene and hexadeuterobenzene are allowed to undergo electrophilic substitution under similar conditions and the rates of the reaction are measured. Since C – D bond is stronger than C – H bond, the two

compounds will show different rate if C – H bond or C – D bond cleavage occurs in the rate determining step. However, in nitration and halogenation, the rates are found to be the same for C_6H_6 and C_6D_6 (i.e., no kinetic isotope effect is observed). This means that C–H bond cleavage does not take place in the rate determining step in these reactions. Due to the reversible nature, sulphonation reactions shows small kinetic isotope effect.

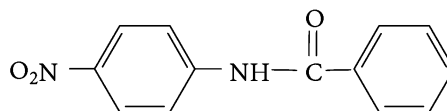
124. (i) The ring next to the oxygen will get nitrated, due to activating effect.



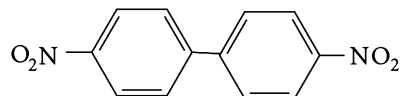
- (ii) Benzylic ring will get nitrated because of the electron withdrawing inductive effect of the ester function on the other ring.



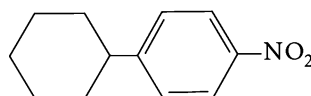
- (iii) Amino group is activating



- (iv) $-\text{NO}_2$ group is deactivating



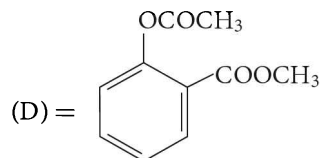
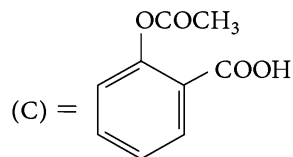
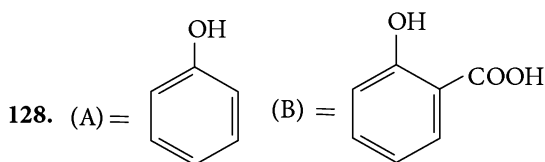
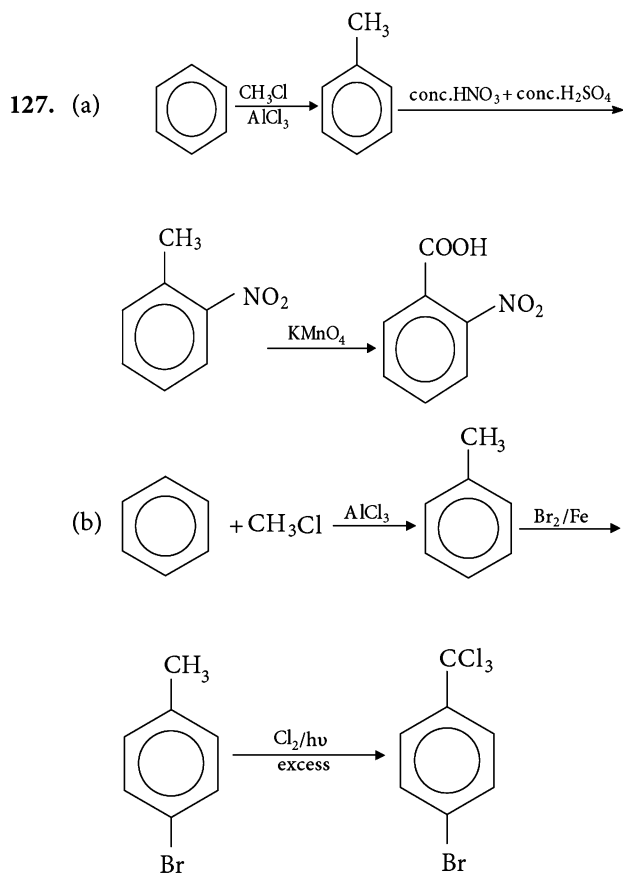
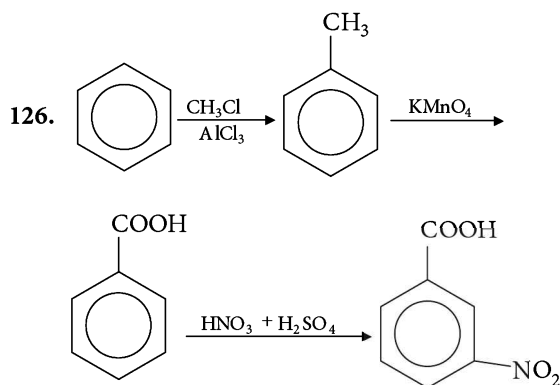
- (v) Cyclohexane ring is not active enough to get nitrated.



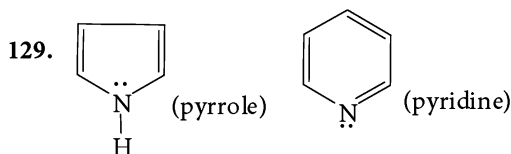
[Note: In all these cases a small amount of the corresponding ortho nitro derivative is also formed.]

3.98 Benzene and Phenols

125. (a) Cyclooctatetraene has 8 pi electrons and is not planar. But the dianion formed obeys Huckel's $(4n + 2) \pi$ - electrons rule with 10pi electrons. So it becomes planar and aromatic.
- (b) Cycloheptatrienone is polarized so that carbon gets positive charge and the cation according to Huckel rule is aromatic, but in Cyclopentadienone the polarization leads to cation which does not obey Huckel rule and hence it dimerizes to form Diels Alder adduct.

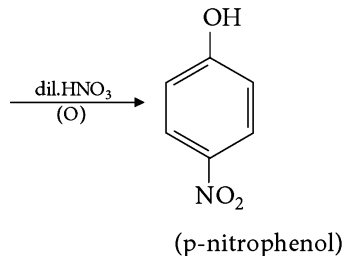
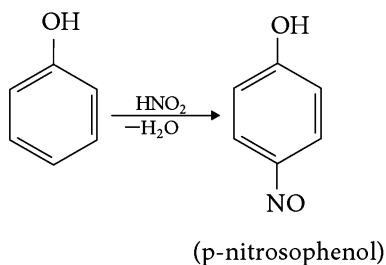


Along with (B), o-hydroxy benzoic acid, a small amount of the para isomer is also obtained which is separated. Diazomethane (CH_2N_2) converts the free acid to the methyl ester (D).

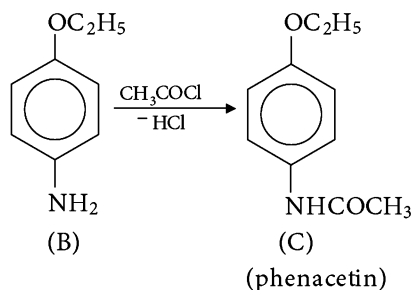
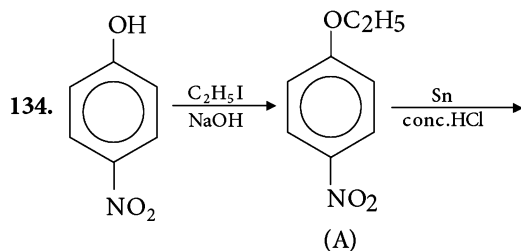


The lone pair of electron on nitrogen in pyrrole is also needed for aromatic sextet. Since the lone pair is involved in delocalisation to give it aromatic stability, it is not readily available for protonation. So pyrrole is less basic. But in pyridine the lone pair on nitrogen is not involved in giving it aromatic stability.

130. There is intramolecular hydrogen bonding in ortho fluoro phenol. Since the phenolic hydrogen is involved in intramolecular hydrogen bonding, the acidic strength of o-fluorophenol is slightly less than that of o-chlorophenol
131. The ring has 6π electrons, obeys Huckel's $(4n + 2)$ rule and is aromatic.
132. The reaction of phenol with nitrous acid gives p-nitrosophenol. The reaction is known as nitrosation. The mild oxidation of p-nitrosophenol leads to the formation of p-nitrophenol. Benzene cannot be directly nitrosated to give nitrosobenzene.



133. Phenol is a stronger acid than alcohol. However, it is soluble only in aqueous sodium hydroxide solution and not in saturated NaHCO_3 solution. Only stronger acids like carboxylic acids are soluble in weaker bases like NaHCO_3 solution.



135. The migratory aptitude of the $\text{H}_3\text{CO}-$ group is high because of higher activation. So the ketone remaining will be This is similar to cumene hydroperoxide rearrangement to give phenol and acetone.

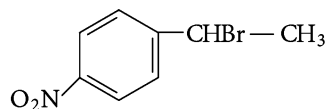
136. The only correct statement is (a).

137. Reimer-Tiemann reaction is the introduction of an aldehyde group in benzene ring containing a $-\text{OH}$ substituent. This is an aromatic electrophilic substitution reaction involving dichlorocarbene intermediate. This electrophile $:\text{CCl}_2$ is generated from chloroform by the action of a base.

138. Phenol is less acidic than p-nitrophenol. The nitro group by its electron withdrawing effect enhances the acidity of phenol.

139. Vapours of naphthalene when mixed with air and passed over V_2O_5 at 673 – 773 K gives phthalic anhydride (A). It reacts with phenol to form phenolphthalein (B)

140. Under the influence of heat and light, bromination occurs in the side chain to give

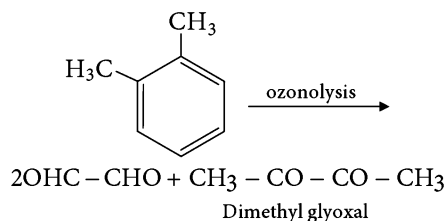
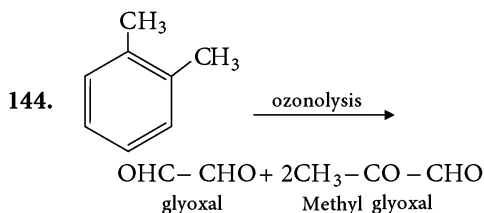


Bromination is selective and only monobromination occurs, unless excess bromine is added.

141. Since $-\text{OCH}_3$ group is a stronger electron donating group than $-\text{CH}_3$ group, the acid strength of I is less than that of III. II is the most acidic due to strong electron withdrawing nature of $-\text{NO}_2$ group.

142. $-\text{O}^-$ is more activating due to the presence of negative charge on oxygen. $-\text{O}-\text{COCH}_3$ is less activating than $-\text{OH}$ due to the electron withdrawing nature of $-\text{C}(=\text{O})-$ group. $-\text{COCH}_3$ is a deactivating group.

143. Phenol can be converted to quinol by oxidation with alkaline $\text{K}_2\text{S}_2\text{O}_8$ followed by acidification. The reaction is known as Elbs persulphate oxidation



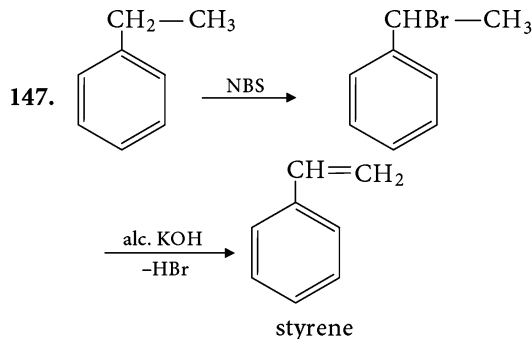
3.100 Benzene and Phenols

145. Benzene is converted to biphenyl when passed through a red hot tube (973 – 1073K)



146. $3\text{C}_6\text{H}_6 + \text{CHCl}_3 \xrightarrow{\text{AlCl}_3} (\text{C}_6\text{H}_5)_3\text{CH} + 3\text{HCl}$
Triphenylmethane

Triphenylmethane is also known as tritane.



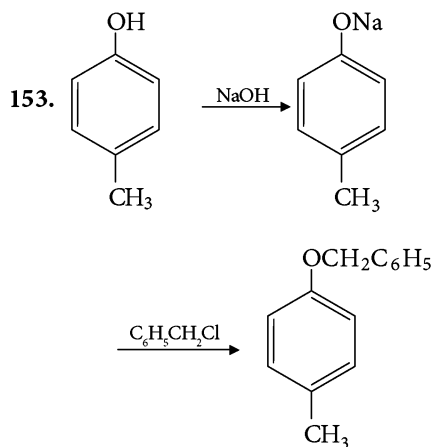
148. $-\text{CCl}_3$ is a meta directing group

149. When $-\text{OCH}_3$ group is at the meta position of phenol, donation of lone pair by resonance and consequent destabilization of phenoxide ion is not possible. Instead, oxygen of $-\text{OCH}_3$ withdraws electrons by $-\text{I}$ effect and stabilizes the phenoxide ion to a certain extent.

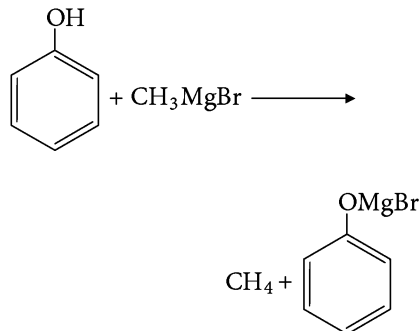
150. 2,4,6-trinitrophenol is more acidic than carbonic acid. So it reacts with NaHCO_3 solution to form the corresponding sodium salt with the liberation of CO_2 .

151. NBS gives allylic substitution. In (b), Br is substituted at the allylic carbon of both the double bonds.

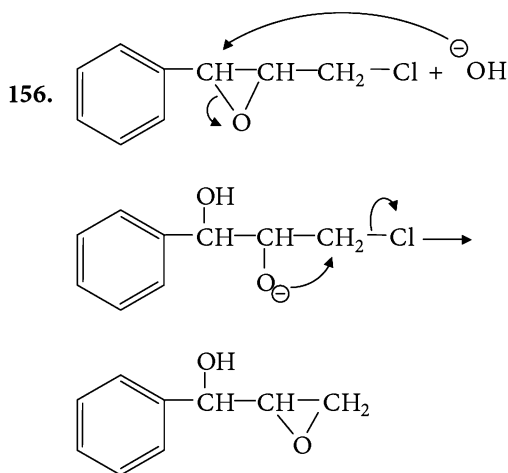
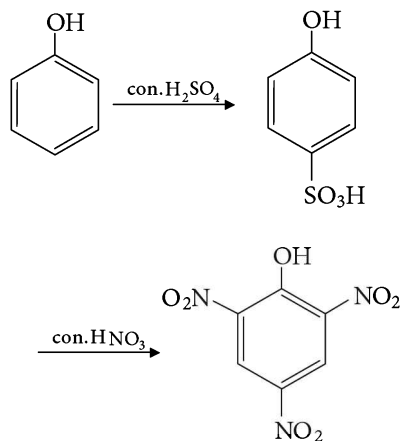
152. Chlorophenol is the most acidic. This is due to the electron withdrawing influence of chlorine



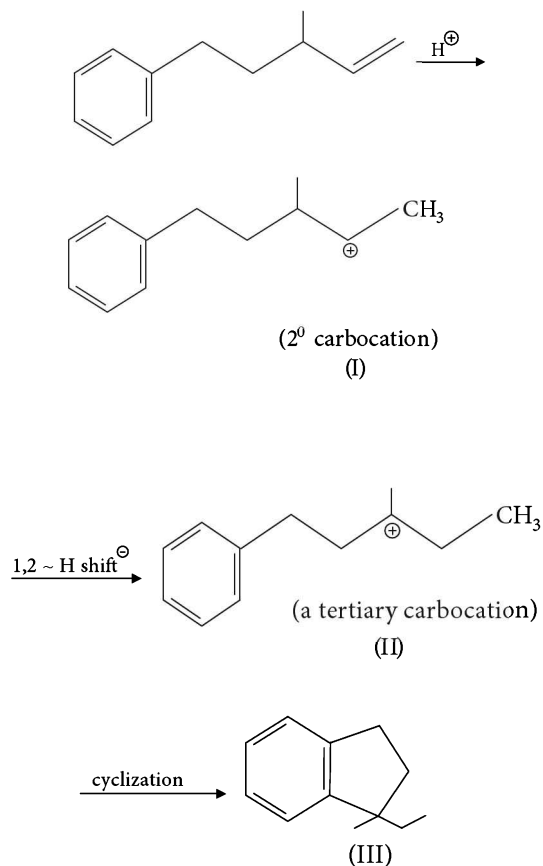
154. Anisole ($\text{C}_6\text{H}_5\text{OCH}_3$) is not formed in the reaction of phenol with CH_3MgBr



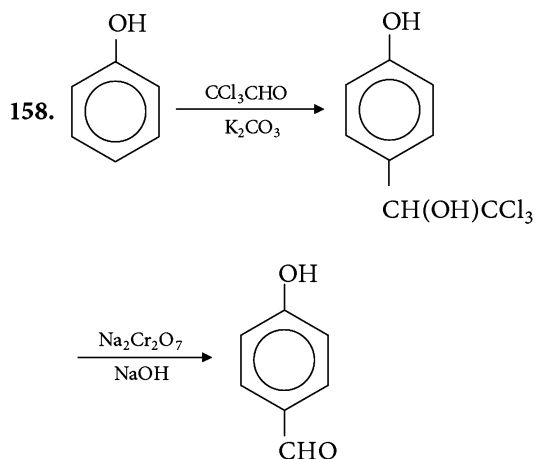
155. Picric acid is generally prepared by first treating phenol with con. H_2SO_4 and then with con. HNO_3



157. A cyclized product is expected. A five membered ring is formed on cyclization. This can be explained by the following steps.



Electrophilic addition of H^+ on to the double bond takes place which results in the formation of a secondary carbocation (I). By the 1,2-shift of a hydride ion, this changes to a more stable tertiary carbocation (II). Then a cyclization occurs to give a cyclic structure (III).

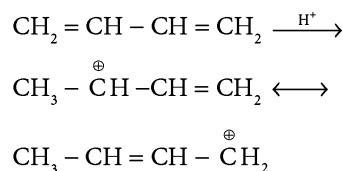


159. Salicylaldehyde when treated with alkaline H_2O_2 followed by acidification gives catechol. It is a convenient laboratory method of preparation of catechol. It is known as Dakin reaction.

160. Phenol condenses with formaldehyde in the presence of dilute acid or alkali to form mainly p-hydroxybenzyl alcohol together with small amount of the ortho isomer. The formation of these products is the basis for the preparation of bakelite.

161. Both $-\text{OH}$ and $-\text{CH}_3$ groups are ortho, para orienting. The major dinitro derivative is (b). (a) has more steric crowding and will be only a minor product.

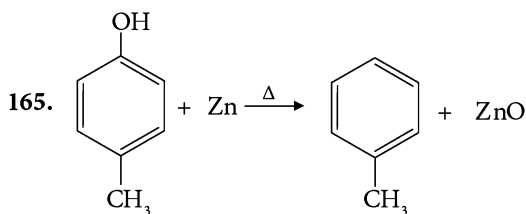
162. It is Friedel-Crafts alkylation reaction



The carbocation attacks the benzene ring to form (a) as one of the products.

163. When toluene is treated with CH_3Cl in presence of anhydrous AlCl_3 , xylene is formed.

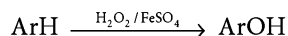
164. A very convenient method of introducing n-propyl group into an aromatic ring is to use cyclopropane as the alkylating agent. It is Friedel-Crafts alkylation.



166. Planar, conjugated cyclic compounds having $4n$ π electrons are unstable and are antiaromatic. For example, cyclobutadiene, a cyclic conjugated diene, is antiaromatic.

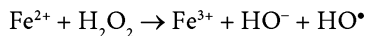
167. Fluorescein is prepared by heating phthalic anhydride with resorcinol to 473K.

168. Fenton's reagent (a mixture of H_2O_2 and FeSO_4) can be used to hydroxylate aromatic rings, but yields are usually not high



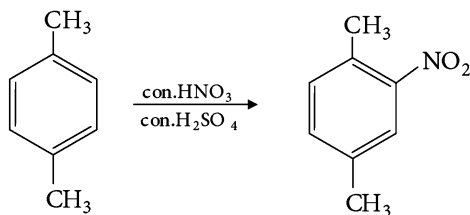
3.102 Benzene and Phenols

The reaction takes place by the attack of HO radical produced from Fenton's reagent on the aromatic ring.



Trifluoroperacetic acid ($\text{F}_3\text{C}-\text{CO}_3\text{H}$) can also bring about hydroxylation at an aromatic carbon.

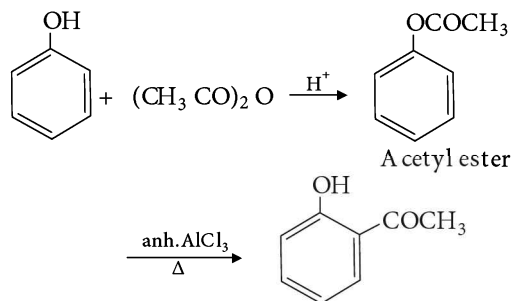
169. p-xylene can give only one mononitro derivative



o-xylene will give two mononitro derivatives while meta xylene will give three isomers of the mononitro derivative. Ethyl benzene can give three mononitro derivatives.

170. It is an example of Friedel-Crafts reaction used to effect ring closure. The product formed is tetralin.
171. Both statements 1 and 2 are correct, but statement 2 is not the reason for statement 1.
172. Both statements are correct and statement 2 is the reason for statement 1. Phenol is slowly oxidized by air to quinones which gives colour to old samples of phenol.
173. Due to resonance involving lone pair on oxygen, C–O bond in phenol has partial double bond character and it is stronger than the C–O bond in alcohols. So the bond is not readily broken in the case of phenol and the yield of chlorobenzene is less with PCl_5 .
174. Statement (1) is correct while statement (2) is not correct.
Phenol contains an activating group in benzene. It makes the ring electron rich for aromatic electrophilic substitution. On the other hand, benzene does not have any activating group. Hence phenol is more active than benzene in electrophilic substitutions.
However, statement (2) is not correct as the acidity of phenol has no influence on substitution.
175. Both statements (1) and (2) are correct. However, statement (2) is not supportive of statement (1).
The ring acylation of phenol is effected under Friedel Crafts conditions because the O–acylated product

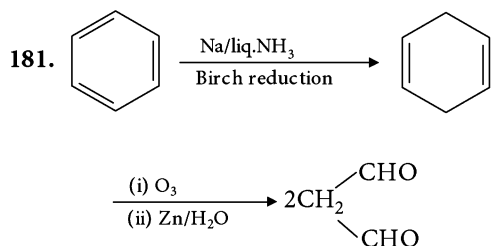
rearranges to a C–acylated product by Fries rearrangement, which occurs under thermodynamically controlled conditions. The sequence of reactions are represented as shown



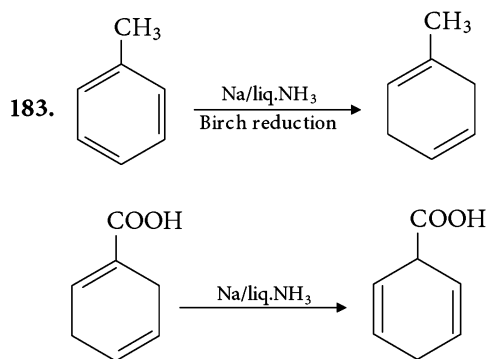
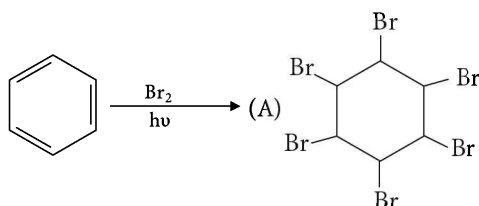
So both statements (1) and (2) are correct though statement (2) is not supportive of (1).

176. Statement 1 is true but statement 2 is not fully correct. Most of the deactivating groups are meta orienting groups. But $-\text{Cl}$, $-\text{Br}$ etc are deactivating groups but at the same time ortho, para directing.
177. Statement 1 is wrong while statement 2 is correct. Among the halogens, fluorine is the least deactivating and fluorobenzene usually shows a reactivity almost same as that of benzene towards electrophilic substitution. This is probably because of the very effective overlap of the 2p orbital containing lone pair of fluorine and 2p orbital of carbon resulting in greater +R effect compared to chlorine.
178. Both statements are correct, but statement 2 is not the reason for the easier electrophilic substitution in phenoxide. Phenoxide is more reactive because it activates the ortho and para positions of benzene ring more due to the negative charge of oxygen.
179. Statement 1 is correct, but statement 2 is not correct. Sulphonation reaction is reversible. That is why benzene sulphonic acid when heated with superheated steam gives back benzene.

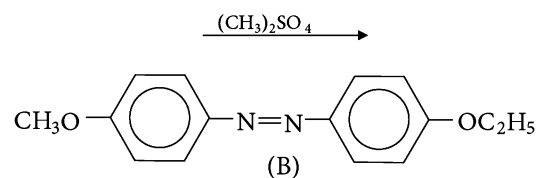
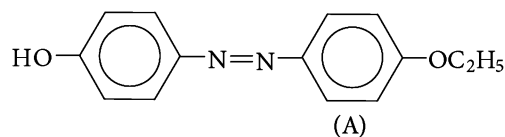
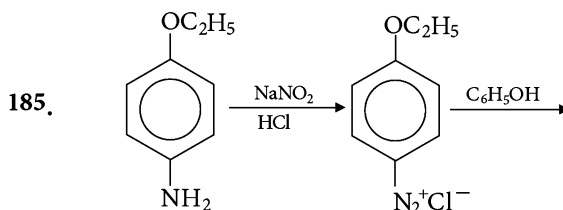
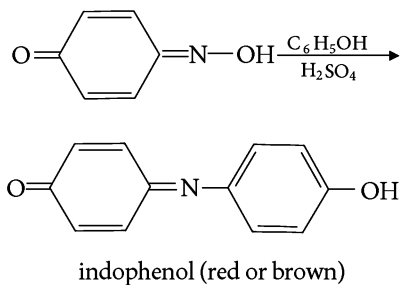
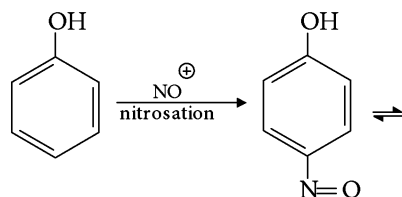
Since sulphonation is reversible, some kinetic isotope effect is found in the case of sulphonation reaction.
180. Statement 1 is true, but statement 2 is not true. Phenol undergoes Kolbe's reaction which is an electrophilic substitution reaction. Statement 2 is wrong because phenoxide ion ($\text{C}_6\text{H}_5\text{O}^-$) is less basic than ethoxide ($\text{C}_2\text{H}_5\text{O}^-$) ion.



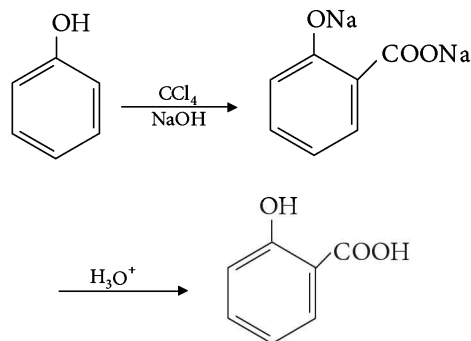
182. Benzene reacts with bromine in presence of sunlight to produce crystalline benzene hexabromide, $\text{C}_6\text{H}_6\text{Br}_6$



184. A red or brown indophenol is obtained. The sequence of reactions is given below.



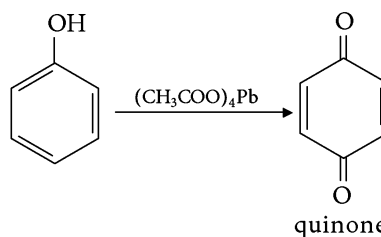
186. Salicylic acid is formed as the main product.



187. Under mild conditions (Br_2 in CS_2 or CCl_4 at low temperatures), cresol undergoes only mono substitution. A para bromo derivative (para to phenolic group) is obtained as a major product.

188. The carbon of the aromatic ring is sp^2 . Greater the 's' character, shorter is the C – O bond length. In alcohols, carbon is sp^3 hybridized.

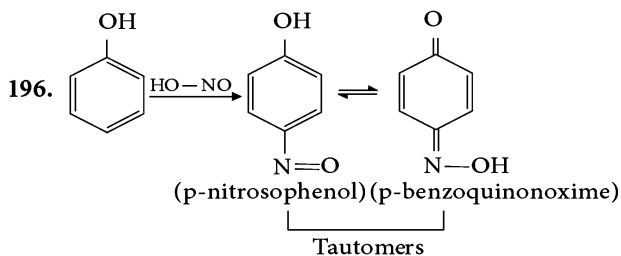
189. Lead tetraacetate, $(\text{CH}_3\text{COO})_4\text{Pb}$, converts phenols to quinones.



3.104 Benzene and Phenols

- 190.** All the four methods given will result in phenol as the product.
- 191.** (a) and (d) are examples of aromatic electrophilic substitution. The other two reactions represented by (b) and (c) are not electrophilic substitutions.
- 192.** Maleic anhydride is industrially prepared by oxidation of benzene with air in presence of V_2O_5 at about 700K. Kinetic isotope effect is not observed for nitration reaction. Distillation of both o-cresol and p-cresol will give toluene. So statements (a), (b) and (d) are correct. Benzene hexachloride is a saturated compound as it does not contain any double bond.
- 193.** Compound (b) is azulene and (c) is thiophene. Both of them are aromatic and satisfy Huckel's rule. (a) and (b) are antiaromatic species containing 4 delocalized electrons.
- 194.** Ethyl benzene, anisole ($C_6H_5 - OCH_3$) and naphthalene are more reactive than benzene towards electrophilic substitution reaction.

- 195.** In (b), $(CH_3)_2CHCH_2OH$ first produces a 1° carbocation and it rearranges to the more stable $(CH_3)_3C^+$ (3° carbocation) which undergoes electrophilic substitution reaction with benzene to form tert-butyl benzene. In (d) protonation of $Me_2C=CH_2$ gives mainly $(CH_3)_3C^+$ and forms tert-butyl benzene.
- (a) cannot produce tert-butyl benzene and no reaction occurs in (c).



- 197.** o-cresol, o-fluorophenol and p-methoxyphenol are less acidic than o-nitrophenol. But p-nitrophenol is more acidic than o-nitrophenol.

CHAPTER

4

ALCOHOLS, ALKYL HALIDES AND HALOARENES

■■ CHAPTER OUTLINE

Preview

STUDY MATERIAL

Introduction

Preparation of alcohols

Reactions of alcohols

Methods to distinguish 1°, 2° and 3° alcohols

Pinacol-pinacolone rearrangement

- Concept Strands (1-3)

Introduction

Classification of alkyl halides

HALOALKANES (ALKYL HALIDES)

Preparation of alkyl halides

Nucleophilic substitution at saturated carbon atom

Mechanism of nucleophilic substitution reactions

Rearrangements observed in S_N1 reactions

Haloarenes

Preparation of haloarenes

Aromatic nucleophilic substitution in haloarenes and substituted haloarenes

Elimination-addition mechanism (EA mechanism)

Additional reactions of haloarenes

Reactions of aralkyl halides

Grignard reagents

Reactions of the Grignard reagents

- Concept Strands (4-12)

TOPIC GRIP

- Subjective Questions (10)
- Straight Objective Type Questions (5)
- Assertion–Reason Type Questions (5)
- Linked Comprehension Type Questions (6)
- Multiple Correct Objective Type Questions (3)
- Matrix-Match Type Question (1)

IIT ASSIGNMENT EXERCISE

- Straight Objective Type Questions (80)
- Assertion–Reason Type Questions (3)
- Linked Comprehension Type Questions (3)
- Multiple Correct Objective Type Questions (3)
- Matrix-Match Type Question (1)

ADDITIONAL PRACTICE EXERCISE

- Subjective Questions (10)
- Straight Objective Type Questions (40)
- Assertion–Reason Type Questions (10)
- Linked Comprehension Type Questions (9)
- Multiple Correct Objective Type Questions (8)
- Matrix-Match Type Questions (3)

INTRODUCTION

Alcohols are compounds containing -OH group. They are represented by the general formula R-OH , where R is a simple alkyl group or substituted alkyl group. The R group can be open chain, branched chain or alicyclic. Alcohols may be aliphatic or aromatic.

Alcohols are classified as monohydric, dihydric, trihydric and polyhydric alcohols depending on the number of -OH groups present in them.

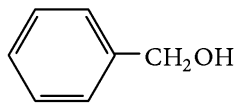
Monohydric alcohols are further classified as primary (1°), secondary (2°) and tertiary (3°) alcohols depending on the carbon to which -OH group is attached.

A primary alcohol is one in which the -OH group is attached to a primary carbon atom in the molecule.

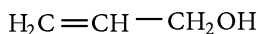
Examples are



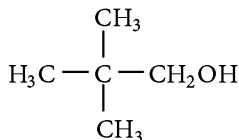
ethyl alcohol
(ethanol)



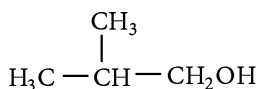
benzyl alcohol
(phenylmethanol)



allyl alcohol
(prop-2-en-1-ol)



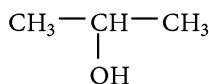
neopentyl alcohol
(2,2-dimethyl-1-propanol)



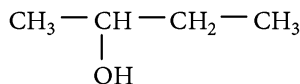
isobutyl alcohol
(2-methyl-1-propanol)

A secondary alcohol is one in which the -OH group is attached to a secondary carbon atom.

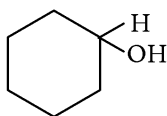
Examples are



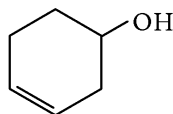
isopropyl alcohol
(2-propanol)



sec-butyl alcohol
(2-butanol)



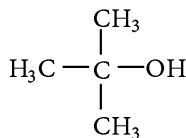
cyclohexyl alcohol
(cyclohexanol)



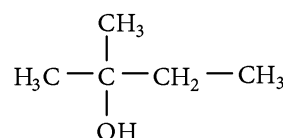
cyclohex-3-en-1-ol

A tertiary alcohol is one in which the -OH group is attached to a tertiary carbon atom.

Examples are



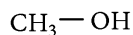
tert-butyl alcohol
(2-methyl-2-propanol)



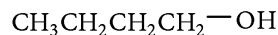
(2-methyl-2-butanol)

If only one -OH group is present in an alcohol, it is known as monohydric alcohol.

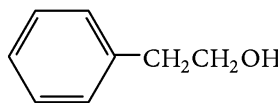
Examples are



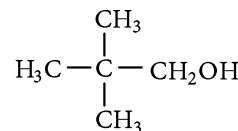
methyl alcohol
(methanol)



n-butyl alcohol
(1-butanol)



β -phenylethanol
(2-phenyl ethanol)

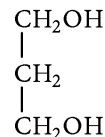


2,2-dimethyl-1-propanol

If two -OH groups are present, it is known as a diol or a dihydric alcohol.

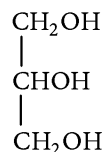


ethylene glycol
(ethane-1,2-diol)



propane-1,3-diol

If three hydroxyl groups are present, then it is known as a triol or trihydric alcohol. The most common example of a triol is glycerol.

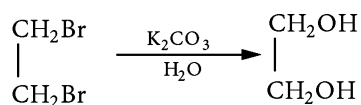
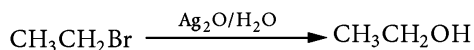


glycerol
(propane-1,2,3-triol)

PREPARATION OF ALCOHOLS

Hydrolysis of alkyl halides

Hydrolysis of alkyl halides with aqueous alkali or moist silver oxide or aqueous potassium carbonate yield alcohol.

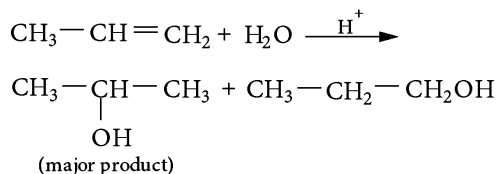


Primary alkyl halides give good yield of alcohols, while tertiary alkyl halides mainly give alkene by dehydrohalogenation.

Hydration of alkenes

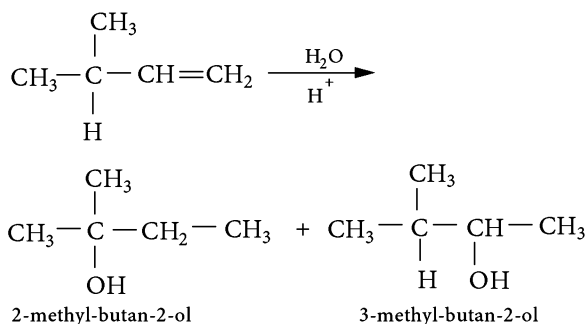
(a) Acid catalyzed hydration

Dilute acid catalyzed hydration of alkenes give alcohols.



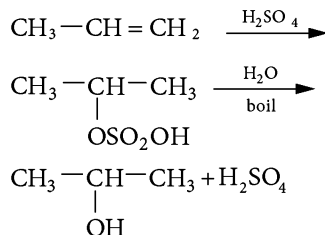
The major product is formed in accordance with Markovnikov's rule.

The reaction proceeds via the formation of a carbocation intermediate and rearrangement of carbocation could be observed.



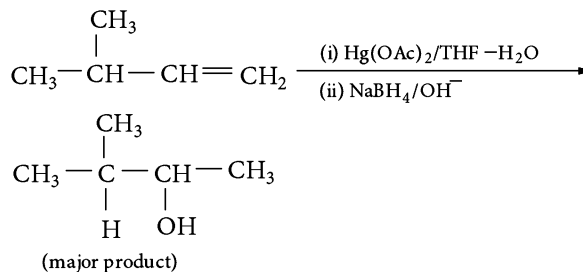
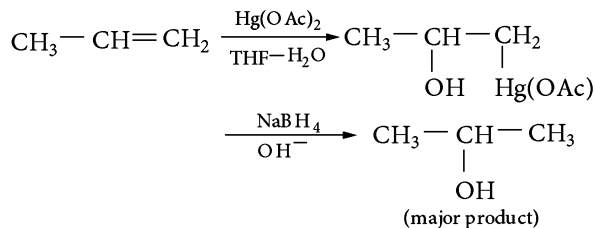
(b) Indirect hydration

In this method, alkenes are passed into $\text{con. H}_2\text{SO}_4$ to form alkyl hydrogen sulphates. These are then hydrolyzed with boiling water to give alcohols



(c) Oxymercuration-demercuration

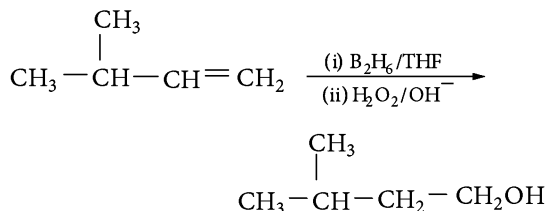
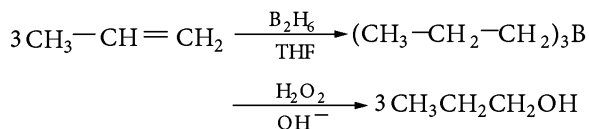
Mercuric acetate in THF- H_2O medium reacts with alkenes to form hydroxy alkylmercury adduct which on reduction with NaBH_4 in alkaline medium undergoes demercuration. Addition of water occurs according to Markovnikov's rule. Since carbocation intermediates are not involved, rearrangement does not occur in the reaction.



(d) Hydroboration-oxidation

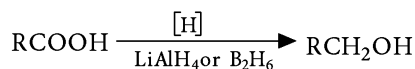
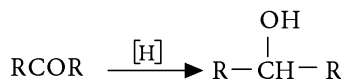
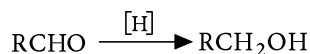
Alkenes form trialkyl borane with diborane which on oxidation with alkaline H_2O_2 yields alcohols. The net reaction involves addition of water to the double bond contrary to Markovnikov's rule. No rearrangement occurs in the reaction.

4.4 Alcohols, Alkyl Halides and Haloarenes



Reduction of compounds having carboxyl or carbonyl groups

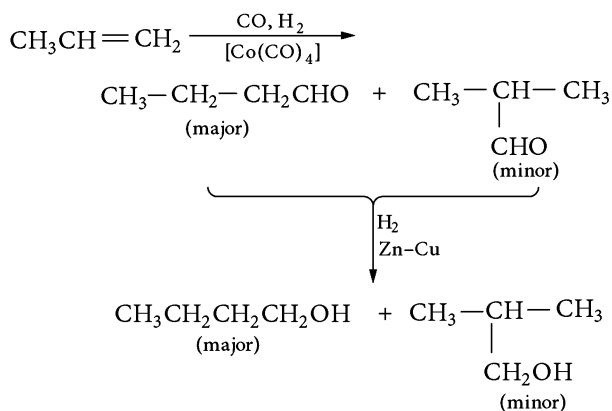
Aldehydes, ketones, acids or acid derivatives on reduction yield alcohols. A number of reducing agents like Zn and conc. HCl, sodium in ethanol, LiAlH_4 , NaBH_4 , B_2H_6 in THF, etc. is used.



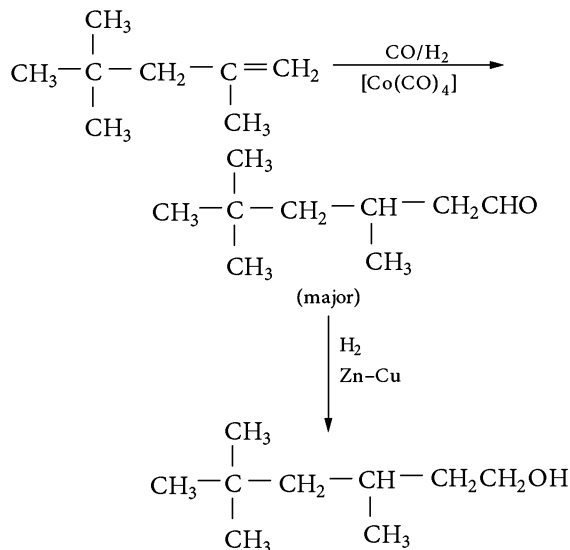
If sodium in ethanol is used as the reducing agent, then the reaction is known as **Bouveault-Blanc reduction**.

Oxo process or carbonylation or hydroformylation reaction.

In this process, a mixture of alkene, carbon monoxide and hydrogen under pressure and elevated temperature, is passed over a catalyst to form aldehyde. The common



catalyst used is cobalt tetracarbonyl, $[\text{Co(CO)}_4]$. A mixture of isomeric straight chain and branched chain aldehydes are formed, which on catalytic hydrogenation yields alcohols.

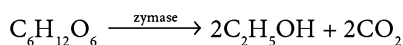
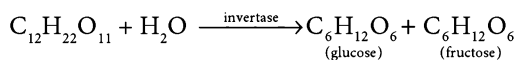


Addition of Grignard reagents to aldehydes and ketones.

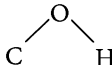
Grignard reagents form addition compounds with aldehydes and ketones, which on hydrolysis yield alcohols. Formaldehyde gives primary alcohol, other aldehydes give secondary alcohols while ketones give tertiary alcohols. [Note: This topic is discussed in detail later in this chapter under "reactions of Grignard reagents"].

Fermentation of carbohydrates (Manufacture of ethanol)

Ethanol is manufactured by the fermentation of molasses or starch. Molasses is the mother liquor left behind after the crystallization of sugar from sugarcane juice. It still contains dissolved sucrose. It is diluted to about 10% concentration of sucrose. Yeast is added and the temperature maintained at about 305K. Yeast supplies the enzymes invertase and zymase which bring about the fermentation.



Properties of alcohols

- (i) The oxygen atom of the -OH group in alcohol is sp^3 hybridized and the  bond angle is slightly less than the tetrahedral angle due to strong lone pair-bond pair repulsion. The bond angle in methanol is 108.9° .
- (ii) The lower alcohols are soluble in water due to their ability to form hydrogen bonds with water.

- (iii) The boiling points of alcohols are generally higher than those of hydrocarbons, alkyl halides and ethers of comparable molecular masses. This is because alcohol molecules are associated through intermolecular hydrogen bonding.

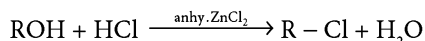
Among isomeric alcohols, boiling points are in the order $1^\circ > 2^\circ > 3^\circ$

REACTIONS OF ALCOHOLS**Reactions involving C – OH bond cleavage**

In reactions involving C – OH bond cleavage, the order of reactivity of alcohols follows the sequence tertiary (3°) > secondary (2°) > primary (1°).

(i) Reaction with hydrogen halide and halogen acids

Alcohols react with halogen acids in the presence of a dehydrating agent, such as anhydrous zinc chloride to form haloalkanes. For example

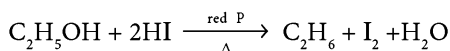


For a given alcohol the reactivity of the halogen acids is in the order $\text{HI} > \text{HBr} > \text{HCl}$

The reaction of 1° and 2° alcohols with hydrogen chloride in presence of anhydrous ZnCl_2 to form alkyl chloride is known as Groves' process.

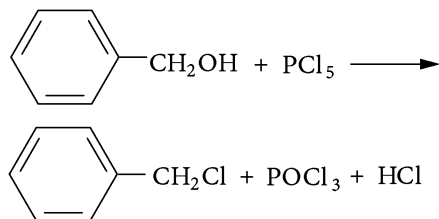
Tertiary alcohols, being very reactive, produce the corresponding halide even without the presence of anhydrous zinc chloride.

However, if alcohol is heated with con. HI in presence of red phosphorus, hydrocarbon is produced

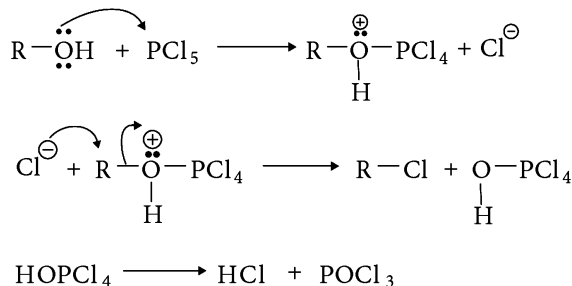
**(ii) Reaction with phosphorus pentahalide**

Alcohols react with phosphorus pentachloride (PCl_5) to give alkyl chloride.

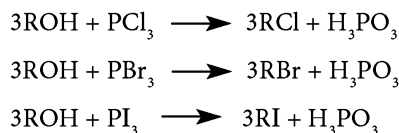
For example,



Here, apart from the main product (alkyl chloride), POCl_3 is also formed, which is fairly nonvolatile and has to be distilled off carefully to separate the alkyl chloride.

Mechanism**(iii) Reaction with phosphorus trihalide**

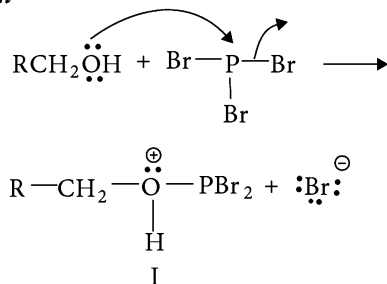
Alcohols react with phosphorus trihalides to give the corresponding alkyl halide.



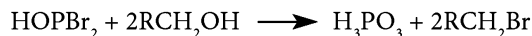
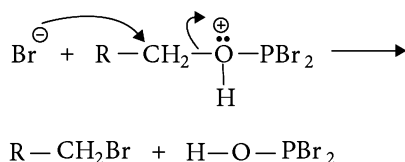
4.6 Alcohols, Alkyl Halides and Haloarenes

Generally, red phosphorus and Br_2 is used in place of PBr_3 and red P and I_2 is used instead of PI_3 .

Mechanism

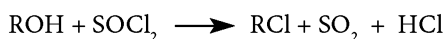


The intermediate (I) obtained is a protonated alkyl dibromophosphate.

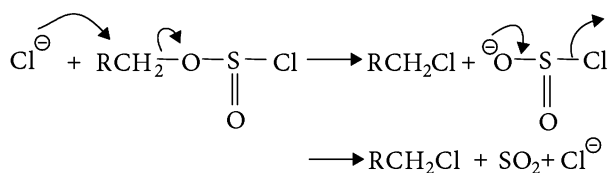
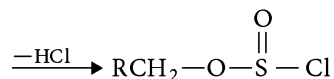
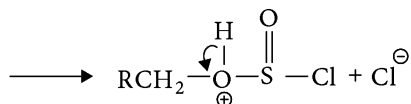
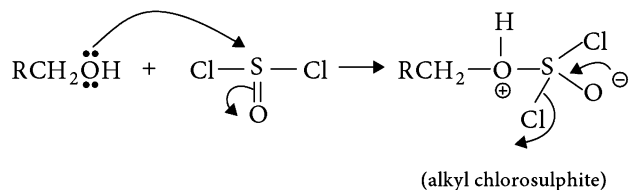


$\text{HO}-\text{PBr}_2$ is a very good leaving group. This can react with two more moles of alcohol to give two more moles of the product.

(iv) Reaction with thionyl chloride (SOCl_2)



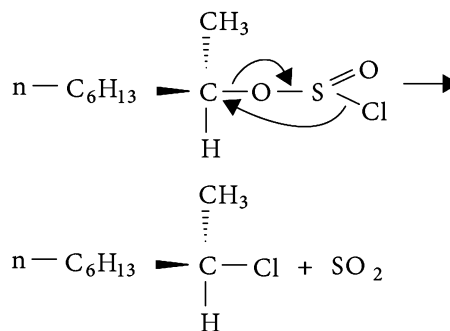
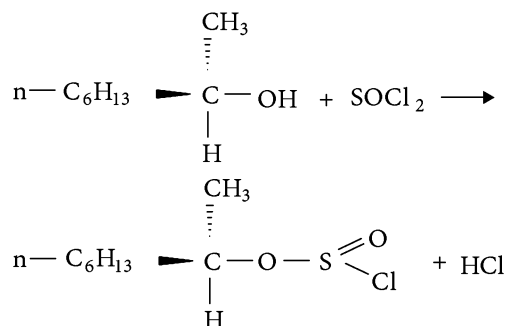
Mechanism



The mechanism involves the formation of alkyl chlorosulphite (RCH_2OSOCl). The advantage of using SOCl_2 over PCl_3 or PCl_5 method in preparing the alkyl chloride from the alcohol is that the other two side products formed namely, SO_2 and HCl , are volatile and can be removed easily. Hence the main product, the alkyl chloride, will be pure enough.

The stereochemical course of conversion of alcohol to haloalkane by the use of thionyl chloride provides an interesting and useful example in stereochemistry. The reaction of optically active 2-octanol with thionyl chloride in ether results in 2-chlorooctane with retention of configuration.

The mechanism is depicted as follows.



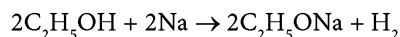
This type of substitution of a chloride in the place of OH with retention of configuration is termed as $\text{S}_{\text{N}}\text{i}$ (substitution nucleophilic internal).

Reactions involving O – H bond cleavage

The general order of reactivity of alcohols in these type of reactions is $1^\circ > 2^\circ > 3^\circ$.

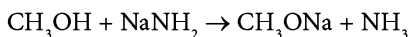
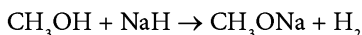
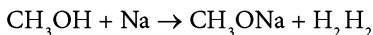
(i) Reaction with active metals

Highly electropositive metals such as Na, K, Ca, Al, etc. can displace hydrogen from alcohols to form alkoxides.



This reaction shows the acidic nature of alcohols. But alcohols are weaker acids than water. Therefore, alkoxides (RO^-) are stronger bases than hydroxide ion (OH^-).

Since alcohol is a weaker base than water, an alkoxide cannot be prepared by the reaction of an alcohol with NaOH but it can be prepared by reaction with active metals, metal hydrides and metal amides.



The order of acidity is $\text{H}_2\text{O} > \text{C}_2\text{H}_5\text{OH} > \text{CH} \equiv \text{CH} > \text{NH}_3 > \text{RH}$

The order of basicity is $\text{HO}^- < \text{C}_2\text{H}_5\text{O}^- < \text{CH} \equiv \text{C}^- < \text{NH}_2^- < \text{R}^-$

Among 1° , 2° and 3° alcohols, acid strength follows the order

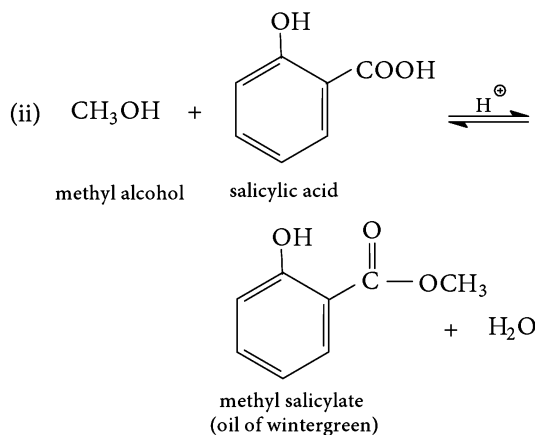
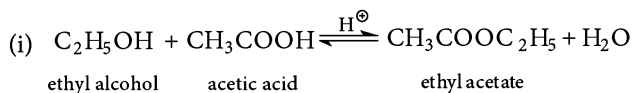
Primary > secondary > tertiary

This can be explained by the +I effect of alkyl group and consequent destabilization of the corresponding alkoxide ions.

(ii) Esterification of alcohols

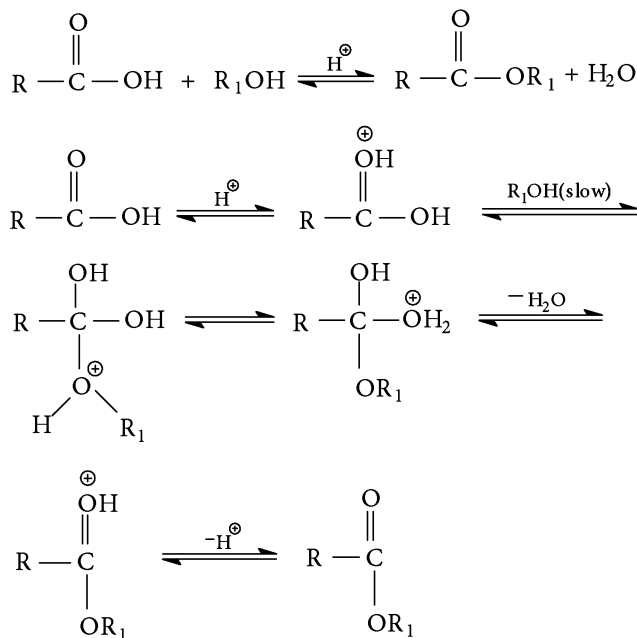
Alcohols react with inorganic and organic acids to form esters. The reaction between an alcohol and a carboxylic acid to form an ester is known as esterification. The esterification reaction is catalyzed by mineral acids. When HCl gas is used as catalyst, the reaction is known as Fischer-Speier esterification and is more satisfactory than H_2SO_4 for 2° and 3° alcohols.

A few typical examples of esterification are



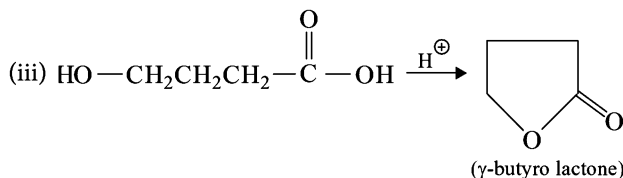
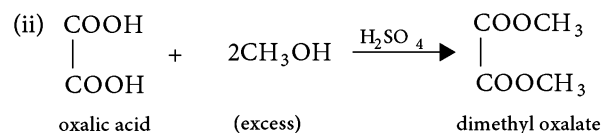
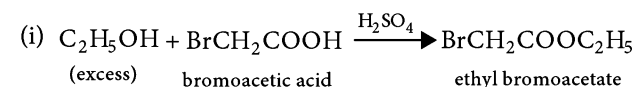
Mechanism of esterification

The esterification reaction involves the substitution by an alkoxy group in the place of hydroxy group in a carboxylic acid. The alkoxy group is supplied by the alcohol.



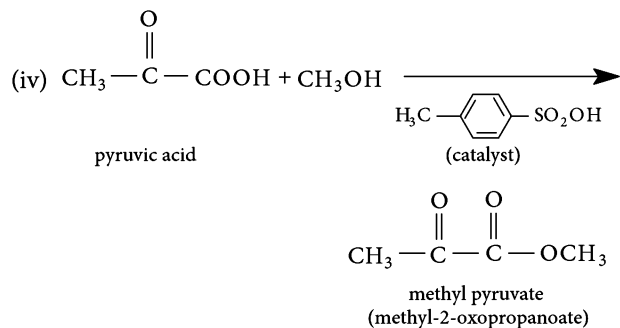
A nucleophilic addition of alcohol to the protonated carboxylic group of the acid occurs initially. A tetrahedral intermediate is formed. This tetrahedral intermediate cannot be isolated, but leads to the final product, ester, by the loss of a water molecule.

A large number of esters are formed by this method. The common acid catalysts used are sulphuric acid, hydrochloric acid and p-toluenesulphonic acid (PTSA).

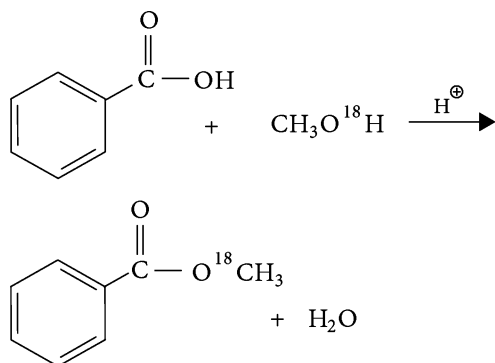


Cyclic esters are known as lactones. γ-butyro lactone is an example of a cyclic ester. This is formed by an intramolecular esterification.

4.8 Alcohols, Alkyl Halides and Haloarenes



- (v) When benzoic acid is treated with methanol labelled with O^{18} ($\text{CH}_3\text{O}^{18}\text{H}$) in the presence of a protonic acid as a catalyst, the product, methyl benzoate, contained the labelled O^{18} and the water obtained was unlabelled.



For the same alcohol, the rate of esterification decreases as the crowding increases near the carboxy group of the acid. There will be significant decrease in the rate of esterification of the following acids:

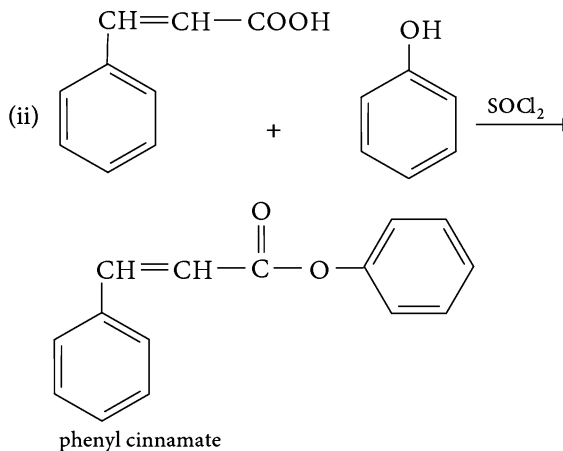
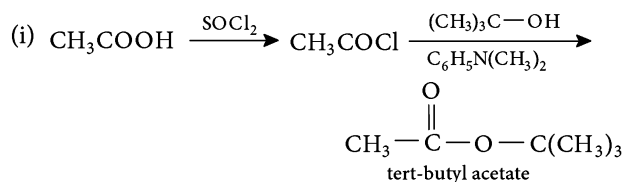


This decrease in rate is due to steric crowding near the carboxylic acid group which is actually the site of esterification.

Esterification from a carboxylic acid and an alcohol is always a reversible process and the isolation of the ester from the reaction mixture may require a complicated procedure.

Instead the acid can be converted to a more reactive acid chloride, so that the base catalyzed reaction with an alcohol to form an ester becomes essentially an irreversible process.

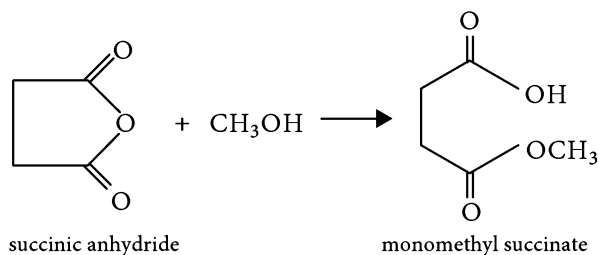
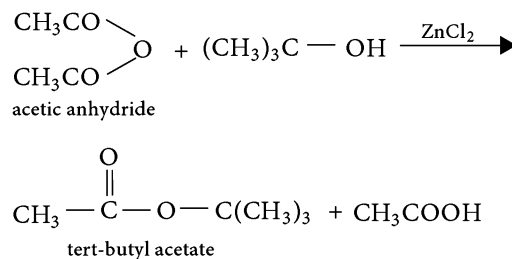
For example,



The carboxylic acid is treated with thionyl chloride (SOCl_2) and the alcohol is added without isolating the acid chloride formed. A base, usually a tertiary amine like N,N-dimethylaniline or pyridine is added to absorb the hydrogen chloride generated in the process.

Instead of acid chlorides sometimes anhydrides of carboxylic acids are used as starting materials. Anhydrides are less reactive than acid chlorides.

Example

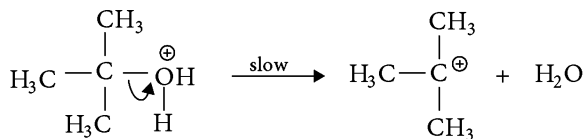


When anhydrides are part of a cyclic structure, the reaction with one mole of an alcohol occurs leading to a half ester. So the product obtained is a half acid-half ester.

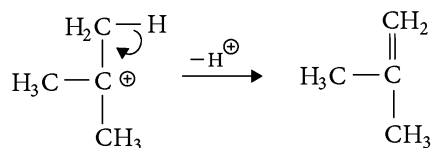
There is an interesting method of converting one ester into another ester of the same acid. This process is known as transesterification. Such a method is followed when direct esterification methods are not successful. This method is also known as alcoholysis. Trans esterification can be acid catalyzed or base catalyzed (using sodium alkoxide as catalyst).

4.10 Alcohols, Alkyl Halides and Haloarenes

In the second step, the carbon-oxygen bond gets cleaved resulting in a carbocation.



In the third and final step, a proton is lost from the carbocation to result in an olefin.



The ease of dehydration of the alcohols is $3^\circ > 2^\circ > 1^\circ$, which also explains the order of stability of carbocations, $3^\circ > 2^\circ > 1^\circ$.

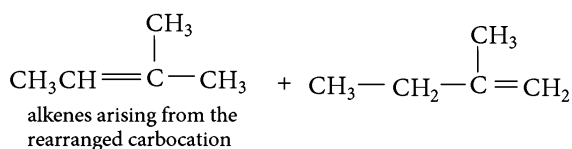
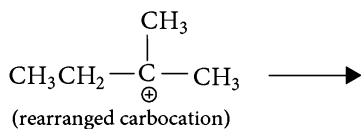
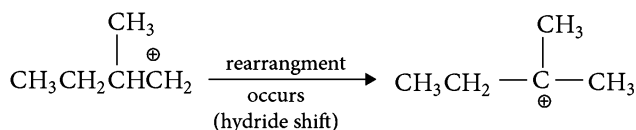
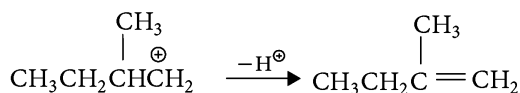
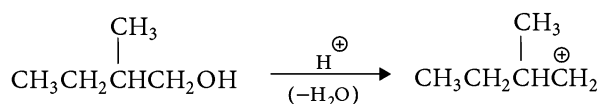
The elimination of a molecule of water from the protonated alcohol to form the carbocation is the rate determining step in the dehydration process.

Dehydration is acid catalyzed. Acid converts the poor leaving group (OH) to a good leaving group (OH_2^+).

Further, *acid catalyzed dehydration of alcohol is reversible*.

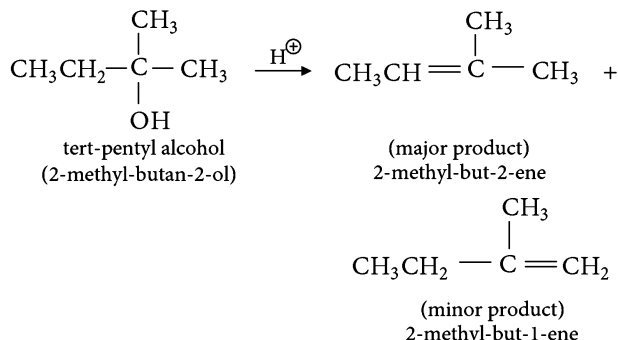
Whenever the structure of the alkyl group permits, rearrangement occurs.

For example,



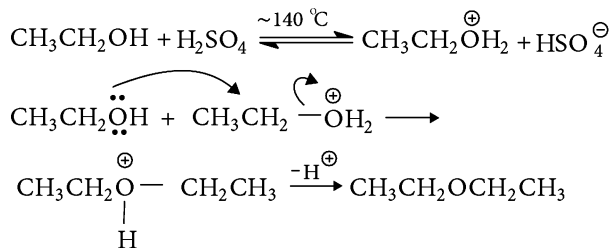
Whenever an alkene is formed by dehydration of an alcohol, the major product formed is the most substituted alkene (Saytzeff's rule).

For example,



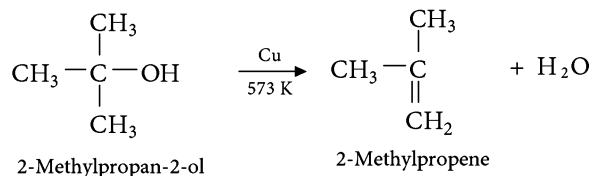
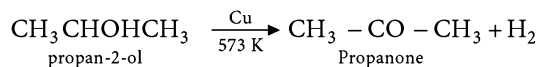
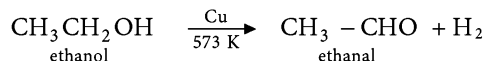
The hydrogen that is eliminated in a dehydration process is always a β -hydrogen. When more than one type of β -hydrogen are available, the β -hydrogen will be eliminated so as to result in a most stable alkene.

The Williamson's method is best method for preparing unsymmetrical ethers. When symmetrical ethers are required, acid catalyzed dehydration of alcohols is preferred. The dehydration procedure for the preparation of symmetrical ethers is generally limited to primary alcohols, since secondary and tertiary alcohols undergo elimination at higher temperature. The ether formation is depicted as follows.



Dehydrogenation (Action of hot copper)

When alcohol vapours are passed over copper catalyst heated to 573K, dehydrogenation occurs. Primary alcohols



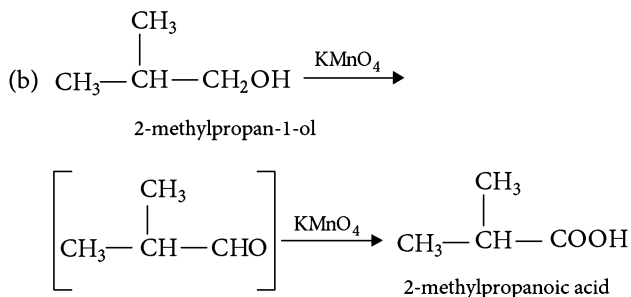
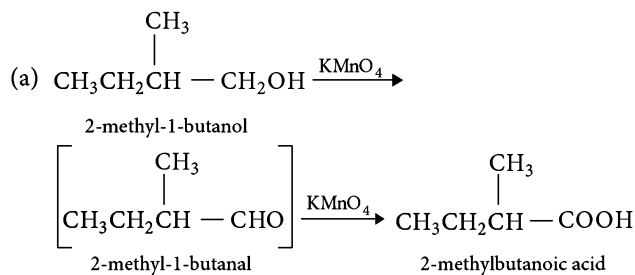
are dehydrogenated to aldehydes while secondary alcohols form ketones. Tertiary alcohols, however, undergo dehydration when passed over hot copper to form alkenes.

Oxidation of alcohols

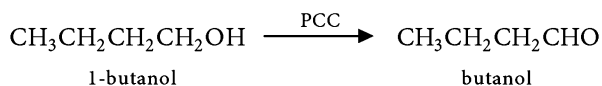
In general, a primary alcohol on oxidation gives an aldehyde with the same number of carbon atoms which on further oxidation gives a carboxylic acid with the same number of carbon atoms. A secondary alcohol on oxidation gives a ketone with the same number of carbon atoms which on drastic oxidation gives acids with lesser number of carbon atoms. Tertiary alcohols are oxidized with acidic oxidizing agents under very strong conditions to form ketones and then acids.

(i) Oxidation of primary alcohols

Aqueous KMnO_4 in the presence of an acid or an alkali and acidified $\text{K}_2\text{Cr}_2\text{O}_7$ oxidizes a primary alcohol, first to an aldehyde and then the oxidation proceeds to give an acid. Generally, the reaction cannot be stopped at the aldehyde stage.

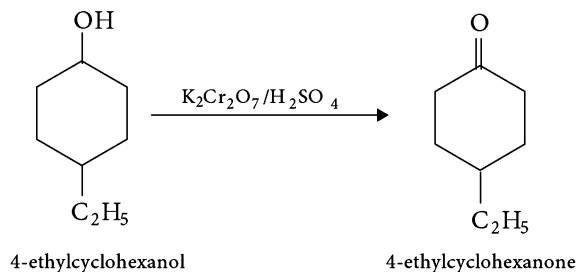


Primary alcohols can be oxidized to the aldehyde stage by using PCC (pyridinium chloro chromate) in methylene chloride. PCC is prepared by mixing $\text{C}_5\text{H}_5\text{N}$ (pyridine), CrO_3 and HCl and is represented as $\text{C}_5\text{H}_5\text{NHCrO}_3\text{Cl}^+$

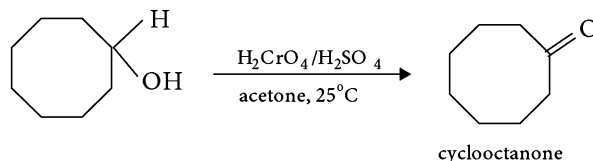


(ii) Oxidation of secondary alcohols

Secondary alcohols can be oxidized to ketones, when the oxidizing agent used is $\text{K}_2\text{Cr}_2\text{O}_7$ or $\text{Na}_2\text{Cr}_2\text{O}_7$ in H_2SO_4 medium.



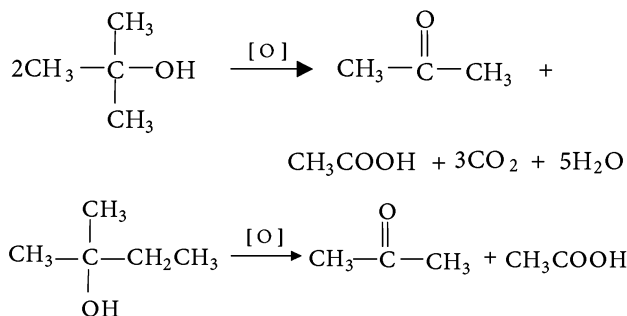
A very useful reagent in the oxidation of secondary alcohols to ketone is the Jones reagent, which is a solution of chromic acid (H_2CrO_4) in H_2SO_4 and acetone. The oxidation is rapid and efficient.



Ketone like benzophenone $\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$ can be obtained by the oxidation of secondary alcohol $\text{C}_6\text{H}_5\text{CHOHC}_6\text{H}_5$ by means of dichromate.

(iii) Oxidation of tertiary alcohols

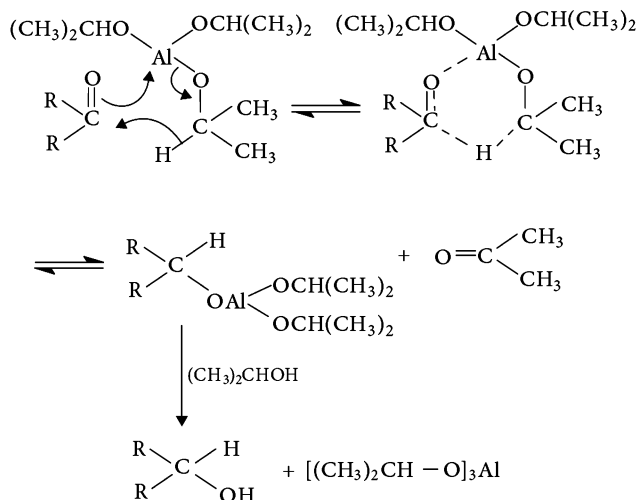
Tertiary alcohols are resistant to oxidation in neutral or alkaline solution, but are readily oxidized by acidified oxidizing agents to a mixture of ketone and acid, each containing fewer carbon atoms than the original alcohol.



The strong oxidizing agents used are acidified KMnO_4 , acidified dichromate, or nitric acid.

(iv) Oppenauer oxidation and Meerwin-Ponndorf-Verley reduction

Oppenauer oxidation and Meerwin-Ponndorf-Verley (MPV) reduction are two reversible oxidation-reduction processes. Aluminium tert-butoxide in acetone and aluminium isopropoxide in isopropyl alcohol are used as reagent for oxidation and reduction, respectively. In MPV reduction, the aldehyde or ketone is heated with the reagent and is highly specific for aldehydes and ketones, so that other reducible groups like carbon-carbon double bonds, $-\text{NO}_2$ – COOR , etc. are not affected. Oppenauer oxidation is mainly used for oxidizing 2° alcohols to ketones. The oxidation and reduction usually involves a cyclic transition state.



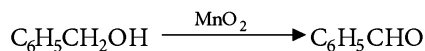
This is a case of *hydride transfer* from aluminium isopropoxide to the carbonyl compound via a cyclic transition state.

(v) Oxidation with MnO_2

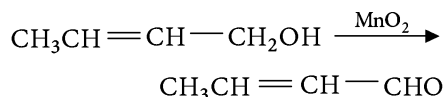
MnO_2 can be used as a specific oxidizing agent for the oxidation of allylic or benzylic (primary or secondary) alcohols to the corresponding carbonyl compounds.

A few interesting oxidations of alcohols influenced by MnO_2 are given below.

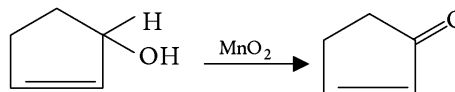
- (a) Benzylic primary alcohol is oxidized to benzaldehyde.



- (b) An allylic primary alcohol is oxidized to an aldehyde by MnO_2 . The double bond is not affected by MnO_2 .



- (c) α,β -unsaturated ketone is obtained by the oxidation of the allylic secondary alcohol by MnO_2 .

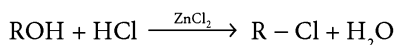


An important industrial method of converting an alcohol to an aldehyde or ketone is to treat the alcohol at high temperature with Ni or chromium oxide-copper catalyst.

METHODS TO DISTINGUISH 1° , 2° AND 3° ALCOHOLS**Lucas test**

In this test, the alcohol is treated with a solution of anhydrous ZnCl_2 in con. HCl (Lucas reagent). Tertiary alcohols give a turbidity immediately at room temperature. Secondary alcohols develop turbidity in a few minutes (about 5 minutes) while primary alcohols do not develop any turbidity at room temperature.

The principle of this test is based on the formation of alkyl chloride from alcohol by reaction with con. HCl in the presence of ZnCl_2 .



Alkyl chlorides are insoluble in water and their formation is indicated by the appearance of turbidity or cloudiness. The rate of reaction of alcohol with HCl is in the

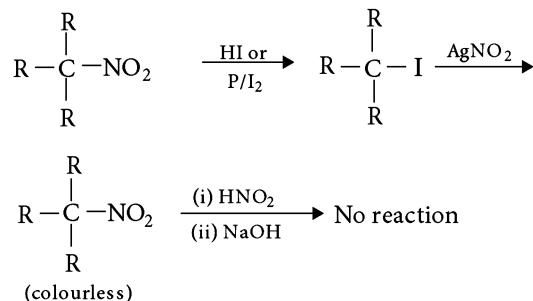
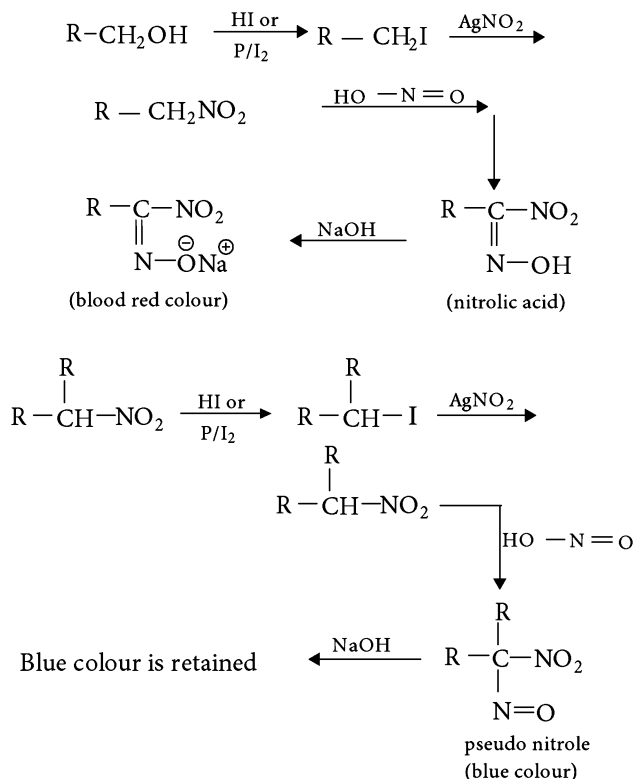
order $3^\circ > 2^\circ > 1^\circ$. Hence tertiary alcohols give turbidity immediately.

Note: This method cannot be employed for alcohols insoluble in aqueous medium.

Victor-Meyer's test

In this test the following steps are involved.

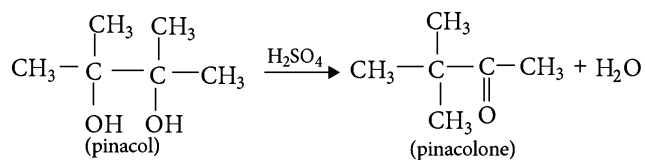
- The alcohol is treated with conc. HI or red phosphorous and iodine to obtain the corresponding alkyl iodide.
- The alkyl iodide is treated with silver nitrite to get the corresponding nitro alkane.
- The nitro alkane is treated with nitrous acid ($\text{NaNO}_2 + \text{H}_2\text{SO}_4$ (or HCl)) and the solution is made alkaline by addition of excess caustic soda or caustic potash.



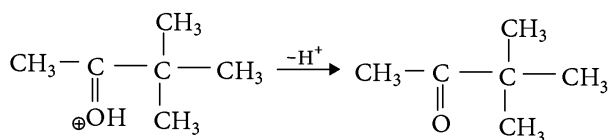
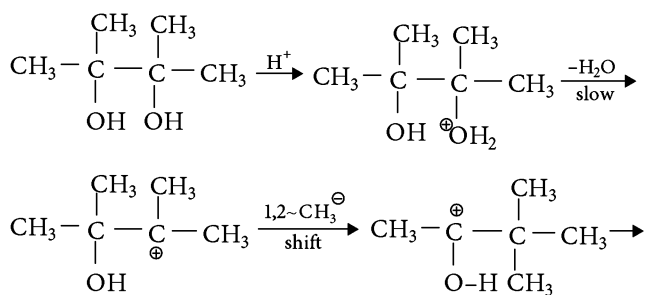
Primary alcohols give blood red colour due to the formation of sodium salt of nitrolic acid, secondary alcohols give blue colour due to the formation of pseudo nitroles while tertiary alcohols form colourless nitro alkanes.

PINACOL-PINACOLONE REARRANGEMENT

1,2-glycols under acidic conditions undergo rearrangement to give aldehydes or ketones. This is known as pinacol-pinacolone rearrangement.

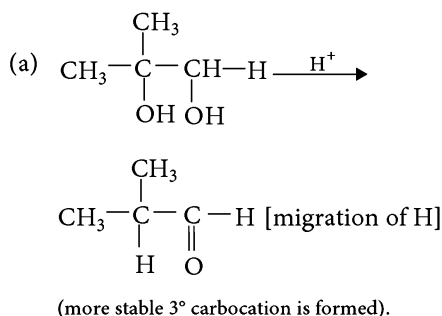


The mechanism involves formation of a stable carbocation, followed by 1,2-shift of an alkyl or aryl group.

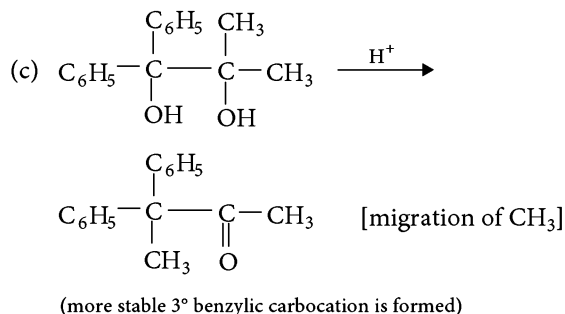
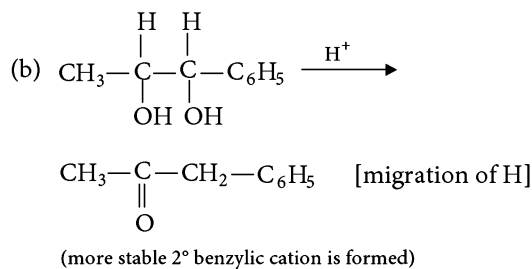


Kinetic measurements have shown that conversion of the protonated alcohol to the carbocation is the rate determining step. Anhydrous ZnCl_2 can also be used instead of H_2SO_4 .

Other examples are



4.14 Alcohols, Alkyl Halides and Haloarenes



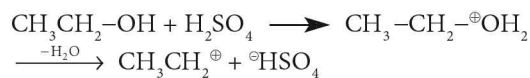
CONCEPT STRANDS

Concept Strand 1

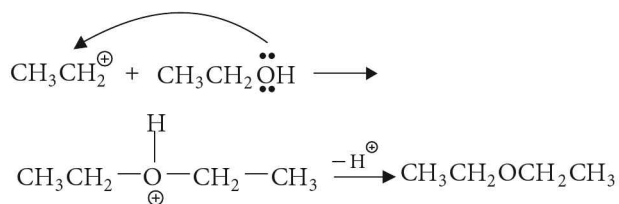
If ethanol is heated with H_2SO_4 , diethylether is formed, whereas, the treatment of ethanol with HI leads to ethyl iodide and not ether. Explain.

Solution

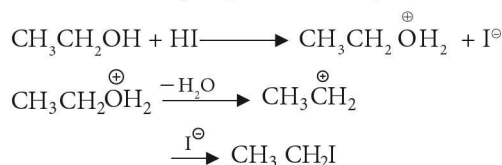
If ethanol is heated with H_2SO_4 , the $-\text{OH}$ group gets protonated to form an oxonium ion.



A molecule of water is lost to give a carbocation CH_3CH_2^+ . The anion generated HSO_4^- is not strong enough nucleophile to combine with the cation to form a stable product. So another molecule of $\text{C}_2\text{H}_5\text{OH}$ attacks the carbocation CH_3CH_2^+ to give a molecule of diethyl ether.



On the otherhand, in the case of HI, (hydroiodic acid), the anion formed I^- is a strong nucleophile and attacks the carbocation CH_3CH_2^+ to form ethyl iodide.

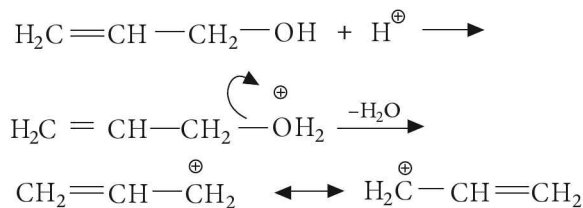


Concept Strands 2

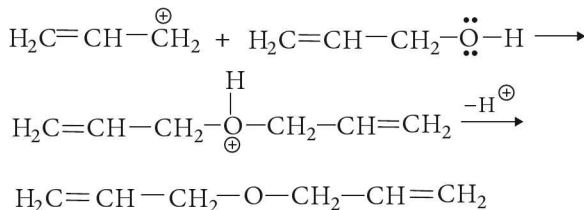
Explain why allyl alcohol forms an ether more rapidly than propyl alcohol?

Solution

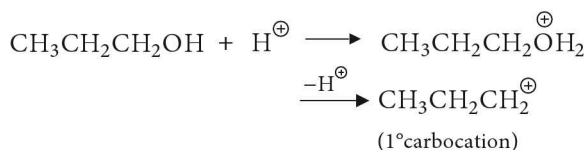
Allyl alcohol, $\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$, produces a resonance stabilized carbocation on protonation.



This stable cation can be attacked by another molecule of allyl alcohol to form ether.



In the case of propyl alcohol, the carbocation formed is a primary carbocation and it is not stabilized readily.



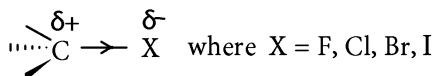
Hence, further reaction proceeds slowly.

HALOALKANES (ALKYL HALIDES)

INTRODUCTION

Alkyl halides are those group of organic compounds where the halogen atom is attached to an sp^3 hybridized carbon. The carbon-halogen bond results from the overlap with an almost pure p-orbital of halogen. The carbon-halogen bond length varies from 1.35 Å to 2.0 Å depending on the size of the halogen, from fluorine to iodine.

Although carbon-halogen bonds in alkyl halides are covalent in nature, they have a partial polar character because of the higher electronegativity of halogen compared to carbon. As a result, the carbon bears a partial positive charge and the halogen bears a partial negative charge.

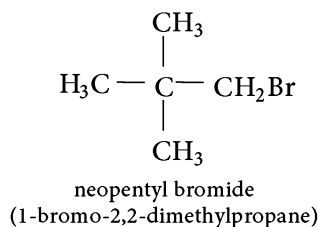
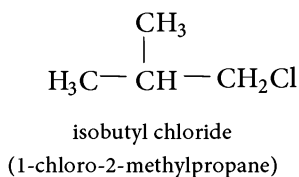
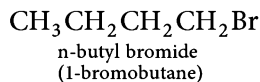


Alkyl halides are used as starting materials for the synthesis of many organic compounds. The halogen atom of an alkyl halide can easily be replaced by other groups, and the presence of a halogen atom affords the possibility of introducing new groups or atoms in the starting molecule. For laboratory purposes, alkyl bromides are more reactive than chlorides. Alkyl iodides are also very useful reagents.

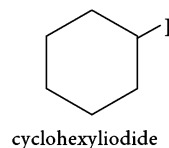
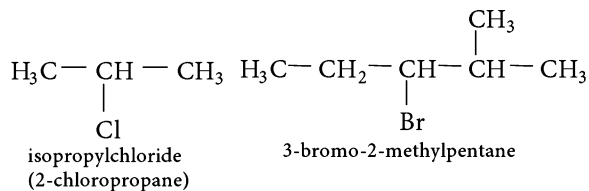
CLASSIFICATION OF ALKYL HALIDES

Alkyl halides are classified as primary, secondary and tertiary halides according to the kind of carbon that bears the halogen.

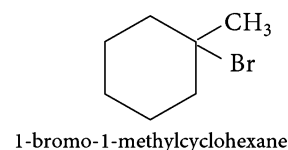
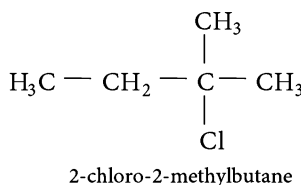
Primary alkyl halides



Secondary halides



Tertiary halides



4.16 Alcohols, Alkyl Halides and Haloarenes

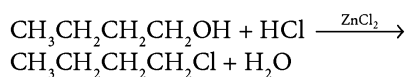
Alkyl halides are soluble in solvents of low polarity. They are generally denser than water. Even though they are solvents of some polarity, they cannot solvate simple ions

appreciably and, therefore, they are not good solvents for inorganic salts.

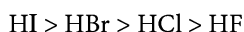
PREPARATION OF ALKYL HALIDES

(i) From alcohols

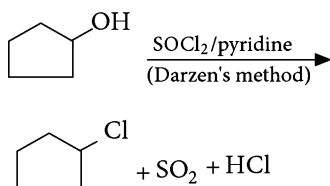
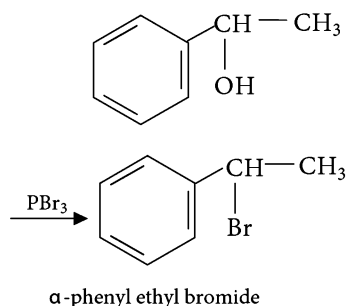
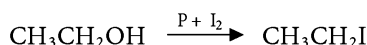
- (a) Alcohols on treatment with concentrated hydrogen halides give alkyl halides.



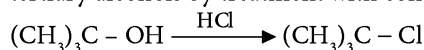
The order of reactivity of the halogen acids and that of alcohols follows the order:



- (b) Alcohols can be converted to alkyl halides by treatment with PCl_3 , PCl_5 , PBr_3 , P and I_2 or SOCl_2

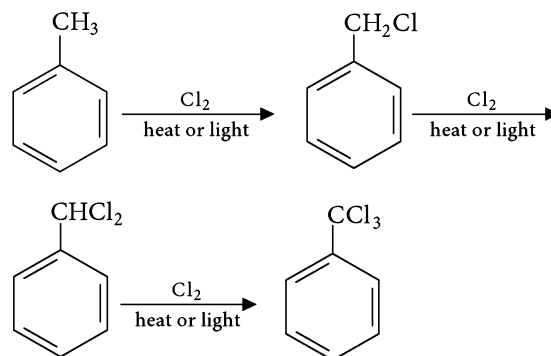


- (c) Tertiary chlorides can be directly obtained from the tertiary alcohols by treatment with conc. HCl .

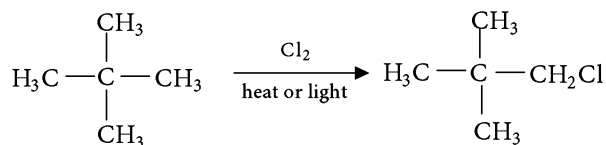


(ii) Halogenation of hydrocarbons

- (a) Toluene can be converted to benzyl chloride on treatment with Cl_2 in the presence of heat or light. This is an example of side chain halogenation.



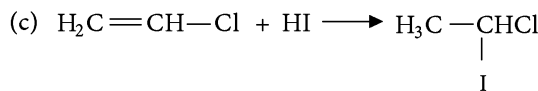
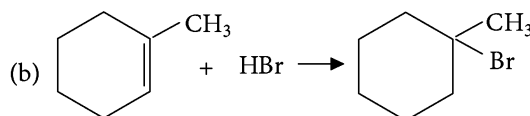
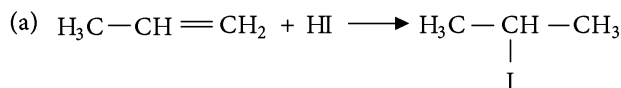
- (b) Neopentane is converted to neopentyl chloride by the action of chlorine in the presence of heat or light (photochemical reactions).

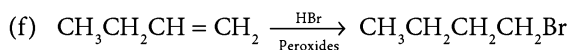
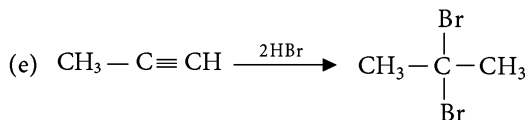
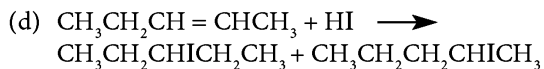


- (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \xrightarrow[\text{heat or light}]{\text{Cl}_2} \text{CH}_3\text{CHClCH}_2\text{CH}_3 + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$

(iii) Addition of hydrogen halides to alkenes and alkynes

This is a regioselective addition occurring according to Markovnikov's rule.

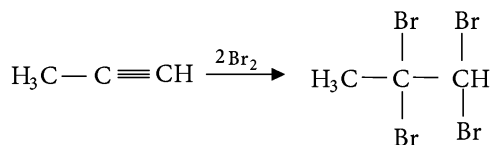




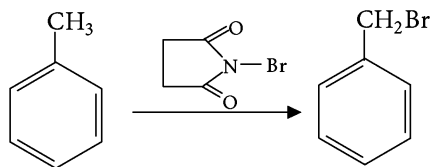
HBr addition in the presence of peroxides takes place contrary to Markovnikov's rule.

(iv) Addition of halogens to alkynes

Alkynes give tetrahalo derivatives upon halogenation..



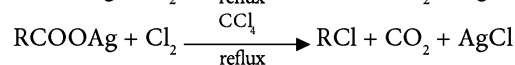
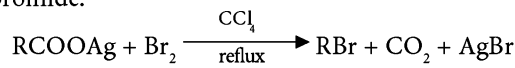
(v) Allylic bromination



When an allylic or benzylic type of compound is treated with N-bromosuccinimide (NBS), bromination occurs in the allylic or benzylic position. Bromination with NBS does not occur at the double bonds.

(vi) Borodine-Hunsdiecker or Hunsdiecker reaction

Silver salts of carboxylic acids in CCl_4 solution are decomposed by chlorine or bromine to form alkyl chloride or alkyl bromide.



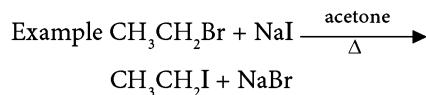
The reaction gives the product with one carbon atom less than the fatty acid and the yield of the halide is primary > secondary > tertiary. Bromine is generally used, while chlorine gives a poor yield of alkyl chloride. The reaction is believed to take place by a free radical mechanism.

Iodine forms esters with the silver salts and this reaction is known as Birnbaum-Simonini reaction.



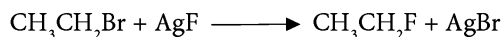
(vii) Finkelstein reaction

Alkyl chlorides or bromides when heated with a solution of sodium iodide in acetone or methanol forms the corresponding alkyl iodide



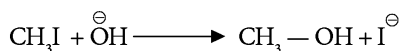
(viii) Swarts reaction

Fluoro alkanes can be prepared by heating the corresponding alkyl chlorides or bromides with inorganic fluorides like AsF_3 , SbF_3 , AgF , Hg_2F_2 , CoF_3 , etc.



NUCLEOPHILIC SUBSTITUTION AT SATURATED CARBON ATOM

Nucleophilic substitution is a characteristic reaction of alkyl halides. Consider the reaction,



This is a substitution reaction, where $\text{I}^\ominus$ is substituted by $\text{OH}^\ominus$. The iodide ion ($\text{I}^\ominus$) leaves with a pair of electrons shared with the carbon in CH_3I . The entering $^\ominus\text{OH}$ ion comes with a pair of electrons needed to form a new bond with the methyl group to result in CH_3OH .

Electron rich reagents that tend to attack a positively polarized carbon centre are called nucleophilic reagents or

nucleophiles. When this attack results in substitution, the reaction is called nucleophilic substitution. A nucleophile that is already attached to the carbon centre and is displaced in the reaction is called the leaving nucleophile. A nucleophile that enters is called the entering nucleophile or attacking nucleophile.

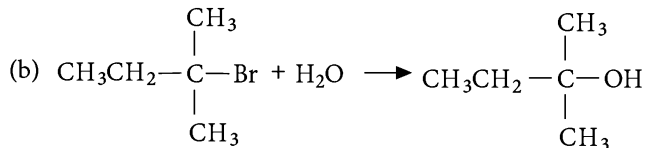
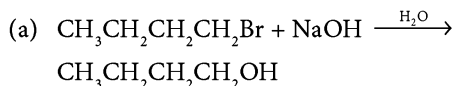
Some important nucleophilic substitution reactions of alkyl halides are given below.

Formation of alcohols

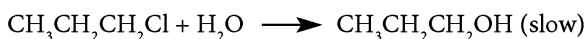
Alkyl halides on hydrolysis give alcohols. The reagent commonly used is dilute aqueous NaOH or aqueous KOH .

4.18 Alcohols, Alkyl Halides and Haloarenes

Tertiary alkyl halides undergo hydrolysis even by boiling with water.



When $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ reacts with water, the formation of $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ is very slow.



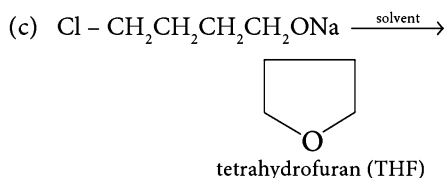
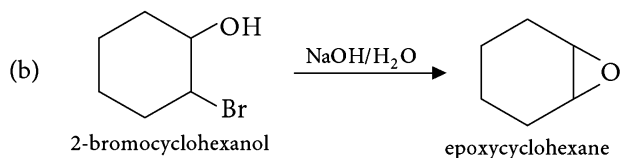
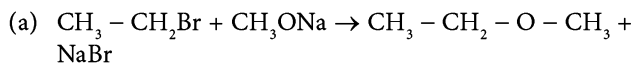
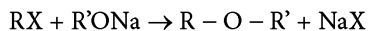
However, if a small quantity of potassium iodide (KI) is added, the reaction becomes faster. The reason is that, at beginning the iodide ion gets substituted for the leaving chloride ion, resulting in the formation of $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$. As I^- is a better leaving group, the reaction becomes faster.

The hydrolysis of alkyl halides by aqueous NaOH or KOH is an irreversible process.

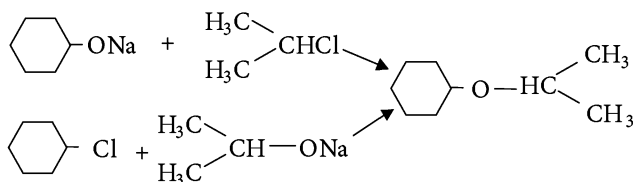
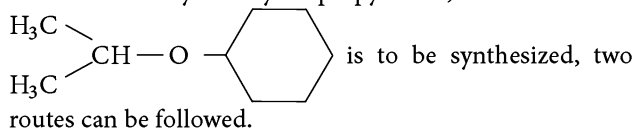
This is because, when $\text{R}-\text{Cl}$ is converted to $\text{R}-\text{OH}$, a weaker leaving nucleophile like Cl^- is replaced by a stronger nucleophile like ^-OH . Once the product $\text{R}-\text{OH}$ is formed, ^-OH being a poor leaving group cannot be easily displaced by a weaker nucleophile like Cl^- . Hence the reverse reaction is not possible.

Formation of ethers

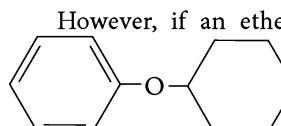
Alkyl halides when treated with sodium or potassium alkoxide form ethers. This reaction is called Williamson's synthesis.

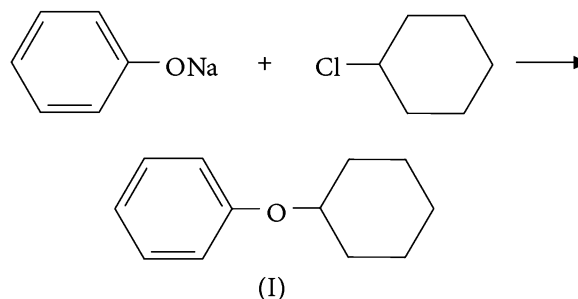


If an ether like cyclohexyl isopropyl ether,



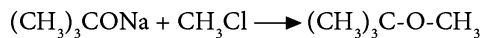
An alkoxide of cyclohexyl alcohol can be treated with isopropyl chloride or an alkoxide of isopropyl alcohol can be treated with cyclohexyl chloride to give the same product namely cyclohexyl isopropyl ether.

However, if an ether like cyclohexyl phenyl ether,  is to be prepared, only one route can be followed, i.e.,

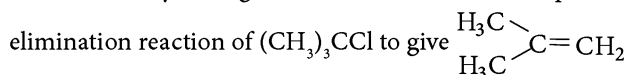


The phenoxide ion has to react with cyclohexyl chloride to get the ether. The other method, namely reacting bromobenzene or chlorobenzene with the alkoxide of cyclohexanol cannot be useful to obtain the same ether (I). This is because, the halogen attached directly to the nucleus of the benzene ring cannot be displaced easily.

For the preparation of tert-butyl methyl ether $(\text{CH}_3)_3\text{C}-\text{O}-\text{CH}_3$, certain special precautions have to be observed. This ether can be prepared only by the following route.



The other method, i.e., from $(\text{CH}_3)_3\text{C}-\text{Cl}$ and CH_3ONa will not be useful because CH_3O^- is not only a nucleophile but also a very strong base. Therefore, there is a parallel



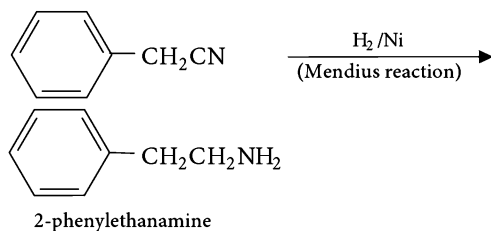
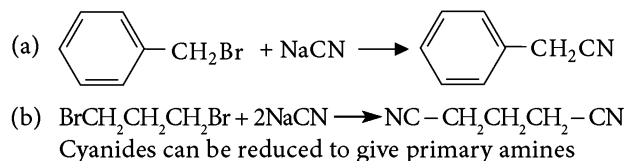
Synthesis of alkyl cyanides

Aliphatic nitriles or cyanides can be prepared by the treatment of an alkyl halide with NaCN or KCN in a suitable solvent like DMSO (dimethyl sulphoxide)

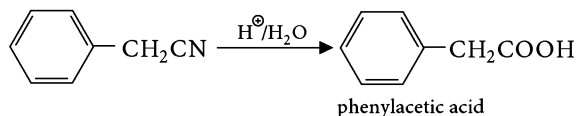
$$\begin{array}{c} \text{H}_3\text{C} \\ \diagup \\ \text{S} \longrightarrow \text{O} \\ \diagdown \\ \text{H}_3\text{C} \end{array}$$

HCN cannot be used in the place of KCN or NaCN, as it is a very weak acid and is not fully ionized as $\text{CN}^\ominus$. Nitriles are often named as cyanides. The term nitrile derives its name from the acids they yield on hydrolysis. For example, CH_3CN is known as acetonitrile, as it yields acetic acid on hydrolysis. $\text{C}_6\text{H}_5\text{CN}$ is known as benzonitrile, as it yields benzoic acid on treatment with water.

Examples are,



Cyanides can also be hydrolyzed to give acids.

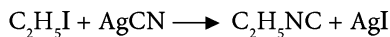


Therefore, conversion of an alkyl halide to cyanide is a very useful route for the preparation of amines and carboxylic acids.

Synthesis of alkyl isocyanides

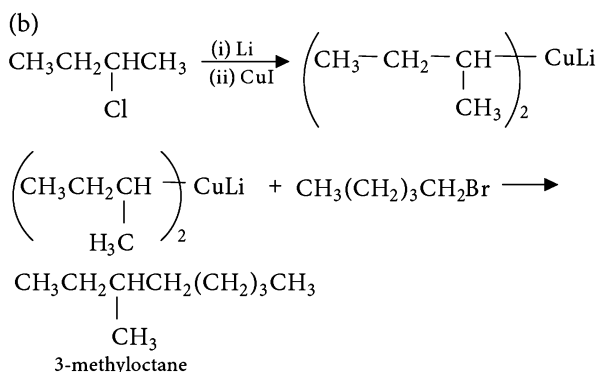
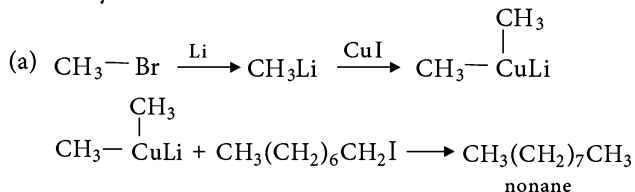
Silver cyanide is predominantly a covalent ($\text{Ag}-\text{C}\equiv\text{N}$) molecule. The lone pair of electrons on nitrogen are available for covalent bonding with the alkyl groups to result in RNC or isocyanides.

An alkyl iodide on heating with AgCN in aqueous ethanolic solution gives foul smelling alkyl isocyanide as the major product.



Corey – House synthesis of alkanes

Corey-House synthesis is used to prepare higher alkanes from alkyl halides.



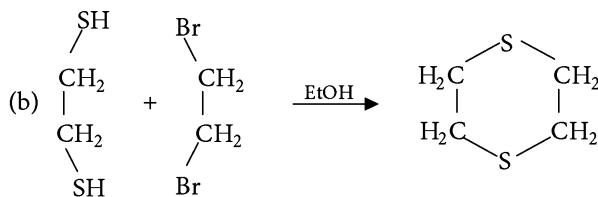
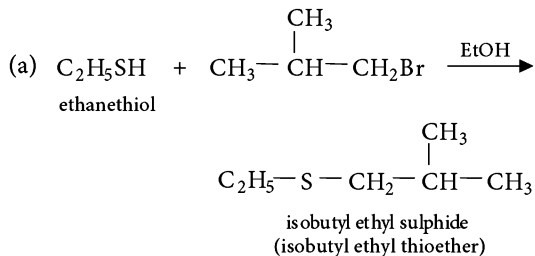
Formation of esters

Silver salt of a carboxylic acid can be converted to an ester when treated with an alkyl halide.



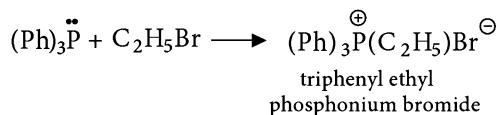
Formation of sulphides or thioethers

Thiols or thio alcohols are very good nucleophiles for substitution at a saturated carbon atom. This reaction is similar to Williamson's ether synthesis. Sulphides are also known as thioethers.



Formation of phosphonium salts

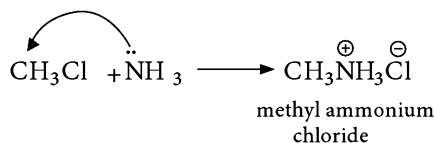
Triphenylphosphine, $\ddot{\text{P}}\text{Ph}_3$ can act as a nucleophile as it has a lone pair of electrons on phosphorus. When triphenylphosphine reacts with an alkyl halide like $\text{C}_2\text{H}_5\text{Br}$, a phosphonium salt is formed.



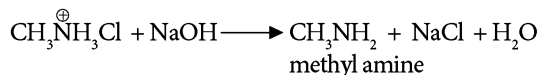
Phosphonium salts are very useful in Wittig reactions for the conversion of carbonyl compounds to olefins.

Synthesis of primary, secondary and tertiary amines

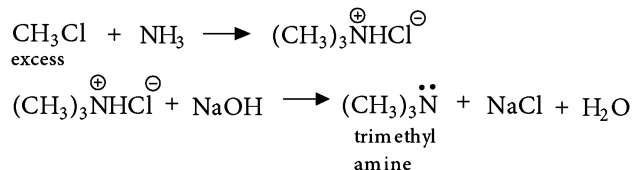
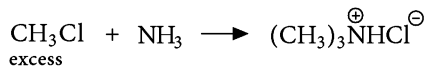
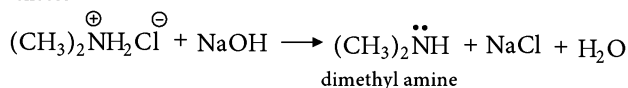
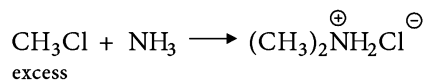
When heated with ethanolic solution of ammonia under pressure, alkyl halides first form primary amines. For example



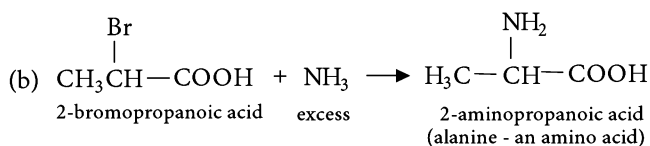
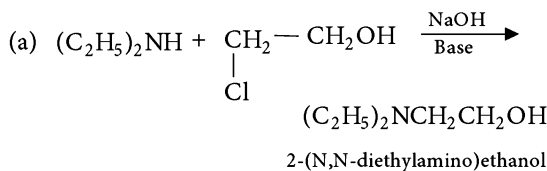
The free amine can be obtained from the ammonium salt by treatment with a strong base



The primary amine formed behaves as a nucleophile and can further react with alkyl halide if present in excess to form secondary and tertiary amines and finally quaternary ammonium salt.

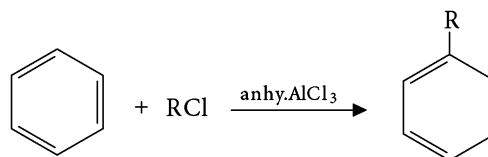


The following examples are also illustrative of the application of alkyl halides in the synthesis of useful amino compounds.



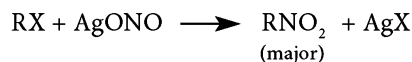
Friedel-Crafts alkylation

Friedel-Crafts alkylation can be carried out using alkyl halides and an aromatic compound, making use of anhydrous AlCl_3 as a catalyst to give alkylated benzenes.



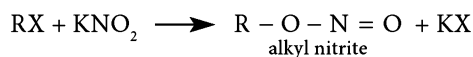
Synthesis of nitroalkanes and alkyl nitrites

When an alkyl halide is heated with silver nitrite in aqueous ethanol solution, nitroalkanes are formed predominantly; a small quantity of alkyl nitrite is also formed. The proportion of the nitrite formed as a side product increases when secondary halides are used and it is about 5% when tertiary halides are used.



N,N-dimethyl formamide, $\text{HCON}(\text{CH}_3)_2$, is also used as a solvent in the place of ethanol.

When an alkyl halide is treated with sodium or potassium nitrite, an alkyl nitrite is obtained.

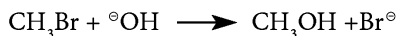


MECHANISM OF NUCLEOPHILIC SUBSTITUTION REACTIONS

Aliphatic nucleophilic substitution reactions proceed either by S_N2 or by S_N1 mechanism.

S_N2 mechanism

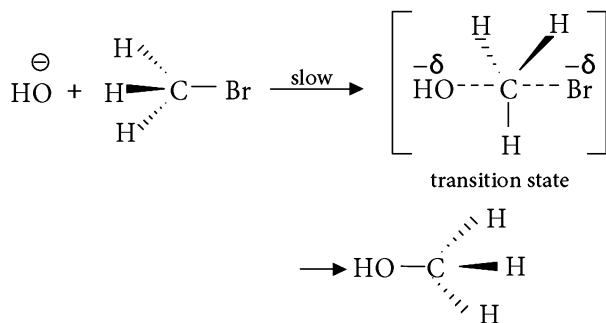
The reaction of methyl bromide with aqueous solution of NaOH can be taken as a specific example for S_N2 mechanism.



This reaction follows second order kinetics, i.e., the rate depends on the concentration of both the substrate (CH_3Br) and the nucleophile (OH^-)

$$\text{Rate} = k[\text{CH}_3\text{Br}][\text{OH}^-]$$

The reaction takes place in a single step. The nucleophile attacks the substrate from the side opposite to that of the leaving group. Bond breaking and bond formation take place simultaneously. The reaction proceeds through a transition state in which both the nucleophile and the leaving group are partially bonded to carbon.



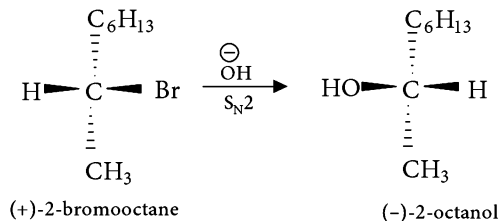
In the transition state the new C – OH bond is not completely formed and the old C – Br bond is not completely broken. The ${}^\ominus\text{OH}$ and ${}^\ominus\text{Br}$ are located as far apart as possible. The three other bonds with carbon lie in the same plane, the bond angle being 120° . The C – H bonds are arranged like the spokes of a wheel with C – OH and C – Br bonds lying along the axle.

This mechanism is known as S_N2 , meaning substitution nucleophilic bimolecular. It is bimolecular because the rate determining step involves both the species ${}^\ominus\text{OH}$ and CH_3Br .

(i) Inversion in S_N2 process

An S_N2 reaction proceeds with inversion of configuration. When (+)-2-bromooctane is treated with aqueous NaOH,

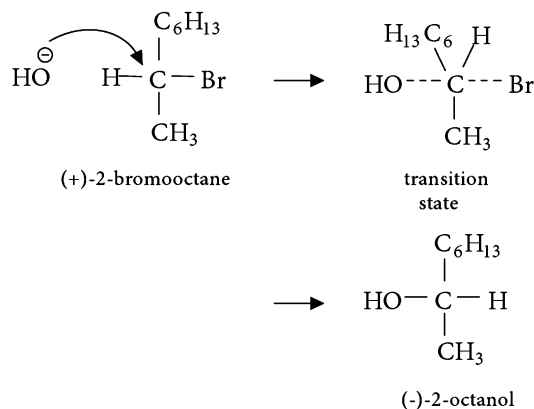
the product obtained is (–)-2-octanol, with inversion of configuration from the starting material.



In the product, namely 2-octanol, the –OH group has not occupied the position previously occupied by the Br. The alcohol obtained has a configuration opposite to the configuration of the starting bromide. (It is coincidental that there is also a reversal of sign of rotation)

A reaction, which yields a product, whose configuration is opposite to that of the starting material is said to proceed with inversion of configuration.

It is to account for this inversion of configuration that the back side or rear side attack was proposed for an S_N2 reaction.



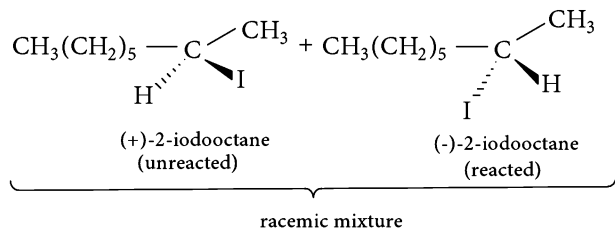
The inversion of configuration in an S_N2 reaction is compared to the turning inside out of an umbrella in a gale. This is known as Walden inversion.

When optically active 2-iodooctane is allowed to react with iodide ion in acetone medium, the substrate loses its optical activity.

When one molecule of 2-iodooctane reacts with iodide in an inversion process, its enantiomer is produced. The optical rotation of the product exactly cancels the rotation of the unchanged molecule. Thus the reaction of the molecule accounts for the cancellation of the optical

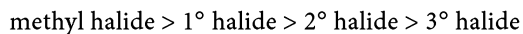
4.22 Alcohols, Alkyl Halides and Haloarenes

rotation of two molecules. Optical activity is lost twice as fast as the iodide exchange reaction occurs.

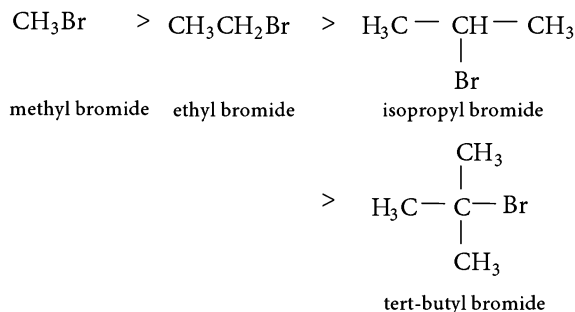


(ii) Reactivity in S_N2 reaction

In S_N2 reaction, the presence of bulky group on the carbon containing the leaving group tends to hinder the approach of the nucleophile and slow down the reaction. Thus the order of reactivity of alkyl halides in S_N2 reaction is

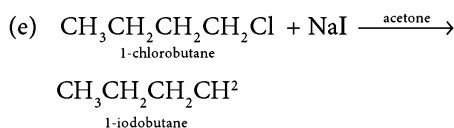
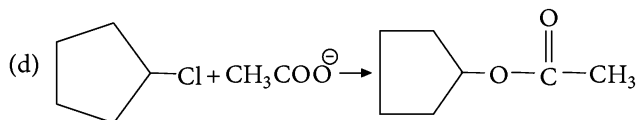
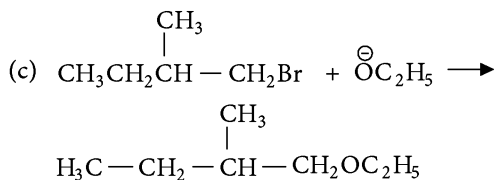
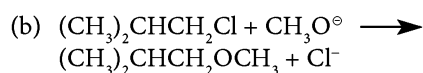
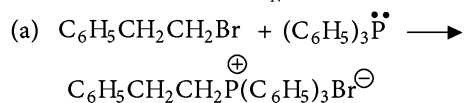


For example



As we proceed from methyl bromide, through ethyl bromide and isopropyl bromide to t-butyl bromide, the hydrogen atoms are replaced by methyl groups and hence there is increased crowding about the central carbon. The back side of the molecule, where the entering nucleophile attacks, becomes increasingly crowded and gets inaccessible. This crowding is particularly severe in the transition state. The net result is that the energy of activation for the reaction is higher and the rate of the reaction is slower. The differences in the rates of S_N2 reactions are mainly due to steric factors and not due to polar factors.

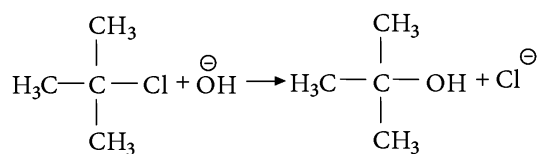
A few examples of S_N2 reactions are given below



A reaction proceeded by S_N2 mechanism is a concerted process, with rear side attack of the nucleophile. If an optically active substrate is used, the product obtained is with inversion of configuration. The reaction follows second order kinetics.

S_N1 mechanism

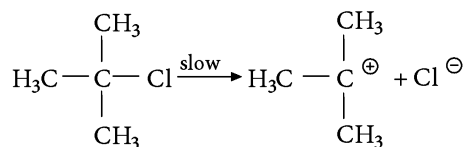
The rate of S_N1 reaction depends only on the concentration of substrate (alkyl halide). For example, the hydrolysis of tertiary butyl chloride follows first order kinetics. Since the reaction follows a first order mechanism, it means that the rate of the reaction depends on the concentration of only one reactant, i.e., tert-butyl chloride.



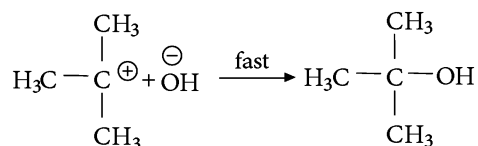
$$\text{Rate} = k[(\text{CH}_3)_2\text{CCl}]$$

The entire reaction occurs in two steps. In step I, the starting material tert-butyl chloride slowly dissociates into a carbocation and a chloride ion.

Step I



This carbocation rapidly combines with the $^{\ominus}\text{OH}$ ions in step II to form the final product, tert-butyl alcohol.

Step II

Thus, $\text{S}_{\text{N}}1$ reaction involves two steps.

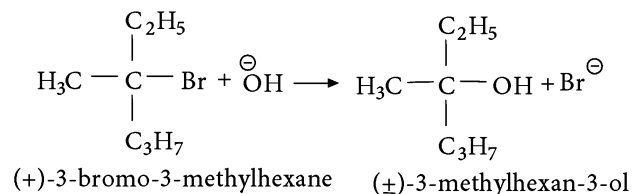
The rate of the overall reaction is determined by the slow step involving the breaking of the C – Cl bond. In the step I, we are actually measuring the rate. This does not involve the $^{\ominus}\text{OH}$ ions. A *single step, whose rate determines the overall rate of a stepwise reaction is called the rate determining step.*

This mechanism is called substitution nucleophilic unimolecular ($\text{S}_{\text{N}}1$). The term unimolecular is used because the rate determining step involves only one molecule. The mechanism is consistent with first order kinetics. The rate of the entire reaction is determined by how fast the alkyl halide ionizes and hence depends only on the concentration of the alkyl halide.

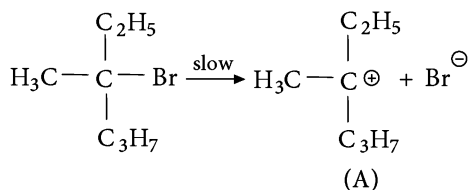
Carbocation (group of atoms that contains a carbon atom bearing only six electrons and a positive charge) is the important intermediate in the $\text{S}_{\text{N}}1$ reaction. Like free radicals, carbocation is an exceedingly reactive species. Carbocation tends to become stable by acquiring a pair of electrons to complete the octet.

Stereochemistry of $\text{S}_{\text{N}}1$ reaction

Let us consider a nucleophilic substitution reaction proceeding by $\text{S}_{\text{N}}1$ mechanism

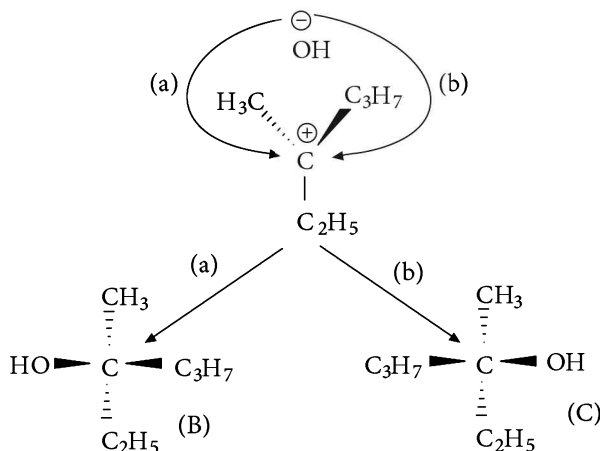


The substrate is optically active. The product obtained is racemic, a mixture of (+)- and (–)- hexanols. The reaction proceeds in two steps. In the step I, a carbocation (A) is formed by a slow ionization process.

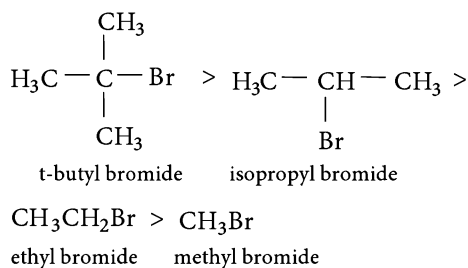


This carbocation (A) is planar. The central carbon bearing the positive charge is sp^2 hybridized.

In the next step, which is a fast step, the nucleophile $^{\ominus}\text{OH}$ gets attached to the carbocation to form the product. Since the carbocation is planar, the attacking nucleophile can attach itself to two sides of the carbocation to give two enantiomeric products (B) and (C). So the final product obtained is a racemic mixture.



In an $\text{S}_{\text{N}}1$ process, a tertiary cation is more favourably formed and stable. Therefore, the order of reactivity is

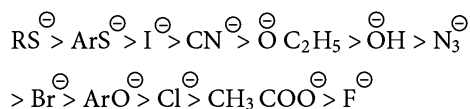
**Factors affecting $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ reactions****1. Nature of the substrate**

We have already seen that substrates, that can produce stable carbocations, show high reactivity towards $\text{S}_{\text{N}}1$ reactions. Thus tertiary alkyl halides, allylic and benzylic halides undergo substitution mainly by $\text{S}_{\text{N}}1$ mechanism. Primary alkyl halides, which do not form stable carbocations undergo substitution by $\text{S}_{\text{N}}2$ mechanism. Secondary alkyl halides may undergo substitution by $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$ mechanism depending on other factors.

2. Nature of the nucleophile

Any species containing a non-bonded pair of electrons can act as a nucleophile. The rates of S_N1 reactions are independent of the nature of the nucleophile because it does not appear in the rate determining step. But the rate of S_N2 reaction is affected by the nature of the nucleophile.

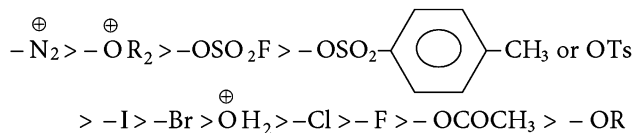
The ability of a nucleophile to form bond with carbon, in nucleophilic substitution reactions, is called the nucleophilicity of the reagent. The nucleophilicity of a reagent depends on the nature of the solvent used in the reaction and, in general, is in the following order :



It has been found that strong nucleophile favour S_N2 while weak nucleophiles favour S_N1 reactions.

3. The effect of the leaving group

The rate of any nucleophilic substitution reaction (S_N1 or S_N2) depends on the nature of the leaving group. The leaving group comes out more readily if it is more stable as a free entity. The order of ease of displacement of groups is not fixed, it depends on the nature of the R group to which it is attached and also on the nature of the solvent. The approximate order of decreasing leaving ability of some groups are given below.

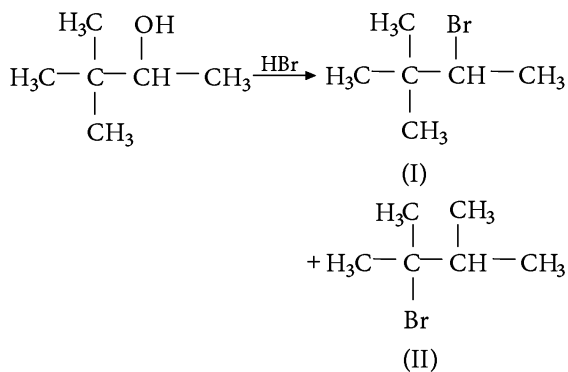


4. Nature of the solvent

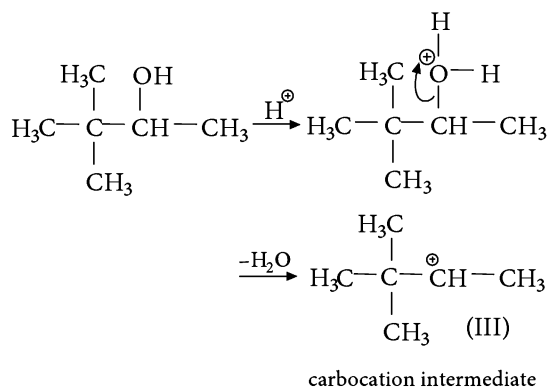
Polar solvents favour ionization and hence favour S_N1 reactions while non polar or weakly polar solvents favour S_N2 reactions.

REARRANGEMENTS OBSERVED IN S_N1 REACTIONS

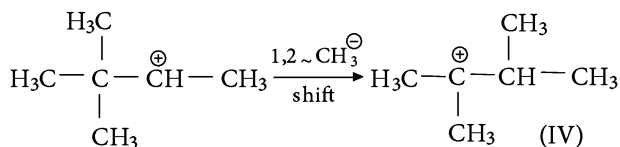
- (i) When 3,3-dimethyl-2-butanol is treated with HBr, the expected product, 3-bromo-2,2-dimethylbutane (I), is formed. In addition to this, another product, 2-bromo-2,3-dimethylbutane (II), is also formed.



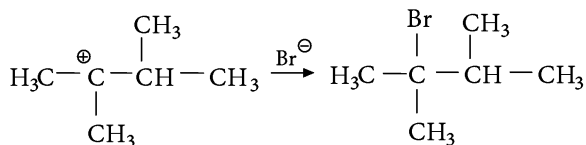
The formation of (II) can be explained by the rearrangement occurring during the reaction. In the first step, a carbocation (III) is formed.



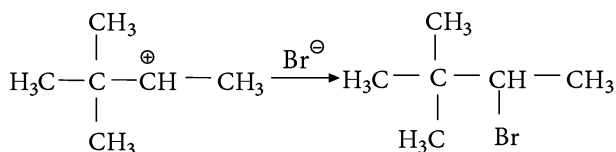
This carbocation (III) is a secondary carbocation and therefore rearranges to a more stable tertiary carbocation (IV) by the 1, 2-shift of a $^\ominus CH_3$ group.



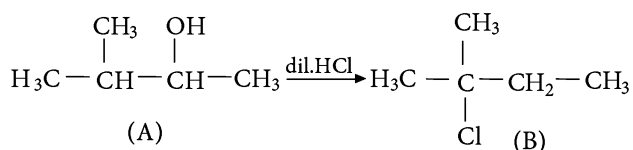
In the second step, the nucleophile $\text{Br}^\ominus$ attacks the carbocation (IV) to produce the product (II).



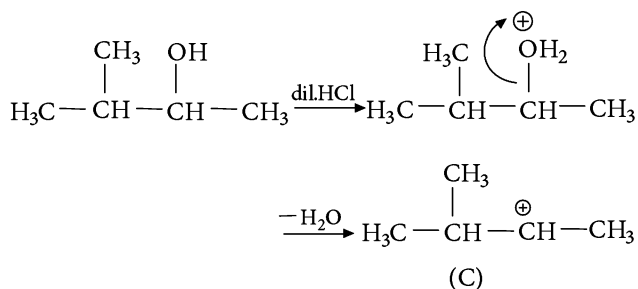
Product (I) is formed by the attack of $\text{Br}^\ominus$ on the carbocation (III).



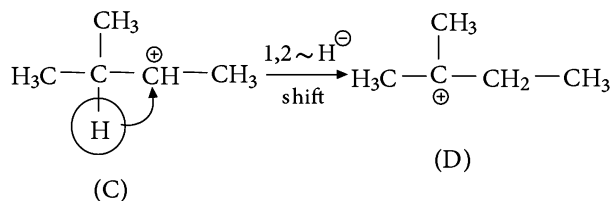
- (ii) The treatment of 3-methyl-2-butanol (A) with hot dilute HCl gives 2-chloro-2-methylbutane (B) as the main product.



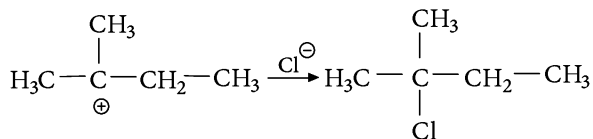
The formation of (B) as a major product can be explained in terms of rearrangement. When the alcohol (A) is treated with aqueous HCl, a carbocation (C) is formed.



This carbocation (C) arises by the loss of a water molecule from the protonated alcohol. The carbocation (C) is a secondary carbocation and therefore rearranges to a more stable tertiary carbocation (D) by a 1,2-hydride shift.

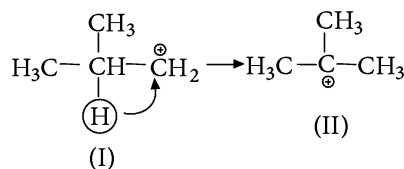


Now the nucleophile $\text{Cl}^\ominus$ adds on to this carbocation to give the final product namely 2-chloro-2-methylbutane.

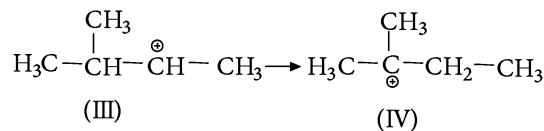


Rearrangements in general can occur in the following ways

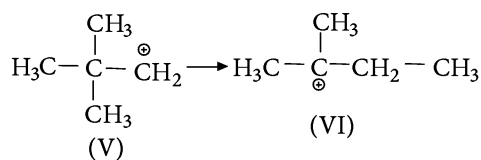
- (a) A primary carbocation like isobutyl cation (I) can rearrange to a more stable, tert-butyl cation (II).



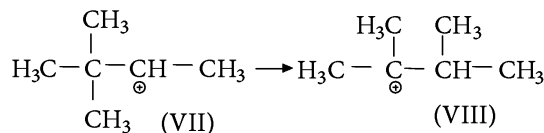
- (b) 3-Methyl-2-butyl cation (III) can rearrange to 2-Methyl-2-butyl cation (IV).



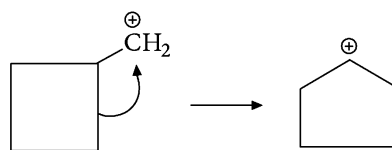
- (c) Neopentyl cation (V) can rearrange to a tert-pentyl cation (VI).



- (d) 3,3-Dimethyl-2-butyl cation (VII) can rearrange to 2,3-Dimethyl-2-butyl cation (VIII).

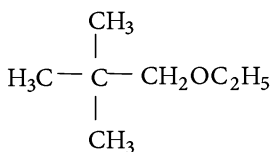
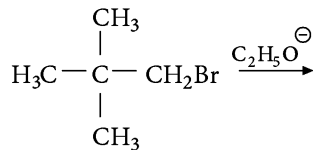


- (e) Rearrangements can occur via a ring expansion also so as to form a stable five or six membered ring.

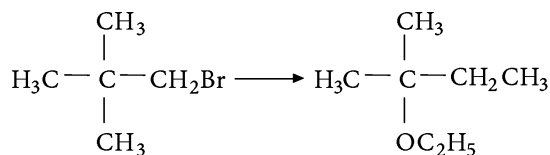


4.26 Alcohols, Alkyl Halides and Haloarenes

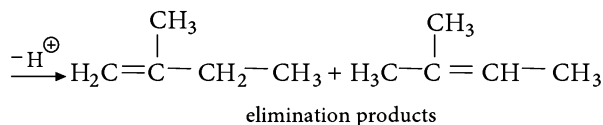
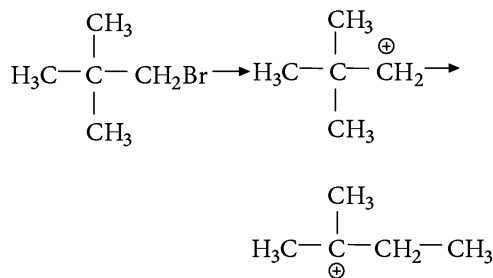
Whenever carbocations are formed there is also a possibility of a competing reaction involving eliminations. For example when neopentyl bromide is treated with a nucleophile like $\text{C}_2\text{H}_5\text{O}^\ominus$, different products are formed. They are a normal substitution product without rearrangement, a substitution product after a rearrangement and finally two elimination products.



substitution product
without rearrangement



substitution product
with rearrangement



Substitution and elimination are competing reactions in alkyl halides. A carbocation can

- combine with a nucleophile.
- rearrange to give another more stable carbocation.
- undergo elimination to give an olefin.

The following factors contribute to an increased elimination product in a reaction that accompanies a nucleophilic substitution.

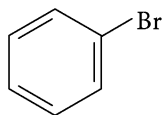
- Increased basicity of the nucleophile.
- Higher temperatures.
- Crowding of the atoms at the substitution centre.

HALOARENES

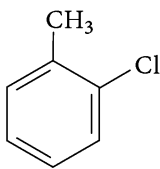
Halogen derivatives of aromatic compounds can be divided into two types, namely aryl halides and aralkyl halides.

Aryl halides

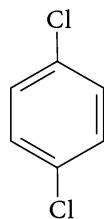
In this type of compounds, the halogen atom is directly attached to the aromatic ring system. For example



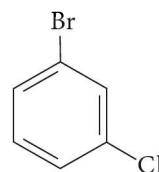
bromobenzene



2-chlorotoluene



1,4-dichlorobenzene



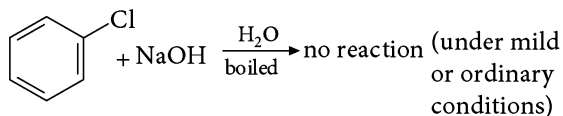
1-bromo-3-chlorobenzene

substitution. This is in contrast to the facile nucleophilic substitution observed with alkyl halides.

For example, chlorobenzene fails to undergo the conversion to give phenol, when boiled with aqueous NaOH solution.

Simple aryl halides are similar to vinyl halides, in that they are relatively unreactive towards nucleophilic

In a similar way, vinyl chloride, $\text{H}_2\text{C}=\text{CH}-\text{Cl}$, also does not undergo a substitution reaction with alkali to give vinyl alcohol.



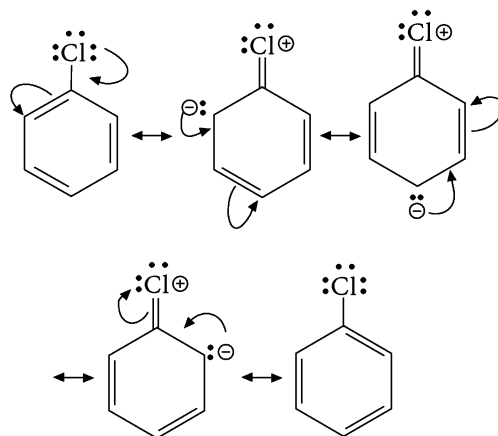
The lack of reactivity of a nuclear halogen can be explained as follows. Phenyl cation, c1ccccc1[CH2+], is very unstable. Therefore, S_N1 reaction does not occur. The C-Cl bond in general C-X bond (where X is a halogen) in aryl halides and vinyl halides are shorter (C-Cl bond length = 1.69 Å whereas C-Cl bond length = 1.78 Å in alkyl halides) and stronger than those found in alkyl, allyl (H2C=CH-CH2-) and benzyl halides.

The carbon-halogen bond is stronger in aryl and vinyl halides because of two reasons

- (i) The carbon to which the halogen is attached is sp^2 hybridized and therefore the electrons of the carbon

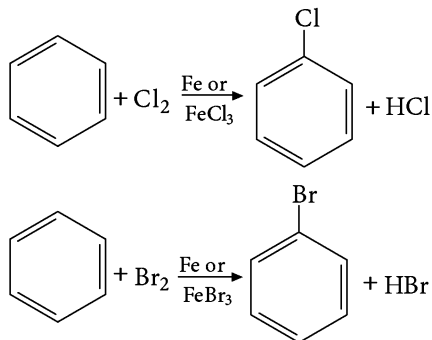
orbital are closer to the nucleus compared to the orbitals of carbon which are sp^3 hybridised.

- (ii) Resonance strengthens the C-Cl bond giving a partial double bond character.

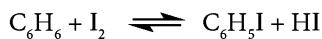


PREPARATION OF HALOARENES

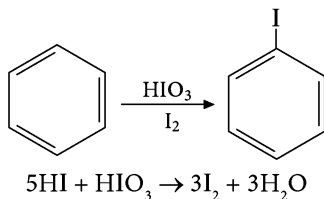
(i) By direct halogenation



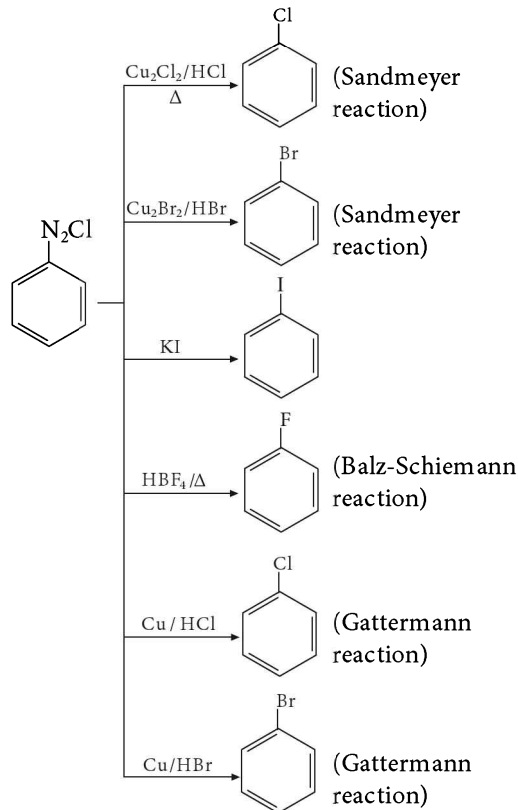
Iodo derivatives cannot be obtained by direct reaction with iodine as the reaction is reversible.



Iodobenzene can be obtained if the reaction is carried out in presence of an oxidizing agent like HIO3 or HNO3, etc. The oxidizing agent oxidizes HI to I2



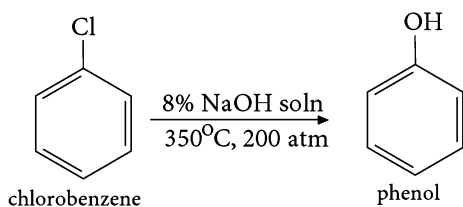
(ii) From diazonium salts



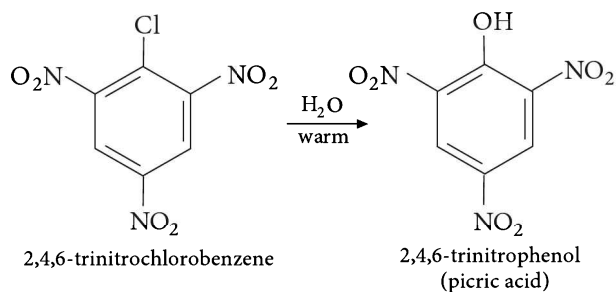
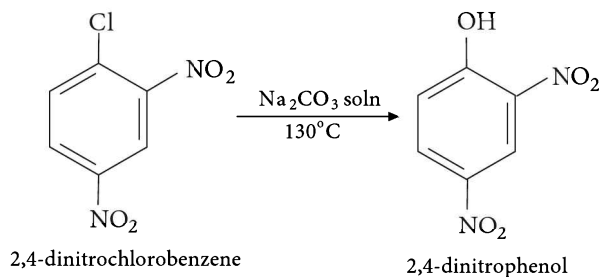
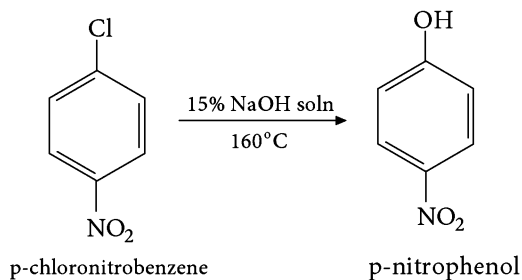
AROMATIC NUCLEOPHILIC SUBSTITUTION IN HALOARENES AND SUBSTITUTED HALOARENES

Aryl halides can be made active towards aromatic nucleophilic substitution if they bear certain substituents. Nucleophilic substitution in haloarenes can occur when strong electron withdrawing groups are present at ortho or para positions to the halogen atom attached to the nucleus.

For example, simple chlorobenzene can be converted to phenol by sodium hydroxide solution only at temperatures over 300°C and higher pressure.



However, the presence of electron withdrawing group at ortho and para positions increases the rate of nucleophilic substitution.

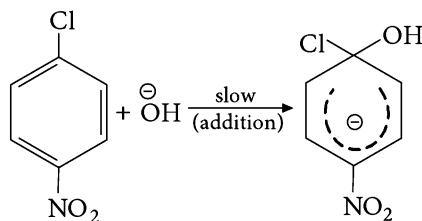


The presence of an electron withdrawing nitro group, ortho or para to the chlorine very much increases the reactivity. As the number of ortho and para nitro groups on the ring is increased the reactivity of substitution increases. 2,4-dinitrophenol is formed from the corresponding 2,4-dinitrohalogen compound at a temperature of 130°C, while picric acid (trinitrophenol) is formed just simply by warming the trinitrohalogen compound with water. When three nitro groups are present, the reaction becomes facile.

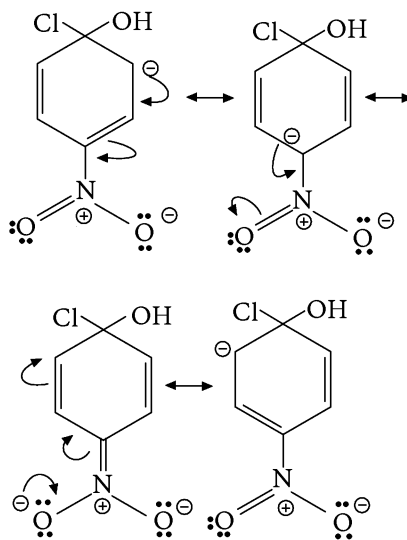
It is important to note that a meta nitro group does not produce a similar activating influence. For example, m-chloronitrobenzene has no activating influence.

The displacement of the nuclear halogen in the presence of $-\text{NO}_2$ groups by an $-\text{OH}$ group to give a nitrophenol involves an addition-elimination mechanism.

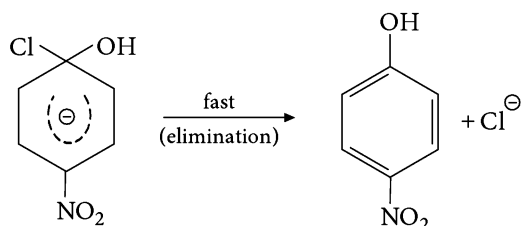
A carbanion with delocalized electrons known as *Meisenheimer complex* (compound or salt) is formed as an intermediate.



The carbanion is stabilized by electron withdrawing groups like $-\text{NO}_2$ by resonance as shown.

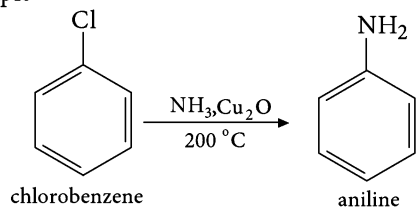


The carbanion undergoes a fast elimination of the Cl^- to give the phenol.



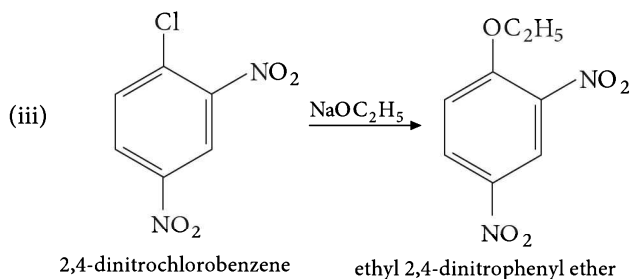
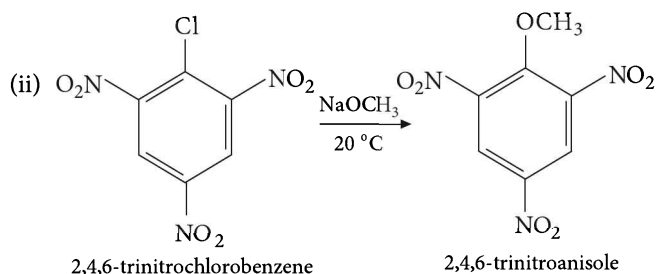
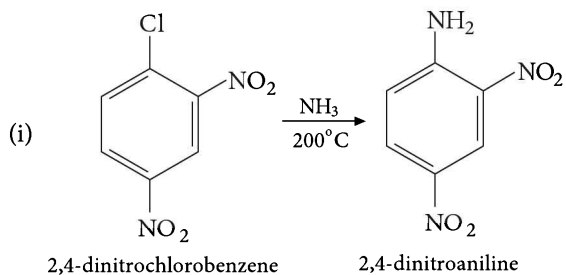
Similar effects are observed when other nucleophilic reagents are used.

For example



The reaction occurs under drastic conditions, at a temperature of 200°C under pressure

If the ring contains nitro group, preferably more than one, ortho or para to the nuclear halogen, the reaction proceeds quite readily under mild conditions.



Aryl or vinyl halides cannot be used in place of alkyl halides in Friedel-Crafts reaction.

Like the nitro group, some other electron withdrawing groups like $-\text{CN}$, $-\text{SO}_3\text{H}$, $-\text{COOH}$, $-\text{CHO}$, etc. located either ortho or para to the halogen can also activate the nucleophilic substitution occurring in an aromatic ring.

Hydrogen is not displaced as H^+ in a nucleophilic aromatic substitution since this would require the separation of a very strong basic hydride ion, H^- .

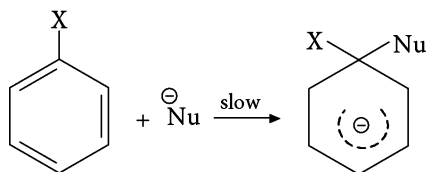
Electron withdrawing groups activate an aromatic nucleophilic substitution, while electron releasing groups deactivate the process. Groups like $-\text{NH}_2$ and $-\text{OH}$ deactivate strongly and groups like $-\text{CH}_3$ and $-\text{OR}$ moderately deactivate the process. The type of effect that each group (whether electron withdrawing or electron releasing) exerts in nucleophilic aromatic substitution is exactly opposite to that in electrophilic aromatic substitution. To be precise, in nucleophilic aromatic substitution electron withdrawal causes activation and electron release causes deactivation.

Evidence for two steps in addition-elimination mechanism

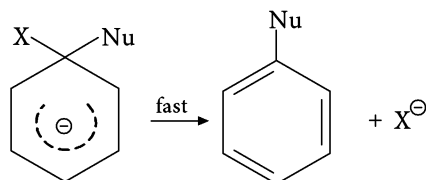
In an aromatic nucleophilic displacement, two steps are involved. It is known as addition-elimination (AE) mechanism.

The first step is a slower step which involves the addition of a nucleophile, which is the rate determining step. The second step is fast, which involves the removal of the leaving nucleophile.

Step - I



Step - II



In $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ reactions, the reactivity of the alkyl halides follows the order, $\text{R-I} > \text{R-Br} > \text{R-Cl} > \text{R-F}$

In nucleophilic aromatic substitution, this difference in the order of reactivity of halogens is not observed. In fact, the C-F bond, which is very slow to react in aliphatic substitution, is the most reactive in aromatic nucleophilic substitution.

4.30 Alcohols, Alkyl Halides and Haloarenes

Effectively, the rate of the reaction in aromatic substitution is independent of the breaking of the carbon-halogen

bond. The rate is determined by the rate of attachment of the attacking nucleophile to the ring.

ALTERNATIVE MECHANISM: ELIMINATION-ADDITION MECHANISM

Aromatic nucleophilic substitution can happen by the elimination-addition mechanism also. This is also known as benzyne mechanism. In this mechanism, elimination of the nucleophile occurs in the first step leading to a benzyne intermediate, which is followed by the addition of the entering nucleophile.

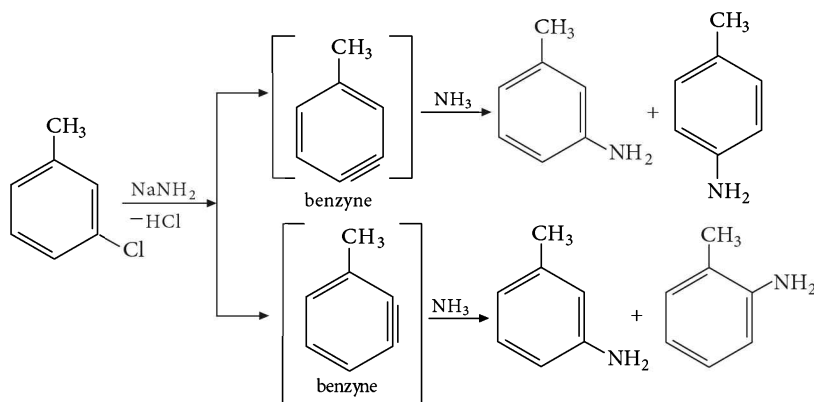
Benzyne mechanism

Reactions of halobenzene with a strong base lead to nucleophilic substitution products. Investigations revealed that

the reaction involves the initial elimination of HX. A *highly energetic, unstable intermediate which contains a triple bond within the benzene ring known as benzyne or 1,2-dehydrobenzene* is formed. Addition of nucleophile in the second step occurs leading to products.

For example

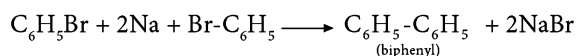
A strong support for the existence of the benzyne is the formation of three different substitution products in the reaction.



ADDITIONAL REACTIONS OF HALOARENES

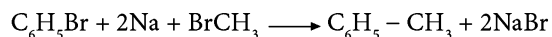
(i) Fittig reaction

Coupling reaction of aryl halides in presence of metallic sodium to give diaryl.



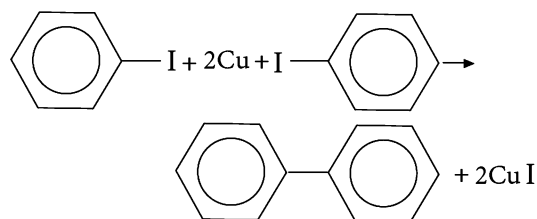
(ii) Wurtz-Fittig reaction

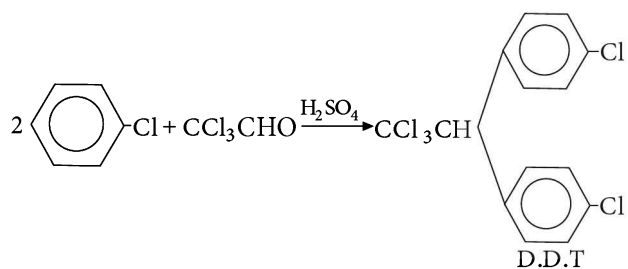
Aryl halides couple with alkyl halides in presence of metallic sodium to form alkyl arenes.



(iii) Ullmann reaction

Iodobenzene on heating with copper in a sealed tube gives biphenyl.

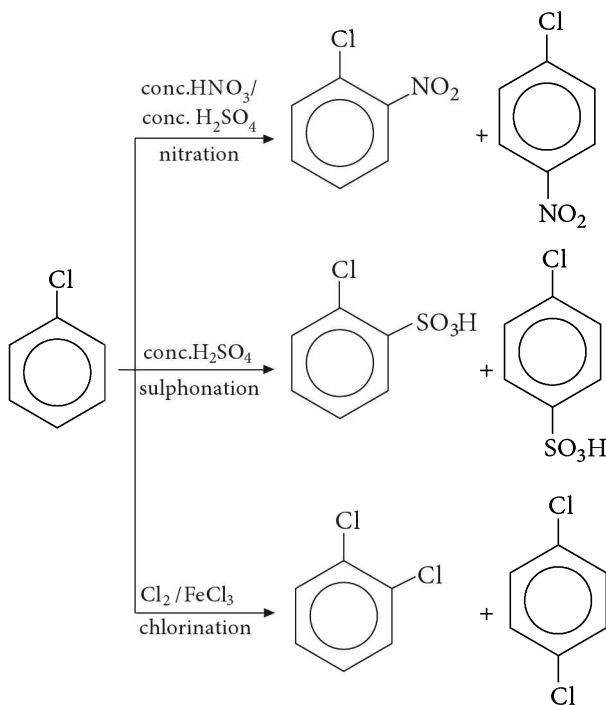


(iv) Reaction with chloral

D.D.T is p,p'-dichlorodiphenyltrichloroethane or 1,1,1-trichloro-2,2-bis(4-chlorophenyl) ethane and is used as an insecticide.

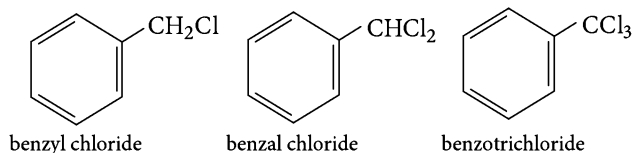
(v) Electrophilic substitution reactions

Halogen is electron withdrawing by inductive effect and electron releasing by mesomeric effect. The reactions are slower compared to benzene and halogen is generally ortho, para directing.

**REACTIONS OF ARALKYL HALIDES**

Aryl alkyl or aralkyl halides are those, which contain a halogen in the side chain. The halogen is not directly attached to the aromatic ring, but through a side chain.

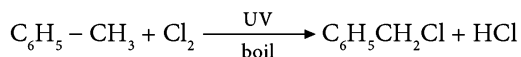
For example



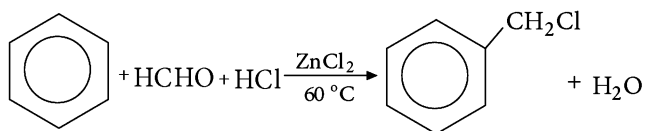
As a typical member of aralkyl halide, benzyl chloride can be considered.

Preparation of benzyl chloride

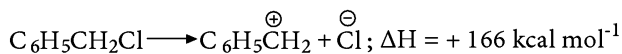
- (i) It is obtained by passing chlorine into boiling toluene in presence of UV light.



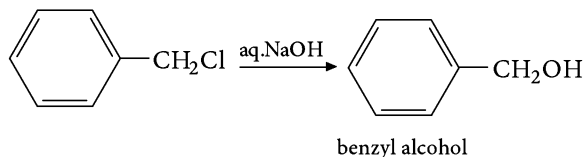
- (ii) By the chloromethylation of benzene with formaldehyde and HCl in presence of anhydrous ZnCl_2 .

**Reactions of benzyl chloride**

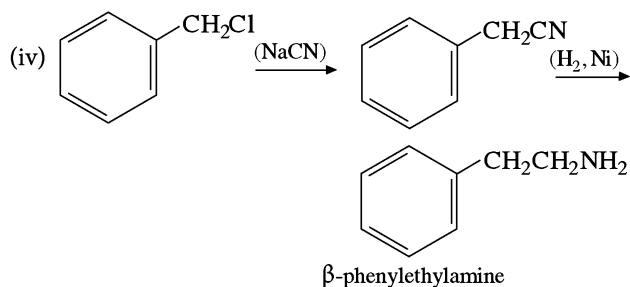
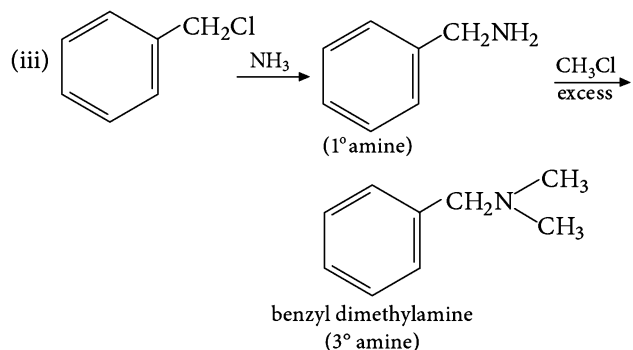
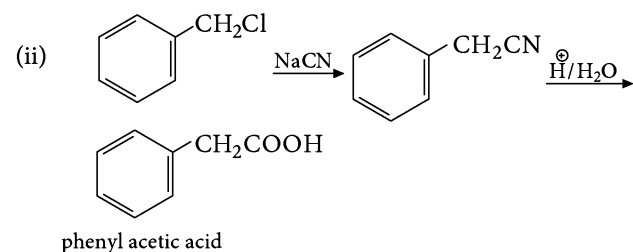
The heterolytic bond dissociation energy of benzyl chloride is $166 \text{ kcal mol}^{-1}$. The benzyl cation is more stable than a primary alkyl cation as it can be stabilized by resonance.



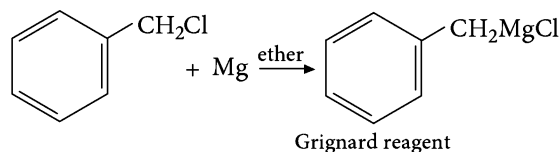
- (i) Hydrolysis of benzyl chloride



4.32 Alcohols, Alkyl Halides and Haloarenes



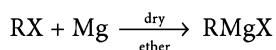
(v) Benzyl chloride can also be converted as a Grignard reagent by reaction with magnesium in ether medium.



In all reactions, benzyl halides behave as though they are alkyl halides.

GRIGNARD REAGENTS

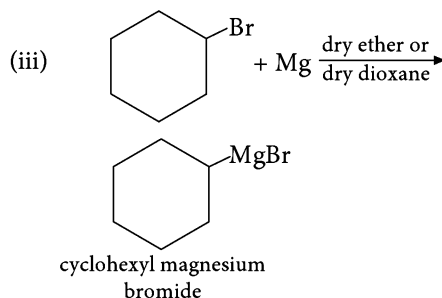
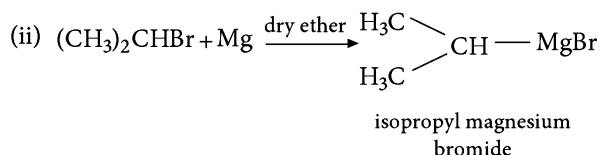
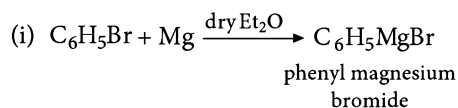
When an alkyl (or aryl or aralkyl) halide reacts with magnesium metal in dry ether medium, the corresponding alkyl (or aryl or aralkyl) magnesium halide is obtained.



An alkyl or aryl (or aralkyl) magnesium halide is known as Grignard reagent. In the formation of the above reagent, magnesium gets inserted between the halogen and the alkyl (or aryl) group. There is a direct link between the metal and the carbon of the alkyl group of the reagent and hence Grignard reagents are examples of organometallic compounds.

Grignard reagents are essentially used for the synthesis of alcohols. The formation of Grignard reagent is one of the important reactions of alkyl halides. Grignard reactions are successful only in totally dry and anhydrous conditions and in an inert atmosphere of nitrogen.

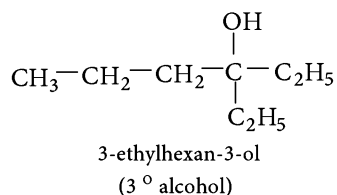
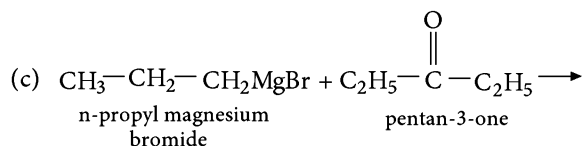
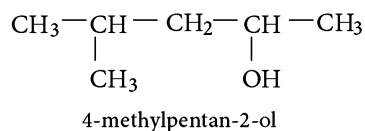
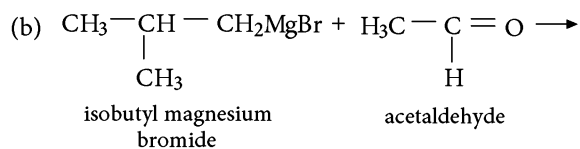
Preparation of Grignard reagents



Bromides and iodides are ideal halides that can be used for the preparation of Grignard reagents. Chlorides are comparatively less reactive and need slightly higher temperatures for the reaction to be initiated. Diethyl ether, dioxane and tetrahydrofuran (THF) are some of the common solvents used in the dry state (totally free from moisture) for Grignard reactions.

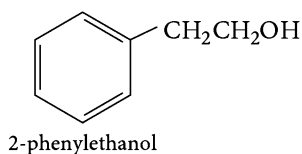
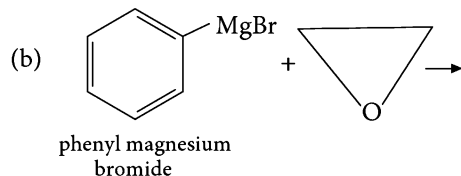
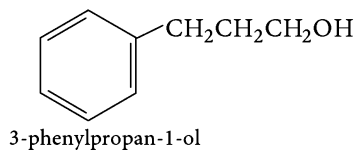
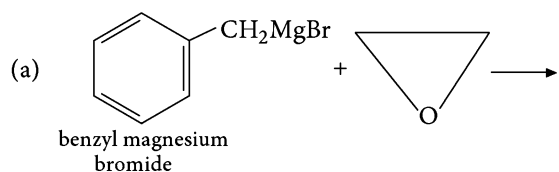
(a)
$$\begin{array}{ccc} \text{CH}_3\text{---CH}_2\text{---CH---CH}_3 & + & \text{H---C=O} \longrightarrow \\ | & & | \\ \text{MgBr} & & \text{H} \\ \text{sec-butyl magnesium} & & \text{formaldehyde} \\ \text{bromide} & & \\ \text{CH}_3\text{---CH}_2\text{---CH---CH}_3 & & \\ | & & \\ \text{CH}_2\text{OH} & & \\ \text{2-methylbutan-1-ol} & & \end{array}$$

4.34 Alcohols, Alkyl Halides and Haloarenes



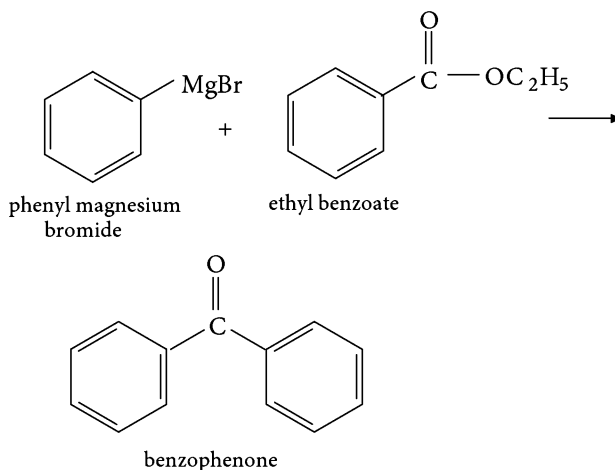
(ii) Reaction with epoxides

When Grignard reagents are treated with ethylene oxide, CH_2-CH_2 , the product obtained is a primary alcohol with two carbons extended.

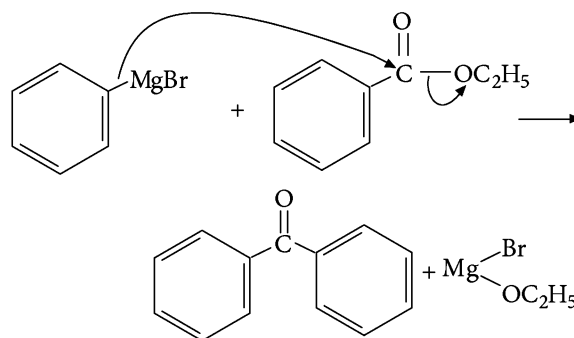


(iii) Reaction with esters

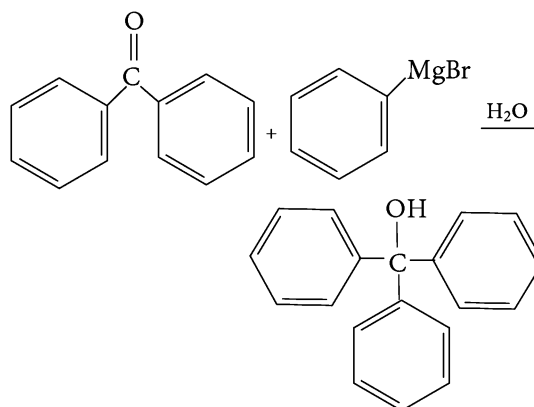
When Grignard reagents react with an ester (other than esters of formic acid), the first product formed is a ketone, which then reacts with another molecule of Grignard reagent to give tertiary alcohol.



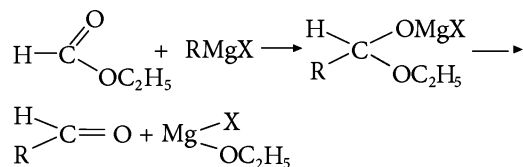
Mechanism



Benzophenone reacts further with excess Grignard reagent to give 3° alcohol as the final product.



Grignard reagent reacts with ethyl formate to form an aldehyde first, which may react with excess Grignard reagent to form secondary alcohols.



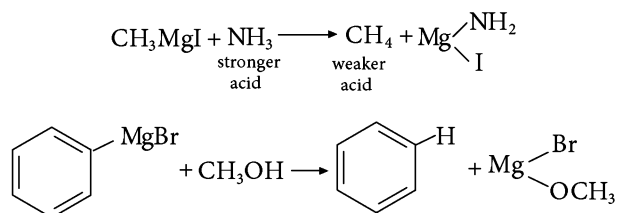
(iv) Reaction with compounds having acidic hydrogen

Grignard reagents are very sensitive to active or acidic hydrogen compounds like H_2O , terminal alkynes, alcohols, acids and amines. They react with them to give the respective hydrocarbons.

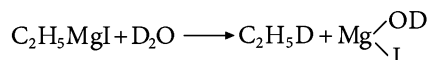
The reaction of a Grignard reagent with water to form an alkane is typical of the reagent. The reaction, $\text{RMgX} + \text{H}-\text{OH} \longrightarrow \text{R}-\text{H} + \text{Mg}(\text{OH})\text{X}$, is simply a displacement of a weaker acid ($\text{R}-\text{H}$) from its salt RMgX by a stronger acid, $\text{H}-\text{OH}$ (water).

Any compound containing hydrogen attached to a more electronegative element like nitrogen or oxygen is significantly more acidic than an alkane (which is a weak acid) and therefore such acidic compounds can decompose a Grignard reagent to the corresponding hydrocarbon.

For example,



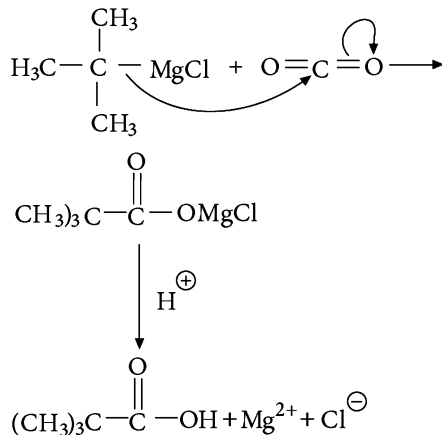
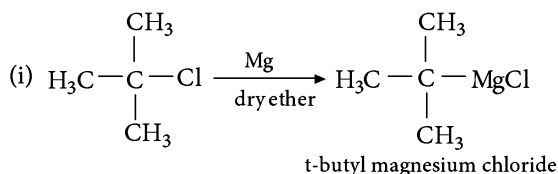
If D_2O is used in the place of H_2O , then



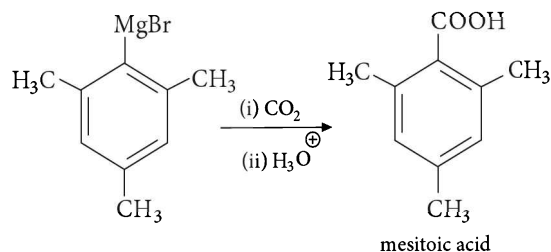
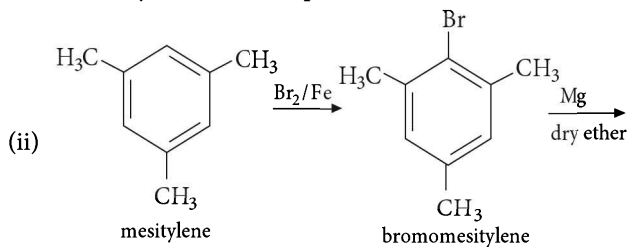
(v) Reaction with CO_2

Synthesis of a carboxylic acid is effected by treating an ether solution of a Grignard reagent with dry CO_2 gas at low temperature.

For example



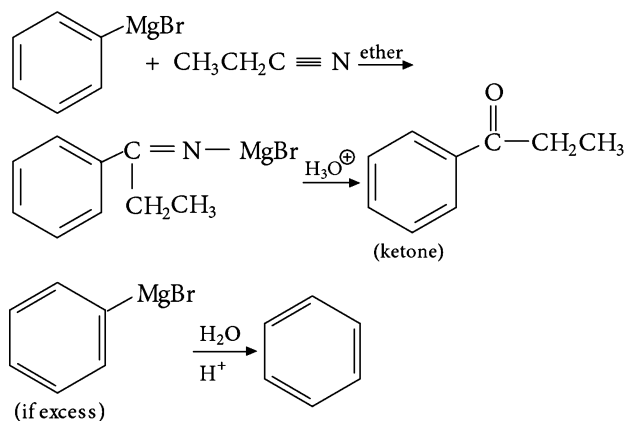
Trimethylacetic acid or pivalic acid is obtained.



(vi) Reaction with nitriles

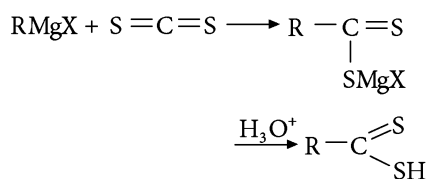
Grignard reagents add on to nitriles in a slow reaction to form an imine ($-\text{HC}=\text{N}-$) initially, which then hydrolyses to a ketone. The reaction does not proceed beyond the ketone stage, since the excess Grignard reagent (even if present) is converted to the corresponding hydrocarbon in presence of water.

4.36 Alcohols, Alkyl Halides and Haloarenes



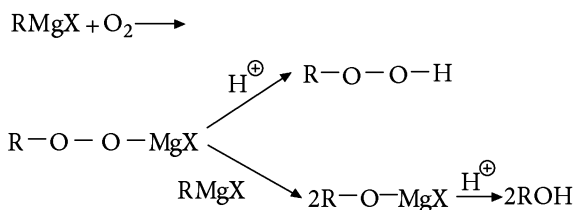
(vii) Reaction with CS₂

Grignard reagents add to CS₂ to give salts of dithiocarboxylic acids, which can be hydrolyzed to give dithioacids.



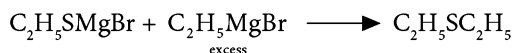
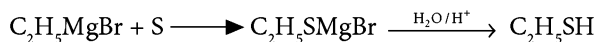
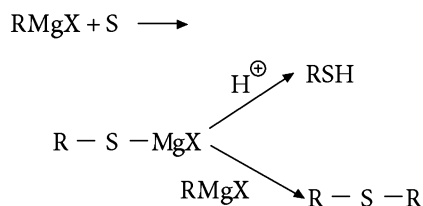
(viii) Reaction with oxygen

Grignard reagents are very sensitive to oxygen and give either alcohols or hydroperoxides.



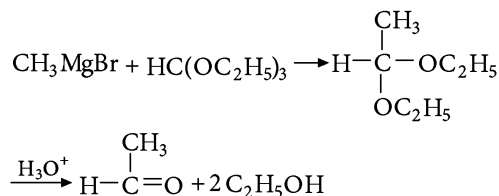
(ix) Reaction of Grignard reagents with sulphur

Grignard reagents react with sulphur to form thio alcohol or dialkylsulphides.



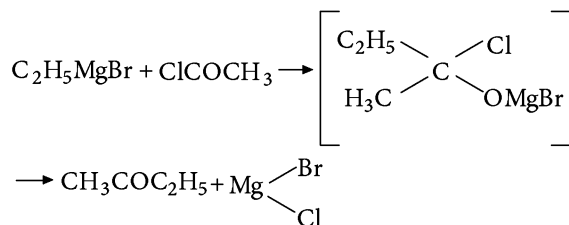
(x) Reaction with ortho esters

Grignard reagents react with ortho esters like ethyl orthoformate HC(OC₂H₅)₃ to give acetals which on hydrolysis give aldehydes.



(xi) Reaction with acid chlorides

The reaction of acid chloride with Grignard reagents yields ketones.

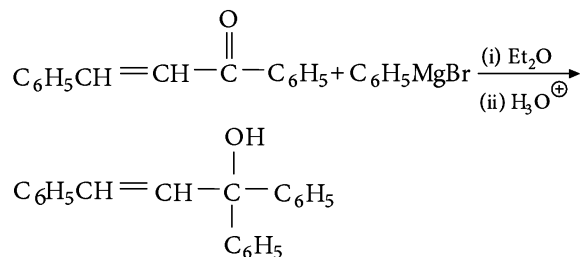


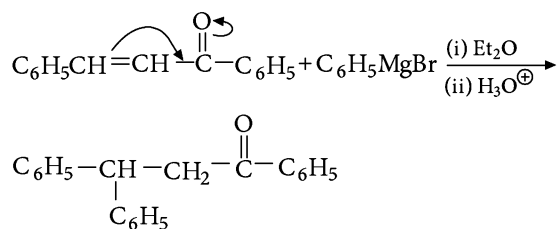
Ketones on further reaction with Grignard reagents give tertiary alcohols.

(xii) Conjugate addition reactions of Grignard reagents

When α,β-unsaturated carbonyl compounds react with Grignard reagents, the reaction takes by two pathways, one involving the normal carbonyl addition while the other involving a conjugate addition or 1,4-addition. For example.

Normal carbonyl addition

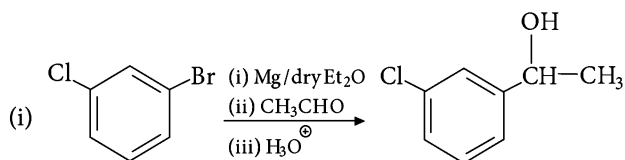


Conjugate addition or 1,4-addition

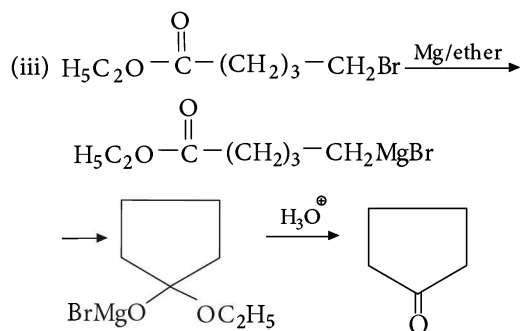
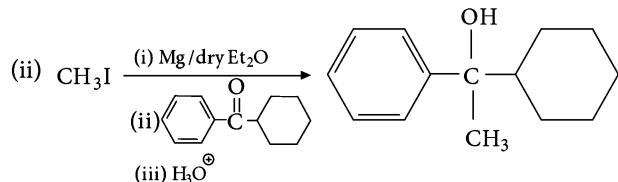
An alcohol is formed in the normal carbonyl addition, while in the conjugate addition the carbonyl group of the starting carbonyl compound is not affected.

The major factor in deciding the course of addition is steric hindrance. 1,4-addition can be made to predominate by carrying out the reaction in presence of cuprous chloride.

Few typical examples of Grignard reactions

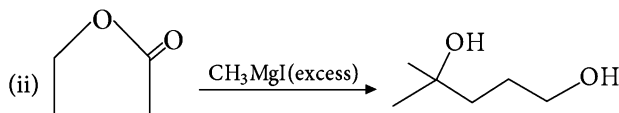
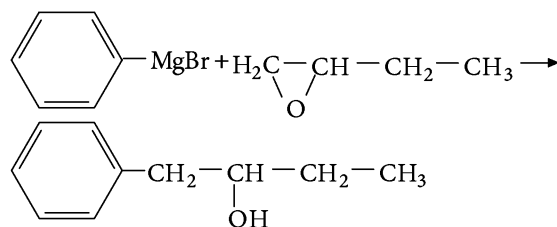
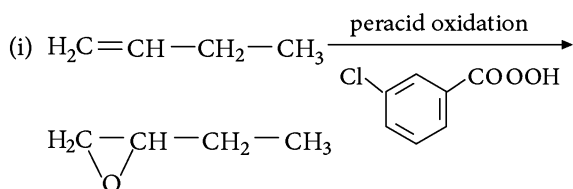


In this reaction, Cl is less reactive than Br. When only one equivalent is reacted, it is the Br which reacts.

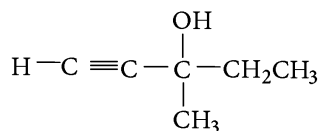
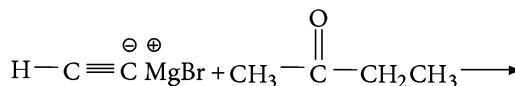
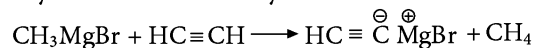


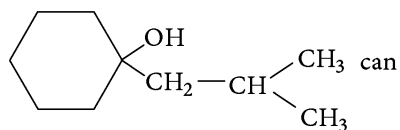
This is an intramolecular Grignard reaction.

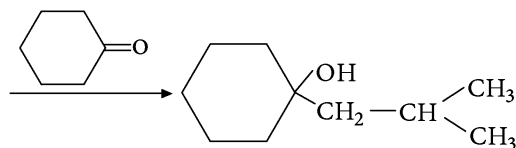
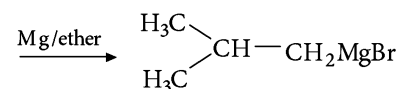
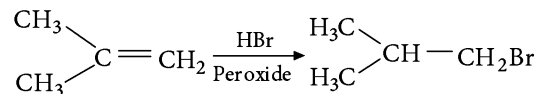
Grignard reactions are very useful in the synthesis of highly branched alcohols of higher molecular weight as shown by the following examples.

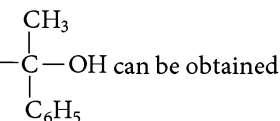


(iii) An acetylene alcohol can be synthesized as follows.

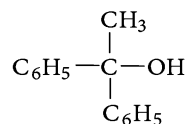
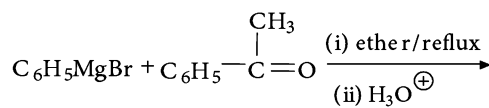


(iv) An alcohol like  can be synthesized as follows.



(v) A tertiary alcohol like  can be obtained

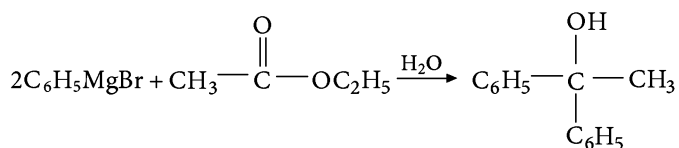
by the following route.



methyl diphenyl carbinol

4.38 Alcohols, Alkyl Halides and Haloarenes

Alternatively,



CONCEPT STRANDS

Concept Strands 3

- Arrange the halide ions in the decreasing order of nucleophilicity.
- Give two examples of unusual reagents, which are strong acids as well as very reactive nucleophiles.

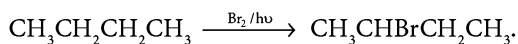
Solution

- $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$
Generally good nucleophiles are strong bases.
- HI and HBr.

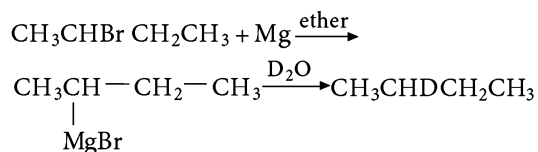
Concept Strands 4

How is $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ converted to $\text{CH}_3\text{CHDCH}_2\text{CH}_3$?

Solution

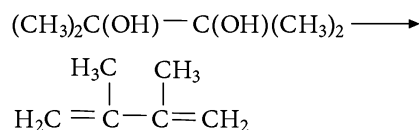


Free radical bromination is highly selective and only a secondary hydrogen gets displaced by bromine.

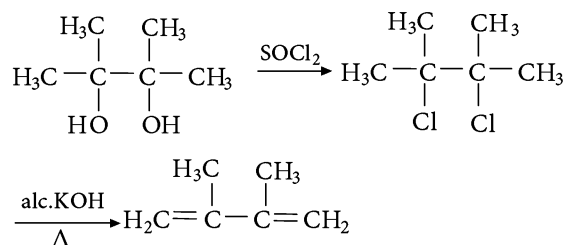


Concept Strands 5

How is the following conversion effected?



Solution



The precaution to be observed in the above conversion is that the alcohol cannot be directly dehydrated by means of an acid to give an olefin. Treatment of the alcohol with the acid gives a carbocation, which undergoes pinacol-pinacolone rearrangement. Therefore, the diol is first converted to a dichloride by means of PCl_5 or SOCl_2 and then dehydrohalogenated by means of a hot alcoholic KOH to give the diolefin.

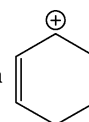
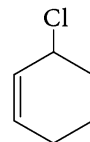
Concept Strands 6

Propose a chemical test to distinguish between

- 3-chlorocyclohexene and 1-chlorocyclohexene
- 1-bromo-1-methylcyclohexane and bromomethylcyclohexane

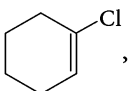
Solution

- 3-chlorocyclohexene is allylic chloride



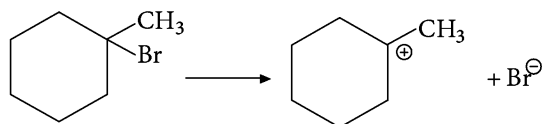
This can lead to a stable allyl cation by a

facile leaving of Cl as Cl^- . Hence alcoholic AgNO_3 solution gives a white precipitate readily. In the case of

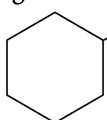
1-chloro-cyclohexene, it is a vinylic halide, ,

where chlorine is attached to an sp^2 carbon, which is difficult to be displaced. Hence $AgNO_3$ solution does not give a white precipitate with this compound.

- (b) 1-bromo-1-methylcyclohexane is a tertiary halide. Bromine can get easily replaced forming a stable tertiary carbocation.



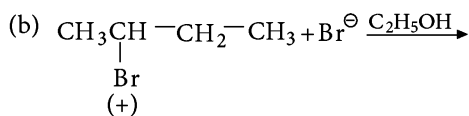
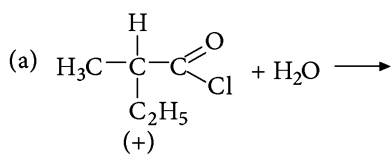
Hence alcoholic $AgNO_3$ readily gives a pale yellow precipitate of $AgBr$. In the case of

bromomethylcyclohexane,  it is a

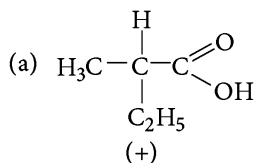
primary halide and $AgNO_3$ solution does not give a ready precipitate as bromine is not ready to leave as Br^- .

Concept Strands 7

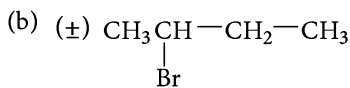
Give the structures of the products in the following reactions. Indicate stereochemistry wherever necessary.



Solution



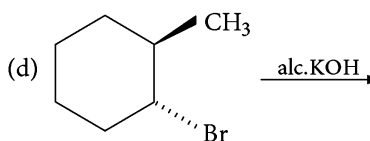
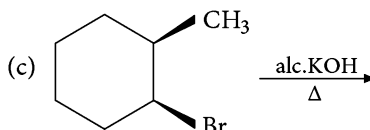
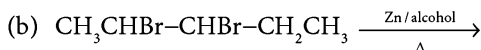
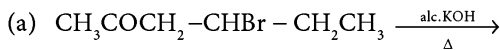
There will be no change in the stereochemistry of the product as the optically active centre does not undergo any substitution.



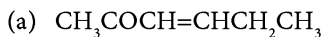
The product is also 2-bromobutane, but the product loses its optical activity because of the formation of a racemic mixture.

Concept Strands 8

Give the major products in the following reactions.

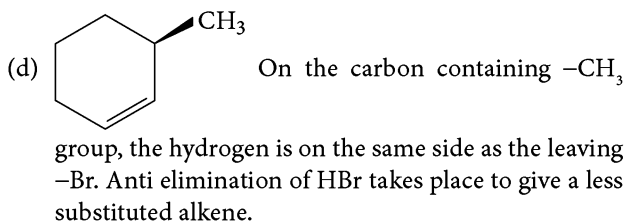
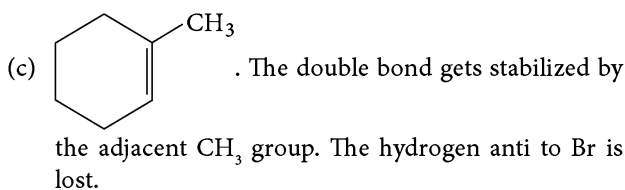


Solution



The hydrogen adjacent to the carbonyl group is more acidic to get displaced in the loss of HBr , to get a conjugated system as the major product.

- (b) $CH_3CH=CHCH_2CH_3$. It is a dehalogenation reaction resulting in an olefin.

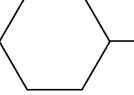


Concept Strands 9

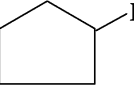
Which of the following reactions is/are expected to proceed very slowly if dilute sulphuric acid is added to the reaction mixture?

4.40 Alcohols, Alkyl Halides and Haloarenes

(a) $\text{CH}_3\text{CH}_2\text{Br} + \text{KCN}$ in methanol

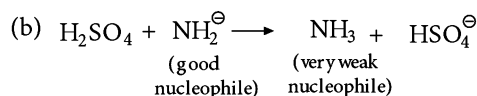
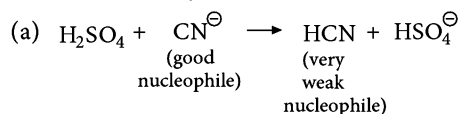
(b)  + KI in methanol

(c) $\text{H}_3\text{C}-\text{CH}(\text{H}_3\text{C})-\text{Br} + \text{CH}_3\text{NH}_2$ in methanol

(d)  + NaSH in ethanol

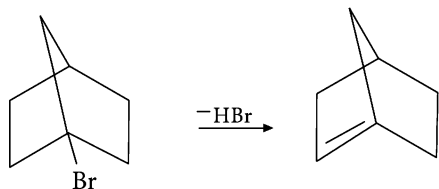
Solution

Reactions (a) and (c) are expected to proceed slowly. Under acidic conditions, in the presence of $\text{dil. H}_2\text{SO}_4$, active nucleophiles with basic properties like $\text{CN}^\ominus$ and $\text{NH}_2^\ominus$ get protonated and they are converted into unreactive forms like HCN or NH_3 which are no longer good nucleophiles.



In the case of reactions (b) and (d), nucleophiles like $\text{I}^\ominus$ and $^\ominus\text{SH}$ are not easily protonated and their nucleophilic character is maintained. Addition of acid does not affect the rate.

Concept Strands 10



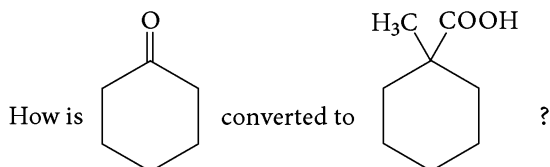
Is the reaction given above possible? Explain.

Solution

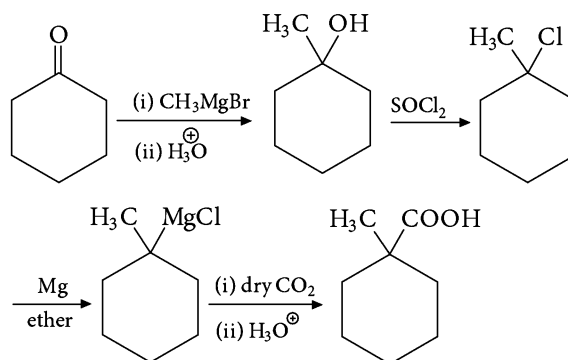
The reaction given is not possible. This is in violation of Bredt's rule, which states that a double bond cannot

be formed at a bridge head, unless the ring size is large enough.

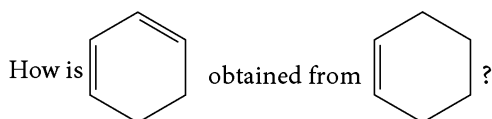
Concept Strands 11



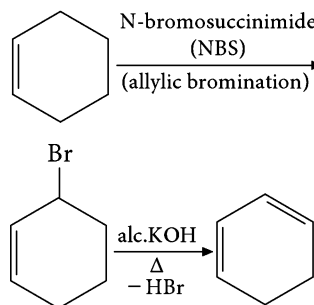
Solution



Concept Strands 12



Solution



SUMMARY

Classification of alcohols	Monohydric, dihydric, trihydric and polyhydric alcohols with examples. 1°, 2° and 3° alcohols.
Preparation of alcohols	Hydrolysis of alkyl halides, acid catalyzed hydration of alkenes and its mechanism, indirect hydration, oxymercuration-demercuration, hydroboration-oxidation, oxo process, reduction of carbonyl compounds, addition of Grignard reagents to carbonyl compounds. Manufacture of ethanol by fermentation.
Reactions of alcohols involving C–OH bond cleavage	Reaction with Lucas reagent, phosphorus tri and pentahalides, thionyl chloride. Reactivity order of alcohols in such reactions is $3^\circ > 2^\circ > 1^\circ$.
Reactions of alcohols involving O–H bond cleavage	Reaction with active metals, Esterification and its mechanism, trans-esterification, Reaction with Grignard reagent. In all these reactions reactivity order is $1^\circ > 2^\circ > 3^\circ$.
Reactions of alcohols involving both alkyl and hydroxyl groups	Dehydration of alcohols and its mechanism. Ease of dehydration of alcohols is $3^\circ > 2^\circ > 1^\circ$. Dehydrogenation of alcohols, Oxidation of alcohols-difference in the behaviour of 1°, 2° and 3° alcohols. Oppenauer oxidation and M.P.V reduction, oxidation with MnO_2 , pinacol-pinacolone rearrangement.
Methods to distinguish 1°, 2° and 3° alcohols	Lucas test, Victor Meyer's test. Theory of the two tests.
Classification of alkyl halides	Primary, secondary and tertiary alkyl halides with examples.
Preparation of alkyl halides	Preparation from alcohols, Halogenation of hydrocarbons, allylic bromination using NBS, preparation from alkenes by using hydrogen halides. Hunsdiecker reaction, Finkelstein reaction and Swarts reaction.
Nucleophilic substitution reactions	Formation of alcohols by reaction of alkyl halides with aqueous alkali, formation of ethers by Williamson's synthesis, synthesis of alkyl cyanides by reaction with NaCN or KCN. Synthesis of isocyanide by reaction with AgCN. Corey-House synthesis, Formation of esters by reaction with silver salt of carboxylic acids. Formation of thioethers, preparation of 1°, 2° and 3° amines from alkyl halides, Friedel-Crafts alkylation, Synthesis of nitroalkanes and alkyl nitrites.
Mechanism of nucleophilic substitution	$\text{S}_\text{N}2$ mechanism: It takes place in one step. Inversion of configuration takes place if substitution occurs at chiral carbon in $\text{S}_\text{N}2$ reaction. Reactivity of alkyl halides in $\text{S}_\text{N}2$ reaction is methyl halide $> 1^\circ$ halide $> 2^\circ$ halide $> 3^\circ$ halide. $\text{S}_\text{N}1$ mechanism: It takes place in two steps. The rate determining step is the heterolysis of the alkyl halide to form a carbocation. Racemization generally occurs in $\text{S}_\text{N}1$ reactions. Rearrangement generally takes place in $\text{S}_\text{N}1$ reactions. In cycloalkanes, rearrangement can lead to ring expansion and ring contraction in certain cases.
Preparation of aryl halides	Preparation by direct halogenation of aromatic hydrocarbons, preparation from diazonium salts–Sandmeyer, Gattermann and Balz-Schiemann reactions.

Aromatic nucleophilic substitution reactions

Aryl halides are less reactive than alkyl halides because of the partial double bond character of C – Cl bond due to resonance. The less reactivity is also due to the sp^2 hybridization of the carbon containing the halogen. Presence of electron withdrawing groups at ortho and para positions with respect to the halogen increases the reactivity of aryl halides towards nucleophilic substitution reactions. Mechanism of nucleophilic aromatic substitution reaction (addition–elimination mechanism). Benzyne mechanism-formation of benzyne intermediate.

Electrophilic substitution reaction of aryl halides

Halogen is electron withdrawing by inductive effect and electron releasing by mesomeric effect. Thus halogen is deactivating and at the same time ortho, para directing. Examples of nitration, sulphonation and halogenation reactions.

Other reactions of aryl halides

Fittig reaction, Wurtz-Fittig reaction and Ullmann reaction. Reaction of chlorobenzene with chloral to form DDT.

Grignard reagents

Alkyl magnesium halides are known as Grignard reagents. Preparation of Grignard reagents.

Reactions of Grignard reagents

Reaction with HCHO followed by hydrolysis give 1° alcohols, other aldehydes give 2° alcohols, while ketones give 3° alcohols. Reaction with ethylene oxide gives 1° alcohol containing two more carbon atoms. Reaction with esters give carbonyl compounds and finally alcohols if Grignard reagent is present in excess. Reaction with compounds containing active hydrogen give hydrocarbons. Reaction with CO_2 gives carboxylic acids. Reaction with nitriles is used to prepare ketones. Examples showing the synthetic utility of Grignard reagents.

TOPIC GRIP



Subjective Questions

- How will you convert?
 - propan-1-ol to propan-2-ol
 - 3-methylbutan-2-ol to 2-methylbutan-2-ol
- Suggest a method to prepare 2-methyl-2-propanol using Grignard reagent.
 - What happens when this alcohol is passed over copper heated to 573K?
- Arrange the following compounds in the increasing order of the property indicated against each. Give reasons for your answer
 - $\text{CH}_3\text{CH}_2\text{OH}$, $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$, $\text{C}_6\text{H}_5\text{OH}$: solubility in water
 - Propan-1-ol, propan-2-ol, 2-methyl-2-propanol : Reaction with Lucas reagent
 - $\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{OH}$, $(\text{CH}_3)_3\text{CCH}_2\text{OH}$, $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{OH}$: Boiling point
- When 3-methylbutan-2-ol is heated with HBr, the major product formed is 2-bromo-2-methylbutane. Explain the formation of the product from the mechanism of the reaction
- Predict the products (A)–(C) in the following reactions.
 - $$\text{C}_3\text{H}_7-\text{CH}_2-\underset{\text{Br}}{\underset{|}{\text{CH}}}-\text{CH}_2\text{Br} \xrightarrow[\text{dry ether}]{\text{Mg}} \xrightarrow{\text{C}_6\text{H}_5\text{NH}_2} \text{(A)}$$
 - $$\text{(b)} \quad \begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{CO}-\text{C}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} \end{array} \xrightarrow[\text{dry ether}]{\text{Mg}} \text{(B)}$$
 - $$\text{(c)} \quad \text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} \xrightarrow{\text{NaOH}/\text{H}_2\text{O}} \text{(C)}$$
- Which of the following pairs of compounds would proceed faster in an $\text{S}_{\text{N}}2$ reaction? Justify.
 - $$\text{(i)} \quad \text{CH}_3\text{CHBr}.\text{CH}_2\text{CH} \begin{array}{l} \nearrow \text{CH}_3 \\ \searrow \text{CH}_3 \end{array} + ^-\text{OH} \xrightarrow[\text{medium}]{\text{acetone}}$$

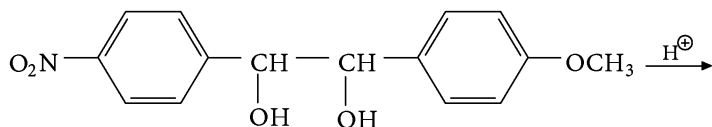
$$\text{(or)} \quad \text{CH}_3\text{CHBr}.\text{CH}_2\text{CH} \begin{array}{l} \nearrow \text{CH}_3 \\ \searrow \text{CH}_3 \end{array} + ^-\text{OH} \xrightarrow[20\% \text{ of water mixture}]{80\% \text{ alcohol}}$$
 - $$\text{(ii)} \quad \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{Cl} + ^-\text{CN} \longrightarrow$$

$$\text{(or)} \quad \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{I} + ^-\text{CN} \longrightarrow$$
 - $$\text{(iii)} \quad \text{Cyclopentyl-Cl} + ^-\text{CN} \longrightarrow$$

$$\text{(or)} \quad \text{Cyclopent-1-en-1-yl-Cl} + ^-\text{CN} \longrightarrow$$

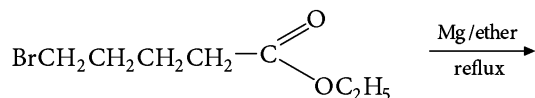
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7. Complete the reaction and propose a mechanism.



8. Starting with ethylene glycol, how is 1,4-dioxane prepared?

9. Give the structure of the product in the following reaction.



10. Two sets of nucleophiles (i) and (ii) are given below. Arrange the nucleophiles in each set in the increasing order of reactivity towards an alkyl halide.

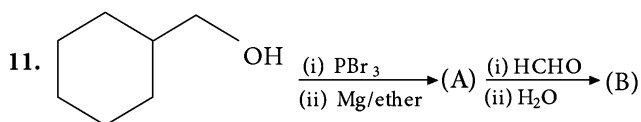
(i) H_2O , H_2S and NaSH

(ii) $\text{CH}_3\text{CH}_2\text{NH}_2$, $\text{CH}_3\text{CH}_2\text{OH}$ and $\text{CH}_3\text{CH}_2\text{SNa}$

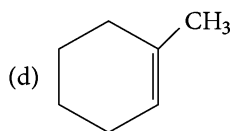
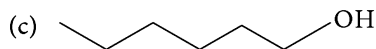
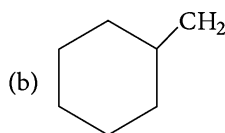
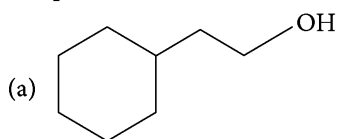


Straight Objective Type Questions

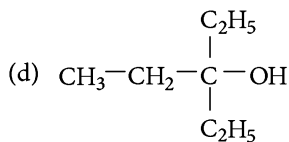
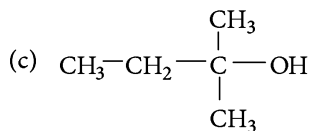
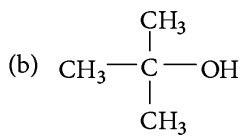
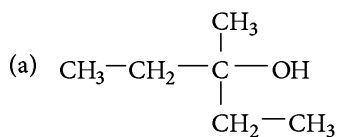
Directions: This section contains multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.



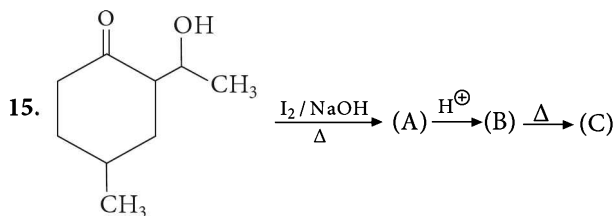
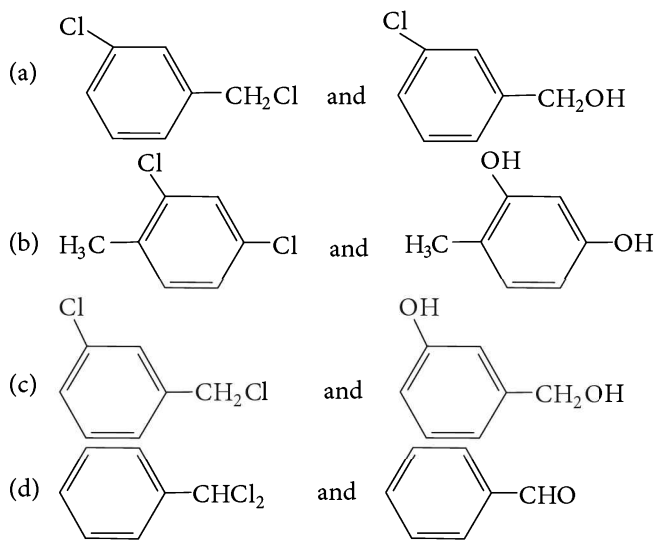
The product (B) is



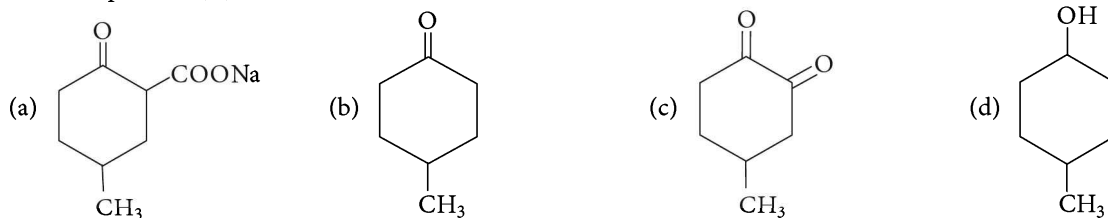
12. The product formed when ethyl acetate is treated with excess CH_3MgBr followed by hydrolysis is



13. The increasing order of reactivity to undergo substitution by S_N2 mechanism of the following halides is
- (a) $(CH_3)_2CHCl < CH_3CH_2Cl < CH_3Br < CH_3Cl$ (b) $CH_3CH_2Cl < (CH_3)_2CHCl < CH_3Cl < CH_3Br$
 (c) $CH_3Cl < CH_3Br < CH_3CH_2Cl < (CH_3)_2CHCl$ (d) $(CH_3)_2CHCl < CH_3CH_2Cl < CH_3Cl < CH_3Br$
14. When chlorine is passed into boiling toluene in the presence of light until the increase in weight corresponds to roughly two chlorine atoms, a product (A) is obtained. When (A) is hydrolyzed with $Ca(OH)_2$ solution, it is converted to (B). The product (A) and (B) are respectively



The final product (C) is



Assertion-Reason Type Questions

Directions: Each question contains Statement-1 and Statement-2 and has the following 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

4.46 Alcohols, Alkyl Halides and Haloarenes

16. Statement 1

Ethanol is a stronger nucleophile than phenol.

and

Statement 2

Ethoxide ion is a stronger base than phenoxide ion.

17. Statement 1

Acid catalysed hydration and oxymercuration reduction of 3-methyl but-1-ene gives the same major product.

and

Statement 2

In oxymercuration-reduction of alkene, the net effect is the addition of water in accordance with Markovnikov's rule.

18. Statement 1

P-bromo nitrobenzene reacts with sodium hydroxide solution more readily than bromobenzene.

and

Statement 2

Nitro group present at the para position stabilizes the intermediate carbanion by resonance.

19. Statement 1

Benzyl bromide gives benzyl alcohol when treated with water in formic acid solution.

and

Statement 2

Benzyl bromide undergoes hydrolysis mainly by S_N2 mechanism.

20. Statement 1

Benzene reacts with chlorine in the presence of bright light to form an insecticide BHC or gammexane.

and

Statement 2

In the formation of gammexane, benzene undergoes an aromatic electrophilic substitution.



Linked Comprehension Type Questions

Directions: This section contains 2 paragraphs. Based upon the paragraph, 3 multiple choice questions have to be answered. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

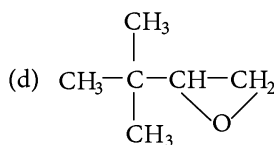
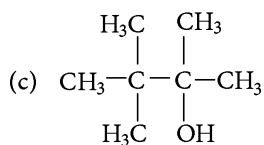
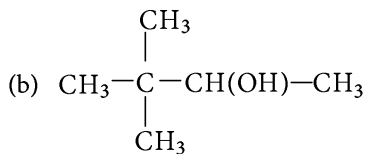
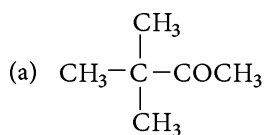
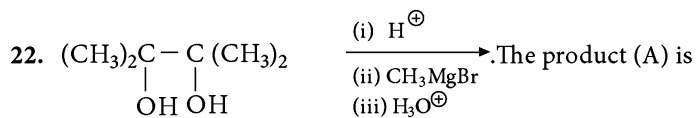
Passage I

Reaction of alcohols

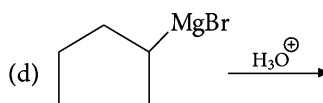
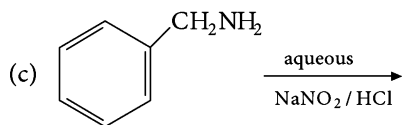
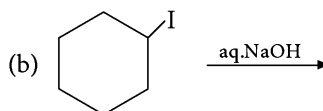
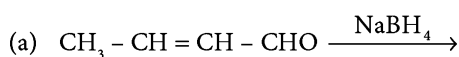
Alcohols can be obtained from aldehydes, ketones, carboxylic acids, halo alkanes, etc. by suitable means. Also alcohols can be converted to other organic compounds by treating with suitable reagents. They also undergo acid catalyzed dehydration with or without rearrangement.

21. The structural isomer of $C_4H_{10}O$, which cannot be dehydrogenated by Cu at $300^\circ C$ is

- (a) $CH_3CH_2CH_2CH_2OH$ (b) $CH_3-\underset{\substack{| \\ OH}}{CH}-CH_2CH_3$ (c) $CH_3-\underset{\substack{| \\ CH_3}}{CH}-CH_2OH$ (d) $(CH_3)_3C-OH$



23. Which of the following reactions does not give alcohol as a product?

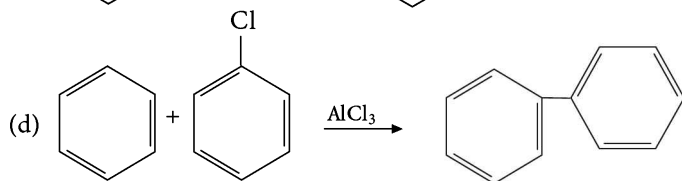
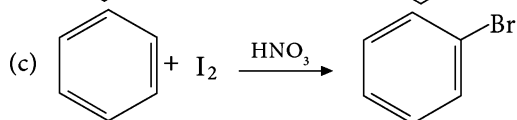
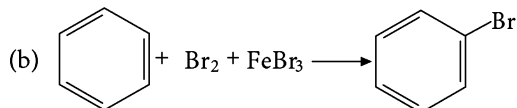
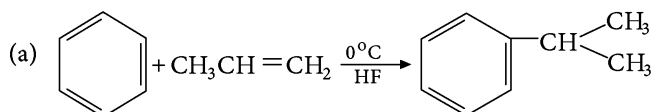


Passage II

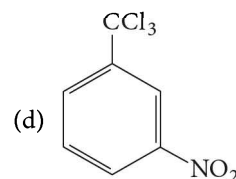
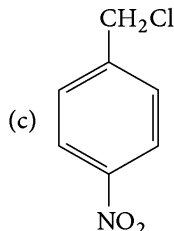
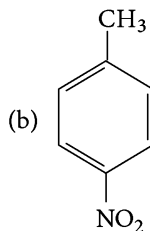
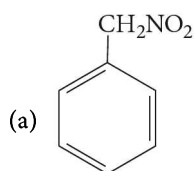
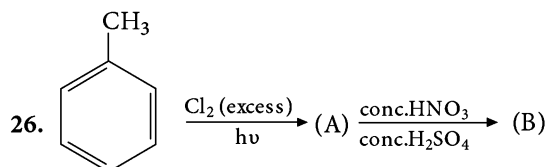
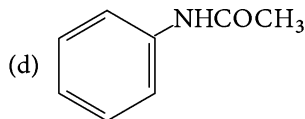
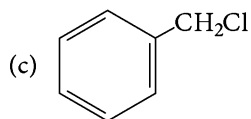
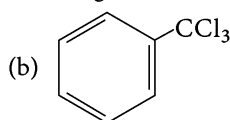
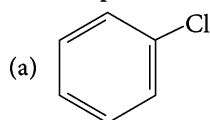
Preparation of halobenzenes

When the halogen is attached directly to the benzene ring, the compound is different from the normal alkyl halides. The ring halides can be prepared by aromatic electrophilic substitution. For aromatic rings, which are not so reactive, a Lewis acid such as ferric salt is used to catalyze the reaction. The position of entry of the halogen in the aromatic ring depends on the groups, which are already present in the ring. Some cases lead to a mixture of ortho and para directed products.

24. A reaction which is not feasible, under the conditions indicated, is



25. The compound containing meta directing group among the following is



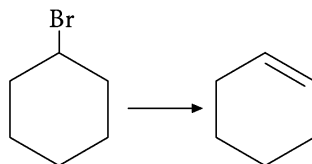
Multiple Correct Objective Type Questions

Directions: Each question in this section has four suggested answers of which ONE OR MORE answers will be correct.

27. The feasible reaction (s) among the following is/are

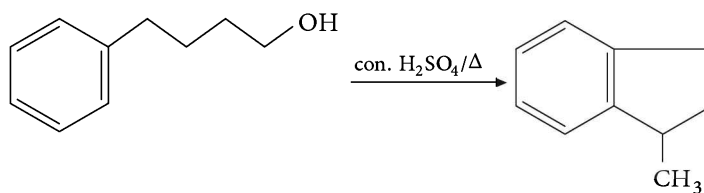
- (a) $\text{C}_6\text{H}_5\text{Br} + \text{CH}_3\text{ONa} \rightarrow \text{C}_6\text{H}_5\text{OCH}_3 + \text{NaBr}$
 (b) $\text{C}_6\text{H}_5\text{OK} + \text{CH}_3\text{I} \rightarrow \text{C}_6\text{H}_5\text{OCH}_3 + \text{KI}$
 (c) $(\text{CH}_3)_3\text{CONa} + \text{CH}_3\text{CH}_2\text{Br} \rightarrow (\text{CH}_3)_3\text{COCH}_2\text{CH}_3 + \text{NaBr}$
 (d) $(\text{CH}_3\text{CH}_2)_3\text{CBr} + \text{OH}^- \xrightarrow{\text{CH}_3\text{OH}} (\text{CH}_3\text{CH}_2)_3\text{COH} + \text{Br}^-$
 (major product)

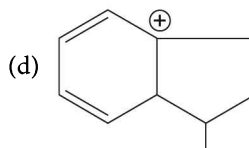
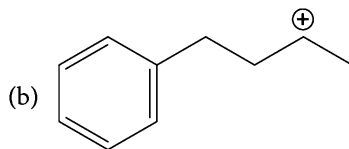
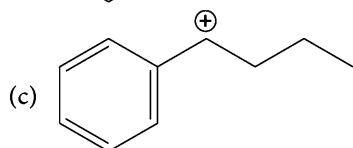
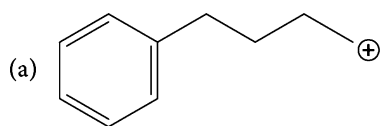
28. The reagent (s) used in the following conversion is/are



- (a) Con. H_2SO_4 (b) NH_4OH (c) NaNH_2 (d) alc. KOH

29. The carbocations involved in the following reaction are





Matrix-Match Type Questions

Directions: Match the elements of Column I to elements of Column II. There can be single or multiple matches.

30.

Column I

- (a) $\text{C}_6\text{H}_5\text{MgBr} + \text{CH}_3\text{CHO} \longrightarrow$
 (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{SOCl}_2 \longrightarrow$
 (c) $(\text{CH}_3)_2\text{CHCl} \xrightarrow[\Delta]{\text{Ag}_2\text{O}/\text{H}_2\text{O}}$
 (d) $(\text{CH}_3)_2\text{C}(\text{OH})-\text{C}(\text{CH}_3)_2(\text{OH}) \xrightarrow{\text{H}_2\text{SO}_4}$

Column II

- (p) Nucleophilic substitution
 (q) Nucleophilic addition
 (r) Molecular rearrangement
 (s) Dehydration
 (t) 2° alcohol

IIT ASSIGNMENT EXERCISE



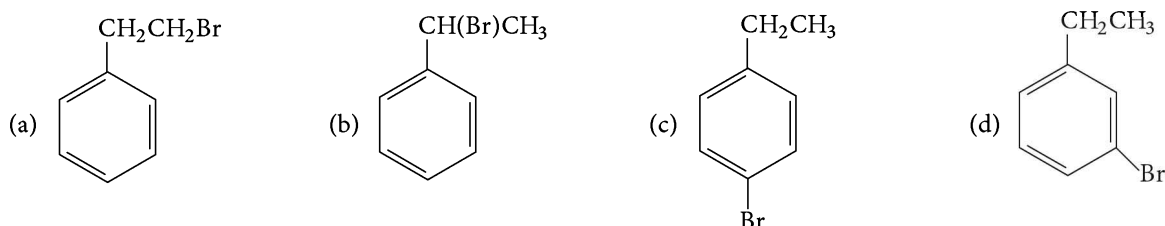
Straight Objective Type Questions

Directions: This section contains multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

31. t-butyl bromide $\xrightarrow{\text{aq. KOH}}$ (X). The main product (X) is

- (a) tertiary butyl alcohol (b) 1-butoxy butane (c) iso-butylene (d) propene

32. When ethyl benzene is treated with one equivalent N-bromosuccinimide in CCl_4 , the major product obtained is



33. $\text{C}_6\text{H}_6 + \text{HCl} + \text{O}_2 (\text{air}) \xrightarrow[500\text{K}]{\text{CuCl}_2} \text{C}_6\text{H}_5\text{Cl}$. The process is called

- (a) Oxo process (b) Dow's process (c) Raschig process (d) Baeyer's process

34. Hydrogen chloride gas is passed through an organic compound of molecular formula $\text{C}_4\text{H}_{10}\text{O}$ at room temperature to obtain the product $\text{C}_4\text{H}_9\text{Cl}$. The product is

- (a) 1-chlorobutane (b) 2-chlorobutane
(c) 1-chloro-2-methyl propane (d) 2-chloro-2-methyl propane

35. $\text{CH}_3\text{-CH=CH}_2 \xrightarrow{\text{H}^+/\text{H}_2\text{O}}$ product. The major product is

- (a) $\text{CH}_3\text{-CH(OH)-CH}_3$ (b) $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-OH}$
(c) (d) $\text{CH}_3\text{-CH(OH)-CH}_2\text{-OH}$

36. Lucas reagent is

- (a) anhy. AlCl_3 and conc.HCl (b) anhy. ZnCl_2 and conc.HCl
(c) Zinc amalgam and conc.HCl (d) $\text{H}_2\text{N-NH}_2$ and KOH

37. A test that can be used to distinguish 1° , 2° and 3° alcohols is

- (a) Victor Meyer's test (b) Liebermann's test (c) Hinsberg's test (d) Lassaigne's test

38. The decreasing reactivity order of halides towards dehydrohalogenation is

- (a) $\text{RI} > \text{RCl} > \text{RBr} > \text{RF}$ (b) $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$ (c) $\text{RF} > \text{RCl} > \text{RBr} > \text{RI}$ (d) $\text{RF} > \text{RI} > \text{RBr} > \text{RCl}$

39. $\text{C}_6\text{H}_5\text{-CH}_3 + \text{Cl}_2 \xrightarrow{800\text{K}} \text{C}_6\text{H}_5\text{CH}_2\text{Cl} + \text{HCl}$. This reaction takes place mainly by

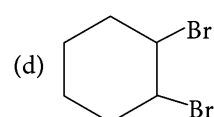
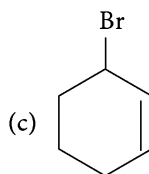
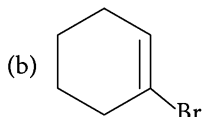
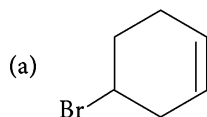
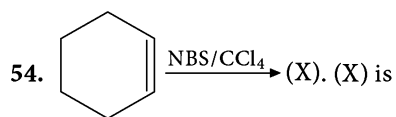
- (a) $\text{S}_{\text{N}}1$ mechanism (b) $\text{S}_{\text{N}}2$ mechanism (c) free radical mechanism (d) $\text{E}1$ mechanism

40. Iodobenzene when heated with Cu powder gives

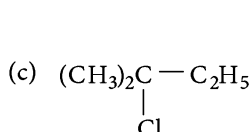
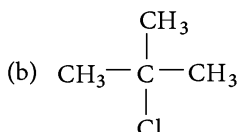
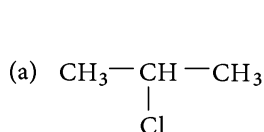
- (a) toluene (b) benzene (c) diphenyl (d) phenyl copper iodide

41. The compound with zero dipole moment is
 (a) 1,2-dichlorobenzene (b) 1,3-dichlorobenzene (c) 1,4-dichlorobenzene (d) 1,4-dihydroxybenzene
42. Benzyl chloride and o-chlorotoluene can be distinguished using
 (a) alcoholic AgNO_3 (b) NaNO_2 and HCl
 (c) hot alkaline KMnO_4 (d) both (a) and (c)
43. But-1-ene $\xrightarrow[\text{(ii) H}_2\text{O}_2/\text{OH}^-]{\text{(i) B}_2\text{H}_6/\text{THF}}$ product. The product is
 (a) n-butyl alcohol (b) iso-butyl alcohol
 (c) sec-butyl alcohol (d) but-1-en-3-ol
44. But-1-ene $\xrightarrow[\text{(ii) NaBH}_4/\text{OH}^-]{\text{(i) Hg}(\text{OAc})_2/\text{THF-H}_2\text{O}}$ (A). The product (A) is
 (a) n-butyl alcohol (b) iso-butyl alcohol
 (c) s-butyl alcohol (d) but-1-en-3-ol
45. Vapours of isomeric butyl alcohols are passed over copper at 573K. The products obtained from normal, sec, iso and tertiary butyl alcohols respectively are
 (a) aldehyde, ketone, aldehyde and ketone, (b) aldehyde, ketone, ketone and aldehyde
 (c) aldehyde, ketone, aldehyde and alkene (d) ketone, aldehyde, aldehyde and alkene
46. Which of the following respectively form primary, secondary and tertiary alcohols by reaction with Grignard reagent followed by hydrolysis?
 (a) Formaldehyde, acetone, acetaldehyde (b) Formaldehyde, acetaldehyde, acetone
 (c) Acetaldehyde, acetone, formaldehyde (d) Acetone, acetaldehyde, formaldehyde
47. The best reagent to replace alcoholic, phenolic or carboxylic $-\text{OH}$ groups with $-\text{Cl}$ is
 (a) PCl_5 (b) SOCl_2
 (c) PCl_3 (d) anhy. ZnCl_2 and conc. HCl
48. $\text{CH}_3\text{CH}_2\text{Cl} + \text{AgF} \rightarrow \text{CH}_3\text{CH}_2\text{F} + \text{AgCl}$. This reaction is called
 (a) Finkelstein reaction (b) Balz-Schiemann reaction
 (c) Swarts reaction (d) Gattermann reaction
49. IUPAC name of allyl chloride is
 (a) 2-chloropropene (b) 3-chloropropene
 (c) 1-chloropropene (d) 1-(chloromethyl)ethane
50. $\text{CH}_3\text{CH}=\text{CH}_2 + \text{HCl} \xrightarrow{\text{peroxide}}$ product. This addition is in accordance with
 (a) Markovnikov's rule. (b) Saytzeff rule
 (c) Kharasch effect (d) Hoffmann's rule
51. Iodoform test may be used to distinguish between
 (a) methanol and ethanol (b) 1-butanol and 2-butanol
 (c) 2-pentanol and 3-pentanol (d) all the above
52. $\text{CH}_3\text{CH}_2\text{Br} \xrightarrow[\text{(ii) H}_2/\text{Ni}]{\text{(i) AgCN}}$ product. The product is
 (a) $\text{CH}_3\text{CH}_2\text{NH}_2$ (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ (c) $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_3$ (d) $\text{CH}_3\text{CH}_2\text{NHCH}_3$
53. (A) $\xrightarrow[\text{(ii) AgNO}_3]{\text{(i) aq. NaOH}}$ white precipitate.
 (A) can be
 (a) vinyl chloride (b) benzyl chloride (c) chlorobenzene (d) o-chlorotoluene

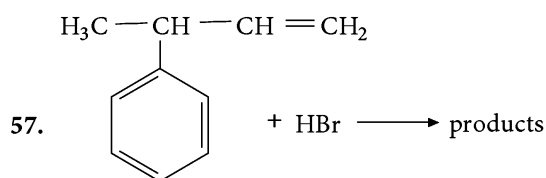
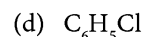
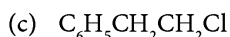
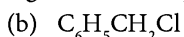
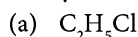
4.52 Alcohols, Alkyl Halides and Haloarenes



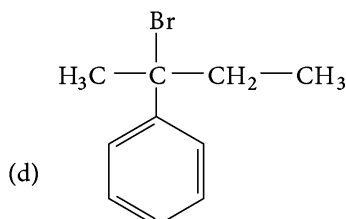
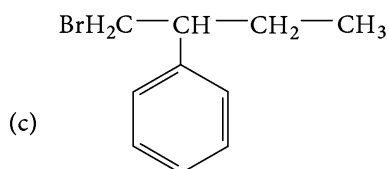
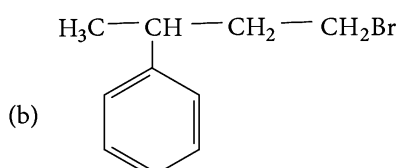
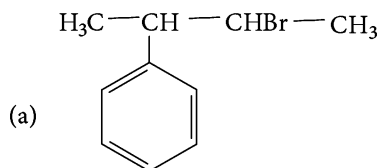
55. Which among the following most readily undergoes $\text{S}_{\text{N}}2$ reaction?



56. Benzyne mechanism is operating in the nucleophilic substitution of



The major product is

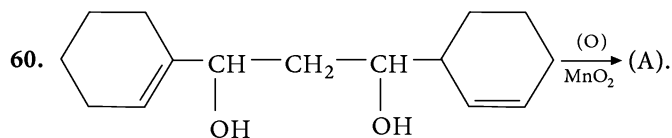


58. It is feasible to prepare tertiary butyl ethyl ether by treating ethyl bromide with sodium tertiary butoxide, rather than treating tertiary butyl bromide with sodium ethoxide because

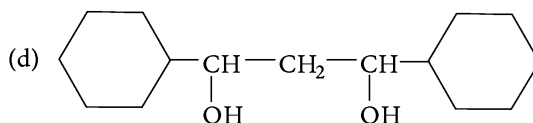
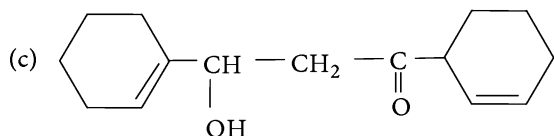
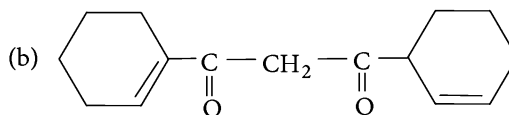
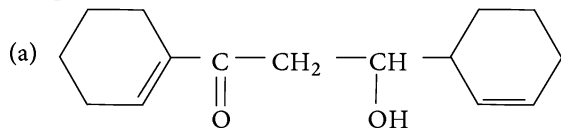
- (a) sodium ethoxide will not react with t-butyl bromide.
- (b) the first reaction is faster and gives more yield.
- (c) t-butyl bromide undergoes dehydrohalogenation to give alkene in presence of sodium ethoxide.
- (d) t-butyl bromide undergoes rearrangement.

59. The haloalkane, 2-iodo-2-methylpentane, can be prepared by treating an alkene (A) with hydroiodic acid. (A) can be

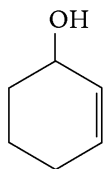
- (a) 2-methylpent-2-ene
- (b) 2-methylpent-1-ene
- (c) 2-methyl-but-2-ene
- (d) both (a) and (b)



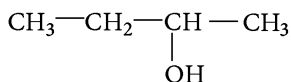
The product (A) is



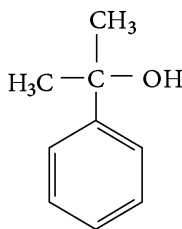
61. When 3,3-dimethyl-2-butanol is treated with dilute acid, the most stable carbocation formed is
 (a) 3,3-dimethyl-2-butyl cation (b) 3,3-dimethyl-1-butyl cation
 (c) 2,3-dimethyl-2-butyl cation (d) 2-methyl-2-pentyl cation
62. When isobutyl bromide loses the bromine to form a cation, it undergoes a 1,2 shift. Which of the following is true?
 (a) Hydride shift is preferred over methyl shift. (b) Methyl shift is preferred over hydride shift.
 (c) Methyl shift results in a tertiary carbocation (d) Hydride shift results in a secondary carbocation.
63. n-butyl bromide can be prepared by treating n-butyl alcohol with KBr and conc. H_2SO_4 . This process cannot be applied to prepare tertiary butyl bromide because
 (a) in tertiary alcohol, C – OH bond cleaves easily.
 (b) conc. H_2SO_4 dehydrates tertiary alcohol to form an alkene.
 (c) tertiary alcohol does not react with KBr.
 (d) in primary alcohol, C – OH bond cleaves easily.
64. The decreasing order of ease of dehydration of the following alcohols is



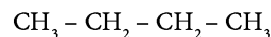
(A)



(B)



(C)

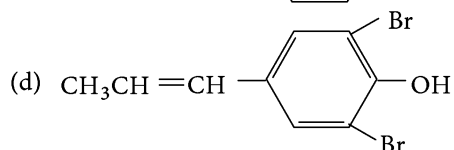
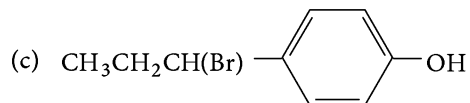
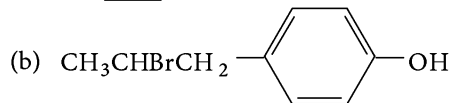
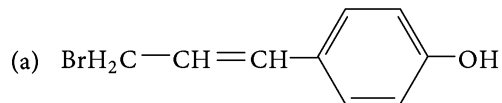


(D)

- (a) (A) > (C) > (B) > (D) (b) (D) > (B) > (A) > (C) (c) (C) > (A) > (B) > (D) (d) (C) > (D) > (B) > (A)
65. When an alkyl chloride (A) is treated with alcoholic potash, 2-methyl-2-butene is obtained as the main product. (A) is
 (a) 1-chloro-3-methylbutane (b) 2-chloro-2-methylbutane
 (c) 2,3-dichloro pentane (d) 1-chloro-2-methylbutane
66. On boiling 2,2-dichloropropane with aqueous alkali, the product obtained is
 (a) 2,2-propanediol (b) acetone (c) propanal (d) 2-chloro-2-propanol
67. The major product of dehydration of hex-4-en-2-ol would be
 (a) 1,4-hexadiene (b) 2,4-hexadiene (c) 1,5-hexadiene (d) 2,3-hexadiene

4.54 Alcohols, Alkyl Halides and Haloarenes

68. The major product formed in the reaction of $\text{H}_3\text{C}-\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{OH}$ with HBr is



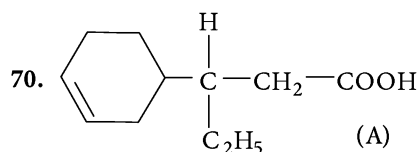
69. Equal quantities of $\text{CH}_3\text{OCH}_2\text{Cl}$ and CH_3Cl are treated with iodide ion in acetone. Which reacts faster?

(a) both react at almost equal rate

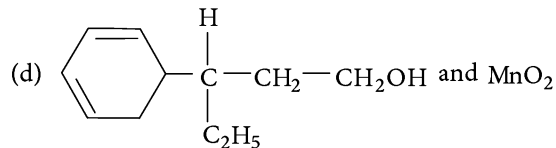
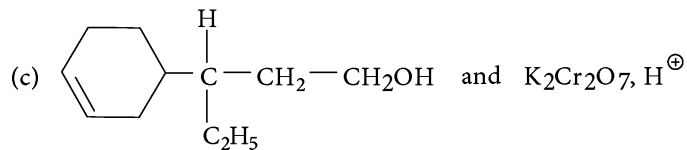
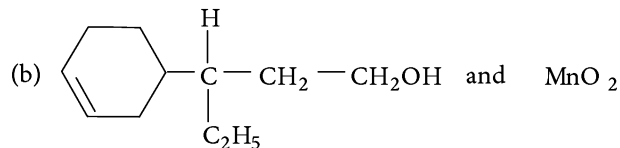
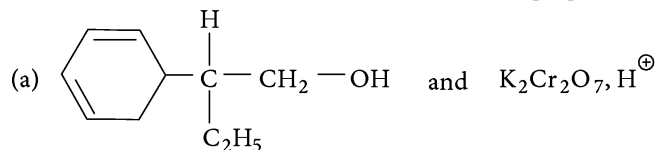
(b) $\text{CH}_3\text{OCH}_2\text{Cl}$ reacts faster

(c) CH_3Cl reacts faster

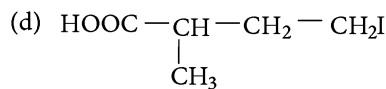
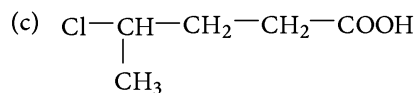
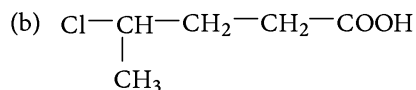
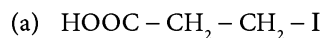
(d) $\text{CH}_3\text{OCH}_2\text{Cl}$ does not react at all



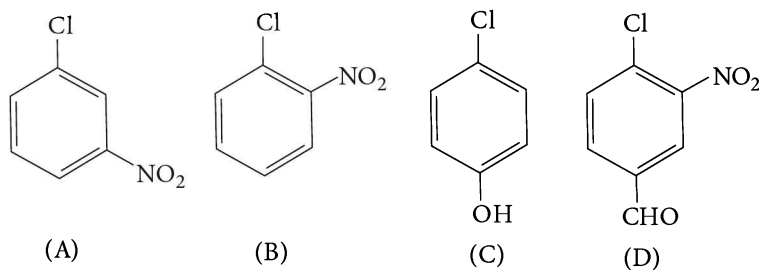
An alcohol and an oxidant, that could be used to prepare (A) is



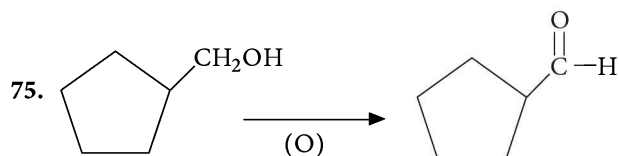
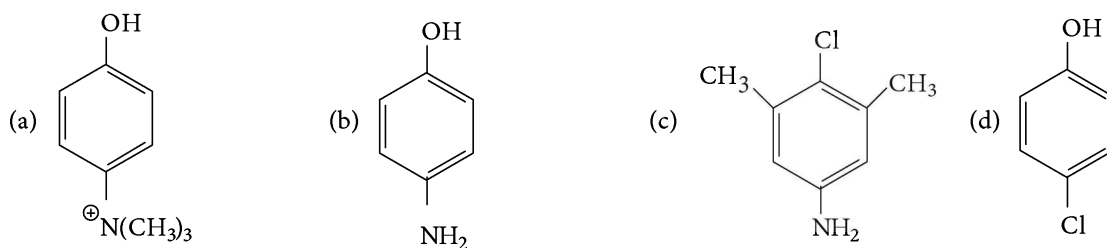
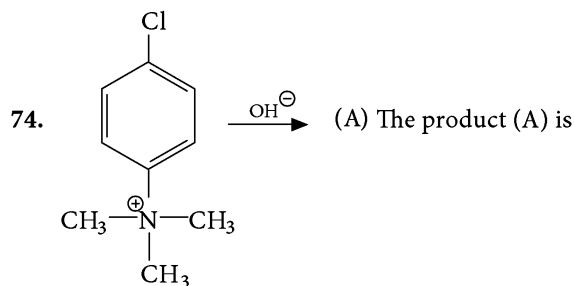
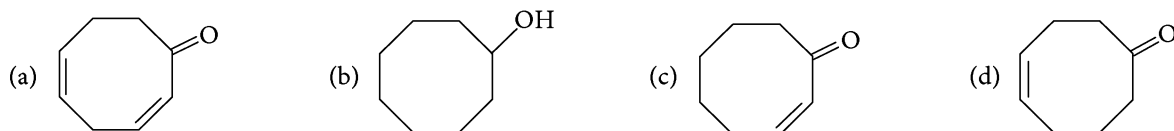
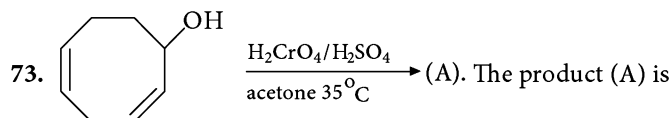
71. $\text{Cl}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{CH}_2-\text{I} \xrightarrow[1 \text{ mole}]{\text{CN}^-} (\text{A}) \xrightarrow{\text{H}_2\text{O}/\text{H}^+} (\text{B})$ The product (B) is



72. What will be the order of reactivity for the nucleophilic substitution of chlorine in the following compounds?

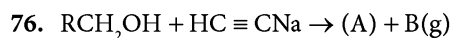


- (a) (A) > (C) > (B) > (D) (b) (D) > (B) > (A) > (C) (c) (C) > (A) > (B) > (D) (d) (D) > (B) > (C) > (A)



The best suitable reagent for this oxidation is

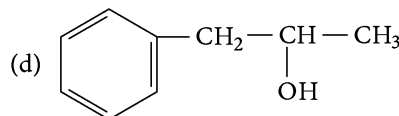
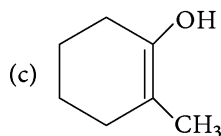
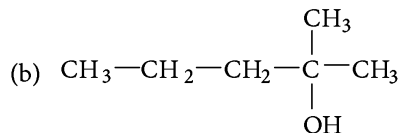
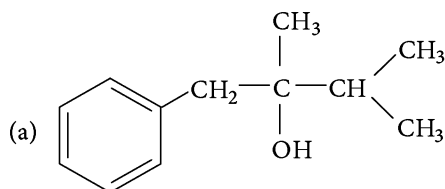
- (a) pyridinium chlorochromate in CH_2Cl_2 (b) KMnO_4
 (c) CrO_3 in aqueous acetone (d) Tollens reagent



(A) $\xrightarrow{\text{H}_2\text{O}}$ (C). (C) is

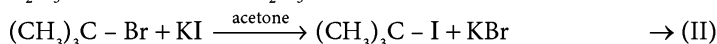
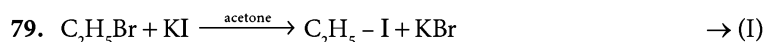
- (a) RCHO (b) RCH_2OH (c) RCOOH (d) $\text{R}-\text{C} \equiv \text{CH}$

77. Which of the following alcohols will give a yellow coloured precipitate with iodine and sodium hydroxide?



78. The most useful reagent to distinguish ethanol from propan-1-ol is

- (a) HCl and ZnCl_2 (b) I_2 and NaOH (c) Cu at 570K (d) KMnO_4



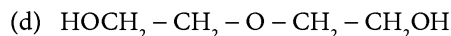
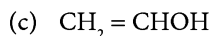
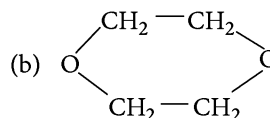
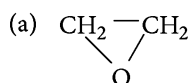
Reaction (II) is much slower than reaction (I) because

- (a) $(\text{CH}_3)_3\text{CBr}$ is sparingly soluble in acetone. (b) (I) follows $\text{S}_{\text{N}}1$ and (II) follows $\text{S}_{\text{N}}2$ mechanism.
(c) (I) follows $\text{S}_{\text{N}}2$ and (II) follows $\text{S}_{\text{N}}1$ mechanism. (d) steric hindrance in the case of reaction (II).

80. The correct decreasing order of acidic strength will be

- (a) $\text{CH}_3\text{CH}_2\text{OH} > \text{H}_2\text{O} > \text{HC} \equiv \text{CH} > \text{H}_2\text{C} = \text{CH}_2$ (b) $\text{H}_2\text{O} > \text{HC} \equiv \text{CH} > \text{CH}_2 = \text{CH}_2 > \text{CH}_3\text{CH}_2\text{OH}$
(c) $\text{H}_2\text{O} > \text{CH}_3\text{CH}_2\text{OH} > \text{HC} \equiv \text{CH} > \text{CH}_2 = \text{CH}_2$ (d) $\text{CH}_3\text{CH}_2\text{OH} > \text{HC} \equiv \text{CH} > \text{CH}_2 = \text{CH}_2 > \text{H}_2\text{O}$

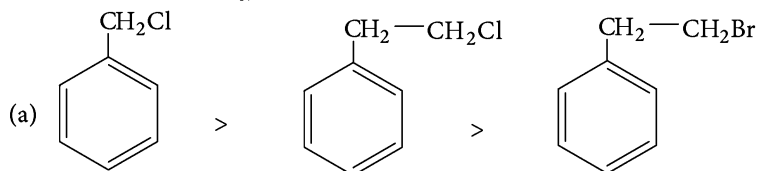
81. The product P in the following reaction is $\text{ClCH}_2-\text{CH}_2\text{OH} \xrightarrow{\text{OH}^-} \text{P}$



82. Reaction of an alkyl halide (A) with alcoholic KOH forms a product which on ozonolysis gives a mixture of propanone and methanal. The structure of the alkyl halide (A) is

- (a) 2-Bromobutane (b) 1, 4-Dibromobutane
(c) 2-Bromo-2-methyl propane (d) 2, 3-Dibromobutane

83. The correct order of $\text{S}_{\text{N}}2$ reactivity among the following is



- (b) $\text{CH}_3\text{Br} > \text{CH}_3\text{CH}_2\text{Br} > (\text{CH}_3)_2\text{CHBr}$
(c) $\text{CH}_3\text{CH}_2\text{Cl} > \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} > \text{CH}_3\text{Cl}$
(d) $(\text{CH}_3)_3\text{CBr} > (\text{CH}_3)_2\text{CHBr} > \text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$

84. Which of the following is the correct order of ease of displacement of groups in substitution reactions?

- (a) $\text{C}_6\text{H}_5\text{SO}_3^- > \text{CH}_3\text{COO}^- > \text{C}_6\text{H}_5\text{O}^-$ (b) $\text{CH}_3\text{COO}^- > \text{C}_6\text{H}_5\text{O}^- > \text{C}_6\text{H}_5\text{SO}_3^-$
(c) $\text{C}_6\text{H}_5\text{SO}_3^- > \text{C}_6\text{H}_5\text{O}^- > \text{CH}_3\text{COO}^-$ (d) $\text{C}_6\text{H}_5\text{O}^- > \text{C}_6\text{H}_5\text{SO}_3^- > \text{CH}_3\text{COO}^-$

85. Which of the following is the correct order of dipole moment of methyl halides?

- (a) $\text{CH}_3\text{F} > \text{CH}_3\text{Cl} > \text{CH}_3\text{Br} > \text{CH}_3\text{I}$ (b) $\text{CH}_3\text{Cl} > \text{CH}_3\text{F} > \text{CH}_3\text{Br} > \text{CH}_3\text{I}$
 (c) $\text{CH}_3\text{I} > \text{CH}_3\text{Br} > \text{CH}_3\text{F} > \text{CH}_3\text{Cl}$ (d) $\text{CH}_3\text{I} > \text{CH}_3\text{Br} > \text{CH}_3\text{Cl} > \text{CH}_3\text{F}$

86. The major product formed when 2-bromopentane is treated with potassium ethoxide in ethanol is

- (a) $\text{CH}_3-\underset{\text{OC}_2\text{H}_5}{\text{CH}}-\text{CH}_2-\text{CH}_2-\text{CH}_3$ (b) pent-1-ene
 (c) cis pent-2-ene (d) trans pent-2-ene

87. 2-Bromopentane $\xrightarrow{(\text{CH}_3)_3\text{COK}/(\text{CH}_3)_3\text{COH}}$ P

The major product (P) formed in the above reaction is

- (a) pent-1-ene (b) cis pent-2-ene
 (c) trans pent-2-ene (d) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{OC}(\text{CH}_3)_3$

88. The major product formed when 2-Fluoropentane is treated with $\text{C}_2\text{H}_5\text{O}^-/\text{C}_2\text{H}_5\text{OH}$ is

- (a) pent-1-ene (b) cis pent-2-ene
 (c) trans pent-2-ene (d) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{OC}_2\text{H}_5$

89. Chloroform on boiling with NaOH solution gives

- (a) sodium methoxide (b) Methanal (c) sodium methanoate (d) dichloromethanol

90. The compound which gives yellow precipitate when heated with iodine and alkali is

- (a) propan-1-ol (b) methanol (c) tert-butyl alcohol (d) butan-2-ol

91. $[\text{A}] \xrightarrow[\text{(ii) H}_2\text{O}_2/\text{OH}^-]{\text{(i) B}_2\text{H}_6/\text{ether}}$ Isobutyl alcohol.

The compound [A] in the above reaction is

- (a) But-1-ene (b) But-2-ene
 (c) 2-Methyl propene (d) 2,2-Dimethyl but-1-ene

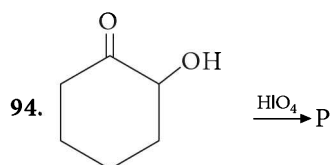
92. Methyl ethanoate $\xrightarrow[\text{(ii) Hydrolysis}]{\text{(i) CH}_3\text{MgCl (excess)}}$ x. The product x in the above reaction is

- (a) $\text{CH}_3-\text{CH}_2-\underset{\text{C}_2\text{H}_5}{\overset{\text{OH}}{\text{C}}}-\text{CH}_2-\text{CH}_3$ (b) $\text{CH}_3-\underset{\text{CH}_3}{\overset{\text{OH}}{\text{C}}}-\text{CH}_3$
 (c) $\text{CH}_3-\text{CH}_2-\underset{\text{CH}_3}{\overset{\text{OH}}{\text{C}}}-\text{CH}_2-\text{CH}_3$ (d) $\text{CH}_3-\text{CH}_2-\underset{\text{CH}_3}{\overset{\text{OH}}{\text{C}}}-\text{CH}_3$

93. Oxidation of one mole of glycerol with periodic acid gives

- (a) 1 mole each of methanol, methanal and methanoic acid.
 (b) 1 mole of methanal and 2 moles of methanoic acid.
 (c) 1 mole of methanoic acid and 2 moles of methanal.
 (d) three moles of methanal.

4.58 Alcohols, Alkyl Halides and Haloarenes



The product P in the above reaction is

- (a) $\text{OHC} - (\text{CH}_2)_4 - \text{CHO}$ (b) $\text{OHC} - (\text{CH}_2)_4 - \text{COOH}$
 (c) $\text{HOOC} - (\text{CH}_2)_4 - \text{COOH}$ (d) $\text{HOH}_2\text{C} - (\text{CH}_2)_4 - \text{COOH}$

95. Ethane-1, 2- diol when heated with PI_3 (or excess HI) gives

- (a) Iodoethane (b) 1, 2 - di iodoethane (c) 2 - Iodoethanol (d) ethene

96. Ethene $\xrightarrow[\text{Ag}/\Delta]{\text{O}_2}$ A $\xrightarrow[\Delta]{\text{dil HCl}}$ B. The product B in the above reaction is

- (a) Ethanol (b) Ethane- 1, 2- diol (c) Ethanal (d) epoxyethane

97. The rate of esterification with acetic acid is highest with

- (a) $(\text{CH}_3)_3\text{COH}$ (b) $(\text{CH}_3)_2\text{CHOH}$ (c) $\text{CH}_3\text{CH}_2\text{OH}$ (d) CH_3OH

98. In which of the following reaction, ethanol acts as a base?

- (a) Reaction with metallic sodium (b) Reaction with Grignard reagent
 (c) Acid catalysed dehydration (d) Reaction with hot copper catalyst

99. Primary, secondary and tertiary alcohols may be distinguished by converting them to the corresponding nitroalkanes and then treating with

- (a) NaNO_2 and dilute HCl (b) $\text{con.H}_2\text{SO}_4$
 (c) Sn and hydrochloric acid (d) Ammonium hydroxide

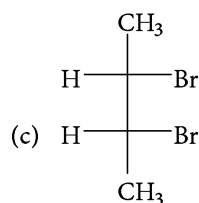
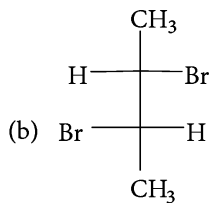
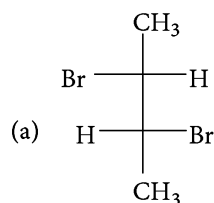
100. $(\text{CH}_3)_2\text{CHBr} \xrightarrow{\text{Mg/ether}} \text{A} \xrightarrow{\text{C}_6\text{H}_5-\text{CO}-\text{CH}_3} \text{B}$

The product B in the above reaction is

- (a) 2-phenyl-3-methyl butan-2-ol (b) 2-phenylpentan-2-ol
 (c) 3-phenyl butan-2-ol (d) propan-2-ol and ethyl benzene

101. $\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_3 \xrightarrow{\text{Na/liq NH}_3} \text{X} \xrightarrow{\text{Br}_2} \text{Y}$

The major product (s) y in the above reaction is/are

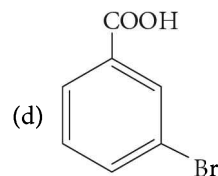
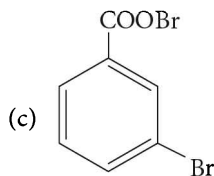
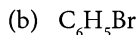
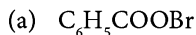
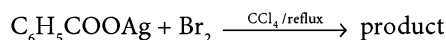


- (d) a mixture of (a) and (b)

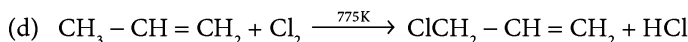
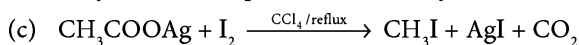
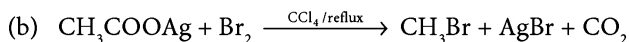
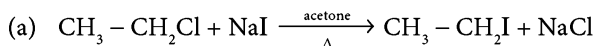
102. A dextrorotatory alkyl halide is hydrolysed under $\text{S}_{\text{N}}2$ conditions to form the corresponding alcohol. The resulting alcohol

- (a) will be levorotary (b) will be dextrorotatory
 (c) will be optically inactive due to racemization (d) may be dextro or laevorotatory

103. The organic compound formed in the following reaction is



104. The reaction which is wrongly represented among the following is



105. Bromobenzene is treated with magnesium in dry ether to form compound x which is then treated with ethanol to form compound y. The compound y is

(a) Benzene

(b) Phenol

(c) Ethylbenzene

(d) ethyl phenyl ether

106. An organic compound (x) was heated with NaOH solution and then acidified with dilute HNO_3 . Addition of silver nitrate solution gave a white precipitate completely soluble in ammonium hydroxide. The compound (x) is

(a) p-chlorotoluene

(b) vinyl chloride

(c) p-dichlorobenzene

(d) benzyl chloride

107. The product formed when isopropyl alcohol is heated with a suspension of bleaching powder in water is

(a) propyne

(b) 2-chloropropane

(c) chloroform

(d) carbon tetrachloride

108. The most nucleophilic but least basic species among the following is

(a) Cl^-

(b) Br^-

(c) I^-

(d) F^-

109. The correct nucleophilicity order among the following is

(a) $\text{NH}_2^- > \text{OH}^- > \text{F}^- > \text{CH}_3^-$

(b) $\text{CH}_3^- > \text{NH}_2^- > \text{OH}^- > \text{F}^-$

(c) $\text{OH}^- > \text{NH}_2^- > \text{CH}_3^- > \text{F}^-$

(d) $\text{CH}_3^- > \text{OH}^- > \text{F}^- > \text{NH}_2^-$

110. Which of the following statement is not correct regarding the solvolysis of 3-bromo-3-methylhexane?

(a) Polar solvents accelerate the reaction.

(b) The intermediate involves sp^2 carbon.

(c) The rate of the reaction at a particular temperature depends only on the concentration of 3-Bromo-3-methylhexane.

(d) The reaction involves inversion of configuration.



Assertion-Reason Type Questions

Directions: Each question contains Statement-1 and Statement-2 and has the following 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

4.60 Alcohols, Alkyl Halides and Haloarenes

111. Statement 1

Nucleophilicity does not always match with basicity.

and

Statement 2

While nucleophilicity is more related to size, polarizability and steric factors, the basicity is the ability to abstract a proton from a substrate.

112. Statement 1

Low reactivity of the haloarenes compared to alkylhalides has been attributed to delocalization of electrons by resonance and the halogens are linked to sp^2 hybridized carbons in haloarenes.

and

Statement 2

The presence of electron withdrawing group like $-CF_3$ at ortho position to the halogen atom makes the aryl halides more susceptible to nucleophilic attack.

113. Statement 1

Dehydration of alcohols is carried out with con. H_2SO_4 and not with con. HCl.

and

Statement 2

Cl^- is a better nucleophile than SO_4^{2-} .



Linked Comprehension Type Questions

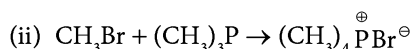
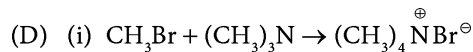
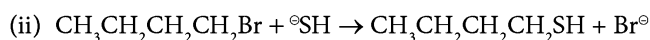
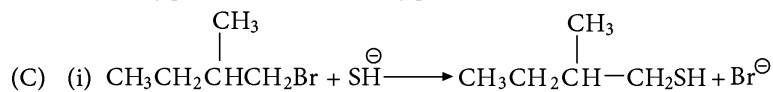
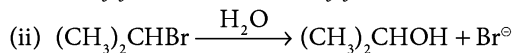
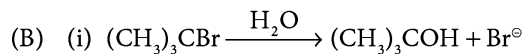
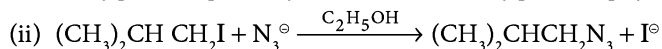
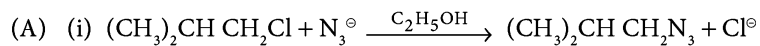
Directions: This section contains 1 paragraph. Based upon the paragraph, 3 multiple choice questions have to be answered. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

Passage I

Mechanism of nucleophilic substitutions

Aliphatic nucleophilic substitutions occur by two different mechanisms namely S_N1 and S_N2 . The various factors like degree of substitution, polarity of the medium, steric factors, nucleophilicity, concentration of the reacting substances etc, determine whether a reaction proceeds by S_N1 or S_N2 mechanism.

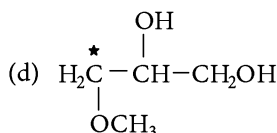
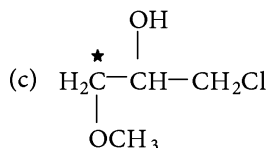
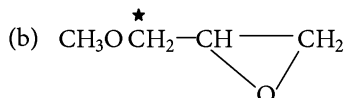
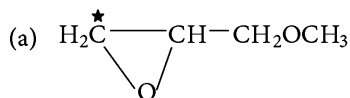
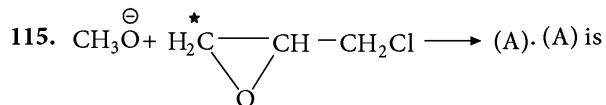
114. Four pairs of reactions (A) – (D) are given below.



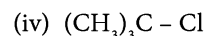
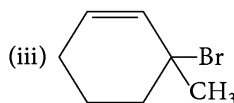
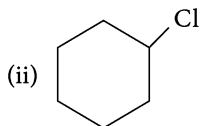
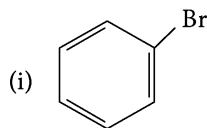
The reaction in each pair, (i) or (ii), which proceeds faster and favourably would be

- (a) (A)–(ii) (B)–(i) (C)–(ii) (D)–(i)
 (c) (A)–(i) (B)–(i) (C)–(ii) (D)–(i)

- (b) (A)–(i) (B)–(i) (C)–(ii) (D)–(i)
 (d) (A)–(ii) (B)–(i) (C)–(i) (D)–(i)



116. Consider that the following substrates undergoing $\text{S}_\text{N}1$ reaction



The increasing order of the rate of reaction will be

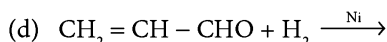
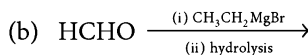
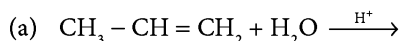
- (a) (iv) < (iii) < (i) < (ii) (b) (i) < (ii) < (iv) < (iii) (c) (iv) < (iii) < (ii) < (i) (d) (iv) < (ii) < (iii) < (i)



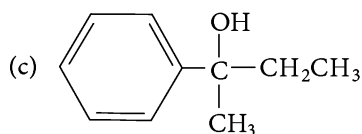
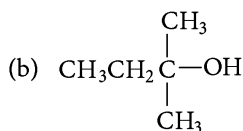
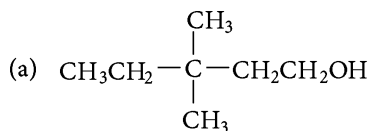
Multiple Correct Objective Type Questions

Directions: Each question in this section has four suggested answers of which ONE OR MORE answers will be correct.

117. Which of the following reactions give n-propyl alcohol as the major product?



118. A compound gives immediate turbidity on treatment with zinc chloride and con.HCl. The compound could be



119. Which of the following will give yellow precipitate when heated with powdered iodine and aqueous NaOH?

- (a) 2-Butanol
 (c) 2-Pentanone

- (b) 2-Methyl-2-propanol
 (d) 3-pentanol

**Matrix-Match Type Question**

Directions: Match the elements of Column I to elements of Column II. There can be single or multiple matches.

120.

Column I

- (a) $(\text{CH}_3)_3\text{CCl} \xrightarrow{\text{C}_2\text{H}_5\text{O}^- / \text{C}_2\text{H}_5\text{OH}} \rightarrow$
(b) $\text{RX} + \text{KNO}_2 \rightarrow \text{Major product}$
(c) $\text{RX} + \text{AgNO}_2 \rightarrow \text{Major product}$
(d) $\text{CH}_3 - \text{CHCl} - \text{CH}_2 - \text{CH}_3 \xrightarrow{\text{alc. KOH}} \rightarrow$

Column II

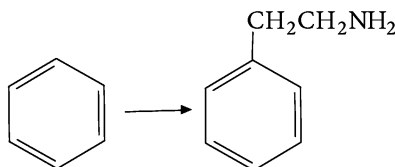
- (p) Nucleophilic substitution
(q) Nitro alkane
(r) Alkyl nitrite
(s) E1
(t) E2

ADDITIONAL PRACTICE EXERCISE



Subjective Questions

121. How is the following conversion effected?



122. In the preparation of $\text{CH}_3\text{--O--C}(\text{CH}_3)_3$, two methods, namely (i) and (ii) are suggested. Which method is preferable and why?

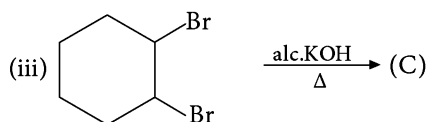
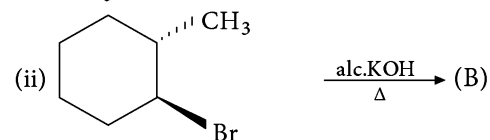
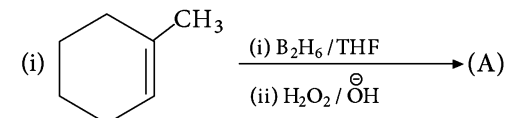


123. If 4-bromo-1-butanol is treated with sodium, a product of molecular formula $\text{C}_4\text{H}_8\text{O}$ is formed. Arrive at the structure and propose a mechanism.

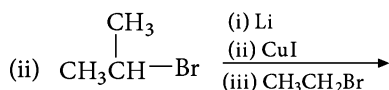
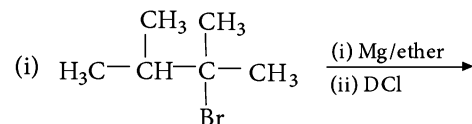
124. Treatment of $(\text{CH}_3)_3\text{CCH}_2\text{MgBr}$ with I_2 gives $(\text{CH}_3)_3\text{CCH}_2\text{I}$ in good yield whereas, $(\text{CH}_3)_3\text{CCH}_2\text{OH}$ on reaction with HBr gives mainly a rearranged product namely $(\text{CH}_3)_2\text{CBrCH}_2\text{CH}_3$ and not $(\text{CH}_3)_3\text{C--CH}_2\text{Br}$. Why?

125. What is the product of addition of HCl to $\text{CCl}_3\text{--CH=CH}_2$?

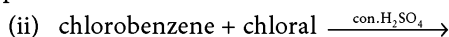
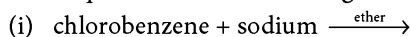
126. Give the structure of the products (A) – (C) in the reactions given below.



127. Give the structure of the main organic product formed in each reaction.



128. Write equations for the following reactions and identify the product formed in each case



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129. Write the steps involved in the conversion of the following

- Ethanol to but-1-yne
- Ethyl bromide to butan-2-one
- 2-chloropropane to propan-1-ol

130. How is $(\text{C}_6\text{H}_5)_2\text{C}=\text{CH}_2$ prepared by a Grignard reaction with $\text{C}_6\text{H}_5\text{Br}$ and $\text{CH}_3\text{COOC}_2\text{H}_5$ as the starting materials?



Straight Objective Type Questions

Directions: This section contains multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

131. The compound that gives a tertiary alcohol on reaction with CH_3MgI is

- (a) $\text{CH}_3-\text{CH}(\text{O})-\text{CH}-\text{CH}_3$ (b) $\text{C}_2\text{H}_5\text{COOH}$
 (c) $\text{C}_2\text{H}_5\text{COOCH}_3$ (d) $(\text{CH}_3)_2\text{CHCHO}$

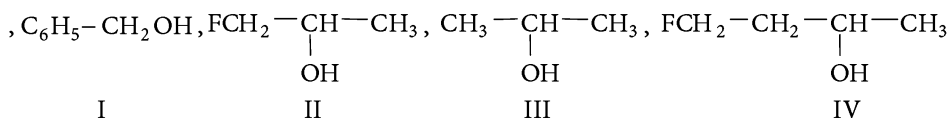
132. Which of the following is the best method to convert 3-methylbut-1-ene to 3-methyl butan-2-ol?

- (a) Acid catalyzed hydration. (b) Addition of con. H_2SO_4 followed by hydrolysis.
 (c) Hydroboration-oxidation. (d) Oxymercuration-demercuration.

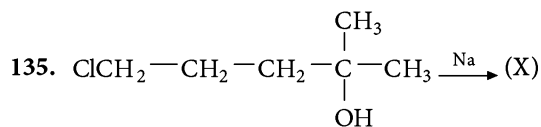
133. Which of the following isomeric alcohols has the highest solubility in water?

- (a) n-butyl alcohol (b) sec-butyl alcohol (c) isobutyl alcohol (d) tert-butyl alcohol

134. The correct decreasing order of reactivity of the following alcohols towards con. HCl is

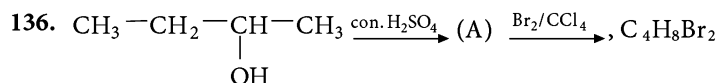


- (a) $\text{III} > \text{I} > \text{IV} > \text{II}$ (b) $\text{I} > \text{III} > \text{IV} > \text{II}$ (c) $\text{I} > \text{III} > \text{II} > \text{IV}$ (d) $\text{III} > \text{I} > \text{II} > \text{IV}$



The product X in the above reaction is

- (a) (b)
 (c) (d)



If five isomers of the final product $\text{C}_4\text{H}_8\text{Br}_2$ are obtained, the number of isomers of (A) formed in the reaction is

- (a) 5 (b) 4 (c) 3 (d) 2

137. The correct order of reactivity of the following alcohols with hydrobromic acid is

1-phenylpropan-1-ol
(I)

1-phenylpropan-2-ol
(II)

3-phenylpropan-1-ol
(III)

- (a) $I > II > III$ (b) $I > III > II$ (c) $III > I > II$ (d) $III > II > I$

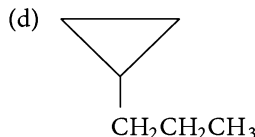
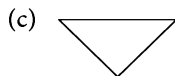
138. Reaction of a compound having the molecular formula $C_4H_{10}O_3$ with acetyl chloride gave a derivative with molar mass 190 g mol^{-1} . The number of hydroxyl groups in the compound is

- (a) 1 (b) 2 (c) 3 (d) 0

139. 1,3-diiodopropane on reaction with sodium in ether gives

(a) $IH_2C - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - I$

(b) $CH_3CH_2CH_2CH_2CH_2CH_3$

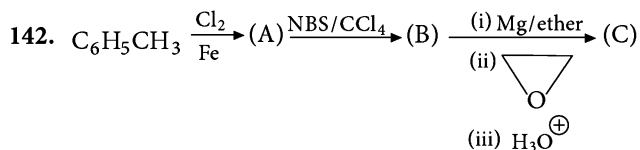


140. Which of the following statements is correct ?

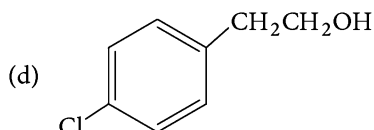
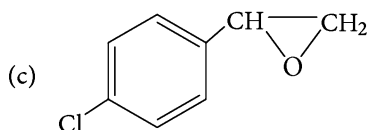
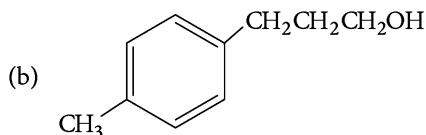
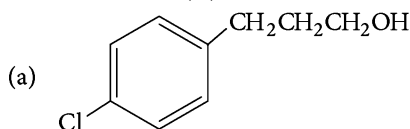
- (a) $CH_3CH_2S^-$ is a stronger base, but weaker nucleophile than $CH_3CH_2O^-$.
 (b) $CH_3CH_2S^-$ is a weaker base, but more nucleophilic than $CH_3CH_2O^-$.
 (c) $CH_3CH_2S^-$ is a stronger base and more nucleophilic than $CH_3CH_2O^-$.
 (d) $CH_3CH_2S^-$ is a weaker base and less nucleophilic than $CH_3CH_2O^-$.

141. Identify the false statement among the following

- (a) The rate of hydrolysis of tert-butyl chloride does not change by increasing the concentration of OH^- .
 (b) 1-phenylethanol reacts with thionyl chloride to give a chloro compound with almost complete retention of configuration.
 (c) Polar solvents generally increase the rate of S_N1 reactions.
 (d) S_N2 reaction of optically active substrate leads to racemization if the leaving group is attached to the chiral carbon.



The structure of (C) is



143. Five alcohols (A) – (E) are given below

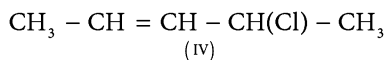
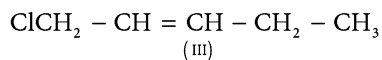
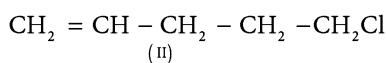
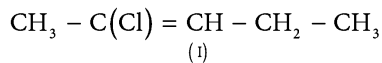
- (A) $CH_3(CH_2)_4CH_2OH$ (B) $C_2H_5CH(OH)C_3H_7$ (C) $(CH_3)_2C(OH)C_3H_7$
 (D) $(CH_3)_2C(OH)CH(CH_3)_2$ (E) $C_2H_5CH(OH)CH(CH_3)_2$

The ease of dehydration in the decreasing order will be

- (a) $D > C > E > B > A$ (b) $C > D > B > A > E$ (c) $D > C > A > B > E$ (d) $D > E > B > A > C$

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144. The correct increasing order of S_N1 reactivity of the following halogen compounds is



(a) $\text{I} < \text{IV} < \text{III} < \text{II}$

(b) $\text{I} < \text{II} < \text{III} < \text{IV}$

(c) $\text{I} < \text{II} < \text{IV} < \text{III}$

(d) $\text{II} < \text{I} < \text{III} < \text{IV}$

145. When the alkyl iodide $\text{CH}_3 - \text{CH}_2\text{I}$ is slowly decomposed by light, the organic product formed is

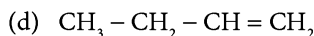
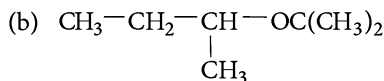
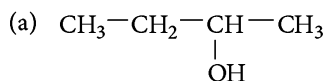
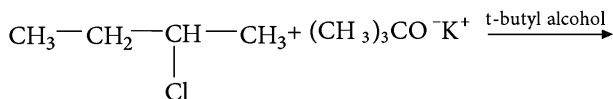
(a) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$

(b) $\text{CH}_3 - \text{CH}_3$

(c) $\text{CH}_3 - \text{CHO}$

(d) $\text{CH}_3 - \text{CH}_2\text{OH}$

146. The major product formed in the following reaction is



147. The correct decreasing order of reactivity of the halides for S_N1 reaction is

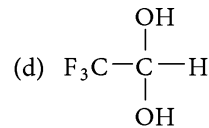
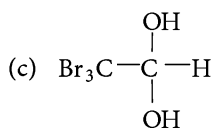
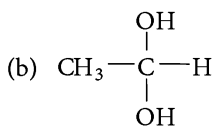
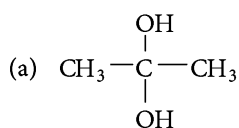
(A) $\text{PhCH}_2\text{Br} > \text{CH}_2 = \text{CHBr} > \text{CH}_3 - \text{CH}_2\text{Br} > \text{CH}_2 = \text{CH} - \text{CH}_2\text{Br}$

(B) $\text{CH}_2 = \text{CHBr} > \text{CH}_2 = \text{CH} - \text{CH}_2\text{Br} > \text{PhCH}_2\text{Br} > \text{CH}_3 - \text{CH}_2\text{Br}$

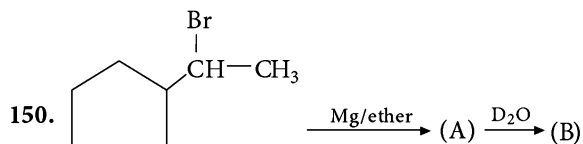
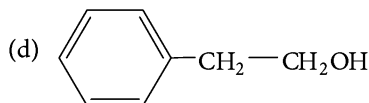
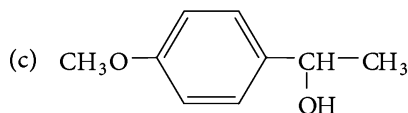
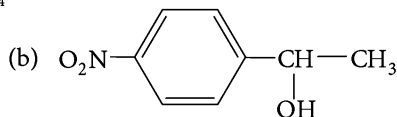
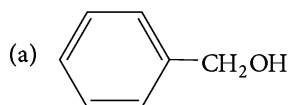
(c) $\text{PhCH}_2\text{Br} > \text{CH}_2 = \text{CH} - \text{CH}_2\text{Br} > \text{CH}_3 - \text{CH}_2\text{Br} > \text{CH}_2 = \text{CHBr}$

(d) $\text{PhCH}_2\text{Br} > \text{CH}_2 = \text{CH} - \text{CH}_2\text{Br} > \text{CH}_2 = \text{CHBr} > \text{CH}_3\text{CH}_2\text{Br}$

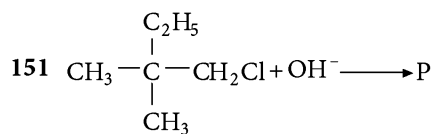
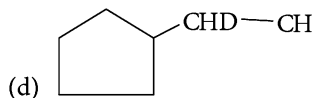
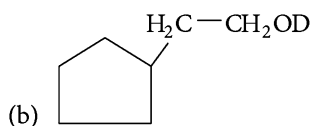
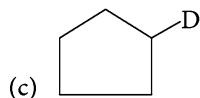
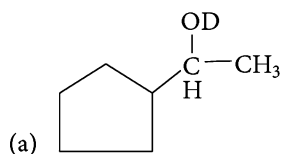
148. The most stable gem diol among the following is



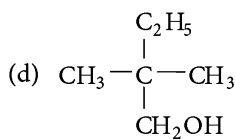
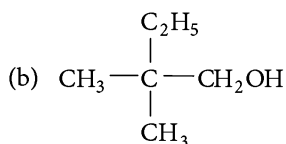
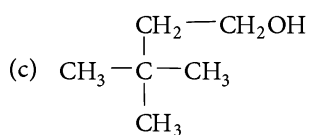
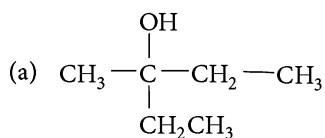
149. The alcohol that is dehydrated most readily with con. H_2SO_4 is



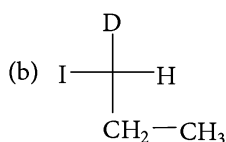
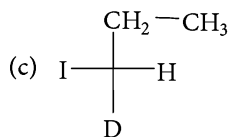
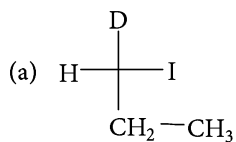
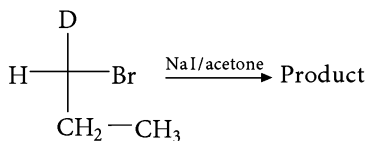
The structure of (B) is



The major product P of the above reaction is

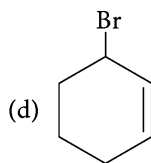
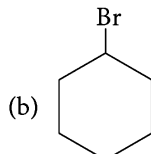
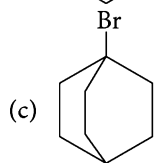
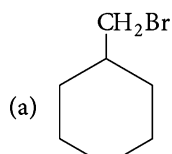


152. The configuration of the product in the following reaction



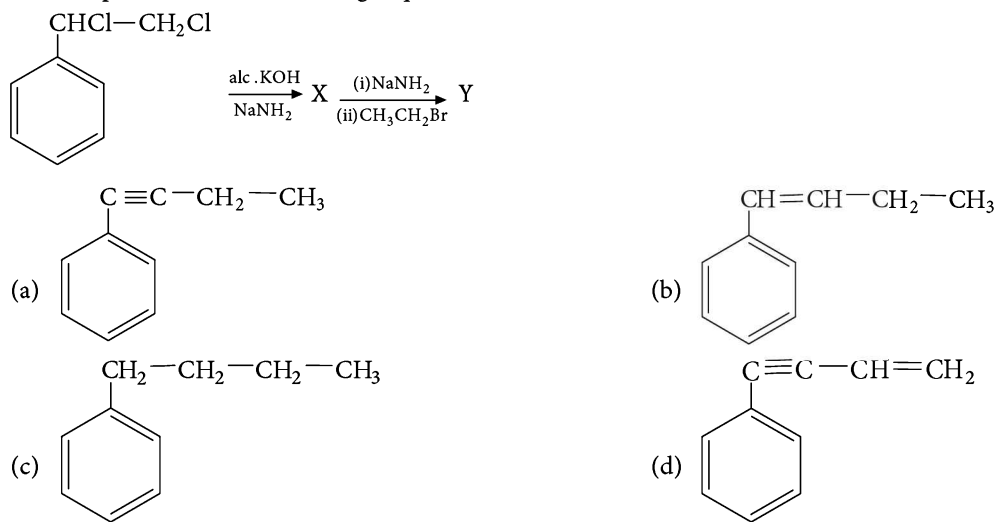
(d) Mixture of (a) and (b)

153. Which of the following will undergo hydrolysis by $\text{S}_{\text{N}}1$ mechanism most readily?

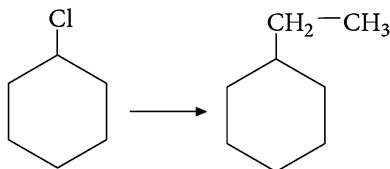


4.68 Alcohols, Alkyl Halides and Haloarenes

154. The compound Y in the following sequence of reaction is

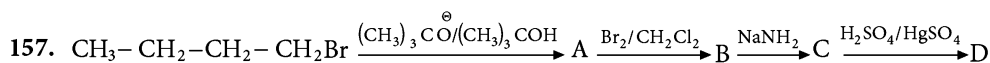
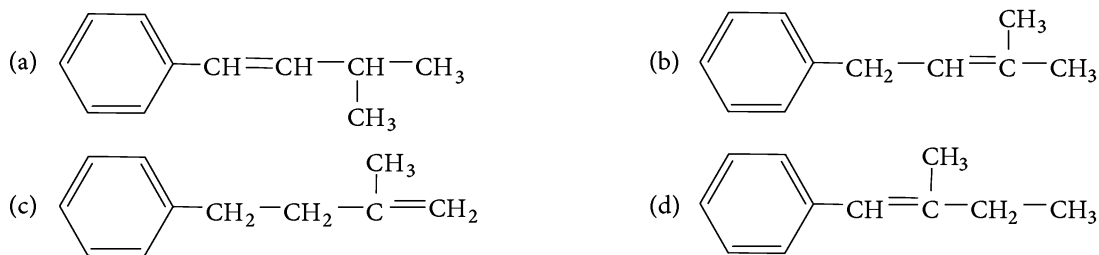


155. The best reagent to bring about the following conversion is



- (a) $\text{C}_2\text{H}_5\text{Br}/\text{Na}$ in ether (b) $(\text{C}_2\text{H}_5)_2\text{CuLi}$ in ether
 (c) Mg in ether/ $\text{CH}_3\text{CH}_2\text{OH}$ (d) $\text{NaOH(aq)}/\text{CH}_3\text{CHO}$

156. The major product formed when 2-bromo-3-methyl-1-phenyl butane is treated with alcoholic KOH is



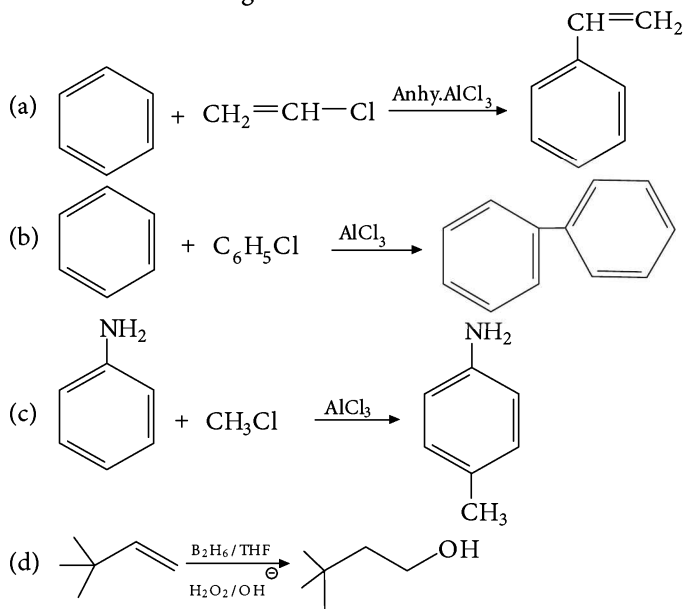
The compound D in the above reaction is

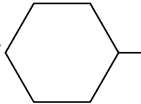
- (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$
 (c) $\text{CH}_3\text{COCH}_2\text{CH}_3$ (d) $\text{CH}_3\text{CH}_2\text{COCHO}$

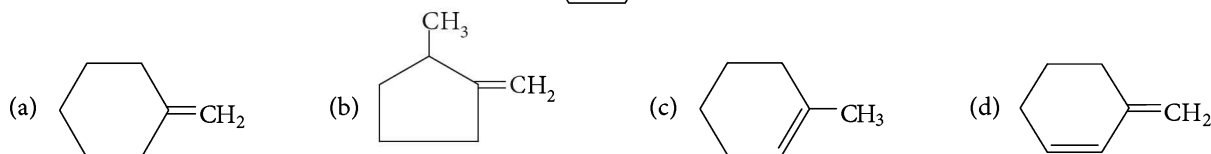
158. The product (Y) in the following reaction is $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{Br} \xrightarrow{\text{H}^+/\text{H}_2\text{O}} (\text{X}) \xrightarrow{\text{Na}} (\text{Y})$



159. Which of the following reactions is feasible?



160. The main product obtained by the dehydration of  under acidic conditions is



161. Meso - 2, 3-dibromobutane when heated with zinc dust in methanol gives mainly

- (a) cis but-2-ene (b) trans-but-2-ene (c) 1, 3-butadiene (d) 2-bromobut-2-ene

162. The correct nucleophilicity order for $\text{S}_{\text{N}}2$ reaction in protic solvents is

- (a) $\text{CH}_3\text{S}^- > \text{C}_6\text{H}_5\text{S}^- > \text{I}^- > \text{CN}^- > \text{CH}_3\text{O}^- > \text{OH}^-$ (b) $\text{CH}_3\text{S}^- > \text{C}_6\text{H}_5\text{S}^- > \text{CN}^- > \text{I}^- > \text{CH}_3\text{O}^- > \text{OH}^-$
 (c) $\text{CN}^- > \text{CH}_3\text{S}^- > \text{C}_6\text{H}_5\text{S}^- > \text{OH}^- > \text{CH}_3\text{O}^- > \text{I}^-$ (d) $\text{OH}^- > \text{CH}_3\text{O}^- > \text{CN}^- > \text{CH}_3\text{S}^- > \text{C}_6\text{H}_5\text{S}^- > \text{I}^-$

163. $\text{CH}_3-\text{CH}=\text{CH}_2 \xrightarrow{\text{Cl}_2, 770\text{K}} (\text{A}) \xrightarrow{\text{NaOH}} (\text{B}) \xrightarrow{\text{MnO}_2/\text{acetone}} (\text{C})$

The major product (C) in the above reaction is

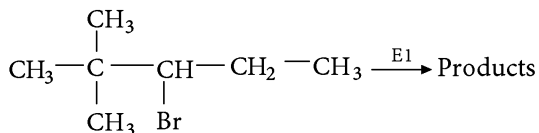
- (a) $\text{CH}_3-\text{CO}-\text{CHO}$ (b) CH_3COOH (c) $\text{CH}_2=\text{CH}-\text{COOH}$ (d) $\text{CH}_2=\text{CH}-\text{CHO}$

164. $\text{CH}_3-\text{CHOH}-\text{CHOH}-\text{CHO} \xrightarrow{\text{NaIO}_4(\text{aq})}$ products

The products formed in the above reaction are

- (a) CH_3-CHO , HCHO , HCOOH (b) CH_3-CHO , HCOOH
 (c) CH_3-CHO , $\text{OHC}-\text{CHO}$ (d) CH_3-COOH , HCOOH

165. The number of isomeric alkenes (structural as well as stereo) that can be formed by dehydrohalogenation of the following alkyl halide under E_1 conditions is



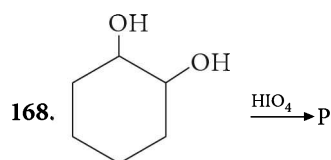
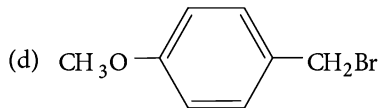
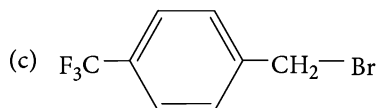
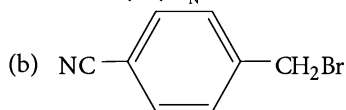
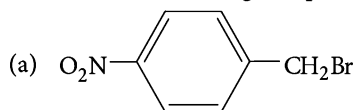
- (a) 1 (b) 2 (c) 3 (d) 4

4.70 Alcohols, Alkyl Halides and Haloarenes

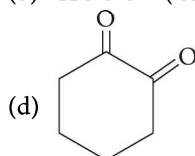
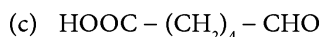
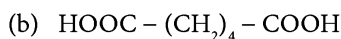
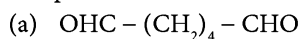
166. Reaction of meso-1, 2-dibromo -1,2-diphenylethane (stilbene dibromide) with alc. KOH (or C_2H_5OK/C_2H_5OH) gives

- (a) cis -1-bromo-1, 2-diphenyl ethene (b) trans-1-bromo-1, 2-diphenyl ethene
(c) 1 : 1 mixture of (a) and (b) (d) 1 : 2 mixture of (a) and (b)

167. Which of the following compounds will undergo hydrolysis most readily by S_N1 mechanism?

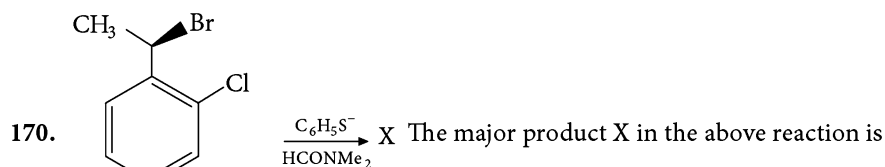


The product P in the above reaction is

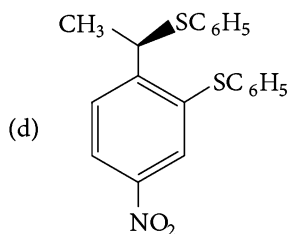
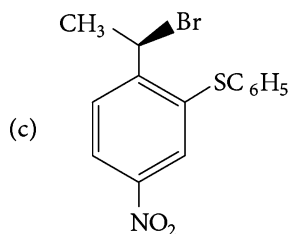
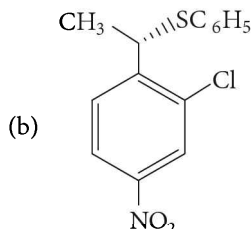
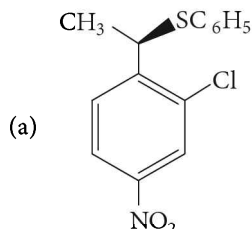


169. The number of possible isomeric compounds that can be formed by substitution of two hydrogen atoms of propane by two chlorine atoms is

- (a) 2 (b) 3 (c) 4 (d) 5



The major product X in the above reaction is





Assertion-Reason Type Questions

Directions: Each question contains Statement-1 and Statement-2 and has the following 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

171. Statement 1

S_N2 reaction of an optically active alkyl halide with aqueous NaOH always gives an alcohol having opposite sign of rotation.

and

Statement 2

S_N2 reaction of an optically active compound always proceed with inversion of configuration.

172. Statement 1

Reaction of bromobenzene with Br_2/Fe gives mainly 1, 4 – dibromobenzene.

and

Statement 2

In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile.

173. Statement 1

$CH_3 - CH_2 - O - CH_2Br$ undergoes hydrolysis faster than $CH_3 - O - CH_2 - CH_2Br$.

and

Statement 2

The carbocation formed by ionization of $CH_3 - CH_2 - OCH_2Br$ is stabilized by resonance.

174. Statement 1

$CH_3 - CH_2 - CH_2Br$ when treated with alcoholic NaCN gives mainly the corresponding cyanide or nitrile.

and

Statement 2

Sodium cyanide being ionic gives cyanide ions having more negative charge on carbon.

175. Statement 1

Reaction of ethyl benzene with chlorine in presence of light and heat gives mainly 1-chloro-1-phenyl ethane.

and

Statement 2

Reaction takes place by the more stable secondary benzylic free radical.

176. Statement 1

Tertiary alcohols produce immediate turbidity with Lucas reagent.

and

Statement 2

The order of reactivity of alcohols is $3^\circ > 2^\circ > 1^\circ$ in all chemical reactions.

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177. Statement 1

Reaction of tert-butyl bromide with sodium ethoxide is not used for the preparation of ethyl t-butyl ether.
and

Statement 2

Tertiary alkyl halide undergoes preferential elimination in presence of bases.

178. Statement 1

When optically active 2-iodooctane is treated with NaI in acetone, it slowly loses its optical activity.
and

Statement 2

Repeated Walden inversions on the reactant and its product finally gives a racemic mixture.

179. Statement 1

The dipole moment of CH_3F is lower than that of CH_3Cl .
and

Statement 2

Since fluorine is more electronegative, C – F bond is more polar than C – Cl bond.

180. Statement 1

Fluorobenzene undergoes nucleophilic substitution much faster than chlorobenzene.
and

Statement 2

Fluorine being more electronegative causes more decrease in electron density at the carbon leading to a faster attack by the nucleophile.



Linked Comprehension Type Questions

Directions: This section contains 3 paragraphs. Based upon the paragraph, 3 multiple choice questions have to be answered. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

Passage I

Alcohols can be prepared by a number of methods. Active metals such as sodium liberate hydrogen from alcohols. The electron releasing inductive effect of the alkyl group makes the alcohols weaker acids than water. Alcohols undergo oxidation under the influence of various reagents and different experimental conditions to give a variety of products. 1,2-diols get cleaved by strong oxidizing agents.

181. Which of the following combination of reactants can be used for the preparation of $\text{C}_6\text{H}_5 - \text{CHOH} - \text{CH}_3$?

(i) $\text{C}_6\text{H}_5 - \text{CHO}$ and CH_3MgBr

(ii) $\text{C}_6\text{H}_5\text{MgBr}$ and $\text{CH}_3 - \text{CHO}$

(iii) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$, Na and CH_3Br

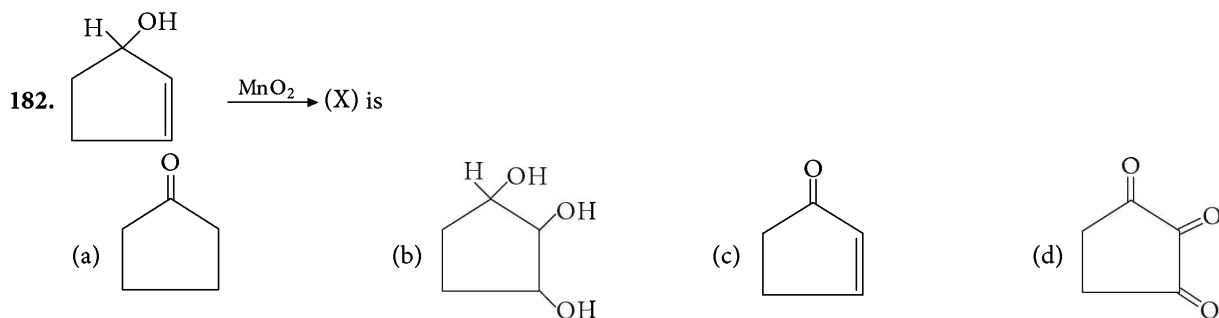
(iv) $\text{C}_6\text{H}_5 - \text{CO} - \text{CH}_3$ and LiAlH_4

(a) (i) and (ii) only

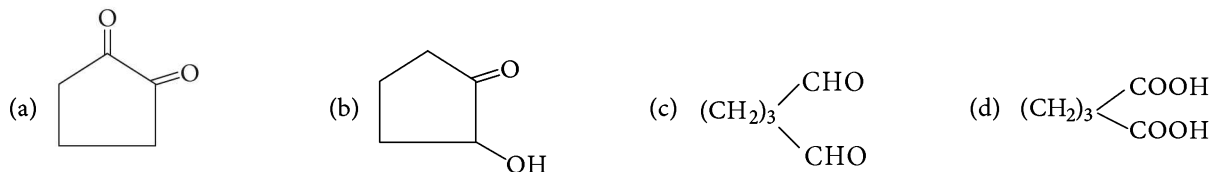
(b) (i), (ii) and (iii) only

(c) (i), (ii) and (iv) only

(d) (i), (ii), (iii) and (iv)



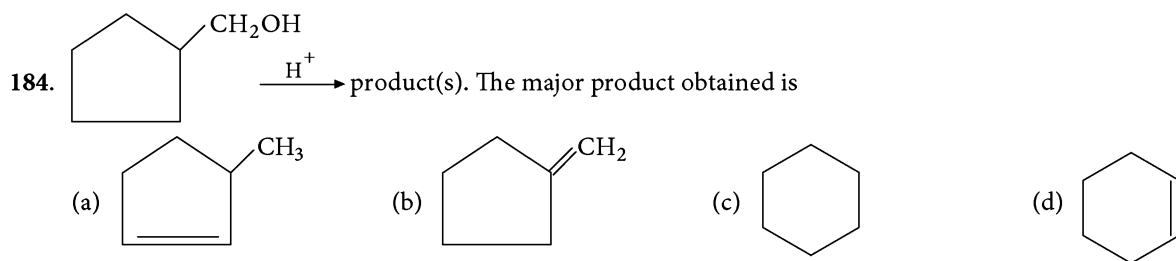
183. Cyclopentane-1,2-diol on oxidation with lead tetraacetate gives



Passage II

Preparation and reactions of alcohols

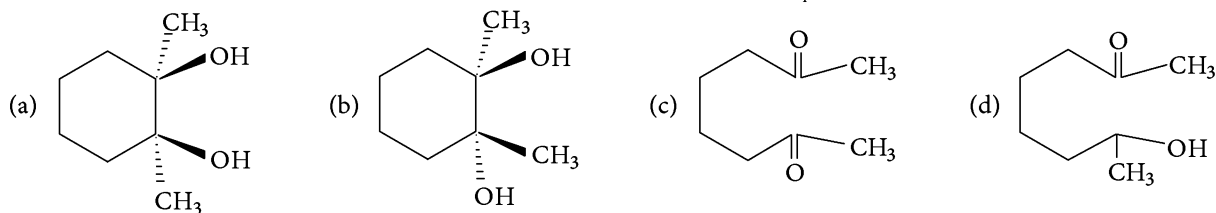
Alcohols can be prepared from alkyl halides, epoxides, alkenes, etc. When treated with acid, C – OH bond is cleaved heterolytically to form a carbocation which could then undergo substitution, elimination or rearrangement depending on the conditions and stability of the carbocation.



185. When $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ is refluxed with metallic sodium in dry ethers the major product obtained is



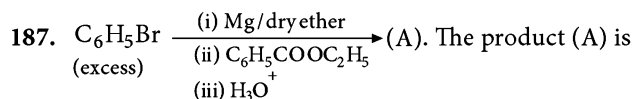
186. When 1,2-dimethyl cyclohexene is treated with cold dilute alkaline KMnO_4 , the product obtained is



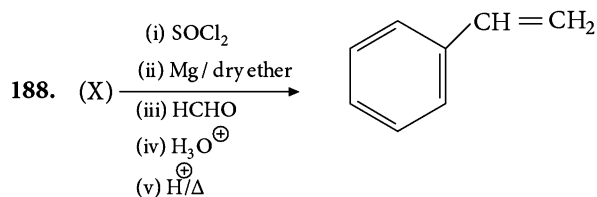
Passage III

Reactions of Grignard reagents

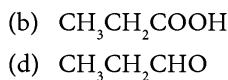
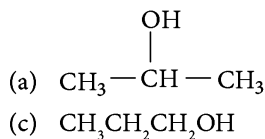
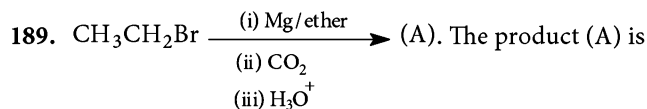
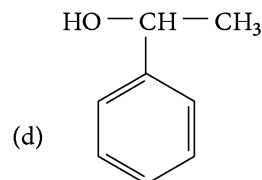
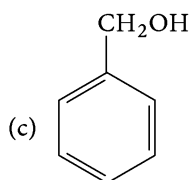
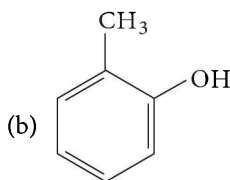
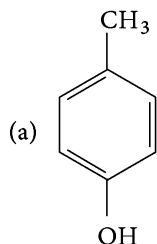
Organic compounds which contain at least one carbon-metal bond are called organometallic compounds. Grignard reagents are very reactive organometallic compounds which are of great synthetic utility. They are used for the synthesis of alcohols, aldehydes, ketones, carboxylic acids, etc. They are however decomposed by compounds which have active hydrogen.



- (a) $(\text{C}_6\text{H}_5)_3\text{C} - \text{OH}$ (b) $(\text{C}_6\text{H}_5)_3\text{C} - \text{COOC}_2\text{H}_5$ (c) $(\text{C}_6\text{H}_5)_2\text{CO}$ (d) $(\text{C}_6\text{H}_5)_2\text{CHOH}$



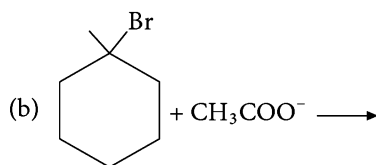
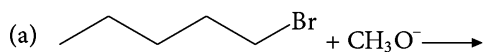
The starting material (X) is

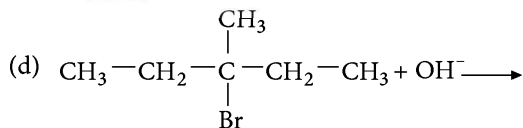
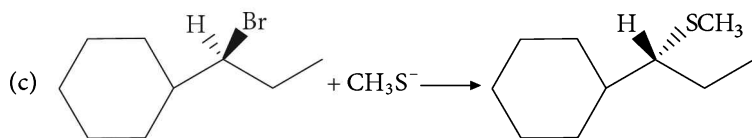


Multiple Correct Objective Type Questions

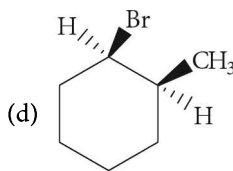
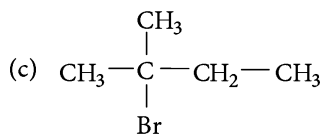
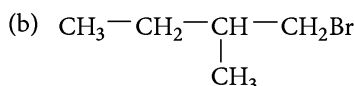
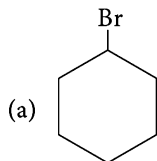
Directions: Each question in this section has four suggested answers of which ONE OR MORE answers will be correct.

190. The rate of which of the following reactions will increase if the concentration of the nucleophile is increased.

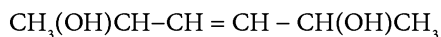




191. Which of the following alkyl halides will give only one alkene in elimination under E_2 conditions?



192. The correct statements about the following compound are

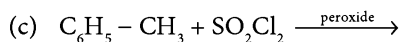
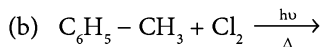


- (a) The total number of stereoisomers possible is 6.
- (b) The total number of diastereomers possible is 3.
- (c) The number of enantiomers possible for the cis isomer is 2.
- (d) The number of enantiomers possible for the trans isomer is 4.

193. Biphenyl is formed when

- (a) bromobenzene is heated with Na in ether.
- (b) iodobenzene is heated with copper powder in a sealed tube.
- (c) chlorobenzene is heated with benzene in presence of anhydrous aluminium chloride.
- (d) phenyl magnesium bromide is treated with bromobenzene in the presence of a small amount of CoCl_2 .

194. Which of the following reactions will give benzyl chloride?



195. Chlorobenzene is less reactive than benzyl chloride towards nucleophilic substitution because

- (a) the carbon of C-Cl bond in $\text{C}_6\text{H}_5\text{Cl}$ is sp^2 hybridized and holds the electron pair more firmly as compared to sp^3 carbon containing chlorine in $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$.
- (b) the C-Cl bond in $\text{C}_6\text{H}_5\text{Cl}$ is less polar compared to that in $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$.
- (c) the C-Cl bond in $\text{C}_6\text{H}_5\text{Cl}$ acquires partial double bond character due to resonance involving the lone pair on chlorine atom.
- (d) the chlorine in $\text{C}_6\text{H}_5\text{Cl}$ is deactivating due to its high electronegativity.

196. The reagent (s) that can be used to distinguish between methanol and ethanol are

- (a) Anhydrous $\text{ZnCl}_2/\text{con.HCl}$
- (b) salicylic acid/con. H_2SO_4
- (c) Acetic anhydride
- (d) I_2/NaOH

197. Which of the following reactions can be used to distinguish between chlorobenzene and benzyl chloride?

- Heating with an alcoholic solution of silver nitrate.
- Boiling with aqueous KOH solution followed by acidification with dilute HNO_3 and addition of AgNO_3 solution.
- Fusion with sodium metal followed by acidification with dilute HNO_3 and addition of AgNO_3 solution.
- Refluxing with alkaline KMnO_4 followed by acidification with HCl .



Matrix-Match Type Questions

Directions: Match the elements of Column I to elements of Column II. There can be single or multiple matches.

198.

Column I

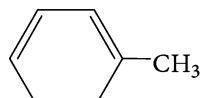
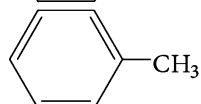
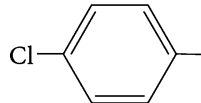
- $\text{S}_{\text{N}}1$ reaction
- $\text{S}_{\text{N}}2$ reaction
- $\text{E}1$ reaction
- $\text{E}2$ reaction

Column II

- Carbocation
- $\text{CH}_3 - \text{CHCl} - \text{CH}_2 - \text{CH}_3 + \text{C}_2\text{H}_5\text{O}^- \xrightarrow{\text{C}_2\text{H}_5\text{OH}}$
Major product
- one step process
- $\text{CH}_3 - \text{CHBr} - \text{CH}_3 + \text{I}^- \xrightarrow{\text{acetone}}$
- Racemisation

199.

Column I

-  $\xrightarrow{\text{Cl}_2/\text{Fe}}$
-  $\xrightarrow[\Delta]{\text{Cl}_2, h\nu}$
-  $\xrightarrow{\text{NaOH}}$
- $\text{CH}_3 - \text{CHOH} - \text{CH}_3 \xrightarrow[440\text{ K}]{85\% \text{ H}_3\text{PO}_4}$

Column II

- Electrophilic substitution
- Nucleophilic substitution
- Carbocations
- Carbanions
- Free radicals

200.

Column I

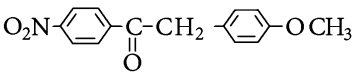
- $\text{CH}_3 - \text{CH}_2 - \text{CHO} \xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) CH}_3\text{MgI}}$
- $\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 - \text{CH}_3 \xrightarrow{\text{H}_2\text{O}/\text{H}^+}$
- $\text{CH}_3 - \underset{\text{CH}_3}{\text{C}} = \text{CH}_2 \xrightarrow{\text{HBr}}$
- $\text{CH}_3 - \text{CH}_2\text{OH} \xrightarrow{\text{PCC/CH}_2\text{Cl}_2}$

Column II

- Regioselective
- Iodoform test
- secondary alcohol
- carbocation
- Markovnikov's rule Topic Grip

SOLUTIONS

ANSWER KEYS

- (i) Dehydration followed by acid catalysed hydration will give the product in both cases
- (i) Acetone is treated with CH_3MgBr and then hydrolysed
(ii) 2-Methyl-2-propene is formed.
- (a) $\text{C}_6\text{H}_5\text{CH}_2\text{OH} < \text{C}_6\text{H}_5\text{OH} < \text{C}_2\text{H}_5\text{OH}$
(b) Butan-1-ol < butan-2-ol < 2-methyl-2-propanol
(c) $(\text{CH}_3)_3\text{CCH}_2\text{OH} < (\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{OH} < \text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{OH}$
- Reaction involves a 1,2-shift of H^- to form a more stable 3° carbocation.
- (a) n-hexane
(b) cyclopentanone
(c) Butane-1,4-diol
- (i) 1st reaction
(ii) 2nd reaction
(iii) 1st reaction
- It is pinacol-pinacolone rearrangement. The major product is

- A part of ethylene glycol is treated with sodium to form $\text{NaOCH}_2\text{CH}_2\text{ONa}$. The remaining part is converted to $\text{ClCH}_2\text{CH}_2\text{Cl}$ by reaction with thionyl chloride. These two compounds on reaction gives 1,4-dioxane.
- Cyclopentanone
- (i) $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{NaSH}$
(ii) $\text{CH}_3 - \text{CH}_2\text{OH} < \text{CH}_3 - \text{CH}_2\text{NH}_2 < \text{CH}_3 - \text{CH}_2\text{SnA}$

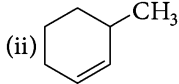
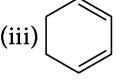
11. (a)	12. (b)	13. (d)
14. (d)	15. (b)	16. (b)
17. (c)	18. (a)	19. (c)
20. (c)	21. (d)	22. (c)
23. (d)	24. (d)	25. (b)
26. (d)		
27. (b), (c)		
28. (c), (d)		
29. (a), (b), (d)		
30. (a) $\rightarrow$ (q), (t)		
(b) $\rightarrow$ (p)		
(c) $\rightarrow$ (p), (t)		
(d) $\rightarrow$ (r), (s)		

IIT Assignment Exercise

31. (c)	32. (b)	33. (c)
34. (d)	35. (a)	36. (b)
37. (a)	38. (b)	39. (c)
40. (c)	41. (c)	42. (d)
43. (a)	44. (c)	45. (c)
46. (b)	47. (b)	48. (c)
49. (b)	50. (a)	51. (d)
52. (d)	53. (b)	54. (c)
55. (d)	56. (d)	57. (d)
58. (c)	59. (d)	60. (a)
61. (c)	62. (a)	63. (b)
64. (c)	65. (b)	66. (b)
67. (b)	68. (c)	69. (b)
70. (c)	71. (c)	72. (b)
73. (a)	74. (a)	75. (a)
76. (b)	77. (d)	78. (b)
79. (d)	80. (c)	81. (a)
82. (c)	83. (b)	84. (a)
85. (b)	86. (d)	87. (a)
88. (a)	89. (c)	90. (d)
91. (c)	92. (b)	93. (c)
94. (b)	95. (d)	96. (b)
97. (d)	98. (c)	99. (a)
100. (a)	101. (c)	102. (d)
103. (b)	104. (c)	105. (a)
106. (d)	107. (c)	108. (c)

109. (b)	110. (d)	111. (a)
112. (b)	113. (a)	114. (a)
115. (b)		
116. (b)		
117. (b), (d)		
118. (b), (c)		
119. (a), (c)		
120. (a) $\rightarrow$ (s)		
(b) $\rightarrow$ (p), (r)		
(c) $\rightarrow$ (p), (q)		
(d) $\rightarrow$ (t)		

Additional Practice Exercise

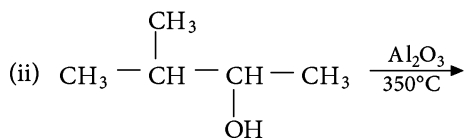
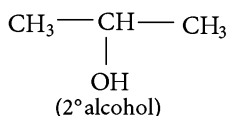
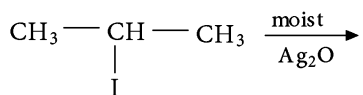
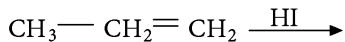
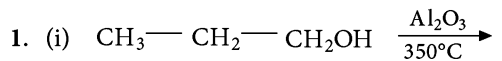
121. Benzene $\xrightarrow[\text{AlCl}_3]{\text{CH}_3\text{Cl}}$ toluene(e)
 $\xrightarrow{\text{NBS}}$ benzylbromide
 $\xrightarrow{\text{KCN}}$ benzyl cyanide
 $\xrightarrow{\text{H}_2/\text{Ni}}$ Product
122. Method (ii)
123. Tetrahydrofuran (THF) is formed
124. Carbocation is formed as intermediate in the reaction of alcohol with HBr
125. $\text{Cl}_3\text{C} - \text{CH}_2 - \text{CH}_2\text{Cl}$
126. (i) Anti Markovnikoff's addition of water takes place
 (ii) 
 (iii) 
127. (i) $\text{H}_3\text{C} - \overset{\text{CH}_3}{\underset{\text{D}}{\text{CH}}} - \text{C} - \text{CH}_3$
 (ii) $\text{CH}_3 - \overset{\text{CH}_3}{\text{CH}} - \text{CH}_2 - \text{CH}_3$
128. (i) Diphenyl (ii) DDT

4.78 Alcohols, Alkyl Halides and Haloarenes

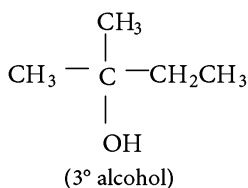
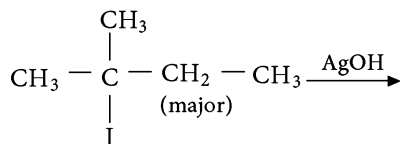
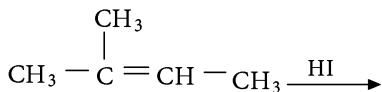
129. (i) Ethanol is treated with SOCl_2 and then with sodium acetylide
(ii) Ethyl bromide is treated with KCN to form ethyl cyanide which is then treated with CH_3MgBr and hydrolysed
(iii) Dehydrohalogenation followed hydroboration-oxidation
130. $\text{C}_6\text{H}_5\text{MgBr}$ is treated with the ester to form 3° alcohol which is then dehydrated.
131. (c) 132. (d) 133. (d)
134. (b) 135. (c) 136. (c)
137. (a) 138. (b) 139. (c)
140. (b) 141. (d) 142. (a)
143. (a) 144. (b) 145. (a)
146. (d) 147. (c) 148. (d)
149. (c) 150. (d) 151. (a)
152. (b) 153. (d) 154. (a)
155. (b) 156. (a) 157. (c)
158. (d) 159. (d) 160. (c)
161. (b) 162. (a) 163. (d)
164. (b) 165. (d) 166. (a)
167. (d) 168. (a) 169. (d)
170. (b) 171. (d) 172. (c)
173. (a) 174. (c) 175. (a)
176. (c) 177. (a) 178. (a)
179. (b) 180. (a) 181. (c)
182. (c) 183. (c) 184. (d)
185. (d) 186. (a) 187. (a)
188. (c)
189. (b)
190. (a), (c)
191. (a), (b)
192. (a), (c)
193. (a), (b), (d)
194. (a), (b), (c)
195. (a), (b), (c)
196. (b), (d)
197. (a), (b), (d)
198. (a) $\rightarrow$ (p), (t)
(b) $\rightarrow$ (r), (s)
(c) $\rightarrow$ (p)
(d) $\rightarrow$ (q), (r)
199. (a) $\rightarrow$ (p), (r)
(b) $\rightarrow$ (t)
(c) $\rightarrow$ (q), (s)
(d) $\rightarrow$ (r)
200. (a) $\rightarrow$ (q), (r)
(b) $\rightarrow$ (r), (s)
(c) $\rightarrow$ (p), (s), (t)
(d) $\rightarrow$ (q)

HINTS AND EXPLANATIONS

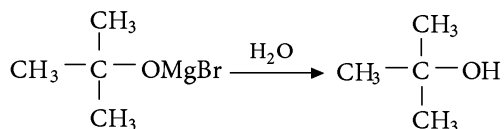
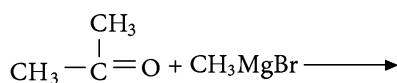
Topic Grip



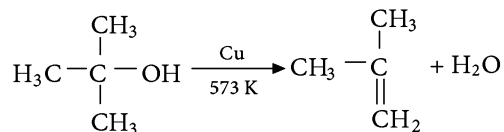
(2° alcohol)



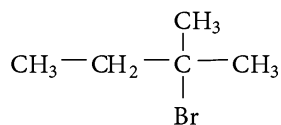
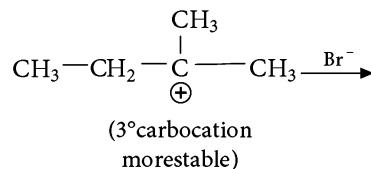
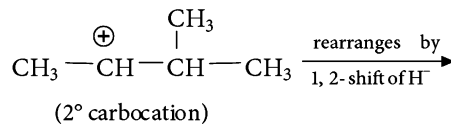
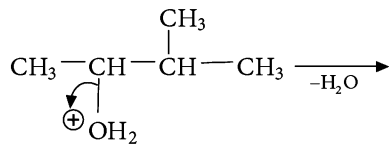
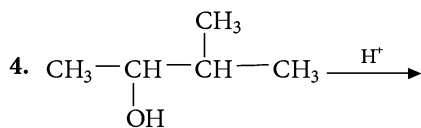
2. (i) Acetone (propanone) on treating with methyl magnesium bromide gives an addition product which on hydrolysis gives 2-methyl-2-propanol

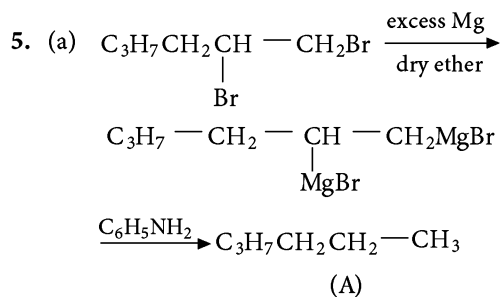


- (ii) When vapours of 2-methyl-2-propanol are passed over copper heated to 573K, dehydration occurs resulting in the formation of the alkene, 2-methyl propene

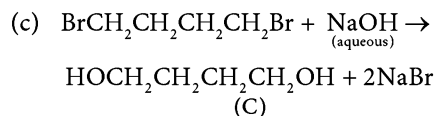
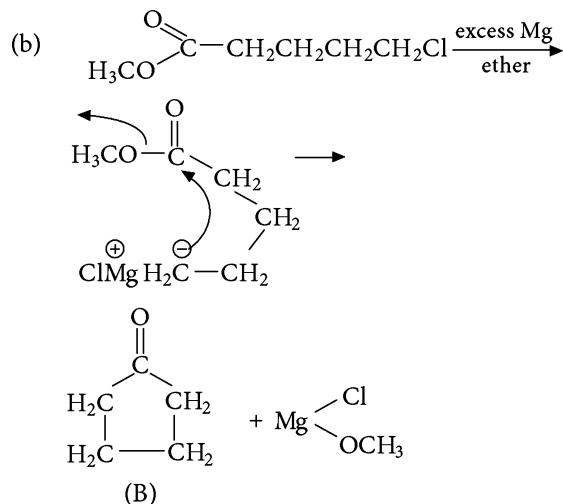


3. (a) $\text{C}_6\text{H}_5\text{CH}_2\text{OH} < \text{C}_6\text{H}_5\text{OH} < \text{C}_2\text{H}_5\text{OH}$
Solubility decreases as the length of the carbon chain increases
- (b) butan-1-ol < butan-2-ol < 2-methyl-2-propanol.
Order of reactivity of alcohols toward's Lucas reagent (i.e., reaction involving C – OH bond cleavage) is $3^\circ > 2^\circ > 1^\circ$
- (c) $(\text{CH}_3)_3\text{CH}_2\text{OH} < (\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{OH} < \text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{OH}$
Among isomeric alcohols, boiling point decreases with branching.



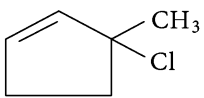
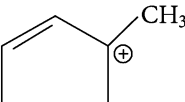


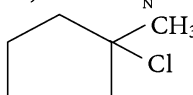
$\text{C}_6\text{H}_5\text{NH}_2$ is a compound having active hydrogen and so a hydrocarbon is produced.



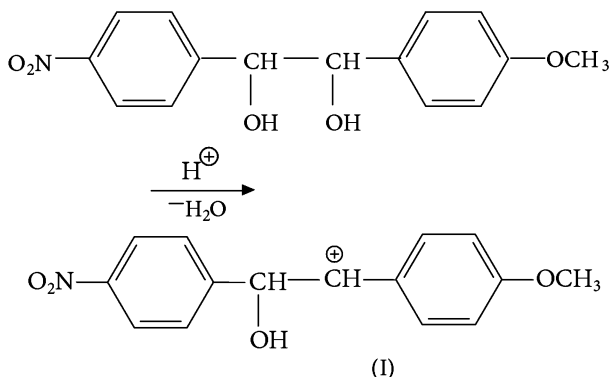
6. (i) Substitution of $-\text{Br}$ by $\text{OH}^\ominus$ in acetone medium would proceed faster in an $\text{S}_\text{N}2$ reaction as the medium is non-polar mixture. In alcohol-water mixture (which it is more polar medium) the reaction condition is favourable for an $\text{S}_\text{N}1$ process.

(ii) Substitution of $-\text{I}$ by $\text{CN}^\ominus$ is more favourable for an $\text{S}_\text{N}2$ process, as the iodide ($\text{I}^\ominus$) ion is a better leaving group than chloride ($\text{Cl}^\ominus$) ion. Since the attacking nucleophile is the same ($\text{CN}^\ominus$), the rate of the $\text{S}_\text{N}2$ process depends on the leaving group.

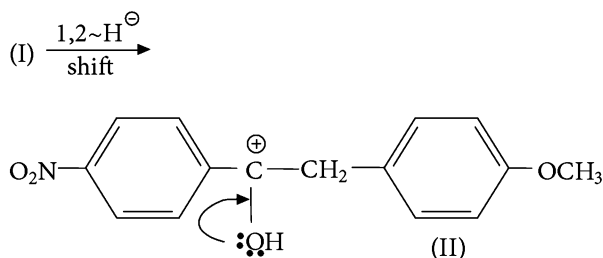
(iii) Substitution of $-\text{Cl}$ by $\text{CN}^\ominus$ in  would be more favourable for a $\text{S}_\text{N}1$ reaction as the carbocation formed,  is more

stabilized due to resonance, whereas $\text{S}_\text{N}2$ reaction is more favourable with 

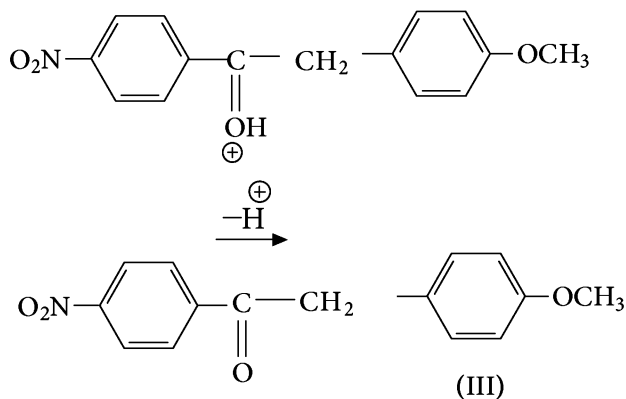
7. The reaction is related to pinacol-pinacolone rearrangements

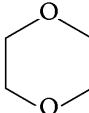


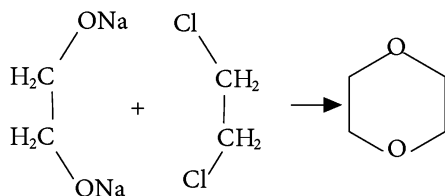
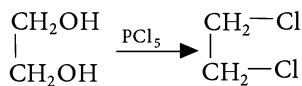
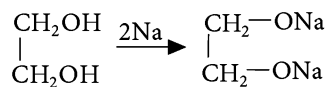
The carbocation is formed on the benzylic carbon of the p-methoxybenzylic group (I), as it is more stabilized by the electron releasing influence of the $-\text{OCH}_3$ group. Now a hydride shift occurs to the adjacent carbon to give (II).



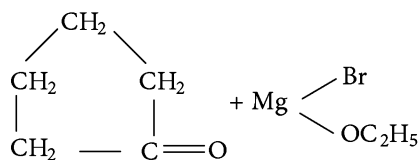
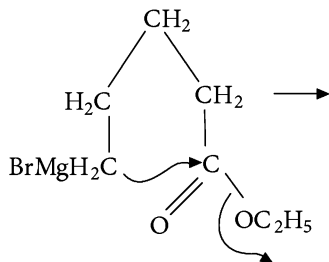
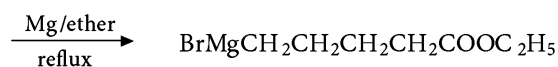
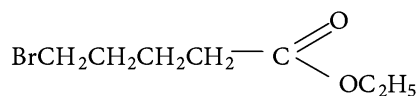
The lone pair of electrons in oxygen stabilize this carbocation, followed by the loss of a proton from oxygen to give the corresponding ketone (III).



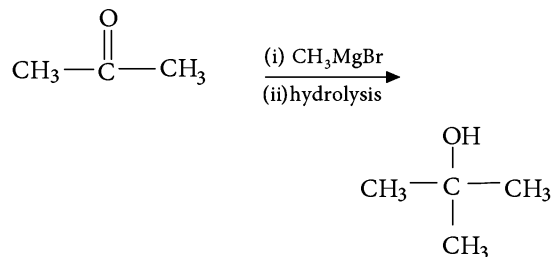
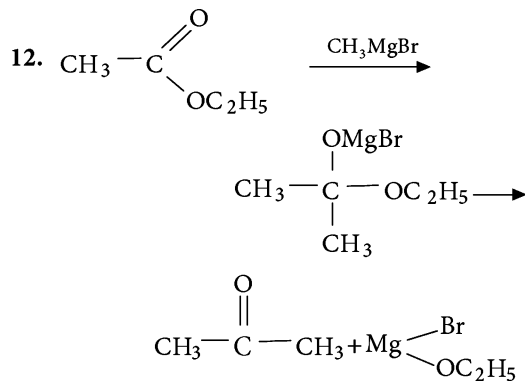
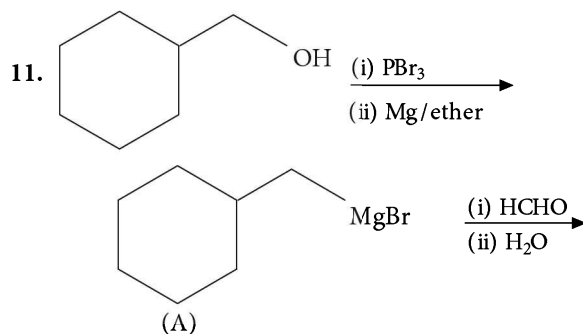
8. 1,4-dioxane is a cyclic ether  It is prepared as follows.



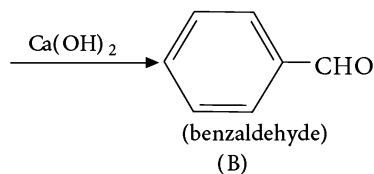
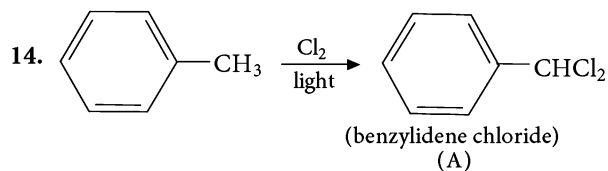
9. The reaction proceeds in two steps. In the first step, a Grignard reagent is formed. In the second step, an intramolecular Grignard reaction occurs leading to the formation of a cyclic ketone.



10. (i) $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{NaSH}$
(ii) $\text{CH}_3\text{CH}_2\text{OH} < \text{CH}_3\text{CH}_2\text{NH}_2 < \text{CH}_3\text{CH}_2\text{SNa}$

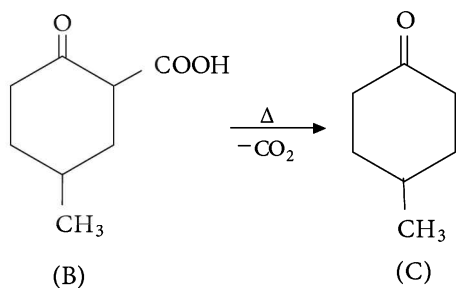
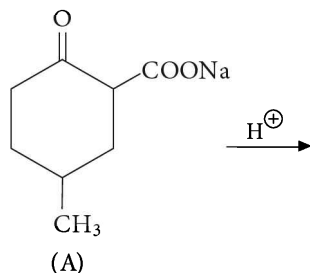
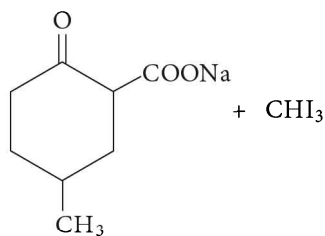
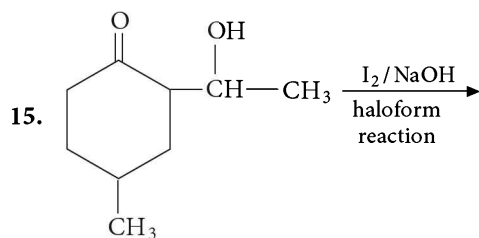


13. As the size of alkyl group increases, the reactivity to undergo substitution by $\text{S}_{\text{N}}2$ mechanism decreases.



4.82 Alcohols, Alkyl Halides and Haloarenes

When two hydrogen atoms of the methyl group in the side chain get substituted by two chlorine atoms, the product (A) is obtained, which is benzylidene chloride. Benzylidene chloride undergoes ready hydrolysis with a weak base like aqueous $\text{Ca}(\text{OH})_2$ solution to give benzaldehyde (B).

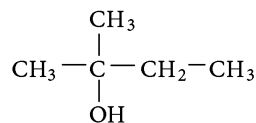
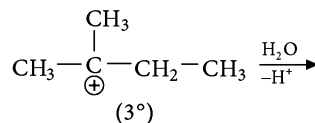
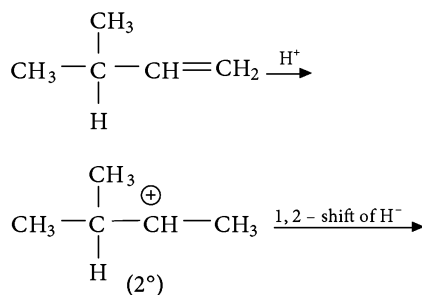


β -keto acid undergoes facile decarboxylation.

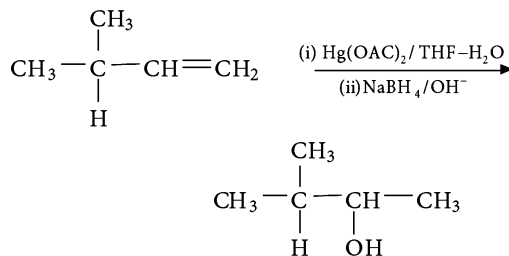
16. Both statements are correct, but statement-2 is not the correct reason for statement-1.

Phenol is a weaker nucleophile because the lone pair of electrons on oxygen in phenol is delocalized with the benzene ring.

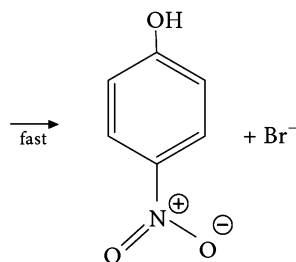
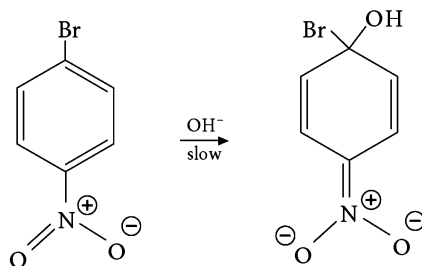
17. Statement-1 is wrong while statement-2 is correct
In acid catalyzed hydration of 3-methylbut-1-ene, rearrangement of initially formed carbocation takes place giving 2-methylbutan-2-ol as the major product



Since carbocations are not involved in oxymercuration reduction, no rearrangement occurs and 3-methyl butan-2-ol is formed as the major product.

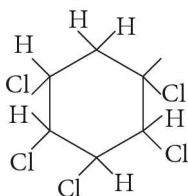


18. Both statements are correct and statement-2 is the explanation of statement-1.



19. Statement-1 is correct while statement-2 is false. In the hydrolysis reaction mentioned, benzyl bromide undergoes hydrolysis by S_N1 mechanism. In the reaction, the nucleophile is weak H_2O . The solvent is polar. So benzyl bromide ionizes to form resonance stabilized benzyl cation and then reacts with water. i.e., the reaction takes place by S_N1 mechanism.

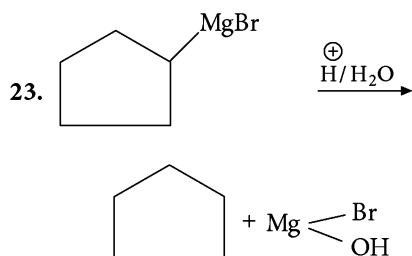
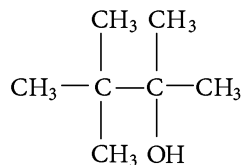
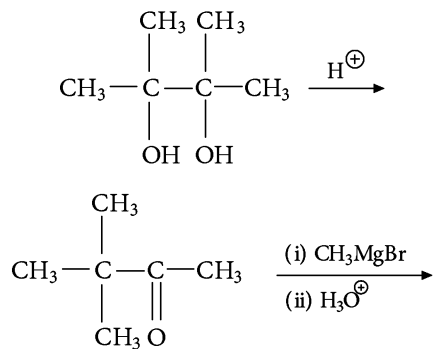
20. Statement-1 is correct, but statement-2 is wrong. Benzene reacts with Cl_2 in the presence of sunlight or heat to give hexachlorobenzene or BHC. This is not a substitution reaction. The double bonds in benzene are utilized in this reaction.



This is not an aromatic electrophilic substitution. The reaction proceeds by a free radical mechanism. This is an addition reaction. Hence reasoning given is not correct.

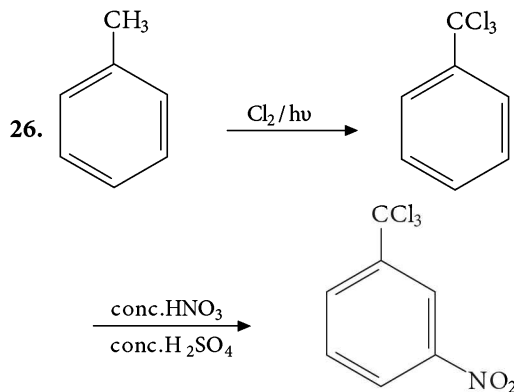
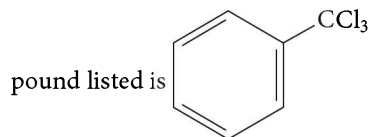
21. Tertiary butyl alcohol $CH_3-C(CH_3)_2-OH$ cannot be dehydrogenated by Cu at $300^\circ C$, but is dehydrated to give isobutylene, $CH_3-C(CH_3)=CH_2$.

22. The starting material is a 1,2-diol. This undergoes, pinacol-pinacolone rearrangement in presence of an acid to give a ketone. The ketone undergoes further reaction with a Grignard reagent to give a tertiary alcohol.



In this reaction, a hydrocarbon is obtained. Alcohol is not the product of reaction.

24. Aryl and vinyl halides cannot be used as halide components in Friedel-Crafts reaction since they do not form stable carbocations readily.
25. A strongly deactivating and a meta directing compound listed is



27. (a) is not feasible because bromine in bromobenzene is not reactive due to the double bond nature of C-Br bond by resonance

The major product in (d) is the elimination product since $(CH_3CH_2)_3CBr$ is a 3° alkyl halide.

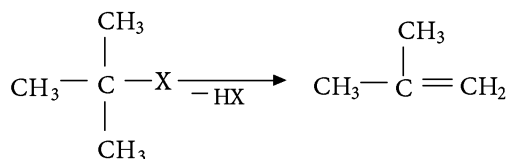
28. The reagents generally used for dehydrohalogenation are alcoholic KOH and sodamide.
29. Protonation of $-OH$ followed by removal of H_2O gives the primary carbocation (a) which rearranges by

4.84 Alcohols, Alkyl Halides and Haloarenes

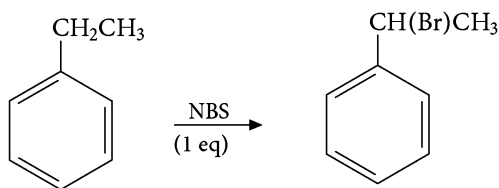
1, 2-shift of hydride ion to form the secondary carbocation (b). Electrophilic attack of the positively charged Carbon on the benzene ring gives (d) which loses a proton to form the product.

IIT Assignment Enquiries: Solutions

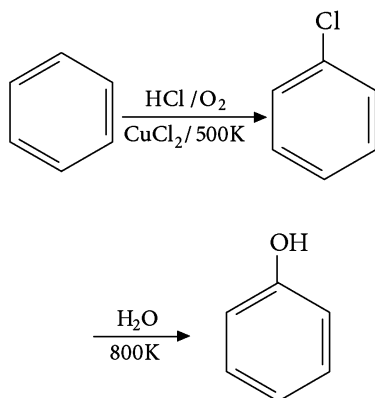
31. In tertiary alkyl halides, the tendency to undergo dehydrohalogenation is much greater than its possibility to undergo hydrolysis.



32. N-bromosuccinimide is a specific brominating agent for allylic or benzylic hydrogen.

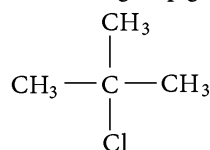


33. In Raschig process benzene vapour is mixed with hydrogen chloride gas and air and passed over cupric chloride at 500K to obtain chlorobenzene, which is then mixed with steam and passed over silica at 800K to obtain phenol.



34. Primary and secondary alcohols react with HCl only in the presence of anhydrous zinc chloride. Only tertiary alcohols form chlorides readily at room temperature when treated with HCl. $\text{C}_4\text{H}_9\text{O}$ is $(\text{CH}_3)_3\text{C}-\text{OH}$ which is tertiary butyl alcohol.

The $-\text{OH}$ group gets readily displaced by $-\text{Cl}$ to give

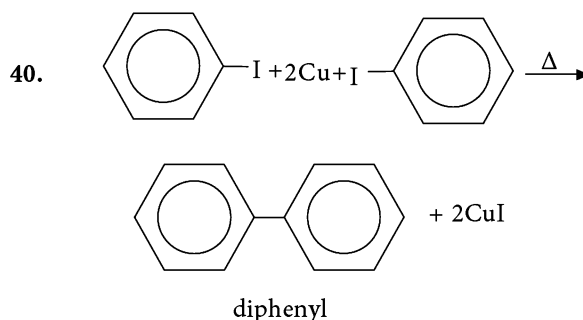


35. $\text{CH}_3 - \text{CH} = \text{CH}_2 \xrightarrow[100\text{atm}]{\text{H}^+ / \text{H}_2\text{O}} \text{CH}_3 - \text{CH}(\text{OH}) - \text{CH}_3$

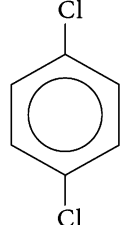
Markovnikov's addition of water takes place to form propan-2-ol as the major product.

36. Mixture of anhydrous ZnCl_2 and conc. HCl is known as Lucas reagent.
37. Victor Meyer's test is used to distinguish primary, secondary and tertiary alcohols. In Victor Meyer's test, the alcohol is reacted with red phosphorous and iodine to get alkyl iodide which is then is treated with AgNO_2 to get the corresponding nitroalkane. The nitroalkane is treated with nitrous acid and the solution is made alkaline with excess NaOH. Primary alcohols give blood red colour (sodium salt of nitrolic acid), secondary alcohols give blue colour (pseudonitroles) and tertiary alcohols form colourless nitro derivatives.

38. The strength of the leaving group decreases in the order $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$.
39. Halogenation of alkyl groups proceeds by free radical mechanism.

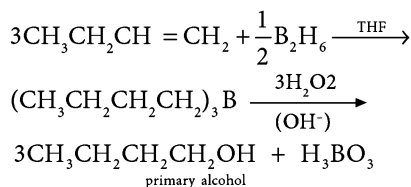


This is an example of Ullmann biaryl synthesis

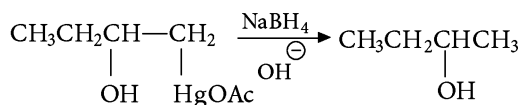
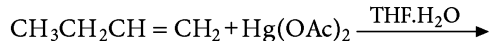
41.  has zero dipole moment as the bond moments get cancelled.

42. Alcoholic silver nitrate on reaction with $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ form white precipitate of AgCl , while chlorotoluene remains unreactive. Products of side chain oxidation are also different. Benzyl chloride gives benzoic acid whereas, o-chlorotoluene gives o-chlorobenzoic acid on side chain oxidation.

43. Hydroboration-oxidation: Alkenes react with diborane (B_2H_6) in ether as solvent to form trialkyl boranes, which on subsequent treatment with alkaline H_2O_2 gives alcohol with terminal $-\text{OH}$, by anti-Markovnikov's addition of H_2O molecule.



44. Alkenes give addition reaction with aqueous mercuric acetate. The adduct on reduction with alkaline NaBH_4 gives alcohol. Addition of H_2O happens according to Markovnikov's rule.



45. Copper at 573K causes the dehydrogenation of primary and secondary alcohols forming aldehydes and ketones respectively. But tertiary alcohols, under the same conditions, undergo dehydration forming alkenes. So normal, sec, iso and tertiary butyl alcohols form butanal, 2-butanone, isobutyraldehyde and isobutene respectively.

46. On reaction with Grignard reagent followed by hydrolysis, formaldehyde gives a primary alcohol, acetaldehyde gives a secondary alcohol and acetone gives a tertiary alcohol.

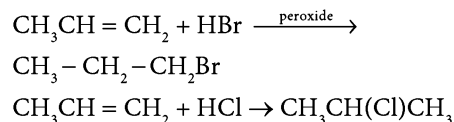
47. $\text{ROH} + \text{SOCl}_2 \rightarrow \text{RCl} + \text{SO}_2 + \text{HCl}$

The main product will be pure as the byproducts formed are gases and escape out.

48. Swarts reaction is the displacement of $-\text{Cl}$ or $-\text{Br}$ of alkyl halides by heating with metallic fluoride as AgF , SbF_3 , CoF_2 , Hg_2F_2 , etc.

49. $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Cl}$ is allyl chloride. Its IUPAC name is 3-chloropropene.

50. In the presence of peroxide, only HBr gives anti-Markovnikov's addition. HCl and HI always obey Markovnikov's rule in the absence or presence of peroxides.



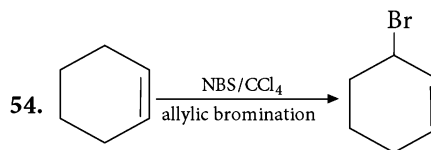
51. Iodoform test is answered by compounds containing

$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{group}$ and $\text{CH}_3-\text{CH}(\text{OH})-\text{group}$. Ethanol, 2-butanol and 2-pentanol, all three alcohols contain $\text{CH}_3-\text{CH}(\text{OH})-\text{group}$.

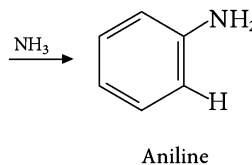
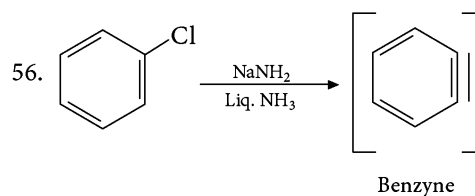
52. $\text{CH}_3\text{CH}_2\text{Br} \xrightarrow{\text{AgCN}} \text{CH}_3\text{CH}_2\text{NC} \xrightarrow{\text{H}_2/\text{Ni}} \text{CH}_3\text{CH}_2\text{NHCH}_3$

53. $\text{C}_6\text{H}_5\text{CH}_2\text{Cl} \xrightarrow{\text{aq. NaOH}} \text{C}_6\text{H}_5\text{CH}_2\text{OH} + \text{NaCl}$
 $\text{NaCl} + \text{AgNO}_3 \rightarrow \text{AgCl} + \text{NaNO}_3$
 (white precipitate)

In vinyl chloride, chlorobenzene and ortho chloro toluene, since the chlorine is attached to a sp^2 hybridized carbon, they do not give this reaction.

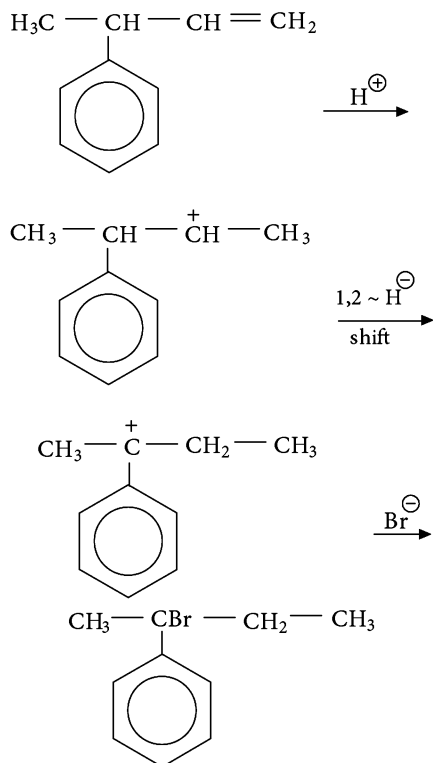


55. $\text{CH}_3-\text{CH}_2-\text{CH}_2\text{Cl}$ (primary alkyl halide) readily undergoes $\text{S}_{\text{N}}2$ reaction.

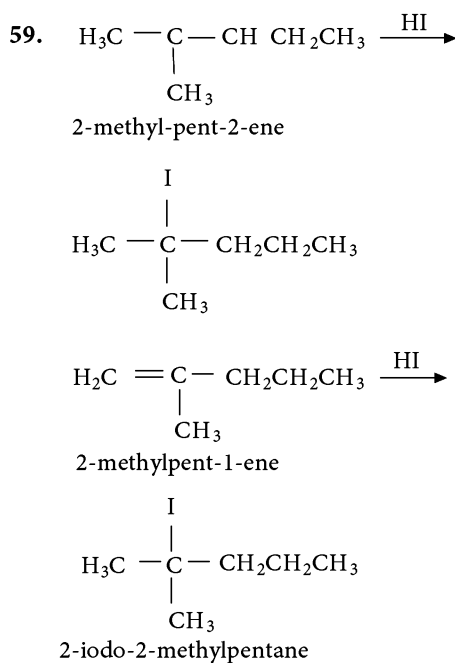


57. H^+ addition occurs to the double bond. But the secondary carbocation formed initially undergoes a rearrangement to give a more stable tertiary benzylic

carbocation, which adds bromide ion to get tertiary bromide.

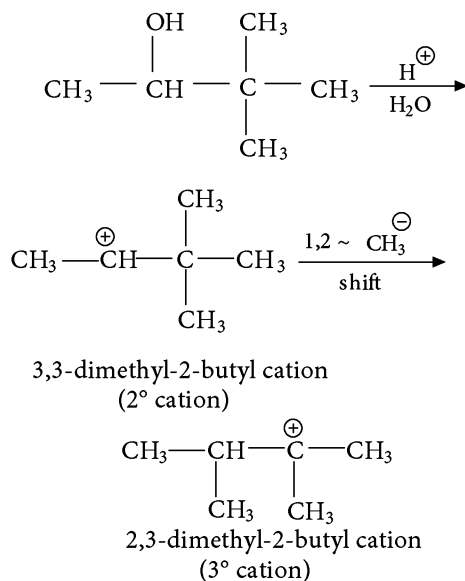


58. Sodium ethoxide is a strong base. So tertiary butyl bromide which is having more tendency to undergo elimination reaction undergoes dehydrohalogenation in presence of NaOEt to form isobutene.

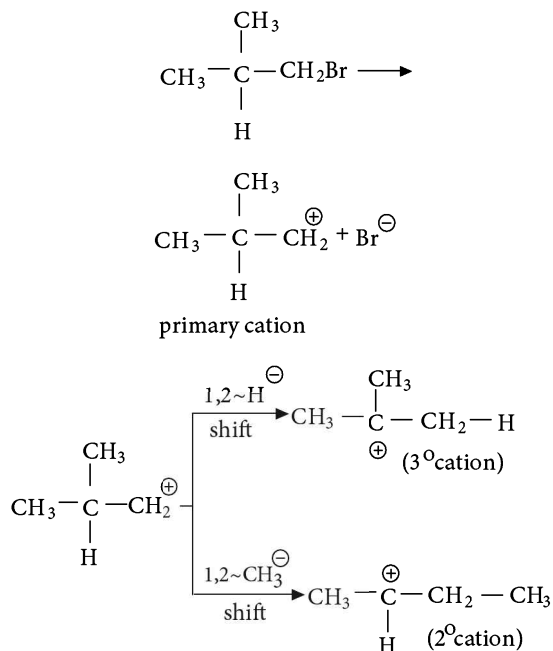


60. MnO_2 selectively oxidises the $-\text{OH}$ group of allylic or benzylic (primary or secondary) alcohol. The $-\text{CO}-$ group formed is in conjugation with the double bond in the system.

61. When 3,3-dimethyl-2-butanol is treated with dilute acid, 3,3-dimethyl-2-butyl carbocation is formed which is a secondary cation. Since tertiary cation is more stable than secondary cation, it will rearrange to give 2,3-dimethyl-2-butyl cation.



62.



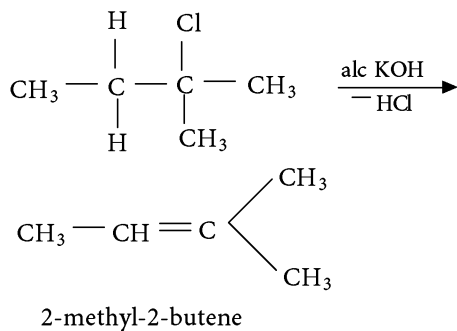
Hydride shift is preferred over methyl shift.

63. Unlike primary alkyl halides, the tertiary halide cannot be obtained from its alcohol because, tertiary alcohols on heating with conc. H_2SO_4 undergo dehydration to form alkenes.

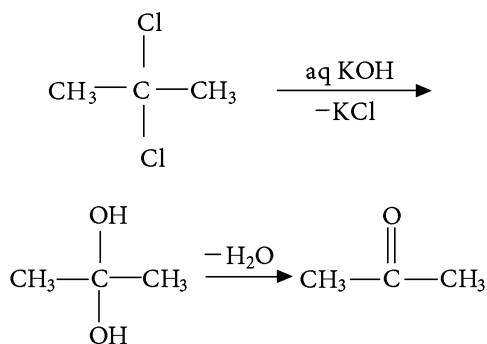
64. (A) and (C) form conjugated unsaturated systems. (C) forms a tertiary benzylic carbocation as the intermediate while (A) forms a secondary allylic carbocation. So, (C) reacts faster than (A). Between (B) and (D), (B) is a secondary alcohol and (D) is a primary alcohol. So, (B) reacts faster than (D). The ease of dehydration is in the order (C) > (A) > (B) > (D).

65. The product is $\text{CH}_3 - \underset{\text{CH}_3}{\text{C}} = \text{CH} - \text{CH}_3$. Ac-

cording to Saytzeff's rule, the alkene which carries more number of alkyl groups attached to the doubly bonded carbon is most preferred. $\therefore$ (A) should be either 2-chloro-3-methylbutane or 2-chloro-2-methylbutane.



66. Acetone is formed when 2,2-dichloropropane is treated with aqueous alkali.

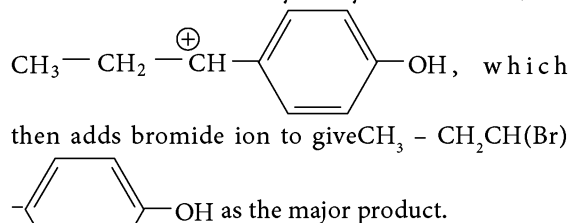


67. $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_2 - \underset{\text{OH}}{\text{CH}} - \text{CH}_3 \xrightarrow{-\text{H}_2\text{O}}$

$$\text{CH}_3 - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{CH}_3$$

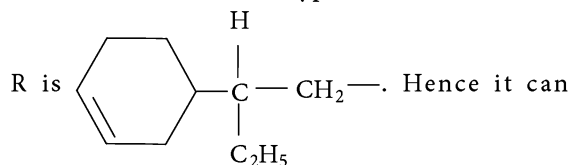
2,4-hexadiene is obtained as the major product as it is a conjugated diene and is more stable.

68. Addition of H^+ to the reactant results in the formation of a more stable secondary benzylic carbocation,

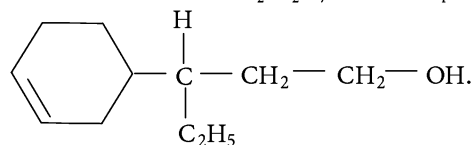


69. In case of the α -alkoxy compounds, the transition states are stabilised by interaction of the p-orbital on the carbon undergoing substitution with the filled 2p orbital of oxygen. So $\text{CH}_3\text{OCH}_2\text{Cl}$ acts faster.

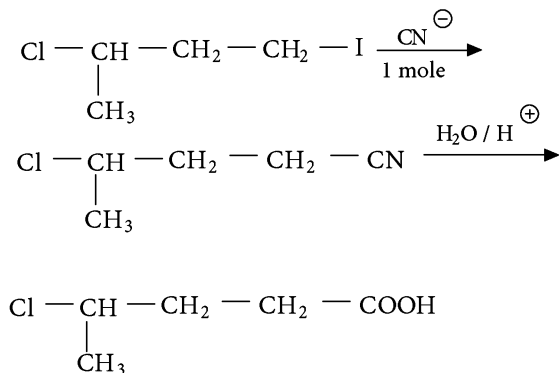
70. The acid (A) is of the type, $\text{R} - \text{COOH}$, where,



be prepared by oxidation of RCH_2OH by an oxidant like acidified $\text{K}_2\text{Cr}_2\text{O}_7$ or KMnO_4 .



71. $\text{I}^\ominus$ is a better leaving group than $\text{Cl}^\ominus$

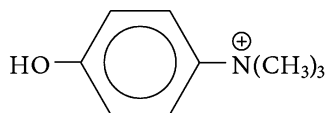


72. (D) contains two electron withdrawing groups at ortho and para position. (B) contains one electron withdrawing group at ortho. (A) contains one electron withdrawing group at metaposition. So effect is reduced when compared to (B) which has one

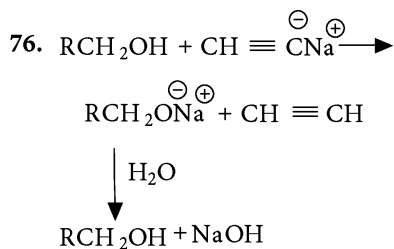
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electron withdrawing group at ortho position. (C) contains electron releasing group, so activity is the least.

73. Chromic acid in sulphuric acid and acetone (Jones reagent) oxidizes secondary alcohols to give ketones in excellent yields under controlled temperatures. This does not affect the double bond.
74. $-N^+(CH_3)_3$ withdraws electrons, stabilizes the carbanion and hence nucleophilic substitution reaction is more favourable, to give

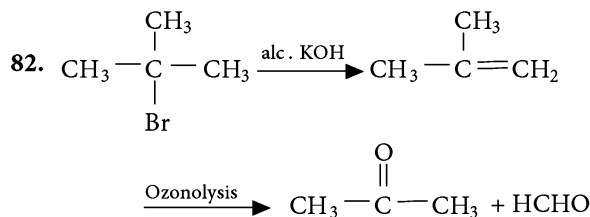
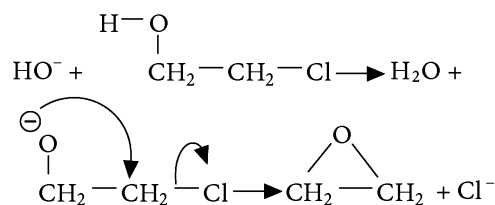


75. Pyridinium chlorochromate, (PCC) when dissolved in methylene chloride will oxidize primary alcohol to aldehyde, and the reaction stop at the aldehydic stage.



The alkoxide formed on hydrolysis gives back the alcohol.

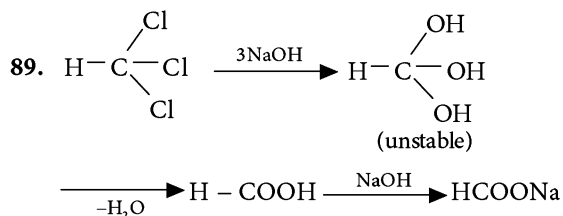
77. This is iodoform reaction. For haloform or iodoform reaction to take place, the alcohol must contain $CH_3-CH(OH)-$ group.
78. Both ethanol and propanol are primary alcohols. Out of these, only ethanol gives iodoform test giving CHI_3 , as it contains $CH_3-CH(OH)-$ group.
79. Both reactions proceed through S_N2 mechanism in a solvent like acetone. With tertiary alkyl halides, S_N2 reactions are slow due to steric hindrance produced by the three alkyl groups. The nucleophile is prevented from rear side attack in the case of (II).
80. The strength can be realized by comparing the relative base strengths of the corresponding conjugate bases
- $$HO^- < CH_3CH_2O^- < HC \equiv C^- < H_2C = CH^-$$
81. Ethylene oxide is the major product formed in the reaction



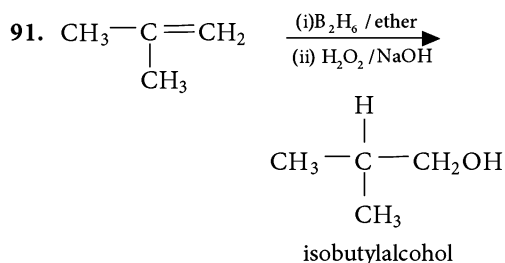
83. Reactivity order of alkyl halide towards S_N2 reaction is
Methyl halide > 1° halide > 2° halide > 3° halide
84. Leaving ability increases with increase in stability of anion.
85. The dipole moments of the various methyl halides are
 CH_3Cl : 1.860 D, CH_3F : 1.847 D
 CH_3Br : 1.830 D, CH_3I : 1.636 D
- The smaller dipole moment of CH_3F is due to shorter C-F bond length (139 pm) compared to C-Cl bond length (178 pm)
86. 2-Bromopentane undergoes elimination reaction (dehydrohalogenation) when treated with potassium ethoxide in ethanol or alcoholic KOH to form mainly trans pent-2-ene. In the dehydrohalogenation of alkyl halides with bases such as alcoholic KOH or $C_2H_5O^-$, more substituted alkene will be formed as the major product (Saytzeff's product). Since trans-pent-2-ene is more stable than cis-pent-2-ene, it is formed as the major product in the elimination of 2-bromopentane.
87. Dehydrohalogenation using bulky bases such as tert-butoxide $(CH_3)_3CO^-$ gives mainly the least substituted alkene (Hofmann product).
88. Dehydrohalogenation of fluoroalkanes gives less substituted alkene (Hofmann product) as the major product.

When a base tries to remove a proton from an alkyl fluoride, the fluoride ion has less tendency to leave compared to other halide ions. As a result, negative charge develops on the carbon that is losing proton and the transition state resembles a carbanion. Carbanions are destabilised by alkyl groups. So

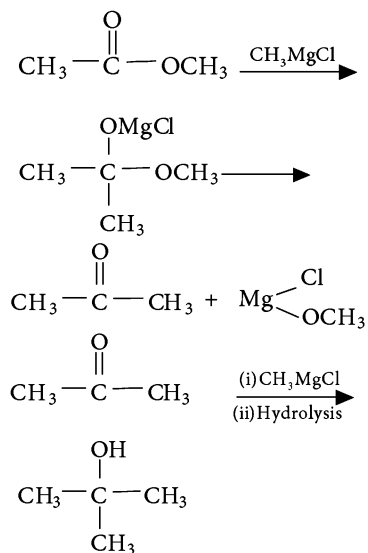
carbanion like intermediate having negative charge on 1° carbon would be more stable. Hence the transition state leading to 1-pentene is more stable in the dehydrohalogenation of 2-fluoropentane and it is formed more rapidly. So it is obtained as the major product (about 80%).



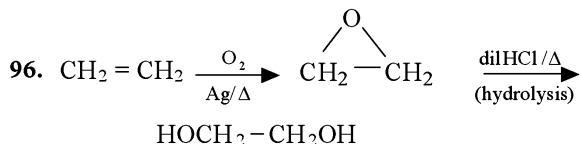
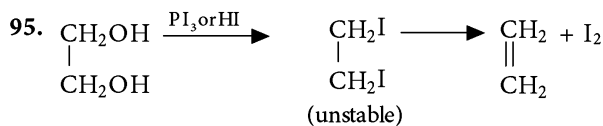
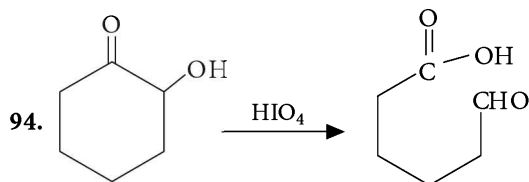
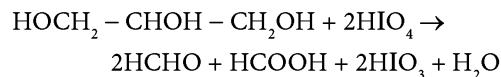
90. Alcohols containing $\text{CH}_3-\text{CHOH}-$ group and aldehydes and ketones having $\text{CH}_3-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-$ group will give yellow precipitate of iodoform when heated with iodine and alkali.



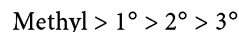
92. Methyl ethanoate reacts with CH_3MgCl to form propanone (acetone) which further reacts with the Grignard reagent to form tert-butyl alcohol (2-methylpropan-2-ol).



93. One mole of glycerol on oxidation with HIO_4 gives two moles of methanal and one mole of methanoic acid



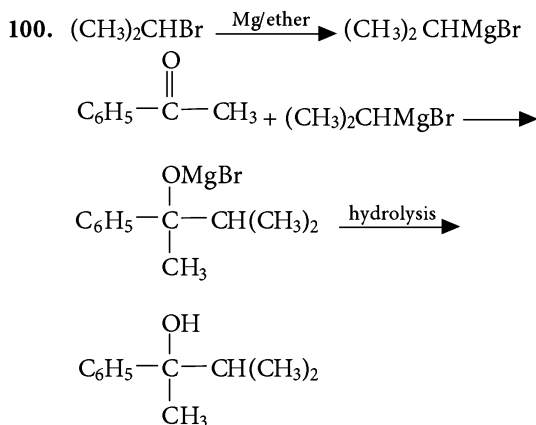
97. Rate of esterification of alcohols:



98. In acid catalysed dehydration, ethanol first accepts proton from acid and thus acts as a base. In reaction with metallic sodium, ethanol acts as an acid.

99. In Victor-Meyer's test for distinguishing 1° , 2° and 3° alcohols, the alcohol is converted to the corresponding nitroalkane and then treated with NaNO_2 and dilute HCl (or HNO_2).

Primary nitroalkanes (obtained from 1° alcohols) give nitrolic acid which gives blood red colour when treated with aqueous NaOH . Secondary nitroalkanes give blue coloured pseudonitrole which is insoluble in NaOH whereas tertiary nitroalkanes do not react with HNO_2 .



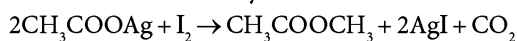
4.90 Alcohols, Alkyl Halides and Haloarenes

101. The major product X in the reaction is trans-but-2-ene which on reaction with bromine gives meso-2,3-dibromobutane

102. Alkyl halide in S_N2 hydrolysis will undergo inversion of configuration. The resulting alcohol will have -OH group attached from the side opposite to that of -Cl of the starting alkyl halide. Inversion of configuration does not mean that the resulting alcohol has opposite configuration. It may be dextrorotatory or laevo rotatory depending on the alcohol formed.

103. $C_6H_5COOAg + Br_2 \xrightarrow{CCl_4 / \text{reflux}} C_6H_5Br + AgBr + CO_2$.
It is called Borodine-Hunsdiecker reaction.

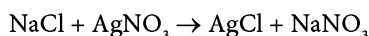
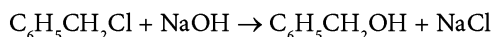
104. Silver salts of carboxylic acids when heated with iodine will form esters and not alkyl iodides



This reaction is called Birnbaum - Simonini reaction.

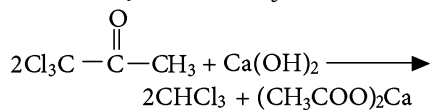
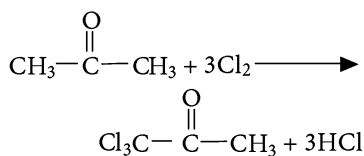
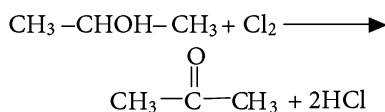
105. $C_6H_5Br \xrightarrow{Mg/ether} C_6H_5MgBr \xrightarrow{C_2H_5OH} C_6H_6 + Mg \begin{smallmatrix} \text{Br} \\ \diagup \quad \diagdown \\ \text{OC}_2\text{H}_5 \end{smallmatrix}$

106. Benzyl chloride ($C_6H_5 - CH_2Cl$) contains chlorine attached to an sp^3 hybridised carbon and it is reactive. So it gives white precipitate of AgCl in the given reaction



AgCl is soluble in NH_4OH due to the formation of the complex $[Ag(NH_3)_2]^+$

107. Isopropyl alcohol is first oxidized to acetone by bleaching powder which further reacts to form chloroform



108. I^- is the strongest nucleophile among the halide ions because of the polarisability of the electron cloud. Since HI is the strongest hydrohalic acid, I^- must be the weakest base among halide ions.

109. As the electronegativity of the atom containing the negative charge increases, it will hold the electron cloud more firmly and hence the nucleophilicity decreases.

110. 3-Bromo-3-methyl hexane is a tertiary alkyl halide and it undergoes solvolysis (i.e., nucleophilic substitution reaction with the solvent) by S_N1 mechanism. Since S_N1 reaction does not involve inversion of configuration, option (d) is not true.

111. Both statements (1) and (2) are correct and statement (2) supports the statement (1).

Nucleophilicity is related to substitution while basicity is related to elimination.

Although both nucleophiles and bases are closely related and sometimes can be found in the same species, there is a difference in their behaviour depending on conditions. For example,

Comparing $-OCH_3$ and $-SCH_3$, the former is more basic while the latter is more nucleophilic. So the statements (1) and (2) are correct and statement (2) is a suitable explanation for statement (1).

112. Both statements (1) and (2) are correct. However statement (2) is not an explanation for statement (1). Poor reactivity or inertness of the haloarenes has been explained by three main reasons, viz.,

- (1) The C-Cl bond assumes a double bond character due to resonance and the electrons are delocalized in the benzene ring.
- (2) In alkyl halides, the halogen is connected to an sp^3 hybridized carbon, while in haloarenes, the halogen is connected to sp^2 hybridised carbon. The carbon halogen bond is shorter and stronger and difficult to break.
- (3) The polarity of the C-X bond in arylhalides is less compared to alkyl halides.

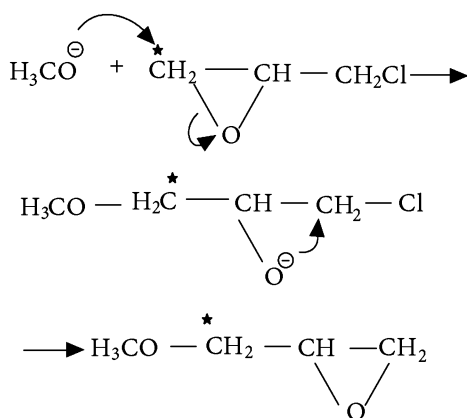
So statement (1) is correct.

Statement (2) is also correct. Aryl halides undergo nucleophilic substitution, when strongly electron withdrawing groups like $-NO_2$, $-CF_3$ etc is present at ortho or para to the halogen atom.

113. Both statements are correct and statement-2 is the correct explanation of statement-1. Protonation of alcohol followed by elimination of water forming carbocation can take place with both con. H_2SO_4 and con. HCl. When HCl is used, the carbocation combines with the powerful nucleophile Cl^- to form alkyl halide. Thus substitution mainly takes place with HCl.

114. In case of (A), $I^\ominus$ is a good leaving group. Hence (ii) proceeds faster. In the case of (B), a tertiary halide proceeds favourably by an S_N1 process. Hence (i) is faster. In the case of (C), the reaction proceeds by an S_N2 mechanism. Hence an unbranched chain is favourable for a rear side attack. Hence the reaction (ii) proceeds faster. In the case of (D), $\ddot{N}(CH_3)_3$ is a stronger nucleophile. In the case of phosphorous, the electrons are distributed over a bigger element. Hence, reaction (i) is faster.

115. The reaction is initiated by an S_N2 displacement on the less substituted carbon of the three membered ring. The $^\ominus OCH_3$ ion then acts as a neighbouring group to displace the chloride ion by an S_N2 mechanism.



116. Phenyl halides are very slow to undergo nucleophilic substitutions. Cyclohexyl halide, a secondary halide is slow to undergo S_N1 process. The tertiary halide proceeds more favourably. A tertiary allylic bromide undergoes S_N1 fastest among those listed.

117. Acid catalysed hydration of propene gives isopropyl alcohol. Hence (a) is not correct. Treating propene with dilute alkaline $KMnO_4$ brings about hydroxylation giving $CH_3CHOH-CH_2OH$. Hence (c) is also not correct. (b) and (d) give n-propyl alcohol as the major product.

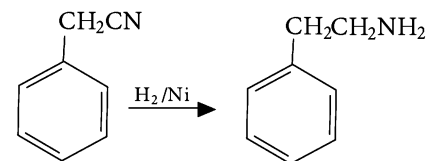
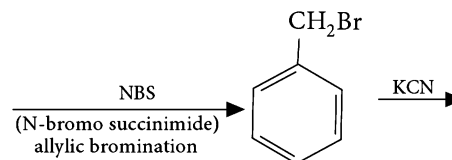
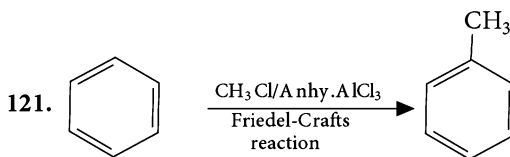
118. Only these two are tertiary alcohols. Only a tertiary alcohol gives an instant turbidity with Lucas reagent ($ZnCl_2$ and con. HCl)

(a)– is a primary alcohol while (d) is a secondary alcohol.

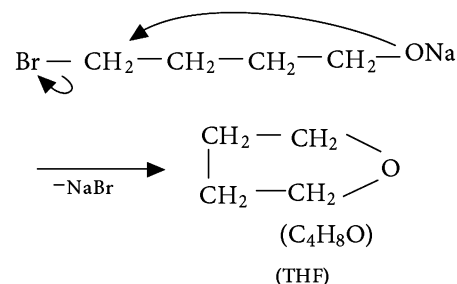
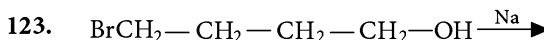
119. Alcohols containing $CH_3-CHOH-$ group and carbonyl compounds containing $CH_3-C(=O)-$ group

will give yellow precipitate of iodoform when heated with iodine and alkali.

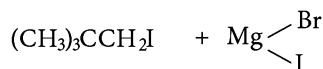
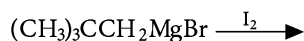
Additional Practice Exercise: Solutions



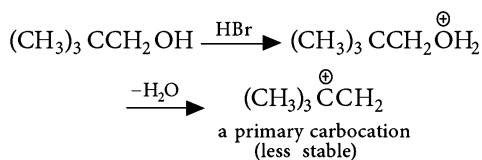
122. Method (ii) is preferable because only a substitution reaction occurs leading to the expected product, namely t-butyl methyl ether $(CH_3)_3C-O-CH_3$. In method (i), since CH_3ONa is a fairly strong base, a competing elimination reaction is also possible. So in addition to the expected substitution product, another product, an olefin $H_2C=C(CH_3)_2$ is also possible arising by elimination.



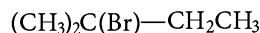
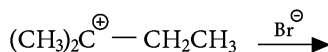
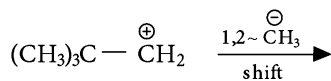
124. In the case of $(CH_3)_3CCH_2MgBr$, an anion $(CH_3)_3C-CH_2^\ominus$ is generated, and does not undergo a rearrangement, as a primary carbanion is the most stable. The primary carbanion adds on to I_2 to form a product without rearrangement.



In the case of $(\text{CH}_3)_3\text{CCH}_2\text{OH}$ which is neopentyl alcohol, the reaction proceeds as follows giving a rearranged product.



The primary carbocation, which is less stable, rearranges to a more stable tertiary carbocation by 1,2- $\text{CH}_3^\oplus$ shift.



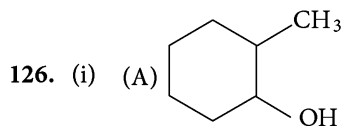
final product

125. Addition of H^+ to $\text{Cl}_3\text{C}-\text{CH}=\text{CH}_2$ results in the formation of two carbocations.

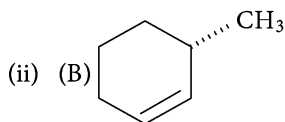


(I) is less stable than (II) due to the presence of a strong electron withdrawing (CCl_3) group attached to the carbocation.

So (II) is formed preferentially. Addition of Cl^- to (II) gives $\text{Cl}_3\text{C}-\text{CH}_2-\text{CH}_2\text{Cl}$



Anti-Markovnikov's addition of water to a double bond takes place. This reaction is known as hydroboration-oxidation.



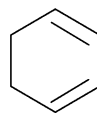
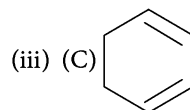
This olefin is obtained by elimination of HBr from trans-1-bromo-2-methyl cyclo-

hexane. The elimination always requires a

beta hydrogen located anti to the leaving

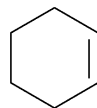
bromide. The olefin cannot be

formed as the hydrogen of the methyl substituted carbon is cis to the leaving bromide and does not depart.



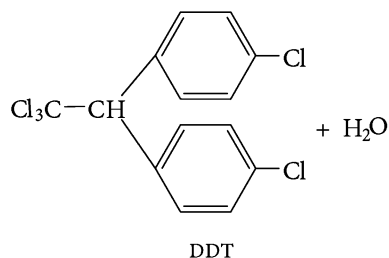
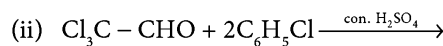
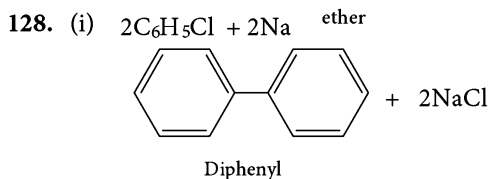
is formed as it is a conjugated olefin.

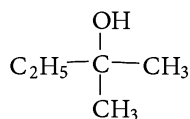
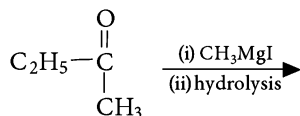
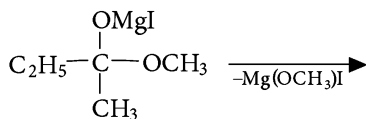
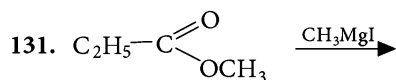
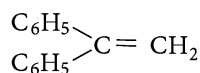
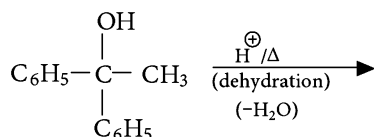
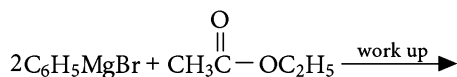
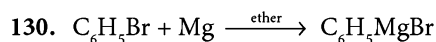
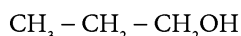
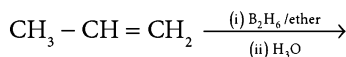
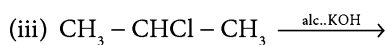
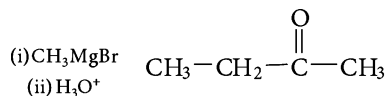
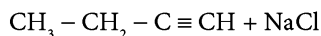
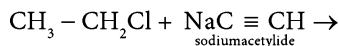
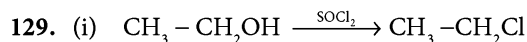
A triple bond is not formed as it cannot be accommodated comfortably in a ring system.



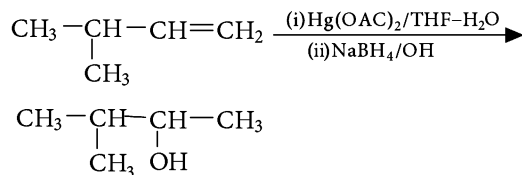
is not a favourable structure.

127. (i) The Grignard reagent formed in the first step is attacked by DCl to give the deuterated product.
(ii) The reaction is known as Corey-House synthesis of hydrocarbons. This method is very useful in the preparation of hydrocarbons having an odd number of carbon atoms which is not easily obtained by Wurtz synthesis or Kolbe's electrolysis or Frankland reaction.





132. In oxymercuration-demercuration, addition of water takes place to alkene in accordance with Markownikoff's rule



Since carbocations are not involved in the reaction, rearrangement does not occur.

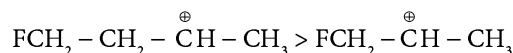
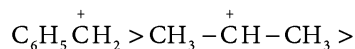
In acid catalysed hydration and addition of H_2SO_4 followed by hydrolysis, carbocations are formed as intermediates and they undergo rearrangement. So considerable quantity of 3° alcohol is formed.

Hydroboration-oxidation gives 1° alcohol with the given alkene

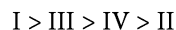
133. Among isomeric alcohols, solubility in water increases with branching. As branching increases, the surface area of the nonpolar hydrocarbon part decreases and this increases the solubility.

However, boiling point decreases with increases in branching among isomeric alcohols.

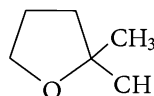
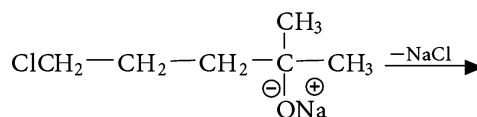
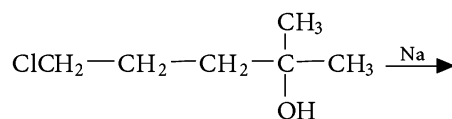
134. The order of reactivity depends on the relative stability of the carbocation intermediate formed. The relative stability of the carbocations formed from the given alcohols is



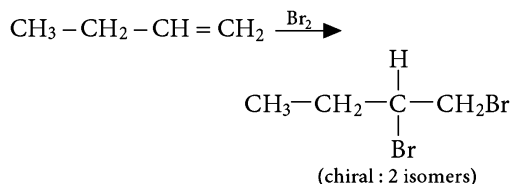
Therefore, the reactivity order of alcohols is



135. This is an example of intramolecular Williamson's ether synthesis. The product is 2, 2 - dimethyl tetrahydrofuran



136. Dehydration of butan-2-ol can give three alkenes: but-1-ene, cis-but-2-ene and trans-but-2-ene. Even though trans-but-2-ene is the major product, other products are also formed in smaller quantities. The formation of five isomeric dibromides ($C_4H_8Br_2$) is explained as follows.



cis-But-2-ene $\xrightarrow{Br_2}$ Racemic mixture of 2,3-dibromobutane (2 isomers)

trans-But-2-ene $\xrightarrow{Br_2}$ Meso-2,3-dibromobutane (one isomer)

137. The reactivity of alcohols with HBr depends upon the relative reactivity of the intermediate carbocation. The carbocations formed from I, II and III respectively are

- (i) $C_6H_5-\overset{\oplus}{CH}-CH_2-CH_3$
 (ii) $C_6H_5-CH_2-\overset{\oplus}{CH}-CH_3$ and
 (iii) $C_6H_5-CH_2-CH_2-CH_2^+$

The relative stability of these carbocations is

(i) > (ii) > (iii)

Therefore, the order of reactivity of alcohols is

I > II > III

138. Molar mass of the compound = 106 g mol^{-1}

Increase in molar mass on acetylation

$$= 190 - 106 = 84 \text{ g mol}^{-1}$$

This corresponds to the introduction of two

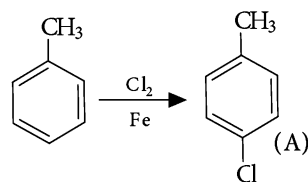
CH_3-CO groups in the compound.

139. This can also be classified as a Wurtz reaction. A cyclopropane ring is formed.

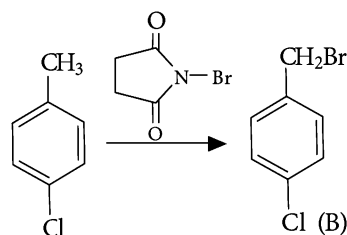
140. Thiols are stronger acids than alcohols. Hence the conjugate base $CH_3CH_2S^\ominus$ is a weaker base than $CH_3CH_2O^\ominus$. But $CH_3CH_2S^\ominus$ is more nucleophilic than $CH_3CH_2O^\ominus$ because the negatively charged electron cloud is more polarizable in the former.

141. Reaction by S_N1 mechanism leads to racemisation. So statement (d) is false. Statement (b) is correct because reaction of an alcohol with thionyl chloride takes place by S_Ni mechanism. Retention of configuration occurs in S_Ni reactions.

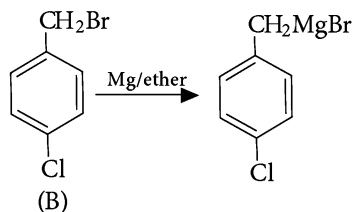
142. The sequence of reactions is



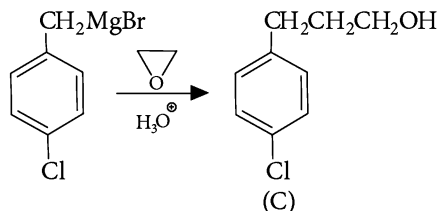
Nuclear halogenation occurs in the first step. Preferably a greater proportion of para substituted product is formed.



Allylic bromination or bromination at the side chain occurs in this step under the influence of NBS (N-bromosuccinimide).

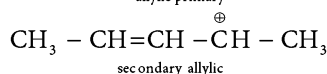
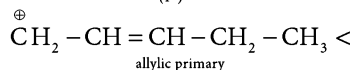
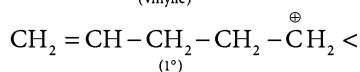


Grignard reaction occurs with the more active halide. In this case, it is the bromide.

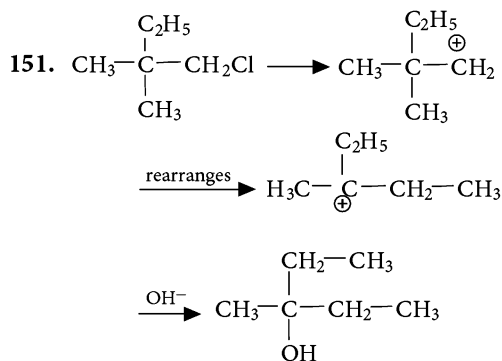
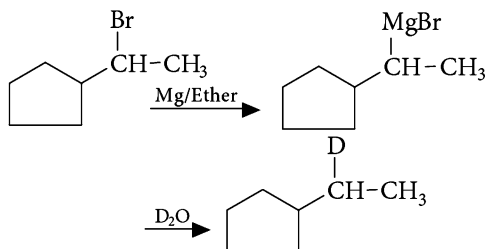


143. Alcohols (D) and (C) are tertiary alcohols, but (D) gives a more substituted olefin. Alcohols (E) and (B) are secondary alcohols, but more substituted olefin is given by (E). The last in the series is (A) which is a primary alcohol.

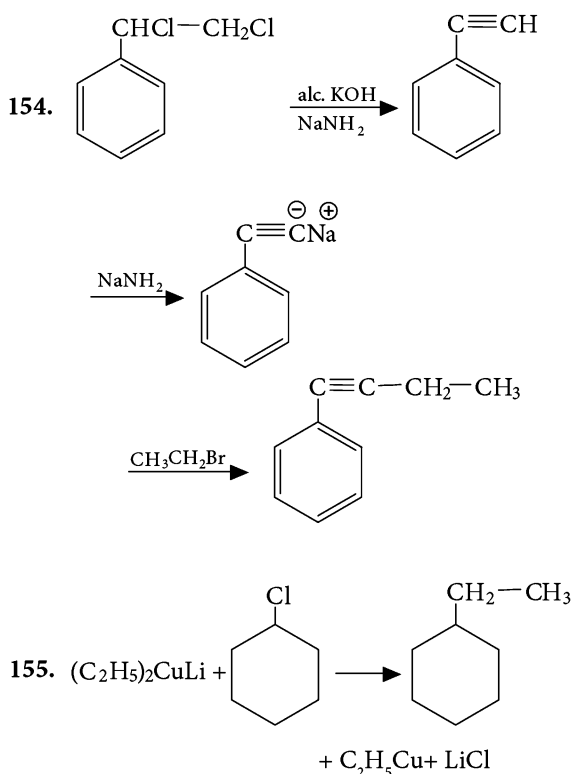
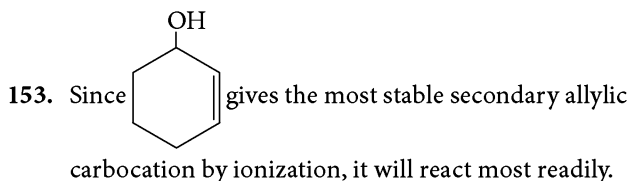
144. S_N1 reactivity is related to the relative stability of the carbocations formed by heterolysis of the C – Cl bond. The greater the stability the more reactive is the halide. The stability of carbocations is in the order



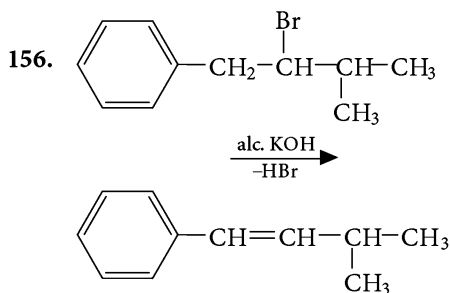
145. In presence of light, homolytic cleavage of C – I bond occurs resulting in the formation of ethyl radical ($\text{CH}_3 - \dot{\text{C}}\text{H}_2$) which combines with each other to form n – butane
146. Dehydrohalogenation using bulky bases gives least substituted alkene as the major product (Hofmann product).
147. The relative order of reactivity of halides in S_N1 reaction is related to the order of stability of carbocations.
148. The presence of highly electron withdrawing groups near the carbon containing the two OH groups makes the diol stable.
149. The most stable carbocation intermediate is formed (c) because of the +R (or + M) effect of $-\text{OCH}_3$ group. Hence (c) undergoes dehydration more readily than others.
150. The reaction sequence will be



152. The reaction (Finkelstein reaction) takes place by S_N2 reaction. Inversion of configuration occurs in S_N2 reaction.

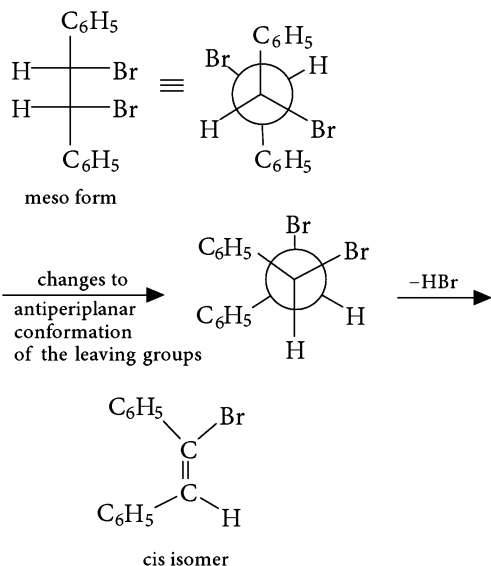


This is known as Corey–House reaction

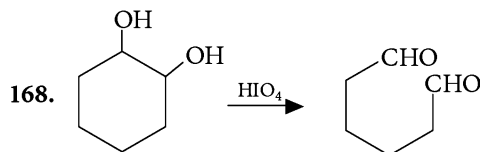


The product with double bond conjugated to the benzene ring is more stable. So it is formed predominantly. Saytzeff's rule of elimination is not obeyed in such cases.

166. Alc.KOH mainly remove one HBr from stilbene dibromide. Elimination takes place from the antiperiplanar conformation to give cis isomer of the alkene



167. The carbocation formed from (d) is stabilized by resonance involving the lone pair of $-\text{OCH}_3$ group. So it undergoes hydrolysis mainly by $\text{S}_\text{N}1$ mechanism



169. The possible isomers of dichloropropane are $\text{CH}_3\text{CH}_2\text{CHCl}_2$ (I), $\text{CH}_3\text{CCl}_2\text{CH}_3$ (II), $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Cl}$ (III), $\text{CH}_3\text{CHClCH}_2\text{CH}_2\text{Cl}$ (IV)

(since the central carbon atom is chiral, two optical isomers are possible for (IV) So total number of isomers = 5

170. Halogen directly attached to the benzene ring is not reactive towards nucleophilic substitution. Since $-\text{NO}_2$ group is at the meta position with respect to chlorine it will not facilitate nucleophilic substitution of chlorine. So substitution occurs at the benzylic position. Since the nucleophile is strong, substitution takes place mainly by $\text{S}_\text{N}2$ mechanism producing inversion of configuration in the product.

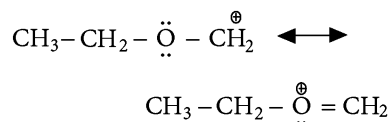
171. Statement 1 is not correct, but statement - 2 is correct. In $\text{S}_\text{N}2$ reaction of an alkyl halide with aqueous NaOH,

an alcohol having opposite configuration is formed. But the sign of rotation may or may not change. Sign of rotation is not directly linked with the configuration R or S.

Each molecule undergoing $\text{S}_\text{N}2$ reaction will undergo inversion of configuration. So statement-2 is correct.

172. Statement-1 is true but statement-2 is false. In bromobenzene, the mesomeric effect is more dominant than the inductive effect in directing the incoming electrophile. Since bromo group has +M effect, it is ortho - para directing. The para product predominates due to steric reasons.

173. $\text{CH}_3 - \text{CH}_2 - \text{O} - \text{CH}_2\text{Br}$ on ionization gives a resonance stabilized carbocation



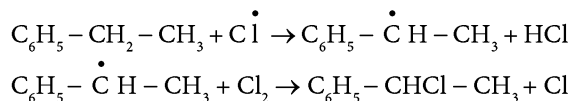
So it undergoes hydrolysis faster.

174. Statement-1 is true but statement-2 is not correct. NaCN, being ionic, will ionize giving cyanide ions (CN^-). Cyanide ion is a resonance hybrid of mainly two structures. The electron cloud and the negative charge may be more on the more electronegative nitrogen.

The formation of cyanide ($\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CN}$) as the major product is due to the greater polarization of the electron cloud on carbon and also due to the more stable C - C bond formation. C - C bond energy is more than that of C - N bond energy

175. Both statements are correct and statement-2 is the correct explanation of statement-1.

Halogenation in presence of light takes place by radical mechanism. In the case of ethylbenzene, the more stable secondary benzylic radical is formed preferentially.



176. Statement-1 is true, but statement-2 is wrong. The order of reactivity of alcohols is $3^\circ > 2^\circ > 1^\circ$ only in reactions which involve C - O bond cleavage. In reactions which involve O - H bond cleavage, the order of reactivity is $1^\circ > 2^\circ > 3^\circ$.

177. Both statements are correct and statement-2 is the correct reason for statement-1

4.98 Alcohols, Alkyl Halides and Haloarenes

Tert butyl bromide undergoes elimination in presence of the base sodium ethoxide to form 2-methyl propene.

178. Both statements are correct and statement-2 is the explanation of statement - 1

2-Iodoctane undergoes exchange of reaction with I^- by S_N2 mechanism. Each molecule undergoing exchange with I^- will undergo inversion of configuration. Since the molecule formed by exchange is the same 2-iodooctane with inverted configuration the sign of rotation also changes. Repeated Walden inversion on the reactant and product 2-iodooctane will finally give a racemic mixture which is optically inactive.

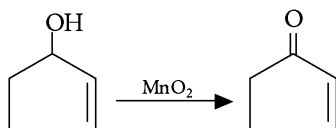
179. Both statements are correct, but statement - 2 is not the reason for statement-1. The reason for the lower dipole moment of CH_3F is the smaller C - F bond length compared to C - Cl bond length.

180. Both statements are correct and statement-2 is the explanation of statement-1

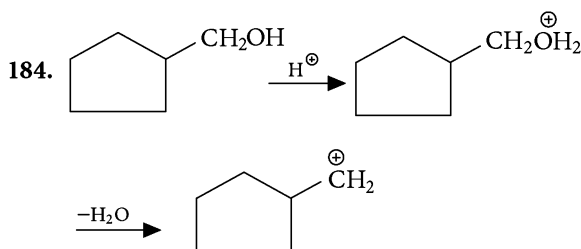
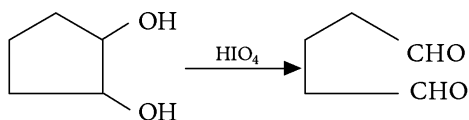
In fluorobenzene, the carbon attached to fluorine will have greater charge due to the high electronegativity of fluorine. So the attack of the nucleophile on this carbon is easier and takes place at a faster rate compared to chlorobenzene. The attack of the nucleophile and resultant formation of carbanion is the rate determining step in aromatic nucleophilic substitution.

181. Reagents given under (iii) can be used to prepare the ether $C_6H_5 - CH_2 - O - CH_3$. Reagents given under (i), (ii) and (iv) will finally give $C_6H_5 - CHOH - CH_3$

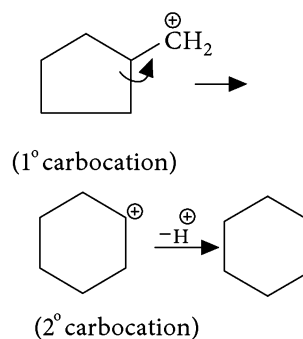
182. MnO_2 is a specific reagent that oxidizes an allylic or benzylic (1° or 2°) alcohol to give the corresponding aldehyde or ketone. This does not affect the olefinic double bond.



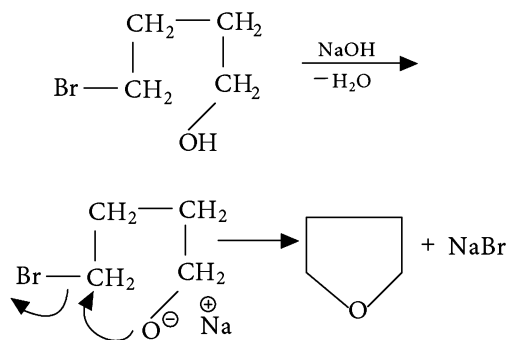
183. 1,2-glycols get readily cleaved by reagents like periodic acid HIO_4 or LTA (Lead tetra acetate) to give either an aldehyde or ketone.



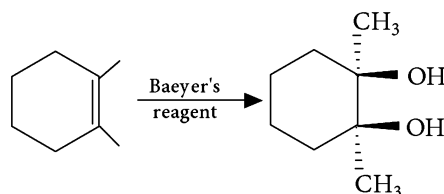
The carbocation shown above, is a primary carbocation and hence it undergoes rearrangement followed by elimination to give a ring expanded product, cyclohexene.

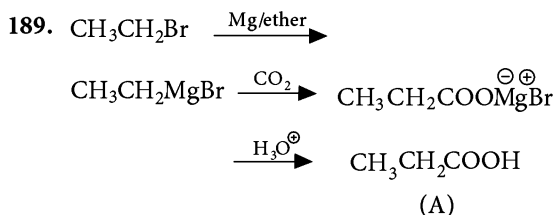
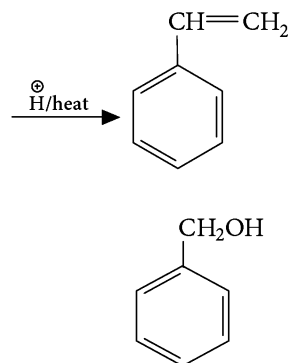
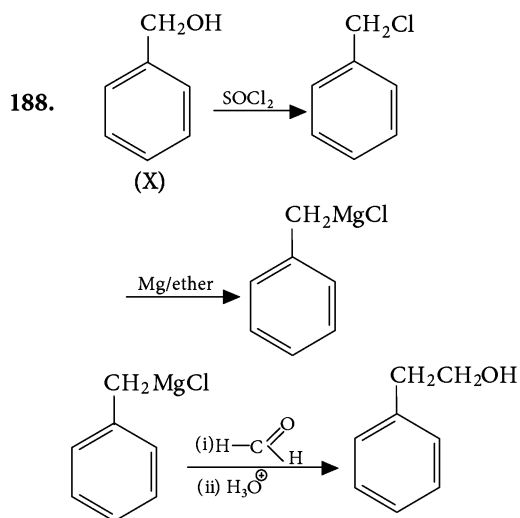
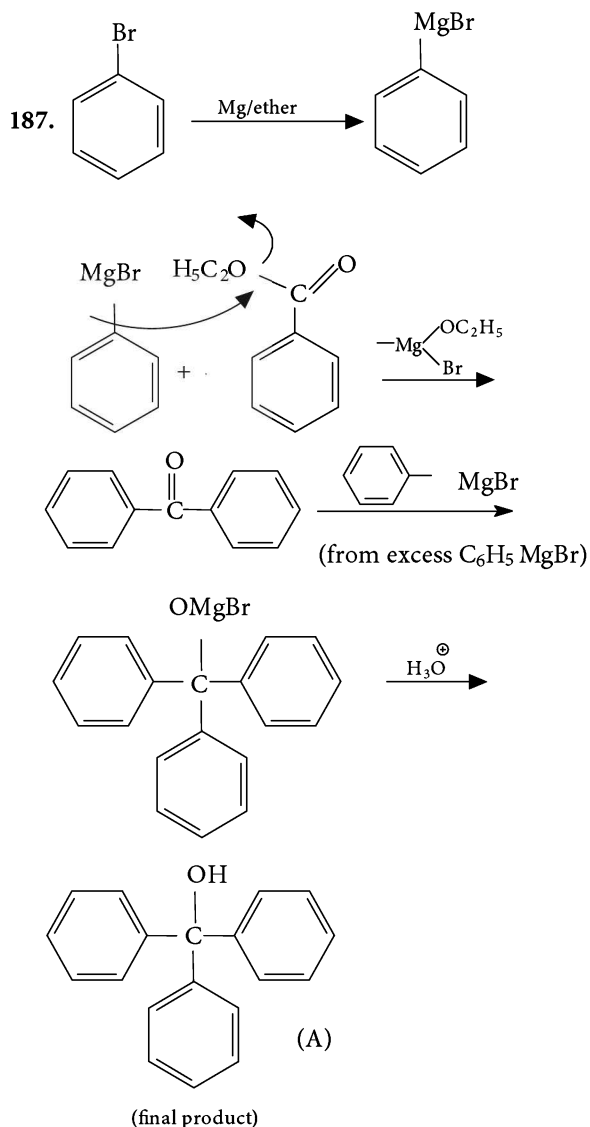


185. Cyclization occurs leading to the formation of tetrahydrofuran (THF), a cyclic ether.



186. Cold dilute alkaline $KMnO_4$ is known as Baeyer's reagent and cis-hydroxylation takes place to give cis-1,2-diol.





190. In (a), the alkyl halide is 1° and it will undergo substitution by S_N2 mechanism. In (c), the product has inverted configuration compared to the reactant and hence it also proceeds by S_N2 mechanism. In these two cases, increase in concentration of the nucleophile will increase the rate.

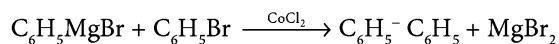
Reaction (b) and (d) proceed by S_N1 mechanism where the rate of the reaction depends only on the concentration of the substrate.

191. Under E2 Conditions (a) and (b) will give only one alkenes. But (c) and (d) can give two different alkenes each.

192. The compound can have two geometrical isomers (cis and trans). Since the compound has two similar chiral carbon atoms, each geometrical isomer can have three different orientations of groups around the two chiral carbon atoms. So six (3×2) stereoisomers are possible. They are R cis R, S cis S, R cis S, R trans R, S trans S and R trans S.

For the cis isomer, R cis R and S cis S are enantiomers. (i.e two enantiomers). For the trans isomer also, two enantiomers only are possible. So statement (d) is not correct. The number of diastereomers possible is 12. So statement (b) is also not correct.

193. (a) is Fittig reaction and (b) is Ullmann biaryl synthesis. Reaction (d) also give good yield of biphenyl.



4.100 Alcohols, Alkyl Halides and Haloarenes

194. (a), (b) and (c)

195. (a), (b) and (c)

196. Methanol gives characteristic smell of oil of winter-green (methyl salicylate) when treated with salicylic acid and a drop of con. H_2SO_4 . Ethanol does not give this special odour.

Ethanol gives yellow precipitate of iodoform when warmed with iodine and alkali. Methanol does not.

197. When heated with alcoholic AgNO_3 , benzyl chloride gives white precipitate of AgCl , but chlorobenzene does not.

When boiled with aqueous KOH , benzyl chloride forms benzyl alcohol producing chloride ions in solution. It gives white precipitate of AgCl with AgNO_3 solution. Chlorobenzene does not give any precipitate.

When refluxed with alkaline KMnO_4 , benzyl chloride is oxidized to potassium benzoate which is precipitated as benzoic acid on acidification and cooling.

Both chlorobenzene and benzyl chloride give NaCl when fused with sodium metal. So both of them will give white precipitate with AgNO_3 . So (c) cannot be used to distinguish between the two.

CHAPTER

5

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

■■ CHAPTER OUTLINE

Preview

STUDY MATERIAL

Introduction

Structure of the Carbonyl Group

Preparation of Aldehydes and Ketones

Nucleophilic Additions to Carbonyl Group

Addition Reaction Followed by Elimination of Water (Addition of Ammonia Derivatives)

Oxidation and Reduction of Aldehydes and Ketones

Name of Reactions of Carbonyl Compounds

- Concept Strands (1-9)

Carboxylic Acids

Nomenclature of Carboxylic Acids

Chemical Kinetics

Preparation of Carboxylic Acids

Properties of Carboxylic Acids

- Concept Strands (10-23)

TOPIC GRIP

- Subjective Questions (10)
- Straight Objective Type Questions (5)

- Assertion-Reason Type Questions (5)
- Linked Comprehension Type Questions (6)
- Multiple Correct Objective Type Questions (3)
- Matrix-Match Type Question (1)

IIT ASSIGNMENT EXERCISE

- Straight Objective Type Questions (80)
- Assertion-Reason Type Questions (3)
- Linked Comprehension Type Questions (3)
- Multiple Correct Objective Type Questions (3)
- Matrix-Match Type Question (1)

ADDITIONAL PRACTICE EXERCISE

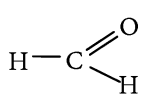
- Subjective Questions (10)
- Straight Objective Type Questions (40)
- Assertion-Reason Type Questions (10)
- Linked Comprehension Type Questions (9)
- Multiple Correct Objective Type Questions (8)
- Matrix-Match Type Questions (3)

INTRODUCTION

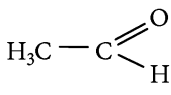
Aldehydes and ketones are compounds containing the carbonyl group and they are generally referred to as carbonyl compounds.

Aldehydes and ketones closely resemble each other in many of their properties. However, there is a basic difference in the structures of the aldehydes and ketones. Aldehydes contain alkyl or aryl group and a hydrogen atom attached to the carbon of the carbonyl group, whereas, in ketone the carbonyl group >C=O is attached to two alkyl or aryl groups. The general formula of aliphatic aldehydes and ketones is $\text{C}_n\text{H}_{2n}\text{O}$.

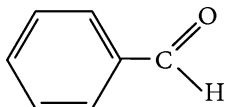
Few examples of aldehydes



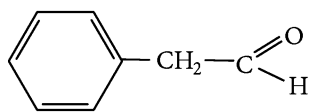
formaldehyde
(methanal)



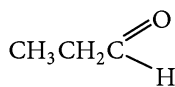
acetaldehyde
(ethanal)



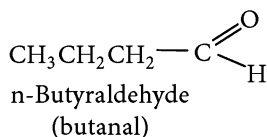
benzaldehyde



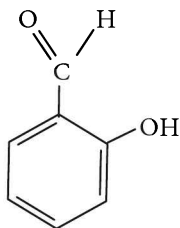
Phenyl acetaldehyde
(2-phenyl ethanal)



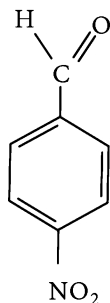
Propionaldehyde
(propanal)



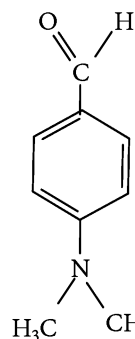
n-Butyraldehyde
(butanal)



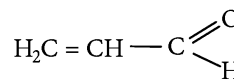
Salicylaldehyde
(2-Hydroxybenzaldehyde)



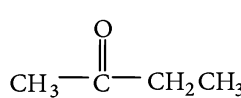
p-nitrobenzaldehyde



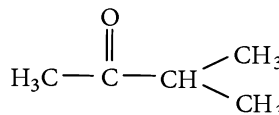
p-(N,N-dimethylamino)
benzaldehyde



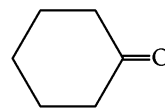
Few examples of ketones



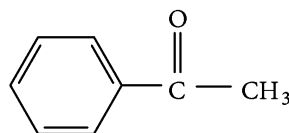
methyl ethyl ketone
(Butanone)



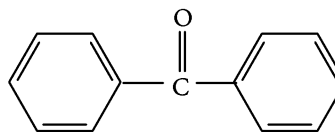
methyl isopropyl ketone
(3-Methylbutan-2-one)



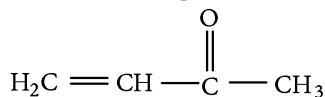
cyclohexanone



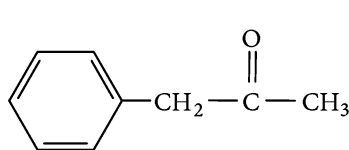
acetophenone



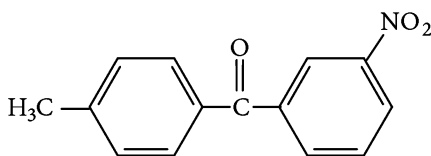
benzophenone



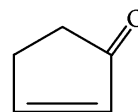
methyl vinyl ketone
(But-3-en-2-one)



benzyl methyl ketone
(1-phenylpropan-2-one)



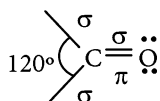
4-methyl-3'-nitro
benzophenone



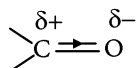
cyclopent-2
-enone

STRUCTURE OF THE CARBONYL GROUP

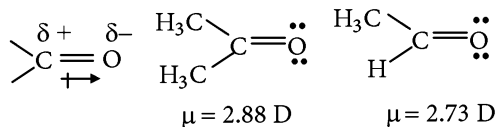
In the carbonyl group, carbonyl carbon is joined to other atoms by three sigma bonds and one pi bond. The three sigma bonds are formed by utilizing the sp^2 hybridized orbitals of carbon. The three hybridized orbitals lie in the same plane at an angle of 120° apart. The remaining one unhybridized p-orbital of carbon overlaps with the p-orbital of oxygen to form a π bond.



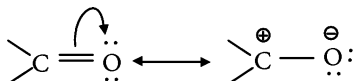
The electrons of the carbonyl double bond hold together two atoms namely carbon and oxygen of quite different electronegativity. Therefore the electrons are not equally shared between carbon and oxygen. The mobile π electron cloud is pulled more towards the more electronegative oxygen.



The carbonyl group is thus polar. The resulting imbalance in the electron density leads to a permanent dipole.

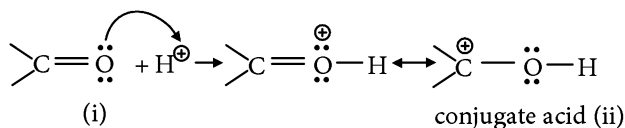


In resonance structures, a carbonyl group can be represented as



The polar representation of the carbonyl group implies that carbon is more electropositive and oxygen is more electronegative. On account of this, electron rich

nucleophiles attack the positively centered or electrophilic carbon and the electron rich oxygen or nucleophilic oxygen can react with electrophiles. Many addition reactions of carbonyl compounds are catalyzed by acids. In acid conditions, a small part of the carbonyl group will be present as its conjugate acid.



The conjugate acid (ii) will be more reactive and more electrophilic than the simple non protonated carbonyl group (i).

Aldehydes and ketones: A comparison of their reactivities

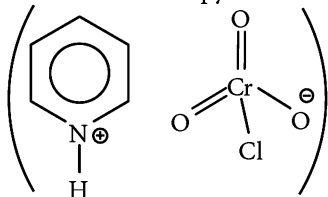
Aldehydes are more reactive than ketones. This is due to a combination of both polar and steric factors. An alkyl group is weakly electron donating. The carbonyl carbon in an aldehydic group is attached to only one alkyl group while the other group attached is a hydrogen. The ketone has two alkyl groups attached to the carbonyl carbon. Therefore, the aldehydic carbon atom is relatively more electron deficient or more electrophilic and has a greater tendency to react with nucleophiles. Steric factors also contribute to a slightly higher reactivity of the aldehydes. There are two fairly bulky (compared to one hydrogen and one alkyl group in an aldehyde) groups in a ketone. This sterically hinders the attack of the carbonyl carbon in a ketone by the nucleophiles. Because of this also, aldehydes are more reactive than ketones. Also the tetrahedral intermediate formed by the attack of a nucleophile on to the carbonyl carbon is less sterically hindered in the case of an aldehyde than ketone. Thus formaldehyde is the most reactive carbonyl compound towards nucleophilic addition reaction.

PREPARATION OF ALDEHYDES AND KETONES

From alcohols

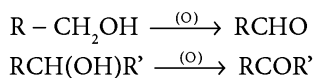
(a) By oxidation

Primary alcohols can be oxidized to aldehydes when treated with pyridinium chlorochromate (PCC)



in dichloromethane or by

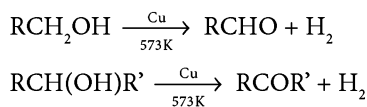
Jones reagent (H_2CrO_4 in H_2SO_4 and acetone) or by Collins reagent (CrO_3 and pyridine in dichloromethane). Secondary alcohols on oxidation yield ketones. These reagents do not affect carbon-carbon double bonds.



Stronger oxidizing agents will oxidize the aldehyde further to acid.

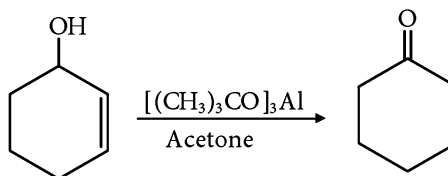
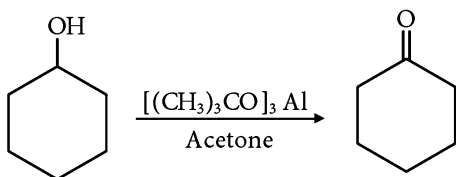
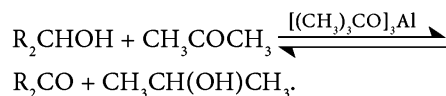
(b) Catalytic dehydrogenation

When vapours of primary or secondary alcohols are passed over copper heated to 573K, aldehydes or ketones are formed, respectively, by dehydrogenation.



(c) Oppenauer oxidation

Oppenauer oxidation involves the oxidation of secondary alcohols to ketones in presence of aluminium tert-butoxide, $[(\text{CH}_3)_3\text{CO}]_3\text{Al}$, in presence of excess acetone or cyclohexanone.



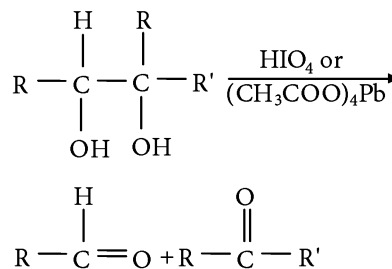
Unsaturated secondary alcohols can be oxidized to unsaturated ketones (without affecting the double bond) by this reagent.

The reverse reaction is known as Meerwein-Ponndorf-Verley (MPV) reduction.

In the MPV reduction, the carbonyl compound is heated with aluminum isopropoxide $[(\text{CH}_3)_2\text{CHO}]_3\text{Al}$ in isopropyl alcohol solution. Then the carbonyl compound is reduced to the corresponding alcohol.

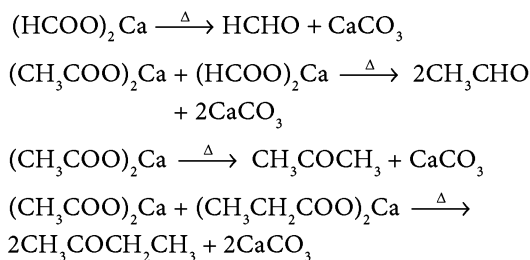
(d) From 1,2-glycols

1,2-glycols undergo cleavage with oxidizing agent like lead tetraacetate or periodic acid to form carbonyl compounds.



From fatty acids

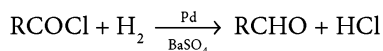
Aldehydes and ketones can be prepared by the dry distillation of calcium salts of fatty acids.



From acid chlorides

(a) Rosenmund reduction

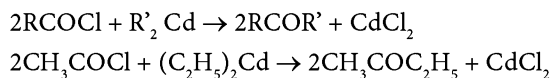
Aldehydes can be obtained by the reduction of acid chloride with hydrogen in boiling xylene using palladium catalyst supported on BaSO_4 , in presence of quinoline or sulphur.



Aldehydes can easily be reduced to alcohols but BaSO_4 in presence of quinoline or sulphur checks the reduction of aldehyde to alcohol, thus acting as a poison to the palladium catalyst. Ketones cannot be prepared by this method.

Formaldehyde cannot be obtained by this method as formyl chloride is unstable and decomposes readily to CO and HCl

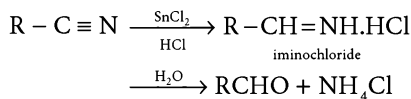
(b) Ketones can be prepared by the action of dialkylcadmium on acid chloride



From alkyl cyanides (or nitriles)

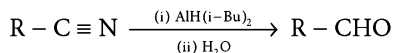
(a) Stephen's reduction

Cyanides are reduced to imine hydrochloride with SnCl_2 and HCl, which on hydrolysis give the corresponding aldehydes.



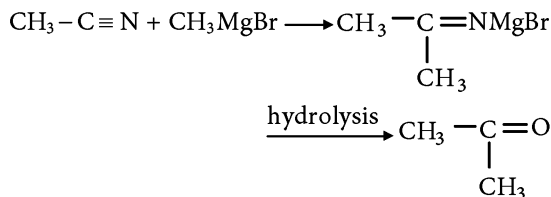
(b) Nitriles (cyanides)

Can also be reduced by diisobutyl aluminium hydride (DIBAL-H) to imines which on hydrolysis give aldehydes



(c) Reaction of cyanides

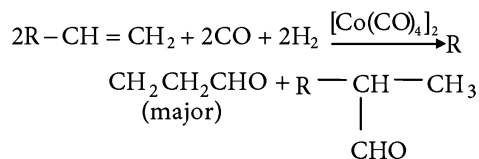
With Grignard reagent followed by hydrolysis gives ketones



From alkenes

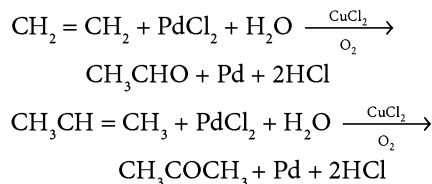
(a) Oxo process or carbonylation or formylation

An alkene reacts with CO and H_2 in presence of cobalt carbonyl as catalyst at high temperature and pressure to form aldehydes (both straight and branched chain).



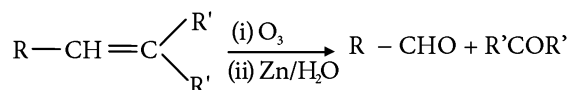
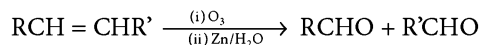
(b) Wacker process

Alkenes are oxidized to their corresponding aldehydes or ketones by treating with an acidified solution of palladium chloride and cupric chloride in presence of oxygen or air.



(c) Ozonolysis

Alkenes on ozonolysis form ozonides which on further hydrolysis with zinc dust and water yield aldehydes or ketones, depending on the structure of alkenes.



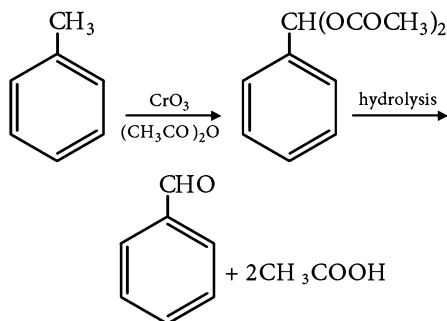
Preparation of aromatic aldehydes and ketones

The simplest aromatic aldehyde, benzaldehyde, is prepared from toluene or benzene

5.6 Aldehydes, Ketones and Carboxylic Acids

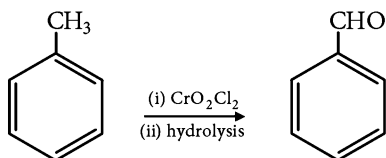
(i) Toluene on oxidation

With CrO_3 in acetic anhydride followed by hydrolysis gives benzaldehyde



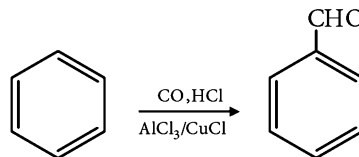
(ii) Etard reaction

Toluene can also be oxidized to benzaldehyde using a solution of chromyl chloride in CS_2



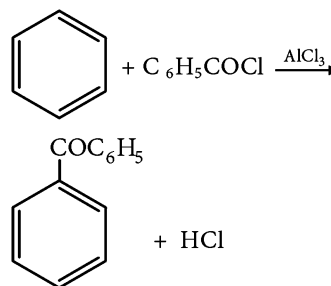
(iii) Gattermann-Koch reaction

When a mixture of CO and HCl gas is passed through benzene in presence of anhydrous AlCl_3 containing cuprous chloride, benzaldehyde is formed.



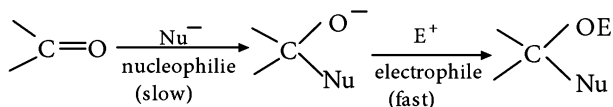
(iv) Aromatic ketones

Can be prepared by Friedel-Crafts acylation reaction

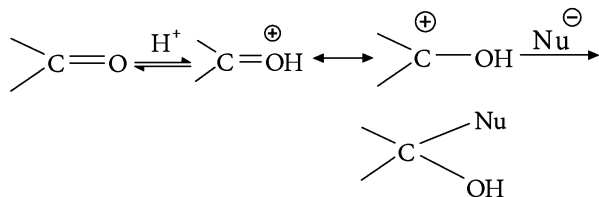


NUCLEOPHILIC ADDITIONS TO CARBONYL GROUP

Due to greater electronegativity of oxygen, the carbon atom of the carbonyl group carries a small positive charge and hence behaves as an electrophile. So a nucleophilic reagent can attack the carbonyl carbon. Thus carbonyl compounds undergo nucleophilic addition reactions. It may be represented as

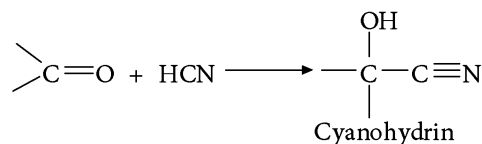


If the attacking nucleophile is weak, the nucleophilic addition reactions are carried out in weakly acidic medium. In the presence of acids, carbonyl group undergoes protonation which increases the positive charge on the carbonyl carbon and thus makes it more electrophilic.

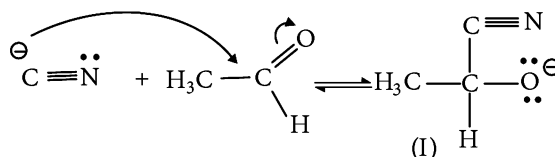


Addition of cyanide

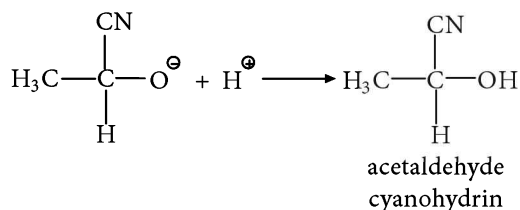
HCN adds to aldehydes and ketones to form a cyanohydrin.



Cyanide ion is the nucleophile and it adds to the carbonyl carbon to produce an oxyanion, (I).



This anion (I) abstracts a proton from solvent or medium (HCN). A cyanohydrin is produced. The reaction follows second order kinetics.

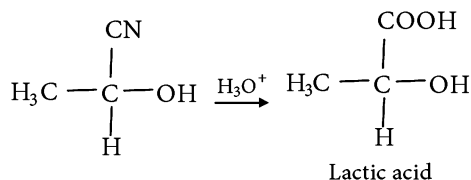


All aldehydes form cyanohydrins. Among ketones, only acetone, butanone, pentan-3-one and pinacolone $[(\text{CH}_3)_3\text{CCOCH}_3]$ form cyanohydrins.

The cyanohydrin formation from aldehydes and ketones is a synthetically very useful reaction because the acid hydrolysis of this cyanohydrin leads to a hydroxy acid.

For example,

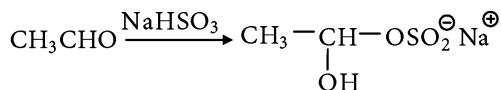
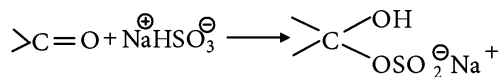
Lactic acid is formed by the hydrolysis of acetaldehyde cyanohydrin.



Mandelic acid $\text{C}_6\text{H}_5-\text{CHOH}-\text{COOH}$ is formed by the reaction of benzaldehyde with HCN followed by hydrolysis.

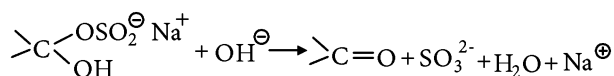
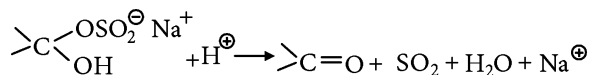
Addition of sodium bisulphite

Aldehydes and ketones add on sodium bisulphite to form crystalline solid bisulphite derivatives.



acetaldehyde bisulphite

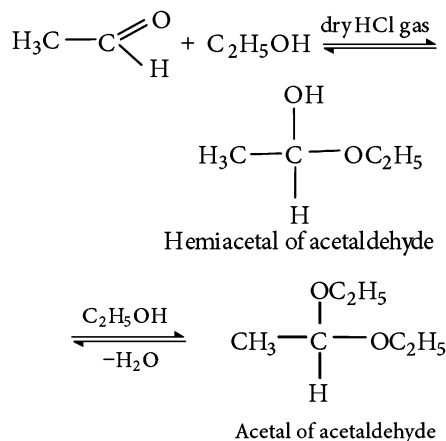
On reacting the bisulphite derivative with dilute acid or alkali, the original aldehyde or ketone is regenerated. Hence this property is used in the separation and purification of aldehyde and ketones.



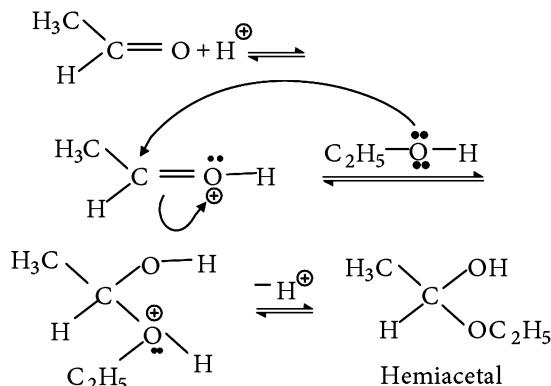
Reaction with alcohols

An aldehyde on reaction with alcohol in the presence of a small amount of dry HCl, gives first a product known as hemiacetal. The hemiacetal formed reacts with a second molecule of the alcohol to produce an acetal.

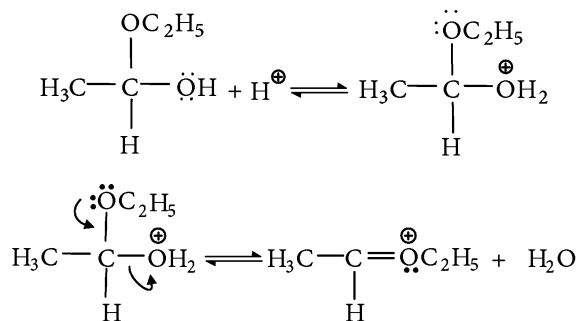
The hemiacetal results by the nucleophilic addition of the alcoholic oxygen to the carbonyl carbon of the aldehyde. For example,



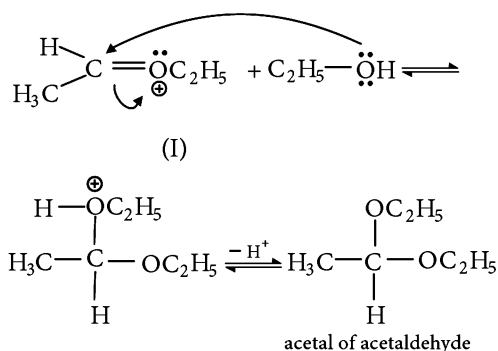
Mechanism of hemiacetal formation



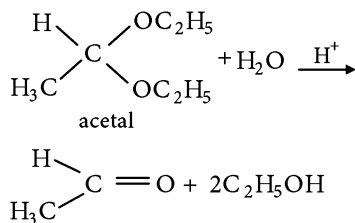
Formation of acetal



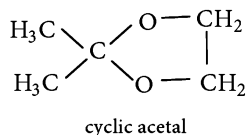
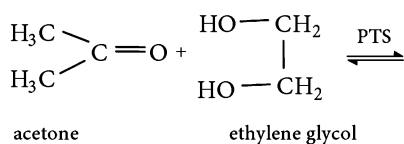
5.8 Aldehydes, Ketones and Carboxylic Acids



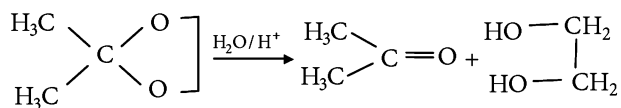
All the steps in the formation of an acetal from acetaldehyde are reversible. If the acetal is placed in water in the presence of a small quantity of an acid, like dil. HCl, acetal is hydrolysed to alcohol and aldehyde.



*Ketones do not react with monohydric alcohols under these conditions. But both aldehydes and ketones form cyclic acetal or ketal when treated with dihydric alcohol such as ethylene glycol in presence of *p*-toluene sulphonic acid (PTS)*

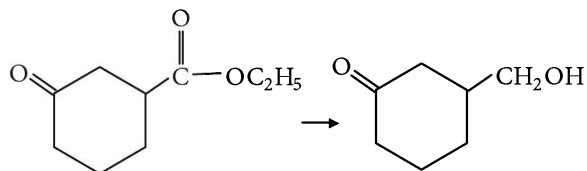


This reaction is also reversible and can give back the ketone and ethylene glycol on treatment with aqueous acid.

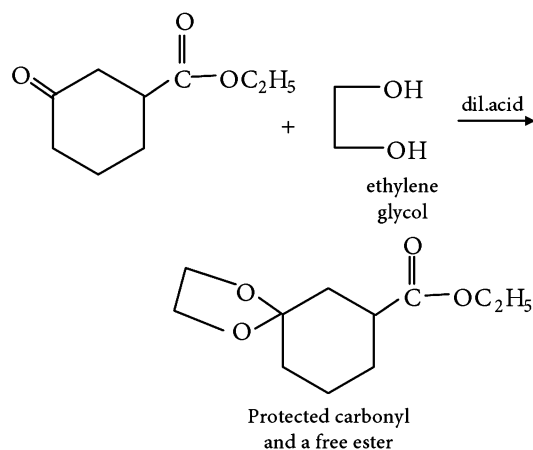


Although acetals or ketals are readily hydrolyzed to aldehydes or ketones respectively in the presence of an aqueous

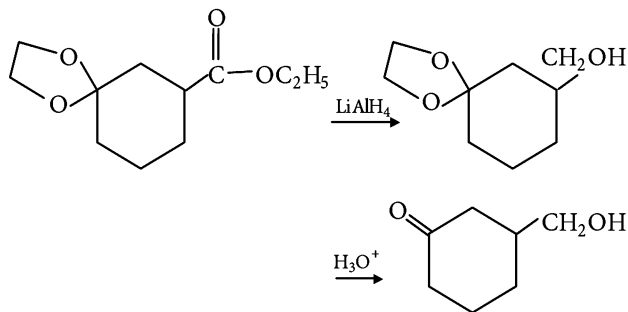
acid, they are very stable in basic solution. So formation of acetals give a convenient method of protecting the aldehydes and ketones from certain reactions in basic medium. For example for the conversion



There are two carbonyl groups in the molecule which can be reduced by reagents like LiAlH_4 . In order to prevent the attack by the reducing agent on the carbonyl group of the ketone, the best method is to protect the free ketone functional group by converting it to a cyclic ketal. The ester carbonyl does not react with the glycol to form the acetal.

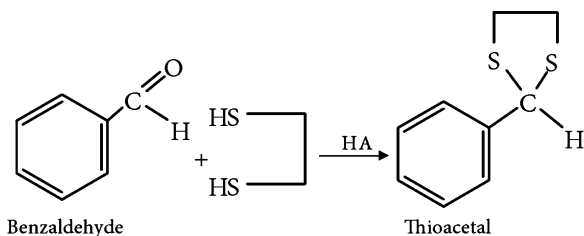


Now when a strong reducing agent like LiAlH_4 is used, only the ester gets reduced to the primary alcohol, whereas the other carbonyl group which is in the form of a ketal is not affected. This cyclic ketal is now hydrolyzed using an acid to liberate the free keto group.

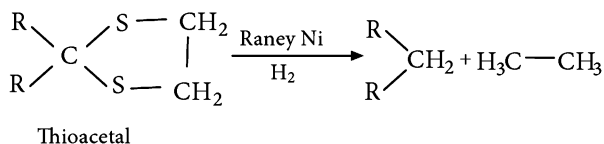


Reaction with thioalcohols

Aldehydes and ketones react with thiols (thioalcohols) to give thioacetal (or mercaptal) and thioketals (or mercaptol), respectively.



Thioacetals are important in organic synthesis because they are reduced by hydrogen (or ethanol) and Raney nickel to give hydrocarbons.

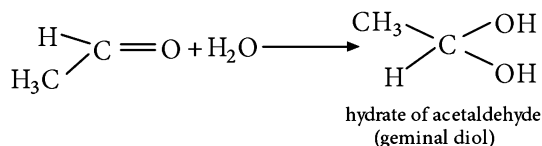


Mercaptals and mercaptols on treatment with aqueous solution of HgCl_2 in presence of CdCO_3 give back the

original aldehydes and ketones. So reaction with thiols is also used to protect carbonyl group.

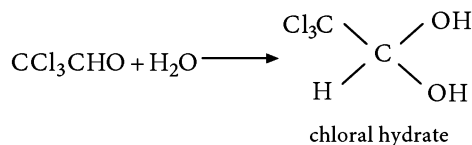
Formation of geminal diols

Aldehydes and ketones react with water and form 1,1-diols or geminal diols (two -OH groups attached to the same carbon atom).



It is not possible to isolate most of the gem diols from aqueous solution because gem diols are unstable and the overall equilibrium is always towards the free aldehyde.

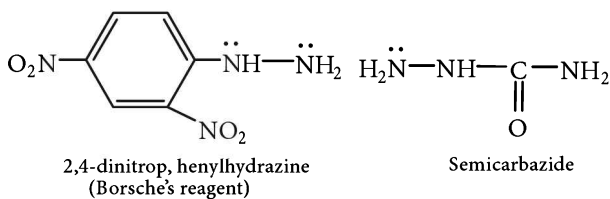
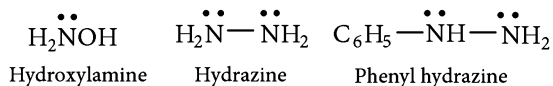
Compounds with strong electron withdrawing groups attached to the carbonyl group can form stable gem diols. For example trichloroacetaldehyde or CCl_3CHO forms a stable gem diols, viz., chloral hydrate.



ADDITION REACTIONS FOLLOWED BY ELIMINATION OF WATER (ADDITION OF AMMONIA DERIVATIVES)

Formation of oximes, semicarbazones and hydrazones

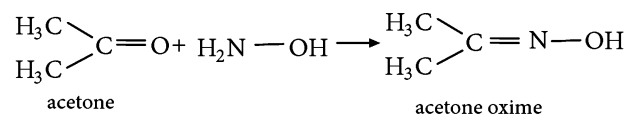
Hydroxylamine, hydrazine, phenylhydrazine, 2,4-dinitrophenylhydrazine (Borsche's reagent) and semicarbazide are the reagents which are commonly used as nucleophilic reagents containing nitrogen. Their structures are given below.



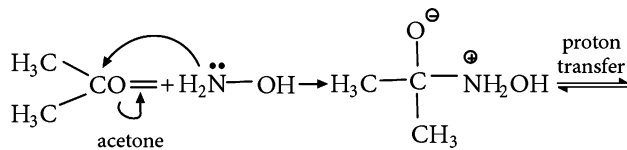
The lone pair of electrons on the nitrogen of these reagents are available for attack on the carbonyl carbon.

The reaction of a carbonyl compound with hydroxylamine ($\text{H}_2\text{N}-\text{OH}$) gives an oxime.

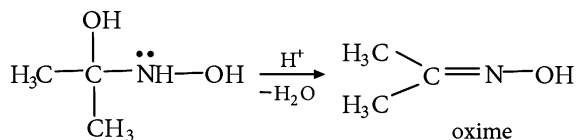
Example



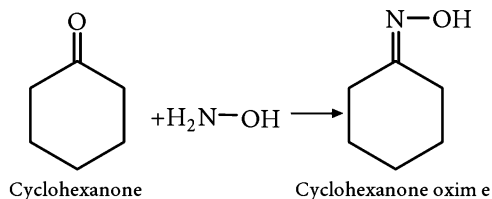
Mechanism



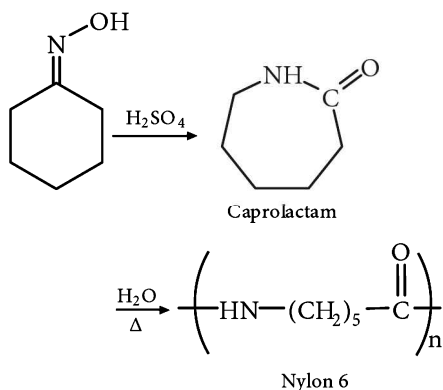
5.10 Aldehydes, Ketones and Carboxylic Acids



Cyclohexanone forms cyclohexanone oxime with $\text{H}_2\text{N}-\text{OH}$.

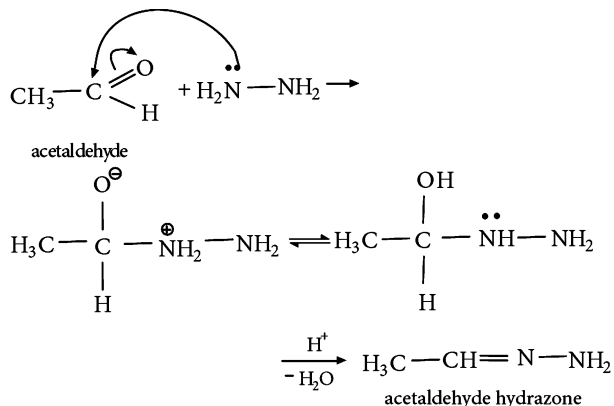


Cyclohexanone oxime undergoes Beckmann rearrangement under the influence of H_2SO_4 to give caprolactam, which undergoes ring opening to give a polymer Nylon 6, when heated with trace of water.

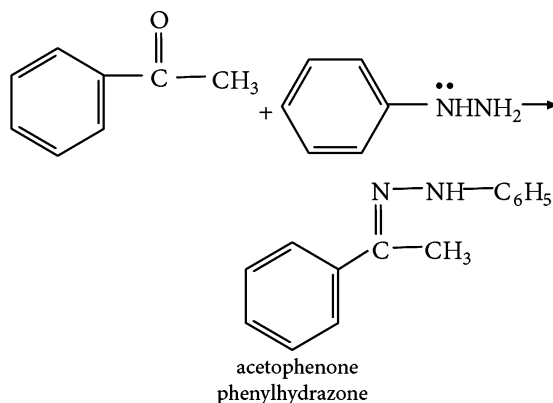


Carbonyl compounds react with hydrazine to form a hydrazone.

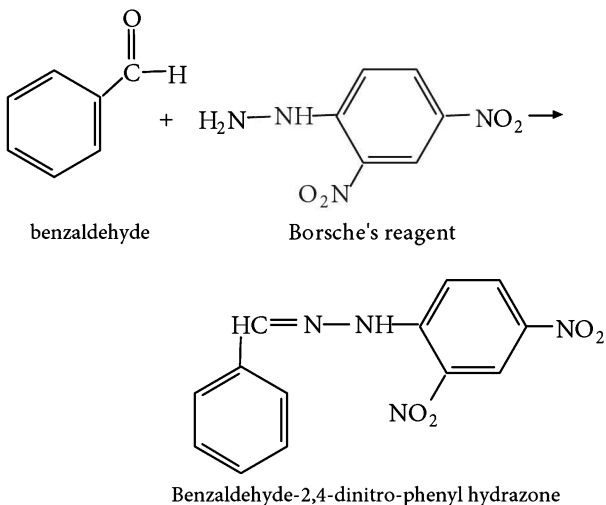
Mechanism



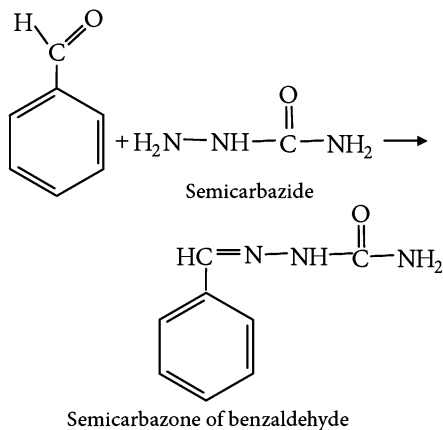
Phenylhydrazine reacts with carbonyl compounds to give phenylhydrazones. For example, acetophenone (liquid) gives a solid derivative acetophenone phenylhydrazone (melting point 105°C) on treatment with phenyl hydrazine.



2,4-dinitrophenylhydrazine (Borsche's reagent) has an advantage over phenylhydrazine in that a yellow or orange solid crystalline derivative of a higher melting point is obtained as a derivative of aldehyde or ketone.



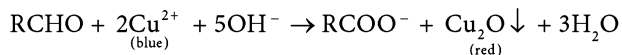
Semicarbazide ($\text{H}_2\text{NNHCONH}_2$) is another important reagent used to form a derivative of an aldehyde or a ketone.



Fehling's solution is an alkaline solution of cupric ion complexed with tartrate. (Fehling's solution A is CuSO_4 solution and Fehling's solution B is alkaline solution of sodium potassium tartrate, also called Rochelle salt). When an aliphatic aldehyde is heated with Fehling's

5.12 Aldehydes, Ketones and Carboxylic Acids

solution, the latter is reduced to a red precipitate of cuprous oxide.



Aromatic aldehydes do not reduce Fehling's solution

(iii) Reaction with Benedict's solution

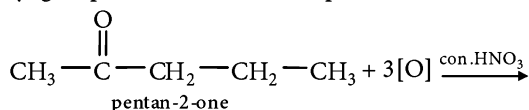
Benedict's solution is a solution of copper sulphate and alkaline sodium citrate. Aldehydes give a red precipitate of Cu_2O when heated with Benedict's solution.

Aldehydes restore the magenta colour to Schiff's reagent (rosaniline hydrochloride is dissolved in water and sulphur dioxide is passed through it until the magenta colour is discharged).

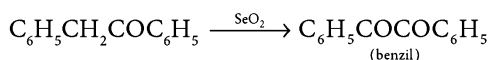
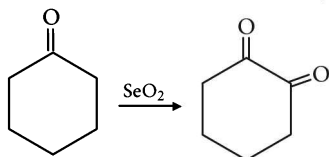
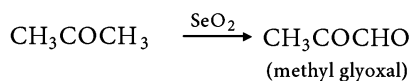
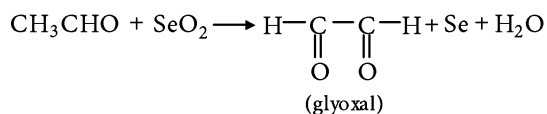
Oxidation of ketones

Ketones are not oxidized by Fehling's solution, Tollens' reagent or Benedict's solution. Ketones do not restore the colour of Schiff's reagent. These tests are thus used to distinguish aldehydes from ketones.

However, ketones can be oxidized by powerful oxidizing agents such as acidified KMnO_4 , acidified $\text{K}_2\text{Cr}_2\text{O}_7$, HNO_3 , etc under vigorous conditions. During these oxidations, cleavage of the C – C bond occurs on any one side of the keto group giving a mixture of carboxylic acids, each containing less number of carbon atoms than the original ketone. In the oxidation of unsymmetrical ketones, the keto group remains preferentially with the smaller alkyl group. This is known as Popoff's rule.



Selenium dioxide oxidizes reactive methylene group adjacent to carbonyl carbon at room temperature to form dicarbonyl compounds.

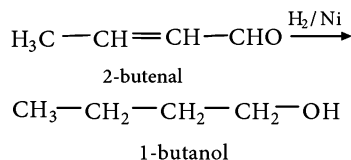


Reduction to alcohols

Aldehydes on reduction give 1° alcohols while ketones on reduction give 2° alcohols.

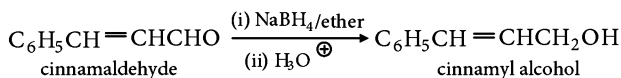
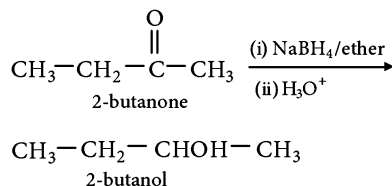
Reduction can be carried out either by catalytic hydrogenation or by using complex metal hydrides.

Unsaturated aldehydes are reduced by hydrogenation in the presence of Raney nickel as a catalyst to give primary alcohols.



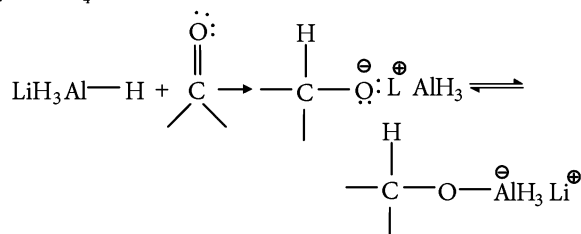
In this case, not only the aldehyde group is reduced to the primary alcohol but the olefinic double bond is also reduced to give the saturated hydrocarbon. So hydrogenation method is not selective.

Lithium aluminium hydride (LiAlH_4) and sodium borohydride (NaBH_4) are two important reducing agents used for the conversion of aldehydes and ketones to alcohols. NaBH_4 is less reactive, mild and more selective than LiAlH_4 . These reagents generally do not reduce the carbon - carbon double bonds.



The reagent (NaBH_4) is highly selective in reducing the aldehyde without affecting the double bond. Lithium aluminium hydride is a very powerful reducing agent which can reduce esters, acids, aldehydes and ketones to alcohols. It can also reduce amides to amines. It reacts violently with water to liberate hydrogen.

The mechanism of reduction of carbonyl compound by LiAlH_4 is shown below.

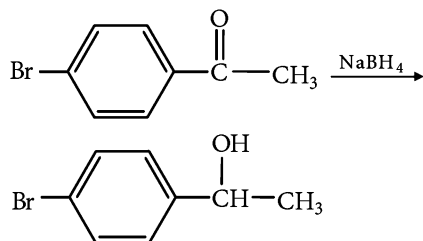


One mole of lithium aluminium hydride or sodium borohydride can reduce four moles of aldehyde or ketone. The

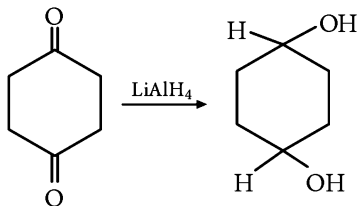
alkoxy lithium aluminium hydride formed in each step provide the hydride for a subsequent step until all four hydrogen atoms are utilized. Final hydrolysis yields the alcohol.

Examples

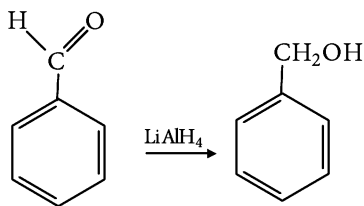
- (i) 4-bromophenyl methyl ketone on reduction with NaBH_4 gives 1-(4-bromophenyl)ethanol.



- (ii) Cyclohexane-1,4-dione on reduction with LiAlH_4 will give cyclohexane-1,4-diol.

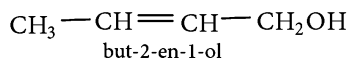


- (iii) Benzaldehyde on reduction with LiAlH_4 gives benzyl alcohol

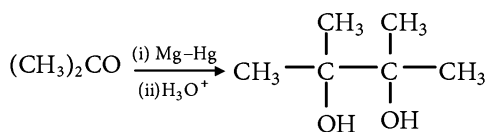


- (iv) $\text{H}_3\text{C}-\text{CH}=\text{CH}-\text{CHO} \xrightarrow{\text{NaBH}_4}$

crotonaldehyde



Reduction of acetone with magnesium amalgam followed by hydrolysis gives pinacol

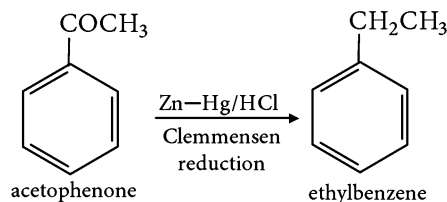


Aldehydes and ketones can be reduced to hydrocarbons by means of two processes

- (i) Clemmensen reduction
- (ii) Wolff - Kishner reduction

Clemmensen reduction

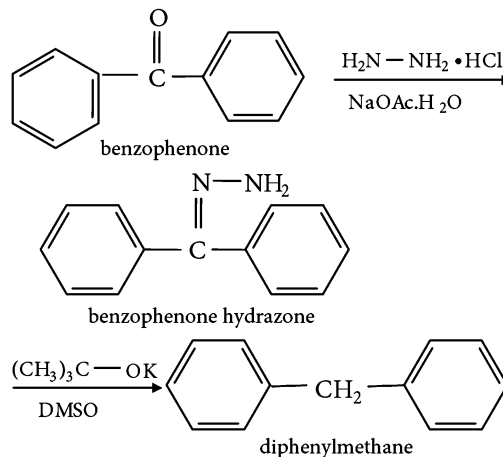
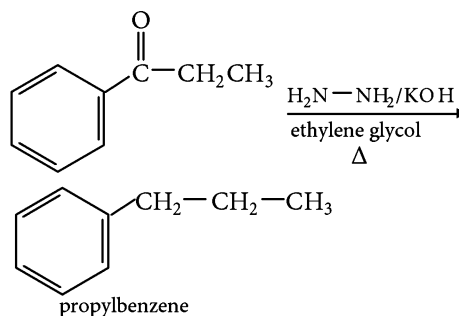
Amalgamated zinc and concentrated hydrochloric acid are the reagents used in this reduction. The carbonyl group is reduced to the hydrocarbon without affecting other reducible group like $-\text{OH}$, $-\text{NO}_2$, $-\text{COOH}$, etc.



Clemmensen reduction is carried out in acid medium. The role of mercury with zinc is to reduce the vigour of the reaction. This works well for ketones than for aldehydes. It fails for acid sensitive and high molecular weight substrates.

Wolff-Kishner reduction

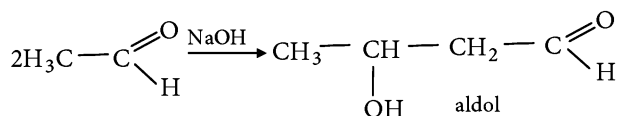
The Wolff - Kishner reduction involves heating of aldehyde or ketone with hydrazine and a strong base like KOH or NaOH in a high boiling solvent such as ethylene glycol. The reduction can be carried out under moderate conditions in dimethyl sulphoxide (DMSO) with potassium t-butoxide as base.



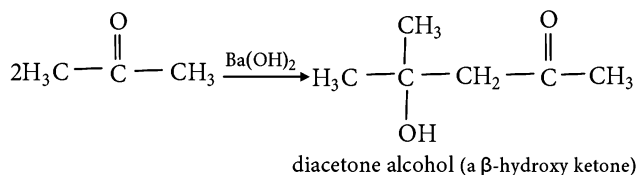
NAMED REACTIONS OF CARBONYL COMPOUNDS

Aldol condensation

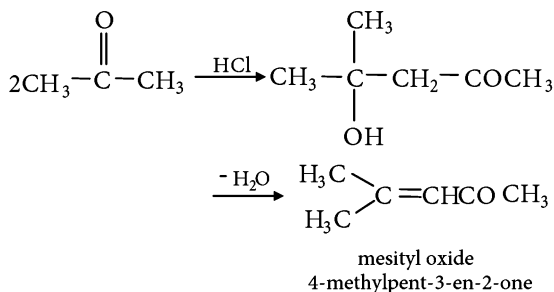
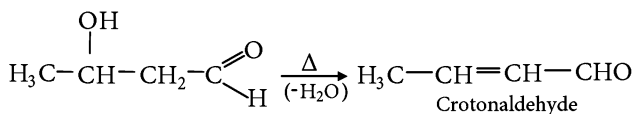
Aldehydes and ketones containing α -hydrogen atoms, when treated with dilute alkali, undergo condensation to form β -hydroxy aldehyde or β -hydroxy ketone. A simple example of an aldol condensation is



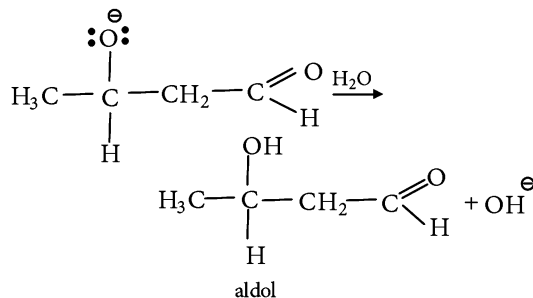
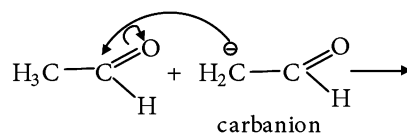
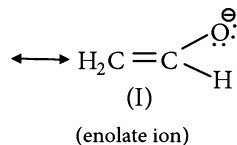
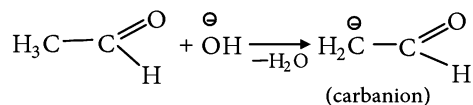
Aldol condensation also takes place in presence of dilute acids such as dilute HCl. Acetone is converted to an aldol namely diacetone alcohol or 4-hydroxy-4-methylpentan-2-one by reaction with barium hydroxide.



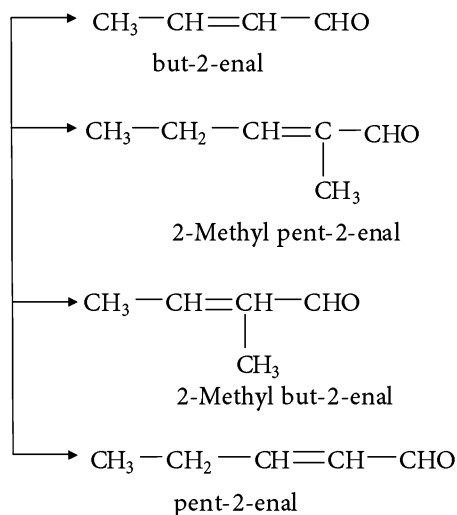
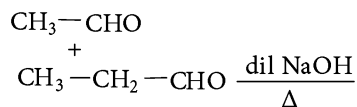
On heating, aldols undergo dehydration to form α , β -unsaturated aldehyde or ketone. When acid catalysts are used, dehydration follows the condensation. For example, the aldol formed from acetaldehyde undergoes dehydration to give crotonaldehyde. Similarly, the aldol formed from acetone gives mesityl oxide after dehydration.



The aldol formation is a dimerization. Examination of the product suggests that the α -carbon (carbon adjacent to carbonyl group) of one aldehyde or ketone forms a bond with the carbonyl carbon of the other aldehyde or ketone. Base catalyzed aldol condensation occurs through the formation of a carbanion intermediate.

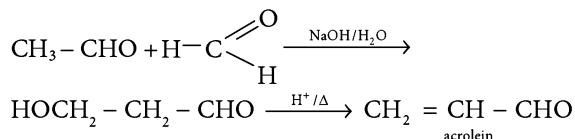


Aldol condensation between two different aldehydes or ketones is known as cross aldol condensation. For example, a mixture of ethanal and propanal when heated with dilute NaOH solution gives four different products.

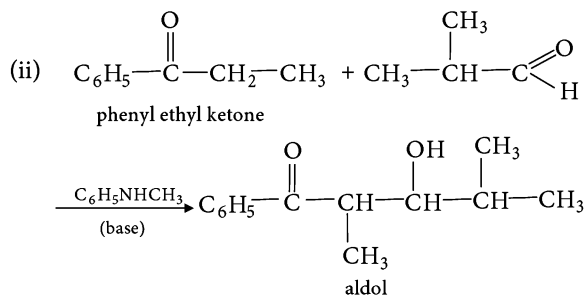
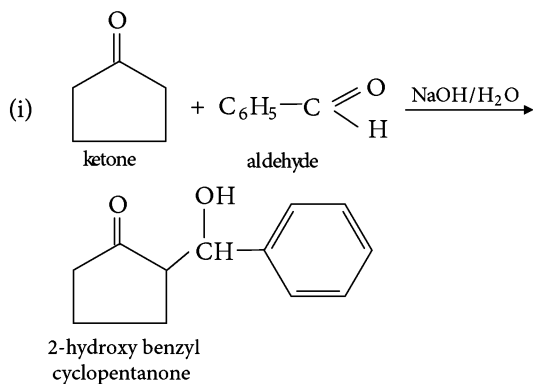


The last two products are the real cross products. If only one carbonyl group contains α -hydrogen, then only one cross product is formed.

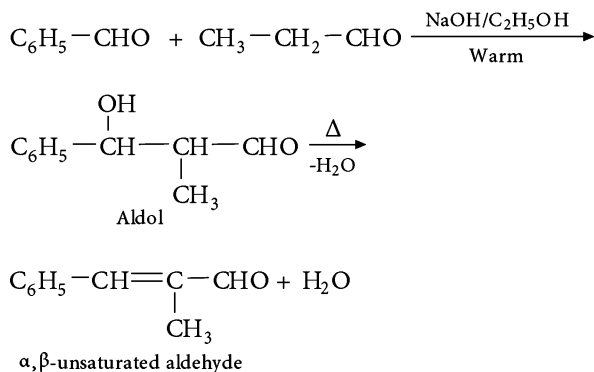
A useful example of crossed aldol condensation to give specific product is to condense acetaldehyde with formaldehyde in the presence of a base.



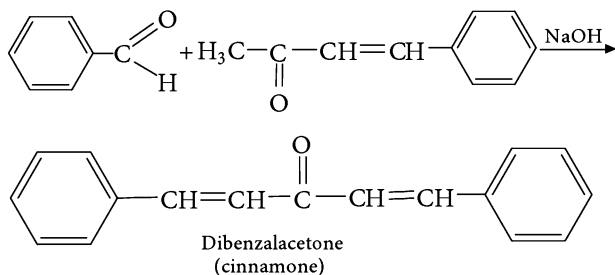
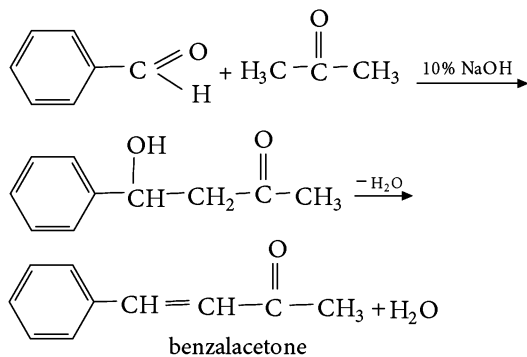
When a mixed aldol condensation occurs between an aldehyde and a ketone, the aldehyde is always the electrophile. The lower activity of the ketone carbonyl group accounts for this result. Two classical examples of an aldol condensation are given



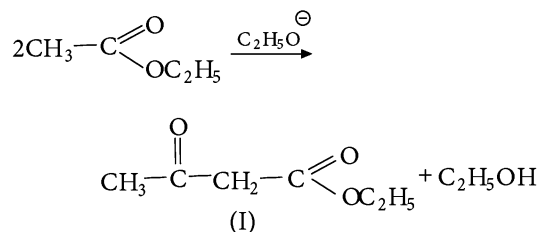
Dehydration or loss of water is a process that usually accompanies immediately after the formation of an aldol.



A useful extension of aldol condensation is Claisen-Schmidt condensation. This is a type of condensation when any aromatic aldehyde (or ketone) is condensed with an aliphatic aldehyde or a ketone with an α -hydrogen in presence of dilute alkali to form an α,β -unsaturated compound.



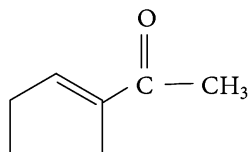
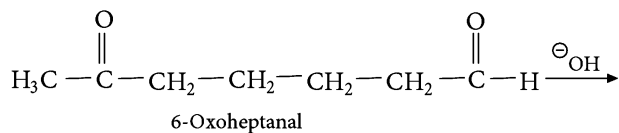
Claisen-ester condensation or Claisen condensation is another useful extension of aldol type condensation. Claisen condensation involves the condensation of an ester with another molecule of ester or ketone or aldehyde. For example, acetoacetic ester (I) is made by the Claisen condensation of ethylacetate under the influence of a base like $\text{C}_2\text{H}_5\text{O}^-$.



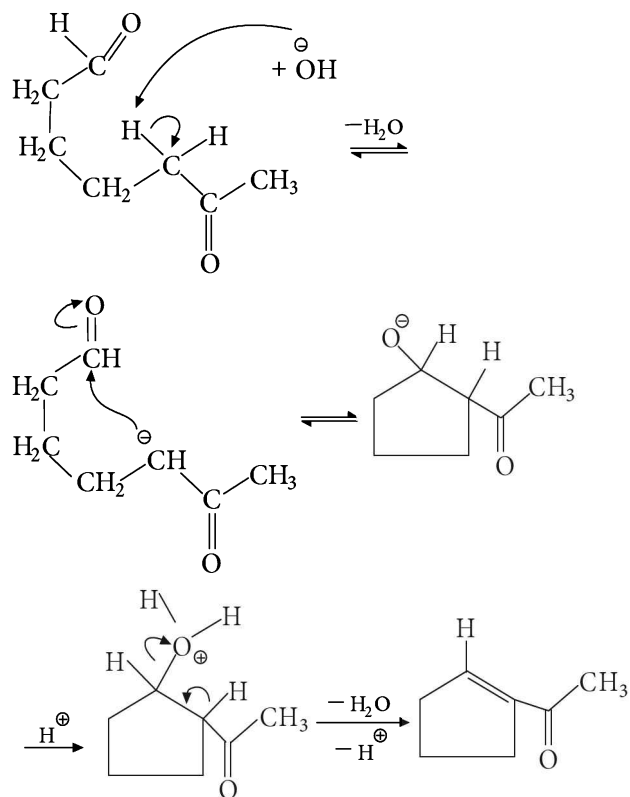
Cyclizations via aldol condensation

Five or six membered rings can be conveniently synthesized by an intramolecular aldol condensation. The following ketoaldehyde cyclizes to give 1-cyclopentenyl methyl ketone

5.16 Aldehydes, Ketones and Carboxylic Acids



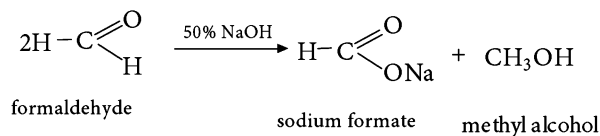
The reaction mechanism involves the formation of enolate anions.



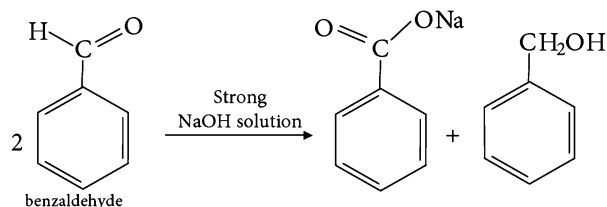
Cannizzaro reaction

Aldehydes which do not contain any α -hydrogen atom undergo self oxidation and reduction when treated with concentrated alkali to form the corresponding acid and alcohol. This type of an oxidation-reduction process is known as disproportionation.

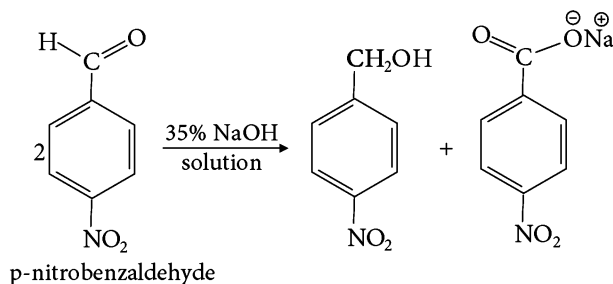
The classical example of a Cannizzaro reaction is the one in which formaldehyde is converted to sodium formate and methanol in presence of sodium hydroxide.



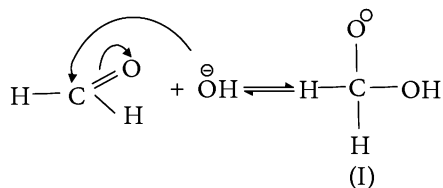
Benzaldehyde undergoes Cannizzaro reaction, to give sodium benzoate and benzyl alcohol, under the influence of strong NaOH.



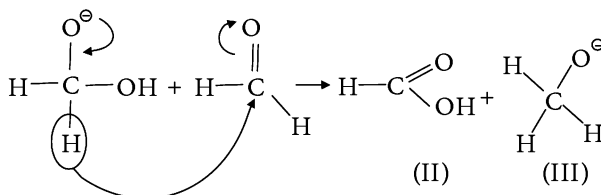
p-nitrobenzaldehyde on reaction with strong aqueous NaOH, gives p-nitrobenzyl alcohol and sodium p-nitrobenzoate.



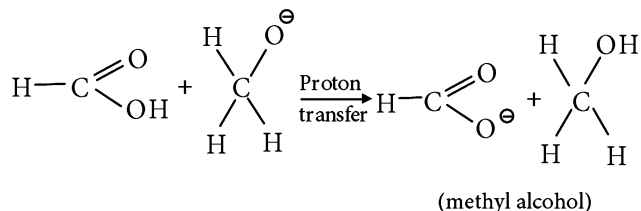
Mechanistically, Cannizzaro reaction is a hydride transfer reaction. The hydroxide ion, OH^- is the nucleophile which attacks the carbonyl carbon in the first step.



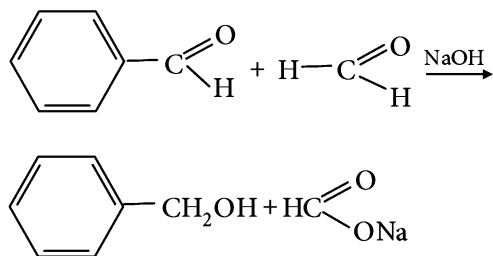
In the second step, the intermediate (I) formed, donates a hydride (H^-) ion to the second molecule of the aldehyde. This is the slow and rate determining step.



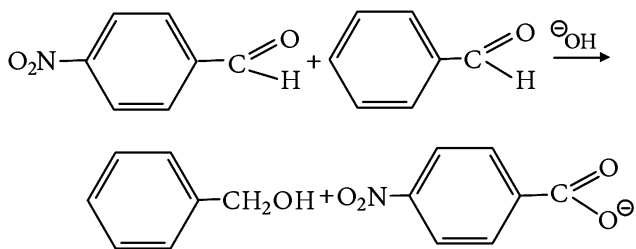
In the third step, there is a rapid proton transfer from (II) to (III) to result in sodium formate and methanol.



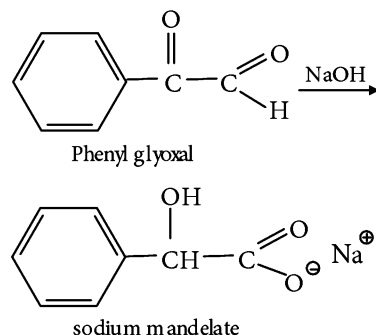
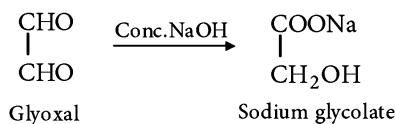
Crossed Cannizzaro reactions can be carried out by using equimolar quantities of two different aldehydes. Whenever, HCHO is used as one of the aldehydes, it is always the HCHO which undergoes the oxidation, while the other aldehyde suffers reduction.



When p-nitrobenzaldehyde is reacted with benzaldehyde in the presence of alkali, the carbonyl carbon of the aldehyde which is more electrophilic will be attacked by the alkali. In this case, the carbonyl carbon of p-nitrobenzaldehyde is more electrophilic. The reaction sequence will be

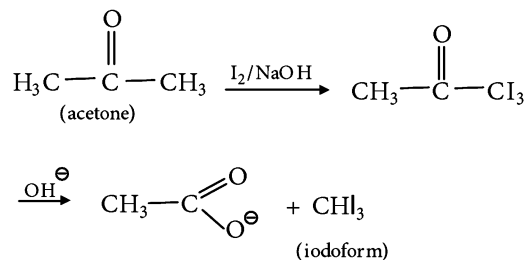


In intramolecular Cannizzaro reaction one part of the molecule undergoes oxidation while the other part suffers a reduction.

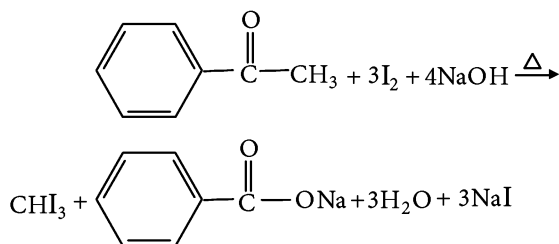


Haloform reaction

Aldehydes and ketones containing the CH_3CO - group and alcohols containing $\text{CH}_3\text{CH}(\text{OH})$ - group when treated with halogen and alkali give the corresponding haloform (chloroform, bromoform or iodoform). This is known as haloform reaction. For example, acetone when heated with iodine and NaOH gives a yellow crystalline precipitate of CHI_3 . This is known as iodoform reaction.

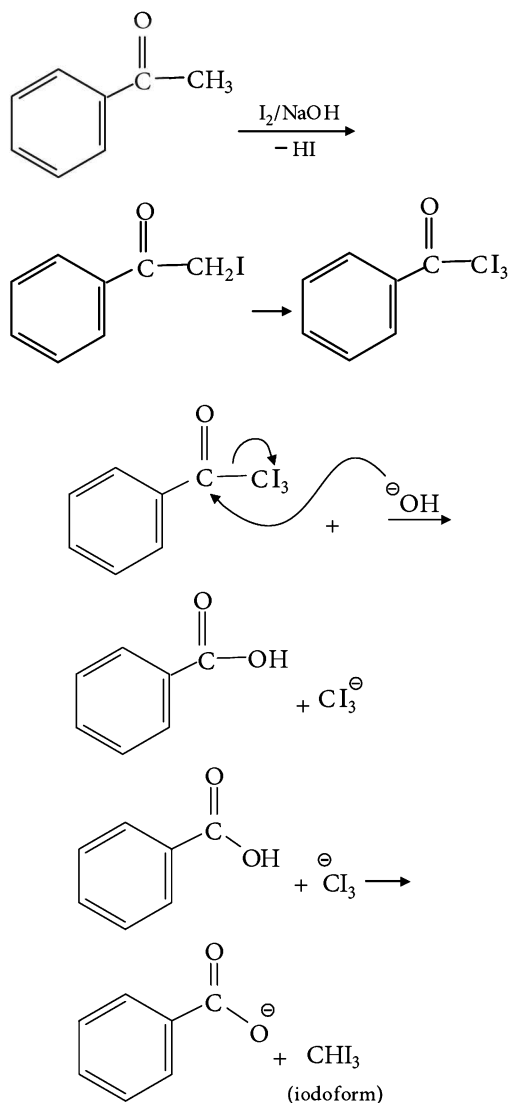


A positive haloform reaction is given by most of the compounds containing an acetyl group attached either to carbon or hydrogen or by compounds, which are oxidized under the conditions of the test to the derivatives containing the acetyl group. For example, compounds which answer iodoform test are ethyl alcohol (on oxidation gives acetaldehyde), isopropyl alcohol (on oxidation gives acetone) and secondary butyl alcohol, $\text{CH}_3\text{CHOHCH}_2\text{CH}_3$ (on oxidation gives methyl ethyl ketone). Another example of iodoform reaction is



5.18 Aldehydes, Ketones and Carboxylic Acids

The mechanism of the reaction involves the following steps. A triiodo compound is formed by the action of iodine in alkali. The triiodo compound obtained undergoes cleavage in presence of NaOH. A carboxylic acid is formed, which loses its proton to Cl_3^- so that CHI_3 and a carboxylate anion are formed as final products.

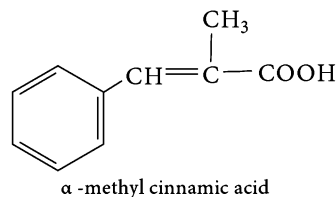
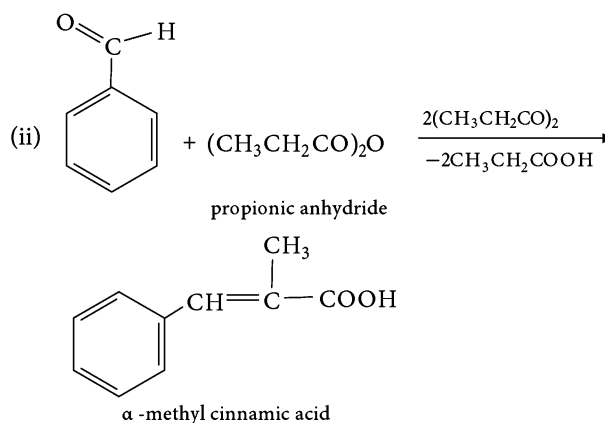
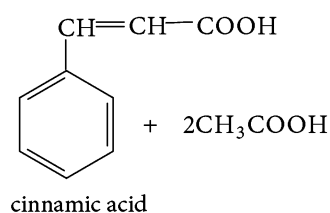
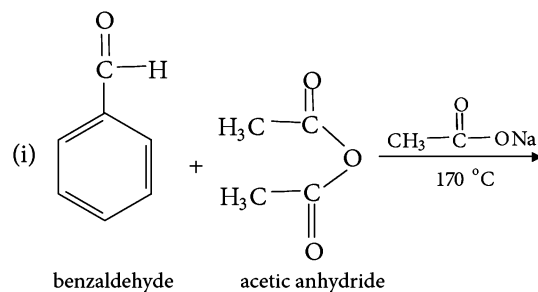


Iodoform is a crystalline yellow solid with a melting point of 120°C . It has a characteristic sharp odour. It is insoluble in water but soluble in ether and alcohol.

Perkin reaction

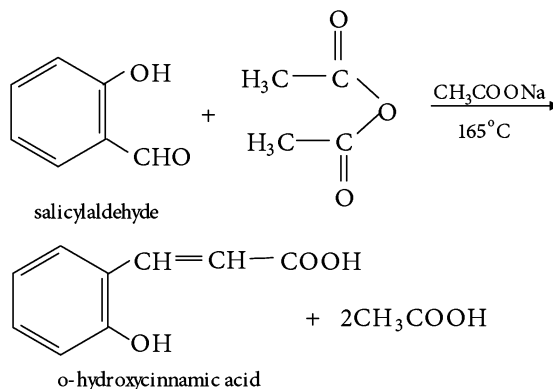
When aromatic aldehydes are heated with the anhydride of an aliphatic acid in the presence of the sodium salt of the same acid, an α, β -unsaturated acid is formed. This reaction is termed as Perkin reaction.

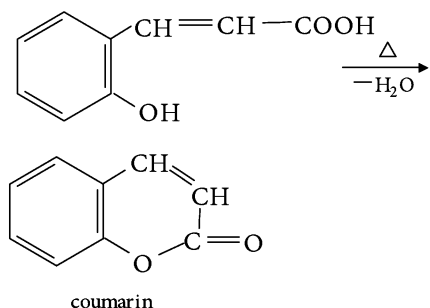
Cinnamic acid is formed by Perkin reaction from benzaldehyde and acetic anhydride in the presence of sodium acetate.



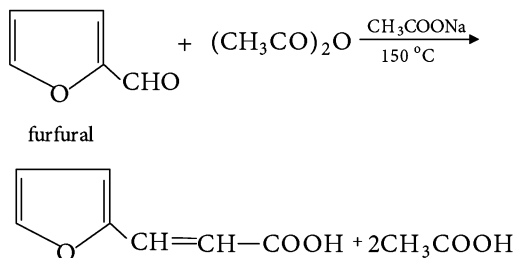
Electron withdrawing substituents on benzaldehyde increase the yield of the correspondingly substituted cinnamic acids and electron releasing substituents decrease the yield of the substituted cinnamic acids.

An important extension of Perkin reaction is in the synthesis of coumarin, which is used in perfumery.



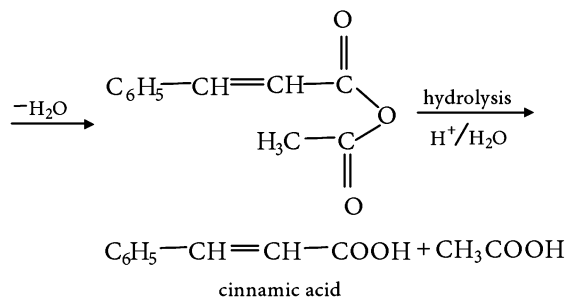
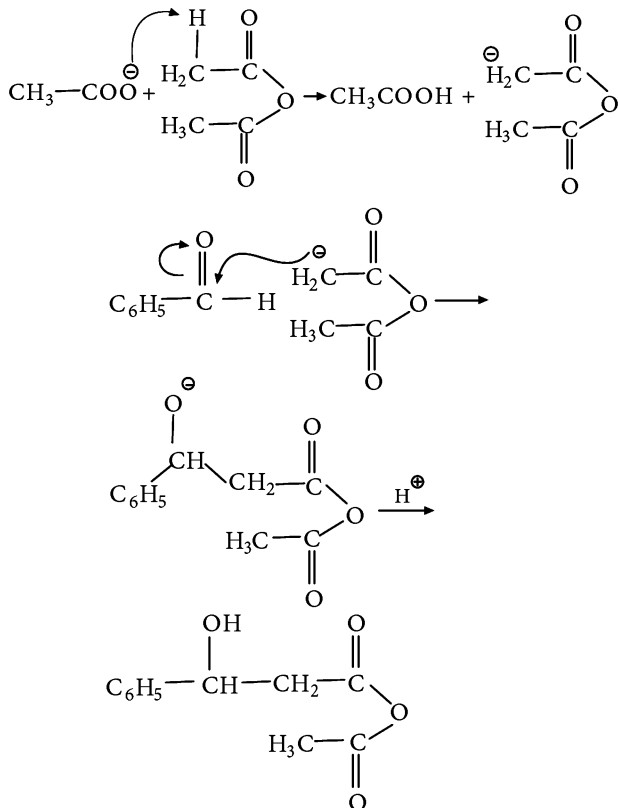


Heterocyclic aromatic compounds like furfural also undergo this reaction.



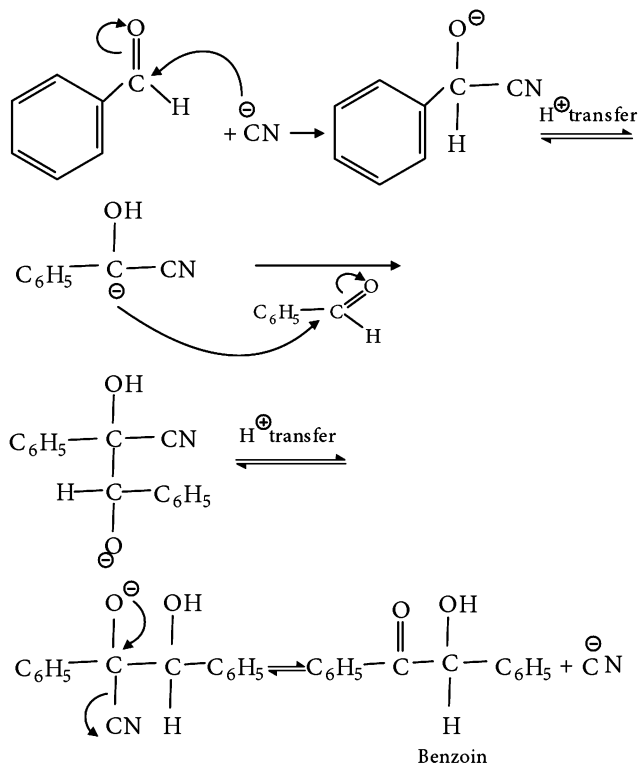
Mechanism of Perkin reaction

Perkin reaction is an aldol type of addition of anhydride to aromatic aldehydes.

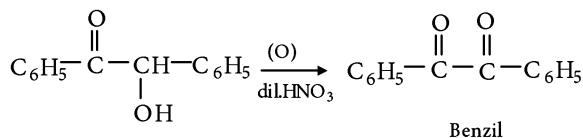


Benzoin condensation

When benzaldehyde is refluxed with aqueous ethanolic KCN or NaCN solution, benzoin is obtained. Aliphatic aldehydes do not undergo benzoin condensation. The importance of this reaction is the specificity in the use of cyanide ion as a catalyst. The reaction fails in the absence of cyanide. Two molecules of benzaldehyde are involved. The mechanism of benzoin condensation is



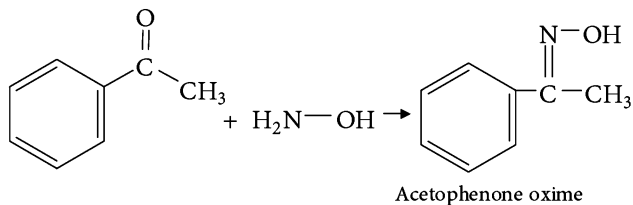
Benzoin can be oxidized to benzil by mild oxidation with dil. HNO_3 .



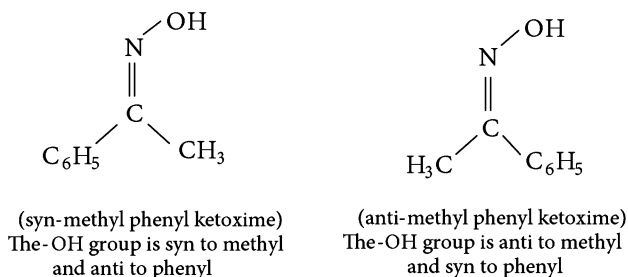
5.20 Aldehydes, Ketones and Carboxylic Acids

Beckmann rearrangement

When a ketone is treated with hydroxylamine, an oxime is formed. Ketoximes when treated with catalysts such as con. H_2SO_4 , polyphosphoric acid, SOCl_2 , PCl_5 , etc undergo a rearrangement to form substituted amides. This is known as Beckmann rearrangement.

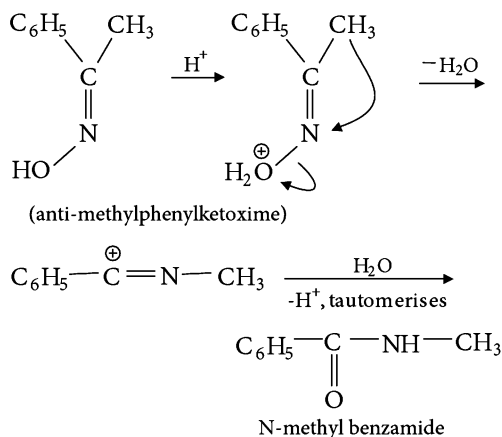


Acetophenone oxime exists in two stereochemical forms namely syn and anti oximes.



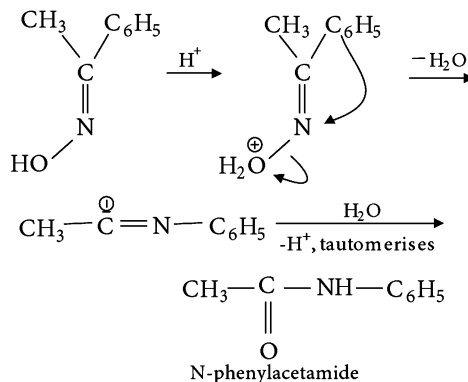
Whenever an oxime undergoes Beckmann rearrangement, the group which is anti to the $-\text{OH}$ undergoes migration. Two different products are likely when oximes of unsymmetrical ketones undergo Beckmann rearrangement, depending on the migrating group which is anti to $-\text{OH}$. From the products obtained, it is possible to obtain information about the stereochemistry of oxime.

For example,



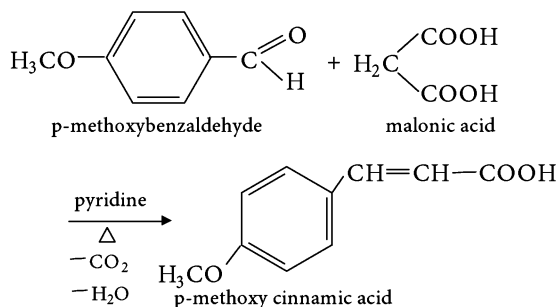
In this case, methyl group migrates from carbon to nitrogen.

The other geometrical isomer of the oxime undergoes Beckmann rearrangement with the migration of phenyl group as shown below.



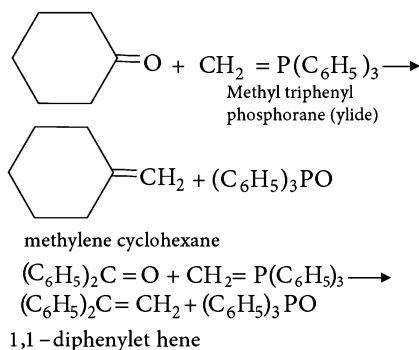
Knoevenagel reaction

Active hydrogen compounds like malonic acid condense with aldehydes to give α,β -unsaturated acids like cinnamic acid. This is also an aldol type condensation, catalyzed by weak organic bases. This reaction is known as Knoevenagel reaction.



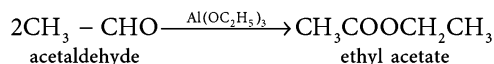
Wittig reaction

The reaction of an aldehyde or ketone with a phosphorus ylide to give a substituted alkene is called Wittig reaction. Phosphorus ylides are prepared by treating phosphonium halides with a base.



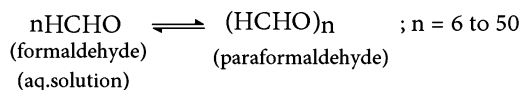
Tischenko reaction

All aldehydes (with or without α -hydrogen) undergo Cannizzaro type disproportionation reaction when treated with aluminium ethoxide. Under these conditions, the acid and alcohol produced by disproportionation combine together to form esters. This is called Tischenko reaction.

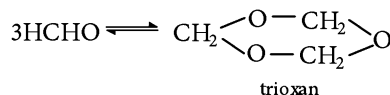


Polymerization

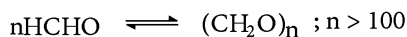
- (a) Formaldehyde solution on evaporation gives a solid, paraformaldehyde, which reforms formaldehyde on heating.



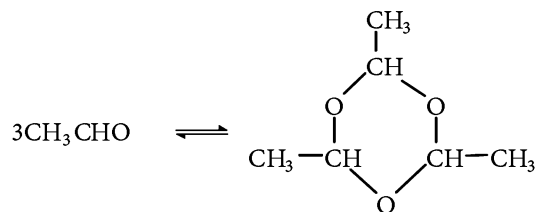
- (b) When allowed to stand at room temperature, formaldehyde gas slowly polymerizes to white solid, metaformaldehyde (or trioxan or trioxymethylene).



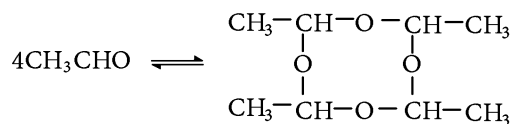
- (c) When formaldehyde solution is heated with concentrated sulphuric acid, polyoxymethylenes, are formed.



- (d) In presence of weak alkalies like $\text{Ca}(\text{OH})_2$, formaldehyde polymerizes to a mixture of sugars of formula, $\text{C}_6\text{H}_{12}\text{O}_6$ which is known as formose or α -acrose.
- (e) When acetaldehyde is treated with a few drops of conc. H_2SO_4 , a vigorous reaction takes place leading to the formation of paraldehyde (trimer).

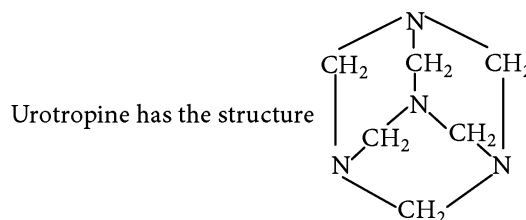
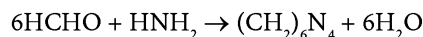


- (f) When acetaldehyde is treated with a few drops of conc. H_2SO_4 at 0°C , the tetramer, metaldehyde, is formed.

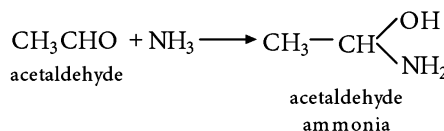


Reaction with ammonia

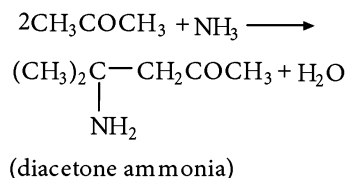
Formaldehyde forms a crystalline compound, hexamethylene tetramine (or urotropine) with ammonia.



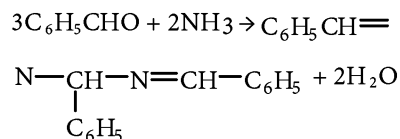
Other aldehydes form addition product with ammonia.



Acetone reacts with ammonia to form diacetone ammonia.



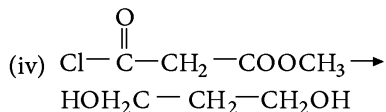
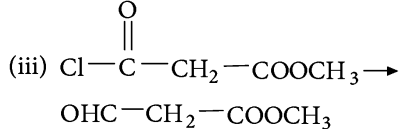
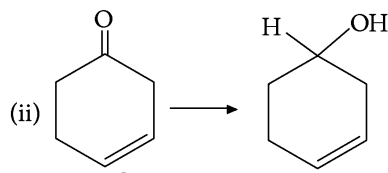
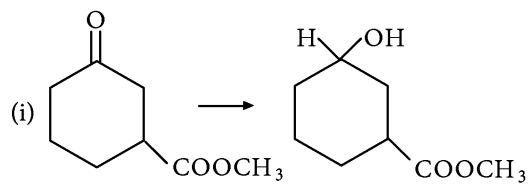
Benzaldehyde forms hydrobenzamide with ammonia



CONCEPT STRANDS

Concept Strand 1

Suggest a suitable reducing agent for the following conversions.



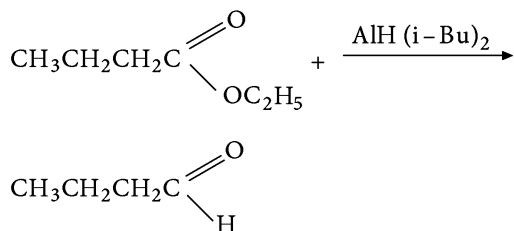
Solution

- (i) NaBH_4
 (ii) LiAlH_4
 (iii) H_2/Pd catalyst supported over BaSO_4 or CaCO_3 poisoned by sulphur or quinoline (Rosenmund reaction)
 (iv) LiAlH_4

Concept Strand 2

How is $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ prepared from ethylbutyrate?

Solution



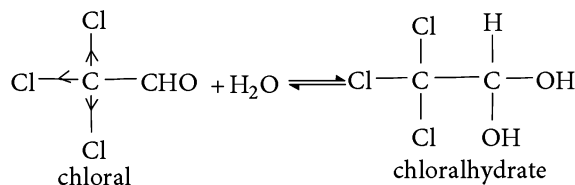
Diisobutyl aluminium hydride, DIBAL – H is used for reducing an ester to an aldehyde.

Concept Strand 3

What is chloral hydrate? Explain the extraordinary stability of chloral hydrate.

Solution

Chloral combines with water to form a very stable hydrate, which can be isolated.

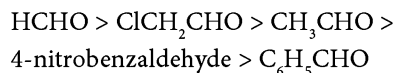


The carbon-chlorine dipole which tends to destabilize the carbon-oxygen bond in chloral reduces the partial positive charge on carbonyl carbon and makes it more stable when it is in the form of a hydrate.

Concept Strand 4

Arrange the following aldehydes in the order of decreasing reactivity towards nucleophilic addition reactions: PhCHO , CH_3CHO , HCHO , ClCH_2CHO and 4-nitrobenzaldehyde.

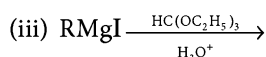
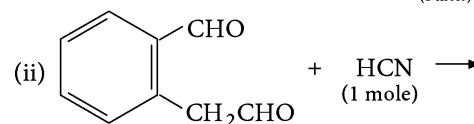
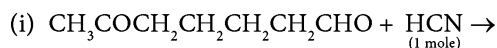
Solution

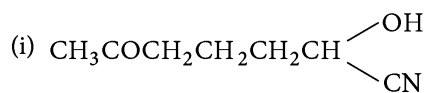


The reaction of the carbonyl group depends on the availability of positive charge on the carbonyl carbon or the electrophilicity of carbonyl cation.

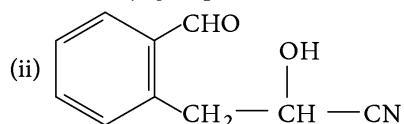
Concept Strand 5

Predict the products of the reactions given below.

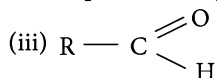


Solution

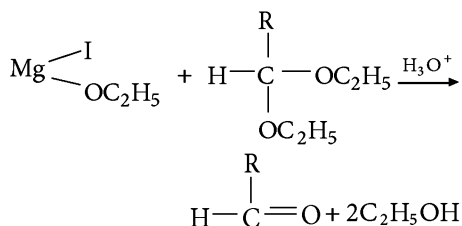
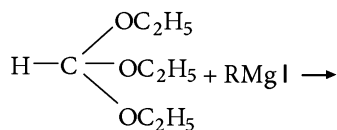
Aldehyde carbonyl is more reactive than a ketone carbonyl group.



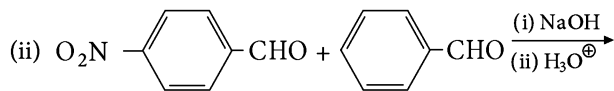
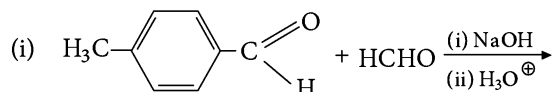
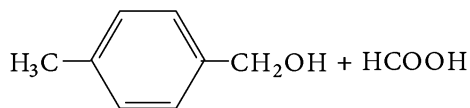
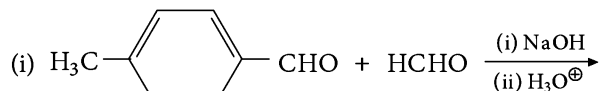
The carbon directly attached to the phenyl is less electrophilic, while the other aldehyde group is like aliphatic aldehyde.



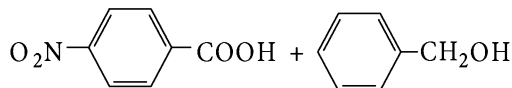
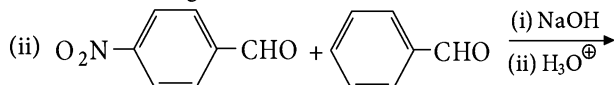
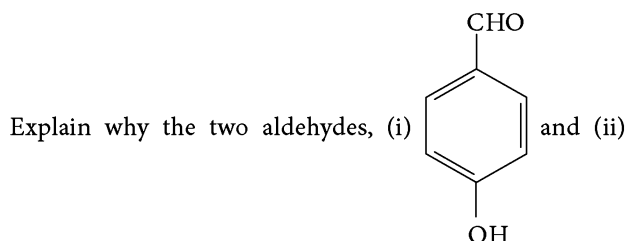
An aldehyde is obtained when a Grignard reagent reacts with an ortho formic ester.

**Concept Strand 6**

What are the products in the following reactions?

**Solution**

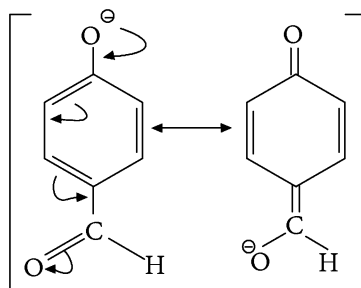
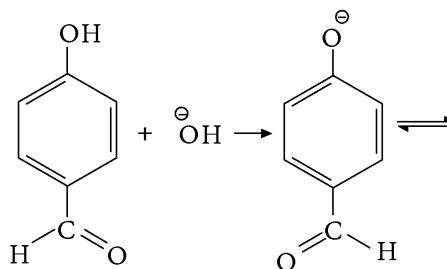
It is the most powerful reducing aldehyde namely HCHO that gets oxidized to an acid.

**Concept Strand 7**

CCl_3CHO fail to undergo Cannizzaro reaction, even though they do not contain any α -hydrogen.

Solution

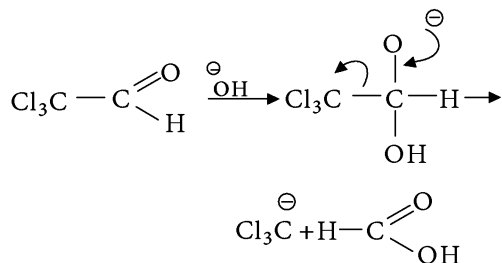
(i) In the case of p-hydroxybenzaldehyde, the presence of a strong base like NaOH (one of the essential reactants in Cannizzaro reaction), removes a proton from the phenolic group thereby making it as a phenoxide ion. This phenoxide ion is stabilized by the electron withdrawing $-\text{CHO}$ group in the para position, thereby making the electrophilicity of the carbonyl carbon to almost nil. So the reaction fails.



5.24 Aldehydes, Ketones and Carboxylic Acids

In the resonance structure of p-hydroxybenzaldehyde, the positive charge on the aldehydic carbon is lost.

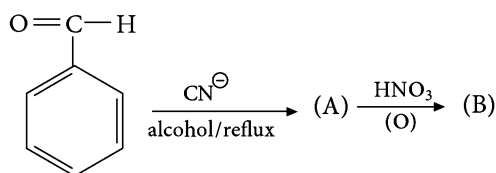
- (ii) Due to the high stability of the ${}^{\ominus}\text{CCl}_3$ due to the inductive effect of three chlorine atoms, the intermediate anion undergoes the cleavage of C – C bond instead of a hydride shift. CHCl_3 is formed in this case.



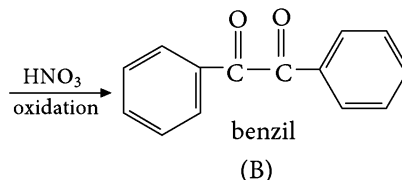
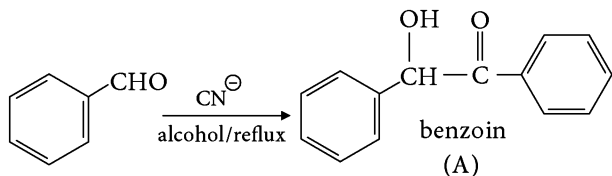
A proton transfer occurs from $\text{H}-\text{C}(=\text{O})\text{OH}$ to ${}^{\ominus}\text{CCl}_3$ to result in CHCl_3 and HCOO^-

Concept Strand 8

Identify the lettered compounds in the following sequence of reactions.



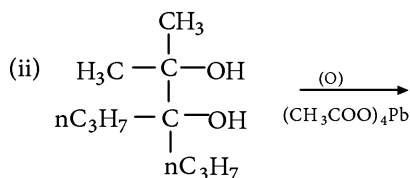
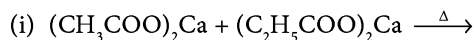
Solution



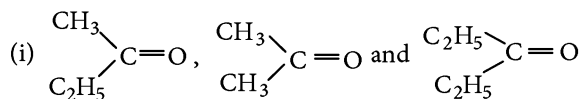
The formation of (A) from benzaldehyde is known as benzoin condensation

Concept Strand 9

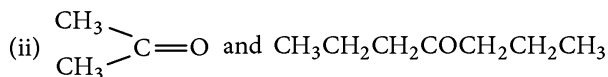
Give the structures of the organic products in the following reactions



Solution



Calcium salts of fatty acids form aldehydes or ketones or their mixture, on distillation depending on the fatty acid used.



Vicinal diols are cleaved by lead tetraacetate, $(\text{CH}_3\text{COO})_4\text{Pb}$. The product formed is aldehyde or ketone, depending on the nature of the diol.

CARBOXYLIC ACIDS

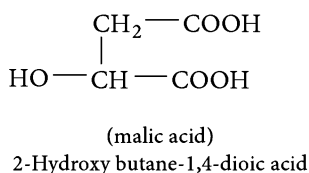
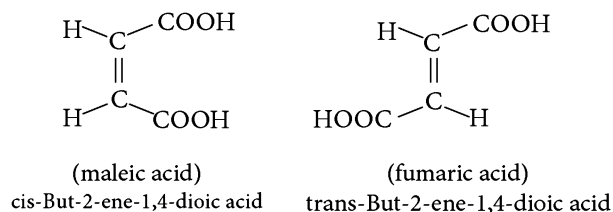
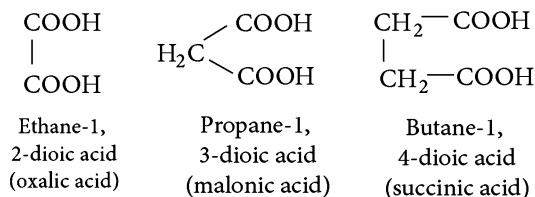
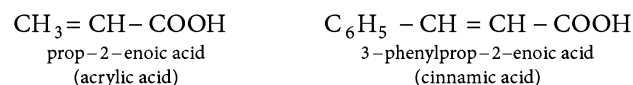
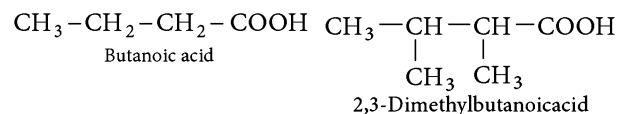
Carboxylic acids are compounds containing -COOH functional group. They are classified as mono, di and tri-carboxylic acids according to the number -COOH groups

present in one molecule. Aliphatic monocarboxylic acids are known as fatty acids because some of their higher members occur in natural fats.

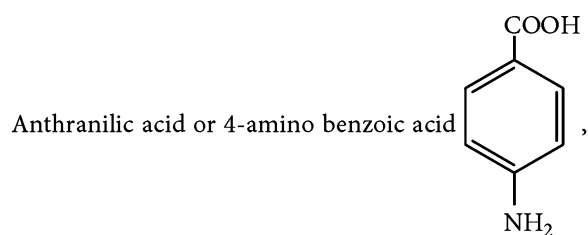
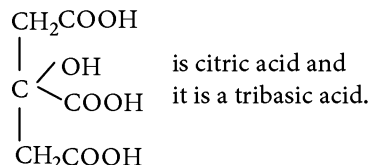
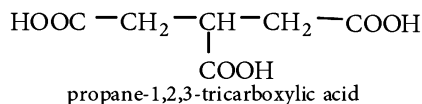
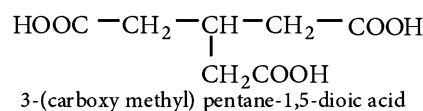
NOMENCLATURE OF CARBOXYLIC ACIDS

The common names of aliphatic monocarboxylic acids are derived from the Greek or Latin name of the source from which they were first isolated. The IUPAC name of saturated aliphatic monocarboxylic acid is derived by replacing the terminal 'e' from the name of the corresponding straight chain alkane by the suffix - oic acid.

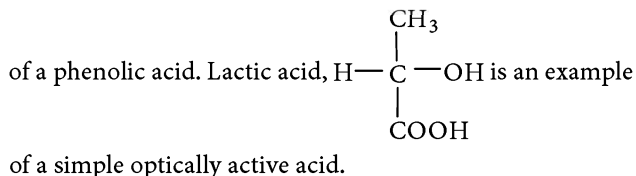
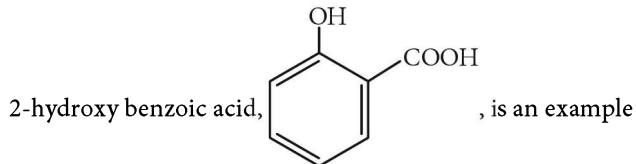
Examples



Maleic acid and fumaric acid are examples of unsaturated dibasic acids. These two acids exhibit geometrical isomerism.



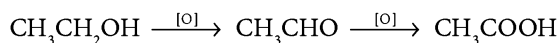
is an example of an aromatic amino acid. Salicylic acid or



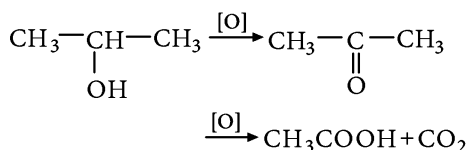
PREPARATION OF CARBOXYLIC ACIDS

Oxidation of alcohols, aldehydes and ketones

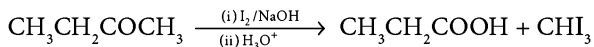
Primary alcohols and aldehydes on oxidation with acidified potassium dichromate or acidified potassium permanganate yield carboxylic acids with the same number of carbon atoms.



Secondary alcohols and ketones on strong oxidation form carboxylic acids with fewer number of carbon atoms.

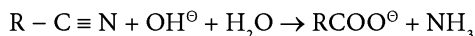
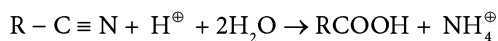


Methyl ketones can be converted to carboxylic acids with one carbon less by haloform reaction.



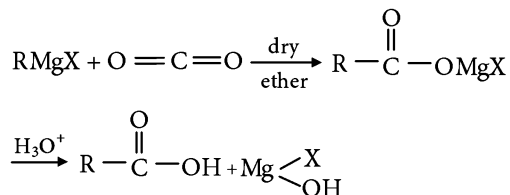
Hydrolysis of cyanides

Acid or base catalysed hydrolysis of cyanides (or nitriles) yield carboxylic acids.



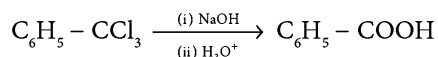
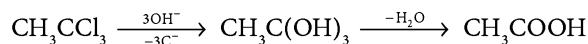
From Grignard reagents

When carbon dioxide is passed through an ethereal solution of Grignard reagent, an addition product is obtained, which on hydrolysis yields a carboxylic acid with one carbon more than the Grignard reagent.



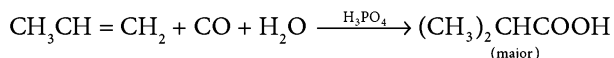
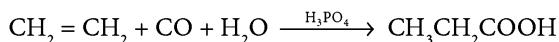
Hydrolysis of trihalogen derivatives of hydrocarbons

Trihalogen derivatives of alkanes, where all the three halogens are on the same carbon atom, on alkaline hydrolysis give monocarboxylic acids.



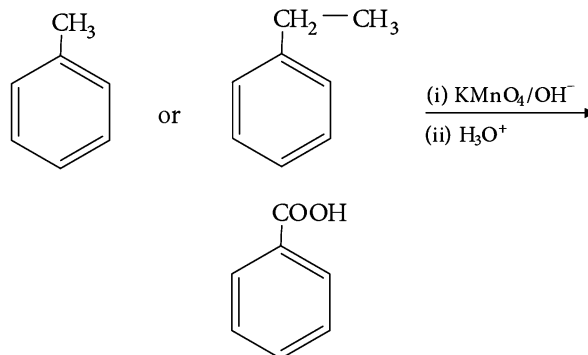
Koch reaction

Koch reaction involves carboxylation of alkenes. When a mixture of alkene, steam and carbon monoxide is heated at 573K under pressure in the presence of phosphoric acid (H_3PO_4), a monocarboxylic acid is formed.



From alkyl benzene

Aromatic carboxylic acids are generally prepared by vigorous oxidation of alkyl benzenes with acidic or alkaline KMnO_4 .



PROPERTIES OF CARBOXYLIC ACIDS

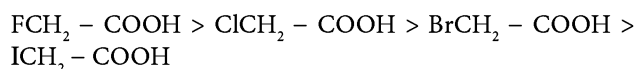
Acidic nature

Carboxylic acids are acidic in nature due to their ionization in aqueous solution to form carboxylate ion and hydronium ions.

The presence of groups with $-I$ effect increases the acidity of carboxylic acids. For example $\text{ClCH}_2 - \text{COOH}$ is a stronger acid than $\text{CH}_3 - \text{COOH}$. Due to the $-I$ effect of chlorine, it would disperse the negative charge on the anion formed by ionization. This would stabilize the anion of chloroacetic acid more than that of acetic acid. So monochloroacetic acid is stronger than acetic acid.

Since the $-I$ effect of halogens decreases in the order $\text{F} > \text{Cl} > \text{Br} > \text{I}$, the acid strength of the halogen substituted acids also decreases in the same order.

For example,



The presence of groups with $+I$ effect decreases the acid strength of carboxylic acids.

For example,

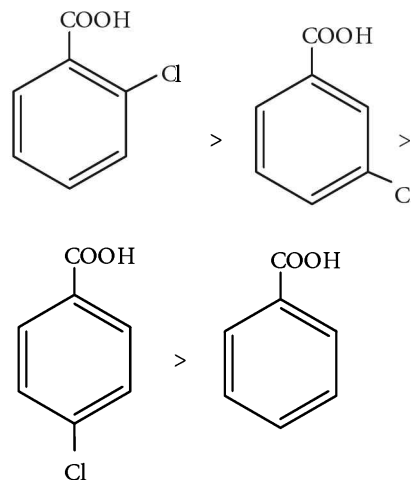
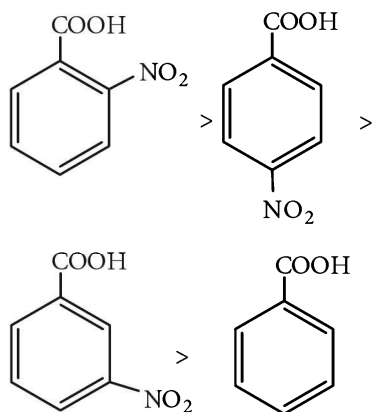


Benzoic acid is slightly stronger than acetic acid but weaker than formic acid.

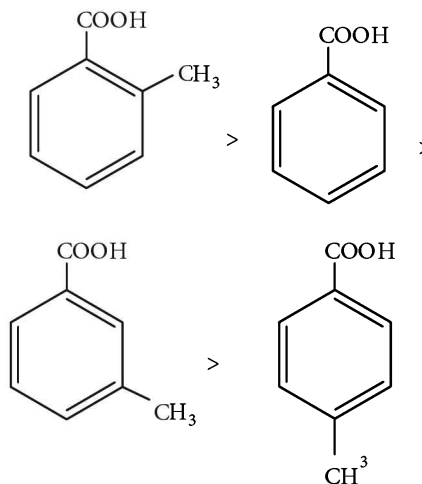
In substituted benzoic acids, electron donating substituents decrease while electron withdrawing substituents increase the acid strength. The effect is more pronounced when the substituent is at para position than at the meta position.

Ortho substituted benzoic acids are usually stronger acids than benzoic acid irrespective of the nature of the substituent. This is called **ortho effect**.

For example,



(In p-chlorobenzoic acid, both $+R$ and $-I$ effect operate, but in m-chlorobenzoic acid, only $-I$ effect operates)

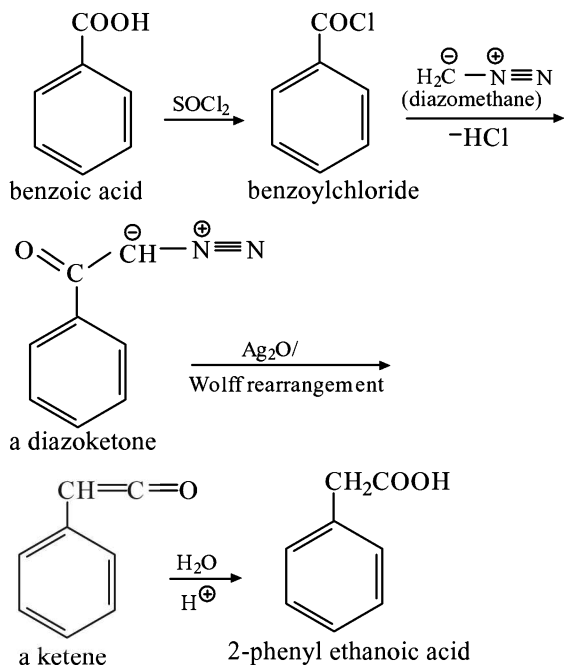


Arndt-Eistert synthesis

Arndt-Eistert synthesis involves the conversion of a carboxylic acid to its next higher homologue. The reaction involves a rearrangement known as Wolff rearrangement.

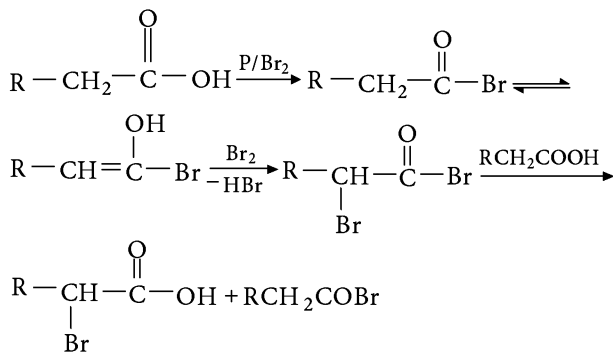
The starting acid is first converted to an acyl halide. Diazomethane reacts with the acyl halide to give the corresponding α -diazoketone, which rearranges to give the higher acid.

5.28 Aldehydes, Ketones and Carboxylic Acids

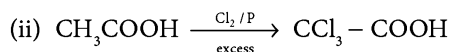
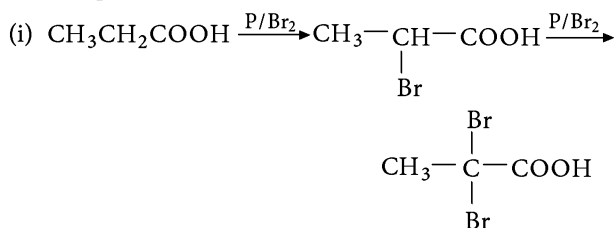


Hell-Volhard-Zelinsky (HVZ) reaction

When carboxylic acids containing α - hydrogen are treated with chlorine or bromine in presence of red phosphorus, α - chloro or α - bromo carboxylic acids are obtained.

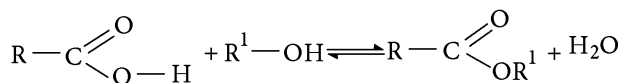


For example

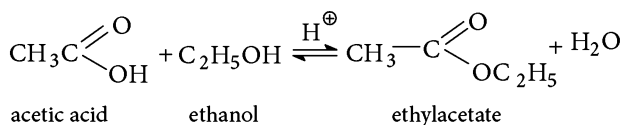


Formation of esters

Esterification of a carboxylic acid is the process by which an alkoxy group is substituted for a hydroxy group in the carboxylic acid.

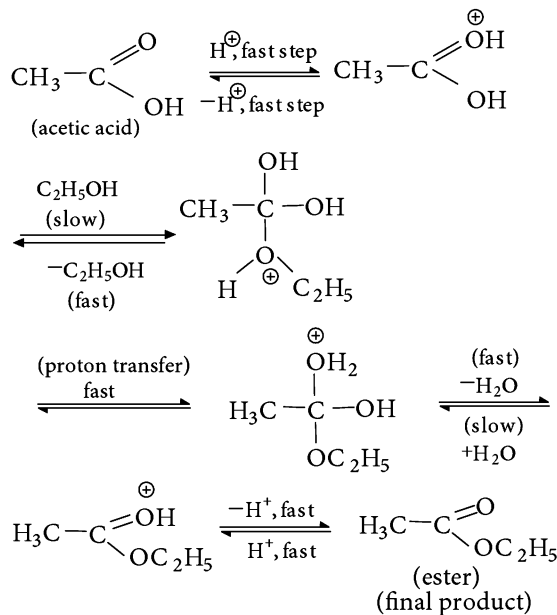


When a carboxylic acid is reacted with an alcohol in the presence of a mineral acid as a catalyst, an ester is formed. This reaction is known as Fischer's esterification.

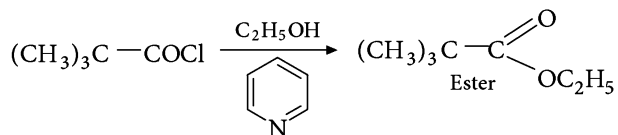
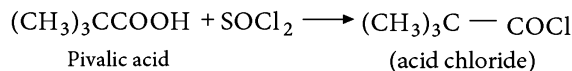


Mechanism of Fischer's esterification

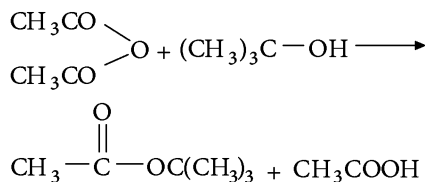
This is illustrated by taking a specific example of the esterification of acetic acid with ethylalcohol in the presence of a trace of mineral acid to give the ester, ethylacetate.



In some instances, the acid is converted to an acid chloride and then utilized for ester formation. For example



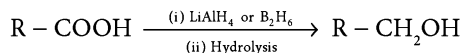
Anhydrides can also be used for the preparation of the esters. They are less reactive than acid chlorides.



These reactions are generally base catalysed and are irreversible and faster than acid catalysed esterification.

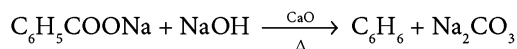
Reduction

Carboxylic acids are reduced to 1° alcohols on treatment with lithium aluminum hydride or diborane.

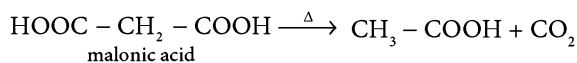


Decarboxylation

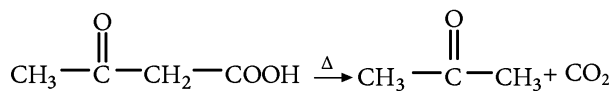
Simple carboxylic acids get decarboxylated when their sodium salts are heated with sodalime.



When two carboxyl groups are attached to the same carbon atom, decarboxylation takes place on heating.

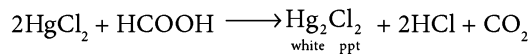


Similarly, β-keto acids undergo decarboxylation on heating



Reducing properties of formic acid

Among fatty acids, formic acid is unique since it contains a hydrogen atom directly attached to -COOH group. Hence formic acid is a reducing agent. It reduces Tollens' reagent to metallic silver, Fehling's solution to a red precipitate of Cu_2O and mercuric salts to mercurous salts.

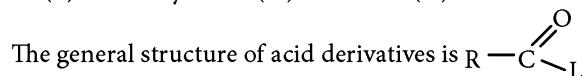


Formic acid also decolourises KMnO_4 solution. These reactions are used to distinguish formic acid from other fatty acids.

Derivatives of carboxylic acids

Functional derivatives of carboxylic acids are formed by the replacement of the -OH group of the carboxyl group by other groups like -Cl, -NH₂, OR, etc.

Important derivatives of carboxylic acids are (i) acyl halides (ii) acid anhydrides (iii) esters and (iv) acid amides.



If L = -Cl, the compound is known as acyl chloride.

If L = -OCOR', it is called acid anhydride.

L = OR' for esters and L = -NH₂ for amides

All the acid derivatives undergo nucleophilic substitution reactions. To differentiate these nucleophilic substitution reactions from those of alkyl halides, these are sometimes referred to as nucleophilic acyl substitution reactions.

The reactivity of acid derivatives towards nucleophilic substitution reactions decrease in the order

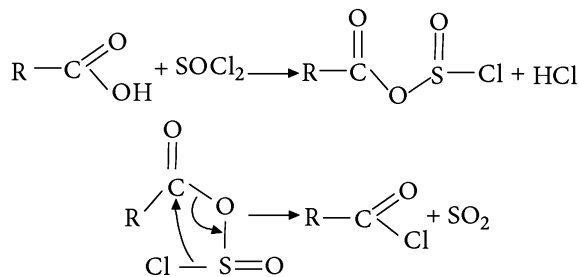
Acid chloride > acid anhydride > esters > amide

(i) Acid chlorides

An acid chloride is prepared by the substitution of -Cl (chloride group) for the -OH (hydroxy group) in a carboxylic acid. The reagents that are commonly used for this purpose are thionyl chloride (SOCl_2), phosphorus trichloride (PCl_3) and phosphorus pentachloride (PCl_5).

Thionyl chloride is the best reagent of all the three, since the products formed, besides the acid chloride, are gases, namely SO_2 and HCl and thus easily separated from the desired product.

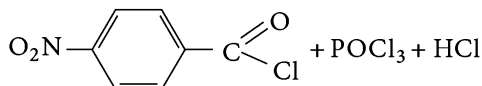
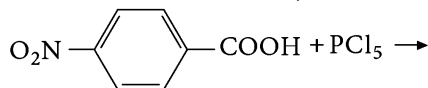
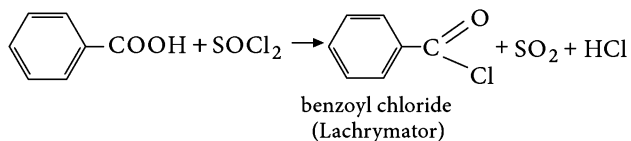
The mechanism of acid chloride formation from a carboxylic acid by means of thionyl chloride is shown below.



5.30 Aldehydes, Ketones and Carboxylic Acids

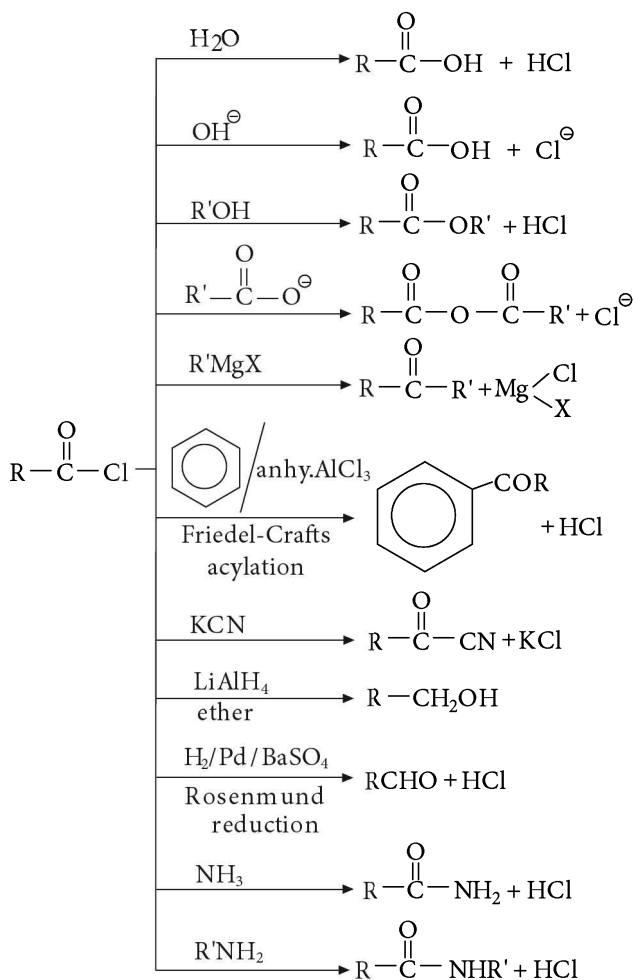
This occurs by S_Ni mechanism (substitution, nucleophilic, internal).

Examples of acid chloride formation



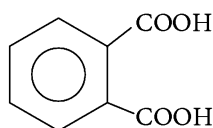
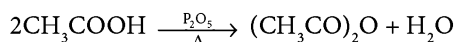
Reactions of acid chlorides

Acid chlorides are very reactive and can be converted to a variety of products depending on the reagents used. The various reactions are summarized below.

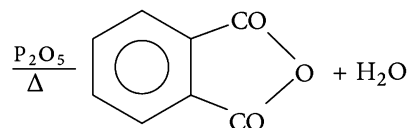


(ii) Acid anhydrides

Acid anhydrides are prepared by heating carboxylic acid with a dehydrating agent like phosphorus pentoxide.

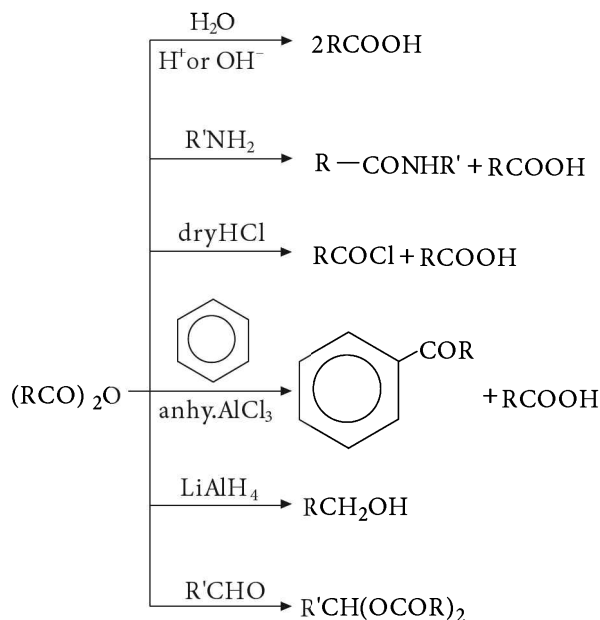


Phthalic acid



Phthalicanhydride

Some of the reactions of acid anhydride are summarized as follows



(iii) Esters

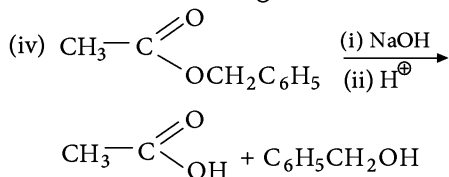
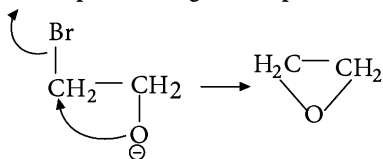
Esters are formed when the hydroxylic hydrogen in carboxylic acids is replaced by an alkyl group. They can be prepared from carboxylic acids or acid chlorides or acid anhydrides as discussed earlier.

Ester hydrolysis

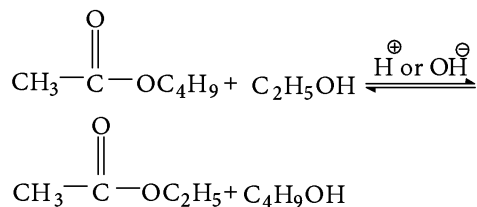
Hydrolysis of esters is the process by which carboxylic esters are broken down under the influence of acids or bases to give free carboxylic acids and alcohols. The hydrolysis is represented by the general equation

5.32 Aldehydes, Ketones and Carboxylic Acids

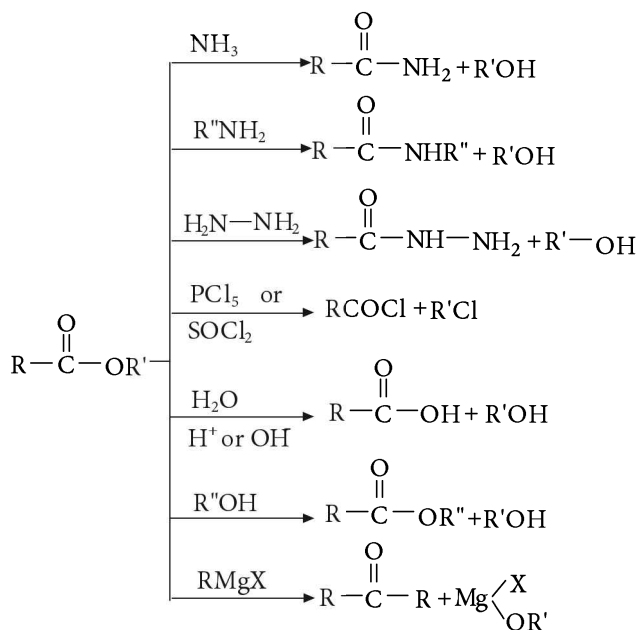
In this example the alcohol product formed is $\text{BrCH}_2\text{CH}_2\text{O}^-$. However, Br^- gets displaced by an intramolecular process to give an epoxide.



By means of alcoholysis, an alcohol residue in an ester can be replaced by another alcohol residue. Alcoholysis is carried out by refluxing the ester with large excess of alcohol in the presence of small amount of acid as catalyst. Alcoholysis is usually effective in replacing a higher alcohol by a lower one. This reaction is also known as *trans-esterification*.

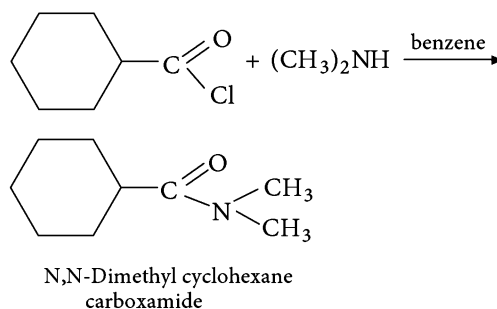
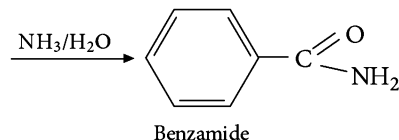
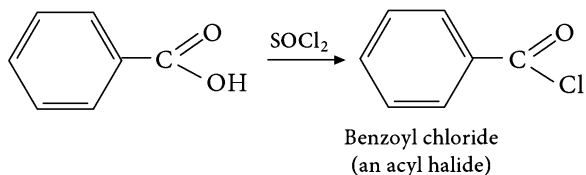


A few reactions of esters are summarized below

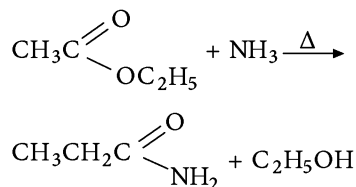


(iv) Acid amides

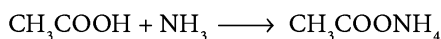
An amide can be prepared by reacting an acyl halide with ammonia or an amine (primary or secondary).



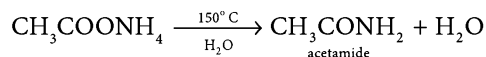
An amide can also be obtained by treating an ester with ammonia.



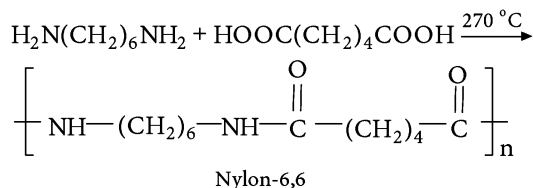
Amides are also prepared by directly reacting a carboxylic acid with NH_3 so that the ammonium salt of the acid is formed, in the first step.



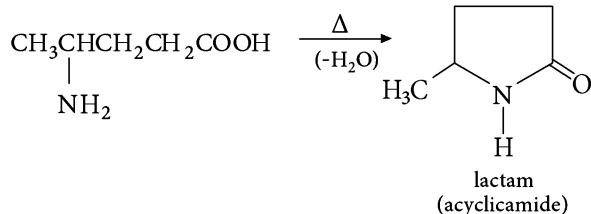
Salt formation is a quick and exothermic process. Removal of water by heating will produce the corresponding amide.



The polyamide Nylon-6,6 is prepared by treating adipic acid with hexamethylenediamine. Nylon-6,6 is a copolymer of adipic acid and hexamethylene diamine.

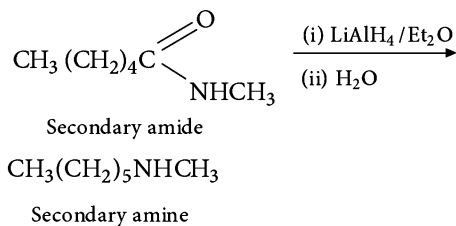


Lactams are cyclic amides containing five or six atoms, which include the amine and carbonyl groups.

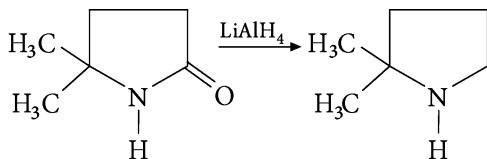


The reaction of an amide with LiAlH_4 gives an amine.

The carbonyl group of the amide $-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-$ is reduced by LiAlH_4 to a methylene group.

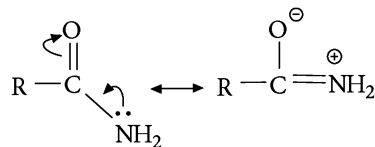


A cyclic amide or a lactam is converted to a cyclic amine, for example,

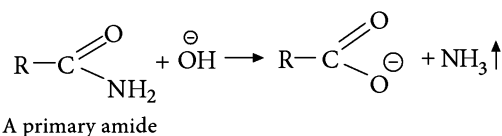


Though an amide contains $-\text{NH}$ group as an amine, the base strength of an amide is far less when compared to an amine.

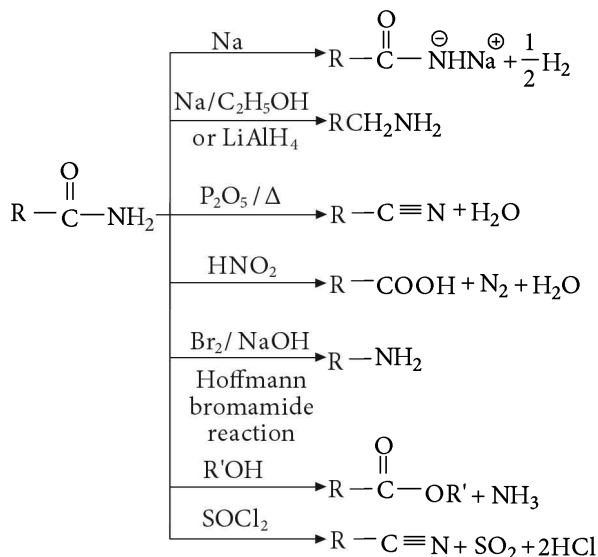
The low basicity of the amides can be accounted in terms of resonance and inductive effects. Amides are much weaker bases than amines because of the powerful electron withdrawing effect of the carbonyl group adjacent to the amine $-\text{NH}_2$ group. The nitrogen atom of the amide is so weakly basic that when an amide accepts a proton, it is more on oxygen than on nitrogen.



Amides undergo hydrolysis to give carboxylic acids liberating NH_3 .



The major reaction of amides can be summarized as follows

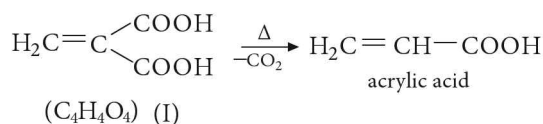


CONCEPT STRANDS

Concept Stand 10

Identify a dibasic acid of molecular formula $\text{C}_4\text{H}_4\text{O}_4$, which on heating gives acrylic acid.

Solution



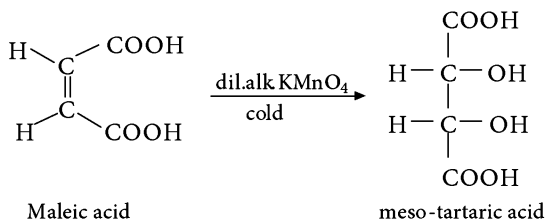
5.34 Aldehydes, Ketones and Carboxylic Acids

(I) is an α -dicarboxylic acid with electron withdrawing group ($-\text{COOH}$) at β -position and therefore undergoes facile decarboxylation.

Concept Strand 11

A dibasic acid of molecular formula $\text{C}_4\text{H}_4\text{O}_4$ on treatment with Baeyer's reagent gives a meso compound. Identify the acid.

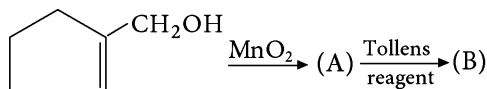
Solution



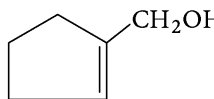
A cis alkene on cis or syn addition gives a meso product.

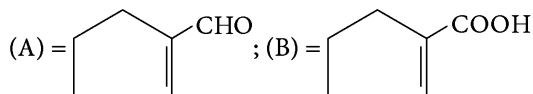
Concept Strand 12

Identify the major organic products (A) and (B) in the following sequence.

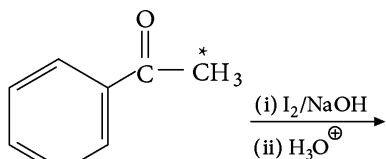


Solution

 is like an allyl alcohol. It is oxidized to an aldehyde by MnO_2 . Double bond is not affected.



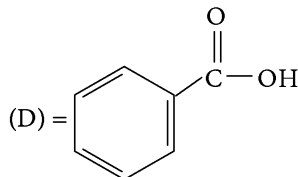
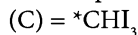
Concept Strand 13



(C) + (D). Identify (C) & (D).
(with labelled carbon)

Solution

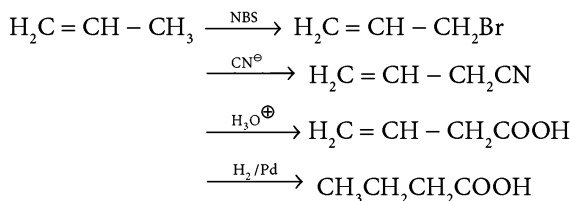
It is an example of iodoform reaction.



Concept Strand 14

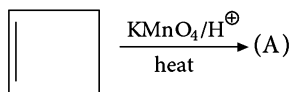
How is $\text{H}_2\text{C}=\text{CH}-\text{CH}_3$ converted to $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$?

Solution

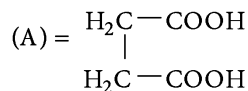


Concept Strand 15

Identify the product (A).



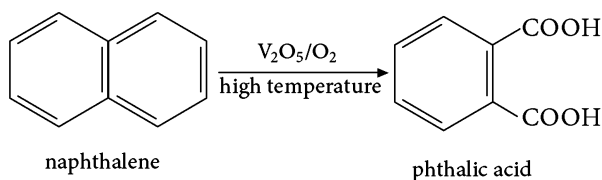
Solution



Concept Strand 16

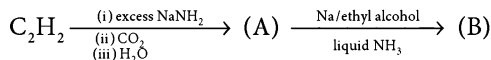
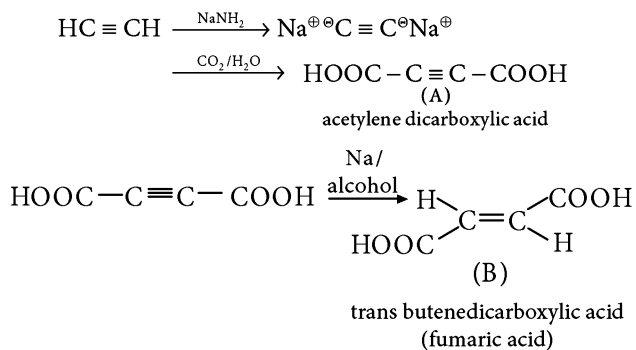
How is naphthalene converted to phthalic acid?

Solution



Concept Strand 17

Identify the compounds (A) – (B) in the sequence.

**Solution**

The conversion from (A) to (B) is an example of Birch reduction, which involves the selective reduction of an alkyne to a trans alkene.

Concept Strand 18

Compare the acids given in each pair and mention which acid in each pair is stronger and why?

- (i) $\text{H}_2\text{C} = \text{CH} - \text{CH}_2 - \text{COOH}$ (or) $\text{CH}_3\text{CH}_2\text{COOH}$
- (ii) $\text{CH}_3\text{CH}_2\text{COOH}$ (or) $\text{CH}_3\text{COCH}_2\text{COOH}$
- (iii) $\text{HC} \equiv \text{C} - \text{CH}_2\text{COOH}$ (or) $\text{H}_2\text{C} = \text{CH} - \text{CH}_2\text{COOH}$
- (iv) ClCH_2COOH (or) $\text{ClCH}_2\text{CH}_2\text{COOH}$

Solution

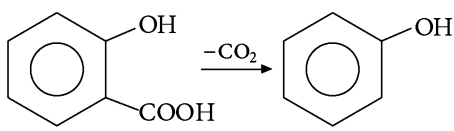
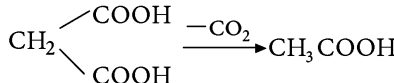
- (i) $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{COOH}$ is a stronger acid than $\text{CH}_3\text{CH}_2\text{COOH}$. This is because the sp^2 hybridized carbon of $\text{H}_2\text{C} = \text{CH}-$ has a stronger electron withdrawing power.
- (ii) $\text{CH}_3\text{COCH}_2\text{COOH}$ is stronger than $\text{CH}_3\text{CH}_2\text{COOH}$ because the carbonyl group has a strong electron withdrawing effect.
- (iii) $\text{HC} \equiv \text{C} - \text{CH}_2\text{COOH}$ is stronger than $\text{H}_2\text{C} = \text{CH} - \text{CH}_2\text{COOH}$ because $\text{HC} \equiv \text{C}-$ group has sp hybridized orbitals which have greater electron withdrawing influence than the sp^2 hybridised orbitals possessed by $\text{H}_2\text{C} = \text{CH} - \text{CH}_2 - \text{COOH}$.
- (iv) ClCH_2COOH is stronger than $\text{ClCH}_2\text{CH}_2\text{COOH}$ because chlorine is nearer to $-\text{COOH}$ group in chloroacetic acid compared to β -chloro propionic acid.

Concept Strand 19

Explain the compounds formed during the decarboxylation of

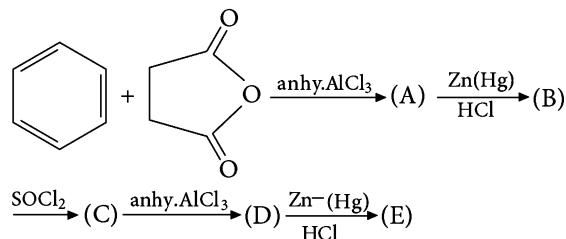
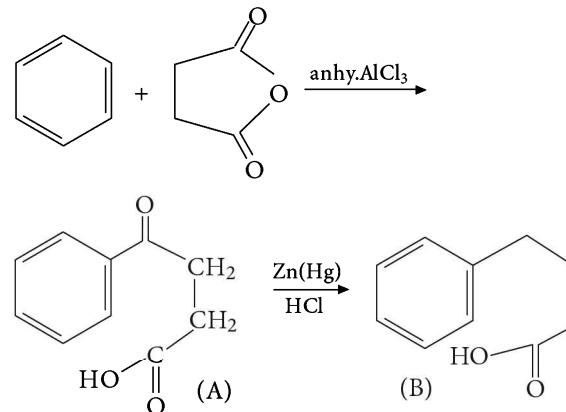
- (i) nitro acetic acid
- (ii) trichloroacetic acid
- (iii) salicylic acid
- (iv) malonic acid

Solution

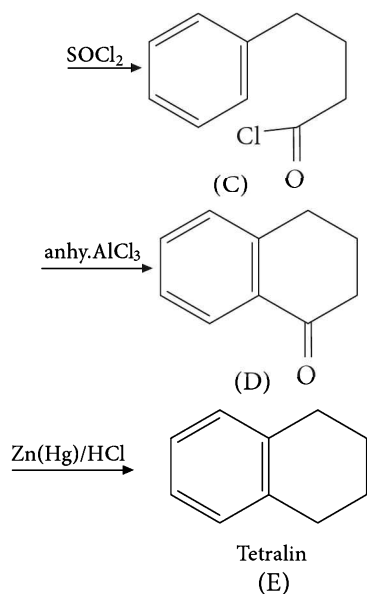
- (i) $\text{O}_2\text{N}-\text{CH}_2-\text{COOH} \xrightarrow{-\text{CO}_2} \text{CH}_3\text{NO}_2$
- (ii) $\text{CCl}_3-\text{COOH} \xrightarrow{-\text{CO}_2} \text{CHCl}_3$
- (iii) 
- (iv) 

Concept Strand 20

Identify the products in the sequence of reactions.

**Solution**

5.36 Aldehydes, Ketones and Carboxylic Acids



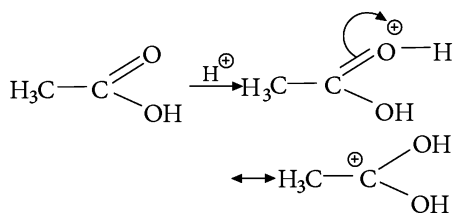
Concept Strand 21

Account for the fact that a trace of mineral acid is needed for esterification of a carboxylic acid.

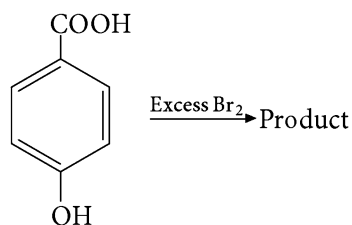
Solution

Adding few drops of a mineral acid promotes the electrophilicity of the carbon of carboxylic acid function by protonation.

For example,

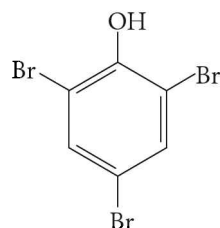


Concept Strand 22



Identify the product.

Solution

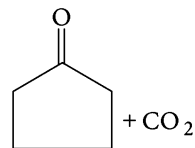


p-hydroxy benzoic acid undergoes decarboxylation to give a white precipitate of 2,4,6-tribromophenol.

Concept Strand 23

Identify the main product, $(\text{CH}_2)_4$  $\xrightarrow{\Delta}$

Solution



(dehydration as well as decarboxylation).

SUMMARY

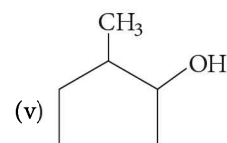
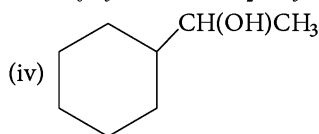
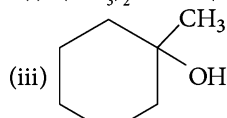
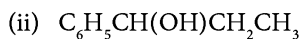
Introduction	Functional group of aldehydes and ketones, examples of aldehydes and ketones.
Structure of the carbonyl group	Carbonyl carbon atom is sp^2 hybridized. Comparison of the reactivities of aldehydes and ketones
Preparation of aldehydes and ketones	(i) From alcohols by oxidation, catalytic dehydrogenation and Oppenauer oxidation (ii) Dry distillation of calcium salts of carboxylic acid. (iii) From acid chloride- Rosenmund's reduction and reaction with dialkyl cadmium (iv) From alkyl cyanides- Stephen's reduction, reduction using $DiBAL-H$, reaction with Grignard reagent. (v) From alkenes-oxoprocess, Wacker's process and ozonolysis (vi) Preparation of aromatic aldehydes and ketones-Etard reaction, Gattermann-Koch reaction and Friedel-Crafts reaction.
Nucleophilic addition to carbonyl group	Addition of HCN , $NaHSO_3$, alcohols, thioalcohols and formation of geminal diols.
Addition reaction followed by elimination of water	Formation of oximes, semicarbazone and hydrazones, Formation of Schiff's bases.
Oxidation and reduction of aldehydes and ketones	Oxidation of aldehydes with Tollens' reagent, Fehling's solution and Benedict's solution. Oxidation of ketones-Popoff's rule. Reduction with H_2/Ni , $LiAlH_4$ and $NaBH_4$, Clem- mensen reduction and Wolff-Kishner reduction.
Name reactions of carbonyl compounds	(i) Aldol condensation (ii) Cannizzaro reaction (iii) Haloform reaction (iv) Perkin reaction (v) Benzoin condensation (vi) Beckmann rearrangement (vii) Knoevenagel condensation (viii) Wittig reaction (ix) Tischenko reaction
Polymerisation	Formation of paraformaldehyde, trioxan, paraldehyde and metaldehyde.
Reaction with NH_3	Formaldehyde forms urotropine, other aldehydes form addition products and acetone forms diacetone ammonia.
Carboxylic acids- introduction	Functional group of carboxylic acids, nomenclature of carboxylic acids.
Preparation of carboxylic acids	(i) By oxidation of alcohols, aldehydes and ketones (ii) Hydrolysis of cyanides (iii) From Grignard reagent (iv) Hydrolysis of trihalogen derivatives of hydrocarbons (v) By Koch reaction (vi) From alkyl benzene
Properties of carboxylic acids	(i) Acidic nature (ii) Arndt-Eistert synthesis (iii) H.V.Z reaction (iv) Formation of esters (v) Reduction (vi) Decarboxylation (viii) Reducing properties of formic acid
Derivatives of carboxylic acids	Preparation and properties of acid chlorides, acid anhydrides, esters and amides.

TOPIC GRIP



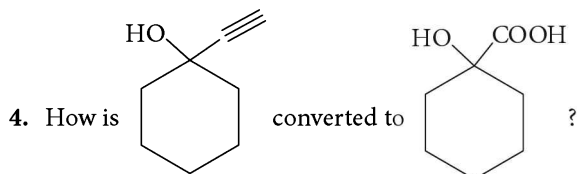
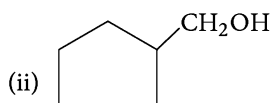
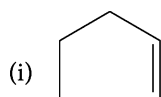
Subjective Questions

1. Write the structures of the products formed, if any, after acidification in the iodoform reaction of following compounds.



2. Account for the fact that aldehydes are more reactive than ketones in nucleophilic additions.

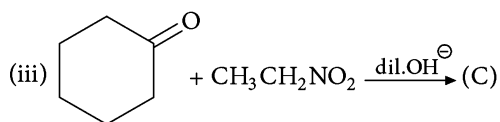
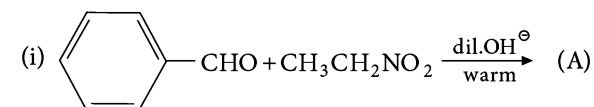
3. How is cyclopentanone converted to



5. An organic compound (C_6H_{10}), on treatment with ozone in the presence of zinc and water gives $\text{C}_6\text{H}_{10}\text{O}_2$, which on

further treatment with base followed by acidification under hot conditions gives . Write the sequence of reactions.

6. Identify the structures of lettered compounds (A) – (C) in the following reactions.



7. How is $(\text{CH}_3)_3\text{C} - \text{Br}$ converted to $(\text{CH}_3)_3\text{C} - \text{CH}_2\text{COOH}$?

8. What is the important organic product formed by the electrolysis of

- potassium succinate
- potassium maleate

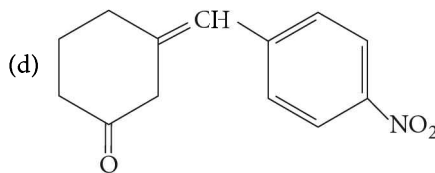
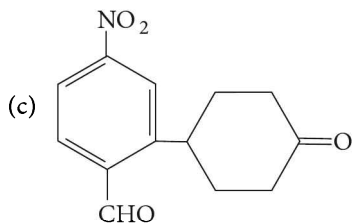
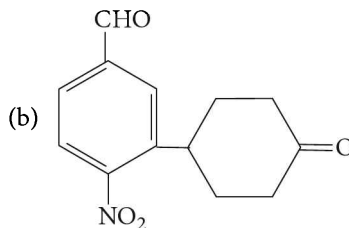
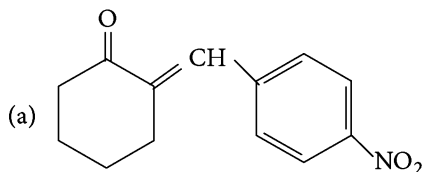
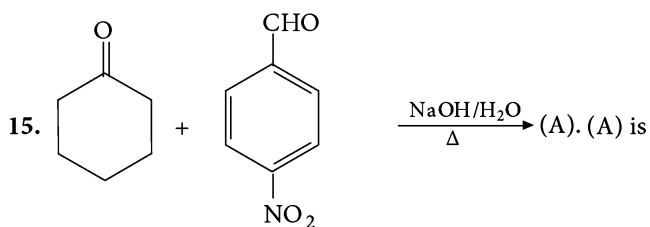
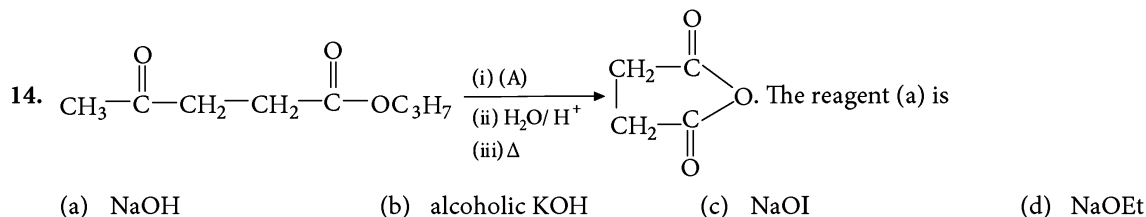
9. Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Why?
10. An organic compound X (MF : $C_6H_{12}O_2$) on acid hydrolysis gave a carboxylic acid Y and an alcohol Z. Oxidation of Z with chromic acid produced Y. Identify the compound (X).



Straight Objective Type Questions

Directions: This section contains multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

11. Propanone is formed when methyl magnesium chloride reacts with
 (a) acetone (b) ethyl iodide (c) acetonitrile (d) methanal
12. $HC \equiv CH \xrightarrow[\text{(iii) } H_3O^+/\Delta]{\text{(i) } Hg^{2+}/H_2SO_4/H_2O, \text{ (ii) } NaOH}$ (A). The major product (a) is
 (a) $CH_3CH = CHCOOH$ (b) $CH_3CH = CHCHO$ (c) $CH_3\overset{OH}{\underset{|}{CH}}-CH_2CHO$ (d) CH_3COOH
13. When calcium propanoate is distilled, the product obtained is
 (a) 2-pentanone (b) 3-pentanone (c) propanal (d) propanone



**Assertion-Reason Type Questions**

Directions: Each question contains Statement-1 and Statement-2 and has the following 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

16. Statement 1

p-nitrobenzaldehyde reacts more readily with HCN than p-methoxybenzaldehyde.
 and

Statement 2

The carbonyl carbon is more electrophilic in p-methoxybenzaldehyde than in p-nitrobenzaldehyde.

17. Statement 1

Chloral forms a stable hydrate with water.
 and

Statement 2

Chloral undergoes hydrolysis when heated with aqueous alkali to form chloroform.

18. Statement 1

During nucleophilic addition to carbonyl compounds, strong acid conditions are not favourable.
 and

Statement 2

Strong acids decrease the reactivity of carbonyl compounds.

19. Statement 1

The first ionization constant of maleic acid is greater than that of fumaric acid.
 and

Statement 2

Maleate anion is stabilized by intramolecular hydrogen bonding.

20. Statement 1

Ethyl acetate is more reactive than acetamide towards nucleophilic substitution.
 and

Statement 2

$-\text{OC}_2\text{H}_5$ is more electron attracting and a better leaving group than $-\text{NH}_2$.

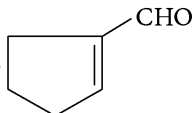
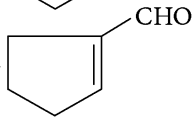
**Linked Comprehension Type Questions**

Directions: This section contains 2 paragraphs. Based upon the paragraph, 3 multiple choice questions have to be answered. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

Passage I

Cannizzarro reaction and aldol condensation are two important reactions of aldehydes. The first reaction is given by carbonyl compounds having no α -hydrogen whereas the second reaction is answered by compounds

containing α -hydrogen atoms. Answer the following questions based on Cannizzarro reaction and intramolecular aldol condensation.

21. When $(\text{CH}_3)_3\text{C} - \text{CHO}$ reacts with HCHO in NaOH followed by acidification, the products are
 (a) $(\text{CH}_3)_3\text{C} - \text{COOH}$ and CH_3OH (b) $(\text{CH}_3)_3\text{C} - \text{CH}_2\text{OH}$ and HCOONa
 (c) $(\text{CH}_3)_3\text{C} - \text{COONa}$ and CH_3OH (d) $(\text{CH}_3)_3\text{C} - \text{CH}_2\text{OH}$ and HCOOH
22. Cyclohexene undergoes ozonolysis in presence of $(\text{CH}_3)_2\text{S}$ to give (A). This undergoes aldol cyclization in NaOH followed by acidification in warm conditions to give (B). (a) and (b) are respectively,
 (a) $\text{CH}_3\text{CO}(\text{CH}_2)_2\text{COCH}_3$ and 3-methylcyclohexanone
 (b) $\text{OHC}(\text{CH}_2)_4\text{CHO}$ and 3-methylcyclohexanone
 (c) $\text{OHCCH}_2\text{COCH}_3$ and 
 (d) $\text{OHC}(\text{CH}_2)_4\text{CHO}$ and 
23. The product $\text{C}_6\text{H}_5\text{CH} = \text{CHCOCH}_3$ is obtained by the mixed aldol reaction of
 (a) benzaldehyde and acetone (b) acetophenone and acetone
 (c) cyclohexanone and propanal (d) benzaldehyde and acetaldehyde

Passage II

Carboxylic acids can be prepared by several methods. Some of these methods are (i) carboxylation of Grignard reagents (ii) ozonolysis of alkenes of the type $\text{RCH} = \text{CHR}'$ in presence of H_2O_2 (iii) hydrolysis of RCN and (iv) oxidative ozonolysis of alkynes.

24. Bromobenzene can be converted to benzoic acid by
 (a) treating with Mg and then carboxylating. (b) treating with NaOH and then carboxylating.
 (c) treating with KCN and then hydrolysing. (d) oxidation with KMnO_4 .
25. $\text{C}_6\text{H}_5\text{CH}_3 \xrightarrow{\text{(A)}} \text{C}_6\text{H}_5\text{CH}_2\text{Br} \xrightarrow{\text{(B)}} \text{C}_6\text{H}_5\text{CH}_2\text{CN} \xrightarrow{\text{(C)}} \text{C}_6\text{H}_5\text{CH}_2\text{COOH}$
 (A), (b) and (c) are respectively,
 (a) NBS , KCN and H_3O^+ (b) Br_2/Fe , KCN and H_3O^+
 (c) Br_2/Fe , HCN and $\text{C}_2\text{H}_5\text{OH}$ (d) NBS , AgCN and H_3O^+
26. Hydroxyacetic acid (HOCH_2COOH) is obtained by
 (a) the reduction of acetic acid by LiAlH_4
 (b) the hydrolysis of ethylene chlorohydrin, by aqueous alkali
 (c) the reaction of CH_3CHO with HCN followed by acid hydrolysis
 (d) Cannizzaro reaction of glyoxal.



Multiple Correct Objective Type Questions

Directions: Each question in this section has four suggested answers of which ONE OR MORE answers will be correct.

27. Which of the following reactions will give acetophenone as a product?
 (a) Acid catalysed hydration of styrene followed by oxidation with hot alkaline KMnO_4 .
 (b) Phenyl acetylene $\xrightarrow{\text{dil H}_2\text{SO}_4/\text{Hg}^{2+}}$

5.42 Aldehydes, Ketones and Carboxylic Acids

- (c) Reaction of benzoyl chloride with dimethyl cadmium.
(d) Dry distillation of a mixture of calcium acetate and calcium benzoate.
28. Carbanion intermediate is involved in
(a) Perkin reaction (b) Friedel-Crafts reaction (c) Cannizzaro reaction (d) Aldol condensation
29. Identify the true statements about methanoic acid.
(a) It is formed by heating glycerol with oxalic acid to about 373K.
(b) It gives formyl chloride when treated with PCl_5 .
(c) It is a stronger acid than benzoic acid.
(d) It gives carbon monoxide on heating with $\text{con.H}_2\text{SO}_4$.



Matrix-Match Type Question

Directions: Match the elements of Column I to elements of Column II. There can be single or multiple matches.

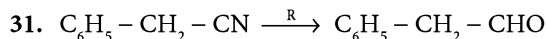
- 30.
Column I	Column II
(a) $\text{C}_6\text{H}_5 - \text{CHO} \xrightarrow{\text{OH}^-}$	(p) Nucleophilic addition
(b) $\text{CH}_3 - \text{CO} - \text{CH}_3 \xrightarrow{\text{OH}^-}$	(q) Nucleophilic acyl substitution
(c) $\text{CH}_3 - \text{CHO} \xrightarrow{\text{HCN}}$	(r) Hydride transfer
(d) $\text{CH}_3 - \text{COOC}_2\text{H}_5 \xrightarrow{\text{C}_2\text{H}_5\text{O}^-}$	(s) Carbanion
	(t) New C – C bond formation

IIT ASSIGNMENT EXERCISE



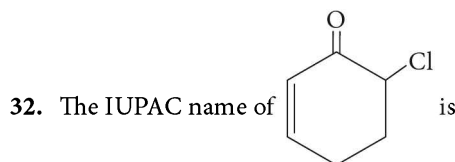
Straight Objective Type Questions

Directions: This section contains multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.



The reagent R used for the above conversion is

- (a) NaBH_4 (b) $\text{H}_2/\text{Pd} - \text{BaSO}_4$ (c) $\text{Na}/\text{liq NH}_3$ (d) SnCl_2/HCl



- (a) 2-chlorocyclohex-5-en-1-one (b) 6-chlorocyclohex-2-en-1-one
(c) 4-chloro-3-oxocyclohex-1-ene (d) 1-chloro-2-oxocyclohex-3-ene

33. The trimer of acetaldehyde is known as

- (a) formalin (b) trioxane (c) paraldehyde (d) metaldehyde

34. 2-phenyl ethanol on oxidation with alkaline KMnO_4 gives

- (a) benzaldehyde (b) 2-phenyl ethanoic acid (c) benzoic acid (d) 2-phenyl ethanol

35. The product obtained when benzene is treated with acetyl chloride in presence of anhydrous AlCl_3 is

- (a) benzophenone (b) benzoyl chloride (c) acetophenone (d) ethyl phenyl ketone

36. Acetaldehyde when heated with NaOH gives

- (a) but-2-enal (b) but-3-enal (c) propenal (d) butanal

37. When distilled with concentrated sulphuric acid, propanone gives

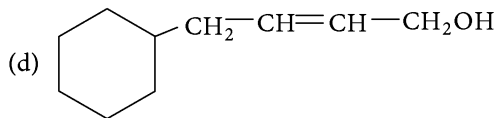
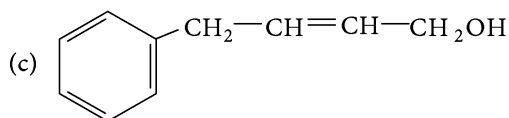
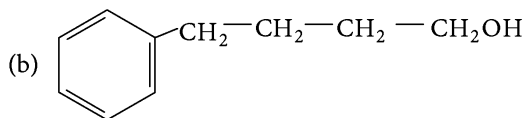
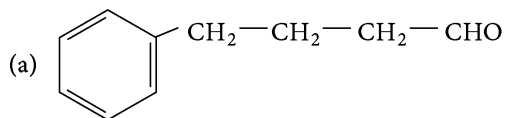
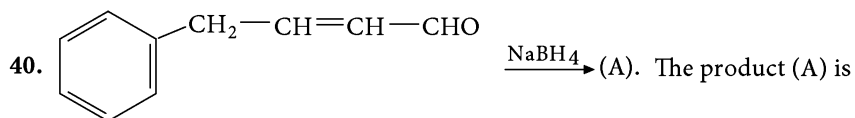
- (a) monomethyl benzene (b) dimethyl benzene (c) trimethyl benzene (d) propanoic acid

38. Iodoform reaction is given by

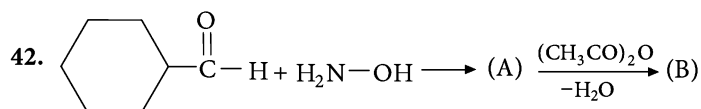
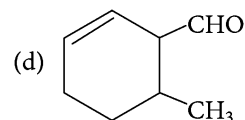
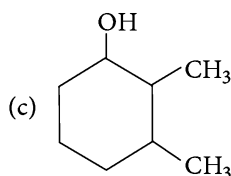
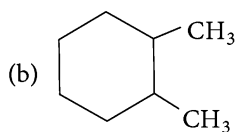
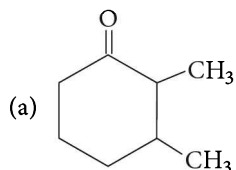
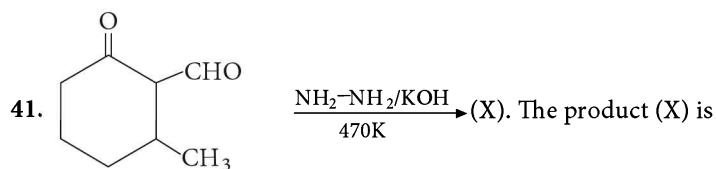
- (a) 2-pentanone (b) 3-pentanone (c) 2-propanol (d) Both (a) and (c)

39. Wolff-Kishner reduction of benzophenone gives

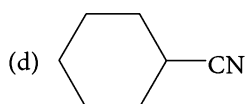
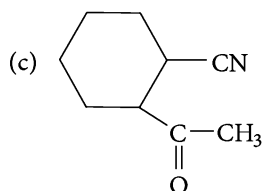
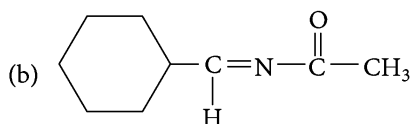
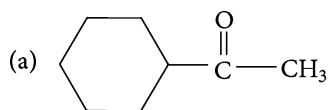
- (a) benzene (b) toluene (c) diphenylmethane (d) ethylbenzene



5.44 Aldehydes, Ketones and Carboxylic Acids



(B) is



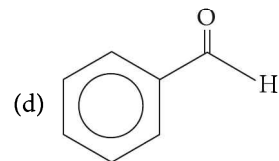
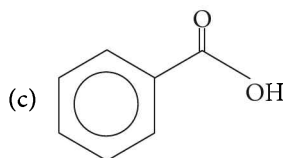
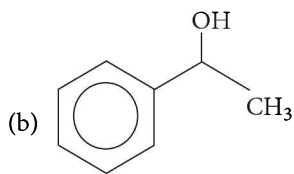
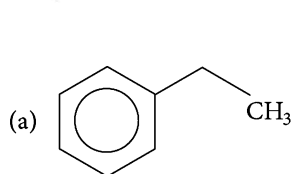
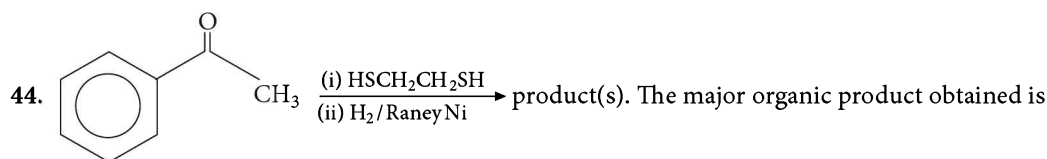
43. Formaldehyde reacts with ammonia to form

(a) formaldehyde ammonia

(b) hexamethylene pentamine

(c) hexamethylene tetramine

(d) tetramethylene hexamine



45. The trimer formed by formaldehyde is

(a) paraformaldehyde

(b) paraldehyde

(c) trioxane

(d) trimethanal

46. A compound, which is known as oil of bitter almonds is

(a) acetaldehyde

(b) acetone

(c) acetophenone

(d) benzaldehyde

47. Acetaldehyde reacts with malonic acid in presence of sodium ethoxide at high temperature to give

(a) acetic acid

(b) propanoic acid

(c) tartaric acid

(d) crotonic acid

48. Acetic acid with HI in presence of red phosphorus gives

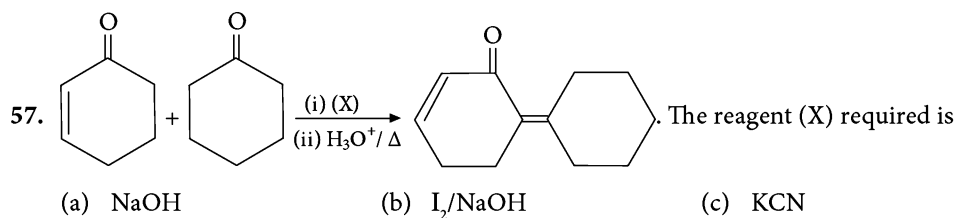
(a) methane

(b) ethane

(c) ethanal

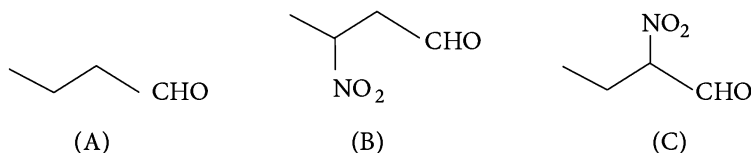
(d) methanal

49. Terephthalic acid is obtained by the oxidation of (X) with acidified $K_2Cr_2O_7$. (X) is
 (a) ortho xylene (b) meta xylene (c) para xylene (d) ethylbenzene
50. Tollens' reagent is reduced by
 (a) methanoic acid (b) ethanal (c) benzaldehyde (d) all the above
51. Claisen condensation is a reaction between
 (a) $HCOOH + HCOOH$ (b) $HCOOH + HCHO$
 (c) $CH_3COOC_2H_5 + CH_3COOC_2H_5$ (d) $CH_3-C(CH_3)_2-COOC_2H_5 + CH_3-C(CH_3)_2-COOC_2H_5$
52. $CH_3COOH \xrightarrow[(ii) (CH_3)_2NH]{(i) SOCl_2}$ product(s). The major organic product is
 (a) $CH_3CH_2CONHCH_3$ (b) CH_3CONH_2
 (c) $CH_3CH_2N(CH_3)_2$ (d) $CH_3CON(CH_3)_2$
53. The products of oxidation of 2-pentanone with concentrated nitric acid are
 (a) propanoic acid and ethanoic acid (b) butanoic acid and methanoic acid
 (c) propanoic acid and methanoic acid (d) 2-methyl propanoic acid and methanoic acid
54. $CH_3-C(=O)-CH_2-C(=O)-OC_2H_5 \xrightarrow[H_3O^+]{\text{excess } CH_3MgBr}$ (A). (A) is
 (a) $CH_3-C(OH)(CH_3)-CH_2-C(OH)(CH_3)-OC_2H_5$ (b) $CH_3-C(=O)-CH_2-C(OH)(CH_3)-OCH_3$
 (c) $CH_3-C(OH)(CH_3)-CH_2-C(=O)-C_2H_5$ (d) $CH_3-C(OH)(CH_3)-CH_2-C(OH)(CH_3)-CH_3$
55. A compound (A) gives a yellow precipitate with iodine and sodium hydroxide. On treating with a Grignard reagent, it gives (B). (B) gives a blue coloured pseudonitrole (C) in the Victor Meyer reaction which does not react with NaOH. (a) is
 (a) acetone (b) acetaldehyde
 (c) benzaldehyde (d) propanal
56. An acid on treating with calcium hydroxide followed by dry distillation gives 2,4-dimethyl-3-pentanone. The acid is
 (a) 2,4-dimethyl pentanoic acid (b) 2,2-dimethyl propanoic acid
 (c) 2-methyl propanoic acid (d) butanoic acid



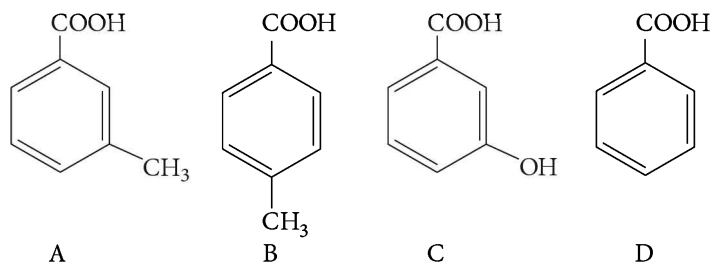
5.46 Aldehydes, Ketones and Carboxylic Acids

58. Arrange the following compounds in the increasing order of reactivity

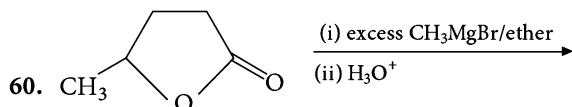


- (a) (A) < (C) < (B) (b) (A) < (B) = (C) (c) (B) < (C) < (A) (d) (A) < (B) < (C)

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



- (a) (A) < (D) < (B) < (C) (b) (A) < (C) < (B) < (D) (c) (C) < (D) < (A) < (B) (d) (B) < (A) < (D) < (C)

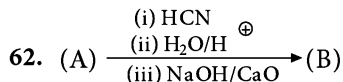


The product would be



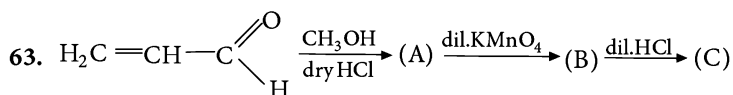
61. Starting with 1-propanol, 2-hydroxypropanoate can be prepared by treating with the reagents, in the order

- (a) Cl_2/P , KMnO_4 and aqueous KOH (b) Cl_2/P , KMnO_4 and alcoholic KOH
 (c) KMnO_4 , Cl_2/P and aqueous KOH (d) KMnO_4 , Cl_2/P and alcoholic KOH



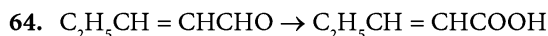
If (b) is 2-chloro ethanol, then (A) is

- (a) 2-chloro propanal (b) chloro propanal
 (c) chloro propanone (d) chloro ethanal



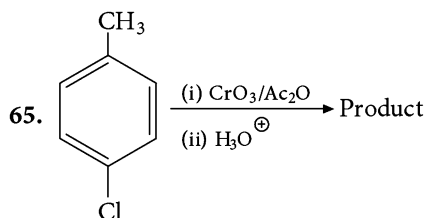
The structure of (C) is

- (a) $\text{H}_2\text{C}=\text{CHCH}_2\text{OH}$ (b) $\text{HOCH}_2-\text{CHOH}-\text{CHO}$
 (c) $\text{OHC}-\text{CH}_2-\text{COOH}$ (d) $\text{CH}_2=\text{CH}-\text{COOH}$

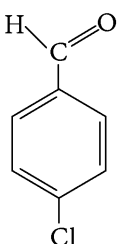
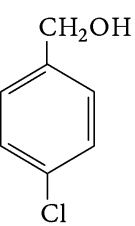
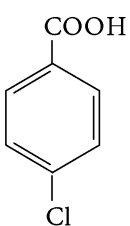
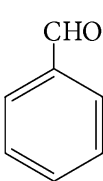


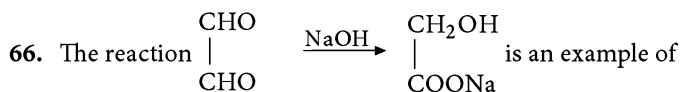
The best oxidizing agent that can be used for the above conversion is

- (a) acidified KMnO_4 solution (b) Tollens' reagent
(c) SeO_2 in AcOH (d) all the above

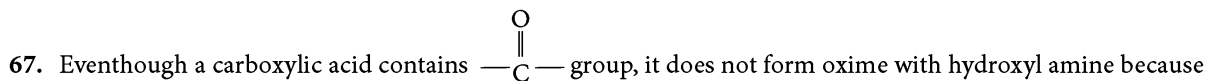


The major product is

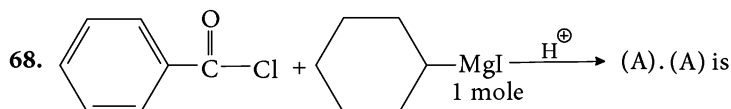
- (a)  (b)  (c)  (d) 

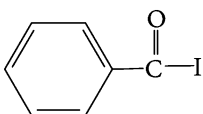
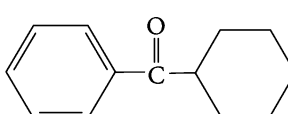
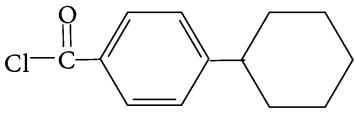
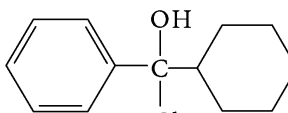


- (a) intramolecular aldol condensation (b) mixed Cannizzaro reaction
(c) intramolecular Cannizzaro reaction (d) crossed Cannizzaro reaction

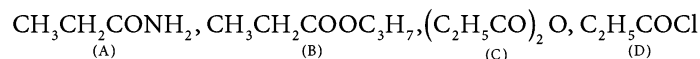


- (a) hydroxyl amine is less reactive to carboxylic acids.
(b) in this case hydroxyl amine acts as a reducing agent, oxidized to HNO_2 .
(c) the >C=O group enters into resonance with lone pairs of —OH group.
(d) the —OH group of carboxylic acid reacts with NH_2OH .



- (a)  (b) 
(c)  (d) 

69. Arrange the following in the increasing rate of hydrolysis

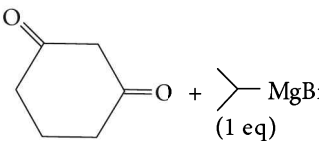


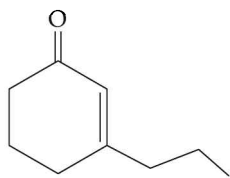
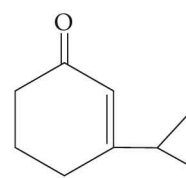
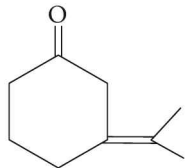
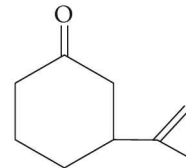
- (a) $(A) < (C) < (B) < (D)$ (b) $(C) < (D) < (A) < (B)$ (c) $(A) < (B) < (C) < (D)$ (d) $(C) < (A) < (D) < (B)$

5.48 Aldehydes, Ketones and Carboxylic Acids

70. $\text{C}_6\text{H}_5\text{CH}_2\text{Br} \xrightarrow[\text{(ii) CO}_2, \text{(iii) H}_3\text{O}^+]{\text{(i) Mg/ether}} (\text{A}) \xrightarrow[\text{(ii) CH}_3\text{NH}_2]{\text{(i) SOCl}_2} (\text{B})$. The major organic product (B) is

- (a) $\text{C}_6\text{H}_5\text{CONHCH}_3$ (b) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CONHCH}_3$
 (c) $\text{C}_6\text{H}_5\text{CH}_2\text{NHCOCH}_3$ (d) $\text{C}_6\text{H}_5\text{CH}_2\text{CONHCH}_3$

71.  (A) is

- (a)  (b) 
 (c)  (d) 

72. A compound (A) (which gives haloform reaction), on reduction with zinc amalgam and conc. HCl gives (B). (B) is also obtained by treating 1,1,2,2-tetrachlorobutane with zinc dust. The compound (A) is

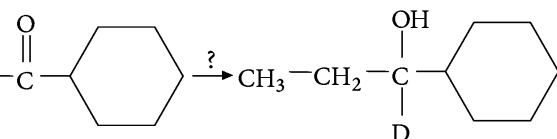
- (a) $\text{CH}_3\text{CH}(\text{OH})\text{C}\equiv\text{CH}$ (b) $\text{CH}_3\text{C}(\text{O})\text{CH}=\text{CH}_2$
 (c) $\text{CH}_3\text{CH}(\text{OH})\text{CH}=\text{CH}_2$ (d) $\text{CH}_3\text{C}(\text{O})\text{C}\equiv\text{CH}$

73. A carboxylic acid gives a ketone on heating through formation of a cyclic transition state. The ketone formed gives yellow precipitate with I_2 and NaOH and does not give addition product with NaHSO_3 . The acid is

- (a) $(\text{CH}_3)_2\text{CH}-\text{C}(=\text{O})-\text{CH}_2-\text{C}(=\text{O})-\text{OH}$ (b) $\text{C}_6\text{H}_5-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-\text{OH}$
 (c) $\text{C}_6\text{H}_5-\text{C}(=\text{O})-\text{CH}_2-\text{C}(=\text{O})-\text{OH}$ (d) $(\text{CH}_3)_2\text{CH}-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-\text{OH}$

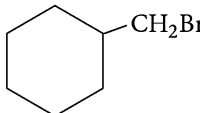
74. The acylating species in the Friedel-Crafts acylation of benzene to give acetophenone is

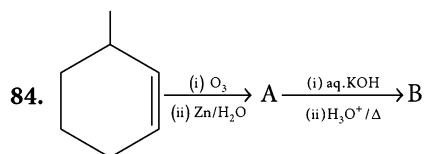
- (a) $\text{CH}_3-\text{C}\equiv\text{O}^+$ (b) AlCl_4^- (c) $\text{CH}_3-\text{C}^+=\ddot{\text{O}}$ (d) $\text{CH}_3-\text{CCl}^+-\text{O}-\text{AlCl}_4^-$

75. 

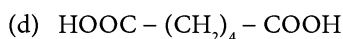
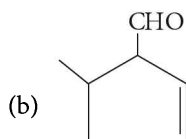
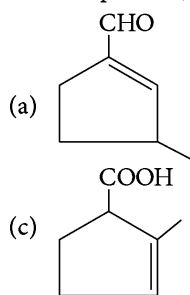
The reagents required for this conversion are

- (a) NaBH_4 and D_2O (b) NaBD_4 and H_2O (c) NaBD_4 and D_2O (d) LiAlD_4 and H_2O

76. $\text{CH}_3\text{CH}_2\text{COCl} + (\text{CH}_3)_2\text{Cd} \rightarrow \text{product(s)}$. The major organic product obtained is
 (a) CH_3COCH_3 (b) $\text{CH}_3\text{COCH}_2\text{CH}_3$
 (c) $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$ (d) $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$
77. The IUPAC name of is $\text{CH}_3-\text{CH}_2-\underset{\text{CHO}}{\text{CH}}-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$
 (a) 2-ethyl-4-methylpentanal (b) 4-methyl 2-ethylpentanal
 (c) 2-methylhexanal (d) 2-ethylhexanal
78. In the industrial preparation of benzoic acid from toluene with air, the reaction takes place in the presence of
 (a) Pt (b) V_2O_5 (c) Cl_2 (d) Cu
79. Malonic acid on heating at 430K yields
 (a) formic acid (b) succinic acid
 (c) acetic acid (d) lactic acid
80. Which of the following halides will not give good yield of the corresponding acid by the conversion to cyanide, followed by hydrolysis?
 (a) $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ (b) $(\text{CH}_3)_3\text{CBr}$
 (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ (d) 
81. The reagent that can be used to distinguish between pentan-2-one and pentan-3-one is
 (a) $\text{Zn} - \text{Hg}/\text{HCl}$ (b) SeO_2
 (c) I_2/NaOH (d) $\text{KMnO}_4/\text{H}_2\text{SO}_4$
82. The reaction of ethanoyl chloride with sodium ethanoate gives
 (a) Ethyl ethanoate (b) ethanoic anhydride
 (c) Butane-2,3-dione (d) sodium 3-oxobutanoate
83. Which of the following pairs will give effervescence with aqueous sodium hydrogen carbonate solution?
 (a) CH_3COCl and $(\text{CH}_3)_2\text{CO}$ (b) CH_3CONH_2 and $(\text{CH}_3\text{CO})_2\text{O}$
 (c) $\text{C}_6\text{H}_5\text{OH}$ and $\text{CH}_3\text{COOCH}_3$ (d) CH_3COCl and $(\text{CH}_3\text{CO})_2\text{O}$



The compound (B) in the above reaction is

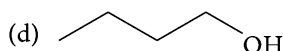
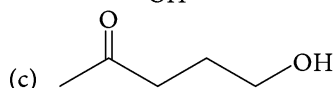
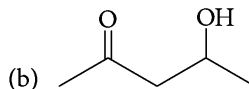
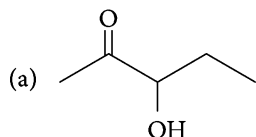


5.50 Aldehydes, Ketones and Carboxylic Acids

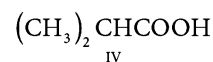
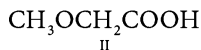
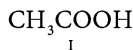
85. When acetic acid is treated with aqueous sodium bicarbonate, CO_2 gas is evolved. The 'Carbon' of CO_2 comes from
 (a) carboxyl group (b) methyl group
 (c) bicarbonate (d) both carboxyl group and bicarbonate

86. Dry distillation of calcium benzoate will give
 (a) acetophenone (b) benzophenone (c) benzaldehyde (d) 2-phenyl ethanol

87. Which of the following will undergo dehydration most readily in presence of acids?



88. The correct decreasing order of acid strength of the following compounds is



- (a) $\text{III} > \text{I} > \text{II} > \text{IV}$ (b) $\text{III} > \text{II} > \text{I} > \text{IV}$
 (c) $\text{III} > \text{I} > \text{IV} > \text{II}$ (d) $\text{II} > \text{III} > \text{I} > \text{IV}$
89. 2-Pentanone can be converted to butanoic acid by reaction with
 (a) Fehling's solution (b) $\text{HCN}/\text{H}_3\text{O}^+$
 (c) $\text{H}_2\text{NNH}_2, \text{KOH}/\text{H}_3\text{O}^+$ (d) $\text{NaOH}, \text{I}_2/\text{H}_3\text{O}^+$
90. Which of the following does not give benzoic acid on hydrolysis?
 (a) Ethyl benzoate (b) Benzene carbonitrile
 (c) Benzyl chloride (d) Benzoyl chloride

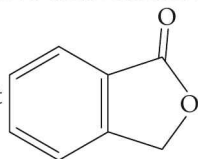


The product P in the above reaction is

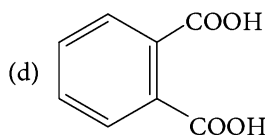
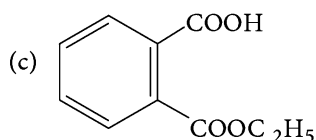
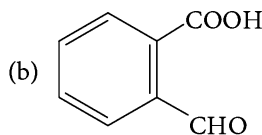
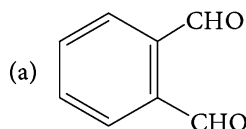
- (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ (b) $(\text{CH}_3)_2\text{CHCOOH}$ (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ (d) $(\text{CH}_3)_2\text{CHCHO}$

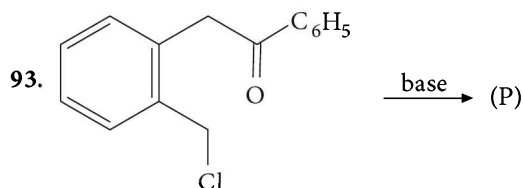
92. An organic compound(X) when heated with concentrated NaOH solution followed by acidification gave the following

lactone as the only organic product

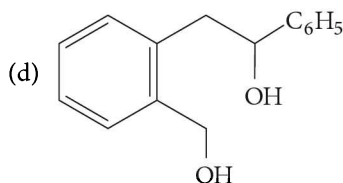
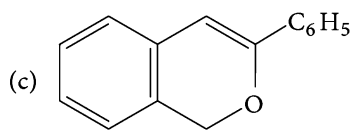
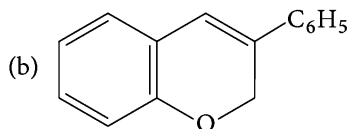
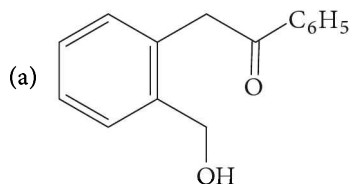


The compound (X) is

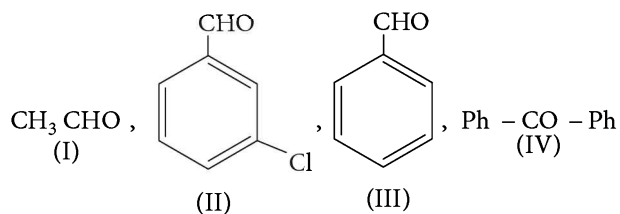




The major product (P) in the above reaction will be



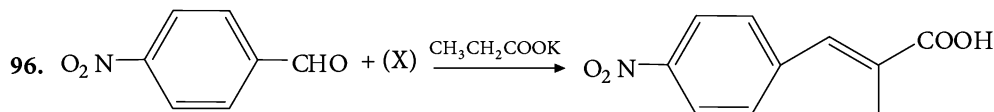
94. The increasing order of the rate of HCN addition to the following carbonyl compounds is



- (a) $\text{II} > \text{IV} < \text{III} < \text{I}$ (b) $\text{IV} < \text{II} < \text{III} < \text{I}$ (c) $\text{IV} < \text{I} < \text{III} < \text{II}$ (d) $\text{IV} < \text{III} < \text{II} < \text{I}$

95. The product formed by the reaction of ethyl acetate with sodium ethoxide is

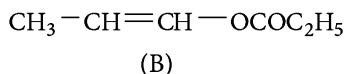
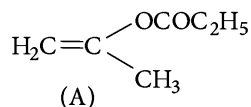
- (a) ethyl acetoacetate (b) ethyl propionate
(c) Propane-2, 3-dione (d) 3-oxobutanal



The reagent (X) in the above reaction is

- (a) $\text{BrCH}_2\text{CH}_2\text{COOH}$ (b) $(\text{CH}_3\text{CO})_2\text{O}$ (c) $(\text{CH}_3\text{CH}_2\text{CO})_2\text{O}$ (d) $(\text{CH}_3\text{CH}_2\text{COO})_2$

97. The reagent that can be used to distinguish between the products obtained by the acid hydrolysis of (a) and (b) given below is



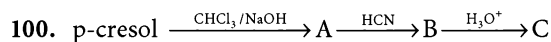
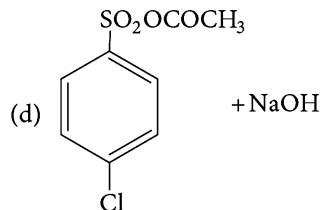
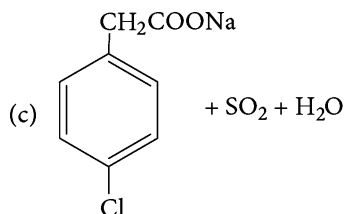
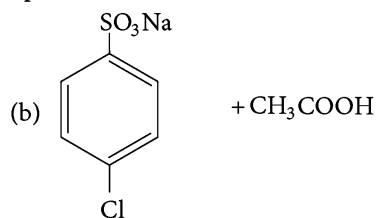
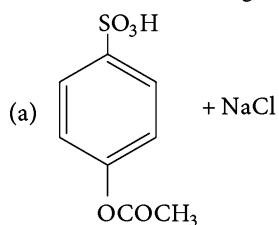
- (a) 2, 4-Dinitrophenyl hydrazine (b) Lucas reagent
(c) Aqueous NaOH (d) Tollens' reagent

98. The strongest acid among the following is

- (a) $\text{C}_6\text{H}_5\text{COOH}$ (b) CH_3COOH (c) $m\text{-CH}_3\text{O C}_6\text{H}_4\text{COOH}$ (d) $p\text{-CH}_3\text{O C}_6\text{H}_4\text{COOH}$

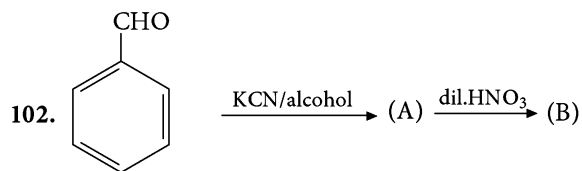
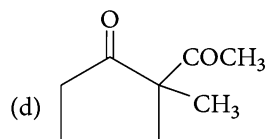
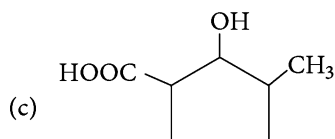
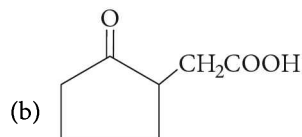
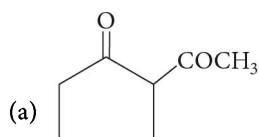
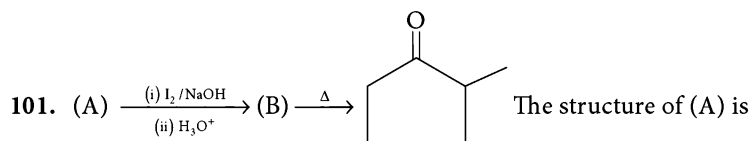
5.52 Aldehydes, Ketones and Carboxylic Acids

99. Which of the following is obtained when 4-chlorobenzene sulphonic acid is treated with excess sodium acetate?

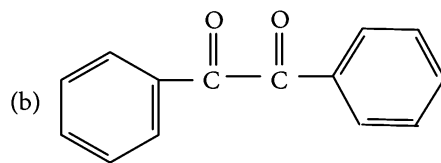
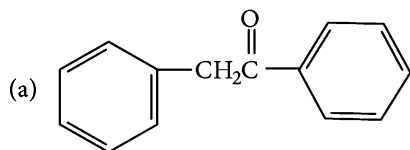


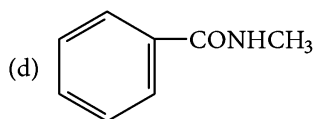
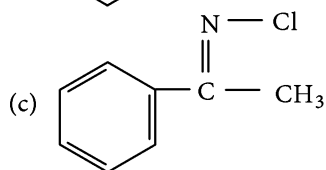
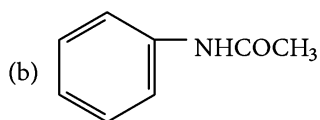
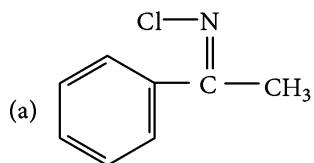
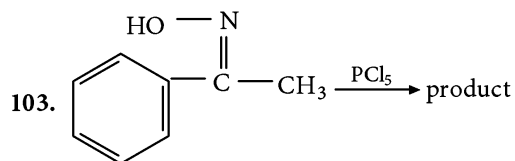
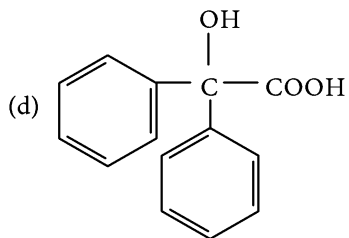
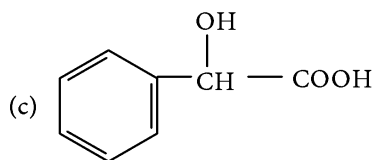
Which of the following statements is not true about the product (C) in the above sequence of reactions?

- (a) It gives violet colour with neutral ferric chloride solution.
- (b) It is optically active.
- (c) There are six sp² hybridised carbon atoms in one molecule of it.
- (d) It liberates CO₂ when treated with NaHCO₃ solution.

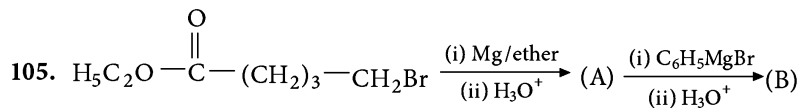
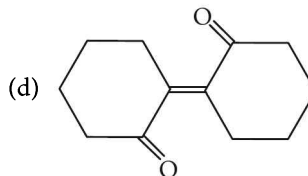
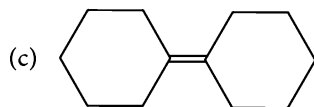
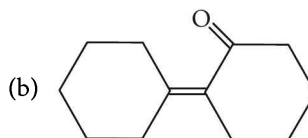
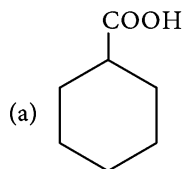


The structure of (B) is

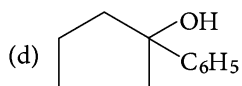
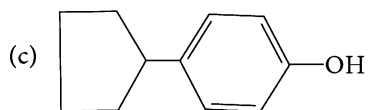
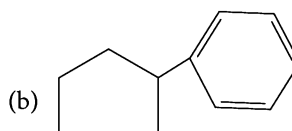
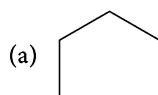




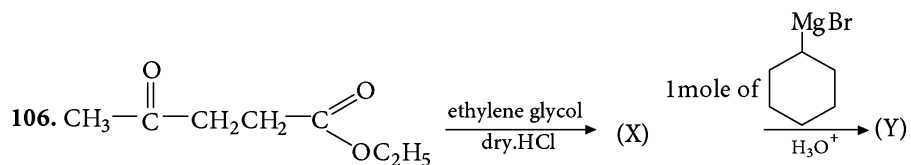
104. The reaction of cyclohexanone with NaOH under hot conditions gives



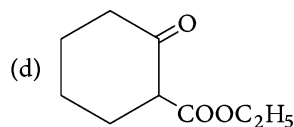
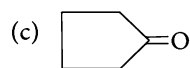
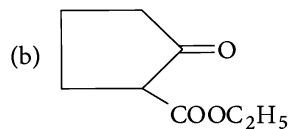
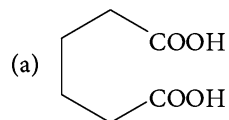
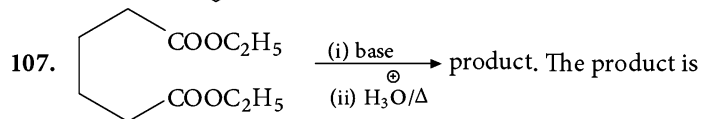
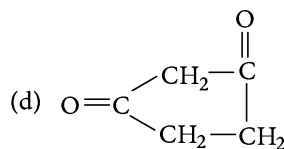
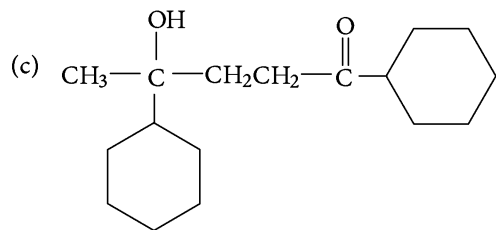
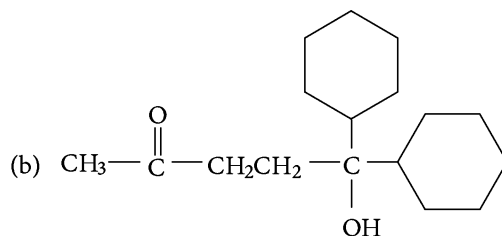
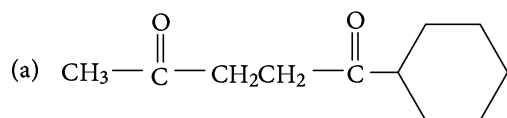
The structure of (b) is



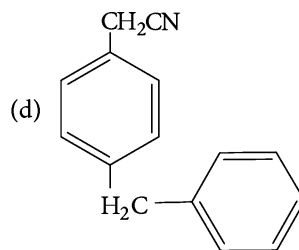
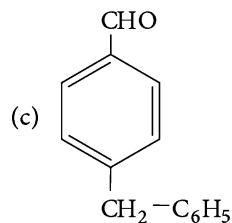
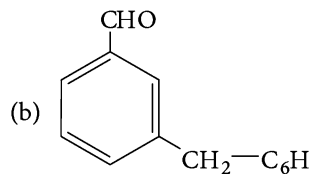
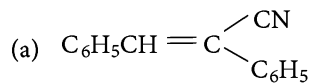
5.54 Aldehydes, Ketones and Carboxylic Acids



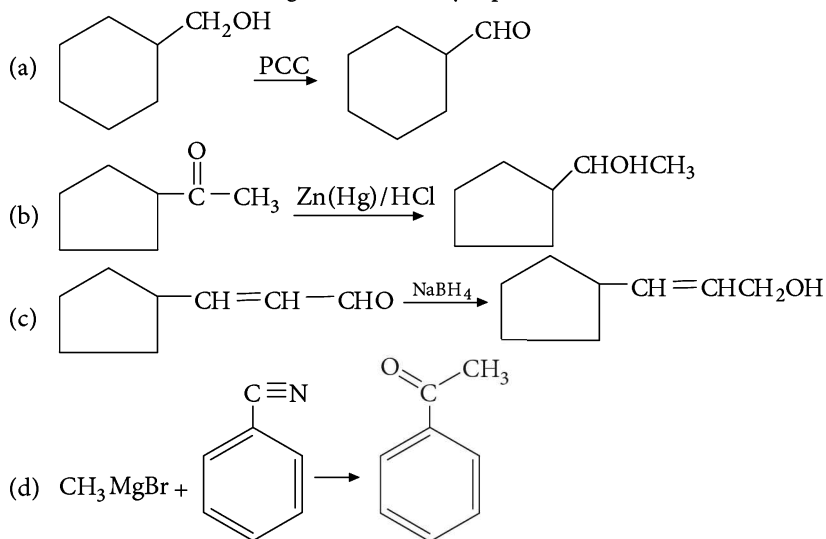
The structure of the product (Y) is



108. The product obtained when benzaldehyde reacts with phenyl acetonitrile in the presence of a base is



109. Which one of the following is not correctly represented?



110. Aspirin (acetyl salicylic acid) is prepared by heating salicylic acid with acetic anhydride. In an experiment, 5 g of salicylic acid is heated with 8 g of acetic anhydride. The theoretical yield of aspirin is

- (a) 5.46 g (b) 3.84 g (c) 6.52 g (d) 4.95 g



Assertion-Reason Type Questions

Directions: Each question contains Statement-1 and Statement-2 and has the following 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

111. Statement 1

Acetals and ketals are unstable in aqueous acid conditions, but quite stable to alkaline conditions.
and

Statement 2

A weaker base like (OH^-) cannot displace a stronger base like (OR^-) found in acetals and ketals.

112. Statement 1

Formic acid produces a white precipitate with HgCl_2 .
and

Statement 2

Mercuric salt of formic acid is insoluble and therefore gets precipitated.

113. Statement 1

p-Fluorobenzoic acid is a weaker acid than p-chlorobenzoic acid.
and

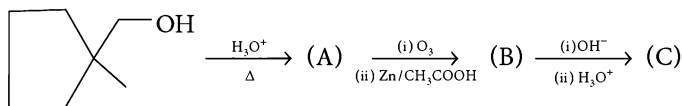
Statement 2

Fluorine in fluorobenzene has greater +R effect than chlorine due to matching sizes of 2p orbitals of carbon and fluorine.

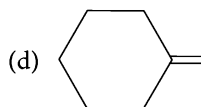
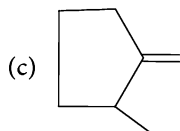
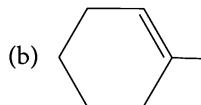
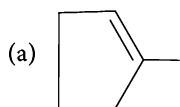


Linked Comprehension Type Questions

Directions: This section contains 1 paragraph. Based upon the paragraph, 3 multiple choice questions have to be answered. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.



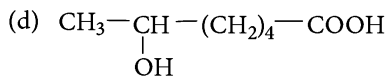
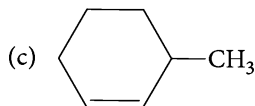
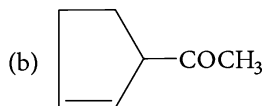
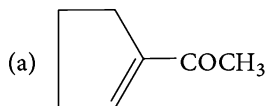
114. The product (A) in the above reaction is



115. The IUPAC name of product (B) is

- (a) Heptane-2, 6-dione (b) 6-oxoheptanoic acid (c) 5-oxohexanal (d) 6-oxoheptanal

116. The structure of the product (C) is



Multiple Correct Objective Type Questions

Directions: Each question in this section has four suggested answers of which ONE OR MORE answers will be correct.

117. Benzophenone does not react with

- (a) NaHSO_3 (b) H_2NOH (c) HCN (d) $\text{C}_6\text{H}_5\text{MgBr}$

118. Which of the following is/are correct about Cannizzaro reaction?

- (a) Step-1 involves attack of $\text{OH}^\ominus$ on carbonyl carbon of aldehyde having no α - hydrogen
 (b) Step-1 is the rate determining step
 (c) Step-2 involves hydride shift
 (d) In crossed Cannizzaro reaction involving formaldehyde, it always undergoes oxidation.

119. Which of the following statements relating to the derivatives of carboxylic acids are correct?

- (a) An amide $\text{R}-\text{C}(=\text{O})\text{NH}_2$ answers all the tests for a primary amine.
 (b) Among the carboxylic acid derivatives, acid chloride is the most reactive.

- (c) Carboxylic acid can be converted to an ester by reacting with alcohol in the presence of a base.
(d) Benzoic acid can be converted to methyl benzoate by using diazomethane.

**Matrix-Match Type Question**

Directions: Match the elements of Column I to elements of Column II. There can be single or multiple matches.

120.

Column I

- (a) $p\text{-NO}_2\text{C}_6\text{H}_4\text{CHO}$
(b) $\text{CH}_3\text{COOC}_2\text{H}_5$
(c) $\text{CH}_3\text{CH}_2\text{COCl}$
(d) $(\text{CH}_3\text{CO})_2\text{O}$

Column II

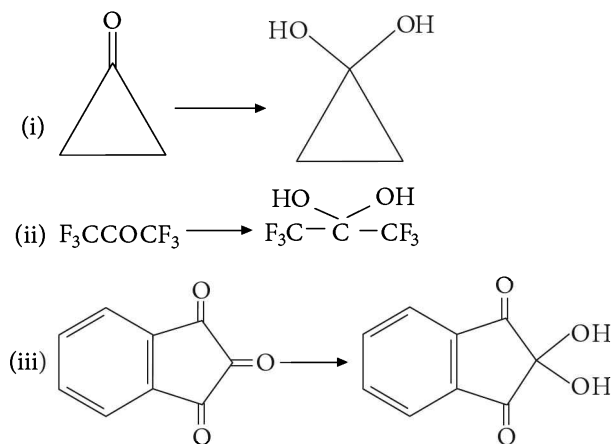
- (p) Friedel–Crafts reaction
(q) Claisen Condensation
(r) Perkin reaction
(s) Benzoin condensation
(t) Rosenmund's reduction

ADDITIONAL PRACTICE EXERCISE

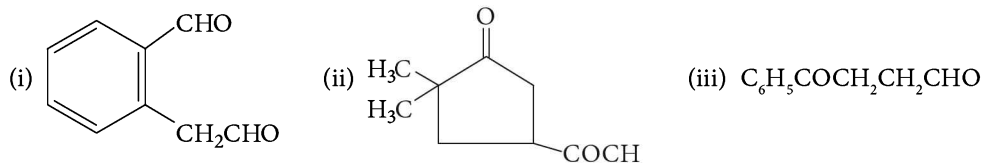


Subjective Questions

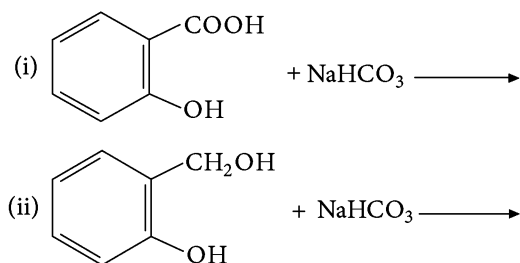
121. How is cyclopentane converted to cyclopentane carbaldehyde?
122. Write the steps involved in the following conversions?
- Benzaldehyde to benzophenone
 - Benzaldehyde to 3-phenylpropan-1-ol
 - Benzene to 2-phenyl ethanoic acid
123. There are two NH_2 groups in semicarbazide. But only one is involved in the formation of semicarbazones. Why?
124. Generally geminal diols are not stable. Account for the fact that the hydrates of the following carbonyl compounds are stable.

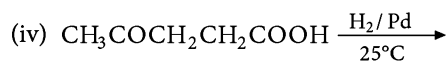
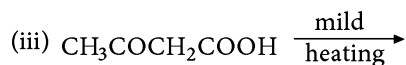


125. What is the product of addition of one equivalent of HCN to each of the following? Give reasons.

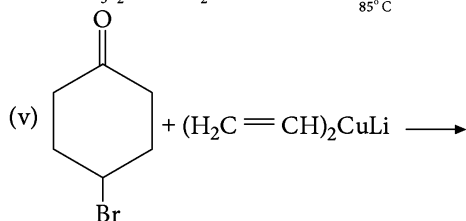
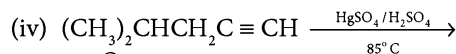
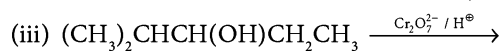
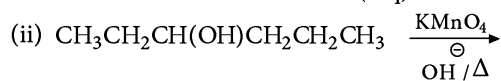
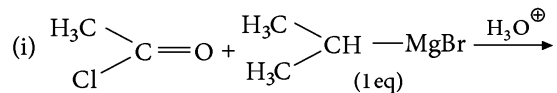


126. Give the major products, if any, in the following reactions



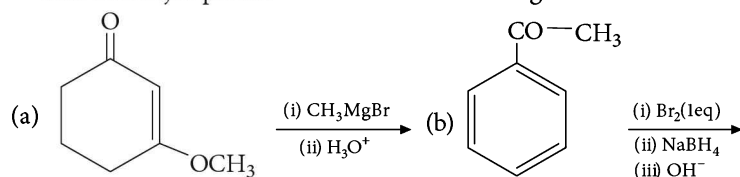


127. Give the structures of the products in the following reactions

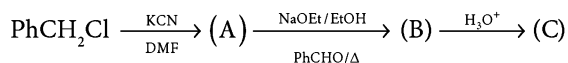


128. Explain why o-hydroxybenzaldehyde is a liquid at room temperature while p-hydroxybenzaldehyde is a solid?

129. Predict the major product in each of the following



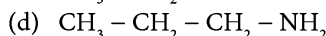
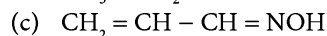
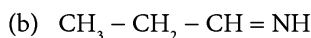
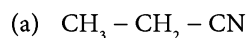
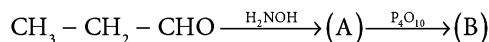
130. Identify the product (c) in the following sequence of reaction



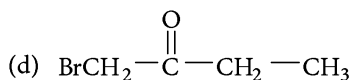
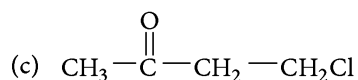
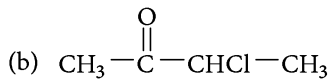
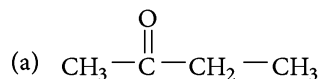
Straight Objective Type Questions

Directions: This section contains multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

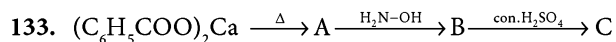
131. Identify the product (b) in the following sequence of reactions.



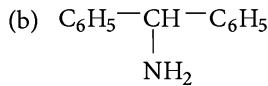
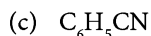
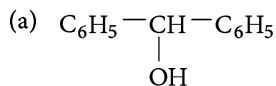
132. Which carbonyl compound among the following is most reactive towards nucleophilic addition?



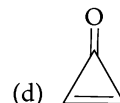
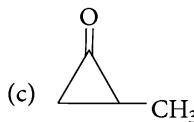
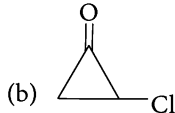
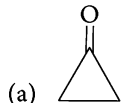
5.60 Aldehydes, Ketones and Carboxylic Acids



The product C in the above reaction series is



134. Which of the following carbonyl compound is most stable?



The above reaction is catalysed by

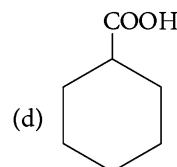
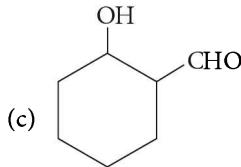
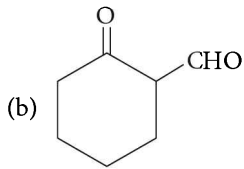
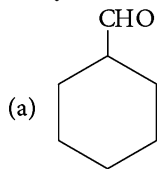
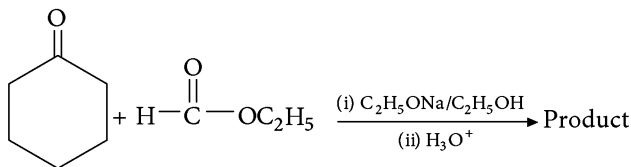
(a) bases only

(b) acids only

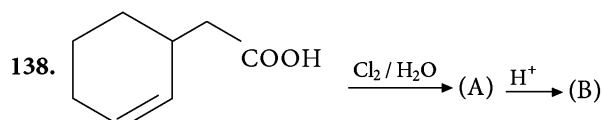
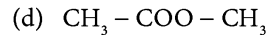
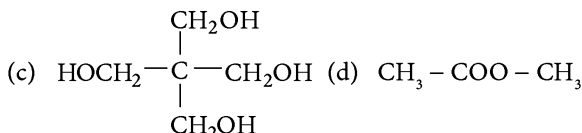
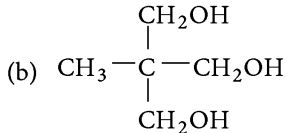
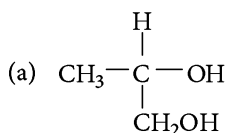
(c) both base and acid

(d) P_2O_5

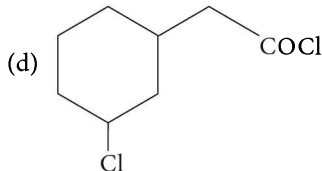
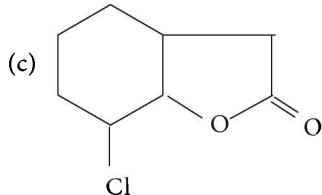
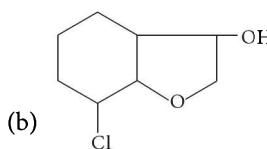
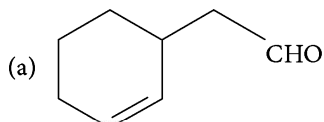
136. The product formed in the following reaction is

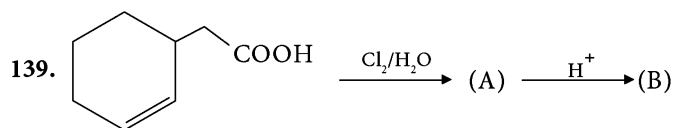


137. When a mixture containing excess formaldehyde and acetaldehyde is treated with $\text{Ca}(\text{OH})_2$, The product formed is calcium formate and

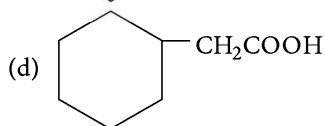
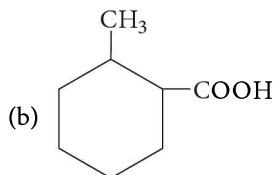
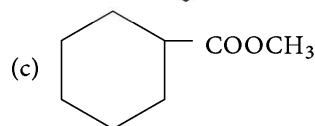
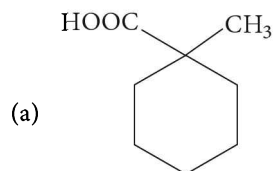


The probable product (B) is

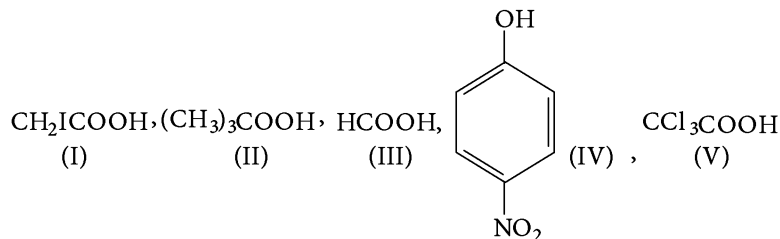




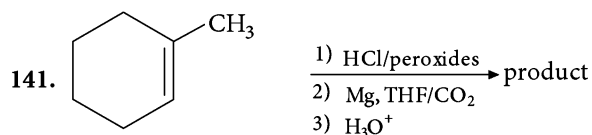
Identify (D)



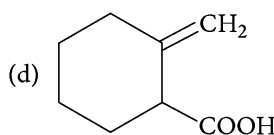
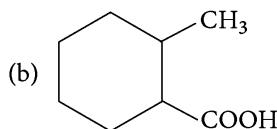
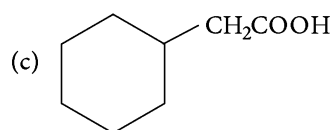
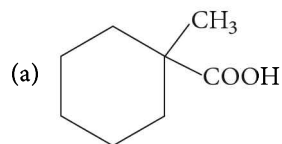
140. The correct order of increasing acidic strength of the following compounds is



- (a) $\text{IV} < \text{II} < \text{I} < \text{III} < \text{V}$ (b) $\text{II} < \text{I} < \text{IV} < \text{III} < \text{V}$ (c) $\text{I} < \text{II} < \text{IV} < \text{III} < \text{V}$ (d) $\text{II} < \text{I} < \text{III} < \text{IV} < \text{V}$



The product is



142. Salicylic acid is more acidic than o-methoxybenzoic acid though both have electron releasing groups i.e., $-\text{OH}$ and $-\text{OCH}_3$. This is because

- (a) $-\text{OH}$ is a stronger electron releasing group compared to $-\text{OCH}_3$.
 (b) salicylate ion is stabilized by intramolecular hydrogen bonding.
 (c) salicylic acid has two replaceable hydrogen atoms.
 (d) $-\text{OCH}_3$ has a stronger steric effect to prevent the stabilization of the carboxylate anion.

143. The conversion of acetaldehyde to Lactic acid involves

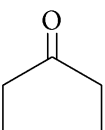
- (a) the addition of HCN followed by acid hydrolysis
 (b) the addition of alkali followed by hydrolysis

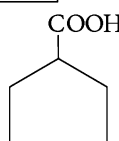
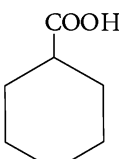
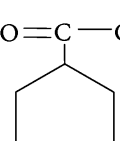
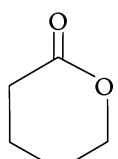
5.62 Aldehydes, Ketones and Carboxylic Acids

- (c) the addition of HCN followed by treatment with Zn/HCl
 (d) the addition of KCN solution followed by treatment with Tollens' reagent

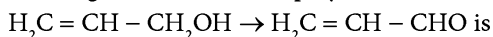
144. Aldol condensation cannot occur between

- (a) two aldehydes
 (b) an aldehyde and a ketone
 (c) two ketones
 (d) an aldehyde and an ester

145.  $\xrightarrow{\text{peracid}}$ product. The structure of the product is

- (a)  (b)  (c)  (d) 

146. The reagent that can be employed for the conversion

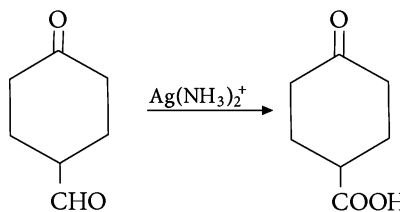
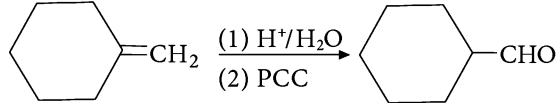
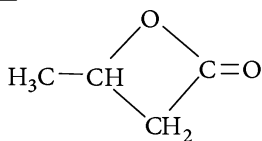
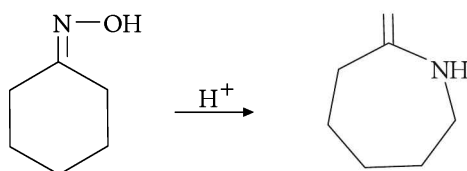


- (a) acidified KMnO_4 (b) alkaline KMnO_4 (c) MnO_2 (d) Ag_2O moist

147. $\text{H}_2\text{C} = \text{CH} - \text{CHO} + \text{HCl} \rightarrow (\text{A})$. (A) is

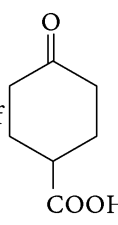
- (a) $\text{ClCH}_2 - \text{CH}_2 - \text{CHO}$ (b) $\text{CH}_3 - \text{CHCl} - \text{CHO}$
 (c) $\text{H}_2\text{C} = \text{CH} - \text{COOH}$ (d) $\text{ClCH}_2 - \text{CHCl} - \text{COOH}$

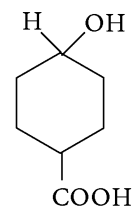
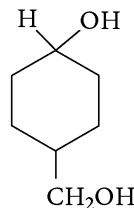
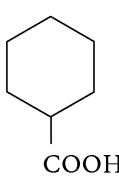
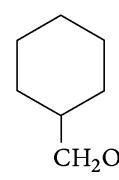
148. Identify the reaction represented incorrectly

- (a) 
- (b) 
- (c) $\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5 \xrightarrow[(2) \text{H}^+]{(1) \text{NaBH}_4} \text{H}_3\text{C} - \text{CH} - \text{C}(=\text{O}) - \text{CH}_2$ 
- (d) 

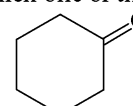
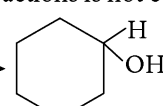
149. Identify the incorrect statement among the following.

- (a) Both pyruvic acid and lactic acid answer the haloform test
 (b) $\text{CH}_3\text{CH}_2\text{COOH}$ can be reduced to $\text{CH}_3\text{CH}_2\text{CH}_3$ using red P and HI
 (c) Kolbe's electrolysis of potassium succinate gives ethylene and CO_2
 (d) Strong heating of ammonium acetate gives methylcyanide

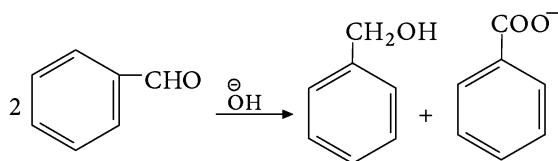
150. The product of the reaction of  with LiAlH_4 is

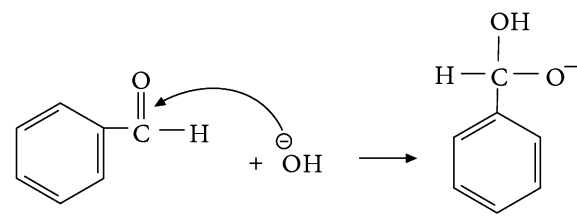
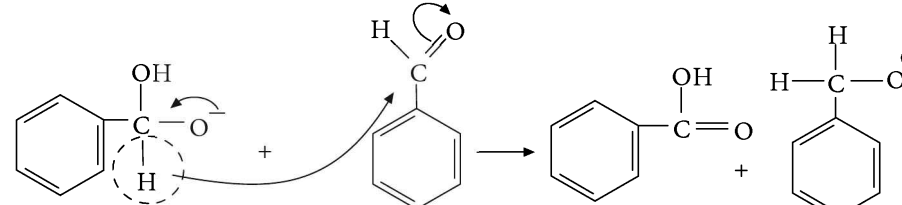
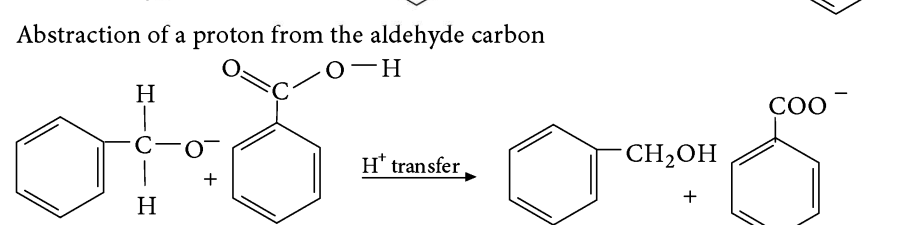
- (a)  (b)  (c)  (d) 

151. Which one of the following reactions is not correctly represented?

- (a)  $\xrightarrow{\text{Zn(Hg)/HCl}}$ 
- (b) $\text{CH}_3\text{COOC}_2\text{H}_5 \xrightarrow{\text{LiAlH}_4} \text{CH}_3\text{CH}_2\text{OH}$
- (c) $\text{CH}_3\text{CN} \xrightarrow[\text{(ii) steam distillation}]{\text{(i) SnCl}_2/\text{HCl}} \text{CH}_3\text{CHO}$
- (d) $\text{CH}_3\text{CH}=\text{CH}-\text{CHO} \xrightarrow{\text{NaBH}_4} \text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$

152. The rate determining step in the reaction given below is

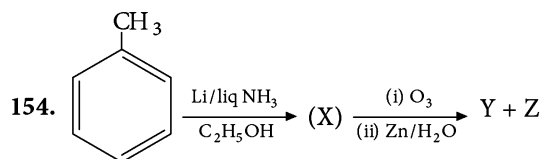


- (a) 
- (b) 
- (c) Abstraction of a proton from the aldehyde carbon
- (d) 

5.64 Aldehydes, Ketones and Carboxylic Acids

153. The reaction which does not involve nucleophilic acyl substitution is

- (a) Claisen reaction (b) Beckmann rearrangement
(c) aldol condensation (d) Saponification of esters

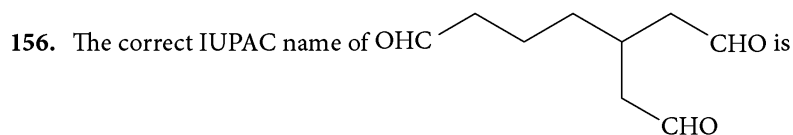


The major products (Y) and (Z) in the above reaction are

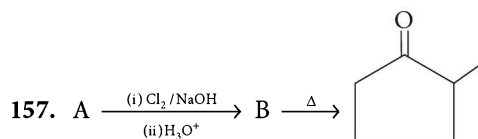
- (a) $\text{OHC}-\underset{\text{CH}_3}{\text{CH}}-\text{CHO} + \text{OHC}-\text{CH}_2-\text{CHO}$
(b) $\text{CH}_3-\text{CO}-\text{CH}_2-\text{CHO} + \text{OHC}-\text{CH}_2-\text{CHO}$
(c) $\text{CH}_3-\text{CO}-\text{CHO} + \text{OHC}-\text{CH}_2-\text{CH}_2-\text{CHO}$
(d) $\text{OHC}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{CHO} + \text{OHC}-\text{CHO}$

155. The compound that forms a stable hemiacetal when treated with CH_3OH and dry HCl is

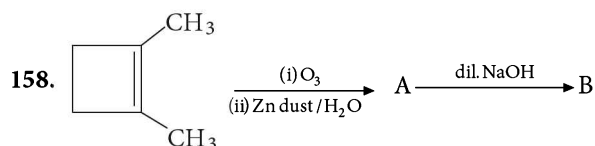
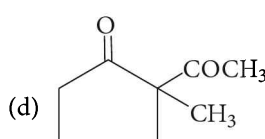
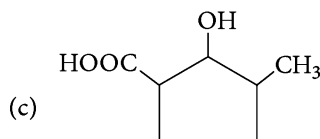
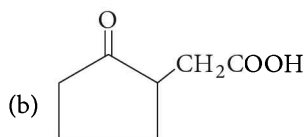
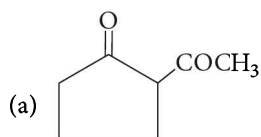
- (a) benzaldehyde (b) cyclohexanone (c) cyclopropanone (d) propanone



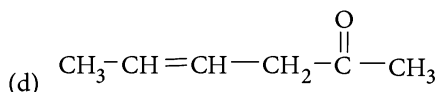
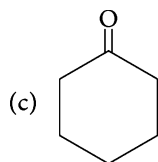
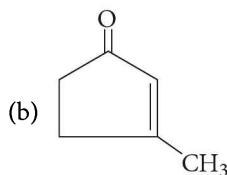
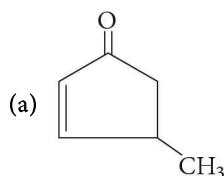
- (a) 2-(formylmethyl) pentane-1,5-dicarbaldehyde (b) 3-(formylmethyl) heptane-1,7-dial
(c) 2-(formylmethyl) pentane-1,5-dial (d) 3-(oxomethyl) heptane-1,7-dial



The compound A in the above sequence of reaction is

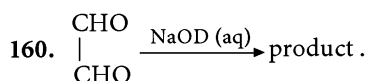


The structure of the product B in the above reaction is



159. Which of the following compounds will give methyl vinyl ketone by aldol condensation followed by dehydration?

- (a) Formaldehyde and acetaldehyde (b) Formaldehyde and acetone
(c) Acetaldehyde and acetone (d) Two molecules of acetaldehyde

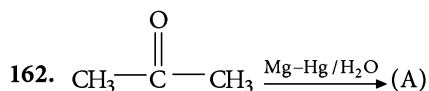


The product is

- (a) $\begin{array}{c} \text{H}_2\text{C---OD} \\ | \\ \text{COO}^- \end{array}$ (b) $\begin{array}{c} \text{H}_2\text{C---OH} \\ | \\ \text{COOD} \end{array}$
(c) $\begin{array}{c} \text{CH}_2\text{OD} \\ | \\ \text{COOH} \end{array}$ (d) $\text{HOH}_2\text{C---CH}_2\text{---CH}_2\text{---COOD}$

161. The reagent that can be used for the conversion of $\text{CH}_3\text{CH=CHCHO}$ to $\text{CH}_3\text{CH=CHCOOH}$ is

- (a) Alkaline KMnO_4 (b) Zn(Hg)/HCl
(c) $\text{PCC/CH}_2\text{Cl}_2$ (d) Tollens' reagent

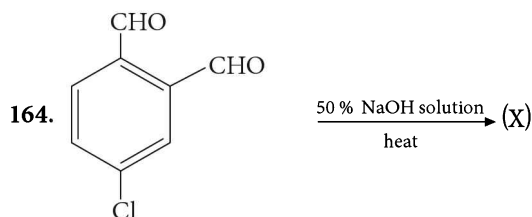


(A) $\xrightarrow{\text{dil. H}_2\text{SO}_4} (\text{B})$ The product (B) in the above reaction is

- (a) Hexan-2-one
(b) 3,3-Dimethyl butan-2-one
(c) 2,3-Dimethyl butan-2-ol
(d) 4-Hydroxy-4-methyl pentan-2-one

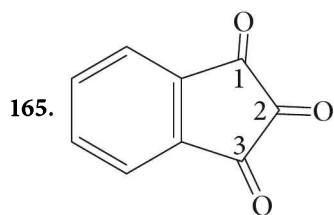
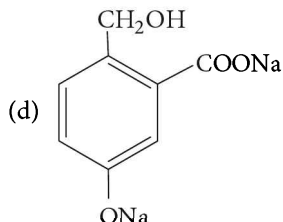
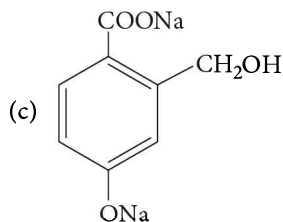
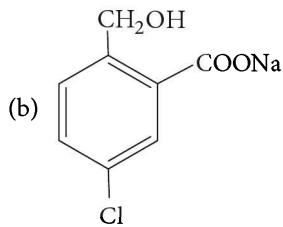
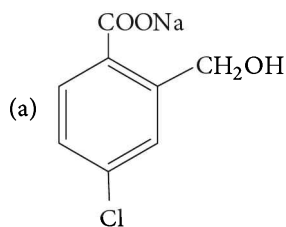
163. The product (P) formed in the following reaction is $\text{CH}_3\text{---C}\equiv\text{CH} \xrightarrow[\text{(ii) HCHO}]{\text{(i) NaNH}_2} (\text{P})$

- (a) $\text{CH}_3\text{---C}\equiv\text{C---CH}_2\text{OH}$ (b) $\text{CH}_3\text{---C}\equiv\text{C---COONa}$
(c) $\text{CH}_3\text{---C}\equiv\text{C---CHO}$ (d) $\text{CH}_3\text{---CH=CH---CHO}$



The major product (x) in the above reaction is

5.66 Aldehydes, Ketones and Carboxylic Acids

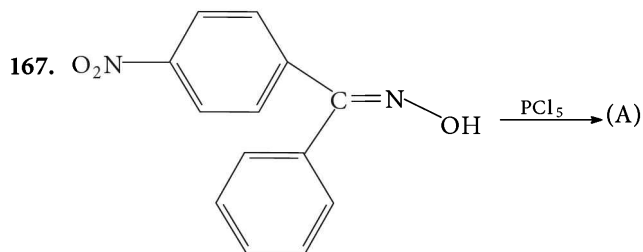


Among the carbonyl groups 1, 2 and 3 marked in the above structure, the most reactive one for nucleophilic addition reaction is

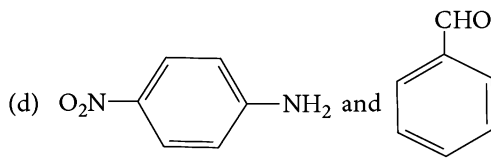
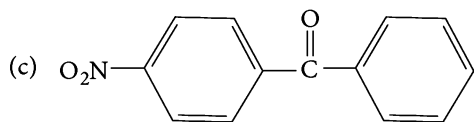
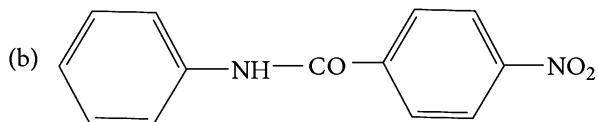
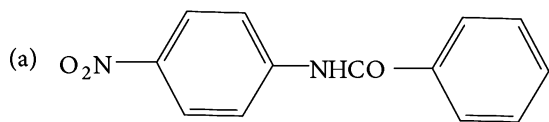
- (a) 1 (b) 2
(c) 3 (d) All have equal reactivity

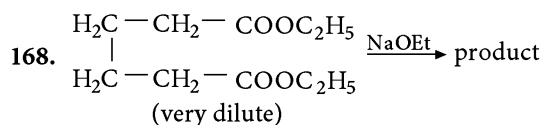
166. The organic compound formed by the dry distillation of calcium adipate is reduced with zinc amalgam and concentrated hydrochloric acid. The final product formed is

- (a) cyclopentane (b) pentane
(c) cyclopentanol (d) cyclohexane

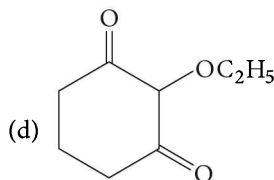
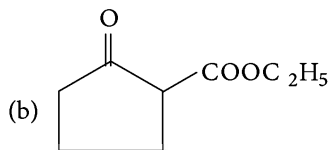
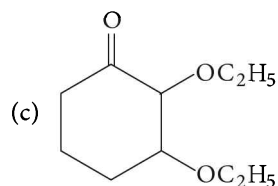
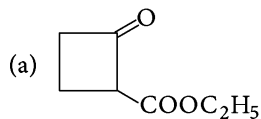


Identify the product(s) (A).

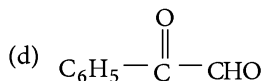
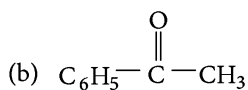
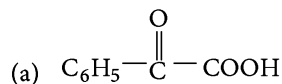
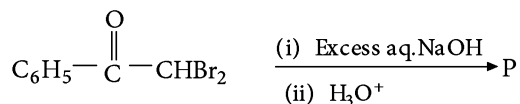




The product is



169. When acetone reacts with chloroform in the presence of alkali like NaOH, the product formed is
 (a) Chloropionium (b) acetic acid (c) Chloreton (d) mesityloxide
170. The product (P) of the following reaction is



Assertion-Reason Type Questions

Directions: Each question contains Statement-1 and Statement-2 and has the following 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

171. Statement 1

o-hydroxy benzene sulphonic acid on heating to 373 K changes to p-hydroxy benzene sulphonic acid
and

Statement 2

Sulphonation of phenol is a reversible process.

172. Statement 1

p-nitrophenol is more acidic than o-nitrophenol.
and

Statement 2

Steric effect due to the presence of $-\text{NO}_2$ group at ortho position of $-\text{OH}$ decreases the acidic strength of o-nitrophenol.

5.68 Aldehydes, Ketones and Carboxylic Acids

173. Statement 1

Between benzamide, $\text{C}_6\text{H}_5\text{CONH}_2$ and benzoyl chloride, $\text{C}_6\text{H}_5\text{COCl}$, the former is more reactive than the latter.
and

Statement 2

$-\text{Cl}$ is a better leaving group than $-\text{NH}_2$.

174. Statement 1

CF_3COONa is more easily decarboxylated than CCl_3COONa on heating with soda lime.
and

Statement 2

Greater the stability of carbanion, higher the ease of decarboxylation.

175. Statement 1

MPV reaction is used for the reduction of ketones to alcohols.
and

Statement 2

Tischenko reaction is similar to MPV reaction used for the reduction of aldehydes to alcohols.

176. Statement 1

Eventhough carboxylic acids contain a $\text{>C}=\text{O}$ group, they do not give the characteristic reaction of carbonyl compounds.
and

Statement 2

The electrophilicity of carbonyl carbon is less in carboxylic acids due to resonance.

177. Statement 1

The $\text{C}=\text{O}$ group of ethanamide is more polar than that in ethylethanoate.
and

Statement 2

$-\text{NH}_2$ group is more electron donating than $-\text{OC}_2\text{H}_5$ by mesomeric effect.

178. Statement 1

The pK_a value of ethanoic acid is lower than that of phenol.
and

Statement 2

Phenoxide ion is more resonance stabilised than ethanoate ion.

179. Statement 1

2-methylpropanal undergoes Cannizzaro reaction when heated with 50% NaOH solution at about 443–473K.
and

Statement 2

2-Methylpropanal contains an α -hydrogen atom.

180. Statement 1

All aldehydes and ketones react with HCN to give a racemic mixture of the corresponding cyanohydrin.
and

Statement 2

Cyanide ion is an ambident nucleophile.

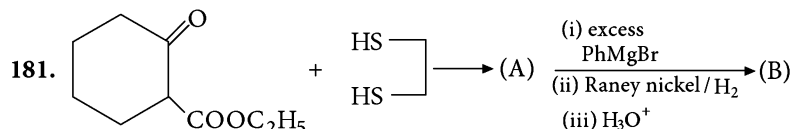


Linked Comprehension Type Questions

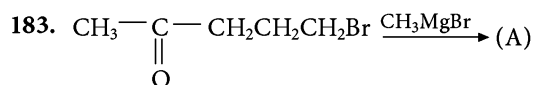
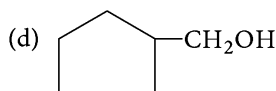
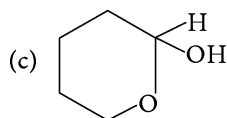
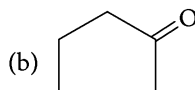
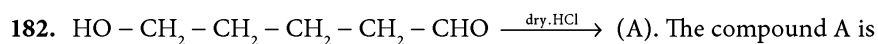
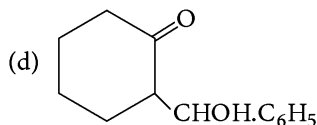
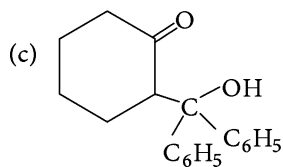
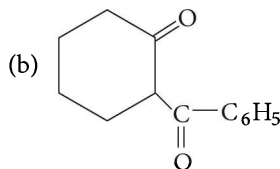
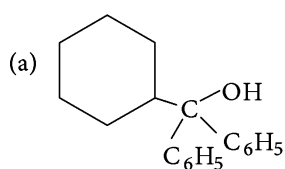
Directions: This section contains 3 paragraphs. Based upon the paragraph, 3 multiple choice questions have to be answered. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

Passage I

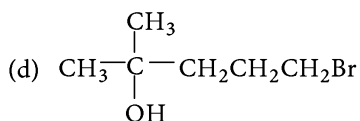
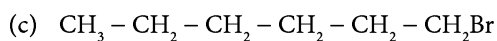
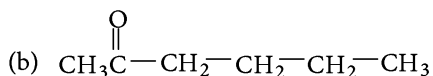
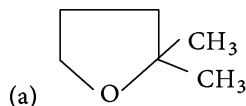
When an aldehyde or ketone is treated with excess of an alcohol in the presence of an acid catalyst, alcohol molecules are added to the carbonyl compound to give an acetal or ketal. The final product is a tetrahedral molecule. Thioacetals or thioketals can be synthesized by treating the aldehyde or ketone with a thiol or a dithiol in the presence of an acid catalyst. The formation of ketal or acetal is one of the methods of protecting a carbonyl group.



The structure of (B) is



The product (A) is



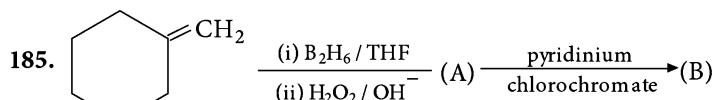
5.70 Aldehydes, Ketones and Carboxylic Acids

Passage II

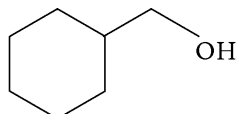
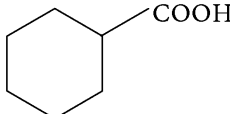
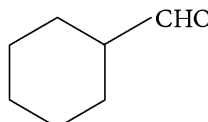
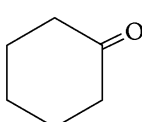
Alkenes and alkynes on reductive ozonolysis yield carbonyl compounds, whereas on oxidative ozonolysis they give carbonyl or carboxyl compounds, depending on the substituents. Aldehydes, ketones and carboxylic acids can also be obtained by the oxidation of alcohols. Aldehydes and ketones undergo a variety of nucleophilic addition reactions.

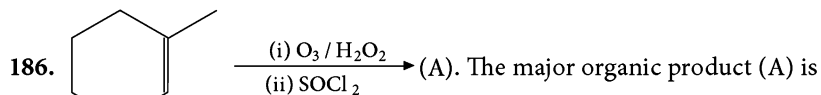
184. Which of the following alcohol will not give a carbonyl compound when the vapours of alcohol are passed through red hot copper tube?

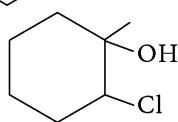
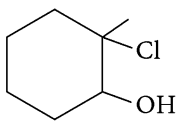
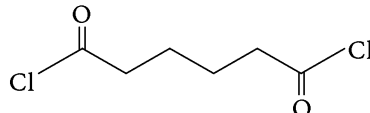
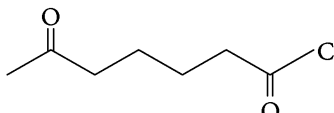
- (a) 3-methyl-pentan-1-ol (b) 4-methyl-hexan-2-ol
(c) Butan-1-ol (d) 2-methyl-propan-2-ol



The major organic product (B) is

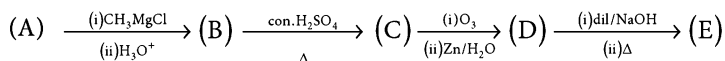
- (a)  (b) 
(c)  (d) 



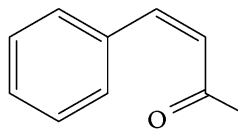
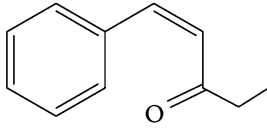
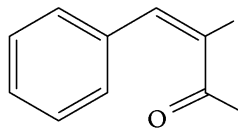
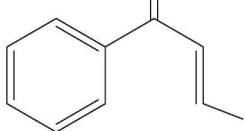
- (a)  (b) 
(c)  (d) 

Passage III

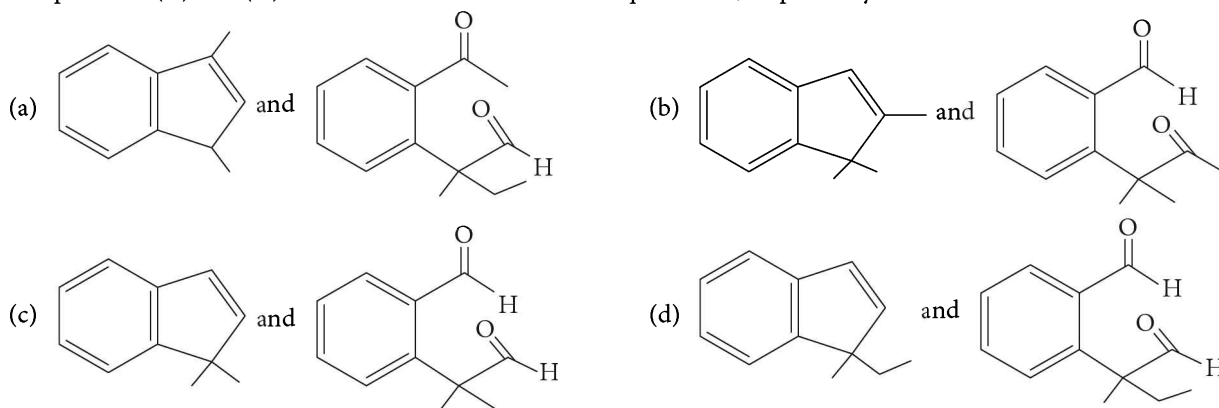
A carbonyl compound (a) which gives yellow precipitate when warmed with powdered iodine and alkali was allowed to undergo the following sequence of reactions



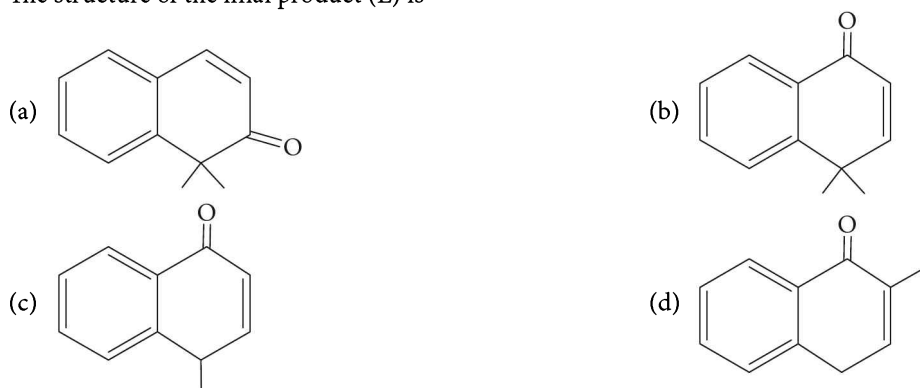
187. The most probable structure of the compound (A) is

- (a)  (b) 
(c)  (d) 

188. The products (C) and (D) formed in the above reaction sequence are, respectively



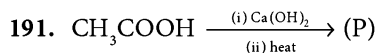
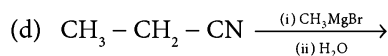
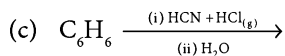
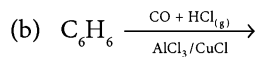
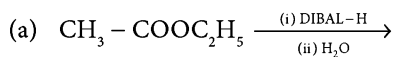
189. The structure of the final product (E) is



Multiple Correct Objective Type Questions

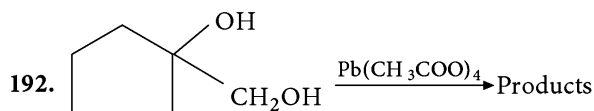
Directions: Each question in this section has four suggested answers of which ONE OR MORE answers will be correct.

190. Which of the following reactions give aldehyde as a product?



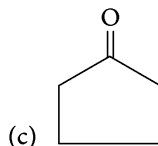
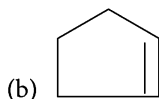
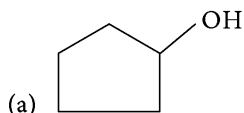
The organic compound (P) formed in the above reaction

- (a) does not reduce Tollens' reagent
- (b) does not undergo aldol condensation
- (c) reacts with chloroform in presence of alkali
- (d) gives two geometrical isomers of the oxime when treated with hydroxylamine



The possible product(s) obtained in the above reaction is/are

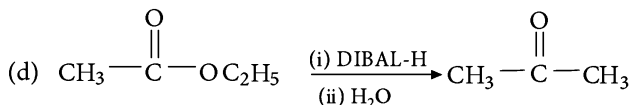
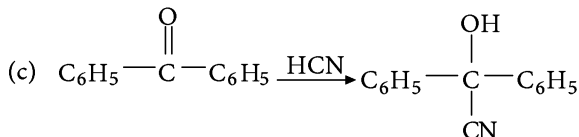
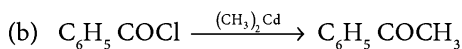
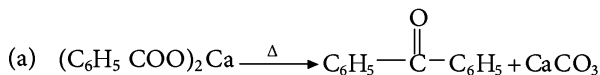
5.72 Aldehydes, Ketones and Carboxylic Acids



193. Identify the correct statements among the following.

- (a) Formaldehyde can react with both -NH_2 groups in semicarbazide.
- (b) In mixed Cannizzaro reaction involving HCHO, it is always the intermediate formed from HCHO which transfers its hydride to the other aldehyde.
- (c) Benzaldehyde reduces both Tollens' reagent and Fehling's solution.
- (d) In Fehling's solution, Cu(II) ions are kept in soluble form of a complex in alkaline medium.

194. Identify the reactions which yield the product shown under the given conditions



195. Acetone can be obtained by

- (a) the decomposition of calcium acetate.
- (b) Rosenmund's reduction of acetyl chloride.
- (c) the hydration of methyl acetylene.
- (d) ozonolysis of 2,3-dimethylbut-2-ene.

196. The carboxylic acid(s) that form anhydride on heating with phosphorus pentoxide is/are

- (a) Malonic acid
- (b) Ethanoic acid
- (c) Maleic acid
- (d) Succinic acid

197. Which of the following statements relating to the derivatives of carboxylic acids are correct?

- (a) An amide $\text{R}-\text{C}(=\text{O})\text{NH}_2$ answers all the tests for a primary amine.
- (b) Esters undergo hydrolysis more readily than acid amides..
- (c) Carboxylic acid can be converted to an ester by reacting with alcohol in the presence of a base
- (d) Benzoic acid can be converted to methyl benzoate by using diazomethane.



Matrix-Match Type Questions

Directions: Match the elements of Column I to elements of Column II. There can be single or multiple matches.

198.

Column I

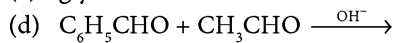
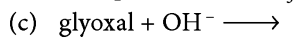
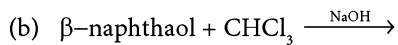
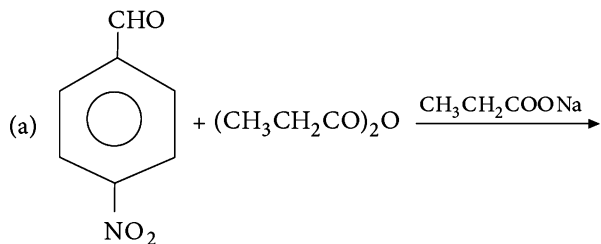
- (a) Cannizzaro reaction
- (b) Perkin reaction
- (c) Kolbe reaction
- (d) $\text{CH}_3\text{CHO} + \text{NaOH}$

Column II

- (p) Crotonaldehyde
- (q) Carbanion intermediate
- (r) Electrophilic substitution
- (s) Disproportionation
- (t) Formation of new carbon-carbon bond.

199.

Column I



Column II

(p) Disproportionation

(q) α, β -unsaturated product

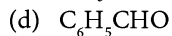
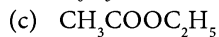
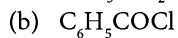
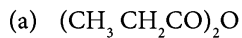
(r) Carbanion intermediate

(s) Hydride shift

(t) Electrophilic substitution

200.

Column I



Column II

(p) Friedel-Crafts reaction

(q) Benzoin condensation

(r) Perkin reaction

(s) Rosenmund's reduction

(t) Claisen condensation

SOLUTIONS

ANSWER KEYS

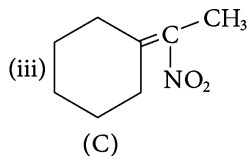
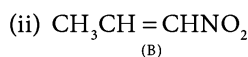
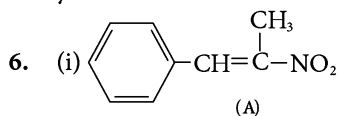
- $(\text{CH}_3)_2\text{CHCOOH} + \text{CHI}_3$
 - Does not undergo iodoform reaction.
 - Does not undergo iodoform reaction.
 - Cyclohexane carboxylic acid and CHI_3
 - Does not undergo iodoform reaction.

- Ketones are less reactive due to the +I effect of two alkyl groups and consequent decrease in the positive charge on the carbonyl carbon atom. Steric crowding also reduces the reactivity of ketones.

- Reduction with NaBH_4 followed by dehydration
 - First converted to cyclopentane by Clemmensen reduction. It is then treated successively with $\text{Br}_2/\text{h}\nu$, Mg/ether and $\text{HCHO}/\text{hydrolysis}$

- It is first treated with dil. $\text{H}_2\text{SO}_4/\text{HgSO}_4$ followed by iodoform reaction.

- The starting material is cyclohexene.



- It is treated successively with Mg/ether , CO_2 , H_3O^+ and PCl_5 to get $(\text{CH}_3)_3\text{C}-\text{COCl}$. Then Arndt-Eistert synthesis is carried out.

- ethylene
 - acetylene
- In the resonance structures of phenoxide ion, the negative charge is delocalised on less electronegative carbon

10. Propylpropanoate

11. (c)	12. (b)	13. (b)
14. (c)	15. (a)	16. (c)
17. (b)	18. (c)	19. (a)
20. (a)	21. (d)	22. (d)
23. (a)	24. (a)	25. (a)
26. (d)		
27. (b), (c), (d)		
28. (a), (d)		
29. (a), (c), (d)		
30. (a) $\rightarrow$ (p), (r)		
(b) $\rightarrow$ (p), (s), (t)		
(c) $\rightarrow$ (p), (t)		
(d) $\rightarrow$ (q), (s), (t)		

IIT Assignments Exercise

31. (d)	32. (b)	33. (c)
34. (c)	35. (c)	36. (a)
37. (c)	38. (d)	39. (c)
40. (c)	41. (b)	42. (d)
43. (c)	44. (a)	45. (c)
46. (d)	47. (d)	48. (b)
49. (c)	50. (d)	51. (c)
52. (d)	53. (a)	54. (d)
55. (b)	56. (c)	57. (a)
58. (d)	59. (d)	60. (d)
61. (c)	62. (d)	63. (b)
64. (b)	65. (a)	66. (c)
67. (c)	68. (b)	69. (c)
70. (d)	71. (b)	72. (d)
73. (c)	74. (a)	75. (b)
76. (b)	77. (a)	78. (b)
79. (c)	80. (b)	81. (c)
82. (b)	83. (d)	84. (a)
85. (c)	86. (b)	87. (b)
88. (b)	89. (d)	90. (c)
91. (b)	92. (a)	93. (c)

94. (d)	95. (a)	96. (c)
97. (d)	98. (c)	99. (b)
100. (c)	101. (d)	102. (b)
103. (d)	104. (b)	105. (d)
106. (a)	107. (c)	108. (a)
109. (b)	110. (c)	111. (a)
112. (c)	113. (a)	114. (b)
115. (d)		
116. (a)		
117. (a), (c)		
118. (a), (c), (d)		
119. (b), (d)		
120. (a) $\rightarrow$ (r), (s)		
(b) $\rightarrow$ (q)		
(c) $\rightarrow$ (p), (t)		
(d) $\rightarrow$ (p), (r)		

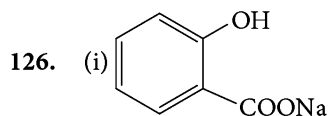
Additional Practics Exercise

- Cyclopentane is successively treated with $\text{Br}_2/\text{h}\nu$, Mg/ether , HCHO , H_3O^+ and PCC
- benzaldehyde is oxidised to benzoic acid and then treated with SOCl_2 and then with benzene in presence anhydrous AlCl_3
 - A mixture of benzaldehyde and CH_3CHO is heated with dilute NaOH solution and the product is reduced with H_2/Ni
 - Benzene is treated successively with $\text{CH}_3\text{Cl}/\text{AlCl}_3$, $\text{Cl}_2/\text{h}\nu$, KCN and H_3O^+
- The lone pair of $-\text{NH}_2$ group near the $\text{C}=\text{O}$ group of semicarbazide is involved in resonance.
- Formation of hydrate relieves part of internal strain in cyclopropanone. In the other cases, the presence of highly electron attracting groups stabilises hydrates.

125. (i) Aldehyde group not directly attached to benzene ring reacts.

(ii) Less hindered keto group reacts preferentially

(iii) Aldehyde group reacts.



(ii) No reaction

(iii) CH_3COCH_3

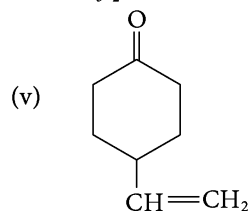
(iv) $\text{CH}_3\text{CHOHCH}_2\text{CH}_2\text{COOH}$

127. (i) $\text{CH}_3\text{COCH}(\text{CH}_3)_2$

(ii) $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_2\text{CH}_3$

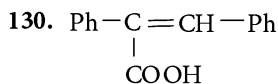
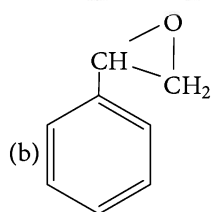
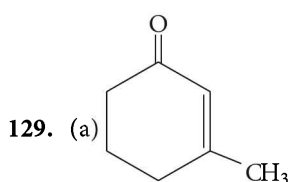
(iii) $(\text{CH}_3)_2\text{CHCOCH}_2\text{CH}_3$

(iv) $(\text{CH}_3)_2\text{CHCH}_2\text{COCH}_3$



(4-vinyl cyclohexanone)

128. Due to intramolecular hydrogen bonding, o-hydroxy benzaldehyde exists as discrete molecules.



131. (a) 132. (b) 133. (d)

134. (d) 135. (c) 136. (b)

137. (c) 138. (c) 139. (d)

140. (a) 141. (a) 142. (b)

143. (a) 144. (d) 145. (d)

146. (c) 147. (a) 148. (b)

149. (d) 150. (b) 151. (a)

152. (b) 153. (b) 154. (b)

155. (c) 156. (b) 157. (d)

158. (b) 159. (b) 160. (a)

161. (d) 162. (b) 163. (a)

164. (b) 165. (b) 166. (a)

167. (a) 168. (b) 169. (c)

170. (c) 171. (b) 172. (c)

173. (d) 174. (d) 175. (c)

176. (a) 177. (a) 178. (c)

179. (b) 180. (d) 181. (a)

182. (c) 183. (a) 184. (d)

185. (c) 186. (d) 187. (c)

188. (b)

189. (a)

190. (a), (b), (c)

191. (a), (c)

192. (c), (d)

193. (b), (d)

194. (a), (b)

195. (a), (c), (d)

196. (b), (c), (d)

197. (b), (d)

198. (a) $\rightarrow$ (s)

(b) $\rightarrow$ (q), (t)

(c) $\rightarrow$ (r), (t)

(d) $\rightarrow$ (p), (q), (t)

199. (a) $\rightarrow$ (q), (r)

(b) $\rightarrow$ (t)

(c) $\rightarrow$ (p), (s)

(d) $\rightarrow$ (q), (r)

200. (a) $\rightarrow$ (p), (r)

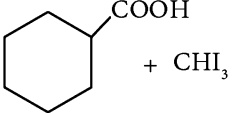
(b) $\rightarrow$ (p), (s)

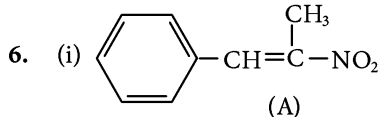
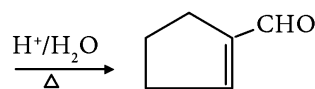
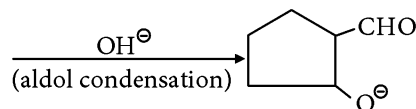
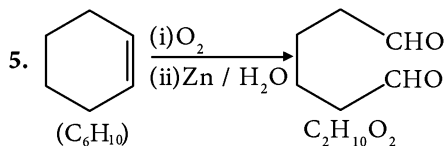
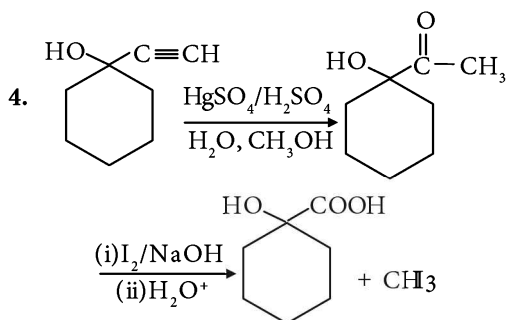
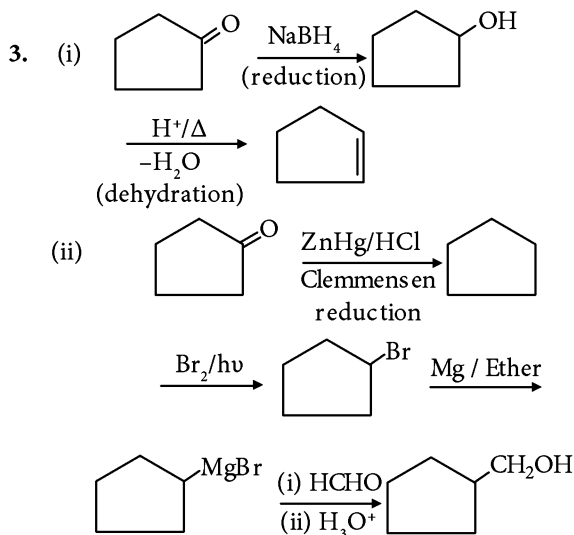
(c) $\rightarrow$ (t)

(d) $\rightarrow$ (q), (r)

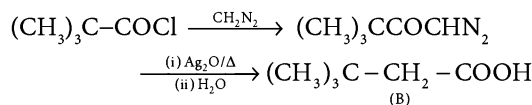
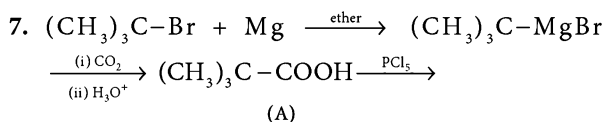
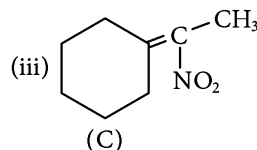
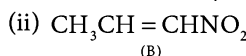
HINTS AND EXPLANATIONS

Topic Grip

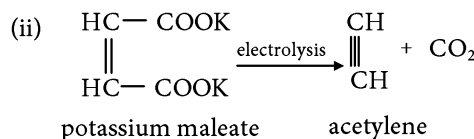
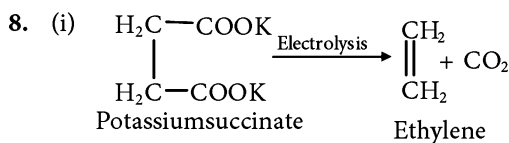
- $(\text{CH}_3)_2\text{CHCOOH} + \text{CHI}_3$
 - Does not undergo iodoform reaction.
 - Does not undergo iodoform reaction.
 - 
 - Does not undergo iodoform reaction.
- There are three reasons, for the less reactivity of ketones.
 - Steric crowding around the sp^2 carbonyl carbon in ketones.
 - Electronic factors—two alkyl groups by electron releasing inductive effects make the carbonyl carbon less electropositive in ketones.
 - By nucleophilic addition, a planar trigonal sp^2 carbonyl carbon is converted to a tetrahedral sp^3 carbon where the steric crowding is more.



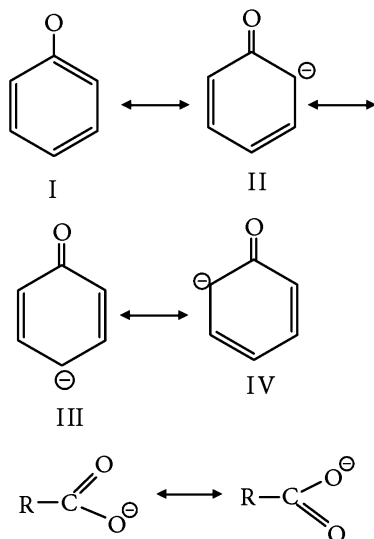
(The hydrogen alpha to the nitro group is acidic and is easily displaced by a base to form a carbanion which undergoes nucleophilic addition on the carbonyl carbon of benzaldehyde).



The conversion from (A) to (B) is stepping up a carboxylic acid which is an example of Arndt-Eistert synthesis. The intermediate diazoketene $(\text{CH}_3)_3\text{C}-\text{COCHN}_2$ undergoes a rearrangement known as Wolff rearrangement to give the higher acid.



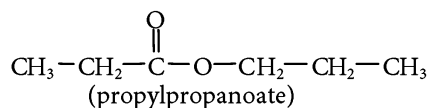
9. The resonance structures of phenoxide ion and carboxylate ion are given below.



In the case of phenoxide ion, structures II, III and IV contain negative charge on a less electronegative carbon and hence their contribution towards resonance is less. But in the case of carboxylate anion, the negative charge is delocalised over two electronegative oxygen atoms. The two structures are equivalent and they contribute equally for resonance. So carboxylate ion is much more resonance stabilised than phenoxide ion. So carboxylic acid ionises to form carboxylate ion more readily and behaves as stronger acid than phenol.

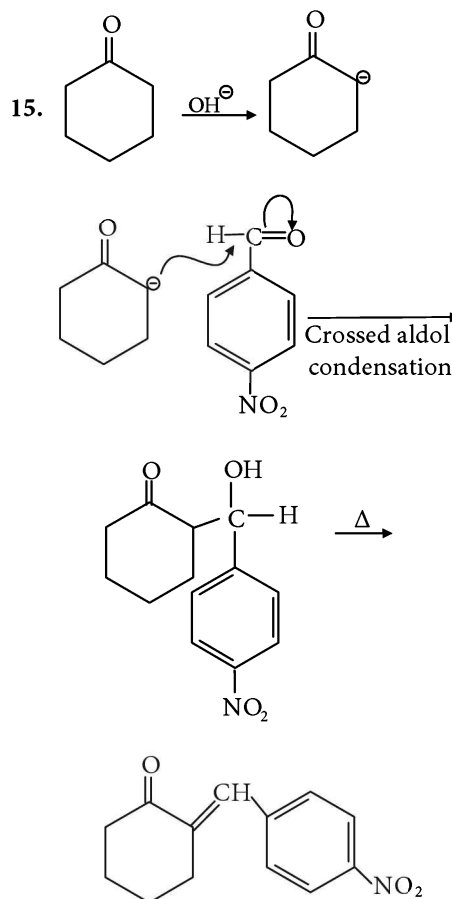
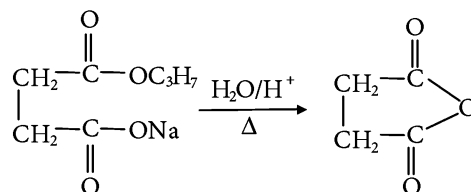
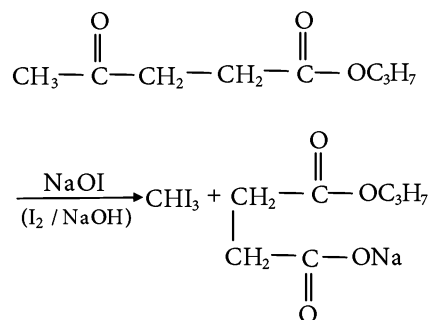
10. Since (X) on acid hydrolysis gives a mixture of acid and alcohol, (X) must be an ester. Since the alcohol (Z) on oxidation gives the carboxylic acid (Y), (Z) and (Y) must contain the same number of carbon atoms. Since the ester contains 6 carbon atoms, the alcohol and acid must contain 3 carbon atoms each.

Therefore, the compound (X) is



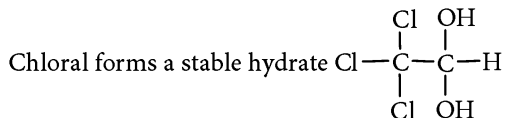
11. $\text{CH}_3-\text{CN} + \text{CH}_3-\text{MgCl} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3-\text{CO}-\text{CH}_3$
12. $\text{HC} \equiv \text{CH} \xrightarrow[\text{H}_2\text{O}]{\text{Hg}^{2+}/\text{H}_2\text{SO}_4} \text{CH}_3\text{CHO}$
- $\xrightarrow[\text{(ii) H}_3\text{O}^+/\Delta]{\text{(i) NaOH}} \text{CH}_3\text{CH}=\text{CHCHO}$
13. $(\text{CH}_3\text{CH}_2\text{COO})_2\text{Ca} \xrightarrow{\text{distill}} (\text{CH}_3\text{CH}_2)_2\text{CO} + \text{CaCO}_3$
- 3-pentanone

14. NaOI is formed from NaOH and I_2 . It involves iodoform reaction followed by acid hydrolysis and dehydration.



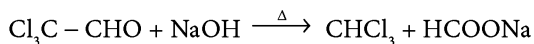
5.78 Aldehydes, Ketones and Carboxylic Acids

16. Statement 1 is true but statement 2 is false. $-\text{OCH}_3$ group present at the para position reduces the positive charge on the carbonyl carbon of p-methoxybenzaldehyde by +R effect. So carbonyl carbon is less electrophilic in p-methoxybenzaldehyde.
17. Both statements are correct, but statement 2 is not the reason for statement 1

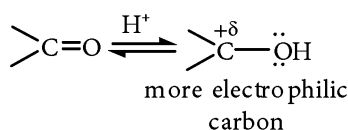


Chloral hydrate is stable because of the strong-I effect of three chlorine atoms. Due to strong-I effect, the electron pair forming the covalent bond of C–OH is more shifted towards carbon. So it is difficult for OH group to leave as OH^- .

Distillation of chloral with aqueous alkali gives chloroform.

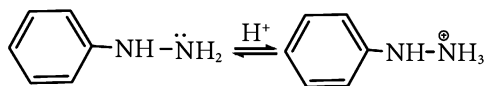


18. Statement 1 is correct but Statement 2 is wrong. During nucleophilic addition to a carbonyl group, mild acidic conditions are favourable because, more electronegative oxygen of the carbonyl group gets preferentially protonated, thereby making the carbonyl carbon more electrophilic compared to a free $>\text{C}=\text{O}$ group.



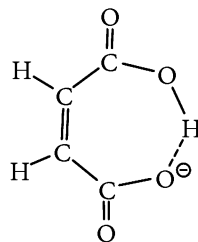
However if the acidic conditions are very strong, it will not only protonate the electronegative oxygen, but also react with the attacking nucleophiles

For example



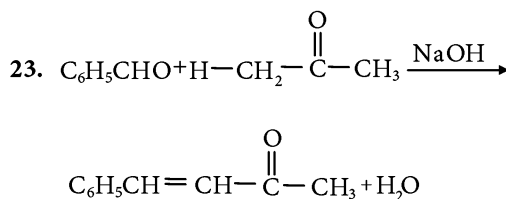
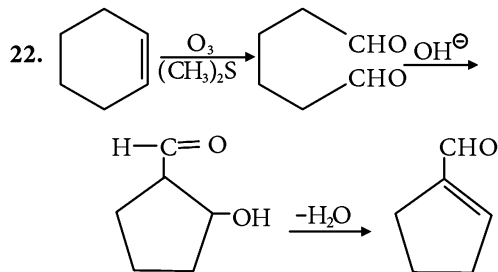
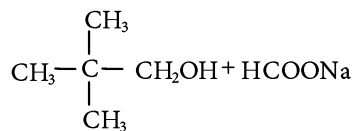
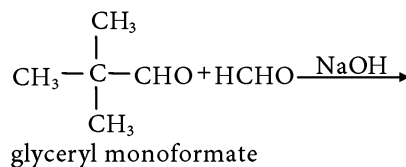
Phenylhydrazine Protonated phenylhydrazine
(a nucleophile) (no longer a nucleophile)

19. First ionization constant of maleic acid is greater than that of fumaric acid. This is because the anion formed by the ionization $-\text{COOH}$ group of maleic acid is stabilized by intramolecular hydrogen bonding.

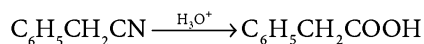
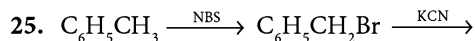


Such a stabilization is not possible for the anion formed from fumaric acid because it is the trans isomer.

20. Both statements are correct and statement 2 is the correct reason for the greater reactivity of ethyl acetate, $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{OC}_2\text{H}_5$. Because of greater electron attracting tendency, $-\text{OC}_2\text{H}_5$ group increases the positive charge on acyl carbon and at the same time $-\text{OC}_2\text{H}_5$ is a good leaving group.
21. Whenever HCHO is used in Cannizzaro reaction it is oxidized and the other aldehyde is reduced.



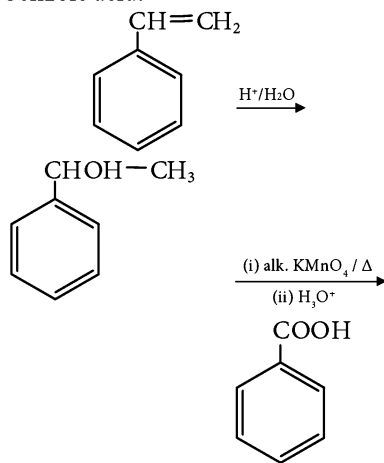
24. Only by formation of Grignard reagent followed by carboxylation, bromobenzene can be converted to benzoic acid.



26. Glyoxal $\text{O}=\text{CH}-\text{CH}=\text{O}$, is a dialdehyde, with both the aldehyde units in the same molecule. When an alkali (strong NaOH solution) is added, an intramolecular Cannizzaro reaction occurs. Cannizzaro reaction is a disproportionation reaction in which one of the $-\text{CHO}$ groups gets oxidised to $-\text{COOH}$ while the other gets reduced to $-\text{CH}_2\text{OH}$. Hence the given product.

27. Acid catalysed hydration of styrene followed by oxidation with alkaline KMnO_4 would bring about side chain oxidation producing potassium salt of benzoic acid.

benzoic acid.

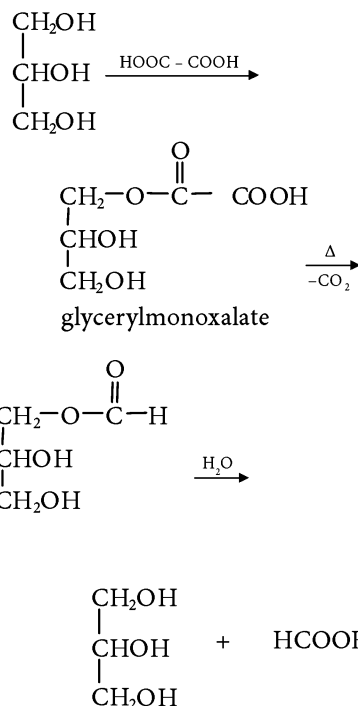


Hence statement (a) is not correct.

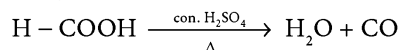
28. In Perkin reaction, carbanion produced from the acid anhydride is added to the carbonyl group of aldehyde and the reaction proceeds to form α, β -unsaturated acid.

In aldol condensation also, carbanion is produced by abstraction of a proton from the α -carbon of the carbonyl compound by the base present.

29. Formic acid is prepared in the laboratory by heating glycerol with oxalic acid to about 373-383K



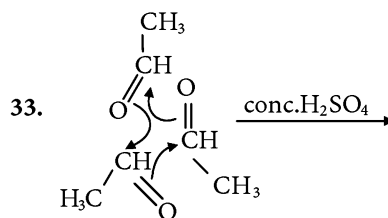
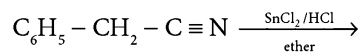
HCOOH is a stronger acid than benzoic acid. Dehydration of formic acid with $\text{con. H}_2\text{SO}_4$ gives CO



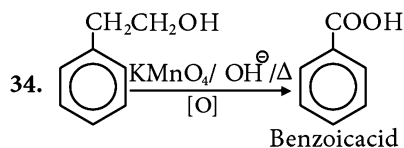
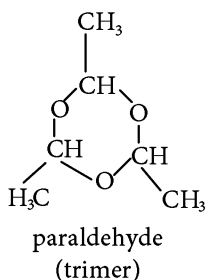
Hence statements (a), (c) and (d) are correct.

IIT Assignment Exercise

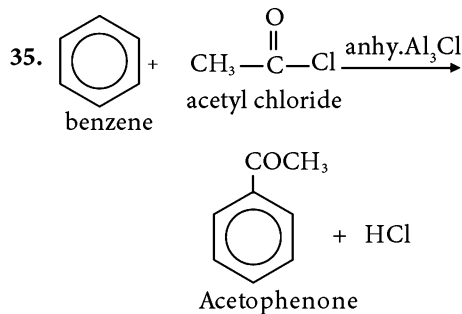
31. Nitriles (cyanides) are reduced to the corresponding imine by SnCl_2/HCl which on hydrolysis give aldehydes.



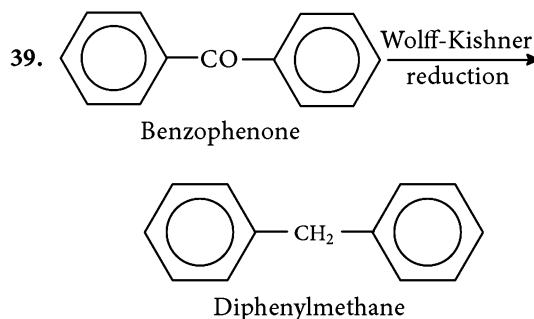
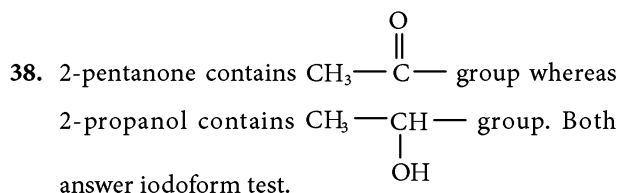
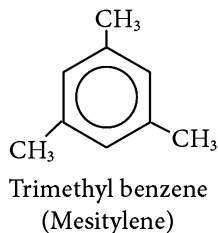
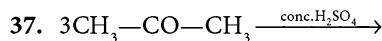
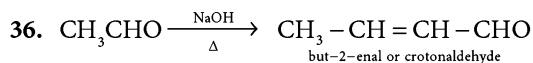
5.80 Aldehydes, Ketones and Carboxylic Acids



This is an example of a side chain oxidation

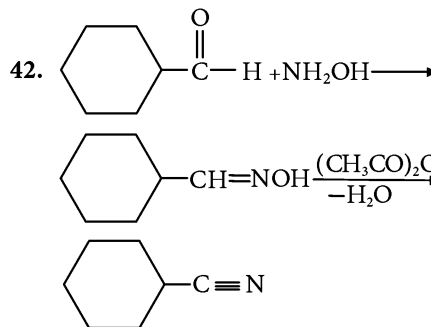
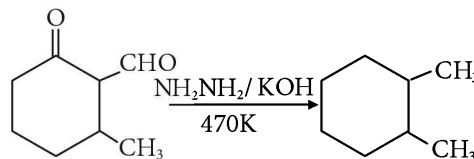


This is an example of Friedel-Crafts reaction.

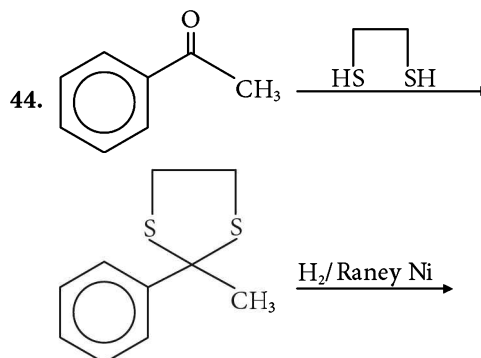


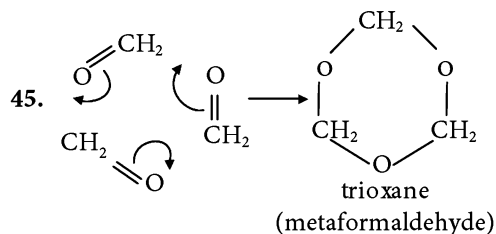
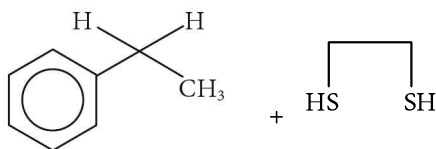
40. Sodium borohydride is a mild reducing agent. It reduces the aldehyde to the alcohol, without affecting the double bond.

41. This is Wolff-Kishner reduction. It reduces the carbonyl group to $-\text{CH}_2-$ group.

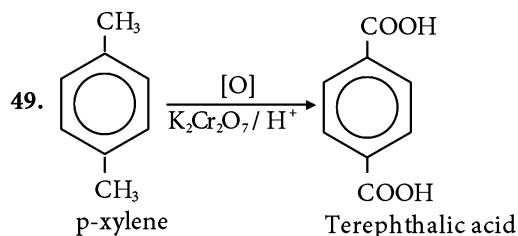
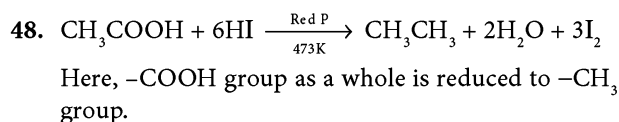
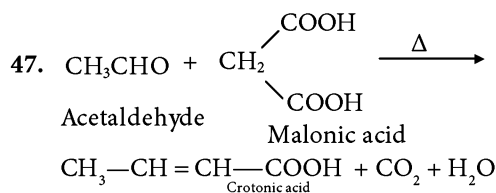


43. $6\text{HCHO} + 4\text{NH}_3 \rightarrow (\text{CH}_2)_6\text{N}_4 + 6\text{H}_2\text{O}$
 $(\text{CH}_2)_6\text{N}_4$ or hexamethylenetetramine (urotropine) is formed which is used as an urinary antiseptic.



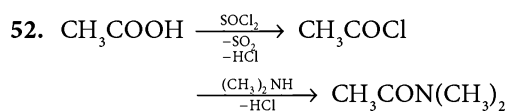
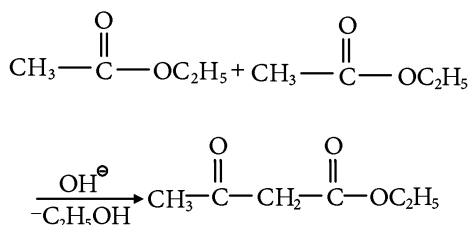


46. Benzaldehyde is known as oil of bitter almonds.

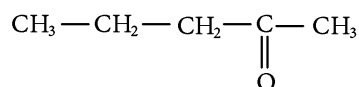


50. Methanoic acid, aliphatic aldehydes and aromatic aldehydes are reduced by Tollens' reagent.

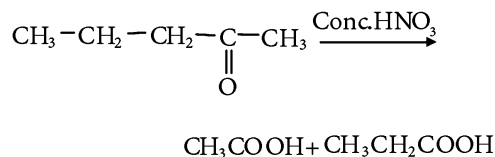
51. Claisen condensation is answered by esters which contains α -hydrogen atoms. The product is β -ketoester.



53. 2-pentanone

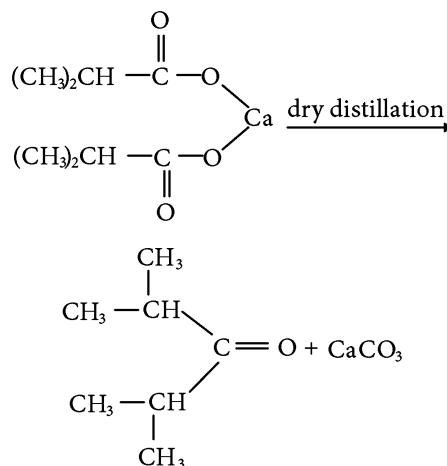
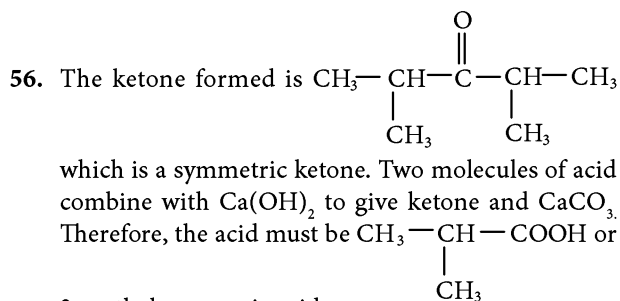


In unsymmetric ketones, the point of cleavage is such that the keto group stays with smaller alkyl group. This is known as Popoff's rule.



54. Both the keto group and ester group undergoes reaction with Grignard reagent. The keto group gives a tertiary alcohol while the ester group first gives a methyl ketone, which is then converted to a tertiary alcohol.

55. (B) obtained gives blue coloured pseudonitrole (C) in Victor Meyer's test and (C) does not react with NaOH $\therefore$ (B) is a secondary alcohol. With Grignard reagent, we get secondary alcohol from aldehydes. The only aldehyde that gives positive iodoform test is acetaldehyde. $\therefore$ (A) is acetaldehyde.



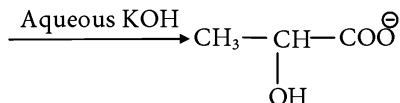
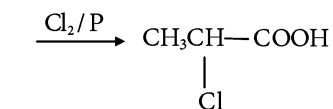
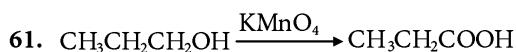
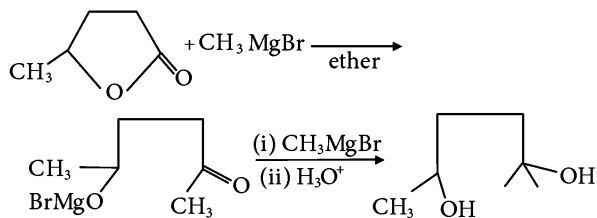
57. The reaction is an example of an aldol condensation.

5.82 Aldehydes, Ketones and Carboxylic Acids

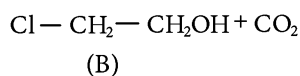
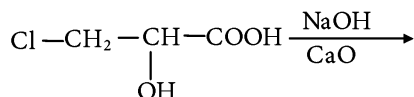
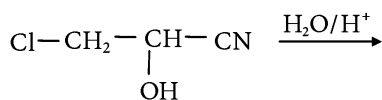
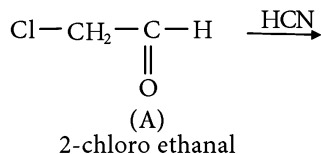
58. $-\text{NO}_2$ is an electron withdrawing group. So on placing it on the α -carbon atom, it makes the carbonyl carbon more positive, and nucleophilic addition is favoured. Moreover the carbanion formed is stabilised by resonance. $-\text{NO}_2$ at β -carbon makes the carbonyl more reactive than the unsubstituted one, but not as reactive as $-\text{NO}_2$ at α -carbon.

59. $-\text{CH}_3$ is electron donating, so decreases the acidity when present in the ring. At the para position, the methyl group has hyperconjugation, so acidity decreases further when compared to the meta position. $-\text{OH}$ group at meta position exerts electron withdrawing inductive effect. Hence acidity is increased.

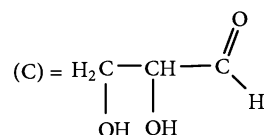
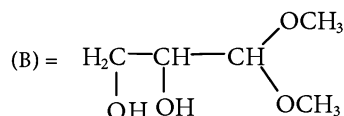
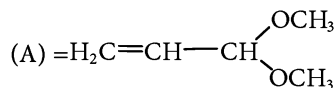
60. This is reaction of Grignard reagent with an ester (lactone)



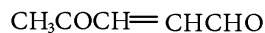
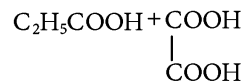
62. (B) is 2-chloro ethanol, $\text{ClCH}_2\text{CH}_2\text{OH}$



63. Glyceraldehyde (C) is the product obtained in this reaction. Direct oxidation of the starting compound namely acrolein by dil. KMnO_4 solution results not only in the formation of the diol, but also in the oxidation of aldehyde to form a carboxylic acid. Hence the aldehyde group is protected, which is effected by the formation of an acetal, by the use of CH_3OH and dry HCl , resulting in (A). Hydroxylation of (A) by means of dil. KMnO_4 results in the diol with the protected aldehyde group which is (B). On hydrolysis with dil. HCl , glyceraldehyde (C) is obtained.



64. Tollens' reagent $[\text{Ag}(\text{NH}_3)_2]\text{OH}$ is best suited for the oxidation given. Tollens' reagent is selective in the oxidation of aldehyde group without affecting the olefinic bond. Products given by the other oxidising agents are



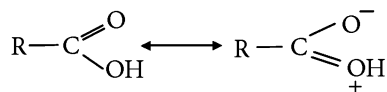
65. Among the oxidising agents used, a mixture CrO_3 and acetic anhydride finds very useful application. The alkyl chain (namely the methyl group) in toluene is oxidised and the reaction stops at the aldehyde stage. The product of oxidation with CrO_3 and Ac_2O is



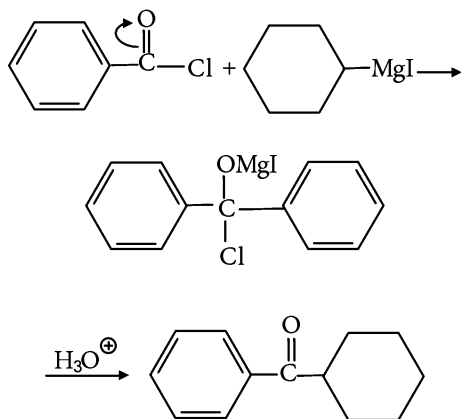
diacetate formed does not undergo further oxidation. When this diacetal is subjected to acid hydrolysis, para chloro benzaldehyde is obtained.

66. Since there is only one reactant molecule involved in this reaction, one part of the molecule gets oxidized while the other gets reduced. Hence this is an example of intramolecular Cannizzaro reaction.

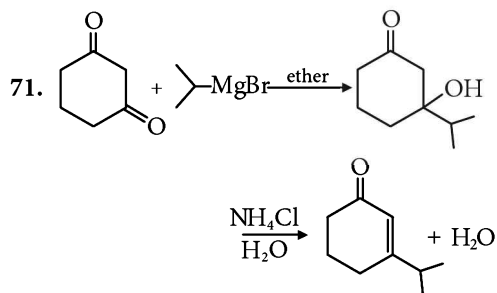
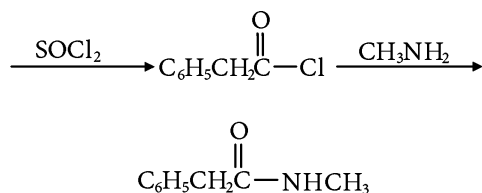
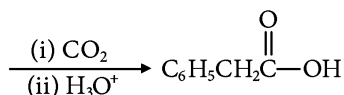
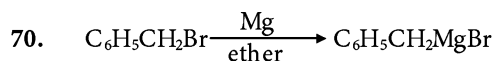
67. The >C=O group in carboxylic acids enters into resonance with the -OH group. So it no longer behaves like a carbonyl group.



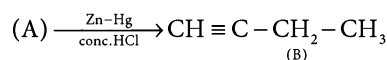
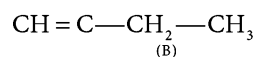
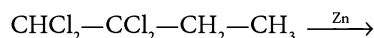
68. Benzoyl chloride reacts with one mole of Grignard reagent, cyclohexyl magnesium iodide, followed by elimination of Cl^- ion to give cyclohexyl phenyl ketone.



69. Cl^- is a better leaving group. As the basicity of the leaving group decreases the rate of hydrolysis increases. Among acid derivatives, the basic strength of the leaving group increases in the order, $\text{Cl}^- < \text{RCOO}^- < \text{RO}^- < \text{NH}_2^-$.

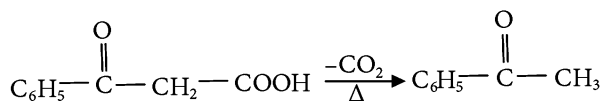


72. (A) gives haloform reaction and is a butane system. So (A) is a ketone with the $\text{CH}_3\text{-CO-}$ group. (B) is obtained on treating $\text{CHCl}_2\text{-CCl}_2\text{-CH}_2\text{-CH}_3$ with zinc dust.

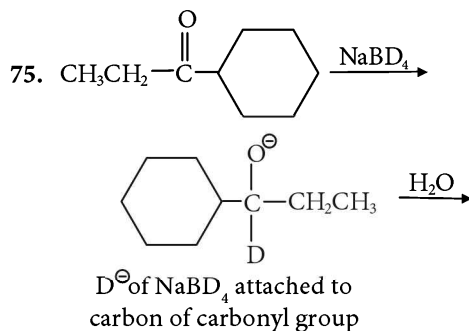


So (A) should be $\text{CH}_3\text{C}(=\text{O})\text{-C}\equiv\text{CH}$ but-3-yn-2-one

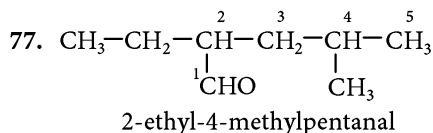
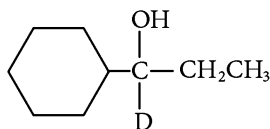
73. The ketone formed gives iodoform reaction, so it has a -COCH_3 group. It does not give addition compound with NaHSO_3 , so it is an aromatic ketone. Ketones are formed by heating β -keto acid (decarboxylation). So the acid should be $\text{C}_6\text{H}_5\text{COCH}_2\text{COOH}$.



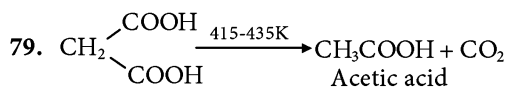
74. In the preparation of acetophenone, the specific acylating species is $\text{CH}_3\text{-C}\equiv\text{O}^+$. This is generated by the reaction between CH_3COCl and anhydrous AlCl_3 to give CH_3CO^+ and AlCl_4^- . The acylating species is an electrophile,



5.84 Aldehydes, Ketones and Carboxylic Acids



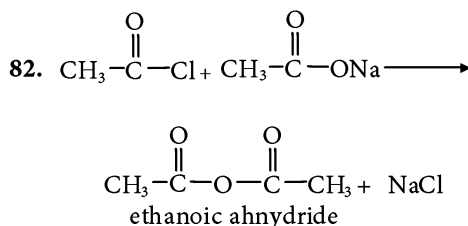
78. Vanadium pentoxide as the catalyst



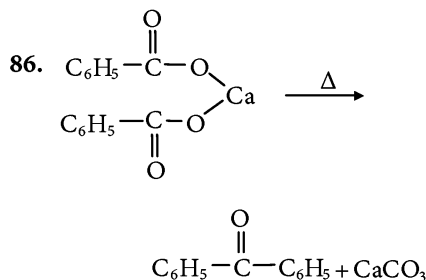
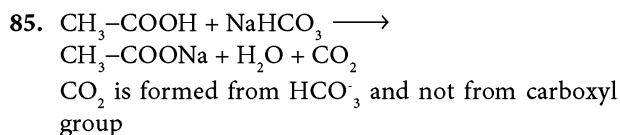
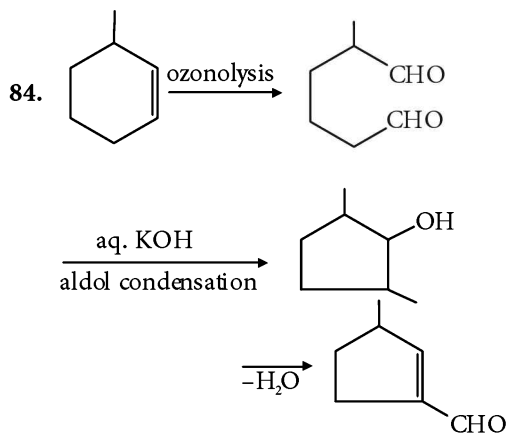
β - keto acids undergo facile decarboxylation

80. $(\text{CH}_3)_3\text{CBr}$ undergoes mainly elimination to give an alkene, 2-methyl propene, when treated with $\text{CN}^\ominus$ ion.

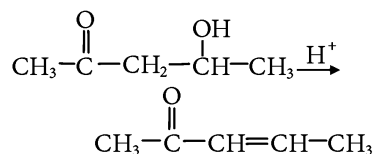
81. Pentan-2-one contains $\text{CH}_3\text{-CO-}$ group and it will give a yellow precipitate of iodoform on heating with iodine and alkali. Pentan-3-one does not give iodoform



83. Both acetyl chloride and acetic anhydride react readily with water to form acetic acid which gives effervescence with NaHCO_3 solution

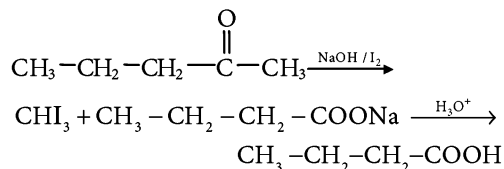


87. β -hydroxy ketones and β -hydroxy aldehydes (aldols) readily undergo dehydration to form α, β -unsaturated ketones and aldehydes

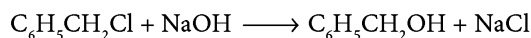


88. $\text{CH}_3\text{OCH}_2\text{COOH}$ is a stronger acid than $\text{CH}_3\text{-COOH}$ because of $-I$ effect of $-\text{OCH}_3$ group. However $-\text{OCH}_3$ group is electron donating when attached to benzene ring or unsaturated system due to $+R$ effect

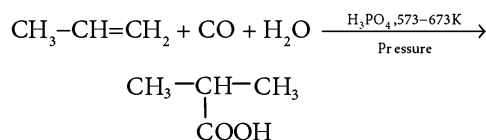
89. 2-pentanone undergoes iodoform reaction when heated with I_2 and NaOH . The reaction mixture, after the separation of iodoform, on acidification gives butanoic acid



90. Benzyl chloride on hydrolysis gives benzyl alcohol

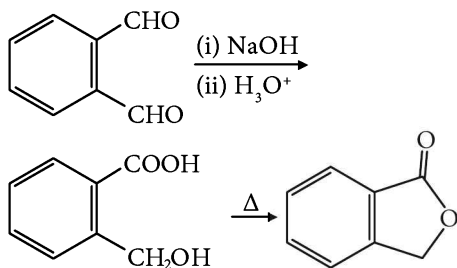


91. Addition of H and COOH takes place in accordance with Markovnikov's rule.

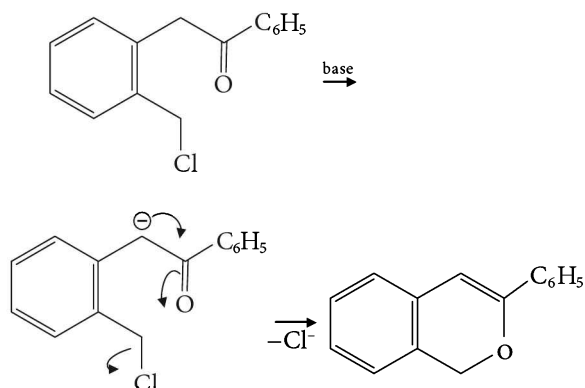


It is known Koch reaction.

92. The compound (a) undergoes Cannizzaro reaction followed by intramolecular ester formation to form the given lactone

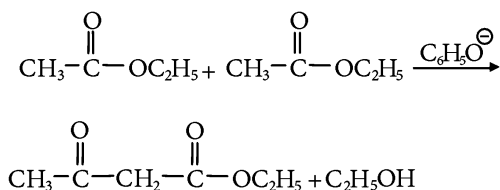


93. Base will abstract the acidic α -hydrogen atom with respect to the carbonyl group resulting in the formation of an enolate anion which then displaces Cl^- to yield the cyclic compound (c)



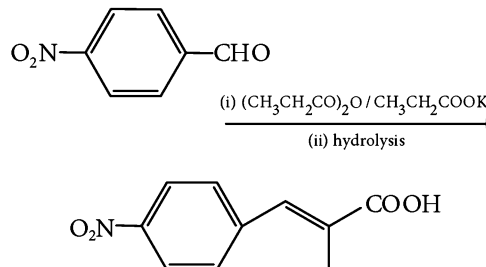
94. Aliphatic aldehydes are more reactive towards nucleophilic addition than aromatic aldehydes. Ketones are less reactive than aldehydes.
m-chlorobenzaldehyde is more reactive than benzaldehyde because $-I$ effect of chlorine increases the electrophilic nature of the carbonyl carbon

95. Esters containing α -hydrogen undergo Claisen condensation when treated with strong bases such as sodium ethoxide.

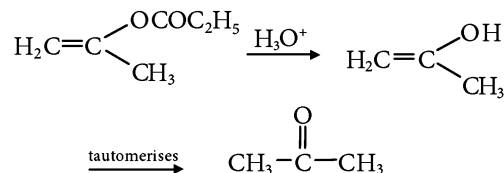


The product formed in this reaction is ethyl acetoacetate or ethyl-3-oxobutanoate

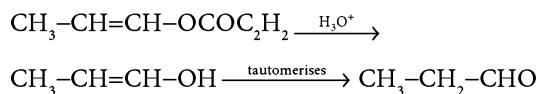
96. It is Perkin reaction. The reagent X required is propionic anhydride



97. Acid hydrolysis of (A) gives acetone

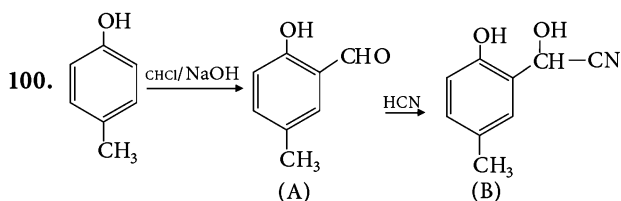
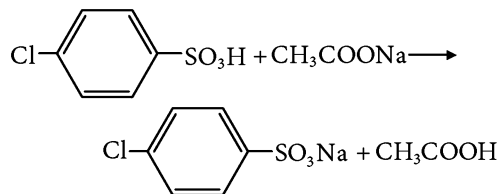


Similar hydrolysis of (B) gives propanal

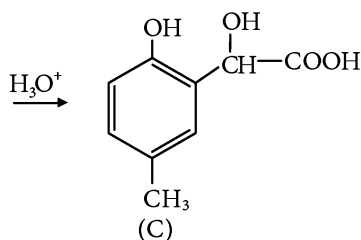


The two can be distinguished with Tollens' reagent, Fehling's solution, I_2/NaOH etc

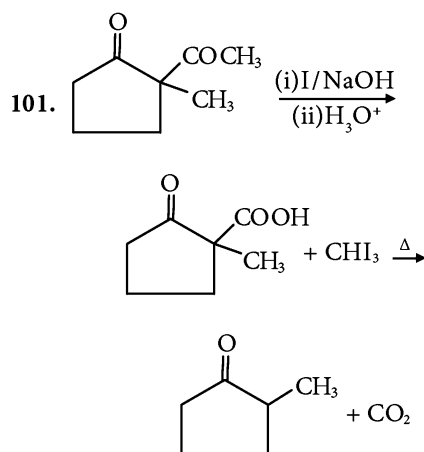
98. Benzoic acid is a stronger acid than acetic acid. m-Methoxy benzoic acid is stronger than benzoic acid due to the $-I$ effect of $-\text{OCH}_3$ group. p-methoxybenzoic acid is weaker than benzoic acid due to the $+R$ effect of $-\text{OCH}_3$ group
99. 4-chlorobenzene sulphonic acid is a stronger acid than acetic acid. Therefore, it displaces acetic acid from sodium acetate



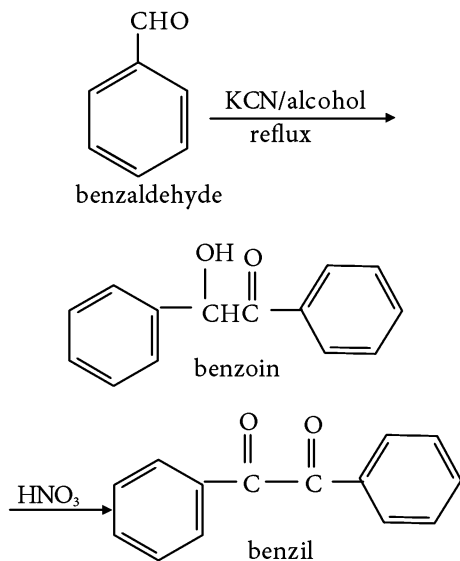
5.86 Aldehydes, Ketones and Carboxylic Acids



One molecule of (C) contains seven sp^2 hybridized carbon atoms



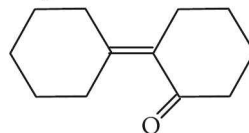
102. Benzaldehyde under the influence of cyanide forms benzoin which is oxidised to benzil by dil. HNO_3 .



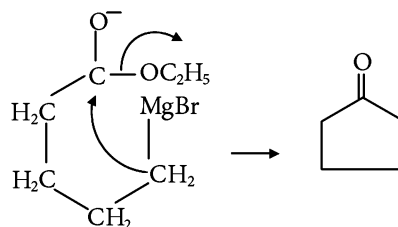
103. This is Beckmann rearrangement of a ketoxime. When Ketoximes rearranges, it is the group which is anti to the $-\text{OH}$ migrates to form the product given,



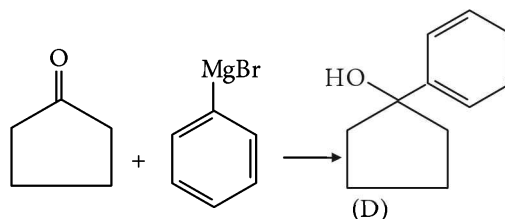
104. This is an instance of aldol condensation of cyclohexanone and the product formed is



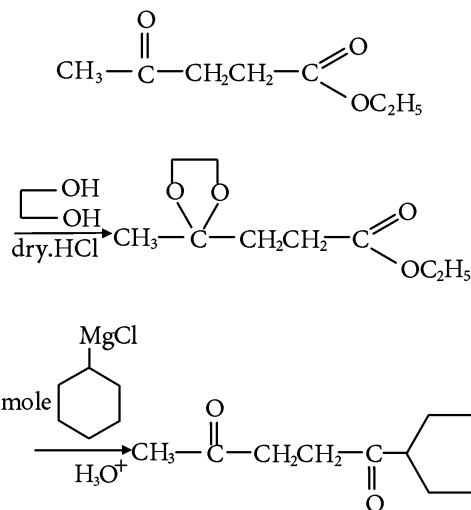
105. The Grignard reagent generated at the end of the chain attacks the ester to form a ketone – (cyclopentanone.)



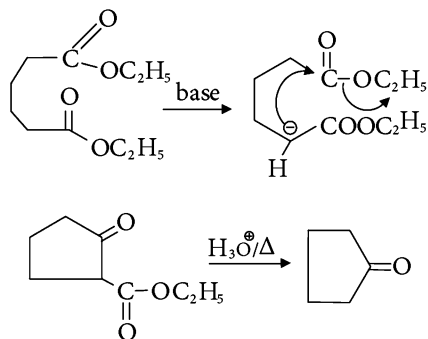
This reacts with phenyl magnesium bromide to give 3° alcohol



106. The starting material is a keto ester. The free keto group is protected by ethylene glycol to form a ketal and the ester is now free to react with one unit of cyclohexyl Grignard reagent. This results in a cyclohexyl ketone and the starting free keto group liberated in the process. This is an example of a Grignard reaction by protecting the keto group already present in the molecule.

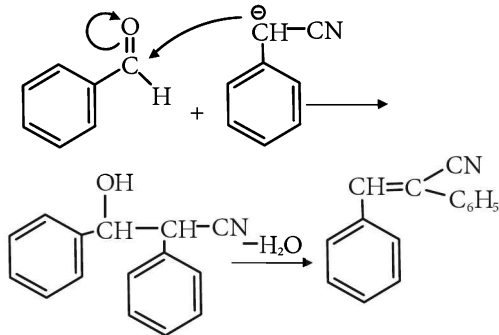


107. This is an example of intramolecular Claisen condensation.

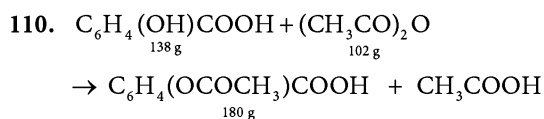


Hydrolysis of ester gives a β -ketoacid, which undergoes facile decarboxylation to give cyclopentanone.

108. This is an example of an aldol type of reaction displayed by the cyanides. The α -hydrogens to the cyano group are acidic and they undergo aldol type of condensation with aldehydes, in the presence of a base.



109. It represents Clemmensen reduction. The product obtained in a Clemmensen reduction is always a hydrocarbon and not an alcohol.



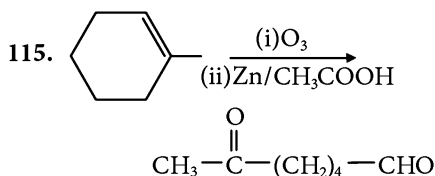
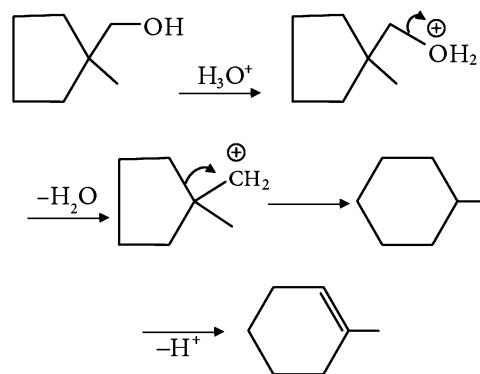
Salicylic acid is the limiting reagent.

138 g of salicylic acid yields 180 g of aspirin. 5 g salicylic acid yields $\frac{180 \times 5}{138} = 6.52 \text{ g}$

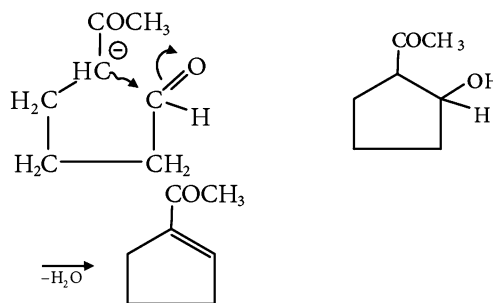
111. Both statement 1 and statement 2 are correct and statement 2 is the correct explanation for the statement 1. When acetals and ketals are hydrolyzed to form a free carbonyl group, there is an initial formation of $\text{—}\overset{\text{OH}}{\underset{\text{OH}}{\text{C}}}\text{—OR}$, which occurs readily in acid medium.

The hemiacetal as shown cannot be formed in basic medium, because —OH is a weaker base and cannot replace a stronger base, namely —OR .

112. Statement 1 is correct, but statement 2 is wrong. Formic acid is a reducing agent. It reduces mercuric salt to mercurous state.
113. Since the lone pair of electrons of fluorine is present in 2p orbital, it can effectively overlap with the 2p orbital of carbon in benzene and hence the +R effect is more compared to chlorine
114. Protonation of alcohol followed by loss of water gives a 1° carbocation which undergoes ring expansion to form a more stable 3° carbocation. This then loses a proton to form 1-methylcyclohexene



116. When treated with alkali, 6-oxoheptanal undergoes intramolecular aldol condensation. The carbanion formed by the removal of α -hydrogen with respect to the keto group attacks the carbonyl groups of aldehyde and the reaction proceeds as follows to form acetyl cyclopentene



5.88 Aldehydes, Ketones and Carboxylic Acids

117. Benzophenone does not undergo addition reaction with NaHSO_3 and HCN . It is due to steric crowding and also due to the less electrophilic nature of carbonyl carbon

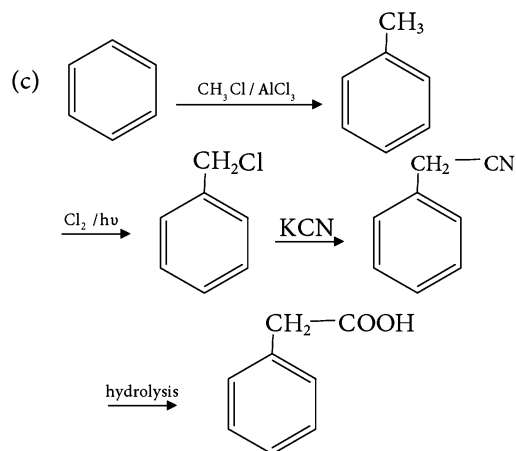
118. In Cannizzaro reaction, step – 2 which involves hydride shift is the slowest and rate determining step. Hence (b) is not correct.

119. (b) and (d) are correct. An amide though it contains a primary amino group does not answer the reactions of an amine.

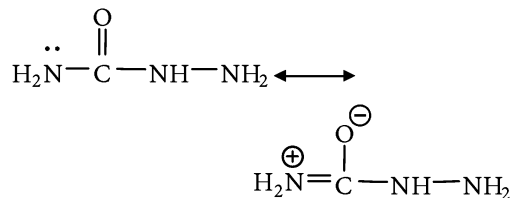
Esters cannot be made from carboxylic acids under the influence of alkali. Only acids-protonic acids catalyse the esterification reaction.

$\text{R}-\text{C}(=\text{O})\text{Cl}$ is most reactive as $-\text{Cl}^\ominus$ is a very good leaving group.

Diazomethane is a very good methylating agent for phenols and carboxylic acids.

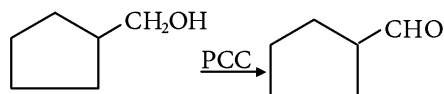
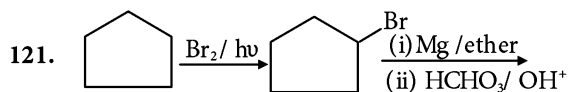


123. The lone pair of $-\text{NH}_2$ group near the $\text{C}=\text{O}$ group of semicarbazide is involved in resonance as shown below

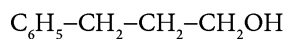
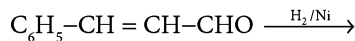
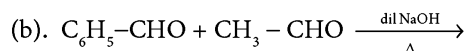
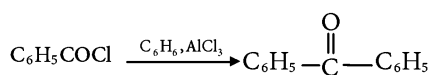
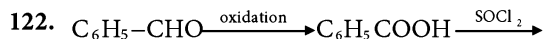
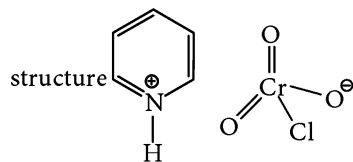


Hence electron density on that $-\text{NH}_2$ group is less and hence it does not act as nucleophile

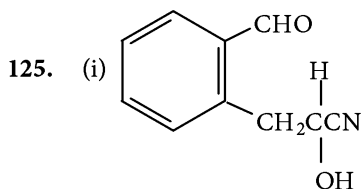
Additional Practice Exercise



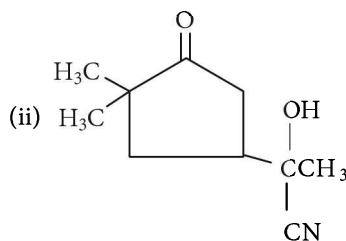
PCC is pyridinium chloro chromate and has the



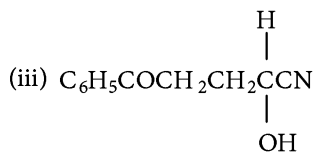
124. In the free carbonyl compounds (ii) and (iii), the dipoles oppose each other and thus has a destabilizing influence. In the hydrates of these carbonyl compounds which are geminal diols (two $-\text{OH}$ groups attached to the same carbon), the dipole of the carbonyl is depleted by a much weaker dipole of the diol. Cyclopentanone forms a stable hydrate because it relieves part of its internal strain.



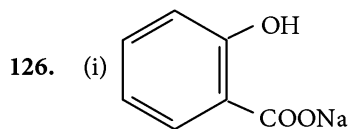
Aromatic aldehydes are less reactive than aliphatic aldehydes, because resonance makes the aromatic aldehyde carbon less electropositive.



The keto group where the cyanohydrin formed is less hindered.



Aldehydes are more reactive than ketones in the addition of nucleophiles to the electrophilic carbon of the carbonyl group. Also, the keto group attached to the benzene ring is less reactive, due to resonance.



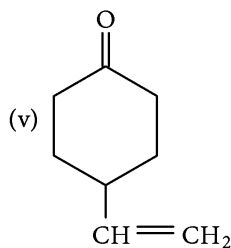
Only the $-\text{COOH}$ is acidic to react with NaHCO_3 and $-\text{OH}$ group is unaffected.

(ii) No reaction. Both $-\text{OH}$ (phenol) and $-\text{CH}_2\text{OH}$ (alcohols) groups are not strongly acidic to react with NaHCO_3 solution.

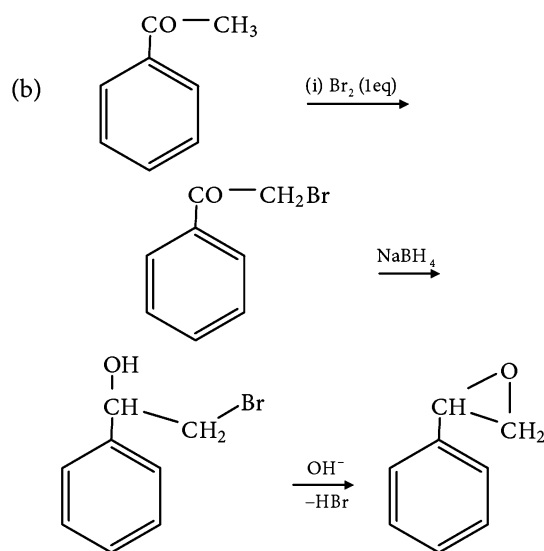
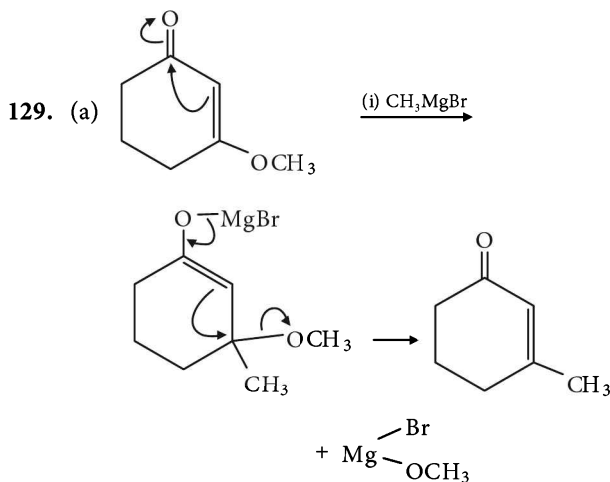
(iii) CH_3COCH_3 is the product. The starting material, $\text{CH}_3\text{COCH}_2\text{COOH}$, a β -keto acid, undergoes decarboxylation readily on mild heating.

(iv) Hydrogenation over Pd at 25°C , affects only the $-\text{CO}-$ group and not the acid group. So the product is $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{COOH}$.

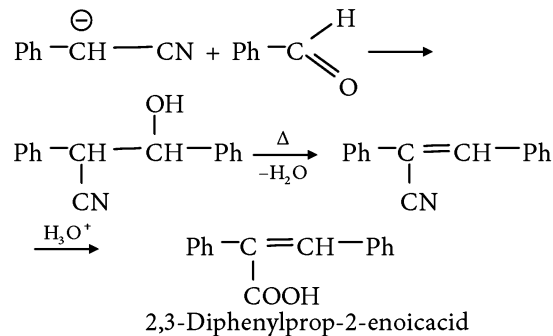
127. (i) $\text{CH}_3\text{COCH}(\text{CH}_3)_2$
 (ii) $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_2\text{CH}_3$
 (iii) $(\text{CH}_3)_2\text{CHCOCH}_2\text{CH}_3$
 (iv) $(\text{CH}_3)_2\text{CHCH}_2\text{COCH}_3$



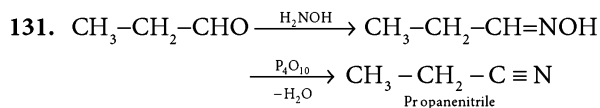
128. Due to intramolecular hydrogen bonding o-hydroxy benzaldehyde exists as discrete molecules. But molecules of p-hydroxybenzaldehyde are associated by intermolecular hydrogen bonding. Since there is considerable intermolecular interaction, p-hydroxy benzaldehyde has higher melting point and exists as solid



Due to the electron withdrawing effect of CN group, the hydrogens on CH_2 group in benzyl cyanide (A) are acidic. So it readily forms carbanion in presence of the base $\text{C}_2\text{H}_5\text{ONa}$ and the carbanion undergoes nucleophilic addition with the carbonyl group of benzaldehyde

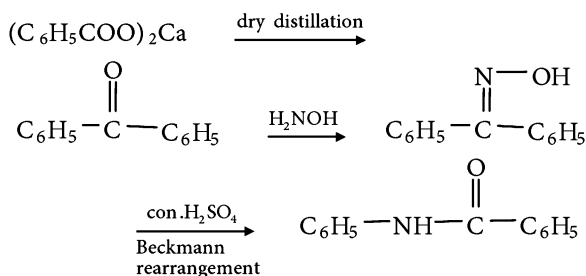


5.90 Aldehydes, Ketones and Carboxylic Acids



132. Presence of chlorine with -I effect at the α -position in compound (b) considerably increases the electrophilicity of the carbon. So it is the most reactive

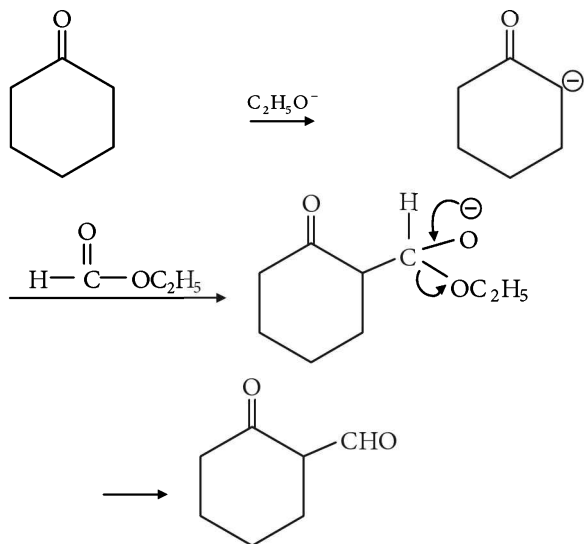
133.



134. Polarisation of the carbonyl carbon will produce positive charge on the carbonyl carbon and that will give the ring aromatic stability in the case of (d)

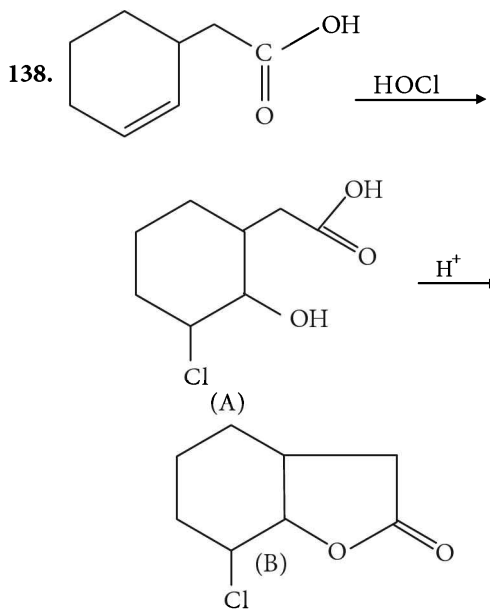
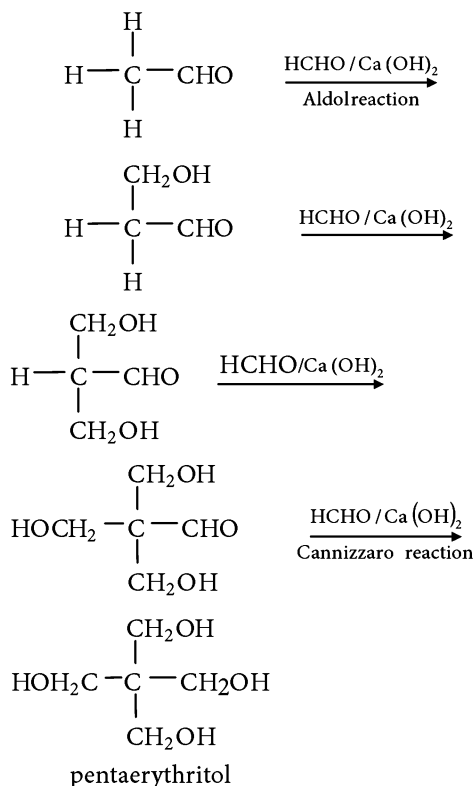
135. Aldol condensation is generally carried out in presence of bases. But it can also be catalysed by acid. The mechanism is entirely different in acid catalysed reaction. In presence of acids, it takes place by the reaction between the conjugate acid and the enol form of the carbonyl compound

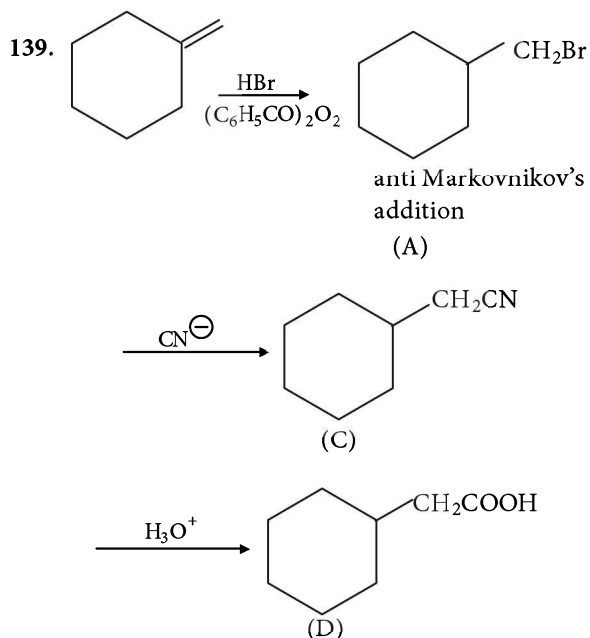
136. The strong base $\text{C}_2\text{H}_5\text{O}^-$ will abstract a proton from the α -carbon of cyclohexanone and the carbanion so formed is added to the carbonyl group of ester. The reaction proceeds as follows



It is an extension of Claisen condensation

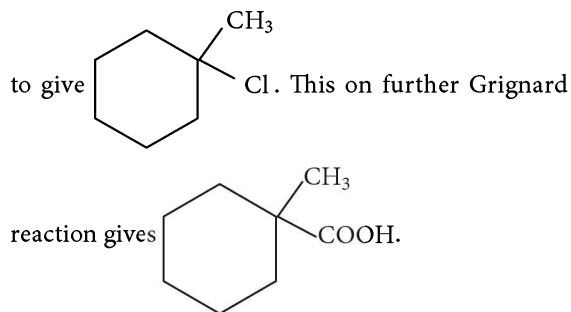
137. Repeated aldol condensation between CH_3CHO and HCHO takes place first till all the three α -hydrogen atoms of $\text{CH}_3\text{-CHO}$ have reacted. The product so formed undergoes crossed Cannizzaro reaction with HCHO to form calcium formate and pentaerythritol



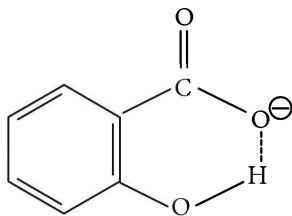


140. (a) p-nitrophenol (IV) though acidic is not as strong as carboxylic acid. Trichloroacetic acid is a very strong acid.

141. Peroxide effect is not observed in the case of addition of HCl. Therefore Markovnikov's addition occurs



142. Though both the $-\text{OH}$ and $-\text{OCH}_3$ groups are electron releasing by nature, the salicylate anion is stabilized by intramolecular H-bonding.



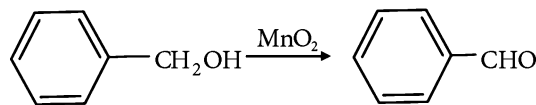
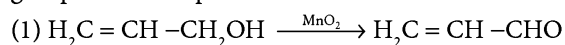
This is not possible with the $-\text{OCH}_3$ group. So salicylic acid is more acidic.

143. HCN is added to CH_3CHO to form a cyanohydrin. This is then hydrolysed to give lactic acid which is a hydroxy acid.

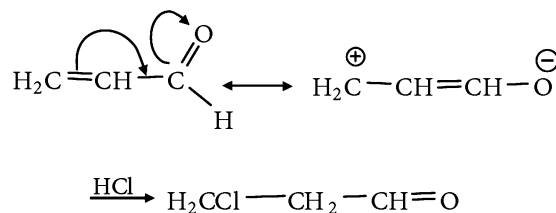
144. Aldol condensation is a reaction that occurs between two aldehydes, ketones or between an aldehyde and a ketone. However an aldol condensation is not noticed between an aldehyde and an ester.

145. This is known as Baeyer-Villiger oxidation/rearrangement. A cyclic ketone gives a ring expanded cyclic ester or a lactone. The reaction occurs in the presence of peracids like perbenzoic acid, MCPBA or peracetic acid.

146. MnO_2 can be used for the selective oxidation of the $-\text{OH}$ group in the presence of allylic and/or benzylic groups. For example

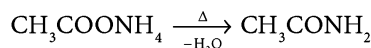


147. The addition of HCl across the double bond occurs contrary to the Markovnikov rule. This is due to the presence of an olefinic double bond in conjugation with the carbonyl group. Resonance operates as shown



148. The only reaction which is incorrectly represented is the hydration of the double bond. Hydration occurs according to Markovnikov rule and a tertiary alcohol is the first product formed which does not lead to the aldehyde on oxidation.

149. Strong heating of ammonium acetate gives only acetamide by dehydration



Acetamide on further dehydration by heating with P_2O_5 gives CH_3CN . Hence statement (d) is not correct.

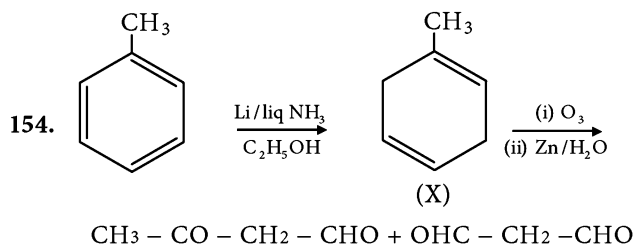
150. LiAlH_4 reduces carbonyl compounds like aldehydes, ketones, acids, esters, to the alcohol. However, LiAlH_4 does not reduce the olefinic bonds.

5.92 Aldehydes, Ketones and Carboxylic Acids

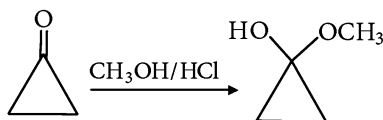
151. Cyclohexanone on Clemmensen reduction gives cyclohexane. So (a) is not correctly matched. The other reactions given in (b), (c) and (d) are correctly represented.

152. Hydride transfer from one carbonyl carbon to the other is the rate determining step in Cannizzaro reaction

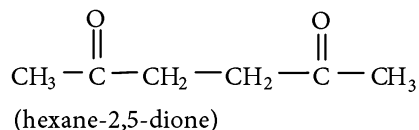
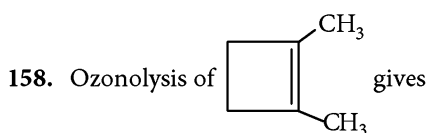
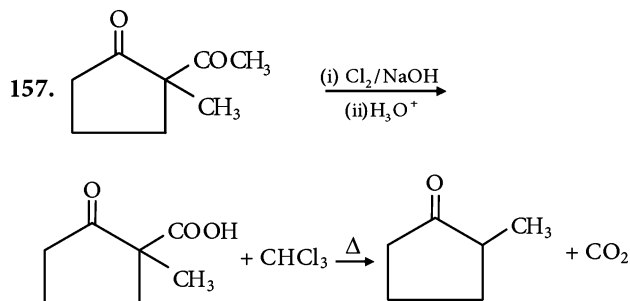
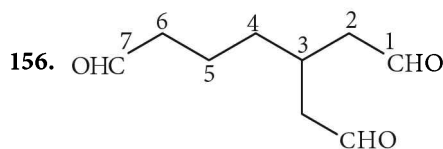
153. The reaction of ketoximes with acidic reagents to form substituted amide is known as Beckmann rearrangement. It does not involve nucleophilic acyl substitution



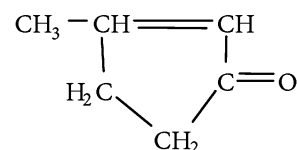
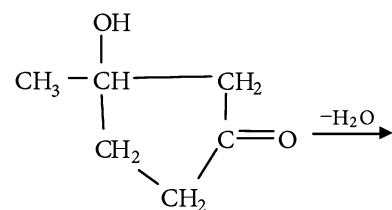
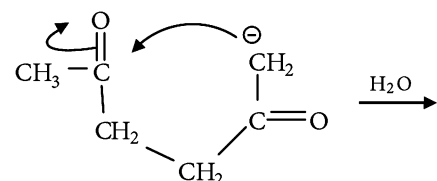
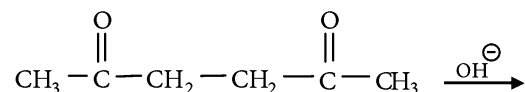
155. The hybridisation of carbonyl carbon in cyclopropanone is sp^2 . The orbitals oriented at 120° apart are forced to form C-C bond of cyclopropane having bond angle of 60° . So there is considerable strain in cyclopropanone. To reduce the angle strain to some extent, it undergoes nucleophilic addition with CH_3OH to form hemiacetal



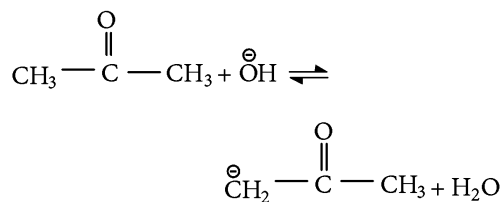
When the hemiacetal is formed, the hybridisation of the carbon changes from sp^2 to sp^3 . Hence the strain involved become less

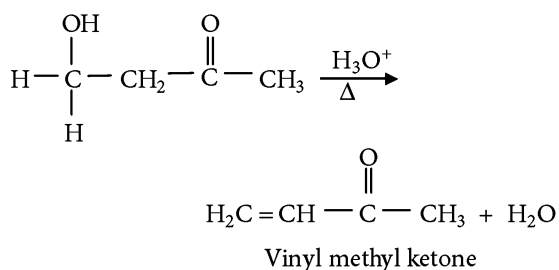
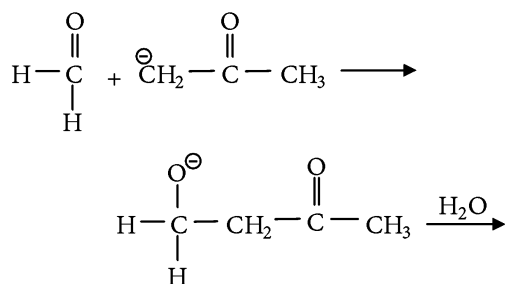


This undergoes intramolecular aldol condensation followed by dehydration to form (b).

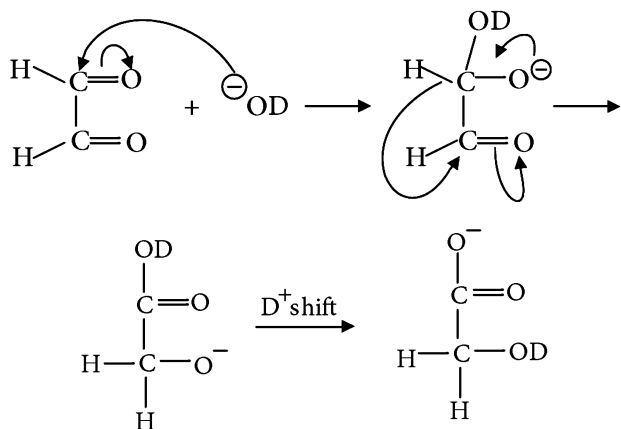


159. When a mixture of formaldehyde and acetone is heated with aqueous NaOH, the carbanion formed from acetone is added to formaldehyde.



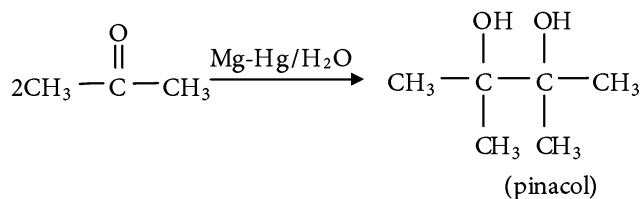


160. The reaction given is an example of intramolecular Cannizzaro reaction. The mechanism of the reaction is

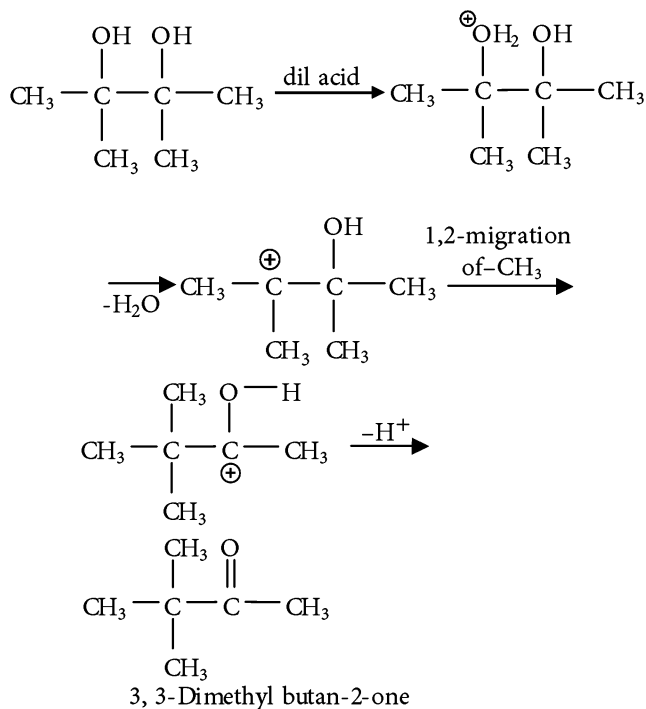


161. Tollens' reagent oxidizes aldehyde group without affecting the double bond.

162. Acetone on reaction with magnesium amalgam and water (or with Mg in benzene followed by hydrolysis) gives pinacol (2, 3 - dimethyl butane - 2, 3 - diol)



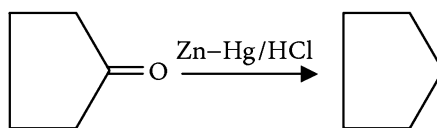
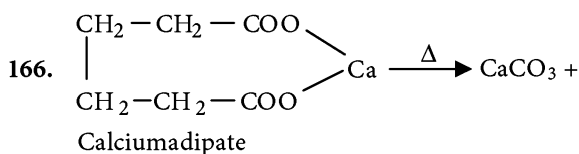
Pinacol undergoes pinacol-pinacolone rearrangement when treated with dilute acid



163. $\text{CH}_3-\text{C}\equiv\text{CH} \xrightarrow{\text{NaNH}_2} \text{CH}_3-\text{C}\equiv\text{C}^-\text{Na}^+ \xrightarrow{\text{H}-\text{CHO}} \text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_2\text{OH}$

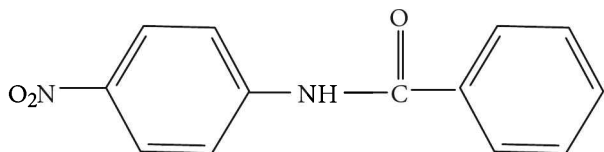
164. Cl is electron attracting by -I effect and electron donating by +M effect. The aldehyde group at the meta position with respect to Cl will experience stronger -I effect but no +M effect from chlorine and hence it will be more reactive than the other aldehyde group. The more reactive aldehyde group gets oxidized in Cannizzaro reaction.

165. Electrophilicity of Carbonyl carbons 1 & 3 are less due to resonance involving the benzene ring. Hence C-2 carbonyl group is the most reactive for nucleophilic addition reaction



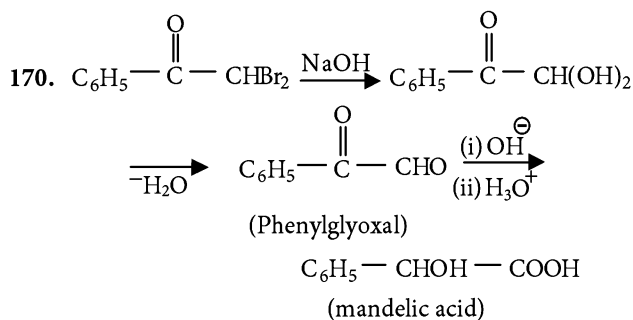
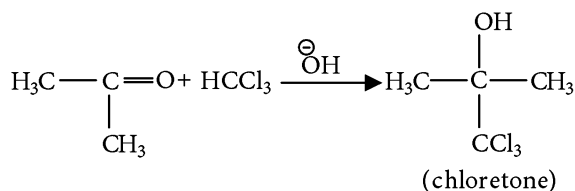
5.94 Aldehydes, Ketones and Carboxylic Acids

167. In Beckmann rearrangement, it is always the group, which is located anti to the $-\text{OH}$ group of the oxime, gets rearranged to the nitrogen from carbon. In this way, it is the paranitrophenyl group that migrate to form the product.



168. This is known as Dieckmann Cyclization. This is an intramolecular cyclization reaction occurring under the influence of a base. A keto ester is the product formed.

169. Chloretonone is formed,



Phenyl glyoxal will undergo intramolecular cannizzaro reaction in presence of alkali to form $\text{C}_6\text{H}_5-\text{CHOH}-\text{COOH}$

171. Both statements are correct, but statement 2 is not the main reason for statement 1

p-Hydroxy benzene sulphonic acid is more stable than the ortho isomer, but the energy of activation for its formation is higher. So when temperature is increased, o-hydroxy benzene sulphonic acid is converted to the more stable p-isomer.

In the sulphonation of phenol, o-hydroxy benzene sulphonic acid is the kinetically controlled product and p-hydroxy benzene sulphonic acid is the thermodynamically controlled product.

172. Statement 1 is true but statement 2 is false.

The formation of intramolecular hydrogen bonding between $-\text{OH}$ and $-\text{NO}_2$ group makes o-nitrophenol slightly less acidic than p-nitrophenol

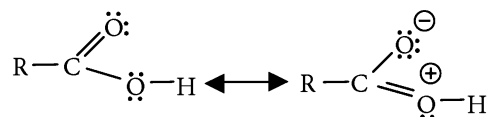
173. Statement 1 is wrong, but statement 2 is correct. In benzamide an $-\text{NH}_2$ group, a poor leaving group is attached to $\text{C}_6\text{H}_5\text{CO}-$ group and so it is not very active.

On the otherhand, in benzoyl chloride, the Cl, which is a poor nucleophile and a good leaving group is attached to the benzoyl group. Here benzoyl chloride is more reactive.

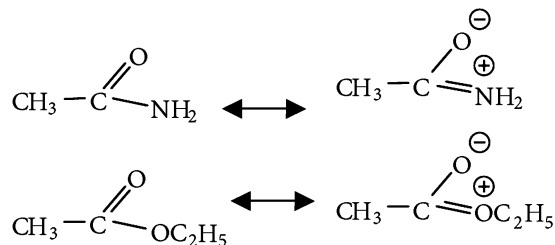
174. Statement 1 is wrong while statement 2 is correct. Cl_3C^- is more stable than F_3C^- because of back bonding.

175. Statement 1 is true, statement 2 is false, Tischenko reaction is used to convert aldehyde into ester, as one molecule of aldehyde is oxidized and other gets reduced to give ester.

176. Both statements are correct and statement 2 is the correct reason for statement 1



177. Both statements are correct and statement 2 is the correct explanation of statement 1. The resonance structures of ethanamide and ethyl ethanoate are given below



Since nitrogen is less electronegative, the ionic structure has greater contribution to resonance in the case of ethanamide. This makes the $\text{C}=\text{O}$ bond in ethanamide more polar. The dipole moments of the two compounds confirm this.

D.M of $\text{CH}_3-\text{CONH}_2$ is 3.6 D while that of $\text{CH}_3-\text{COOC}_2\text{H}_5$ is 1.78D

178. Statement 1 is correct but statement 2 is false. Ethanoate ion is more resonance stabilised than

phenoxide ion. In the three resonance structures of phenoxide ion, the negative charge is delocalized on less electronegative carbon and hence their contribution towards resonance is less. In the case of ethanoate ion, the negative charge is delocalised over two electronegative oxygen atoms and the two structures contribute equally to resonance. Hence ethanoate ion is more resonance stabilised.

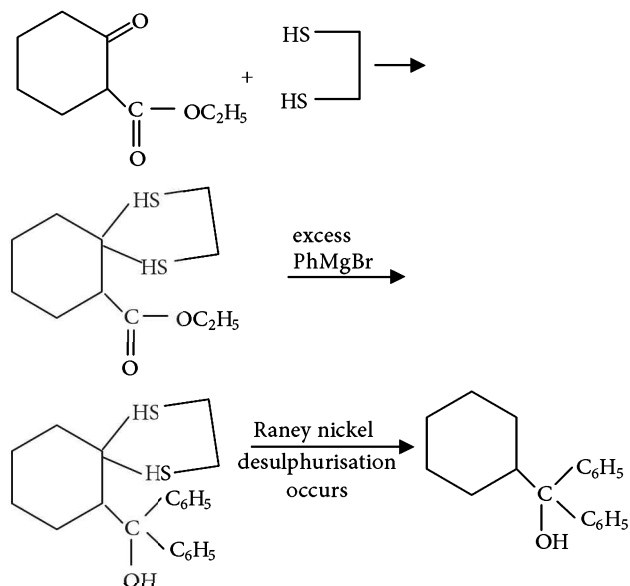
179. Both statements are correct, but statement 2 is not the reason for statement 1

Eventhough 2-methyl propanal contains an α -hydrogen atom, it does not easily undergo aldol condensation because the carbanion formed by the removal of α -hydrogen is quite unstable due to the +I effect of two methyl groups. So it undergoes Cannizzaro reaction

180. Statement 1 is not completely correct but statement 2 is correct

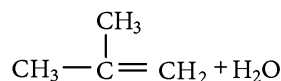
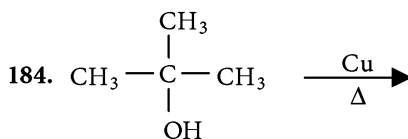
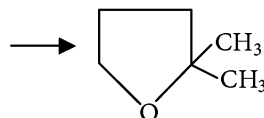
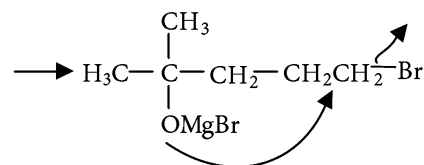
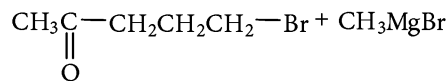
All aldehydes other than formaldehyde when treated with HCN give a racemic mixture of cyanohydrin. But in the case of ketone, only unsymmetrical ketones will give optically active cyanohydrin and hence racemic mixture. The cyanohydrin formed by symmetrical ketones such as acetone is not optically active

181. The free ketone in the six membered ring is protected as a thioketal in the first step. Then a Grignard reaction occurs and on Raney Nickel, reductive desulphurisation occurs. The sequence of reactions can be depicted as shown to give (a)

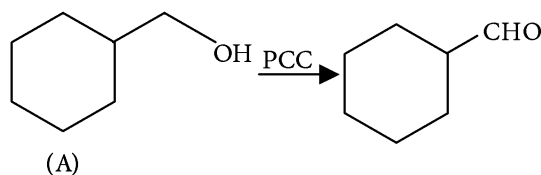
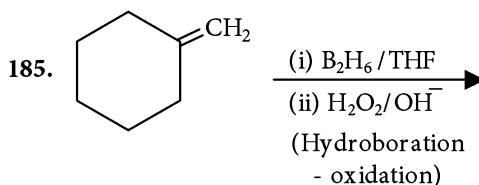


182. This is an example of a hemi acetal formation by an intra molecular condensation. Since there is only one -OH group, the reaction stops with the hemiacetal formation.

183. This is a reaction in which the Grignard reagent attacks the carbonyl group and the intermediate formed cyclises to form a tetra hydrofuran ring.

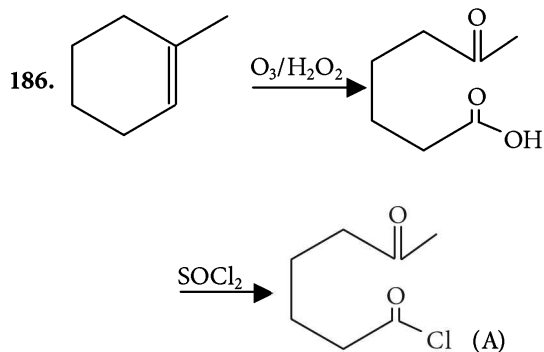


Tertiary alcohols undergo dehydration (to give alkenes) when passed through red hot copper tube.



Hydroboration-oxidation reaction gives a primary alcohol (A) as the major product. (A) on oxidation with pyridinium chlorochromate (PCC) gives an aldehyde (B) as the final product

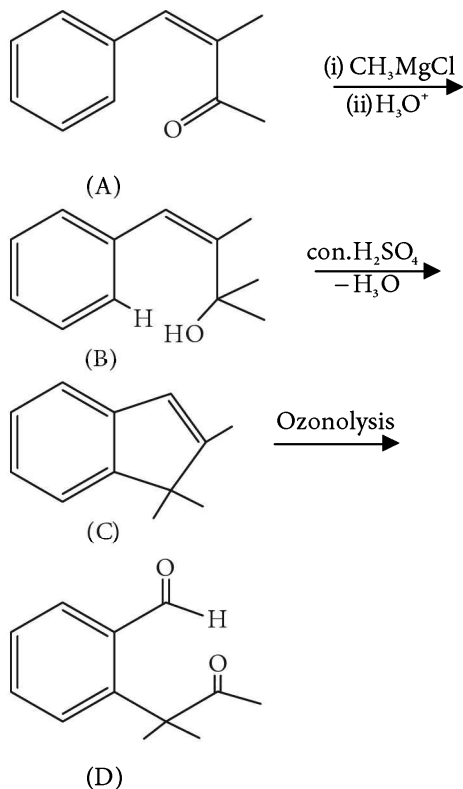
5.96 Aldehydes, Ketones and Carboxylic Acids



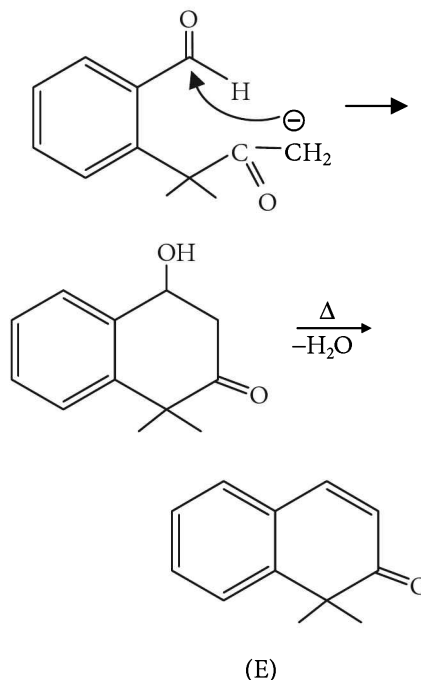
187. Since the compound gives yellow precipitate of iodoform when heated with iodine and alkali, it

must contain $\text{CH}_3-\text{C}(=\text{O})-$ group. So the compound must be either (a) or (c). To explain the given structures of (C), (D) and (E) in the next questions, we have to consider the compound (A) as that given in option (c)

188. Compound (A) on reaction with CH_3MgCl followed by hydrolysis gives a 3° alcohol (B). On heating with con. H_2SO_4 , (B) undergoes dehydration with ring closure to form (C) which on ozonolysis gives (D) as shown below

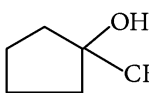


189. The compound (D) on treatment with dilute NaOH solution undergoes intramolecular aldol condensation. The carbanion formed by the removal of α -hydrogen with respect to the keto group undergoes nucleophilic addition at the aldehydic carbonyl group. This undergoes dehydration to form the final product (E)



190. DIBAL-H reduces esters to aldehyde. Reaction (b) and (c) give benzaldehyde. Reaction (b) is known as Gattermann-Koch reaction and reaction (c) is called Gattermann aldehyde synthesis. Reaction (d) gives ketone and not aldehyde.

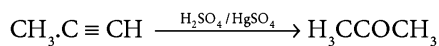
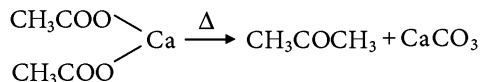
191. The product formed is acetone. It undergoes aldol condensation and reacts with chloroform in presence of alkali to form chloroacetone which is used as a hypnotic. Since it is a symmetrical ketone, it gives only one isomer of the oxime when treated with $\text{H}_2\text{N}-\text{OH}$.

192.  is a 1,2 diol. This is cleaved by $\text{Pb}(\text{CH}_3\text{COO})_4$ to give (c) and (d) as the products.

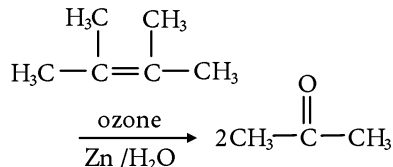
193. Statement (a) and (c) are incorrect. $-\text{NH}_2$ directly attached to $-\text{CO}-$ in semicarbazide cannot react with aldehyde or ketone. Benzaldehyde does not reduce Fehling's solution.

194. Benzophenone does not form cyanohydrin with HCN. DIBAL-H reduces esters to aldehydes. So (c) and (d) are not correct.

195. Methods (a), (c) and (d) lead to acetone. One of the standard methods of preparation of acetone is the dry distillation of calcium acetate.

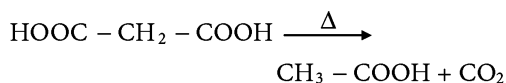


Ozonolysis of 2,3-dimethyl-2-butene gives acetone.



Rosenmund's reduction of acetyl chloride gives acetaldehyde.

196. Malonic acid on heating decomposes to form acetic acid and CO_2



197. (b) and (d) are correct. An amide though it contains a primary amino group does not answer reactions of an amine.

Esters cannot be made from carboxylic acids under the influence of alkali. Only acids-protonic acids catalyse the esterification reaction.

Diazomethane is a very good methylating agent for phenols and carboxylic acids.

198. (a) $\rightarrow$ (s)
 (b) $\rightarrow$ (q), (t)
 (c) $\rightarrow$ (r), (t)
 (d) $\rightarrow$ (p), (q), (t)
199. (a) $\rightarrow$ (q), (r)
 (b) $\rightarrow$ (t)
 (c) $\rightarrow$ (p), (s)
 (d) $\rightarrow$ (q), (r)
200. (a) $\rightarrow$ (p), (r)
 (b) $\rightarrow$ (p), (s)
 (c) $\rightarrow$ (t)
 (d) $\rightarrow$ (q), (r)

CHAPTER

6

AMINES, AMINOACIDS AND PEPTIDES

■■ CHAPTER OUTLINE

Preview

STUDY MATERIAL

AMINES

Classification of Amines

Preparation of Amines

Basicity of Amines

Chemical Properties of Amines

Diazonium Salts

Reactions of Diazonium Salts

- Concept Strands (1-5)

Amino Acids

Preparation of Amino Acids

Properties of Amino Acids

Peptides

Amino Acid Analysis

- Concept Strands (6-9)

TOPIC GRIP

- Subjective Questions (10)
- Straight Objective Type Questions (5)

- Assertion–Reason Type Questions (5)
- Linked Comprehension Type Questions (6)
- Multiple Correct Objective Type Questions (3)
- Matrix-Match Type Question (1)

IIT ASSIGNMENT EXERCISE

- Straight Objective Type Questions (60)
- Assertion–Reason Type Questions (3)
- Linked Comprehension Type Questions (3)
- Multiple Correct Objective Type Questions (3)
- Matrix-Match Type Question (1)

ADDITIONAL PRACTICE EXERCISE

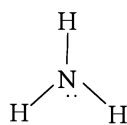
- Subjective Questions (10)
- Straight Objective Type Questions (15)
- Assertion–Reason Type Questions (5)
- Linked Comprehension Type Questions (9)
- Multiple Correct Objective Type Questions (9)
- Matrix-Match Type Questions (2)

AMINES

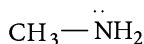
Amines are alkyl or aryl derivatives of ammonia, obtained by replacing one or more hydrogen atoms of ammonia by alkyl or aryl groups.

CLASSIFICATION OF AMINES

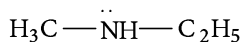
Amines are classified as primary, secondary and tertiary amines depending on the number of hydrogen atoms of ammonia replaced by the organic groups.



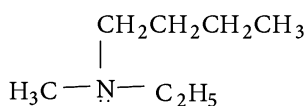
ammonia



a primary amine
(only one hydrogen of ammonia is replaced by an alkyl group)

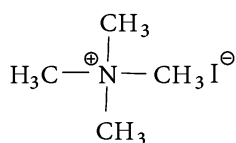


a secondary amine
(two hydrogens of ammonia are replaced by two alkyl groups)

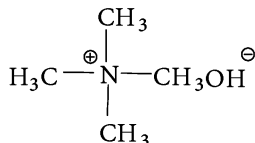


a tertiary amine
(all the three hydrogens of NH_3 are replaced by alkyl groups)

When four alkyl or aryl groups are attached to nitrogen, the lone pair of electrons on nitrogen are also involved in bonding with the organic group. In such a case, it is



tetramethyl ammonium iodide



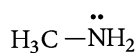
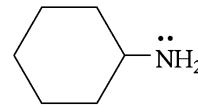
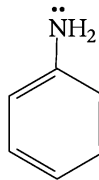
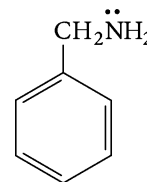
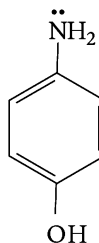
tetramethyl ammonium hydroxide

called a quaternary ammonium salt. A quaternary ammonium compound is a salt and not an amine and the basic character of nitrogen is lost.

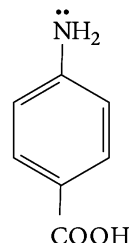
Functional groups of 1°, 2° and 3° amines are $-\text{NH}_2$, $>\text{NH}$ and $>\text{N}$, respectively.

A few examples of primary, secondary and tertiary amines are given below.

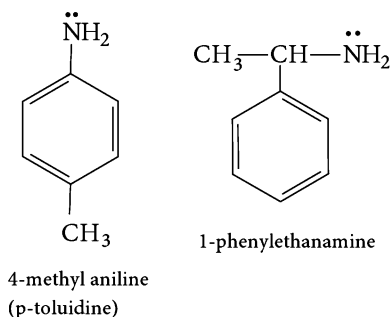
Primary amines

Methyl amine
(Methanamine)Cyclohexylamine
(Cyclohexanamine)Aniline
(an aromatic primary amine)Benzylamine
(Phenyl methanamine)

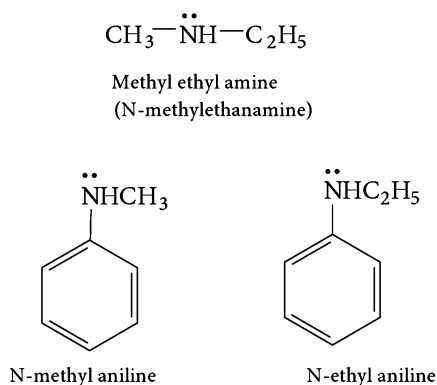
4 - amino phenol



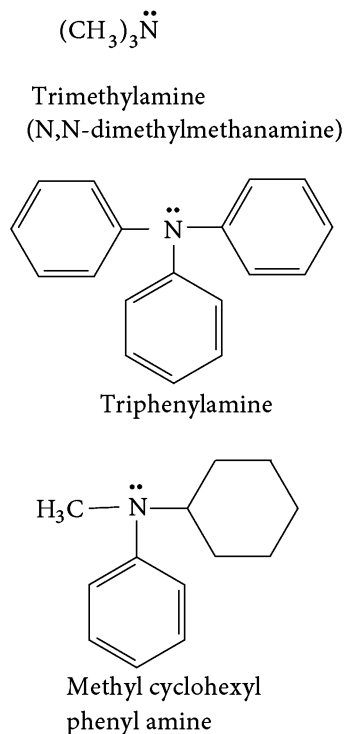
4-aminobenzoic acid



Secondary amines



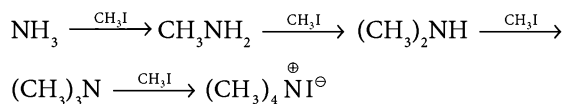
Tertiary amines



PREPARATION OF AMINES

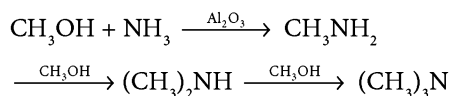
(i) Hoffmann's method

When an alkyl halide is heated to about 373K with alcoholic ammonia in a sealed tube, a mixture of primary, secondary and tertiary amines are formed, along with quaternary ammonium halide. This process is also termed as ammonolysis of alkyl halides.



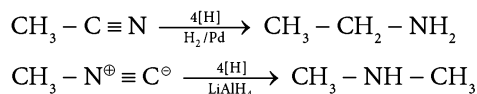
(ii) Ammonolysis of alcohols

A mixture of amines is obtained when the mixture containing vapours of alcohol and ammonia are passed over heated alumina (Al_2O_3) or thoria (ThO_2) at 575 – 600K



(iii) Reduction of cyanides and isocyanides

Primary amines can be obtained by the reduction of nitriles by catalytic hydrogenation or with sodium in alcohol or with LiAlH_4 .



(iv) Reduction of amides

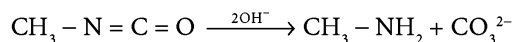
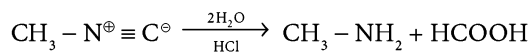
Primary amines can be obtained by the reduction of amides with LiAlH_4



(v) Hydrolysis of isocyanides or isocyanates

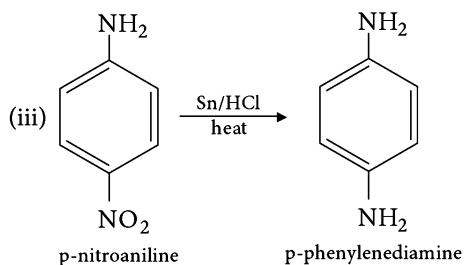
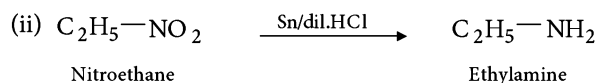
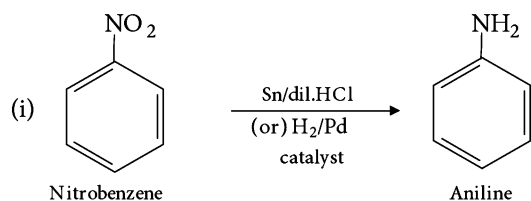
Isocyanides or isocyanates can be hydrolyzed to primary amines.

6.4 Amines, Aminoacids and Peptides



(vi) Reduction of nitro compounds

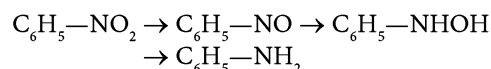
Amines can be prepared by the reduction of nitro compounds. A metal (Sn or Fe) and an acid (HCl) or molecular hydrogen with finely divided metal (Ni, Pd, Pt) catalyst are used to reduce $-\text{NO}_2$ group to $-\text{NH}_2$ group.



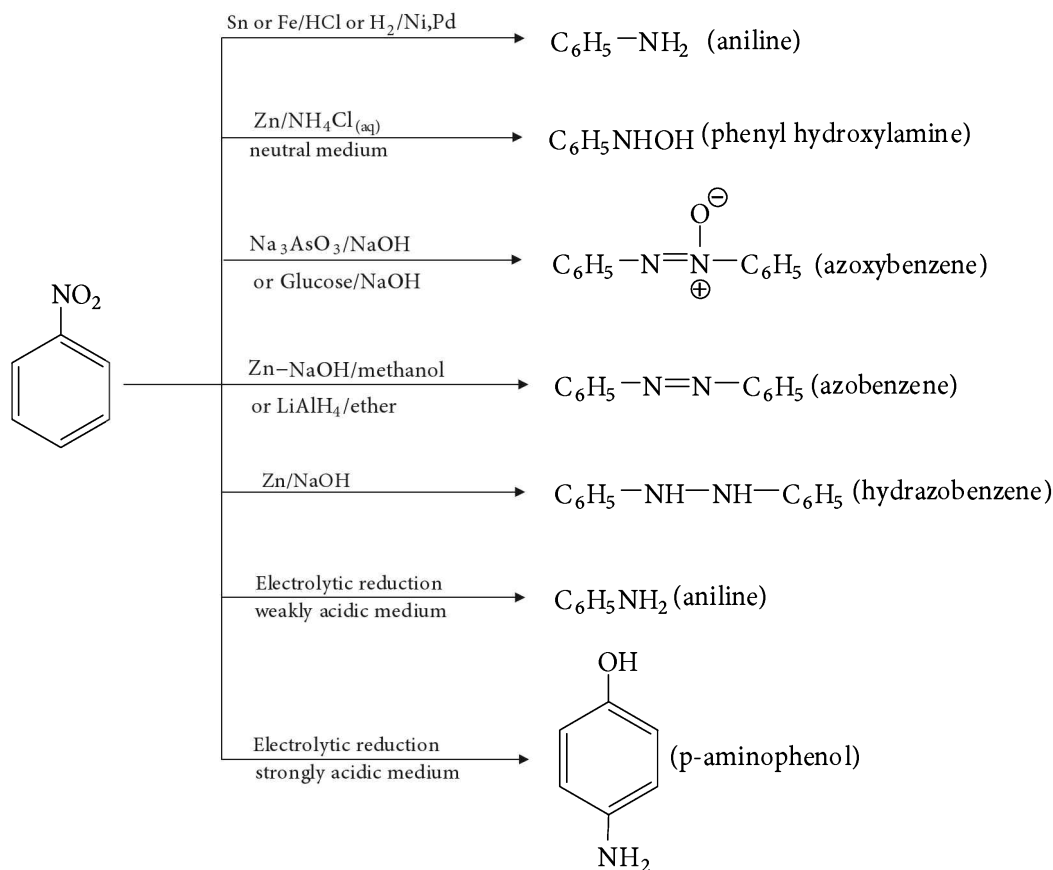
Reduction of nitro compounds to amines is a very important route in organic synthesis as it is the main route to the formation of aromatic and aliphatic amines.

Reduction products of nitrobenzene

The reduction of nitrobenzene ($\text{C}_6\text{H}_5\text{NO}_2$) has been shown to occur through the following stages.



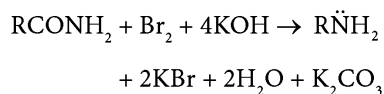
The nature of the product obtained depends on the reducing agent and the pH of the solution in which the reduction is carried out.



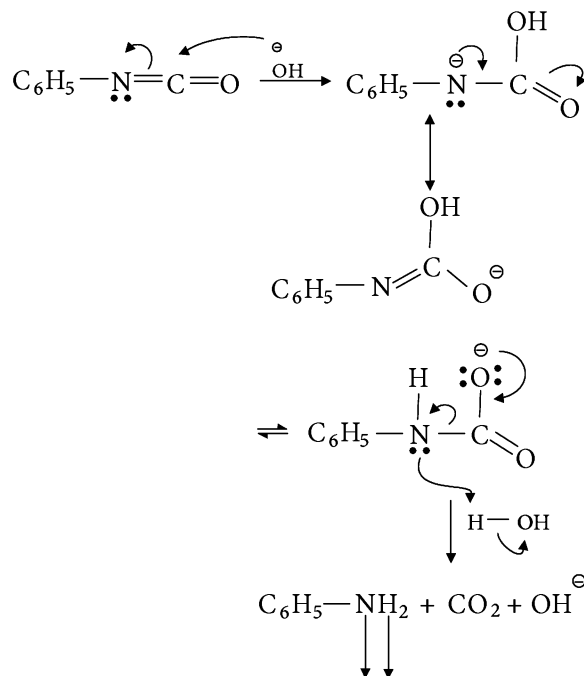
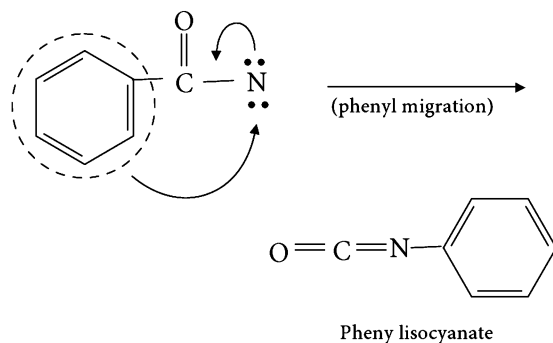
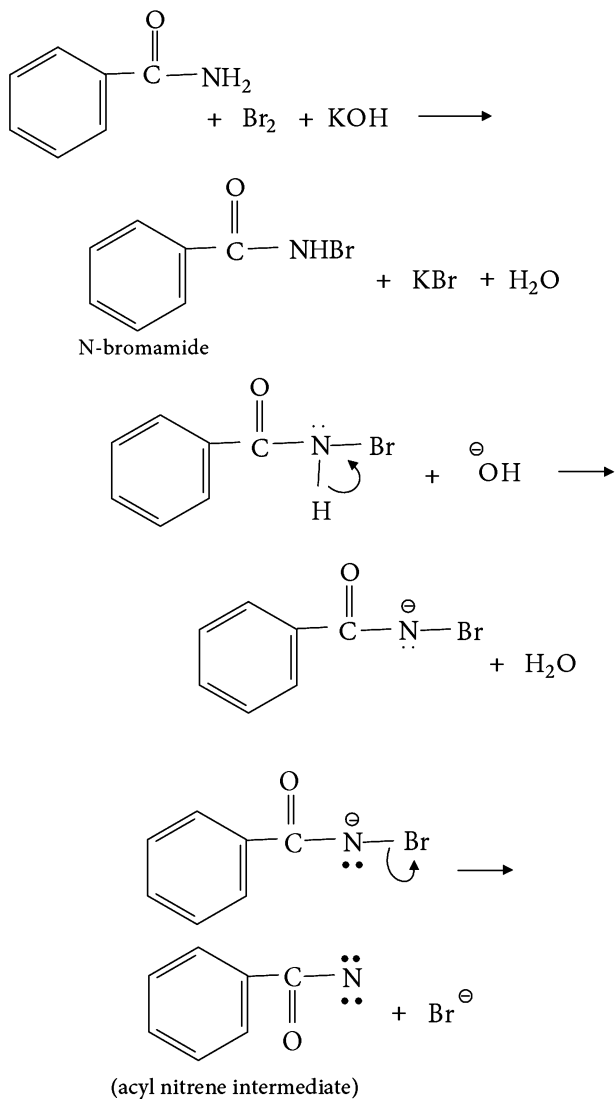
(vii) Hoffmann's bromamide reaction

When an amide is treated with bromine and alkali (or chlorine and alkali), a rearrangement occurs and a primary amine containing one carbon atom less than the amide is formed. This is known as Hoffmann's degradation or Hoffmann's bromamide reaction.

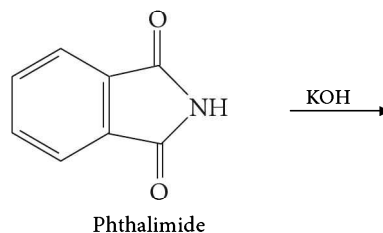
General equation for the rearrangement is



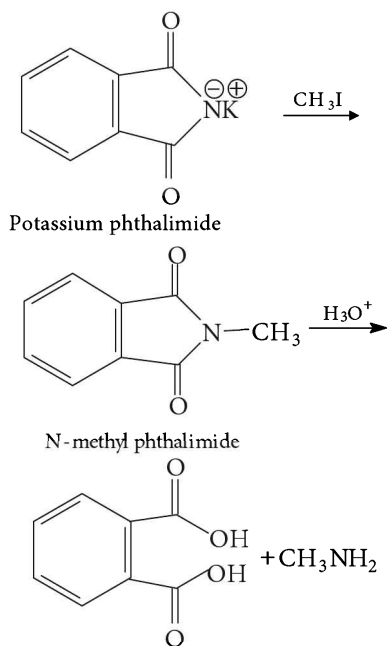
The rearrangement is believed to proceed via a nitrene intermediate. Nitrene is an electron deficient intermediate similar to a carbene. The mechanism of the rearrangement is given below.

**(viii) Gabriel phthalimide reaction**

When phthalimide reacts with KOH solution, the acidic hydrogen attached to the imide nitrogen is displaced by potassium. Now an alkylhalide is added to get N-alkyl phthalimide, which on acid or base hydrolysis gives a primary amine and phthalic acid.



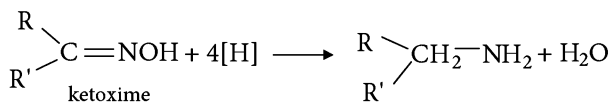
6.6 Amines, Aminoacids and Peptides



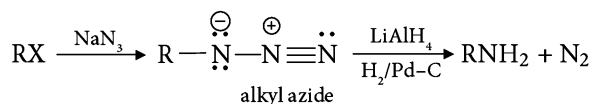
This is one of the convenient methods for the synthesis of pure primary aliphatic and aralkylamines.

(ix) Reduction of oximes

Reduction of aldoxime and ketoxime with LiAlH_4 or sodium and alcohol gives 1° amines



(x) Reduction of azides



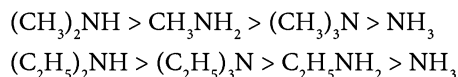
BASICITY OF AMINES

Amines are basic due to the presence of lone pair of electrons on the nitrogen atom.

Basicity of aliphatic amines

All aliphatic amines are stronger bases than ammonia due to the +I effect of alkyl groups. Aliphatic 2° amines are more basic than 1° amines because of the +I effect of two alkyl groups and consequent increase in electron density on nitrogen.

If we consider inductive effect alone, aliphatic 3° amines must be stronger bases. But aliphatic tertiary amines are found to be less basic than 2° amines in aqueous solution. The observed order of basic strength in aqueous medium is



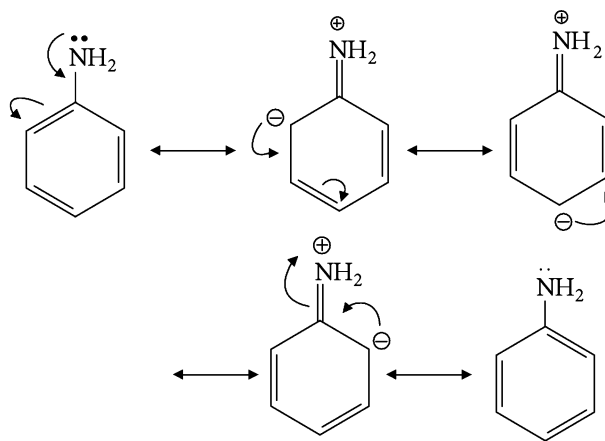
The less basic strength of 3° amine (R_3N) is due to the comparatively less stability of its conjugate acid (R_3NH^+) by hydrogen bonding in aqueous medium. Since the cation formed by the protonation of tertiary amine contains only one hydrogen, it can form only one hydrogen bond with water. Protonated primary and secondary amines can form more hydrogen bonds with water.

In the case of ethylamines, $(\text{C}_2\text{H}_5)_3\text{N}$ is slightly more basic than $\text{C}_2\text{H}_5\text{NH}_2$ due to the greater +I effect of ethyl group compared to methyl group.

In gaseous phase and in non-aqueous solvents where there is no solvation effect, 3° amines are more basic than 1° and 2° amines. In these media, the basicity of amines depends only on the +I effect on alkyl groups.

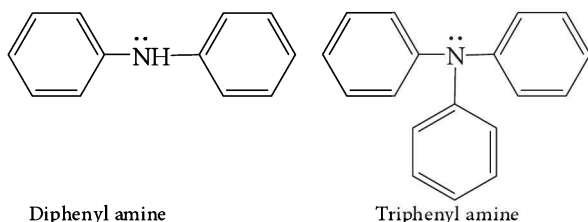
Obviously, presence of an electron-withdrawing group such as Cl reduces the base strength of aliphatic amines.

Basicity of aromatic amines

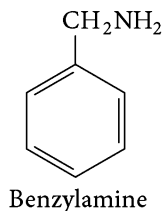


Aromatic amine like aniline is a much weaker base than an aliphatic amine. Aniline is a weaker base because of the delocalization of the lone pair of electrons on nitrogen into the aromatic ring. Aniline gets stabilized by resonance as shown.

Diphenylamine (when two phenyl groups are attached to nitrogen) is less basic than aniline. Triphenylamine (three phenyl groups on nitrogen) is almost neutral.



Benzylamine is a stronger base than aniline.

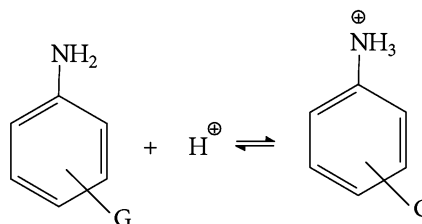


This is because delocalization of electrons from the lone pair on nitrogen into the benzene ring is prevented by an intervening $-\text{CH}_2-$ group between the amine group and the aromatic ring. Benzylamine as a base has a strength almost comparable to that of an aliphatic amine. The lone pair of electrons on nitrogen are easily available for protonation.

The basic character of aniline is affected by the presence of substituents in the benzene ring.

- (i) Electron releasing substituents like $-\text{CH}_3$, $-\text{OH}$, $-\text{OCH}_3$, etc. in the benzene ring at para position increase the basicity of aniline. These substituents tend to disperse the positive charge on the anilinium ion and therefore, stabilize the anilinium ion relative to the free $-\text{NH}_2$ group in aniline. Alternatively, they increase the electron density on nitrogen in $-\text{NH}_2$, making it more basic.
- (ii) Electron withdrawing substituents like $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $-\text{C}(=\text{O})\text{H}$ in the benzene ring decrease the basicity of aniline. Electron withdrawing substituents tend to intensify the positive charge on the anilinium

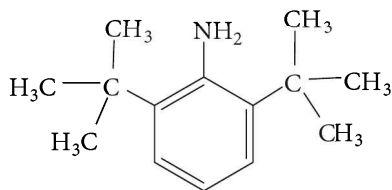
ion and therefore, destabilize the anilinium ion with respect to free aniline. Alternatively, electron withdrawing groups, decrease the electron density on nitrogen, making it less basic.



If G releases electrons, it stabilizes the cation, increases electron density of free $-\text{NH}_2$ and increases the basicity. If G withdraws electrons, it destabilizes the cation, decreases the electron density of free $-\text{NH}_2$ and decreases the basicity.

- (iii) Ortho-substituted anilines are usually weaker bases than aniline irrespective of the nature of the substituent (i.e., whether the group has electron donating or electron withdrawing nature). This is called ortho effect and is due to a combination of steric and electronic factors.
- (iv) *Relative basic strength of nitroanilines*
Aniline > m-nitroaniline > p-nitroaniline > o-nitroanilines
- (v) *Relative basic strength of toluidine*
p-toluidine > m-toluidine > aniline > o-toluidine
- (vi) *Relative strength of methoxy anilines (anisidines)*
o-anisidine is a weaker base than aniline due to ortho effect. Due to +R effect of $-\text{OCH}_3$ group at para position, p-anisidine is a much stronger base than aniline. Presence of $-\text{OCH}_3$ group at the meta position cannot exert its +R effect on $-\text{NH}_2$ group, but it can exert its $-\text{I}$ effect due to the presence of electronegative oxygen. Hence m-anisidine is a weaker base than aniline and it is found to be even weaker than o-anisidine. Thus the basicity order may be written as
p-anisidine > aniline > o-anisidine > m-anisidine.
- (viii) *Relative basic strength of chloroanilines*
Since $-\text{I}$ effect of chlorine outweighs its +R effect, all chloroanilines are weaker bases than anilines. The relative basicity order is
Aniline > p-chloroaniline > m-chloroaniline > o-chloroaniline
2,6-di (tert-butyl) aniline is a much stronger base than aniline.

6.8 Amines, Aminoacids and Peptides

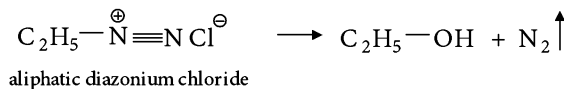
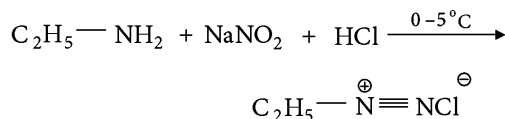


This is due to the fact that the two bulky tert-butyl groups on the two sides of the amino group prevent the nitrogen from being in the same plane as the ring carbon atoms, thereby inhibiting delocalization of electrons by resonance. This is an instance of steric inhibition of resonance.

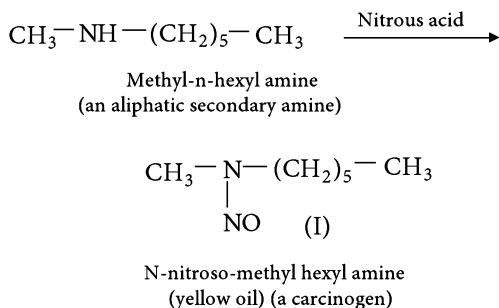
CHEMICAL PROPERTIES OF AMINES

Reactions with nitrous acid

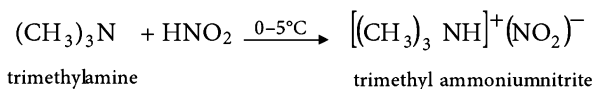
Primary aliphatic amines react with NaNO_2 and dil.HCl at $0-5^\circ\text{C}$, to yield aliphatic diazonium chlorides, which are quite unstable and decompose readily to give alcohols, with the evolution of nitrogen.



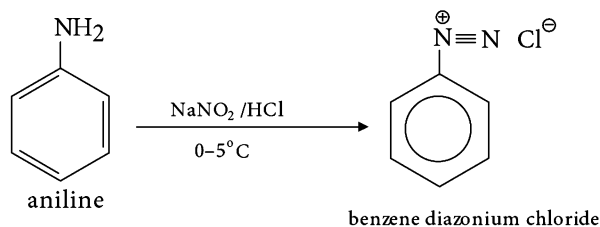
Secondary aliphatic amines react with NaNO_2/HCl or HNO_2 to give N-nitroso compounds.



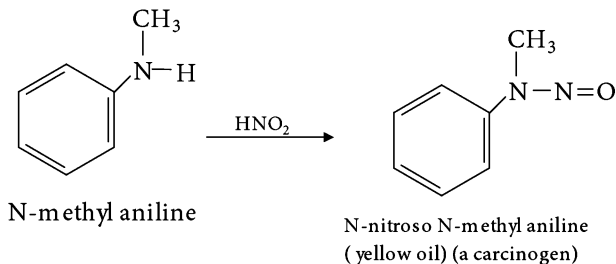
Tertiary aliphatic amines react with HNO_2 to form water soluble nitrite salts.



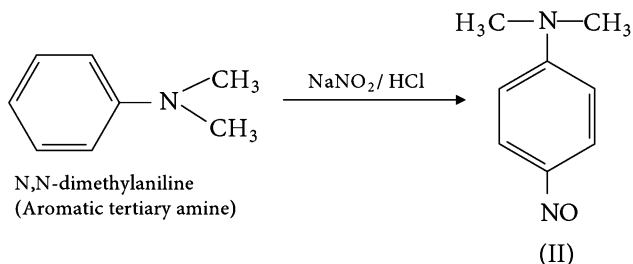
Primary aromatic amines react with NaNO_2 and dil.HCl at $0-5^\circ\text{C}$ to form aryl diazonium salts, which are stable at low temperatures.



Secondary aromatic amines react with nitrous acid to give N-nitroso compounds.



Tertiary aromatic amines react with HNO_2 to give ring nitroso substituted products. For example, N,N-dimethylaniline on reaction with NaNO_2 and dil.HCl , undergoes ring nitrosation to give p-nitroso N,N-dimethylaniline (II).

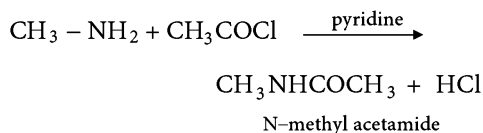


Ring nitrosation is an aromatic electrophilic substitution in which the attacking species is the nitrosonium ion, NO^+ , that can attach itself to the ring. The nitrosonium ion is a weak electrophilic species compared to the electrophilic species involved in nitration (NO_2^+ -nitronium ion) and other electrophiles. Therefore, nitroazation occurs only

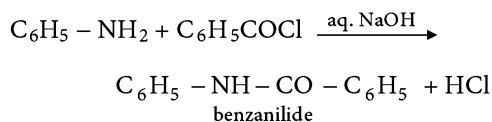
in rings bearing a powerfully activated species like N,N-dimethylamino group or other activating species like phenolic group.

Acylation of amines

Primary and secondary amines are acylated when treated with acid chloride or acid anhydride. Tertiary amines are not acylated as they do not contain a hydrogen atom on nitrogen.

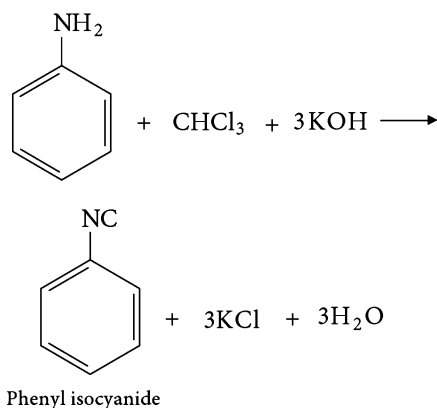
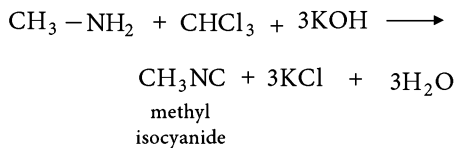


Acylation of aromatic amines using benzoyl chloride in presence NaOH is known as benzoylation or Schotten-Baumann reaction.

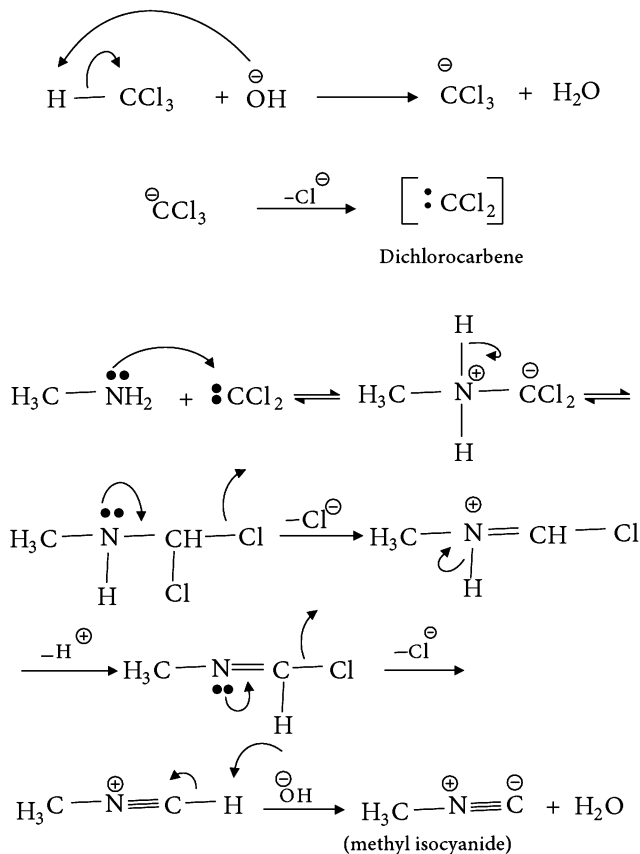


Carbylamine reaction

A primary amine, whether aliphatic or aromatic, when warmed with CHCl_3 and strong alcoholic KOH solution, forms an isocyanide or carbylamine, which are characterized by a strong nauseating odour. Carbylamine formation is a typical reaction of the primary amines, not answered by secondary or tertiary amines.

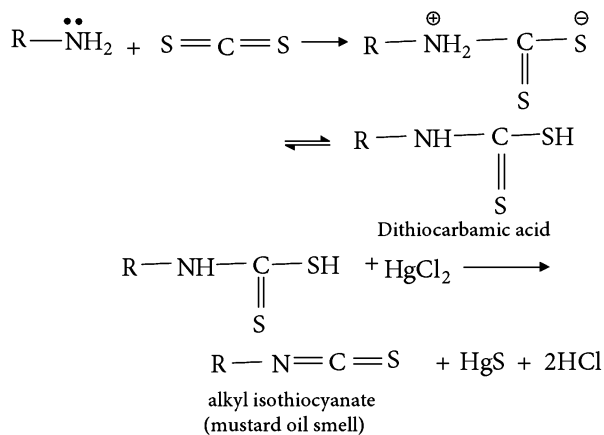


The formation of carbylamine involves the generation of dichlorocarbene $:\text{CCl}_2$ as a reactive electron deficient intermediate. The mechanism is explained by the following steps



Hoffmann's mustard oil reaction

Primary amines form dithiocarbamic acid with CS_2 , which on heating with HgCl_2 , forms isothiocyanates. This is known as Hoffmann's mustard oil reaction.

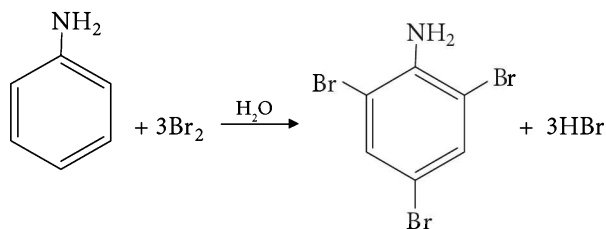


Reactions of the aromatic ring

Amino group is ortho, para directing and it activates the benzene ring towards electrophilic substitution reactions.

(a) Halogenation

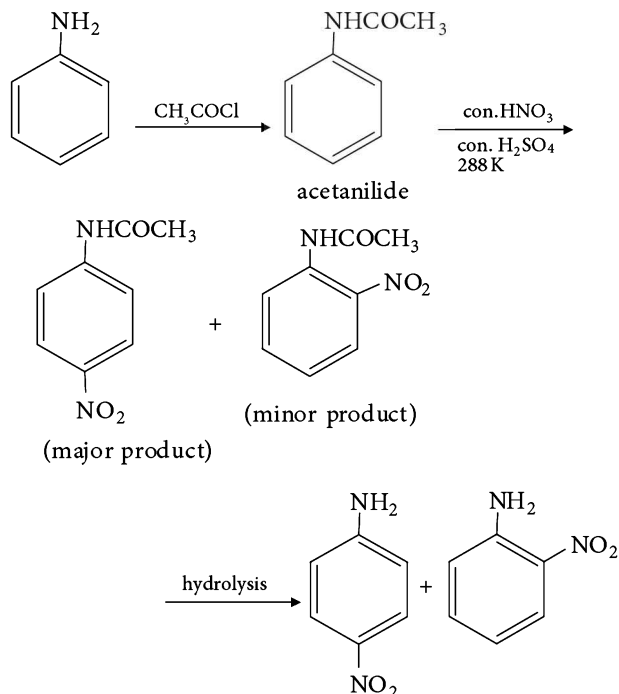
Aniline reacts with bromine water to give a white precipitate of 2,4,6-tribromoaniline



For the preparation of monobromo derivative, the activating effect of amino group is reduced by acetylation and then bromination is carried out.

(b) Nitration

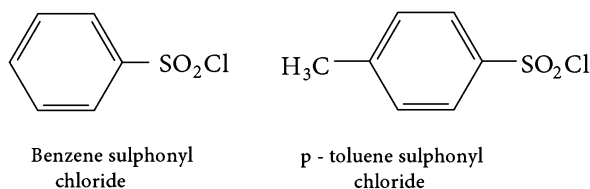
Direct nitration of aniline with con. HNO_3 leads to oxidation of the highly activated benzene ring forming tarry oxidation products along with nitro derivatives. Therefore, before nitration, aniline is first acetylated to protect the amino group. The acetyl group is finally removed by hydrolysis.



Even though $-\text{NH}_2$ group is ortho-para directing, controlled direct nitration of aniline with con. HNO_3 gives considerable amount of m-nitroaniline (about 47%). This is because under strongly acidic conditions, most of aniline is protonated to form anilinium ion ($\text{C}_6\text{H}_5 - \text{NH}_3^+$) and $-\text{NH}_3^+$ group is meta directing.

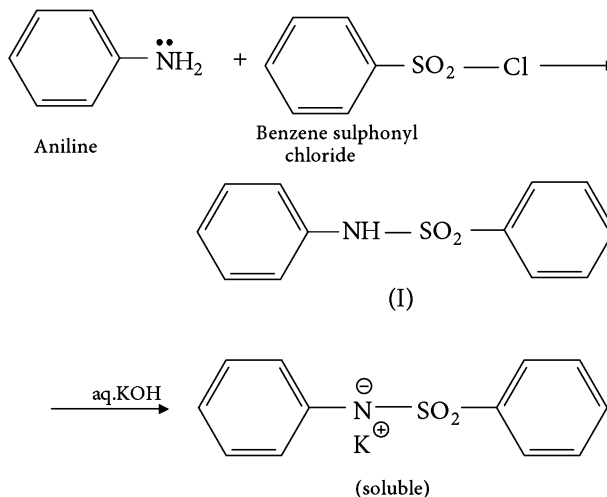
Hinsberg test

Hinsberg's test is used to distinguish 1° , 2° and 3° amines. The amine is shaken with Hinsberg's reagent which is benzene sulphonyl chloride in the presence of aqueous KOH (p-toluene sulphonyl chloride can also be used instead of benzene sulphonyl chloride).

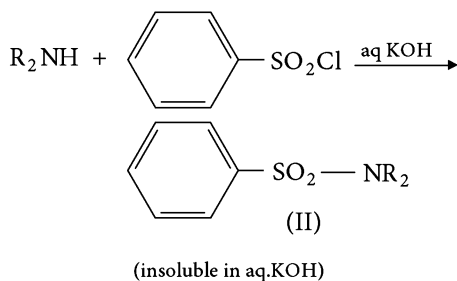


Primary and secondary amines form benzene sulphonamide with benzene sulphonyl chloride while tertiary amines do not form sulphonamides.

The benzene sulphonamide (I) formed from a primary amine has an acidic hydrogen attached to nitrogen. Reaction with aq. KOH converts the benzenesulphonamide into a soluble salt. Thus a 1° amine gives a clear solution when treated with Hinsberg's reagent in presence of aqueous KOH.



The disubstituted benzene sulphonamide (II) formed from 2° amine has no acidic hydrogen and therefore remains insoluble in aqueous alkali.

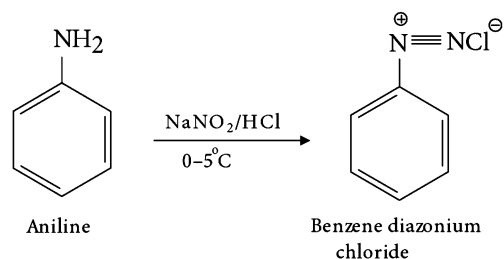


A tertiary amine does not react with Hinsberg reagent due to the lack of any hydrogen attached to nitrogen. Thus a primary amine yields a clear solution, a secondary amine yields an insoluble solid and the tertiary amine does not react when treated with Hinsberg's reagent and aqueous KOH.

DIAZONIUM SALTS

When a primary aromatic amine like aniline, dissolved in cold dil. hydrochloric acid, is treated with aqueous sodium nitrite solution, under ice cold conditions ($0 - 5^\circ\text{C}$), an aryl diazonium salt, namely benzene diazonium chloride is formed.

An aryl diazonium salt is fairly stable at low temperatures, but starts decomposing slowly on storing. Therefore, they are used under cold conditions as and when they are prepared.



REACTIONS OF DIAZONIUM SALTS

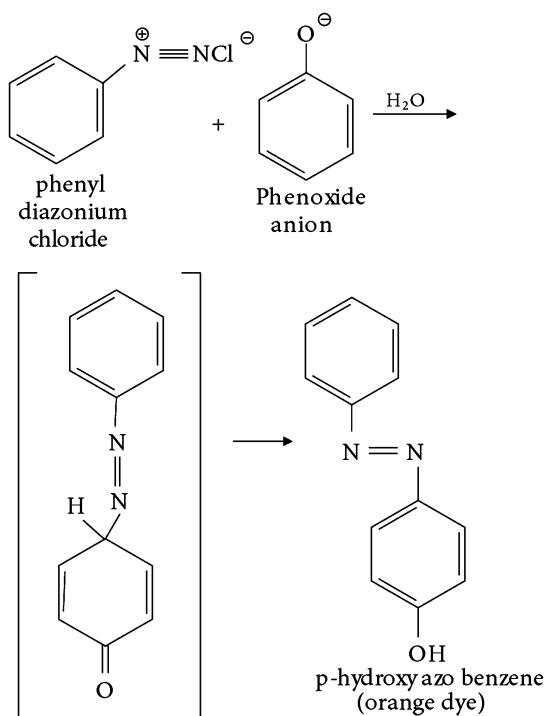
The reactions of diazonium salts can be divided into two types. In one type of reactions, nitrogen is lost as N_2 and there is a replacement by some other atoms or groups in the ring in the place of nitrogen. In another type of reactions known as coupling reactions, nitrogen of the starting diazonium salt is retained in the product also.

Azocoupling reactions

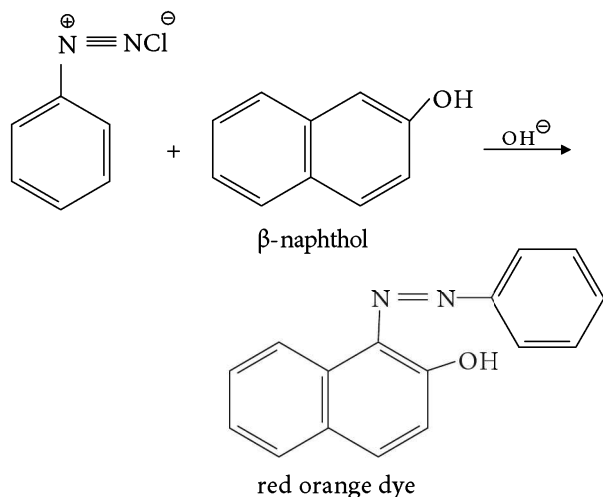
Diazonium salts react with phenols in basic medium to give aryl azo phenols. The overall reaction is an electrophilic aromatic substitution by means of a weak electrophile, namely the phenyldiazonium ion ($\text{C}_6\text{H}_5\text{N}_2^+$) on an aromatic ring that is fairly activated by the phenoxide anion. Such reactions are known as coupling reactions.

Arylazophenols form a group of an important class of azodyes.

Benzene diazonium chloride couples with β -naphthol (or 2-naphthol) in alkaline medium to give a red orange dye.

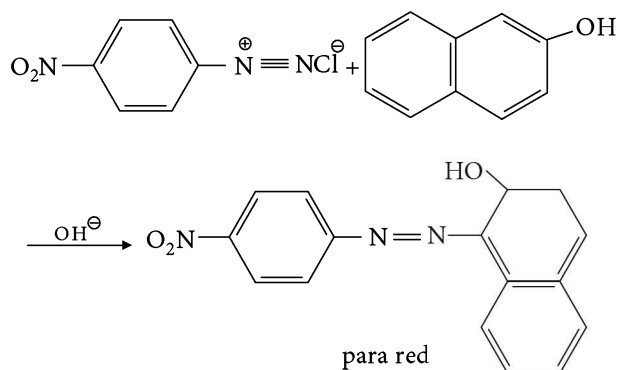


6.12 Amines, Aminoacids and Peptides

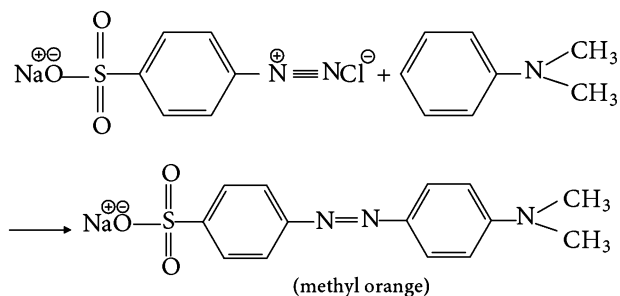


α -naphthol (1-naphthol) undergoes coupling with diazonium salts at position 4.

A red dye known as para red is formed by the coupling of diazotised p-nitroaniline with β -naphthol.



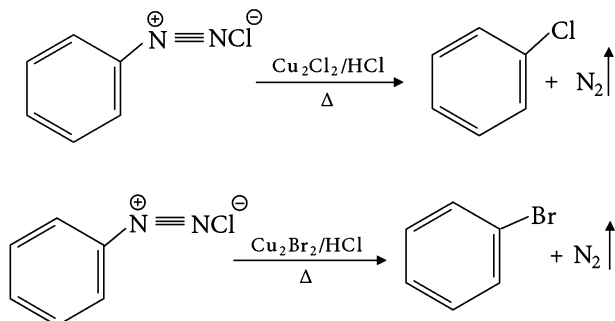
An acid base indicator, methyl orange is obtained by the coupling of diazotized sulphanilic acid with N,N-dimethylaniline in alkaline medium.



Sandmeyer reaction

Replacement of the diazonium group by either $-\text{Cl}$ or $-\text{Br}$ is effected by mixing a freshly prepared diazonium salt

with cuprous chloride or cuprous bromide in presence of hydrogen halides. At slightly higher temperatures, nitrogen is evolved and the aryl chloride or aryl bromide is obtained as the final product. This is generally referred to as Sandmeyer reaction

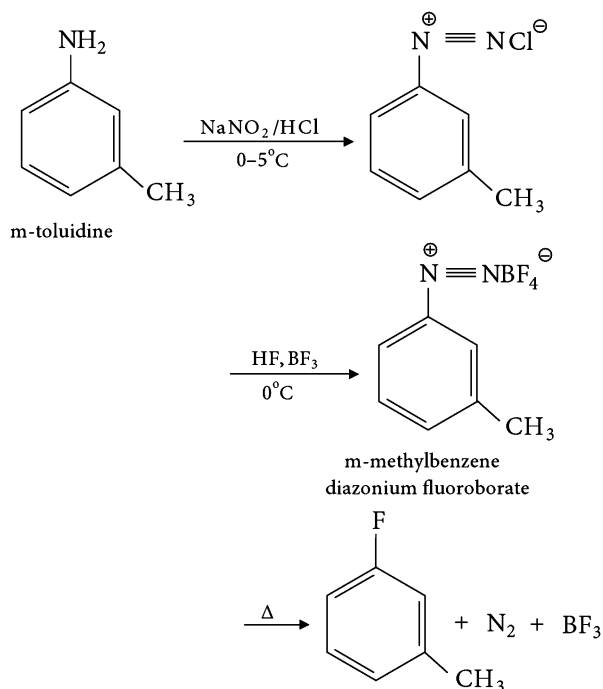


Gattermann reaction

Gattermann reaction is a modification of Sandmeyer reaction by using copper powder (in the place of cuprous halide) and hydrogen halide.

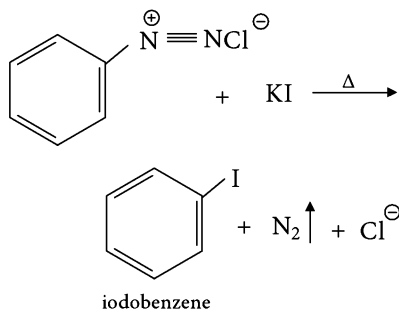
Balz-Schiemann reaction

Replacement of the diazonium group by $-\text{F}$ is effected by adding a mixture of HF and BF_3 or HBF_4 at 0°C to the diazonium chloride to get insoluble diazonium fluoroborate followed by gentle heating. This reaction is called Balz-Schiemann reaction.



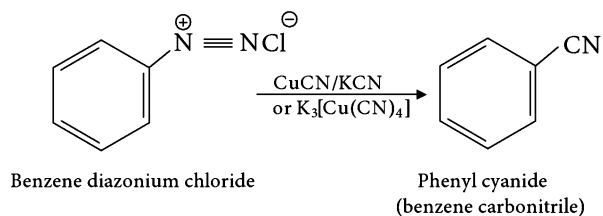
Replacement by iodide

Replacement of the diazonium group by iodide does not require the use of cuprous iodide or copper. Instead the diazonium salt is heated with KI to give iodo substituted benzene.



Replacement by cyanide

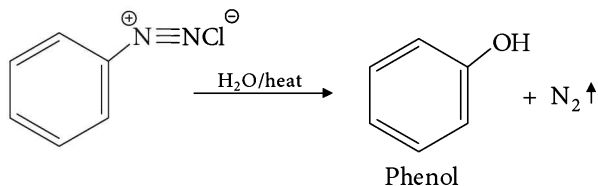
When the aryldiazonium chloride is reacted with cuprous cyanide and potassium cyanide or $K_3[Cu(CN)_4]$, the corresponding aryl cyanide is obtained.



The conversion of aniline to cyanide is a convenient route to the synthesis of aryl carboxylic acids.

Replacement by hydroxyl group

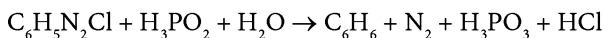
When a diazonium salt is heated with water, phenol is formed.



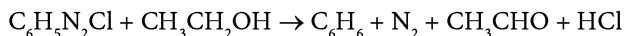
Deamination

One of the most important synthetic utility of the diazonium salt is the replacement of the diazonium group

by $-H$. The reagent generally used is hypophosphorus acid (H_3PO_2), a powerful reducing agent. This reaction is also known as deamination.

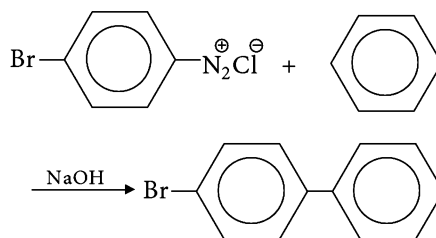


Replacement by hydrogen can also be carried out by heating with ethanol.



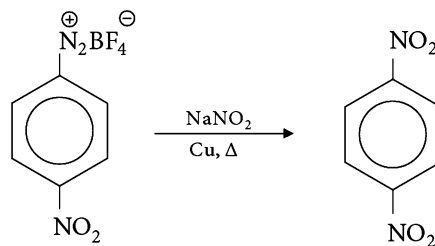
Gomberg reaction

Biaryl can be prepared by adding an aromatic compound to an alkaline solution of a diazonium salt.



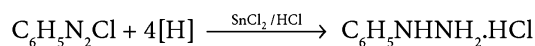
Replacement by nitro group

When diazonium fluoroborate is heated with sodium nitrite solution in presence of copper, the diazonium group is replaced by $-NO_2$ group.



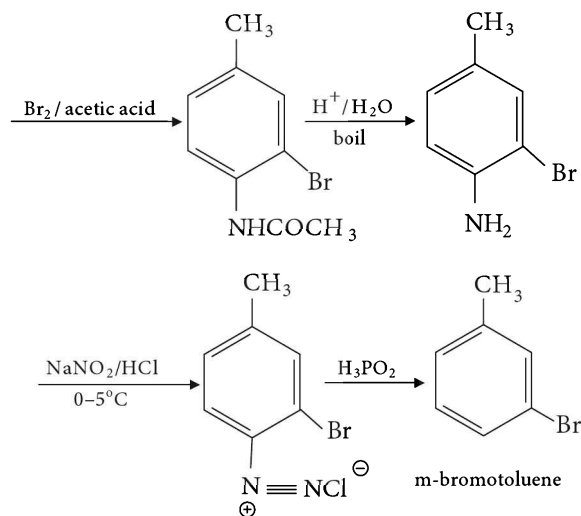
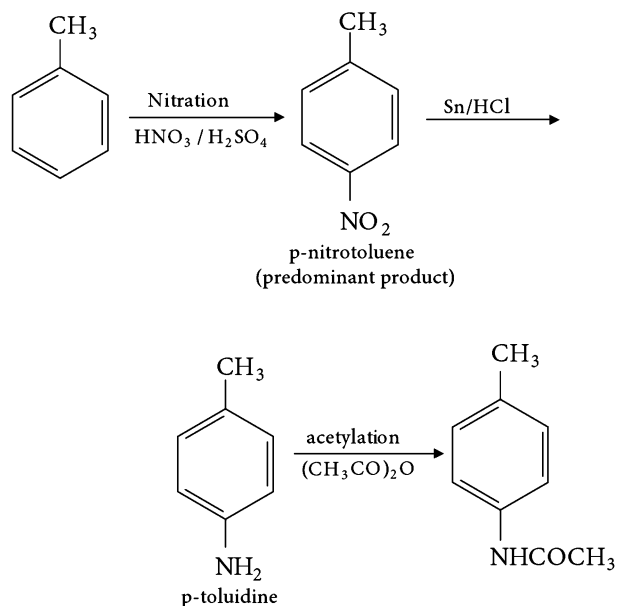
Reduction

When reduced with $SnCl_2$ and HCl or with Na_2SO_3 solution, benzene diazonium chloride gives phenyl hydrazine.



The synthesis of m-bromotoluene starting from toluene is achieved through the diazonium salt. Both the substituents in m-bromotoluene are ortho and para directing groups and these two groups have to be placed in the meta positions in the target molecule.

6.14 Amines, Aminoacids and Peptides

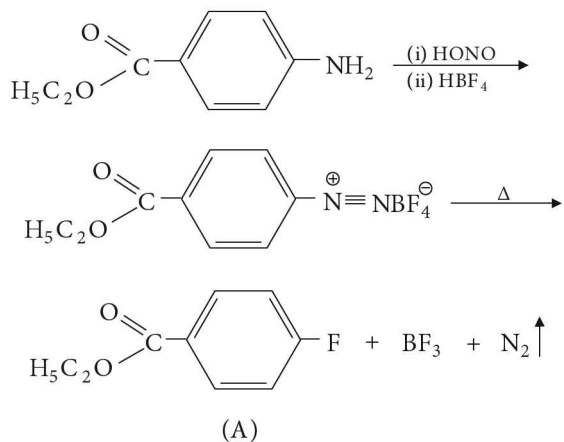


CONCEPT STRANDS

Concept Strand 1

When ethyl p-amino benzoate is reacted with nitrous acid followed by heating with fluoroboric acid, a crystalline compound (A) is formed. Identify the product (A) and name the reaction.

Solution

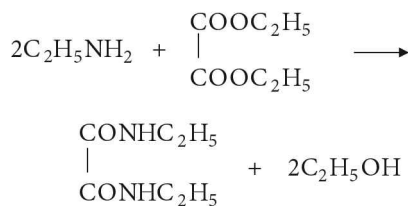


Concept Strand 2

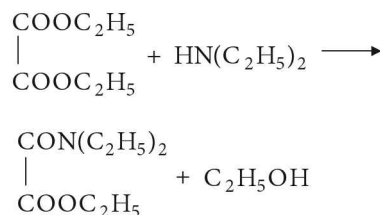
How does diethyl oxalate react with $\text{C}_2\text{H}_5\text{NH}_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$ and $(\text{C}_2\text{H}_5)_3\text{N}$?

Solution

$\text{C}_2\text{H}_5\text{NH}_2$, being a primary amine forms a crystalline solid of N,N-diethyl oxamide.



With diethylamine, which is a secondary amine, N,N-diethyl oxamic ester is formed, which is a liquid.



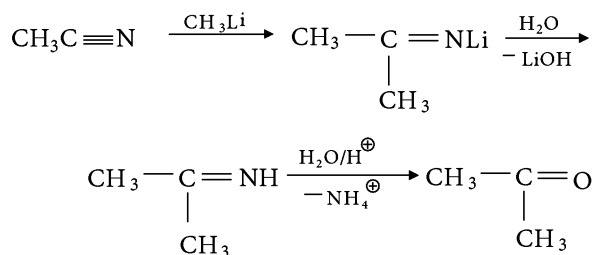
$(\text{C}_2\text{H}_5)_3\text{N}$ being a tertiary amine does not contain a replaceable hydrogen on amine and does not react with diethyl oxalate.

This method of separation of primary, secondary and tertiary amines, is known as Hoffmann's method.

Concept Strand 3

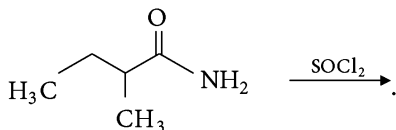
What happens when acetonitrile reacts with CH_3Li , followed by treatment with acidulated water?

Solution

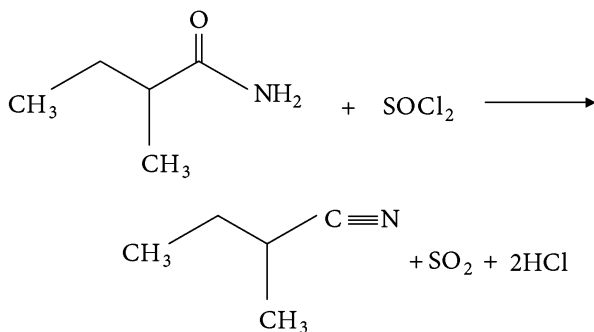


Concept Strand 4

Identify the products formed in the reaction,



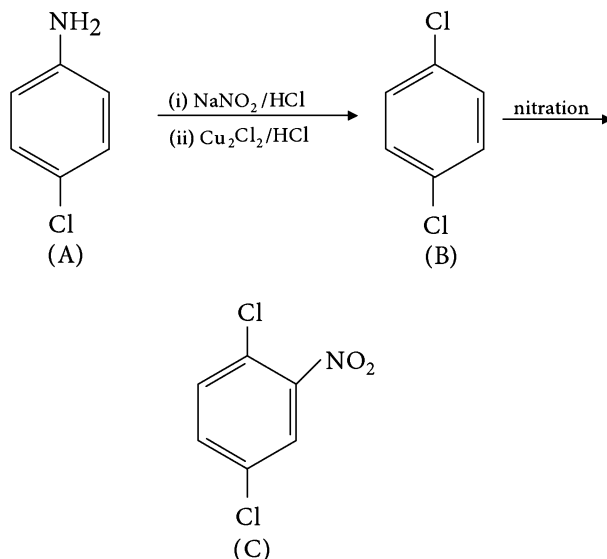
Solution



Concept Strand 5

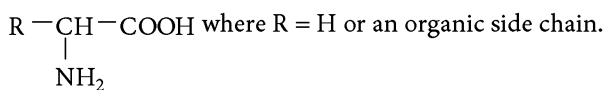
An organic compound (a) $\text{C}_6\text{H}_6\text{ClN}$ when treated with NaNO_2 and HCl at low temperature, followed by treatment with Cu_2Cl_2 in conc. HCl gave (B), $\text{C}_6\text{H}_4\text{Cl}_2$, which gives rise to only one mononitro product (C), $\text{C}_6\text{H}_3\text{Cl}_2\text{NO}_2$, under nitrating conditions. Identify (A), (B) and (C).

Solution



AMINO ACIDS

Amino acids contain both amino ($-\text{NH}_2$) and carboxylic acid ($-\text{COOH}$) groups. Acids in which $-\text{NH}_2$ group is attached to the carbon atom adjacent to the $-\text{COOH}$ group are called α -amino acids. They can be represented by the general formula.



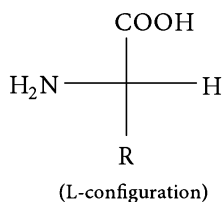
α -Amino acids are the building blocks of proteins. The α -carbon of all amino acids (except glycine) is chiral.

Proteins are made up of α -amino acids combined by peptide linkages. Cells use the different α -amino acids to produce the proteins. *The exact sequence of arrangement of various α -amino acids to form the protein chain is called the primary structure of the protein.*

6.16 Amines, Aminoacids and Peptides

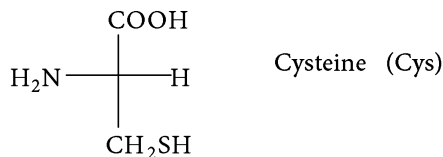
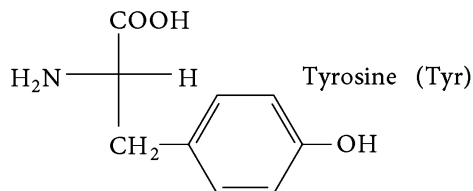
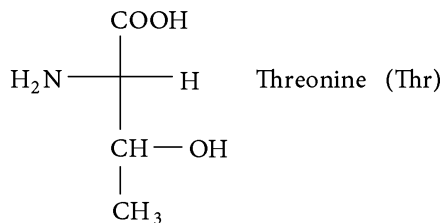
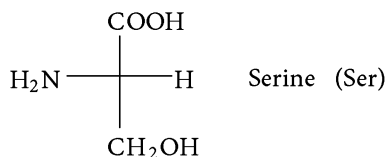
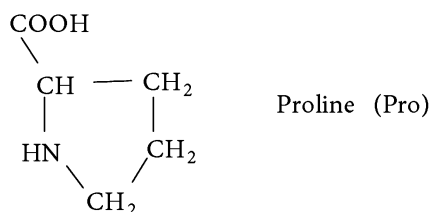
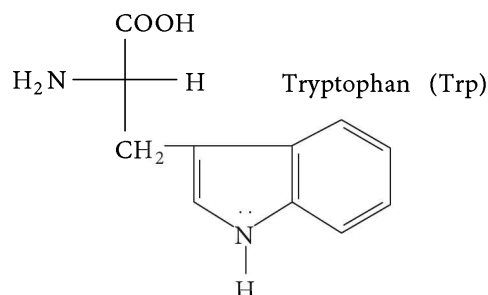
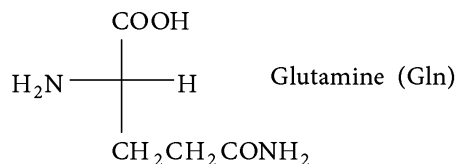
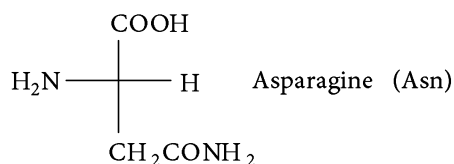
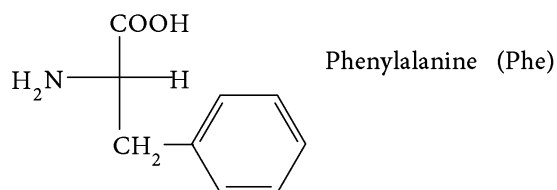
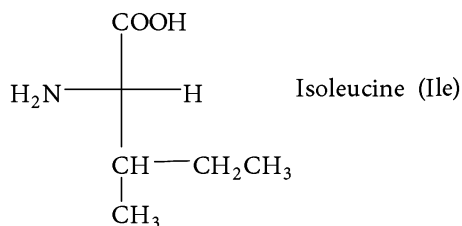
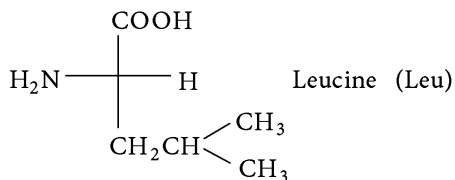
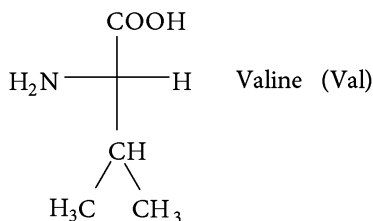
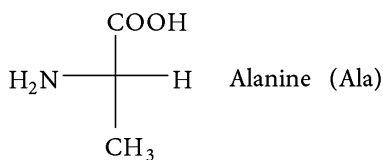
Hydrolysis of proteins either by acid or base gives a mixture of various amino acids. All the α -amino acids that are constituents of proteins have the L-configuration at the α -carbon. The only exception to this is glycine where there is no chiral centre.

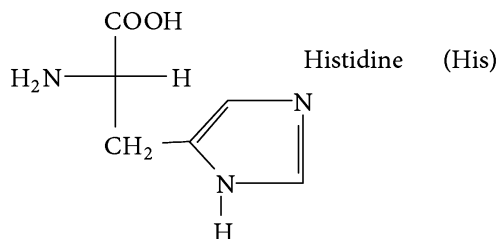
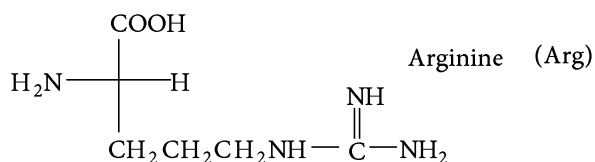
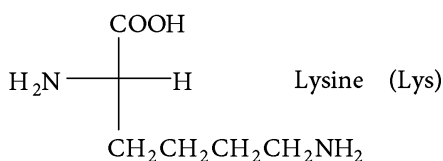
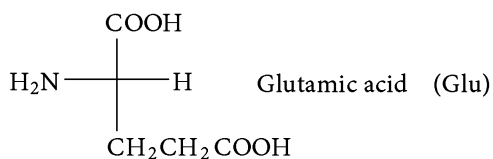
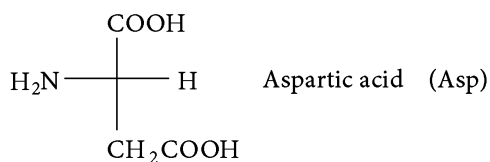
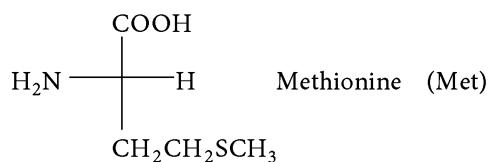
An L-aminoacid is represented by the general formula.



The structures, names and three letter abbreviations of the 20 most commonly occurring amino acids are given below.

$\text{H}_2\text{NCH}_2\text{COOH}$ Glycine (Gly)

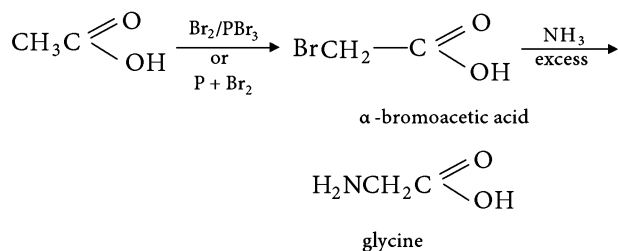




PREPARATION OF AMINO ACIDS

(i) From α -halo acids

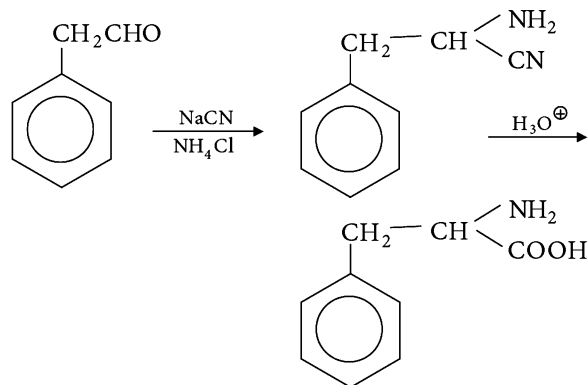
Earlier method involves the conversion of carboxylic acid to α -halo acid by Hell-Volhard-Zelinsky (HVZ) reaction and further treatment with excess NH_3 gives α -amino acid.



(ii) Strecker synthesis

In Strecker synthesis, α -amino acid is prepared from carbonyl compounds. For example, phenyl ethanal on

treatment with sodium or potassium cyanide in the presence of ammonium chloride followed by hydrolysis gives phenyl alanine.

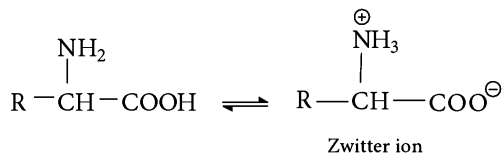


PROPERTIES OF AMINO ACIDS

Amino acids are colourless crystalline solids having high melting points.

Zwitterion structure

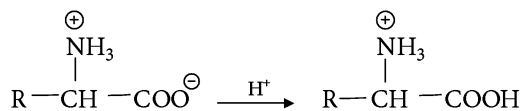
Due to the presence of $-\text{COOH}$ and $-\text{NH}_2$ groups within the same molecule, they neutralize each other and amino acids exist as zwitterions or dipolar ion or inner salt.



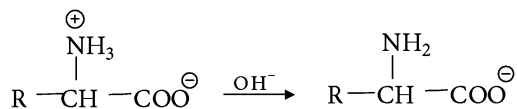
Many properties of amino acids are consistent with this dipolar structure. In zwitterionic form, amino acids show amphoteric behaviour as they react with both acids and bases.

Isoelectric point

In presence of acid (i.e., at low pH), the $-\text{COO}^-$ group of the zwitterion accepts a proton and gets converted into $-\text{COOH}$ group. Thus the zwitterion is converted into a cation.



In presence of a base (i.e., high pH) the $-\text{NH}_3^+$ ion changes to $-\text{NH}_2$ group by losing a proton and this gives a negative ion.

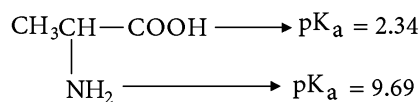


Thus in acidic medium, the amino acid migrates towards the cathode in an electric field and in basic medium it migrates to the anode. For every amino acid, there is an intermediate pH at which it will mainly exist as neutral zwitterion and hence will not migrate to either electrode. This pH is known as the isoelectric point of amino acid. *Thus the pH at which an amino acid shows no tendency to migrate towards cathode or anode when placed in an electric field is known as its isoelectric point.* It is the pH at which the

quantity of negative charge on an amino acid exactly balances the quantity of positive charge. The isoelectric point has a value half way between the pK_{a_1} and pK_{a_2} values for most of the amino acids.

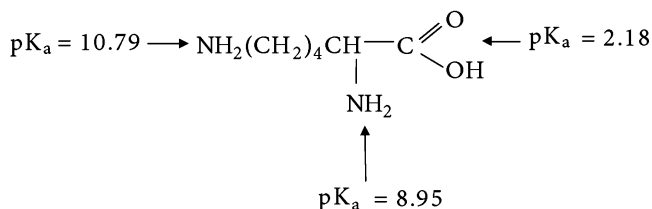
$$\text{Isoelectric point} = \frac{1}{2}(\text{pK}_{a_1} + \text{pK}_{a_2})$$

The isoelectric point of an amino acid like alanine is given by



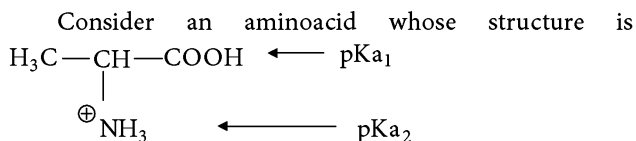
$$\text{Isoelectric point} = \frac{2.34 + 9.69}{2} = 6.02$$

For amino acid like lysine, which has a long alkyl chain containing an amino group, the isoelectric point is the average of the pK_a values of similar ionizing groups.



$$\text{Isoelectric point} = \frac{8.95 + 10.79}{2} = 9.87$$

In the case of glutamic acid, $\text{HOOC}-\text{CH}_2\text{CH}_2-\underset{\text{COOH}}{\overset{\text{NH}_2}{\text{CH}}}$ the isoelectric point is 3.22.



If the pH is less than pK_{a_1} there is no ionization of the acid, the amino acid will exist as $\text{H}_3\text{C}-\underset{\text{NH}_3^+}{\text{CH}}-\text{COOH}$.

If the pH is more than pK_{a_1} but less than pK_{a_2} , then the

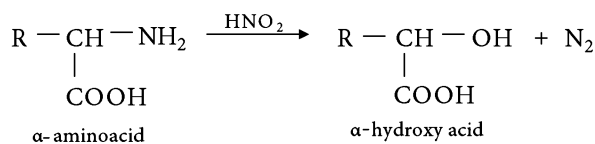
amino acid will exist as, $\text{H}_3\text{C}-\underset{\text{NH}_3^+}{\text{CH}}-\text{C}\begin{smallmatrix} \text{O} \\ // \\ \text{O}^- \end{smallmatrix}$. If the pH

is more than pK_{a_2} , then the amino acid will remain in the

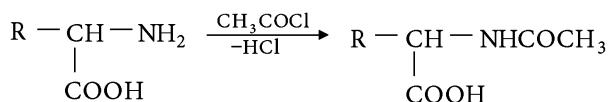
form $\text{H}_3\text{C}-\underset{\text{NH}_2}{\text{CH}}-\text{C}\begin{smallmatrix} \text{O} \\ // \\ \text{O}^- \end{smallmatrix}$

Reactions characteristic of amino group

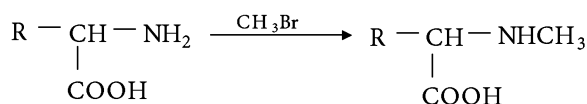
(a) With nitrous acid



(b) Acetylation

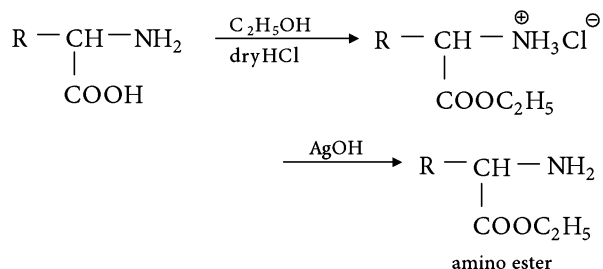


(c) Alkylation

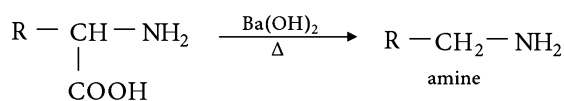


Reactions characteristic of carboxyl group

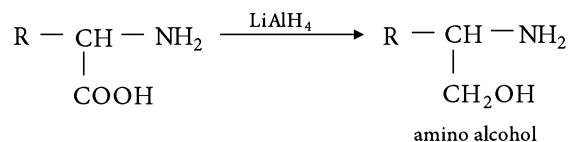
(a) Esterification



(b) Decarboxylation

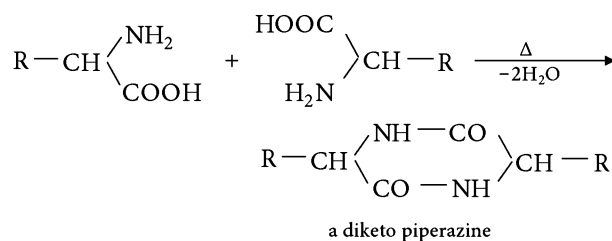


(c) Reduction

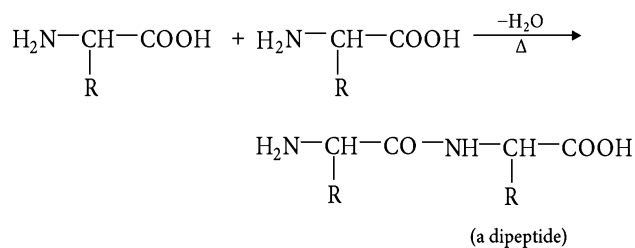


Reactions due to both amino and carboxyl groups

(a) Formation of cyclic amides or 2,5-diketo piperazines

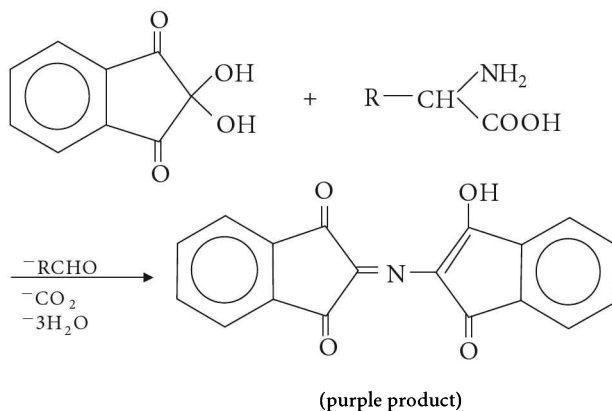


(b) Formation of peptides



(c) Ninhydrin reaction

Ninhydrin (indane-1,2,3-trione hydrate) reacts with amino acids to form a purple coloured product. All amino acids



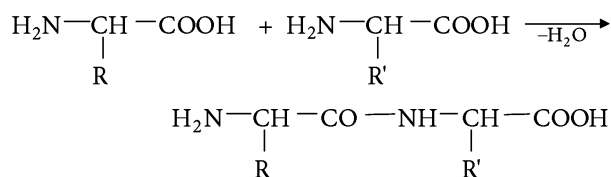
6.20 Amines, Aminoacids and Peptides

(except proline which gives yellow colour) give the same purple coloured product.

This reaction is used in the identification and quantitative estimation of amino acids.

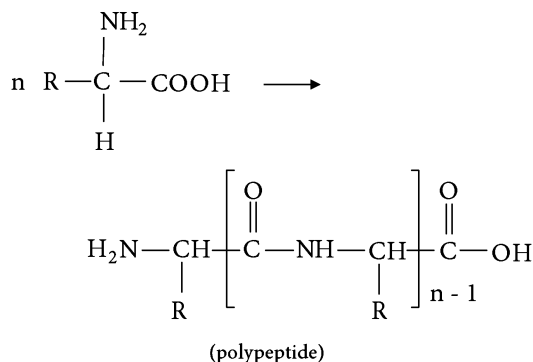
PEPTIDES

Peptides are amides formed by the condensation of amino group of one amino acid molecule with the carboxyl group of another amino acid molecule with the elimination of water molecule.

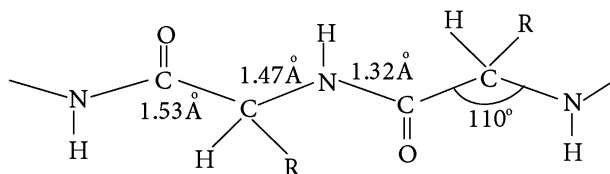


The $\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{NH}- \end{array}$ bond connecting the amino acid molecule in a peptide is called a peptide linkage or peptide bond. Condensation of three amino acid molecules (same or different) forms a tripeptide. Similarly, condensation of a large number of α -amino acids forms a large polyamide molecule called a polypeptide.

The peptide bond, $-\text{CO}-\text{NH}-$ bond, is a covalent linkage that holds the peptide structure together. The atoms in the group, $-\text{CO}-\text{NH}-$, are planar and the 'O' and 'H' are trans. Since the peptide carbon-nitrogen bond length (i.e., C-N of $-\text{CO}-\text{NH}-$) is $1.32\text{\AA}$ and is



shorter than the usual carbon-nitrogen single bond length ($\sim 1.47\text{\AA}$), this bond has some double bond character.



Peptides are the constituent units of proteins. Several enzymes are employed to degrade the proteins into peptide fragments.

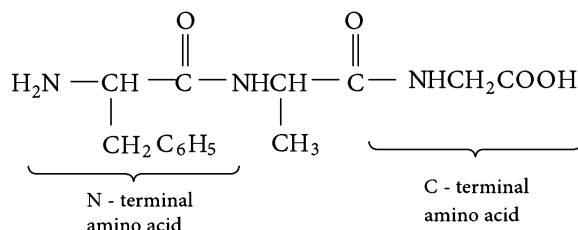
AMINO ACID ANALYSIS

The primary structure of a peptide or protein is the sequence of arrangement of component amino acids in the chain. Hydrolysis of most of the peptides with hot dil. HCl releases the free amino acids, which are then further analyzed.

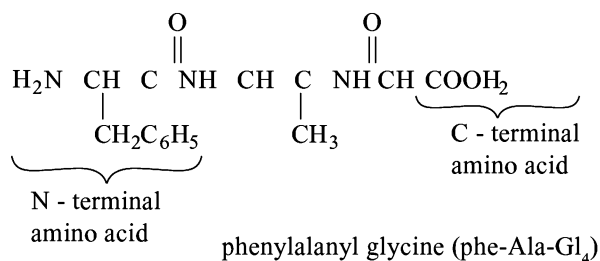
Terminal group analysis

When the structure of the peptide is determined, the usual practice is to write the amino acid with the free amino group (the N-terminal) to the left hand side and the unit with the free carboxy group (the C-terminal) to the right hand side.

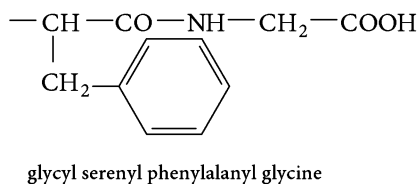
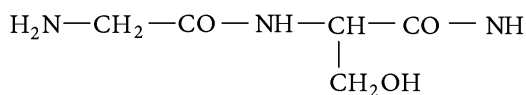
A peptide is named as a derivative of the C-terminal group. Other amino acids in the series are listed as substituents in a sequence beginning with N-terminal unit. For example, a tripeptide can be named as



Phenylalanyl alanyl glycine (Phe-Ala-Gly)



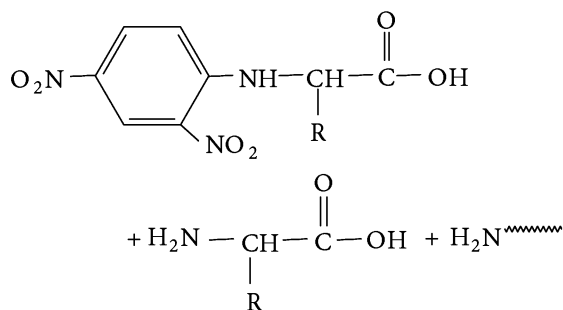
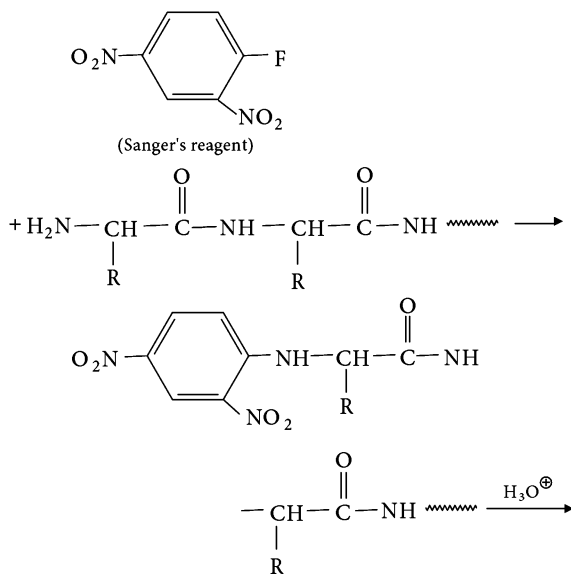
The structure of a peptide where the sequencing is Gly-Ser-Phe-Gly will be



N-terminal analysis

Sanger's method

Sanger's reagent is 2,4-dinitro fluorobenzene. In this method, the polypeptide is treated with Sanger's reagent in presence NaHCO_3 . The N-terminal amino group of the peptide gets substituted for the fluorine atom, to give 2,4-dinitrophenyl (DNP) derivative. This is then completely hydrolyzed to give a DNP-amino acid and a mixture of free amino acids.



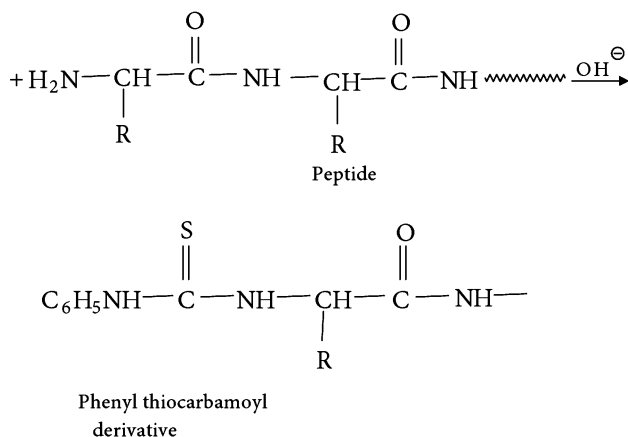
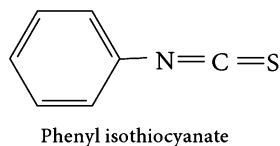
By identifying the DNP-amino acid, the N-terminal amino acid of the polypeptide or protein can be determined.

Edman degradation

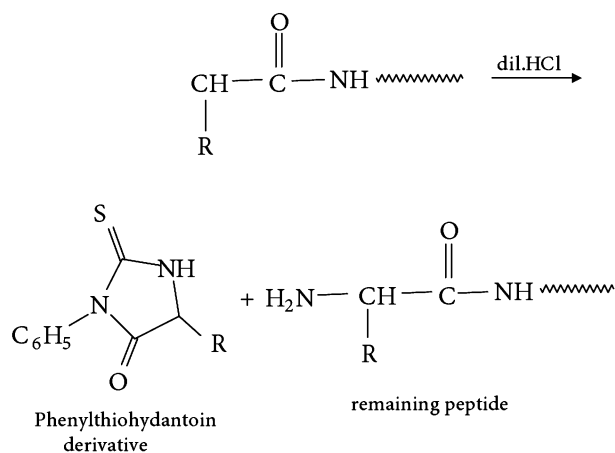
In Edman degradation procedure, the peptide is reacted with phenyl isothiocyanate ($\text{C}_6\text{H}_5\text{N}=\text{C}=\text{S}$). Nucleophilic addition by the N-terminal amino group results in phenyl thiocarbamoyl derivative of the peptide.

Treatment of this derivative with HCl results in the cleavage to produce a phenylthiohydantoin derivative and the N-terminal amino acid is separated from the remaining portion of the peptide. This procedure allows the identification of the N-terminal group while leaving the remaining part of the peptide chain intact.

This method can be repeated again and again until each amino acid, in sequence, is identified.



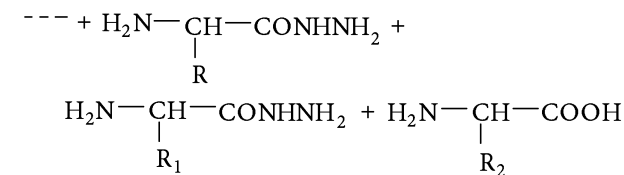
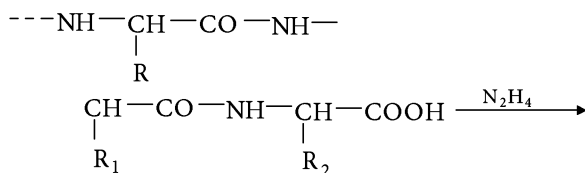
6.22 Amines, Aminoacids and Peptides



C-terminal analysis

Hydrazinolysis

The peptide is heated with anhydrous hydrazine at 100°C. It converts all amino acid residues, except the C-terminal one into amino acid hydrazides.



Cleavage with carboxypeptidase

The C-terminal is removed selectively by the enzyme, carboxypeptidase (obtained from pancreas), which cleaves only the peptide linkage adjacent to the free alpha-carboxyl group in the peptide chain. The analysis can be repeated on the shortened peptide and the new C-terminal residue identified, and so on.

Amino acid sequence

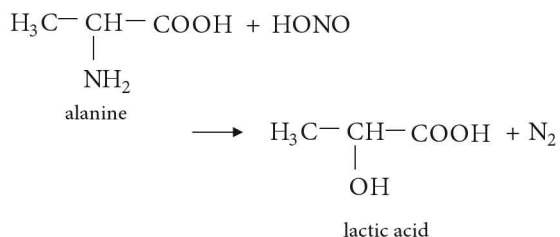
Once when the C-terminal and N-terminal groups are identified, the sequence of amino acids in the peptide chain has to be determined. Edman degradation is used for short peptide chains. Large peptides are broken to smaller units for identification and then the sequence in each of these units is used to arrive at the overall structure. Partial hydrolysis by acid or preferably enzymes is generally used to cleave the large peptide units to smaller units.

CONCEPT STRANDS

Concept Strand 6

Which amino acid reacts with nitrous acid to give lactic acid?

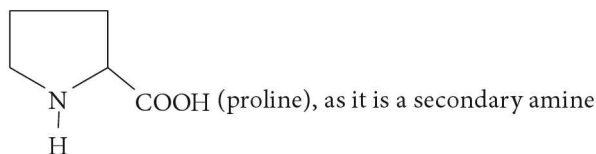
Solution



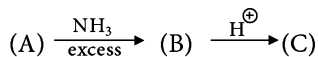
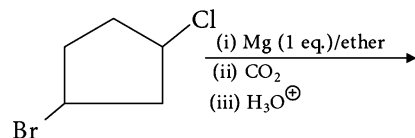
Concept Strand 7

Name the amino acid that does not liberate nitrogen on treatment with nitrous acid.

Solution

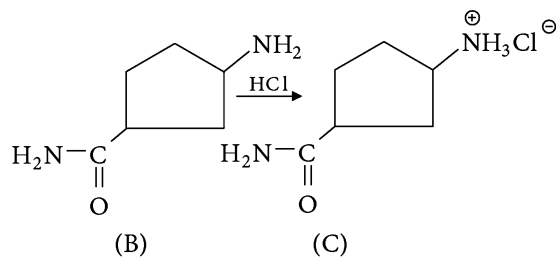
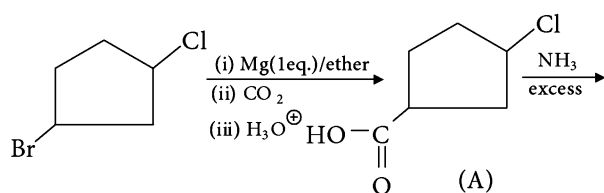


Concept Strand 8



Identify (A) to (C).

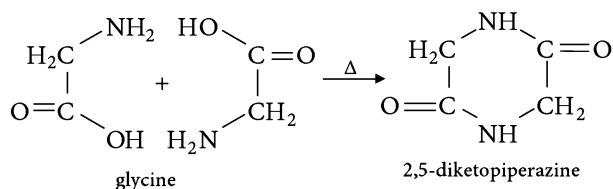
Solution



Concept Strand 9

What happens when glycine is heated?

Solution



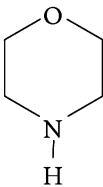
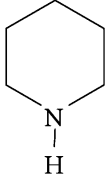
SUMMARY

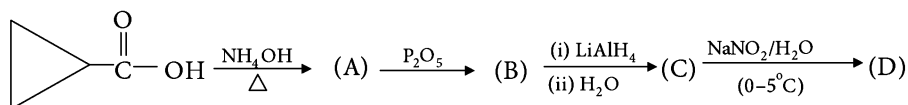
Classification of amines	Primary, secondary and tertiary amines. Examples for each class. Quaternary ammonium salts.
Preparation of amines	Hoffmann's method, ammonolysis of alcohols, reduction of cyanides and isocyanides, reduction of amides, hydrolysis of isocyanides, reduction of nitrocompounds, reduction products of nitrobenzene, Hoffmann's bromamide reaction and its mechanism, Gabriel's phthalimide synthesis.
Basicity of amines	Basicity of aliphatic amines, basicity of aromatic amines and substituted aromatic amines, ortho effect, relative strength of different amines.
Chemical properties of amines	Reaction with nitrous acid, acylation reaction, carbylamine reaction, Hoffmann's mustard oil reaction. Reaction of the aromatic ring in aromatic amines-halogenation and nitration. Hinsberg's test.
Diazonium salts	Preparation of diazonium salts, azocoupling reaction, Sandmeyer reaction, Gattermann reaction, Balz-Schiemann reaction, reaction with KI, replacement of diazonium group with -CN and -OH. Deamination, Gomberg reaction, replacement by -NO ₂ group, reduction.
Amino acids	Importance of α-amino acids Structure and names of α-amino acids which are constituents of proteins, preparation of amino acids.
Properties of amino acids	Reactions due to -NH ₂ group, reactions due to -COOH group, Zwitterion formation, isoelectric point.
Peptides	Formation of peptides, peptide bond.
Amino acid analysis of peptides	N-terminal analysis-Sanger's method and Edman degradation. C-terminal analysis-hydrazinolysis and cleavage with carboxypeptidase.

TOPIC GRIP

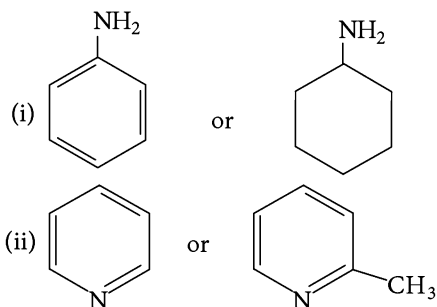


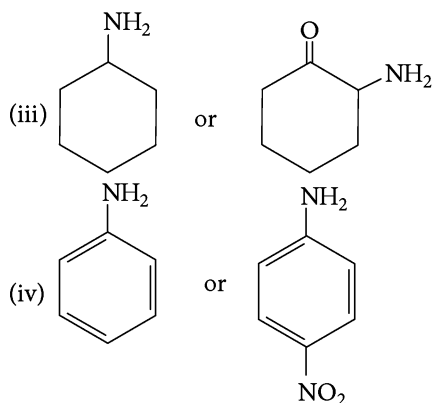
Subjective Questions

- Why aromatic primary amines cannot be prepared by Gabriel's phthalimide synthesis?
- Account for the following
 - Methylamine in water reacts with ferric chloride to give a precipitate of hydrated ferric oxide.
 - Aniline does not undergo Friedel-Crafts reaction.
 - Diazonium salts of aromatic primary amines are more stable than those of aliphatic amines.
- Write equations for the various steps involved in the following conversions
 - Nitrobenzene to benzoic acid
 - Benzene to m - bromophenol
 - Ethanamine to methanamine
 - Nitromethane to dimethylamine
- What are essential and non-essential amino acids?
- Account for the observation that 2,6,N,N-tetramethylaniline is a stronger base than N,N-dimethyl aniline.
- Which among the pairs is a stronger base?
 - $[(\text{CH}_3)_2\text{CH}]_2\text{NH}$ (or) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_3$
 - 
 (or)
 
 - $\text{ClCH}_2 - \text{CH}_2\text{NH}_2$ (or) $\text{H}_3\text{CCH}_2\text{NH}_2$
- Identify the lettered compounds (A)-(D) in the following reactions.

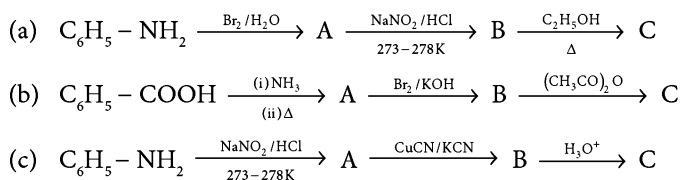


- Identify the stronger base in each of the following pairs.





9. Identify the products A, B and C in each of the following.



10. (i) How is

- (a) $\text{C}_6\text{H}_5\text{CHO}$ converted to $\text{C}_6\text{H}_5\text{CH}_2\text{NHC}_6\text{H}_5$?
 (b) $\text{CH}_3\text{CH}_2\text{CHO}$ converted to $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$?



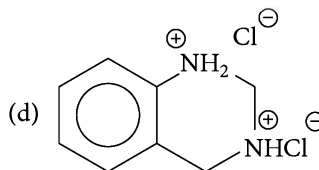
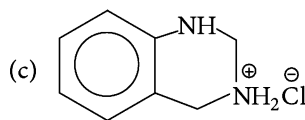
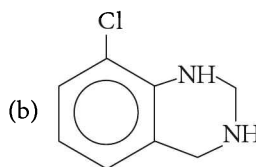
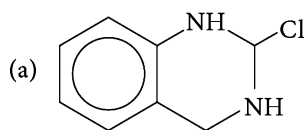
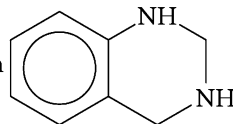
Straight Objective Type Questions

Directions: This section contains multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

11. Which of the following compounds will not give a primary amine when treated with LiAlH_4 ?

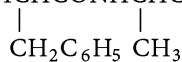
- (a) CH_3NC (b) $\text{CH}_3\text{CH}_2\text{CONH}_2$
 (c) $\text{C}_6\text{H}_5\text{CN}$ (d) $\text{CH}_3\text{CH}_2\text{NO}_2$

12. The major product obtained when one equivalent of HCl is treated with

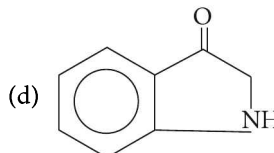
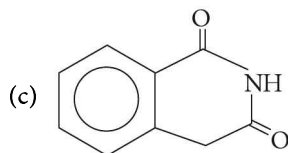
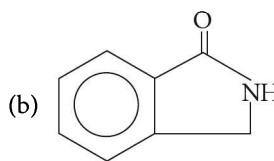
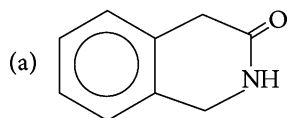
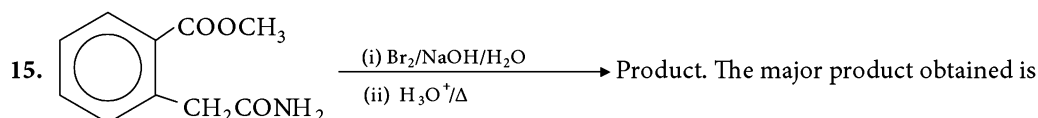
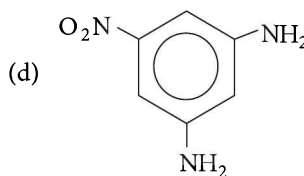
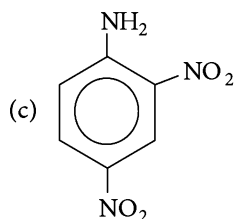
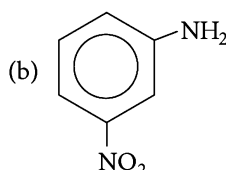
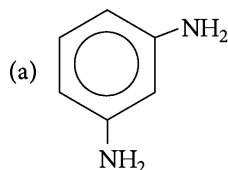
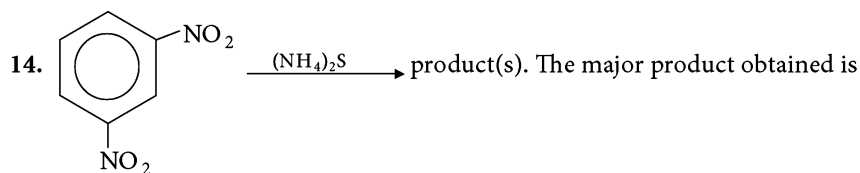


6.26 Amines, Aminoacids and Peptides

13. The name of the tripeptide $\text{H}_2\text{NCH}_2\text{CONHCHCONHCHCOOH}$ is



- (a) glycyl phenylalanyl alanine (b) alanyl phenylalanyl glycine
(c) alanyl glycyl phenyl alanine (d) phenylalanyl glycyl alanine



Assertion–Reason Type Questions

Directions: Each question contains Statement-1 and Statement-2 and has the following 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

16. Statement 1

Nitration of aniline is generally carried out after protecting amino group by acetylation.
and

Statement 2

Acetylation decreases the activating effect of amino group.

17. Statement 1

Anilinium ion ($\text{C}_6\text{H}_5 - \text{N}^+\text{H}_3$) is more acidic than ammonium ion (NH_4^+).
and

Statement 2

Anilinium ion is stabilized more by resonance than aniline.

18. Statement 1

Pyridine is less basic than piperidine.
and

Statement 2

The lone pair of electrons is involved in resonance to give aromatic stability to pyridine.

19. Statement 1

Benzene diazonium chloride undergoes coupling with N, N – dimethyl aniline to form an azodye, but it does not couple with 2, 6 – dimethyl – N, N – dimethyl aniline.
and

Statement 2

The para position of 2, 6 – dimethyl – N, N – dimethyl aniline is not sufficiently activated for coupling reaction.

20. Statement 1

Proline does not liberate nitrogen gas when treated with nitrous acid.
and

Statement 2

Proline does not contain a primary amine group.



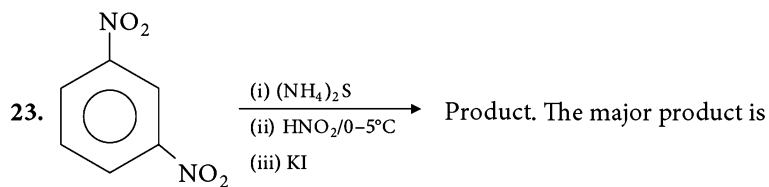
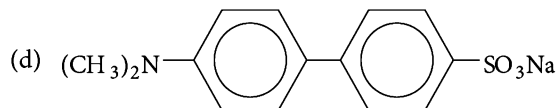
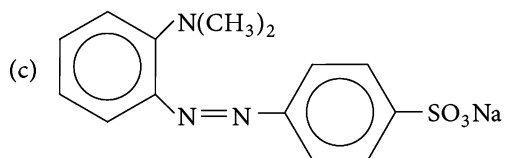
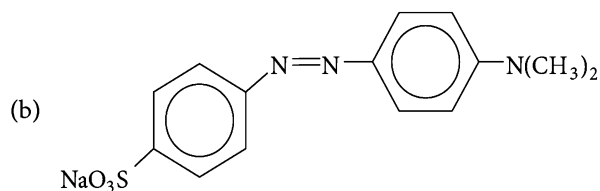
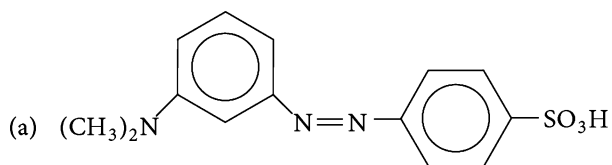
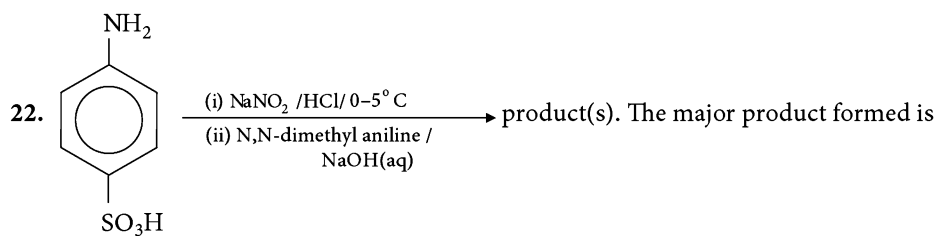
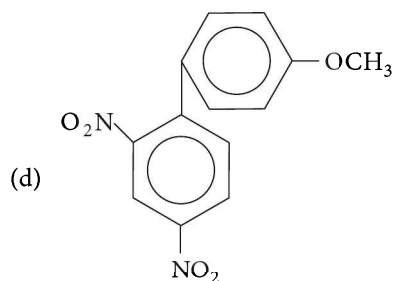
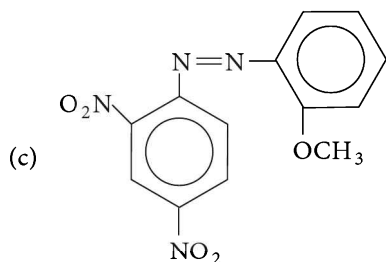
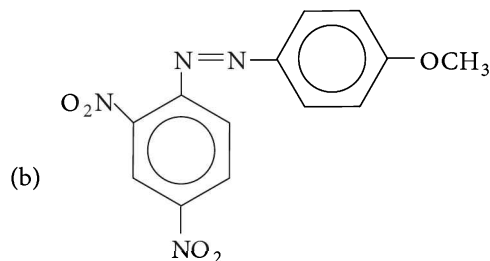
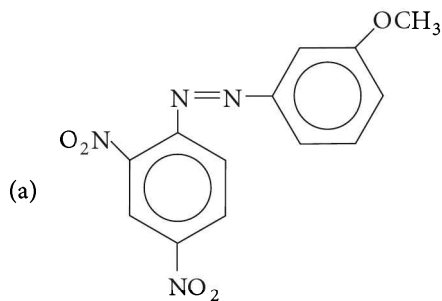
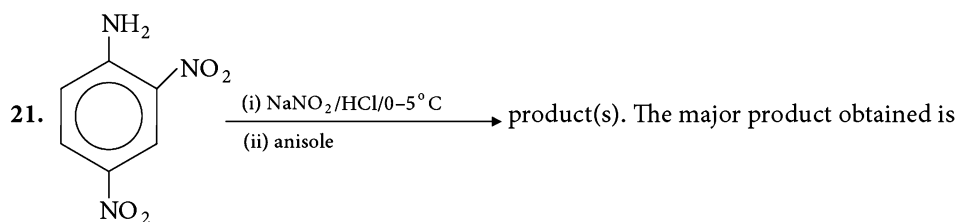
Linked Comprehension Type Questions

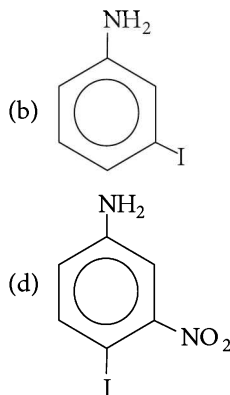
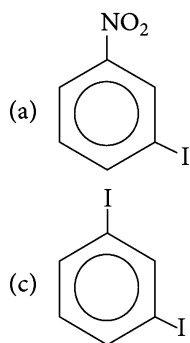
Directions: This section contains 2 paragraphs. Based upon the paragraph, 3 multiple choice questions have to be answered. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

Passage I

Arene diazonium salts are more stable than alkyl diazonium salts, as the positive charge is dispersed on the benzene ring in the former. They can undergo a variety of reactions where the diazo group can be replaced by $-\text{H}$, $-\text{OH}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{F}$, $-\text{CN}$ etc., by reaction with suitable reagents. They also undergo coupling reactions, where the diazo group is retained. Electron withdrawing groups on the diazonium salts increase the reactivity of coupling reactions.

6.28 Amines, Aminoacids and Peptides



**Passage II**

α -amino acids are the building blocks of proteins. All α -amino acids, except glycine, are chiral and have L-configuration. They exist as Zwitterions each of which has a specific isoelectric point. Amino acids join together to form peptides (di, tri etc) and polypeptides. Each polypeptide has a free amino group and a free carboxyl group, called the N-terminal and C-terminal, respectively.

24. Which of the following reagents is used to identify the C-terminal amino acid?

- (a) 2,4-dinitrofluorobenzene (b) Dansyl chloride
(c) hydrazine (d) phenyl isocyanate

25. In L-glutamic acid, $\text{H}_2\text{N}-\underset{\text{CH}_2\text{CH}_2\text{COOH}}{\text{CH}}-\text{COOH}$, the carboxyl groups have a pK_a 's of 2.13 and 4.31, whereas the ammonium

ion has a pK_a of 9.76. The isoelectric point of the amino acid is

- (a) 5.4 (b) 5.95
(c) 3.22 (d) 7.04

26. When three amino acids join to form a tripeptide, such that no amino acid is used more than once, the number of tripeptide(s) is/are

- (a) 3 (b) 6
(c) 9 (d) 12

**Multiple Correct Objective Type Questions**

Directions: Each question in this section has four suggested answers of which ONE OR MORE answers will be correct.

27. The conversion of ethane nitrile to ethanamine can be carried out by using

- (a) LiAlH_4 (b) DIBAL - H
(c) H_2/Pd (d) $\text{Na}/\text{C}_2\text{H}_5\text{OH}$

28. Which of the following compounds are more basic than aniline?

- (a) p - chloroaniline (b) o - toluidine
(c) benzylamine (d) p-anisidine

29. The amino acids containing sulphur are

- (a) leucine (b) cysteine (c) methionine (d) tryptophan

**Matrix-Match Type Question**

Directions: Match the elements of Column I to elements of Column II. There can be single or multiple matches.

30.

Column I**(Amines)**

- (a) $\text{C}_6\text{H}_5\text{NH}_2$
- (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$
- (c) $\text{C}_2\text{H}_5\text{NHC}_2\text{H}_5$
- (d) $\text{CH}_3\text{NHC}_2\text{H}_5$

Column II**(Method of preparation)**

- (p) Hofmann's bromamide reaction
- (q) Reduction of amides
- (r) Reduction of cyanides
- (s) Reduction of isocyanides
- (t) Gabriel's phthalimide synthesis

IIT ASSIGNMENT EXERCISE



Straight Objective Type Questions

Directions: This section contains multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

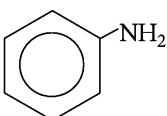
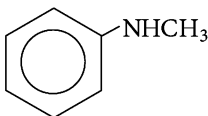
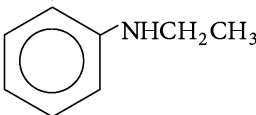
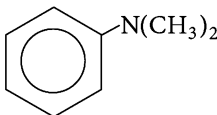
31. The higher boiling points of amines is due to

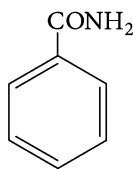
- (a) intermolecular hydrogen bonding (b) +I effect of alkyl groups
(c) basic nature of amines (d) solubility in water

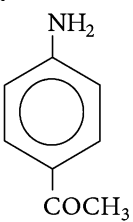
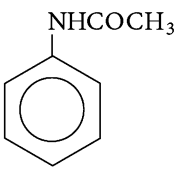
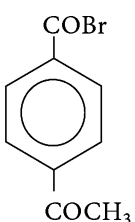
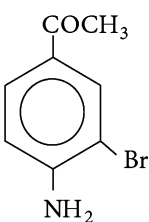
32. $\text{C}_6\text{H}_5\text{NH}_2 + \text{C}_6\text{H}_5\text{COCl} \rightarrow \text{C}_6\text{H}_5\text{NHCOC}_6\text{H}_5 + \text{HCl}$. This reaction is called

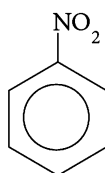
- (a) Schotten Baumann reaction (b) Perkin reaction
(c) Schmidt reaction (d) Claisen reaction

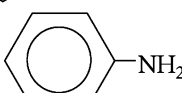
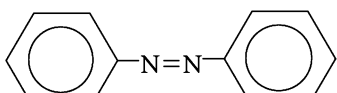
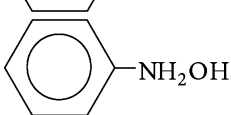
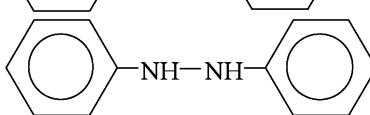
33. Which of the following will form a para nitroso derivative with nitrous acid?

- (a)  (b) 
(c)  (d) 

34.  $\xrightarrow{\text{Br}_2/\text{NaOH}}$ (A) $\xrightarrow{\text{CH}_3\text{COCl}/\text{reflux}}$ (B). Identify the major product (B).

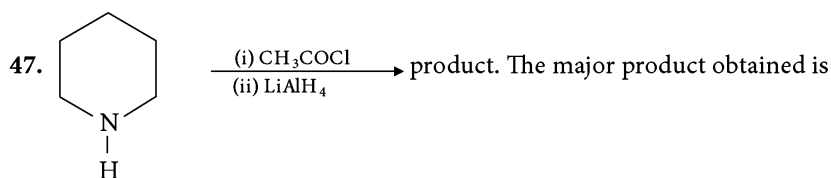
- (a)  (b) 
(c)  (d) 

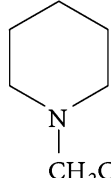
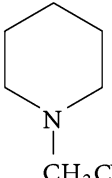
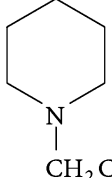
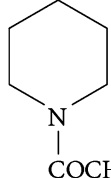
35.  $\xrightarrow[\text{ether}]{\text{LiAlH}_4}$ (X). The compound (X) is

- (a)  (b) 
(c)  (d) 

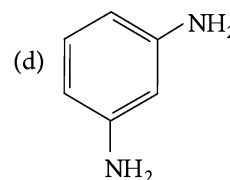
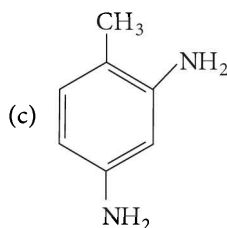
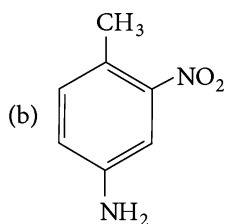
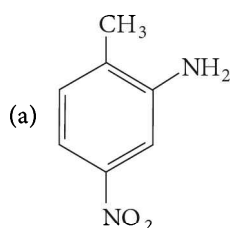
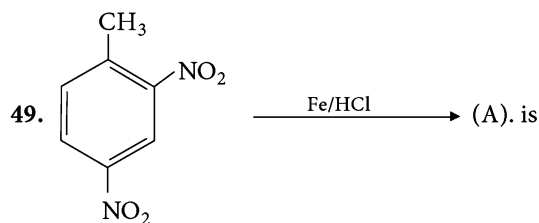
6.32 Amines, Aminoacids and Peptides

36. Para toluidine is treated with HNO_2 at ice cold conditions and then boiled with water. The final product obtained is
 (a) anthranilic acid (b) p-cresol
 (c) toluic acid (d) phenol
37. Ammonium salt of an organic acid (A) is heated to give (B). (B) is treated with bromine and alkali to give (C). (C) with nitrous acid gives ethanol. (A) is
 (a) ethanoic acid (b) methanoic acid (c) propanoic acid (d) propanone
38. 1° , 2° and 3° amines can be separated using
 (a) $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ (b) KMnO_4 (c) NaOH (d) HCl
39. Exhaustive methylation followed by Hoffmann's elimination of n-propyl amine gives
 (a) ethene (b) propene
 (c) N-methylaminopropane (d) butene
40. The hybridization of nitrogen in aniline is
 (a) sp (b) sp^2 (c) sp^3 (d) sp^3d
41. Which of the following reductions does not give an amine?
 (a) $\text{R}-\text{NO}_2 \xrightarrow[\text{Raney Ni}]{\text{H}_2}$ (b) $\text{R}-\text{NO}_2 \xrightarrow[\text{ether}]{\text{LiAlH}_4}$
 (c) $\text{R}-\text{NO}_2 \xrightarrow{\text{Sn/HCl}}$ (d) $\text{R}-\text{NO}_2 \xrightarrow[\Delta]{\text{Zn/NH}_4\text{Cl}}$
42. When RNH_2 is warmed with CS_2 in presence of HgCl_2 , RNCS is formed. This is called
 (a) Hoffmann exhaustive methylation reaction (b) Hoffmann degradation reaction
 (c) Hoffmann carbylamine reaction (d) Hoffmann mustard oil reaction
43. Which of the following can be used to get a diazonium fluoroborate?
 (a) p-toluidine (b) Glycine
 (c) Benzylamine (d) Cyclohexylamine
44. Gabriel phthalimide synthesis is used for the preparation of
 (a) primary amines (b) secondary amines
 (c) α -amino acids (d) both (a) and (c)
45. The structural feature which distinguishes proline from other amino acids is that
 (a) it is optically inactive (b) it is a secondary amine
 (c) it contains two carboxylic acid groups (d) it contains two amino groups
46. When phenyl alanine is treated with nitrous acid, the product obtained is
 (a) 1-amino-2-phenyl-ethanol (b) 3-hydroxy-2-phenyl-propanoic acid
 (c) 2-amino-1-phenyl-ethanol (d) 2-hydroxy-3-phenyl-propanoic acid

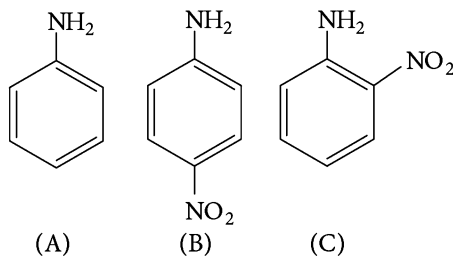


- (a)  (b)  (c)  (d) 

48. For an amino acid $\text{R}-\text{CH} \begin{matrix} \text{NH}_2 \\ \text{COOH} \end{matrix}$, R is an alkyl group. It is made into a solution with water. To the solution a few drops of dil. HCl are added and the solution is electrolysed. Which of the following would happen?
- (a) The amino acid becomes an anion. (b) The protonated amino acid moves to the cathode.
 (c) The protonated amino acid moves to the anode. (d) The amino acid decomposes.

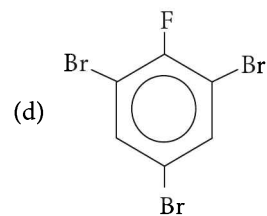
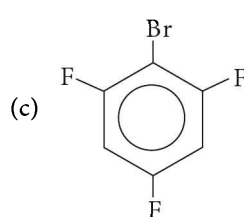
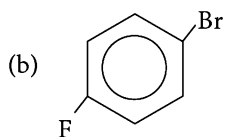
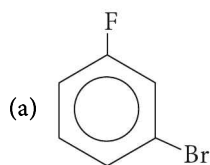
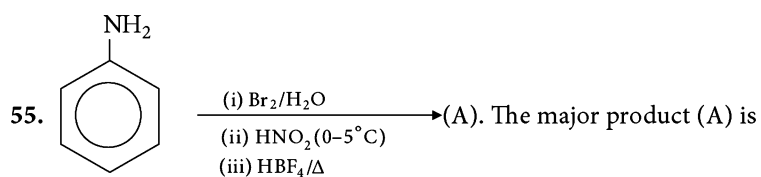
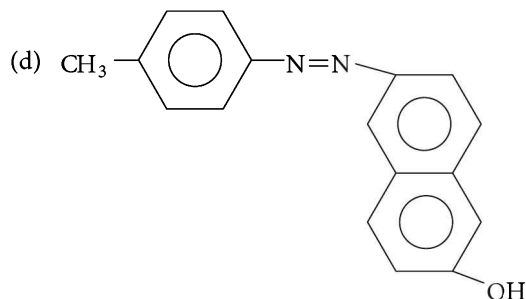
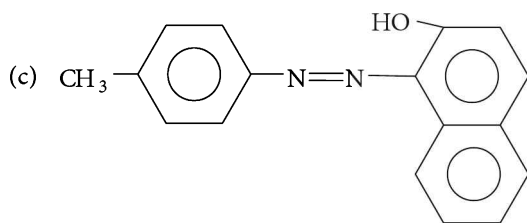
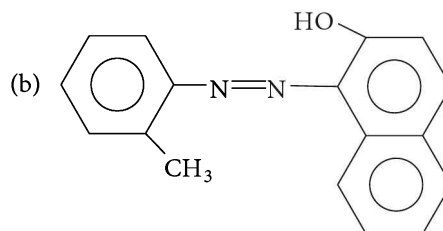
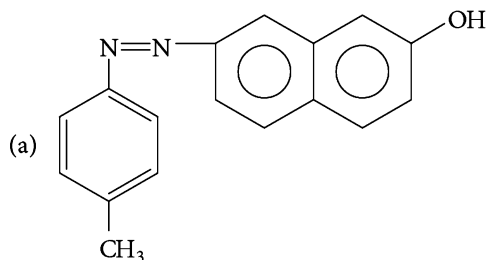
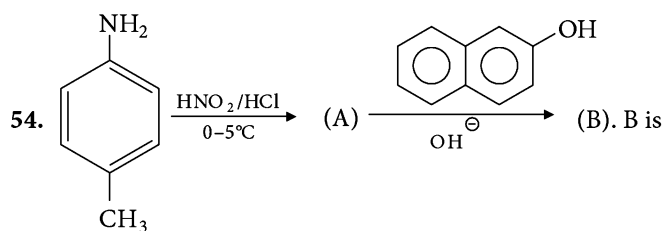


50. Aniline can be prepared from nitrobenzene by treating it with Zn and conc. HCl. If an alkali like NaOH is used instead of conc. HCl, azobenzene is formed. How can aniline be prepared after this stage?
- (a) oxidizing with Caro's acid (b) Reduction under acidic conditions
 (c) Reduction with HI and red phosphorus (d) Heating the mixture.
51. A nitrogen compound containing four carbon atoms dissolves in water on adding dil. HCl. It forms a coloured compound with HNO_2 . If nitrogen does not show chiral properties, the compound may be
- (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ (b) $(\text{CH}_3)_2\text{CHCN}$
 (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NHCH}_3$ (d) $\text{CH}_3\text{CH}_2\text{NHCH}_2\text{CH}_3$
52. The order of basicity decreases with decrease in alkylation in the gas phase. This trend is changed in aqueous medium. The appropriate reason for this change is
- (a) the electron releasing effect of alkyl group.
 (b) difference in behaviour of alkyl group in aqueous phase.
 (c) ammonium ion formed in tertiary amine does not have effective hydrogen bonding.
 (d) alkyl group stabilises only the alkyl ammonium ion.
53. Arrange the following in the increasing order of basicity



- (a) (A) < (C) < (B) (b) (C) < (B) < (A) (c) (B) < (C) < (A) (d) (B) < (A) < (C)

6.34 Amines, Aminoacids and Peptides



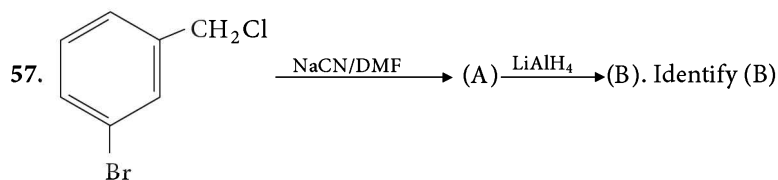
56. Sanger's reagent is used to identify

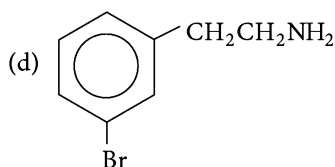
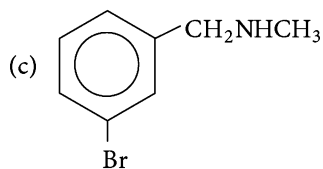
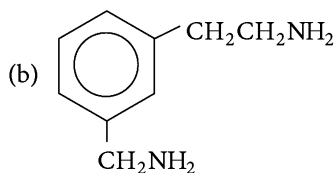
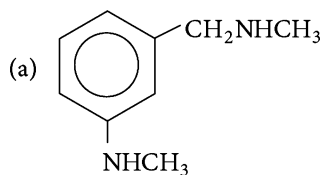
(a) C-terminal of a peptide chain

(b) N-terminal of a peptide chain

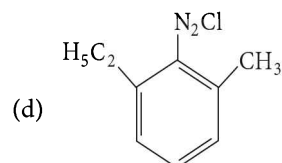
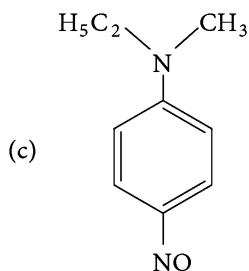
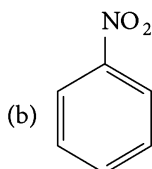
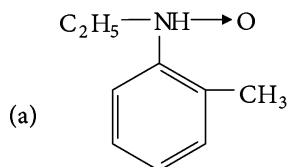
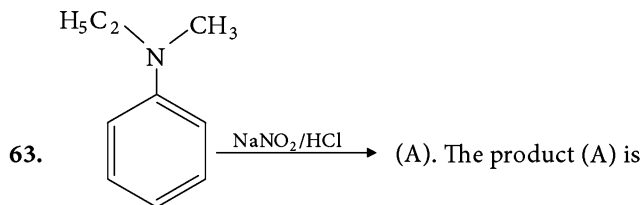
(c) number of amino acids in a peptide chain

(d) side chain of amino acids

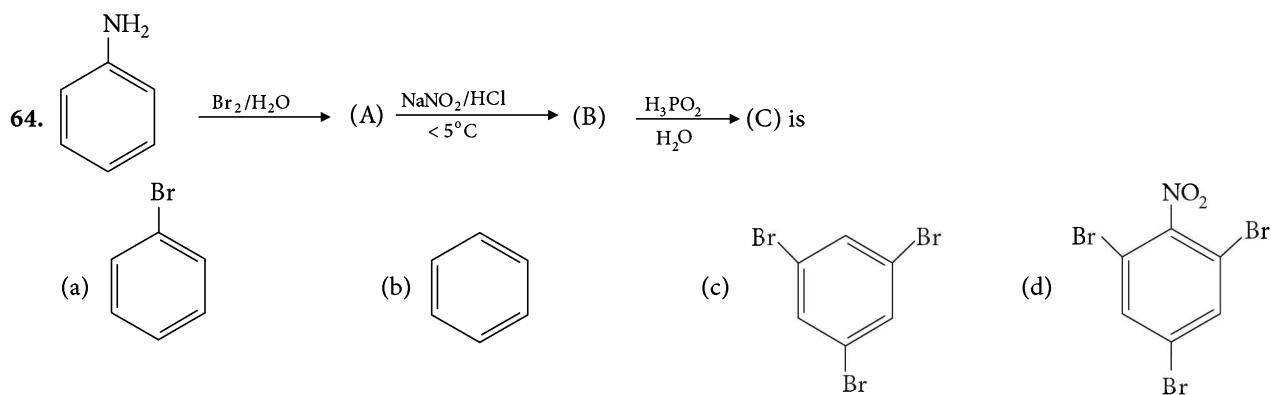




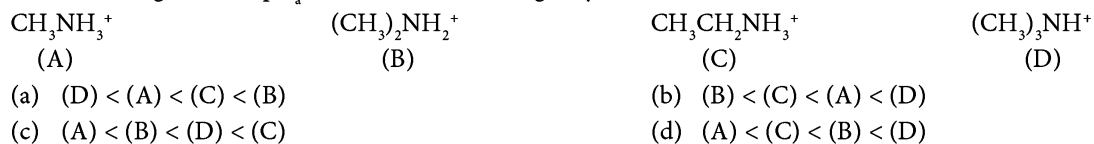
58. Which of the following sequence is best suited to convert benzene to 3-chloro aniline?
- nitration, reduction, chlorination
 - chlorination, nitration, reduction
 - nitration, chlorination, reduction
 - nitration, reduction, acetylation, chlorination, hydrolysis
59. The reaction used to test primary amines is
- Lucas reaction
 - Victor Meyer's test
 - carbylamine reaction
 - Gattermann reaction
60. In amino acid, if a proton migrates from carboxyl group to amino group, the product is called
- dipolar ion
 - Zwitterion
 - internal salt
 - all the above
61. Sandmeyer reaction, is a type of
- unimolecular nucleophilic substitution reaction
 - unimolecular electrophilic substitution reaction
 - bimolecular nucleophilic substitution reaction
 - free radical reaction
62. A compound (X) of formula C_3H_9N was treated with chloroform and alcoholic KOH. The organic product formed was reduced to give a secondary amine. Identify the true statement regarding (X)
- It exists in only one form which is optically inactive.
 - It exists in two isomeric forms and both the forms are optically inactive.
 - It exists in two forms and only one form shows optical activity.
 - It exists in two forms and both forms exhibit optical isomerism.



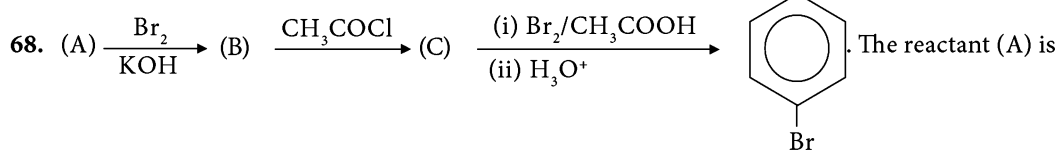
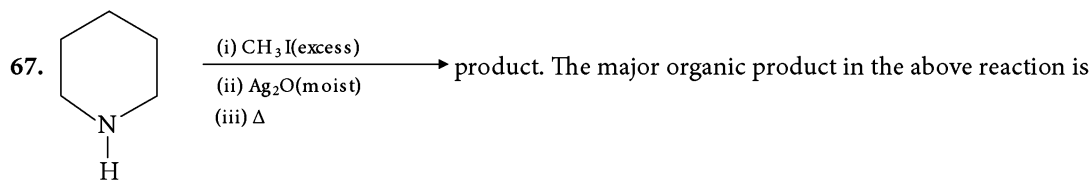
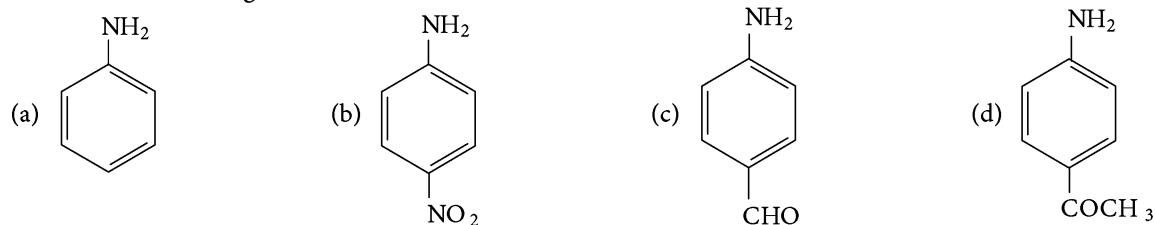
6.36 Amines, Aminoacids and Peptides

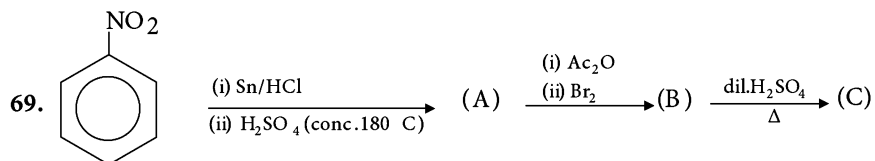
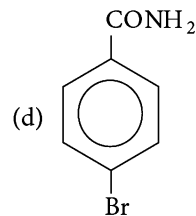
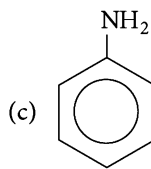
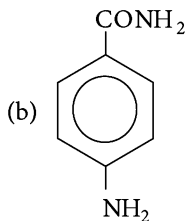
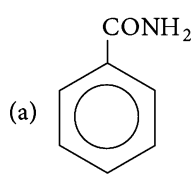


65. The increasing order of pK_a values of the following alkylammonium ions would be

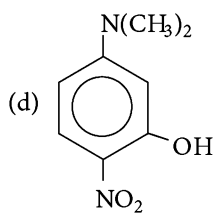
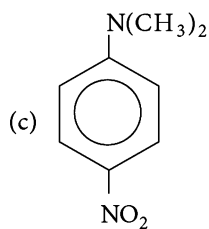
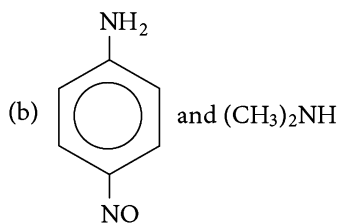
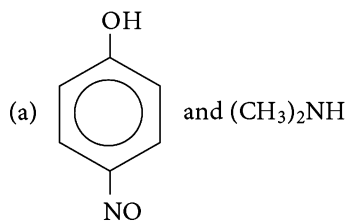
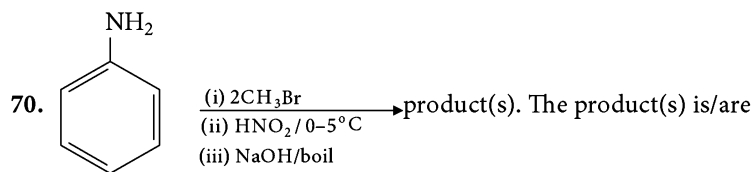
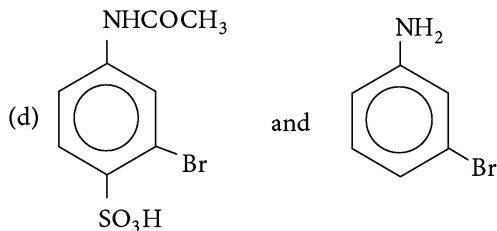
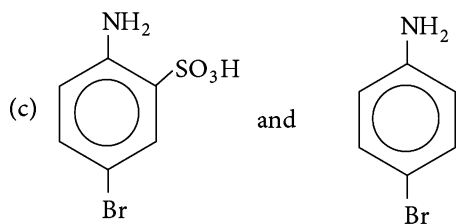
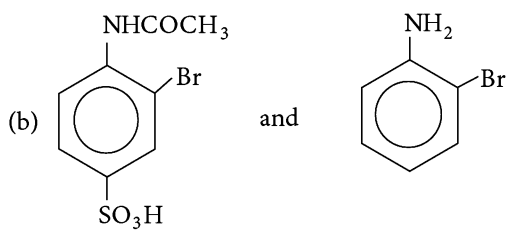
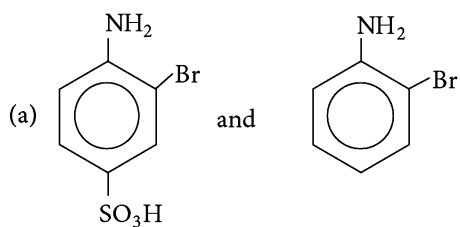


66. Which of the following is most basic?

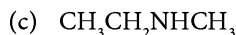
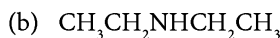
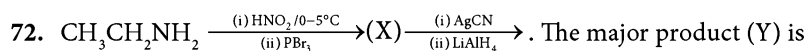
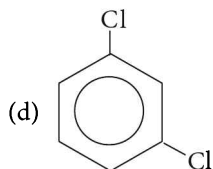
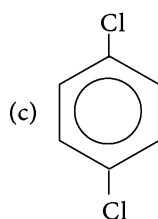
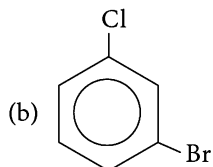
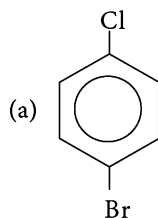
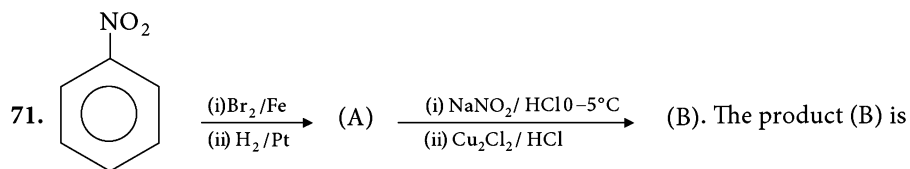




(B) and (C) respectively, are



6.38 Amines, Aminoacids and Peptides



73. Reaction of glycine with NaNO_2 and HCl gives

(a) acetic acid

(b) glycolic acid

(c) oxalic acid

(d) nitroacetic acid

74. An amide having the molecular formula $\text{C}_3\text{H}_7\text{NO}$ on hydrolysis gives an acid (A) and an amine (B). The acid (A) gives silver mirror when warmed with Tollens' reagent and the amine (B) gives foul smelling isocyanide when warmed with chloroform and alcoholic KOH . The amide is

(a) N-methyl acetamide

(b) propionamide

(c) N-ethyl formamide

(d) N,N-dimethyl formamide

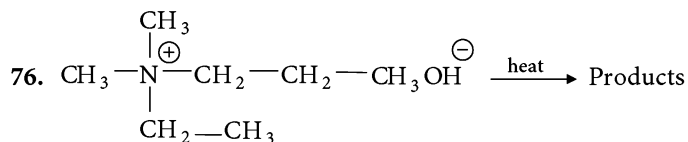
75. Which of the following compounds react with aldehyde to form Schiff's base?

(a) 1° amines

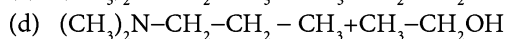
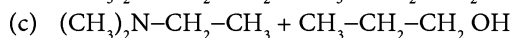
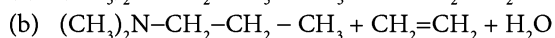
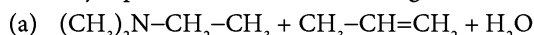
(b) 2° amines

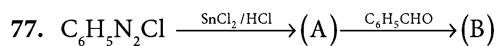
(c) 3° amines

(d) amides

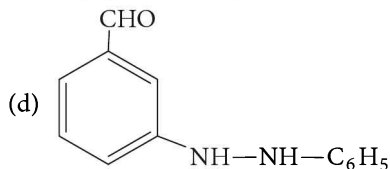
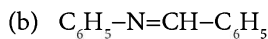
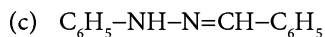
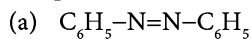


The major products formed on heating the above quaternary ammonium hydroxide are

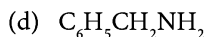
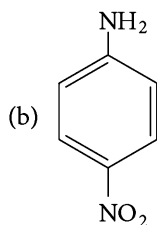
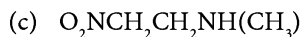
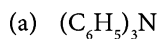




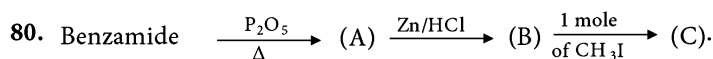
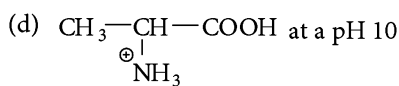
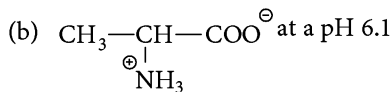
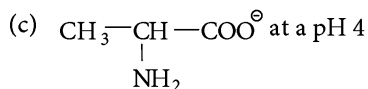
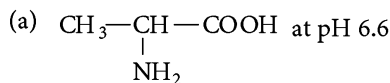
The product (B) in the above sequence of reaction is



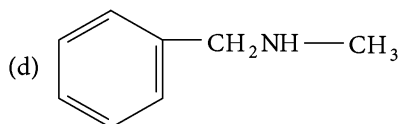
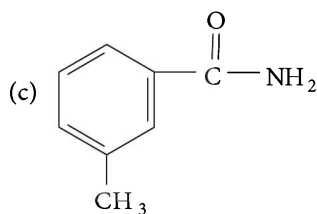
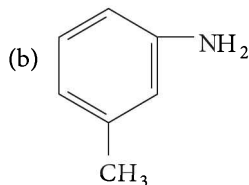
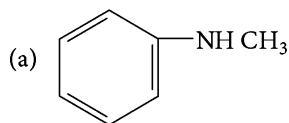
78. The weakest base among the following is



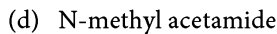
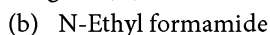
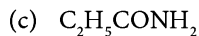
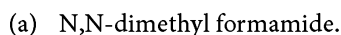
79. The correct representation of alanine is



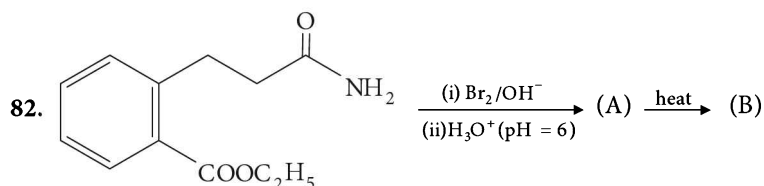
The structure of (C) is



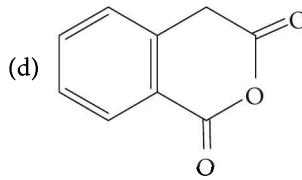
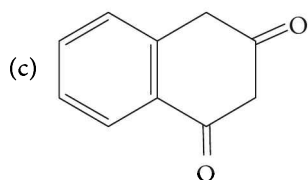
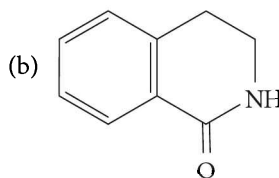
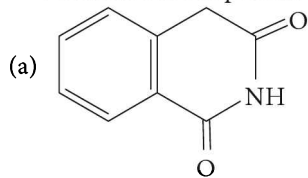
81. An organic compound (A) $\text{C}_3\text{H}_7\text{NO}$ on hydrolysis gives (B) which forms a silver mirror with Tollens' reagent and (C) which fails to dissolve in alkali after reacting with Hinsberg's reagent. (A) is



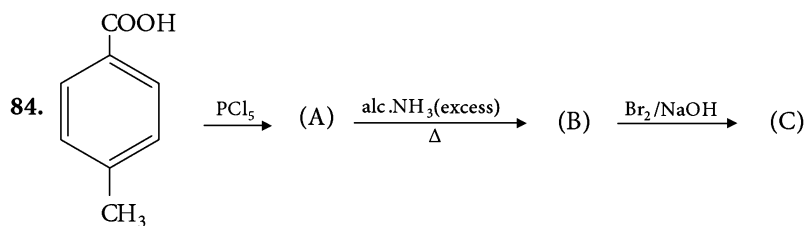
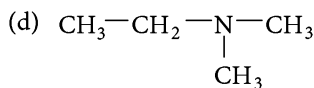
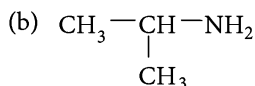
6.40 Amines, Aminoacids and Peptides



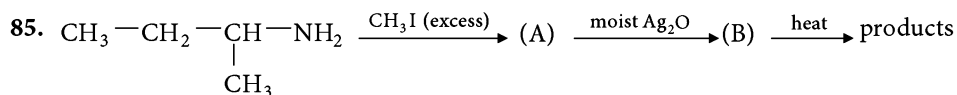
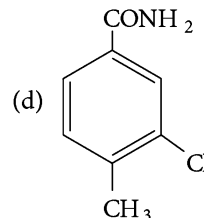
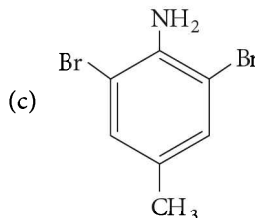
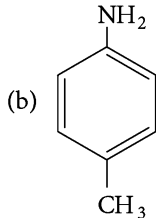
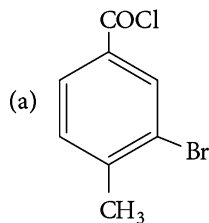
The structure of the product (B) in the above reaction is



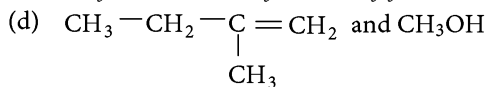
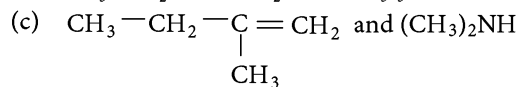
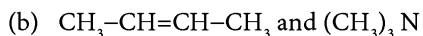
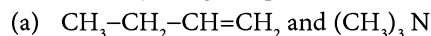
83. Which of the following compounds will give a solid product after treatment with p-toluene sulphonyl chloride and aqueous sodium hydroxide



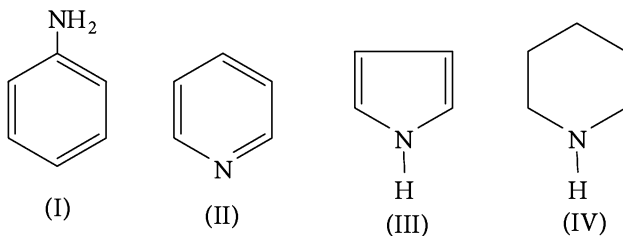
The product (C) in the above reaction sequence is



The final major organic products of the above reaction are



86. The correct decreasing order of basicity of the following compounds is



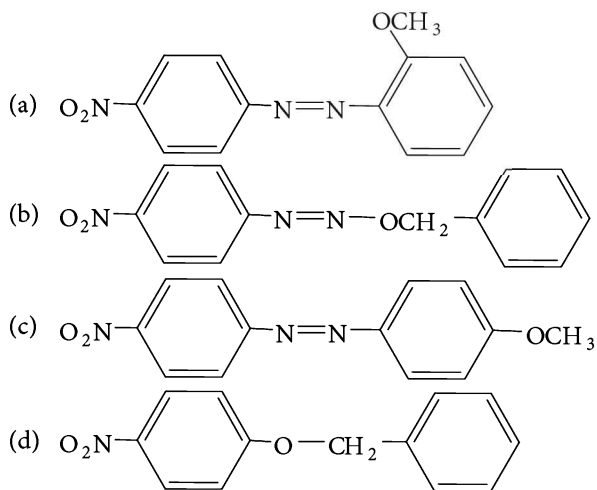
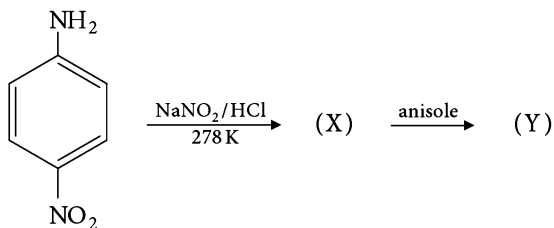
(a) $I > IV > II > III$

(b) $IV > I > III > II$

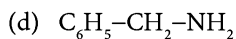
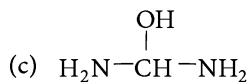
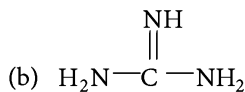
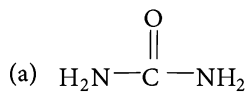
(c) $IV > I > II > III$

(d) $IV > II > I > III$

87. The structure of the final product (Y) formed in the following reaction sequence is



88. Which among the following is the strongest base?



89. Maximum number of tetrapeptides that can be prepared from the 10 essential amino acids is

(a) 10,000

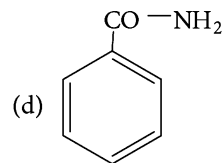
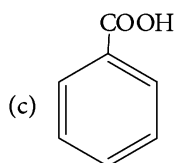
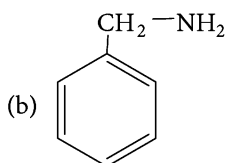
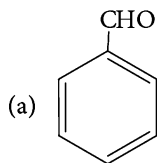
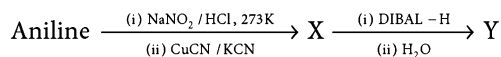
(b) 5000

(c) 2500

(d) 15000

6.42 Amines, Aminoacids and Peptides

90. The major product Y in the following sequence of reactions is



Assertion-Reason Type Questions

Directions: Each question contains Statement-1 and Statement-2 and has the following 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

91. Statement 1

Aniline reacts with concentrated H_2SO_4 to form anilinium sulphate which on heating to about 473K forms mainly p-aminobenzene sulphonic acid (sulphanilic acid).

and

Statement 2

Sulphanilic acid exists as a dipolar ion.

92. Statement 1

Gabriel's phthalimide synthesis can be used for the conversion of $\text{C}_2\text{H}_5\text{Br}$ to $\text{C}_2\text{H}_5\text{NH}_2$.

and

Statement 2

With proper choice of alkyl halides, phthalimide synthesis can be used to prepare 1°, 2° and 3° amines.

93. Statement 1

o-Toluidine is more basic than aniline.

and

Statement 2

Methyl group is an electron donating group.



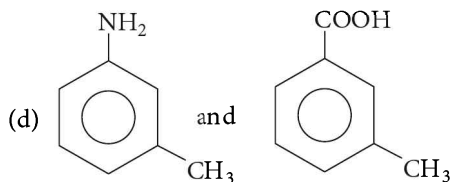
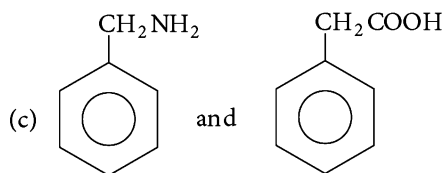
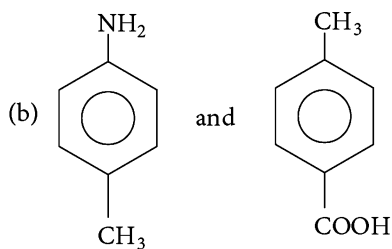
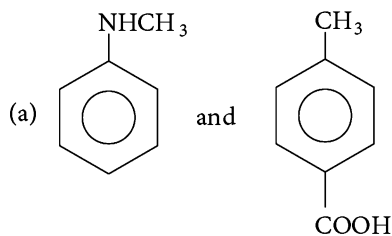
Linked Comprehension Type Questions

Directions: This section contains 1 paragraph. Based upon the paragraph, 3 multiple choice questions have to be answered. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

Passage I

A compound (A), $\text{C}_7\text{H}_9\text{N}$, on diazotization and followed by reaction with CuCN-KCN mixture gives (B), $\text{C}_8\text{H}_7\text{N}$. (B) on acid hydrolysis gives (C) $\text{C}_8\text{H}_8\text{O}_2$. When heated with acidified KMnO_4 , (C) forms terephthalic acid. (C) reacts with SOCl_2 followed by NH_3 to give (D), $\text{C}_8\text{H}_9\text{NO}$, which when treated with bromine in aqueous alkali gives (A). Answer the following questions based on the above passage.

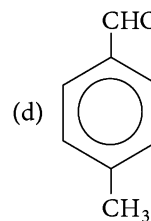
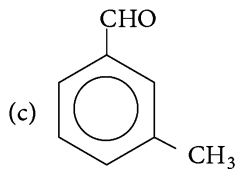
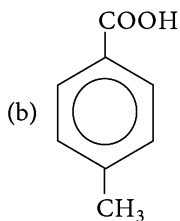
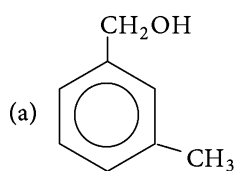
94. (A) and (C) are respectively



95. When (D) is treated with sodium in ether the gas evolved is

- (a) N_2 (b) NH_3
(c) H_2 (d) O_2

96. When (B) is reduced with stannous chloride and hydrochloric acid, followed by hydrolysis, the product obtained is

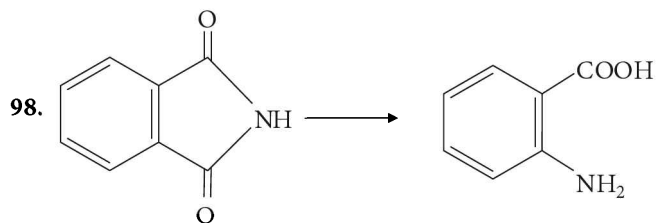


Multiple Correct Objective Type Questions

Directions: Each question in this section has four suggested answers of which ONE OR MORE answers will be correct.

97. Which of the following reactions give only 1° amine?

- (a) Hofmann's bromamide reaction
(b) Reduction of oximes with $LiAlH_4$
(c) Reaction of alcohol with NH_3 at high temperature in presence of alumina
(d) Reduction of nitro compound with Sn and HCl



The reaction(s) involved in the above conversion of phthalimide to anthranilic acid is/are

- (a) Reduction with $NaBH_4$ (b) Alkaline hydrolysis
(c) Reaction with HNO_2 (d) Hofmann bromamide reaction

6.44 Amines, Aminoacids and Peptides

99. The intermediate(s) involved in the reaction of $\text{C}_6\text{H}_5\text{CONH}_2$ with bromine and aqueous KOH is/are
 (a) $\text{C}_6\text{H}_5\text{CONBr}_2$ (b) $[\text{C}_6\text{H}_5\text{CONBr}]^- \text{K}^+$ (c) $\text{C}_6\text{H}_5\text{NCO}$ (d) $\text{C}_6\text{H}_5\text{NC}$



Matrix-Match Type Question

Directions: Match the elements of Column I to elements of Column II. There can be single or multiple matches.

100.

Column I

- (a) $\xrightarrow[\text{(ii) Hydrolysis}]{\text{(i) C}_2\text{H}_5\text{Br}}$
- (b) $\xrightarrow{\text{Br}_2/\text{OH}^-}$
- (c) $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \beta\text{-naphthol} \xrightarrow{\text{NaOH}}$
- (d) $\text{p-toluidine} \xrightarrow{\text{Br}_2/\text{H}_2\text{O}}$

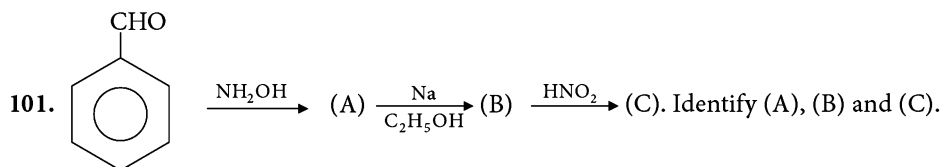
Column II

- (p) Electrophilic substitution
- (q) Nucleophilic substitution
- (r) Rearrangement
- (s) Primary amine
- (t) Coupling

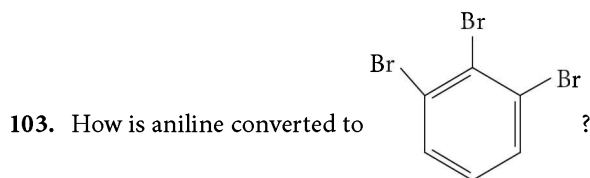
ADDITIONAL PRACTICE EXERCISE



Subjective Questions

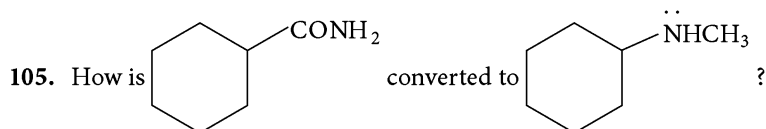


102. What are the products obtained by the oxidation of aniline with (i) chromic acid and (ii) alkaline KMnO_4 ?



104. Account for the following observations

- Acetonitrile is preferred as a solvent for many organic reactions.
- Benzamide is not soluble in hydrochloric acid, whereas aniline is soluble, though both contain the $-\text{NH}_2$ group.

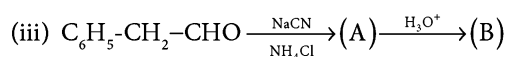
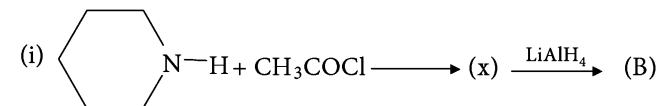


106. Explain any four colour reactions that serve as tests for proteins?

107. How are the following conversions carried out?

- Ethyl amine to methyl amine
- Benzene to phenyl hydrazine
- meta dinitrobenzene to meta bromo phenol

108. Complete the following reaction



109. Write equations for the steps involved in the preparation of m-nitrophenol from nitrobenzene.

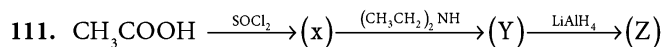
110. How will you convert

- benzene to m-bromo iodobenzene?
- aniline to 3, 5-di iodo nitrobenzene?



Straight Objective Type Questions

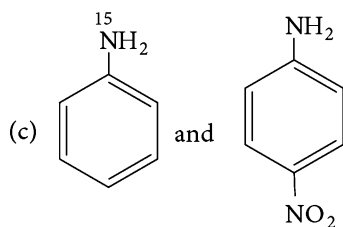
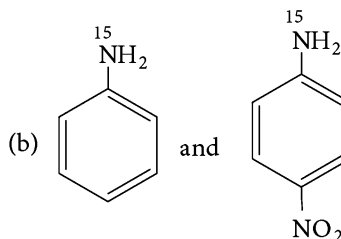
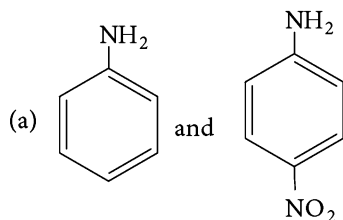
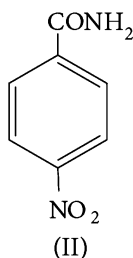
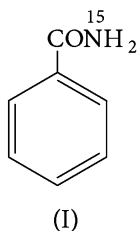
Directions: This section contains multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.



The compound (Z) in the above reaction sequence is

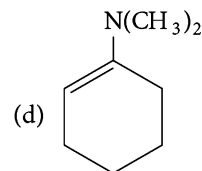
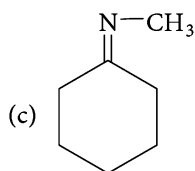
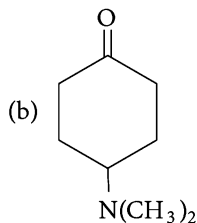
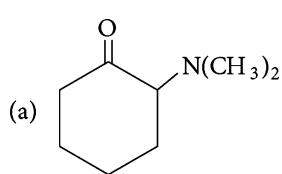
- (a) $(\text{CH}_3\text{CH}_2)_3\text{N}$ (b) $(\text{CH}_3\text{CH}_2)_2\text{N}-\text{CH}_3$
 (c) $(\text{CH}_3\text{CH}_2)_2\text{N}-\text{CH}_2\text{OH}$ (d) $(\text{CH}_3\text{CH}_2)_2\text{N}-\text{CH}_2-\text{CH}_2\text{OH}$

112. The products formed when a mixture of the following two amides (I and II) are treated with bromine and aqueous KOH are



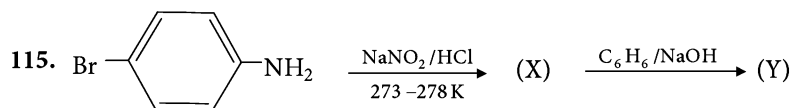
- (d) a mixture of all of these

113. The structure of the product formed when cyclohexanone reacts with dimethylamine in presence of catalytic amount of an acid such as p-toluene sulphonic acid is

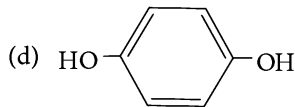
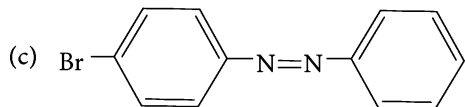
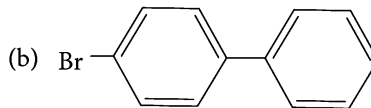
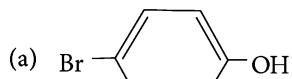


114. The N-terminal amino acid of a peptide can be determined by reaction with

- (a) Hydrazine (b) 2,4-dinitrophenyl hydrazine
 (c) 2,4-dinitrofluorobenzene (d) Acetic anhydride



The product (Y) in the above reaction is



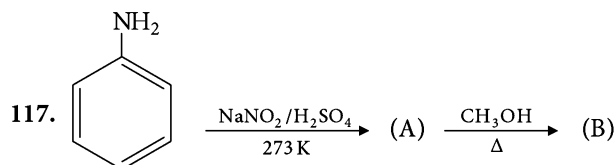
116. Reduction of benzenediazonium chloride with zinc and hydrochloric acid gives

(a) aniline

(b) azobenzene

(c) phenyl hydrazine

(d) benzene



The major product (B) in the above reaction is

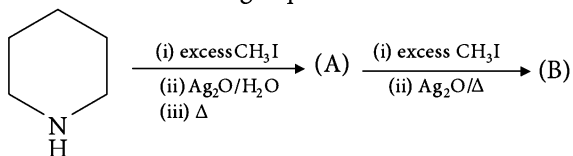
(a) benzene

(b) phenol

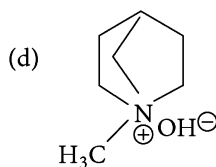
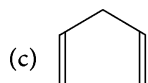
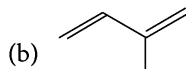
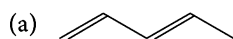
(c) anisole

(d) benzyl alcohol

118. Consider the following sequence of reactions



The final product (B) is

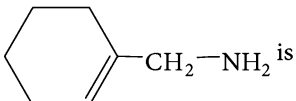


119. The decreasing order of base strength among

(i) $\text{CH}_3-\text{C}\equiv\text{C}-\text{NH}_2$

(ii) $\text{CH}_3-\text{CH}=\text{CH}-\text{NH}_2$

(iii) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{NH}_2$ and

(iv)  is

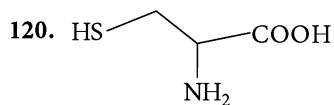
(a) (iii) > (iv) > (ii) > (i)

(b) (iv) > (iii) > (ii) > (i)

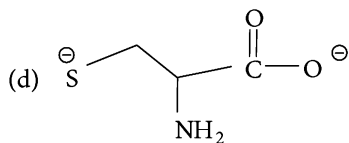
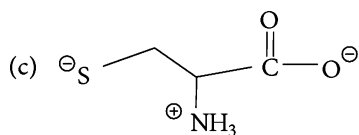
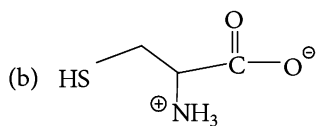
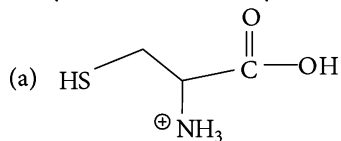
(c) (i) > (ii) > (iii) > (iv)

(d) (iv) > (iii) > (i) > (ii)

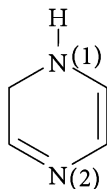
6.48 Amines, Aminoacids and Peptides



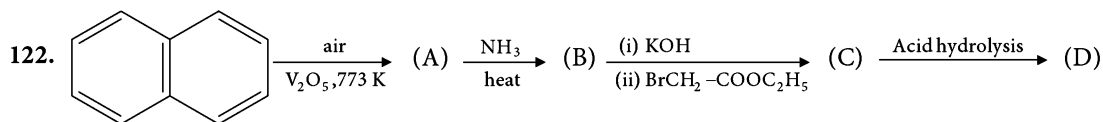
The pKa values of $-\text{COOH}$, $-\text{SH}$ and $-\text{NH}_3^+$ groups present in the amino acid cysteine are 1.8, 8.2 and 10.8 respectively. The structure of cysteine at a pH = 5 will be



121. Identify the correct statement about the basicity of the two nitrogen atoms (1) and (2) marked in the following structure.



- (a) (2) is less basic because the lone pair is present in sp^2 hybridized orbital.
- (b) (2) is more basic because the lone pair of electrons on nitrogen is not involved in resonance.
- (c) (1) is more basic because the lone pair is present in an sp^2 hybridized orbital.
- (d) Both are equally basic as they are part of the same ring system.

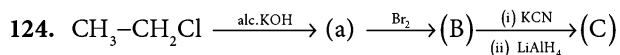


One of the products (D) in the above reaction sequence is

- (a) 2-Amino-1-naphthol
- (b) alanine
- (c) glycine
- (d) 2-phenylethanoic acid

123. Which of the following gives a primary amine on hydrolysis?

- (a) $\text{CH}_3-\text{CH}_2-\text{CN}$
- (b) $\text{CH}_3-\text{CH}=\text{NOH}$
- (c) $\text{CH}_3-\text{CH}_2-\text{NO}_2$
- (d) $\text{CH}_3-\text{CH}_2-\text{NC}$



The product (C) in the above reaction sequence is

- (a) $\text{CH}_3-\text{CH}_2\text{NH}_2$
- (b) $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$
- (c) $\text{H}_2\text{NCH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$
- (d) $(\text{CH}_3-\text{CH}_2)_2\text{NH}$

125. Aniline does not undergo coupling with benzene diazonium chloride at pH < 5 because

- (a) Diazonium salts are less stable at low pH.
- (b) Coupling takes place in neutral solution.

- (c) The azo dye formed is soluble in acid solution.
 (d) Aniline is converted into $\text{C}_6\text{H}_5-\text{N}^+\text{H}_3\text{Cl}^-$ which cannot undergo coupling.



Assertion–Reason Type Questions

Directions: Each question contains Statement 1 and Statement 2 and has the following 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

126. Statement 1

The boiling point of n-propylamine is higher than that of trimethylamine.

and

Statement 2

There is hydrogen bonding in n-propylamine.

127. Statement 1

Benzene diazonium chloride reacts with an alkaline solution of phenol to give a blue coloured dye.

and

Statement 2

The colour of the dye is due to extended conjugation.

128. Statement 1

In the preparation of acetanilide from aniline, acetyl chloride is a more active reagent than acetic anhydride.

and

Statement 2

Among the derivatives of carboxylic acid, acid chloride is the most active as it contains a better leaving group Cl^- (chloride ion), compared to an acetate ion.

129 Statement 1

Ninhydrin in aqueous medium gives a violet coloured product with amino acid.

and

Statement 2

Ninhydrin in aqueous medium reacts with amino acid as it exists as a stable gem-diol.

130. Statement 1

In the conversion of benzene diazonium chloride to iodobenzene, there is no need to treat the diazonium salt with cuprous iodide.

and

Statement 2

Iodide is a strong nucleophile.



Linked Comprehension Type Questions

Directions: This section contains 3 paragraphs. Based upon the paragraph, 3 multiple choice questions have to be answered. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

Passage I

Amines have the formula RNH_2 and can be prepared by different methods. Some of them are (i) reduction of nitriles (ii) reduction of amides (iii) reduction of azides and (iv) Gabriel phthalimide synthesis. The most important property of amines is their basicity due to the presence of lone pair of electrons on nitrogen. Answer the following questions.

131. The method, $RX \xrightarrow{KCN} RCN, \xrightarrow[(ii) H_2O]{(i) LiAlH_4 / ether} RCH_2NH_2$ is not suitable for the preparation of benzyl amine because
- $RX \xrightarrow{KCN} RCN$ reaction is not possible since chlorobenzene does not undergo S_N1 or S_N2 reaction.
 - It is difficult to reduce C_6H_5CN to $C_6H_5CH_2NH_2$
 - Bromobenzene gets oxidized
 - $LiAlH_4$ cannot reduce C_6H_5CN .
132. The conversion of RCH_2CH_2Br to $RCH_2CH_2N_3$ by NaN_3 is an example of
- S_N1 reaction
 - S_N2 reaction
 - nucleophilic addition reaction
 - electrophilic addition reaction

133. Arrange the following amines in the order of their increasing basicity

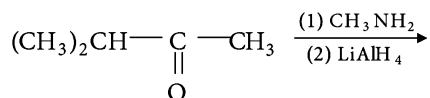


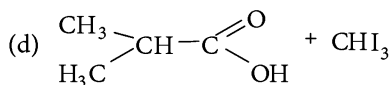
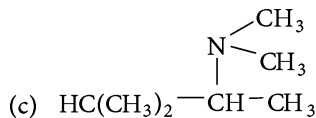
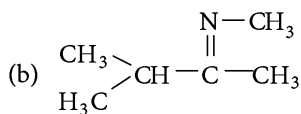
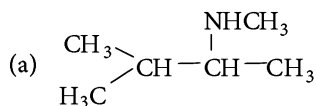
- (iv) < (iii) < (ii) < (i)
- (iii) < (iv) < (ii) < (i)
- (iii) < (ii) < (i) < (iv)
- (i) < (ii) < (iii) < (iv)

Passage II

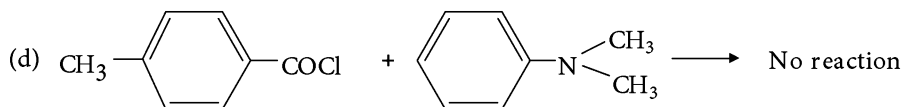
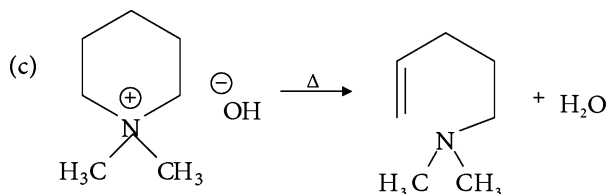
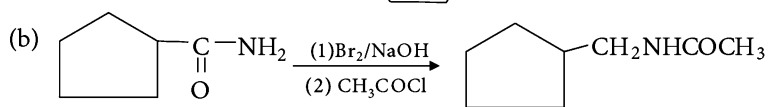
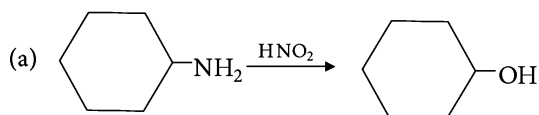
Amines can be separated using Hinsberg method. Amines undergo a wide range of reactions like alkylation, acylation, reaction with nitrous acid, carbylamine reaction and condensation reactions with aldehydes.

134. Which of the following on reduction with $LiAlH_4$ will give N-methylaniline?
- Methyl isocyanide
 - Acetamide
 - Phenyl carbylamine
 - Benzonitrile
135. The major organic product formed from the following reaction is

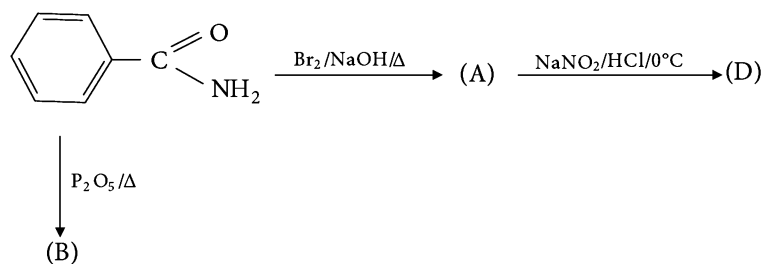




136. Which of the following reactions is not correctly given?



Passage III



137. The intermediates which are involved in the conversion from benzamide to (A) are

- (a) N-bromamide (b) carbocation
(c) carbene (d) isocyanide

138. (B) on treatment with Zn/HCl gives

- (a) aniline (b) benzylamine
(c) phenylisocyanide (d) N-methylaniline

139. (D) on reaction with phenol under alkaline conditions gives

- (a) diazobenzene (b) hydrazobenzene
(c) benzidine (d) para hydroxy azobenzene



Multiple Correct Objective Type Questions

Directions: Each question in this section has four suggested answers of which ONE OR MORE answers will be correct.

140. Which of the following reactions will give phenyl cyanide as a product?
 (a) Reaction of benzene diazonium chloride with cuprous cyanide and KCN
 (b) Heating bromobenzene with alcoholic potassium cyanide
 (c) Dehydration of benzaldoxime by heating with acetic anhydride
 (d) Fusing sodium benzene sulphonate with NaCN
141. The correct statement (s) among the following is/are
 (a) The amino acid tyrosine gives violet colour with neutral ferric chloride solution
 (b) Lysine is a basic amino acid
 (c) Serine is an amino acid containing sulphur
 (d) A tetrapeptide contains four peptide bonds
142. Which of the following compounds will give liberation of nitrogen gas when treated with NaNO_2 and HCl at low temperature?
 (a) Benzylamine
 (b) N,N-Dimethylaniline
 (c) Diethylamine
 (d) Alanine
143. Identify the correct statement(s) regarding amino acids and peptides from the following.
 (a) C–N bond length in peptides is smaller than the usual C–N bond length in amines.
 (b) Atoms in $-\text{CO}-\text{NH}-$ group are not in a plane.
 (c) An important sensitive test for the detection of amino acids is the ninhydrin colour test.
 (d) The isoelectric point of glutamic acid is about 3.2.
144. Which of the following compounds on oxidation with acidified dichromate gives p-benzoquinone?
- (a)

(b)

(c)

(d)
145. Identify the reactions in which both the nitrogen atoms of benzene diazonium chloride are retained in the product.
 (a) Reduction with zinc and hydrochloric acid
 (b) Reduction with SnCl_2 and hydrochloric acid
 (c) Reduction with sodium sulphite
 (d) Coupling reaction
146. The reactions that can be used to prepare benzylamine are
 (a) Reduction of benzamide with H_2/Pd .
 (b) Reduction of benzenecarbonitrile with SnCl_2/HCl .
 (c) Reaction of potassium phthalimide with benzylbromide followed by hydrolysis.
 (d) reaction of benzoyl chloride with ammonia.
147. Coupling reaction takes place when benzene diazonium chloride is treated with
 (a) Benzaldehyde
 (b) α -naphthol
 (c) N,N-dimethylaniline
 (d) anisole
148. Which of the following compounds reacts with benzaldehyde to form a product containing $\text{>C}=\text{N}$?
 (a) $(\text{CH}_3)_2\text{NH}$
 (b) $\text{C}_6\text{H}_5\text{NH}_2$
 (c) $\text{C}_6\text{H}_5\text{NHNH}_2$
 (d) $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$



Matrix-Match Type Questions

Directions: Match the elements of Column I to elements of Column II. There can be single or multiple matches.

149.

Column I

- (a) Coupling reaction
- (b) Liebermann's nitroso reaction
- (c) Hinsberg reaction
- (d) Carbylamine reaction

Column II

- (p) Phenol
- (q) Aniline
- (r) N-methylethanamine
- (s) Tertiary butyl amine

150.

Column I

(Test)

- (a) Hinsberg's test
- (b) Carbylamine test
- (c) Azo dye test
- (d) Liebermann nitroso reaction

Column II

(Distinguish between)

- (p) $\text{C}_6\text{H}_5\text{NH}_2$ and $\text{C}_6\text{H}_5\text{NHCH}_3$
- (q) $\text{C}_6\text{H}_5\text{NH}_2$ and $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$
- (r) $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$ and $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$
- (s) $\text{CH}_3-\text{CH}_2-\text{CH}_2\text{NH}_2$ and $p\text{-CH}_3-\text{C}_6\text{H}_4-\text{NH}_2$
- (t) $(\text{CH}_3\text{CH}_2)_2\text{NH}$ and $(\text{CH}_3\text{CH}_2)_3\text{N}$

SOLUTIONS

ANSWER KEYS

Topic Grip

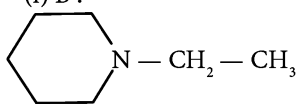
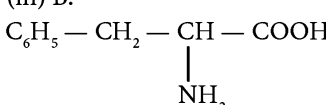
1. Aryl halides do not undergo nucleophilic substitution with phthalimide ion.
2. (a) Methylamine accepts proton from water liberating OH^- ions which give precipitate of $\text{Fe}(\text{OH})_3$
(b) Aniline, being basic, combines with Lewis acid catalyst
(c) Aryl diazonium salts are stabilised by resonance
3. (a) Nitrobenzene is treated successively with Sn/HCl , HNO_2 , CuCN/KCN , and H_3O^+
(b) Benzene is treated successively with nitrating mixture, Br_2/Fe , Sn/HCl , HNO_2 and $\text{H}_2\text{O}/\text{heat}$
(c) Ethanamine is treated successively with HNO_2 , $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$, NH_3/heat and Br_2/KOH
(d) Nitromethane is treated successively with Sn/HCl , $\text{CHCl}_3/\text{alc. KOH}$ and H_2/Pd
4. Amino acids which the human body can synthesise are called non-essential amino acids.
5. Steric inhibition of resonance.
6. (i) $[(\text{CH}_3)_2\text{CH}]_2\text{NH}$
(ii) Piperidine
(iii) Ethylamine
7. $\text{D} = \text{cyclopropyl-CH}_2\text{OH}$
8. (i) cyclohexylamine
(ii) 2-methyl pyridine
(iii) cyclohexylamine
(iv) aniline
9. (a) C = 1, 3, 5-Tribromobenzene
(b) C = $\text{C}_6\text{H}_5\text{NHCOCH}_3$
(c) C = benzoic acid
10. (a) Benzaldehyde is treated successively with aniline, H_2/Ni , NH_3 and H_2/Ni
(b) Propanal is first treated with NH_3 and then reduced with H_2/Ni
11. (a) 12. (c) 13. (a)
14. (b) 15. (b) 16. (a)
17. (c) 18. (c) 19. (a)
20. (a) 21. (b) 22. (b)
23. (a) 24. (c) 25. (c)
26. (b)
27. (a), (c), (d)
28. (c), (d)
29. (b), (c)
30. (a) $\rightarrow$ (p)
(b) $\rightarrow$ (p), (q), (r), (t)
(c) $\rightarrow$ (q)
(d) $\rightarrow$ (q), (s)

IIT Assignment Exercise

31. (a) 32. (a) 33. (d)
34. (b) 35. (b) 36. (b)
37. (c) 38. (a) 39. (b)
40. (c) 41. (d) 42. (d)
43. (a) 44. (d) 45. (b)
46. (d) 47. (b) 48. (b)
49. (c) 50. (b) 51. (d)
52. (c) 53. (b) 54. (c)
55. (d) 56. (b) 57. (d)
58. (c) 59. (c) 60. (d)
61. (d) 62. (b) 63. (c)
64. (c) 65. (a) 66. (a)
67. (b) 68. (a) 69. (b)
70. (a) 71. (b) 72. (c)
73. (b) 74. (c) 75. (a)
76. (b) 77. (c) 78. (a)
79. (b) 80. (d) 81. (a)
82. (b) 83. (c) 84. (b)
85. (a) 86. (d) 87. (c)
88. (b) 89. (a) 90. (a)

91. (b) 92. (c) 93. (d)
94. (b) 95. (c) 96. (d)
97. (a), (b), (d)
98. (b), (d)
99. (b), (c)
100. (a) $\rightarrow$ (q), (s)
(b) $\rightarrow$ (r), (s)
(c) $\rightarrow$ (p), (t)
(d) $\rightarrow$ (p), (s)

Additional Practice Exercise

101. A = benzaldoxime
B = benzylamine
C = benzyl alcohol
102. (i) p-benzoquinone
(ii) azobenzene
103. Aniline is successively treated with CH_3COCl , nitrating mixture, $\text{Br}_2/\text{CH}_3\text{COOH}$, HNO_2 , CuBr/HBr , Sn/HCl , HNO_2 and H_3PO_2
104. (i) CH_3CN is not quite reactive
(ii) Benamide is almost neutral
105. Treated with Br_2/KOH , CHCl_3/KOH and H_2/Pd
106. Biuret test, Xanthoproteic test, Hopkins-cole test and Ninhydrin test.
107. Ethylamine is treated successively with HNO_2 , KMnO_4/H^+ , SOCl_2 , NH_3 and Br_2/KOH
108. (i) B : 
(ii) $\text{HOCH}_2-\text{COOH} + \text{N}_2 + \text{H}_2\text{O}$
(iii) B : 

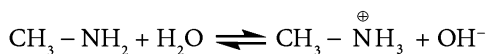
109. Nitrobenzene is treated successively with nitrating mixture, $(\text{NH}_4)_2\text{S}$, HNO_2 and $\text{H} - \text{OH}/\text{heat}$
110. (a) Benzene is treated successively with nitrating mixture, Br_2/Fe , Fe/HCl , HNO_2 and KI
 (b) Aniline is treated successively with CH_3COCl , nitrating mixture, H_3O^+ , ICl , HNO_2 and H_3PO_2
111. (a) 112. (c) 113. (d)
 114. (c) 115. (b) 116. (a)
117. (c) 118. (a) 119. (a)
 120. (b) 121. (b) 122. (c)
 123. (d) 124. (c) 125. (d)
 126. (a) 127. (d) 128. (a)
 129. (a) 130. (a) 131. (a)
 132. (b) 133. (d) 134. (c)
 135. (a) 136. (b) 137. (a)
 138. (b)
 139. (d)
 140. (a), (c), (d)
 141. (a), (b)
 142. (a), (d)
 143. (a), (c), (d)
144. (b), (c), (d)
 145. (b), (c), (d)
 146. (a), (c)
 147. (b), (c), (d)
 148. (b), (c)
 149. (a) $\rightarrow$ (p), (q)
 (b) $\rightarrow$ (p), (r)
 (c) $\rightarrow$ (q), (r), (s)
 (d) $\rightarrow$ (q), (s)
 150. (a) $\rightarrow$ (p), (r), (t)
 (b) $\rightarrow$ (p), (r)
 (c) $\rightarrow$ (p), (q), (s)
 (d) $\rightarrow$ (p), (t)

HINTS AND EXPLANATIONS

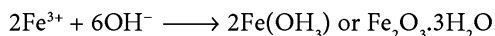
Topic Grip

1. In Gabriel's phthalimide synthesis, alkyl halides undergo nucleophilic substitution with phthalimide ion (produced from potassium phthalimide) to form N-alkyl phthalimide which on hydrolysis gives 1° amine. Since aryl halides do not undergo nucleophilic substitution readily with phthalimide ion, they do not give N-aryl phthalimide. So aromatic 1° amines cannot be prepared by this method.

2. (a) Methylamine, being more basic than water, accepts a proton from water liberating OH⁻ ions

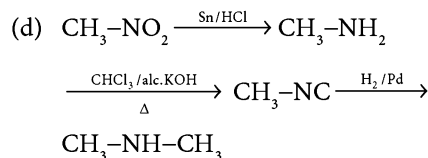
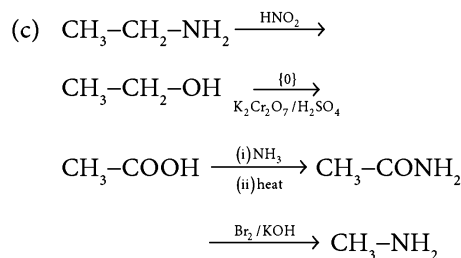
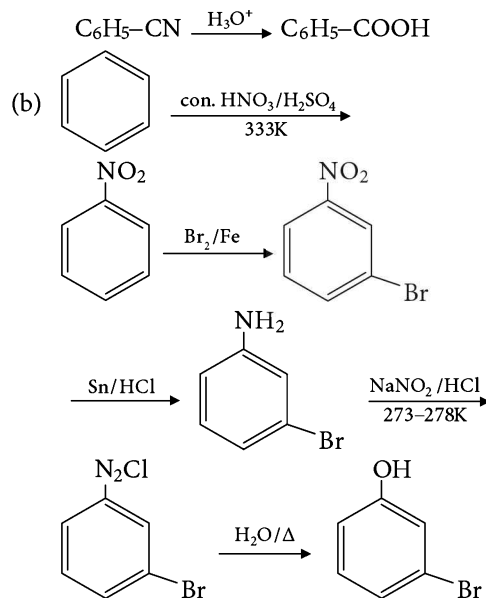
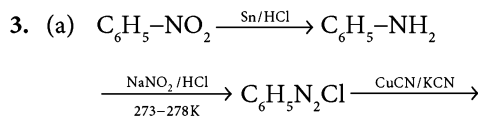
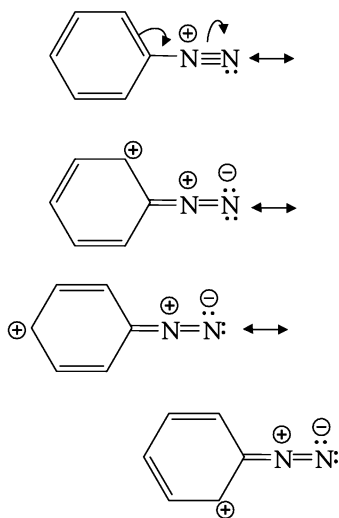


Fe³⁺ ions of ferric chloride combine with these OH⁻ ions to form a reddish brown precipitate of ferric hydroxide or hydrated ferric oxide

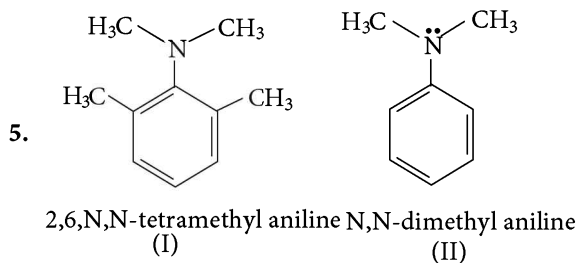


(b) Aniline being basic combines with the Lewis acid catalyst AlCl₃ used in Friedel-Craft reaction. So the catalyst will not be available to produce electrophile. Moreover, due to positive charge produced on the nitrogen atom in the salt, it becomes a deactivating group and so electrophilic substitution such as Friedel-Craft reaction does not take place.

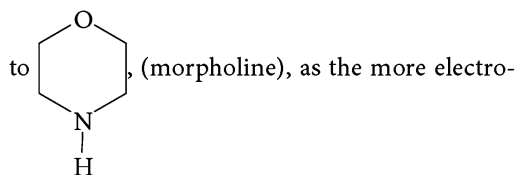
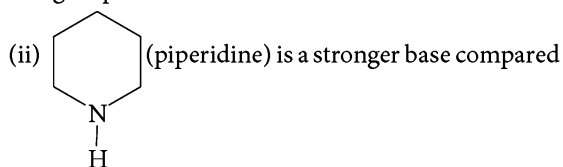
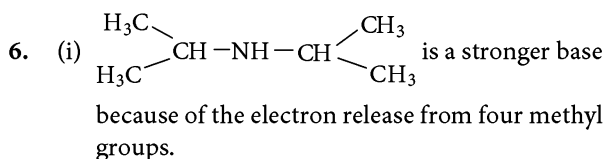
(c) Aryl diazonium salts are stabilised by resonance whereas alkyl diazonium salts are not



4. Amino acids which the human body can synthesise are called non-essential amino acids. Those amino acids which human body cannot synthesise are known as essential amino acids. Hence essential amino acids must be supplied through diet. Valine, leucine, isoleucine, phenylalanine, methionine, tryptophan, threonine, lysine, arginine and histidine are the essential amino acids

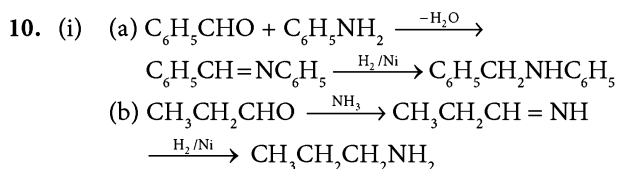
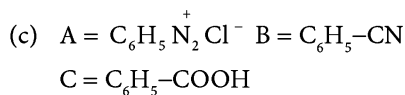
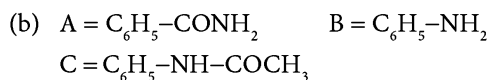
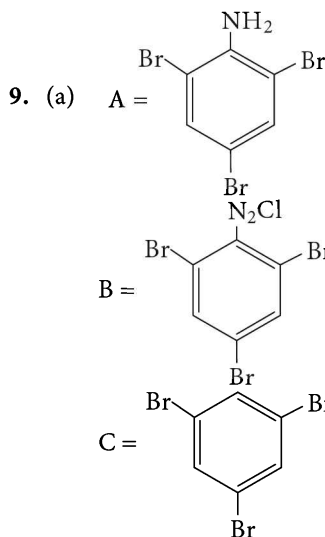
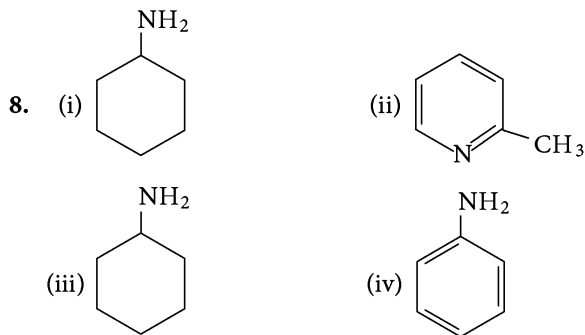
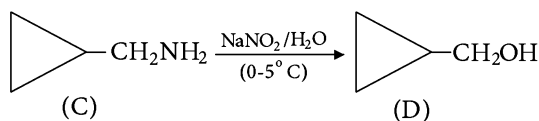
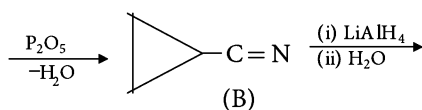
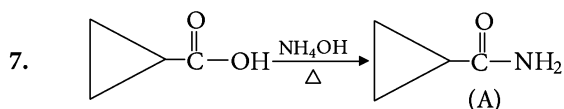


In (I), the amino group is flanked on both sides by two bulky methyl groups. This prevents the molecule from turning planar due to steric hindrance. So the lone pair of electrons is not delocalized into the benzene ring. Hence, 2,6,N,N-tetramethyl aniline is a stronger base. On the other hand, in the case of N,N-dimethyl aniline, (II), the electrons on amine nitrogen can be delocalized and so it is a slightly weaker base. In the case of (I), it is termed as steric inhibition of resonance.

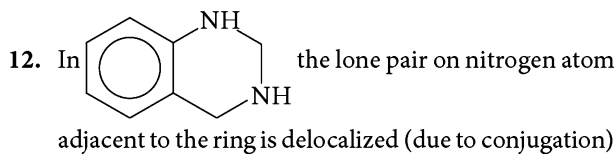
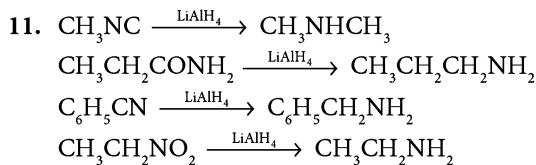


negative oxygen draws electrons towards it.

(iii) $\text{CH}_3\text{CH}_2\text{NH}_2$ (ethylamine) is a stronger base than β -chloroethyl amine, $\text{ClCH}_2\text{CH}_2\text{NH}_2$. This is due to the withdrawal of electrons by chlorine in β -chloroethyl amine.

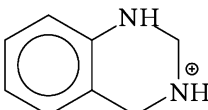


These reactions are known as reductive amination reactions.



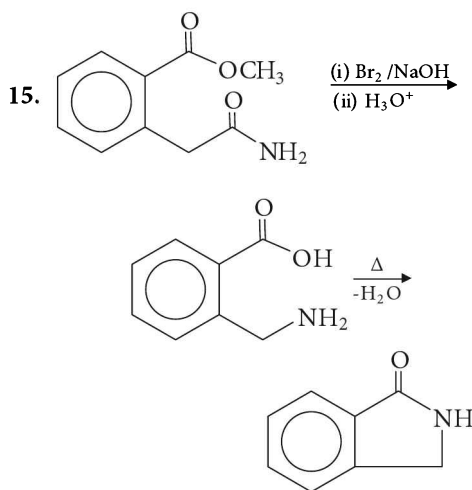
6.58 Amines, Aminoacids and Peptides

and is less available for protonation. The other nitrogen

thus gets protonated to form  as the product.

13. $\text{H}_2\text{NCHCO}-\text{NHCHCO}-\text{NHCHCOOH}$ is glycyl
 $\text{CH}_2\text{C}_6\text{H}_5$ CH_3
 phenylalanyl alanine or (Gly-Phe-Ala)

14. Only one $-\text{NH}_2$ is selectively reduced to give m-nitroaniline.



16. Both statements are correct and statement 2 is the reason for statement 1

Since $-\text{NH}_2$ group is highly activating, direct treatment of aniline with con.HNO_3 leads to oxidation of the benzene ring. Acetylation of $-\text{NH}_2$ group will convert it to $-\text{NH}-\text{COCH}_3$ which is less activating. So nitration can be conveniently carried out and the acetyl group is finally removed by hydrolysis

17. Statement 1 is correct, but statement 2 is false. Anilinium ion, $\text{C}_6\text{H}_5\text{N}^+\text{H}_3$ is the conjugate acid of aniline while ammonium ion is the conjugate acid of ammonia. Since aniline is a weaker base than ammonia, the conjugate acid of aniline must be a stronger acid. Anilinium ion ($\text{C}_6\text{H}_5-\text{NH}_3^+$) does not contain any lone pair of electrons on nitrogen. So it is less stabilised by resonance than aniline so statement 2 is wrong

18. Statement 1 is true while statement 2 is false. Pyridine is less basic than piperidine because the lone pair of electron of nitrogen is accommodated in a sp^2 hybridised orbital in pyridine. The lone pair of electrons is in sp^3 hybridised orbital of nitrogen in the case of

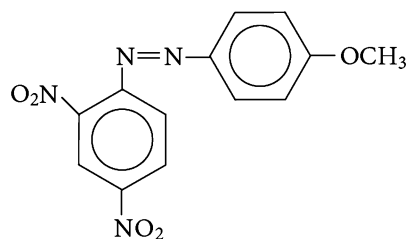
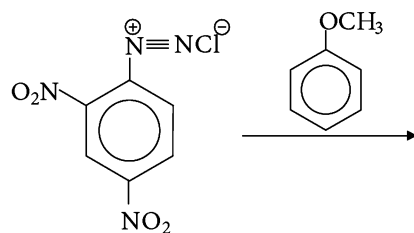
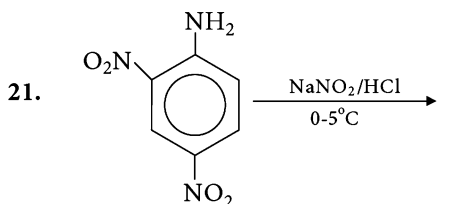
piperidine. Hence the lone pair of electrons is more tightly held in the case of pyridine.

Statement 2 is not correct because the lone pair of electrons is not involved in giving aromatic stability to pyridine

19. Both statements are correct and statement 2 is the correct reason for statement 1

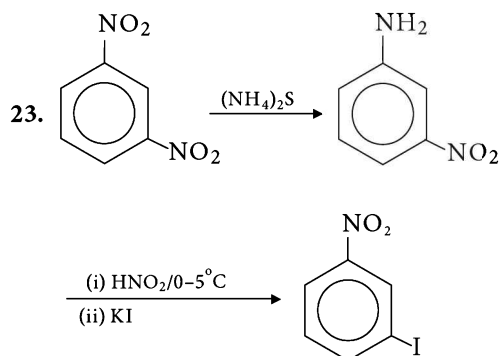
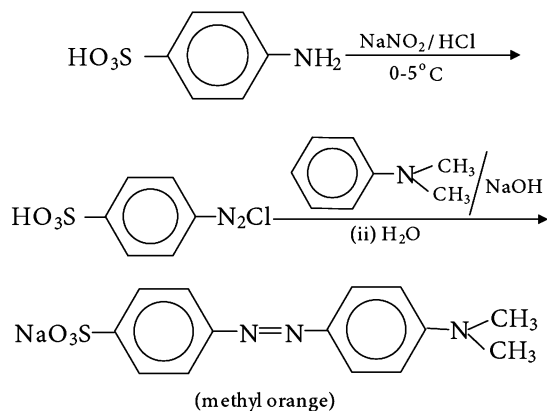
Due to steric crowding the nitrogen atom of 2,6-dimethyl-N,N-dimethylaniline goes slightly out of plane of benzene ring and hence the lone pair of electrons are not effectively involved in resonance. This is known as steric inhibition of resonance. Hence the para position of 2,6-dimethyl-N,N-dimethylaniline is not sufficiently activated for coupling reaction

20. Both statements are correct and statement 2 is the correct reason for statement 2. Among the naturally occurring amino acids, proline does not contain a primary amino group. It contains only a secondary amino group. So it does not liberate N_2 when treated with HNO_2



4-methoxy-2',4'-dinitroazobenzene

22. The product obtained is known as methyl orange and it is prepared by coupling diazotized sulphanilic acid with dimethyl aniline.



$(\text{NH}_4)_2\text{S}$ is a selective reducing agent and it reduces one of the two nitro groups to $-\text{NH}_2$.

24. The C-terminal amino acid can be identified by hydrazine. The polypeptide gets hydrolysed and all amino acid units except the C-terminal amino acid is converted to the corresponding hydrazones. This is known as hydrazinolysis.

25.
$$\text{pI} = \frac{\text{pK}_{a_1} + \text{pK}_{a_2}}{2} = \frac{2.13 + 4.31}{2} = 3.22$$

 pK_a 's of similar groups are considered.

26. Six different sequence of tripeptides can be obtained.

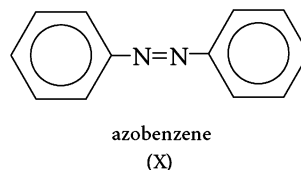
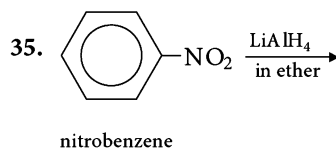
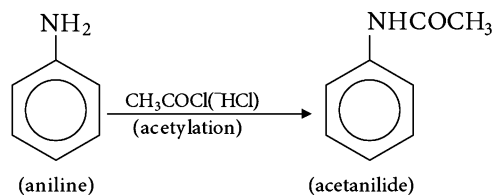
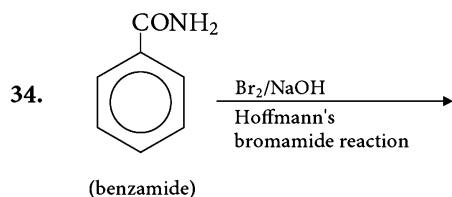
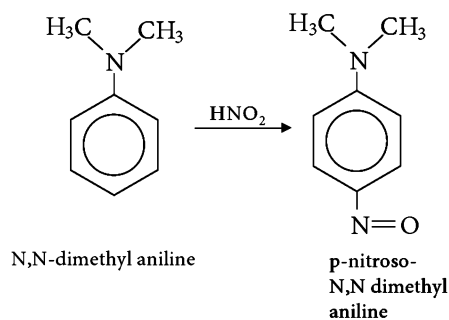
27. DIBAL-H will reduce cyanides(nitriles) to imines which on hydrolysis give aldehydes. All other reducing agents given will reduce cyanides to 1° amines

28. Benzylamine is more basic because the lone pair on nitrogen is not delocalized by resonance. p-anisidine or p-methoxyaniline is more basic than aniline due to the +R effect of $-\text{OCH}_3$ group

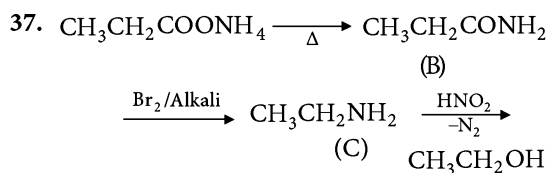
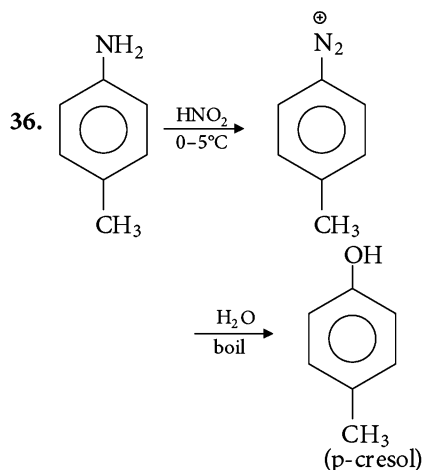
29. Cystein and methionine are sulphur containing α -amino acids

IIT Assignment Exercise

31. Intermolecular hydrogen bonding in amines results in higher boiling point. The hydrogen bonding is however less effective compared to oxygen and fluorine.
32. Schotten Baumann reaction is the benzoylation of phenols or anilines.
33. Tertiary aromatic amines form para nitroso derivatives with nitrous acid.

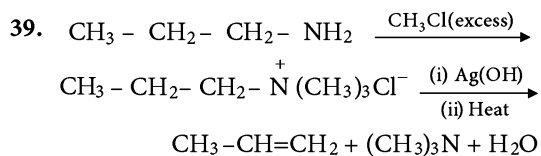


6.60 Amines, Aminoacids and Peptides



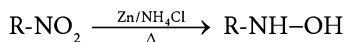
Hence (A) is $\text{CH}_3\text{CH}_2\text{COOH}$ (propanoic acid).

38. Using $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ (Hinsberg's reagent) 1°, 2° and 3° amines can be separated.



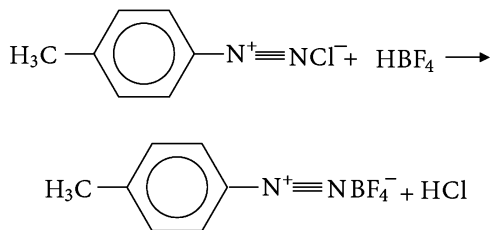
40. Nitrogen is sp^3 hybridised in aniline.

41. Reduction of nitro compounds with Zn and NH_4Cl give the corresponding hydroxyl amines.

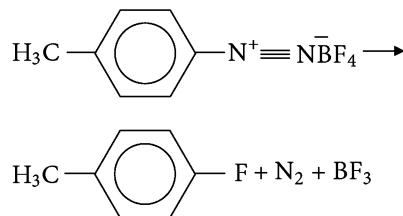


42. Hoffmann mustard oil reaction

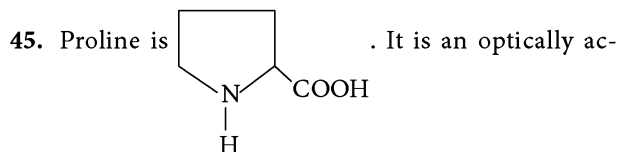
43. p-toluidine being aromatic 1° amine undergoes diazotisation. The diazonium salt on treatment with HBF_4 (fluoroboric acid) gives diazonium fluoroborate.



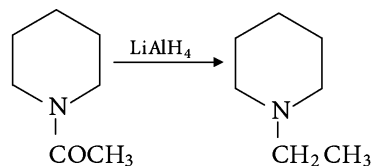
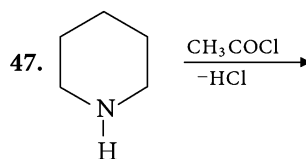
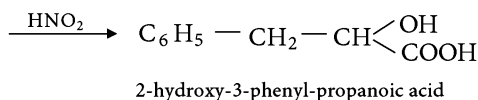
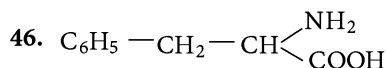
Diazonium fluoroborate on heating gives p-fluorotoluene.



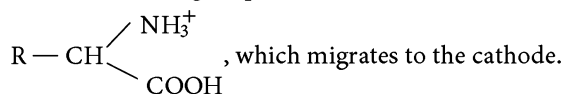
44. Primary amines and α -amino acids can be synthesized by Gabriel phthalimide synthesis.



It is an optically active compound with a secondary amino functional group.



48. The medium is acidic due to addition of HCl. So the amino acid gets protonated to form a cation,

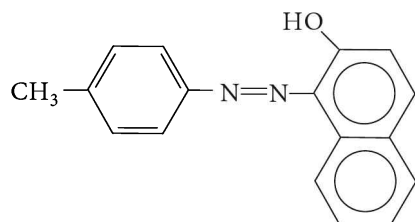
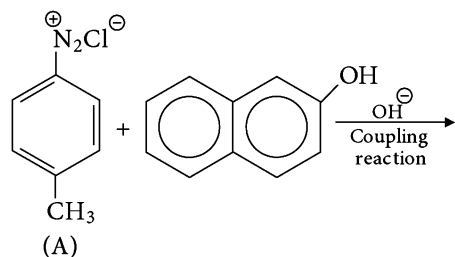
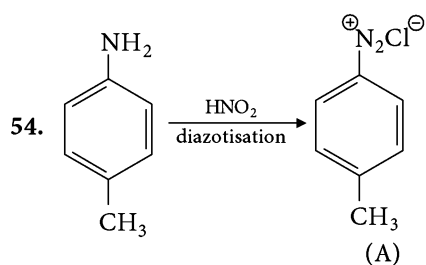


49. When a ring containing two $-\text{NO}_2$ group is reduced using metals like Fe or Zn in HCl, both the $-\text{NO}_2$ groups are reduced. $-\text{CH}_3$ group remains unaffected.

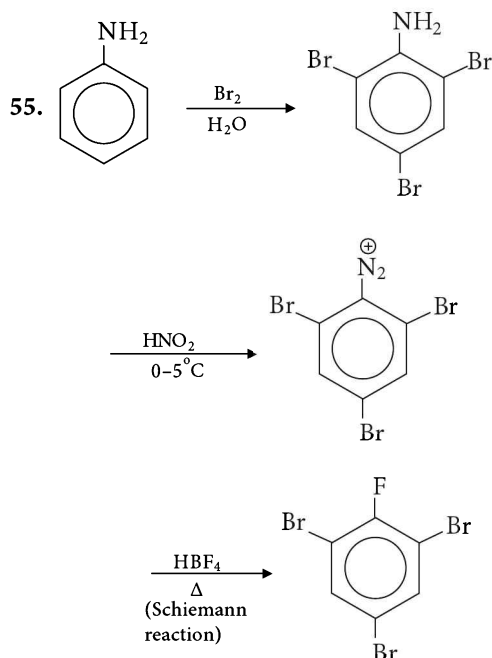
50. Aniline is the reduction product of nitro benzene under acidic conditions. Azobenzene formed can

be converted to aniline by reduction under acidic conditions.

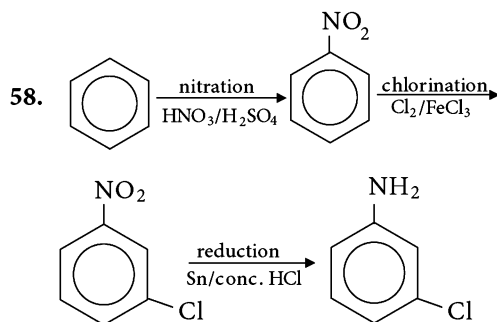
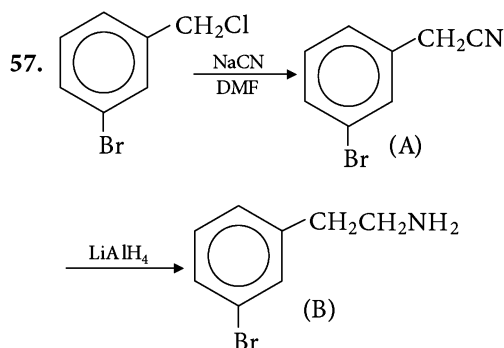
51. Since it dissolves in water on adding acid and contains nitrogen, it is an amine. It gives coloured compound with HNO_2 due to the formation of nitroso compound, which indicates the presence of a secondary amine. As the amine is not chiral it should contain two same groups. Hence the compound is $\text{CH}_3\text{CH}_2 - \text{NH} - \text{CH}_2\text{CH}_3$.
52. In aqueous solution, the substituted ammonium ions formed from secondary or primary amines are stabilized by solvation through hydrogen bonding much more effectively than the ammonium ions formed from tertiary amines, as tertiary amines have no hydrogen. There is no such possibility in gas phase. Hence the trend is reversed.
53. $-\text{NO}_2$ group possesses an electron withdrawing effect and forces the lone pair of electrons on the nitrogen on $-\text{NH}_2$ into conjugation. This decreases the basic nature of nitrogen. The effect is pronounced in ortho position than in para position. So aniline is most basic among the three.



Since the para position in 2-naphthol is not available, coupling occurs at the ortho position.



56. Sanger's reagent is 2,4-dinitrofluorobenzene and is used to identify the N-terminal of a peptide chain.

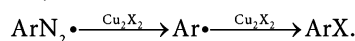


59. $\text{RNH}_2 + \text{CHCl}_3 + 3\text{KOH (alc)} \xrightarrow{\Delta} \text{R} - \text{N} \equiv \text{C} + 3\text{KCl} + 3\text{HO}_2$
Foul smelling carbonylamine or isocyanide is formed.

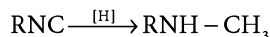
6.62 Amines, Aminoacids and Peptides

60. $\text{R}-\underset{\text{NH}_3^+}{\overset{\ominus}{\text{CH}}}-\text{COO}^-$ is known as zwitterion or internal salt or dipolar ion.

61. Sandmeyer reaction is a free radical reaction.

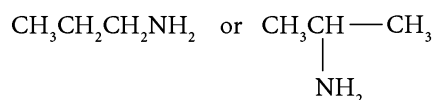


62. Molecular formula is $\text{C}_3\text{H}_9\text{N}$. The product obtained from carbylamine reaction (CHCl_3 and alc.KOH) gave on reduction a secondary amine. Isocyanides on reduction give secondary amine.



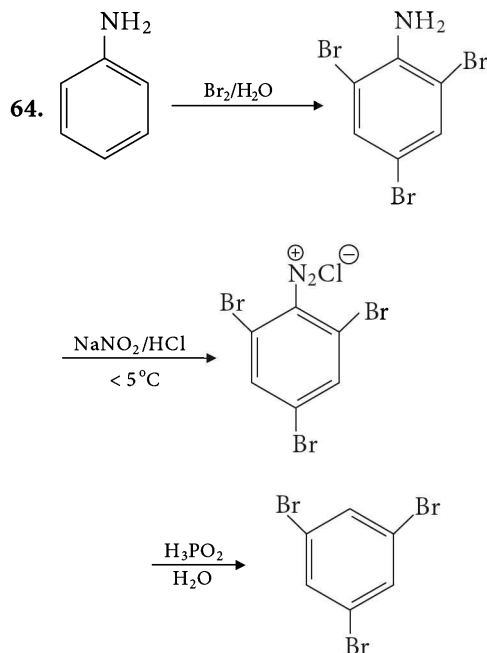
Therefore (X) is a primary amine with formula $\text{C}_3\text{H}_9\text{N}$.

We can have



Both the isomeric forms are not optically active.

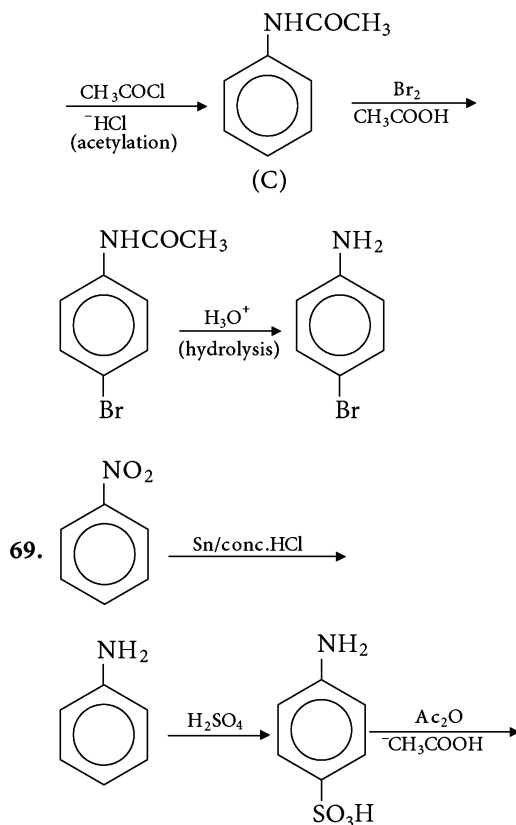
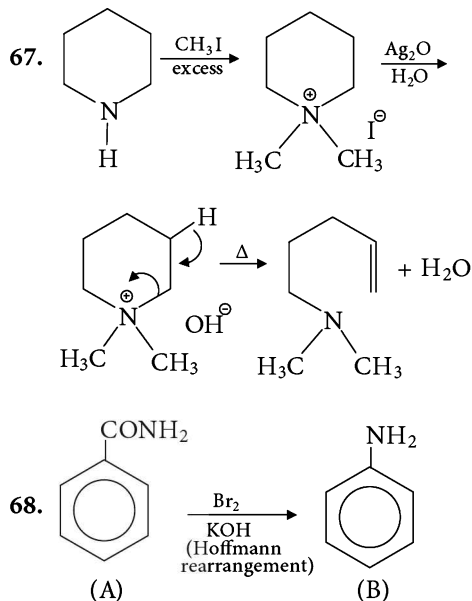
63. N-ethyl-N-methyl aniline on treatment with nitrous acid gives para nitroso derivative.



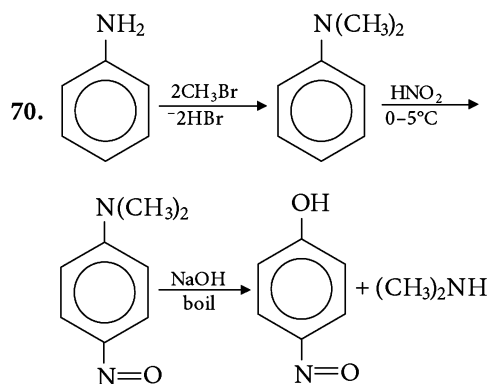
65. More basic the amine, less acidic would be the conjugate base.

66. Electron withdrawing groups on the ring at para position decreases the basicity, as the lone pair of electrons on nitrogen get involved in resonance with these

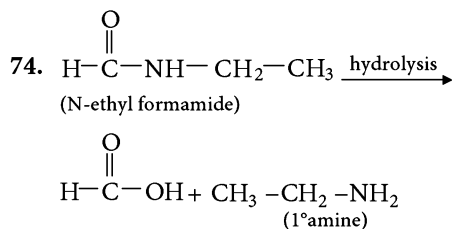
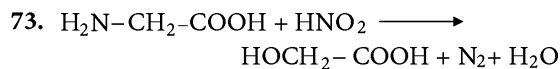
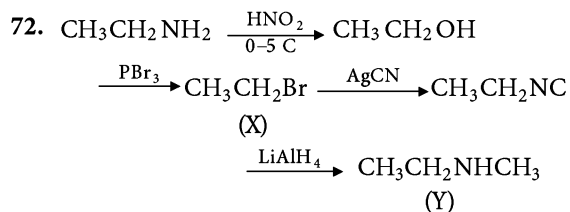
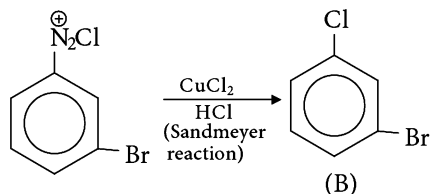
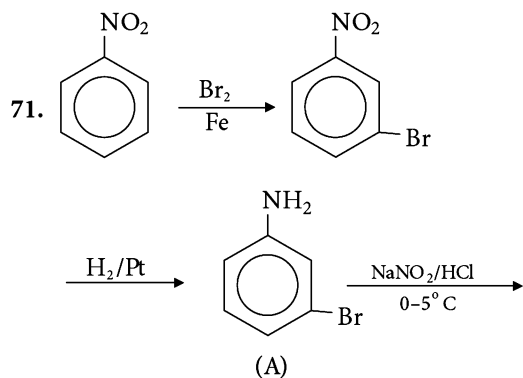
groups. Aniline is more basic than aromatic amines with electron withdrawing groups.



In the conversion from (B) to (C), hydrolysis with dil. H_2SO_4 not only hydrolyses the $-\text{NHCOCH}_3$ to the free NH_2 , but $-\text{SO}_3\text{H}$ is also removed.

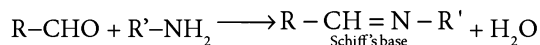


Aniline is heated with methyl bromide followed by reaction with nitrous acid to form 4-nitroso-N,N-dimethyl aniline. When this is boiled with sodium hydroxide, pure dimethyl amine and p-nitrosophenol are formed. This is one of the best methods of preparing pure secondary amines.



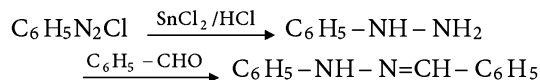
HCOOH reduces Tollen's reagent and 1° amine answers carbylamine test

75. 1° amines react with aldehydes to form aldimines or Schiff's bases



76. On heating quaternary ammonium hydroxide elimination reaction takes place. The elimination follows Hofmann rule, according to which the predominant alkene formed will be the least substituted alkene. About 98% of alkene formed in the above case is ethylene

77. Reduction of benzene diazonium chloride with SnCl_2 and HCl gives phenyl hydrazine which reacts with benzaldehyde to form phenyl hydrazone of benzaldehyde

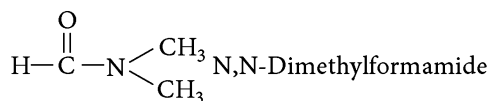


78. Triphenylamine is a very weak base and it is almost neutral, as the central nitrogen in triphenylamine is bonded with three phenyl groups.

79. (b) Alanine exists as a Zwitter ion at the isoelectric point.

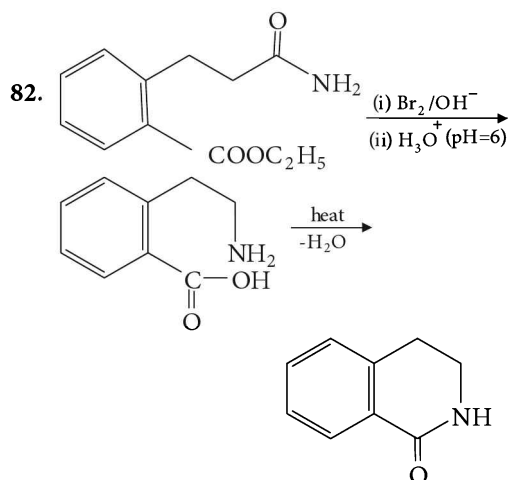
80. Benzamide on dehydration with P_2O_5 gives benzonitrile or phenyl cyanide, which on reduction gives benzylamine. This on treatment with one mole of CH_3I undergoes N-methylation to give N-methylbenzylamine.

81. Compound (A) is N,N-dimethylformamide (DMF).

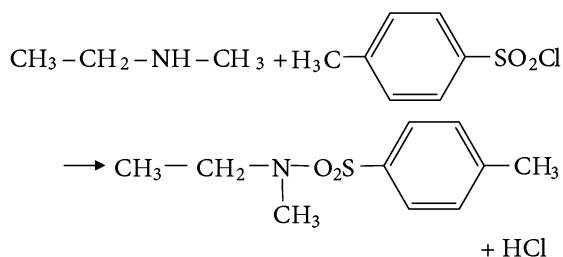


undergoes hydrolysis to give $\text{H}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{OH}$ and $\text{HN}(\text{CH}_3)_2$ (dimethyl amine)

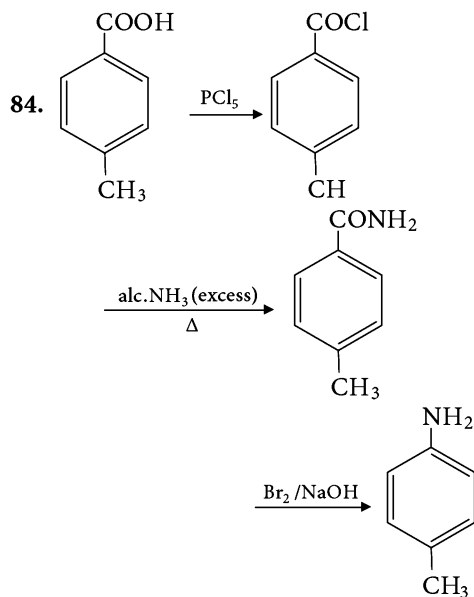
6.64 Amines, Aminoacids and Peptides



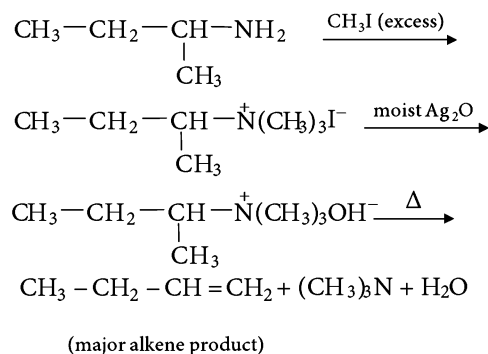
83. Secondary amines react with p-toluene sulphonyl chloride to form a sulphonamide derivative which is insoluble in aqueous alkali



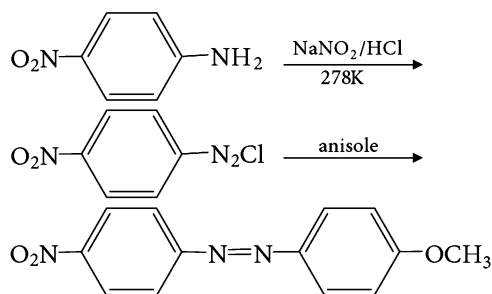
The sulphonamide derivative formed by 1° amine is soluble in NaOH solution while 3° amines do not react with p-toluene sulphonyl chloride



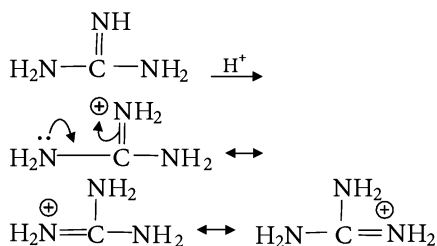
85. Exhaustive methylation of 1° amine with CH_3I gives quaternary ammonium iodide which is converted to quaternary ammonium hydroxide by treating with moist silver oxide. Quaternary ammonium hydroxide on heating undergoes elimination. The major alkene formed will be the less substituted alkene (Hofmann rule)



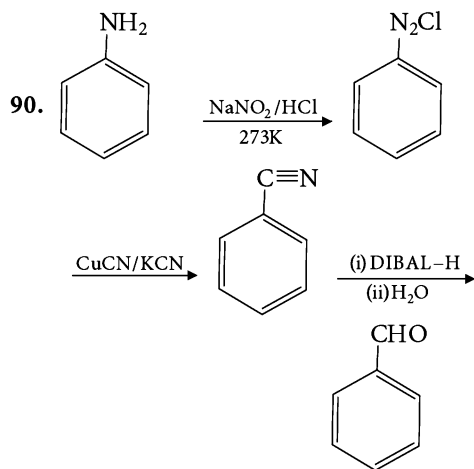
86. Piperidine (IV) is a cyclic secondary amine and the lone pair is in a sp^3 hybridised orbital. So it is most basic. Pyrrole (III) is the least basic compound because the lone pair on nitrogen is involved in giving it aromatic stability. Pyridine (II) is more basic than aniline because the lone pair of nitrogen in pyridine is not delocalized as in aniline
87. Diazotisation of p-nitroaniline gives p-nitrobenzene diazonium chloride and this couples with anisole giving mainly the azo dye (C)



88. The compound given in (b) is guanidine. It is a very strong base because the cation formed by protonation of guanidine is considerably stabilised by resonance



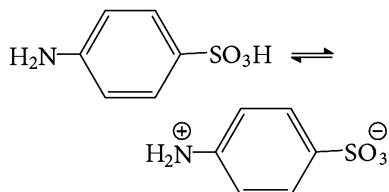
89. Maximum number of tetrapeptides that can be prepared from 10 different amino acids is $10^4 = 10,000$



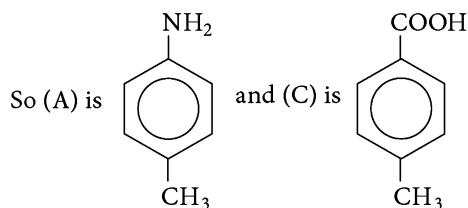
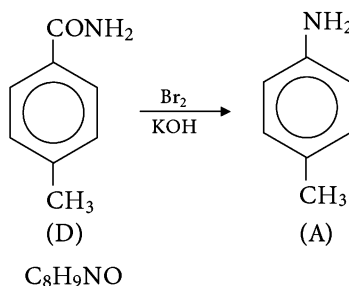
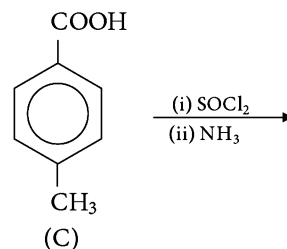
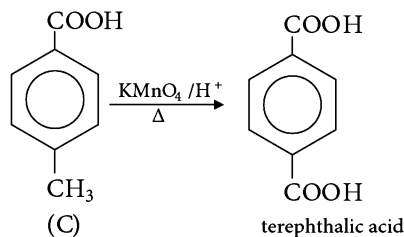
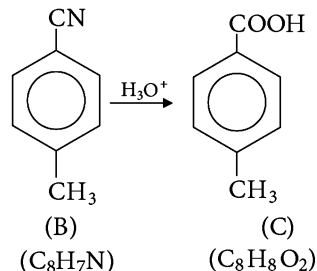
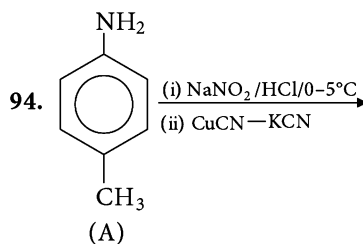
91. Both statements are correct, but statement 2 is not the correct reason for statement 1

Sulphanilic acid is prepared by the sulphonation of aniline. At lower temperature, aniline forms the salt, anilinium hydrogen sulphate which on heating gives a mixture ortho and para amino benzene sulphonic acid. The major product will be the para isomer

p-aminobenzene sulphonic acid (sulphanilic acid) exists as a dipolar ion (Zwitter ion)

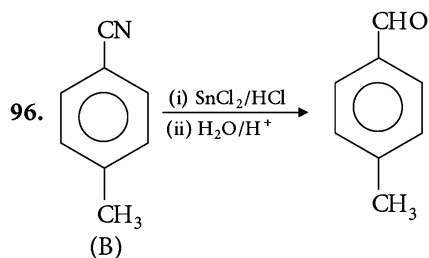
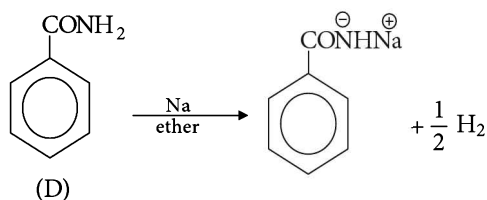


92. Statement 1 is correct, but statement 2 is wrong. Gabriel's phthalimide synthesis can be used only for the synthesis of aliphatic primary amines.
93. Statement 1 is wrong whereas statement 2 is correct. o-Toluidine is less basic than aniline due to ortho effect

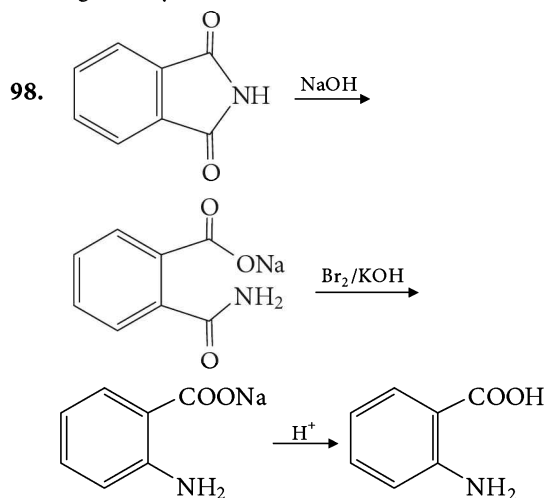


6.66 Amines, Aminoacids and Peptides

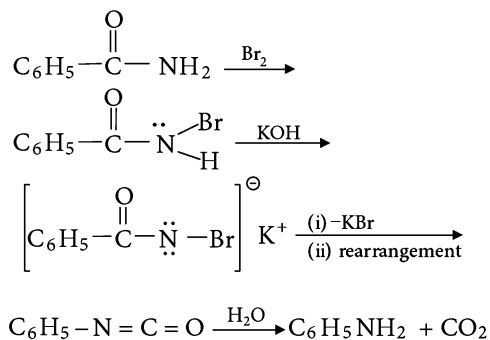
95. Amides react with sodium in ether to form the corresponding sodium salt of amide with the evolution of hydrogen.



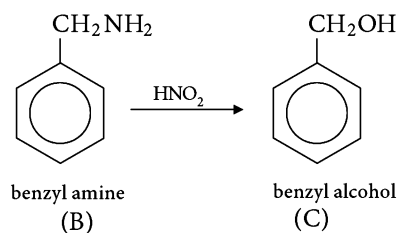
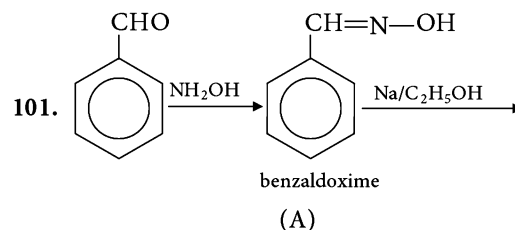
97. When excess alcohol vapours are mixed with ammonia and passed over heated alumina, a mixture of 1°, 2° and 3° amines is formed. All other methods a, b and c give only 1° amines



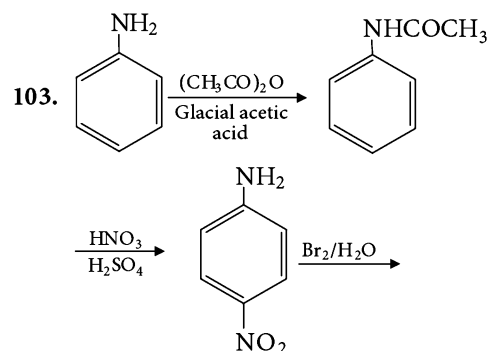
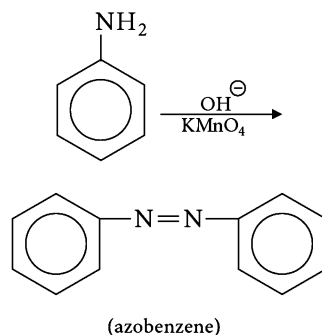
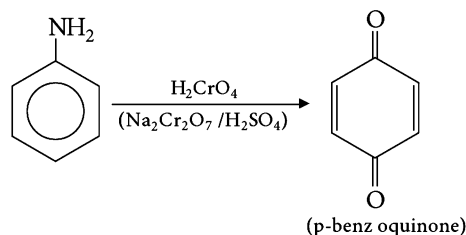
99. The reaction is Hofmann's bromamide reaction. The reaction is believed to take place as follows

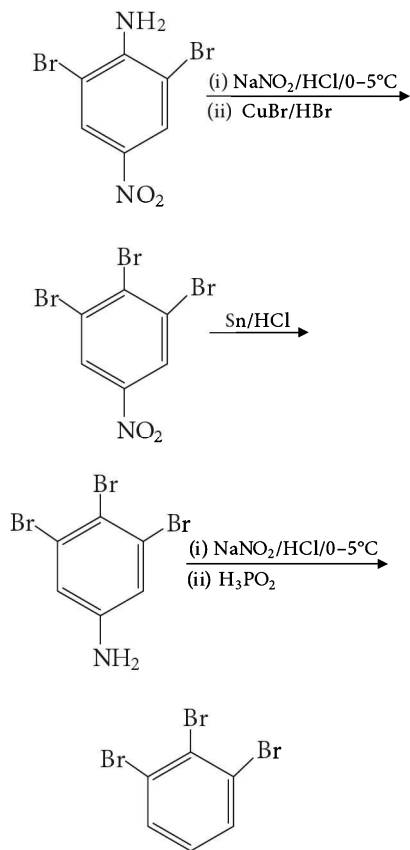


Additional Practice Exercise

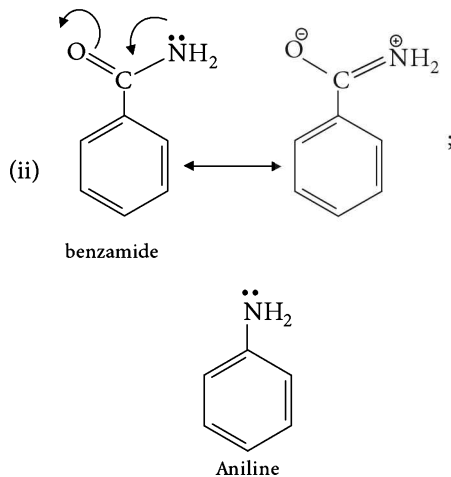


102. The oxidation products of aniline depends on the nature of oxidizing agent.

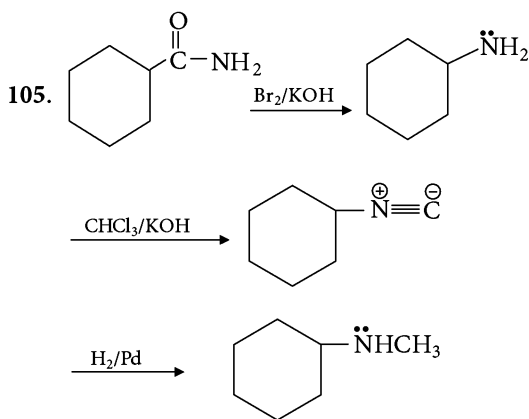




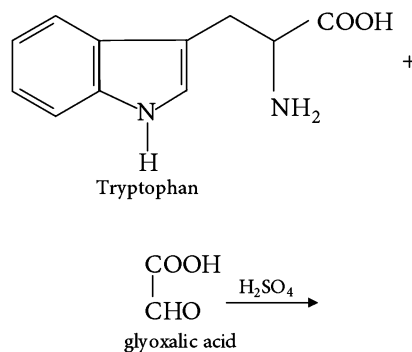
104. (i) CH_3CN is acetonitrile. This is used as a solvent in many organic reactions because it is not quite reactive with other reagents under mild acidic or basic conditions. Acetonitrile is fairly a strong polar solvent and so a variety of compounds readily dissolve in acetonitrile. The boiling point of acetonitrile is 82°C and can easily be removed during the work up. It is readily miscible with water and other organic solvents.



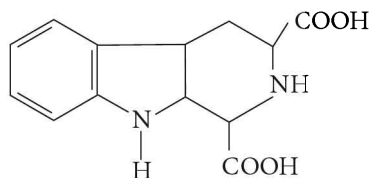
In benzamide, the electrons on the amide nitrogen is being drawn by the carbonyl group and nitrogen assumes a partial positive charge by resonance. So the lone pair on nitrogen is no longer available for protonation and hence it is not soluble as a base in an acid. On the other hand, in aniline, the lone pair of electrons, though partially delocalized into the benzene ring, is still available for protonation by an acid. Hence aniline dissolves in acid like HCl forming anilinium chloride salt.



106. (i) Biuret test: On adding a dilute solution of CuSO_4 to an alkaline solution of protein, a red or a violet colour is developed. This is due to the formation of biuret ($\text{H}_2\text{NCONHCONH}_2$) and indicates the presence of peptide ($-\text{CO}-\text{NH}$) linkage.
- (ii) Xanthoproteic test: When a protein solution is warmed with concentrated nitric acid, a yellow colour is obtained. The formation of yellow colour is due to the nitration of benzene ring in phenylalanine, tyrosine or tryptophan.
- (iii) Hopkins-Cole test: When a protein containing tryptophan is mixed with glyoxalic acid and when conc. H_2SO_4 is allowed to slide along the test tube, a bluish violet colour is observed.

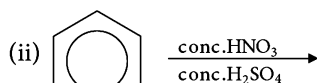
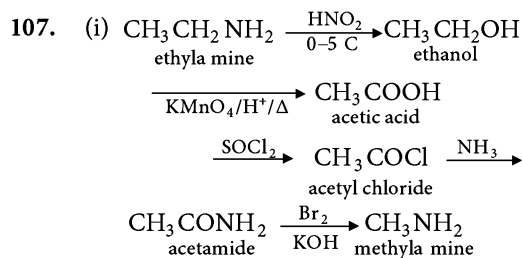
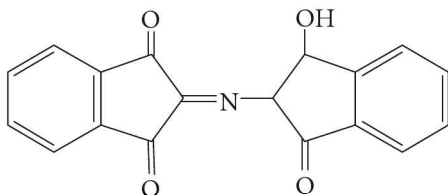


6.68 Amines, Aminoacids and Peptides

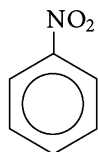


(Bluish violet colour)

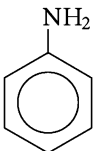
- (iv) **Ninhydrin test:** This test is given by all proteins. When a solution of a protein is treated with ninhydrin, a violet or deep blue colour is formed, due to the formation of



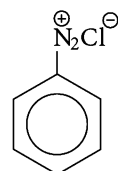
benzene



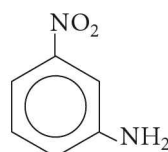
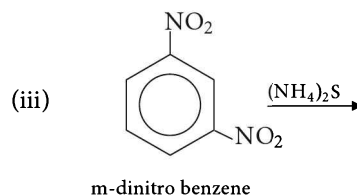
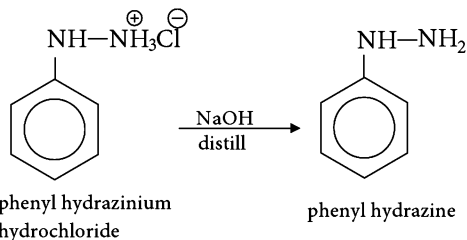
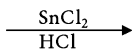
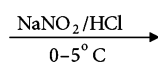
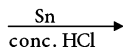
nitrobenzene



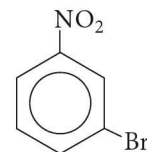
aniline



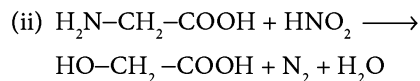
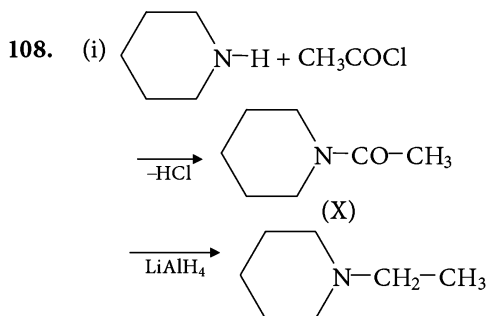
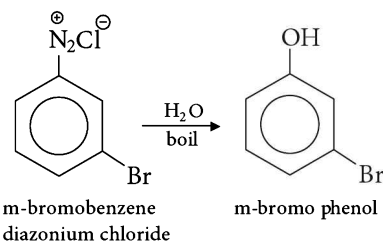
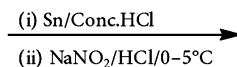
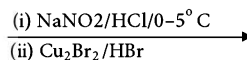
benzene
diazonium chloride

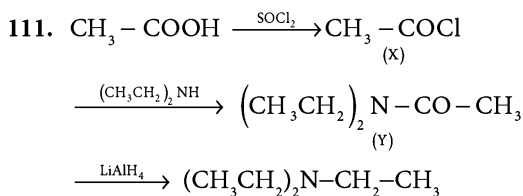
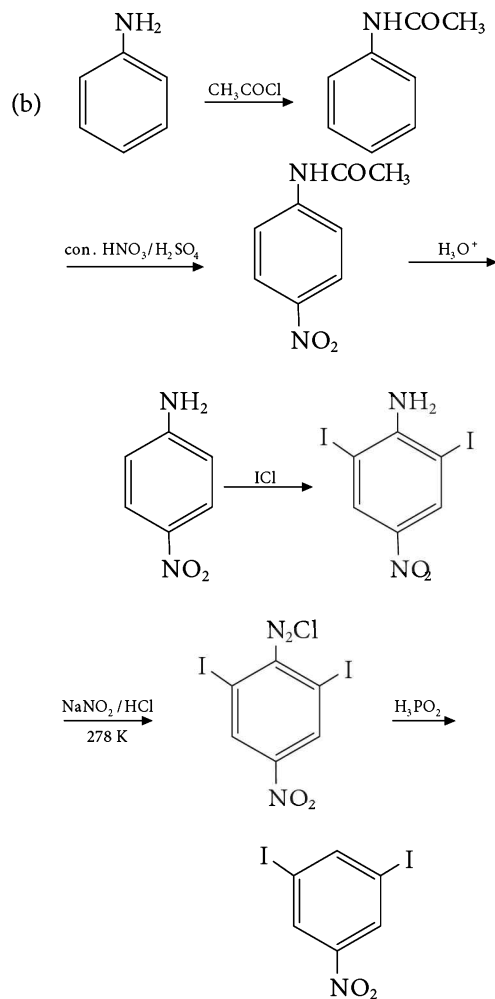
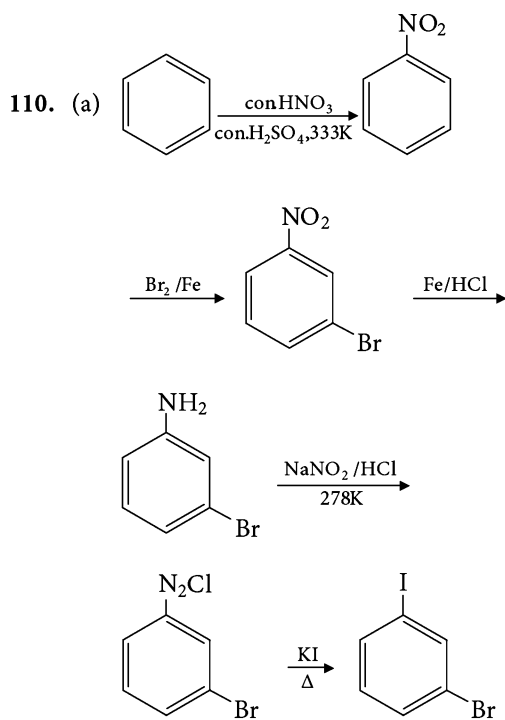
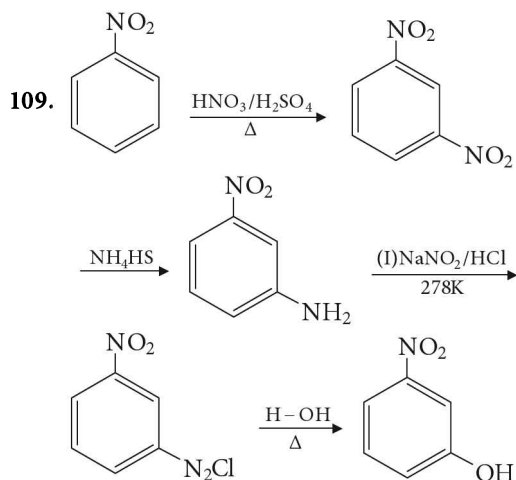
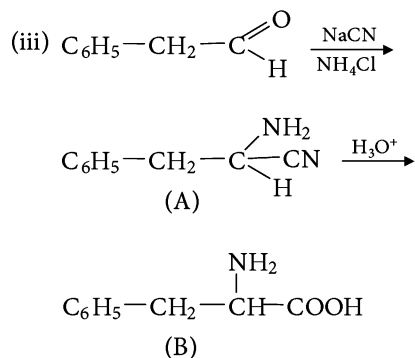


m-nitro aniline



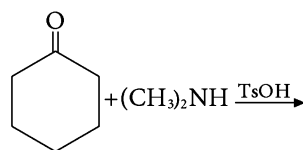
m-bromo nito benzene



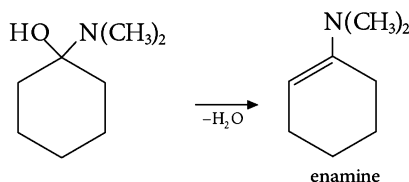


112. It is Hofmann bromamide reaction. Hofmann bromamide reaction involves an intramolecular rearrangement. So no cross products are formed even if we mix together two different amides in the reaction

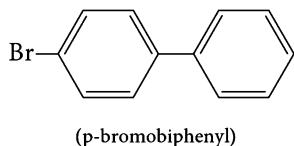
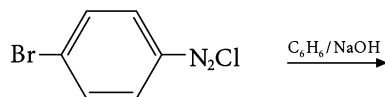
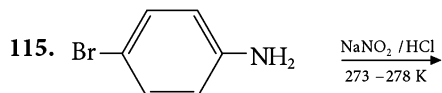
113. Ketones containing α -hydrogen when treated with secondary amines form enamines



6.70 Amines, Aminoacids and Peptides

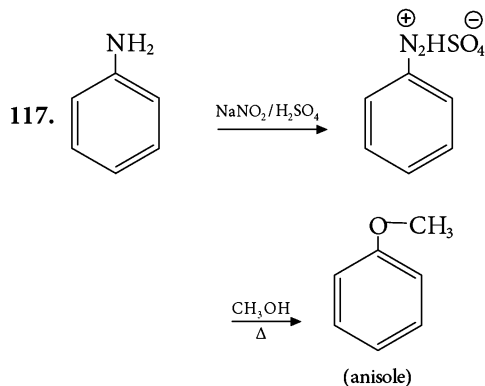


114. 2, 4-dinitrofluorobenzene is used in Sanger's method for the determination of N-terminal amino acid of a protein or peptide



The second step in the reaction is Gomberg reaction

116. Strong reducing agents such as Zn/HCl reduce benzene diazonium chloride to aniline

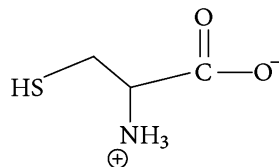


If ethanol is used benzene and $C_6H_5-O-C_2H_5$ are formed as products

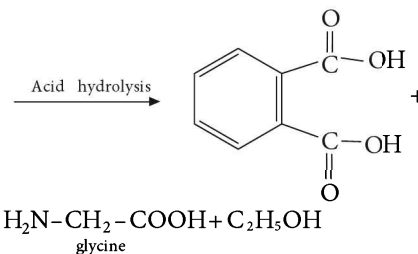
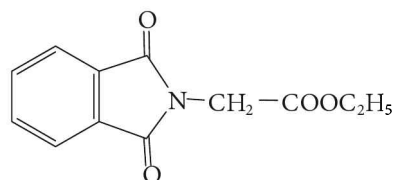
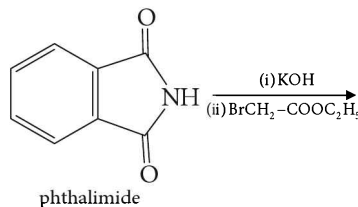
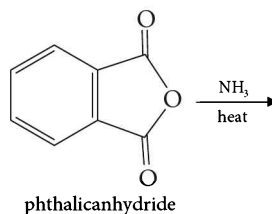
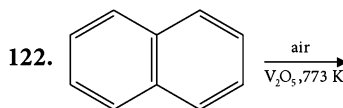
118. Penta-1,4-diene is first obtained which rearranges to form conjugated penta-1,3-diene.

119. The significant difference in the strength of the bases is the type of hybrid orbitals used by the carbon to the amino group. The more s-character it has, the more electron withdrawing inductive effect thereby base weakening effect. The increasing order of electron withdrawal by the carbon and decreasing order of base strength will be observed in (a).

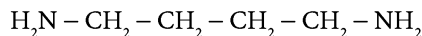
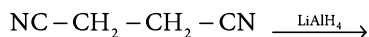
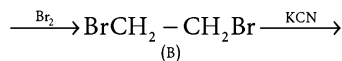
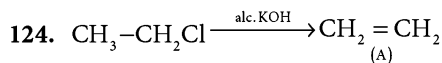
120. Isoelectric point of the aminoacid is $\frac{1.8 + 8.2}{2} = 5$
At the P_1 , it exists as neutral dipolar ion.



121. The lone pair of electrons on nitrogen is not involved in resonance and hence lone pair availability is more on (2). So (2) is more basic. The lone pair on (1) is involved in resonance and it gives aromatic stability to the ring.



123. (d) Isocyanides on acid hydrolysis give 1° amine and formic acid

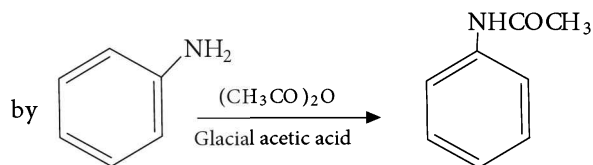
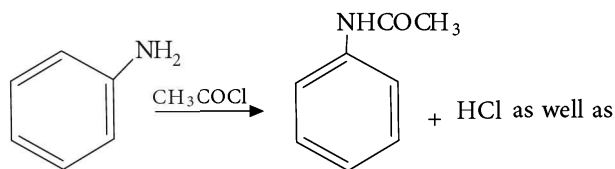


125. In strong acid medium aniline is converted anilinium ion. Since $-\text{NH}_3^+$ is electron withdrawing and deactivating, it does not undergo coupling reaction

126. n-propylamine ($\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{NH}_2$) molecules are associated by intermolecular hydrogen bonding. So higher energy is required to separate the molecules and the boiling point is high. Since there is no hydrogen directly attached to nitrogen in trimethylamine ($(\text{CH}_3)_3\text{N}$), there is no hydrogen bonding possible so its boiling point is lower

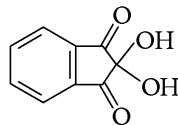
127. Statement 1 is incorrect while statement 2 is correct. Benzene diazonium chloride undergoes coupling reaction with alkaline solution of phenol to form an orange red coloured azo dye. The colour of the dye is due to extended conjugation

128. Both statements are correct and the reasoning given is the correct explanation for the statement 1. Acetanilide can be made from aniline by



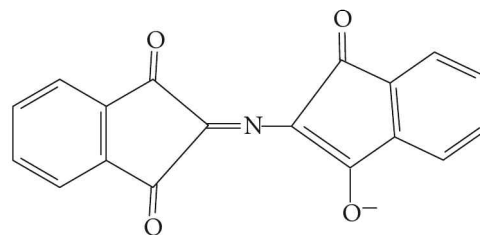
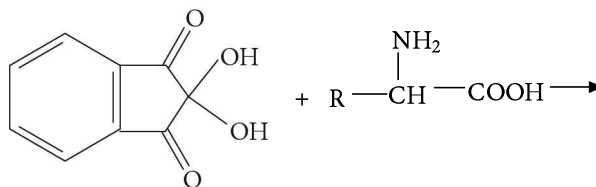
Between the two reagents acetyl chloride is more reactive because of the presence of a good leaving group.

129. Both statement 1 and 2 and reasoning are correct. Statement 2 is the correct explanation for the assertion made. ninhydrin is

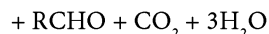


Generally gem diols are not stable, and they readily decompose. However ninhydrin is a very stable compound because of the two carbonyl groups at the α -positions.

When an aqueous solution of an amino acid is treated with ninhydrin, a violet colour is produced.

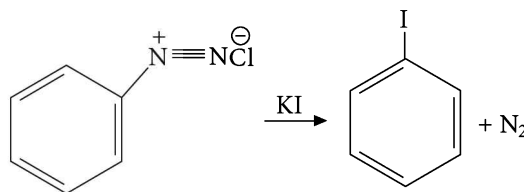


(Violet colouration)



130. Both statements are correct and the statement 2 is the correct explanation for the statement 1. In Sandmeyer's reaction, benzene diazonium chloride is converted to chlorobenzene or bromobenzene by treatment of the diazonium salt with cuprous halide in the presence of hydrohalic acid.

However, in the synthesis of iodobenzene from the diazonium salt, KI will be enough to effect the conversion.



I^- is a strong nucleophile to remove the nitrogen from diazonium and get substituted to form iodobenzene.

6.72 Amines, Aminoacids and Peptides

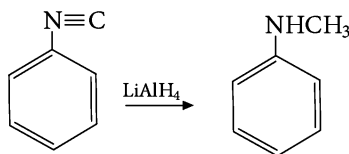
131. $RX \rightarrow RCN$ is not possible in aryl halides, since chlorobenzene do not undergo S_N1 or S_N2 reactions.

132. $RCH_2CH_2Br \xrightarrow[-NaBr]{NaN_3} RCH_2CH_2N_3$ is an example of S_N2 reaction.

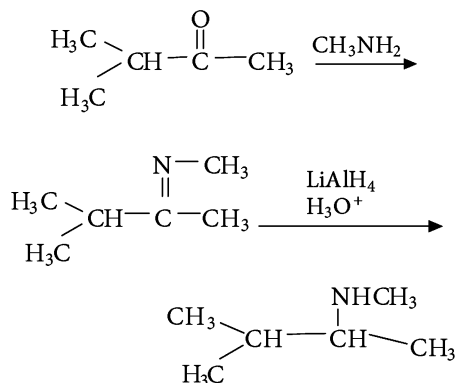
133. (i) < (ii) < (iii) < (iv).

Aromatic amines are less basic than aliphatic amines. In (iii), fluorine being electronegative, pulls the electrons away from nitrogen and reduces basicity.

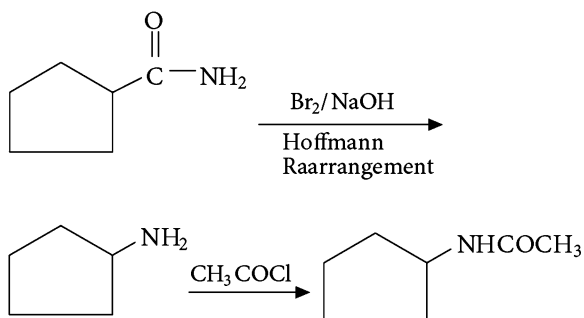
134. Phenyl carbylamine is phenyl isocyanide. This on reduction gives N-methyl aniline



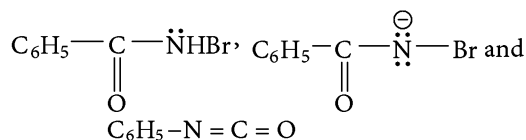
135. A Schiff's base is formed initially which undergoes reduction to give the secondary amine



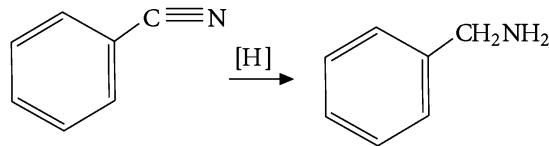
136. The reaction which is not correctly represented is (b)
The correct representation will be



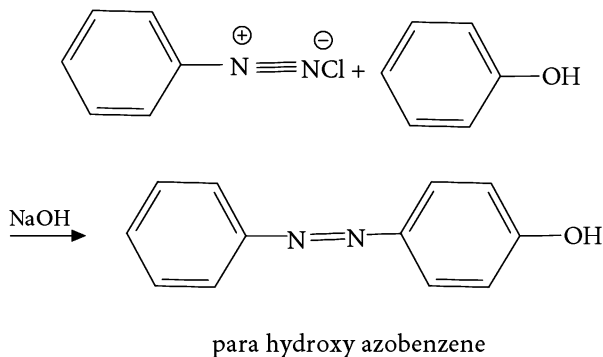
137. The reaction represented is Hoffmann rearrangement and the intermediate involved are



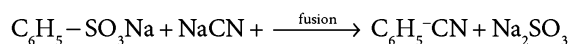
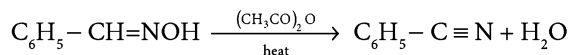
138. (B) is phenylcyanide. This on reduction gives benzylamine



139. (D) is benzene diazonium chloride and this undergoes coupling reaction with phenol to give para hydroxy azobenzene (a red dye)



140. $C_6H_5N_2Cl \xrightarrow{CuCN/KCN} C_6H_5-CN + N_2 Cl^-$
(sandmeyer)

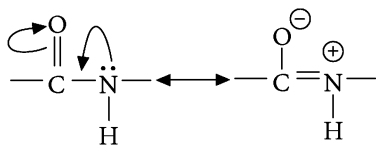


141. Tyrosine contains a phenolic group and hence it gives violet colouration with neutral $FeCl_3$ solution. Lysine contains $2NH_2$ groups and one $COOH$ group. So it is a basic amino acid

142. Benzylamine ($C_6H_5-CH_2NCH_3$) and alanine ($CH_3-CH(NH_2)-COOH$) contain primary amino group

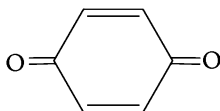
linked to sp^3 hybridised carbon. Hence these compounds liberate N_2 when treated with nitrous acid at any temperature

143. C-N bond length in peptides is slightly smaller because of the partial double bond character due to resonance

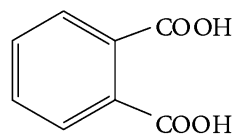
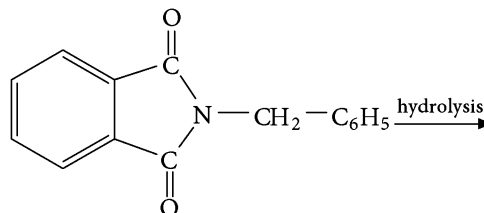
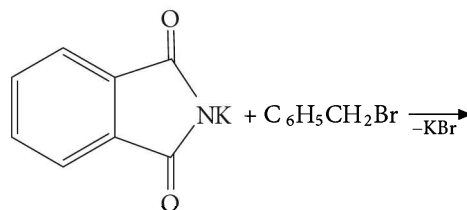
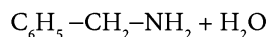


Hence statement (a) is correct. Atoms of $\text{—}\overset{\text{O}}{\parallel}\text{C—NH—}$ group are in the same plane. Hence statement (b) is not correct. Statements (c) and (d) are also correct. Glutamic acid is an acidic amino acid. Hence its iso-electric point is about 3.2

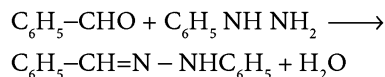
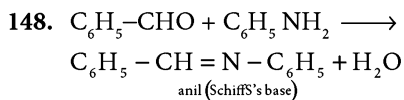
- 144 Aniline, quinol and p-aminophenol on oxidation with acid dichromate give para benzoquinone



145. Reduction of benzene diazonium chloride with SnCl_2/HCl or Na_2SO_3 give phenyl hydrazine ($\text{C}_6\text{H}_5\text{NHNH}_2$). Reduction with Zn and HCl gives aniline. So (A) is not correct



147. Diazonium salts couple with aromatic compounds containing activating groups



CHAPTER

7

CARBOHYDRATES, POLYMERS AND PRACTICAL ORGANIC CHEMISTRY

■■ CHAPTER OUTLINE

Preview

STUDY MATERIAL

Carbohydrates

Classification of Carbohydrates

Glucose

Reactions of Glucose

Structure of Fructose

Sucrose

Starch

Cellulose

- Concept Strands (1-2)

Polymers

Condensation Polymers

Addition polymers

- Concept Strands (3-4)

Practical Organic Chemistry

Detection of Elements-Qualitative Analysis

Detection and Identification of the Functional Groups

Chemical Methods of Separation of Mono Functional Organic Compounds from Binary Mixtures

Analysis of Organic Mixtures

Concept Strands (5-7)

TOPIC GRIP

- Subjective Questions (10)
- Straight Objective Type Questions (5)
- Assertion-Reason Type Questions (5)
- Linked Comprehension Type Questions (6)
- Multiple Correct Objective Type Questions (3)
- Matrix-Match Type Question (1)

IIT ASSIGNMENT EXERCISE

- Straight Objective Type Questions (60)
- Assertion-Reason Type Questions (3)
- Linked Comprehension Type Questions (3)
- Multiple Correct Objective Type Questions (3)
- Matrix-Match Type Question (1)

ADDITIONAL PRACTICE EXERCISE

- Subjective Questions (5)
- Straight Objective Type Questions (10)
- Assertion-Reason Type Questions (5)
- Linked Comprehension Type Questions (6)
- Multiple Correct Objective Type Questions (3)
- Matrix-Match Type Questions (1)

CARBOHYDRATES

Carbohydrates are an important group of biomolecules made up of three elements carbon, hydrogen and oxygen. Most of the carbohydrates can be represented by the general formula $C_x(H_2O)_y$ where, x and y are whole numbers. Carbohydrates are also known as saccharides.

Carbohydrates contain essentially two main functional groups namely the carbonyl group and the hydroxyl groups. Carbohydrates are made in natural green plants by a process known as photosynthesis under the influence of chlorophyll and sunlight. By photosynthesis, CO_2 is converted to glucose. In the process of photosynthesis, oxygen is liberated.

Carbohydrates are defined as polyhydroxy aldehydes or ketones or substances which yield these on hydrolysis and they may have one or more chiral carbons in the structure.

The names of simple carbohydrates end in -ose. Those with aldehyde structure are known as aldoses and those with ketone structure are known as ketoses. They are further classified depending upon the number of carbon atoms present. For example, a sugar with five carbons with an aldehyde function is known as an aldopentose. A sugar with six carbons including a ketone function is known as a ketohexose.

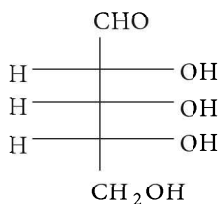
CLASSIFICATION OF CARBOHYDRATES

Carbohydrates are classified into three categories depending on their behaviour towards hydrolysis.

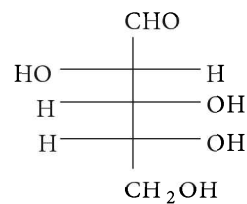
A carbohydrate that cannot be hydrolyzed to simpler compounds is called a **monosaccharide**. A carbohydrate which can be hydrolyzed to give two to ten units of monosaccharides is called an **oligosaccharide** and can be further classified as a disaccharide (two same or different monosaccharides on hydrolysis), trisaccharide, etc. A carbohydrate which can be broken down by hydrolysis to give a large number of monosaccharides is known as a **polysaccharide**.

Monosaccharides and oligosaccharides are crystalline solids, highly soluble in water and sweet in taste. They are generally called sugars. They may be reducing or non reducing.

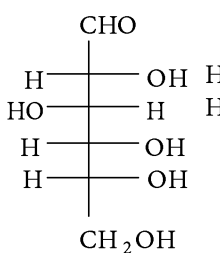
Carbohydrates which reduce Fehling's solution or Tollens' solution are known as reducing sugars. Glucose is an aldohexose and is a reducing sugar. Fructose is also a reducing sugar though it is a ketohexose.



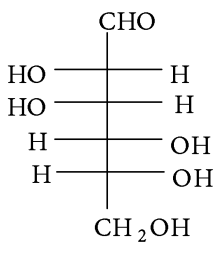
D-ribose
(aldopentose)



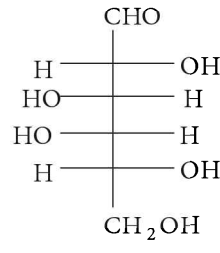
D-arabinose
(aldopentose)



D-glucose
(aldohexose)

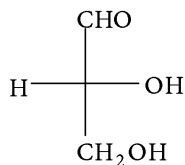


D-mannose
(aldohexose)

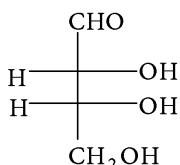


D-galactose
(aldohexose)

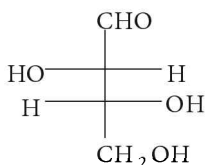
Examples of monosaccharides



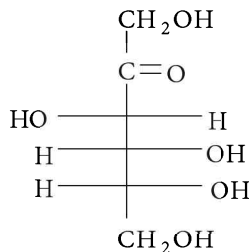
D-glyceraldehyde
(aldotriose)



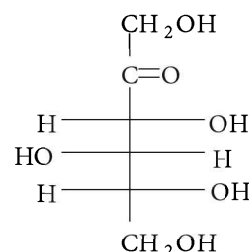
D-erythrose
(aldotetrose)



D-threose
(aldotetrose)

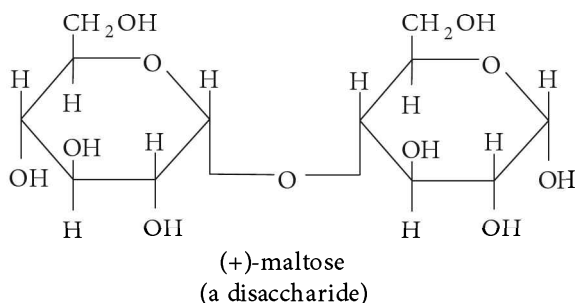
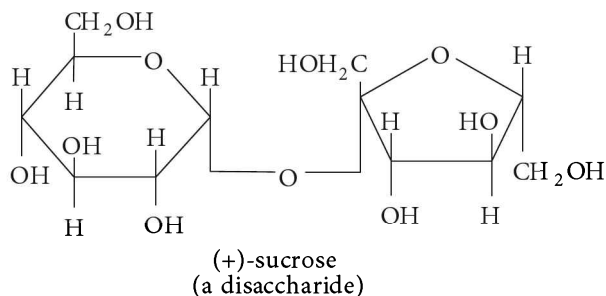


D-fructose
(ketohexose)



D-sorbose
(ketohexose)

Examples of disaccharides



Polysaccharides

Polysaccharides are high polymers of monosaccharide units and have molecular weights that may range from a few thousand to several millions. Many polysaccharides contain 80 to 100 monosaccharide units. Some materials like cellulose may contain about 2000 glucose units per molecule. Many monosaccharide units are joined together by glycosidic linkages. Cellulose and starch are the most common polysaccharides.

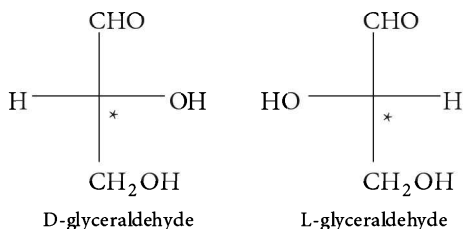
Different types of polysaccharides are linear polysaccharide, branched polysaccharide and cyclic polysaccharide.

GLUCOSE

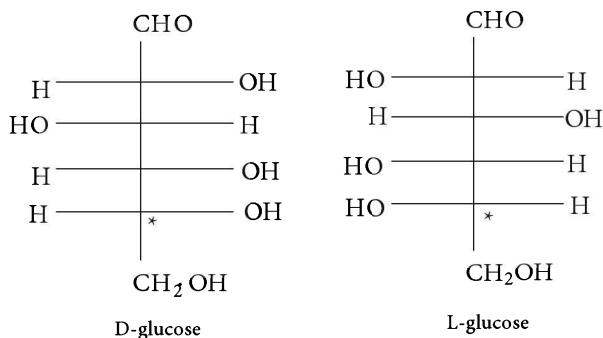
D and L – designations for glucose

The symbols D and L refer to the configuration of the molecule. D- glyceraldehyde and L- glyceraldehyde serve as reference points for the assignment of relative configuration to all the monosaccharides.

D-monosaccharide has the same configuration at its penultimate carbon (coming from the top in a vertical arrangement) as D-glyceraldehyde which has a chiral carbon with the most oxidized group on the top, most reduced group at the bottom, –H to its left and –OH on the right. Similarly, an L-monosaccharide has the same configuration as L-glyceraldehyde with the most oxidized group on the top, most reduced group on the bottom –OH on its left and –H on the right on the chiral carbon. So the D-and L-glyceraldehydes are represented by Fischer convention as follows.



On this basis, D-and L-configurations are assigned for glucose as shown.



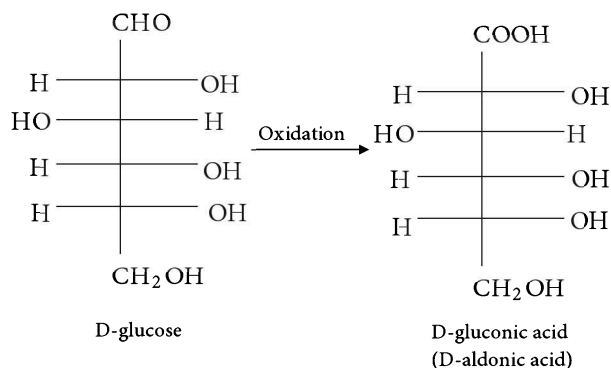
Glucose has a molecular formula $C_6H_{12}O_6$. It has four chiral centres. Glucose is a reducing sugar. It is an aldohexose. D- glucose is one of the sixteen stereoisomers, that can arise from four chiral centres, which are aldohexoses. D- glucose is also known as dextrose since it is dextrorotatory.

REACTIONS OF GLUCOSE

Oxidation

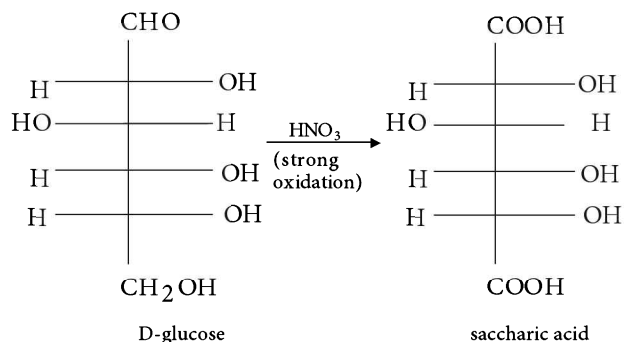
(a) With mild oxidizing agents

Mild oxidising agents such as Benedict's solution (copper sulphate with alkaline sodium citrate), Fehling's solution (copper sulphate with alkaline sodium potassium tartarate) and Tollens' reagent (ammoniacal AgNO_3 solution) oxidize glucose to gluconic acid. Other oxidizing agents like bromine water or iodine under alkaline conditions (sodium hypoiodite) also oxidize glucose to gluconic acid. Gluconic acid is also known as aldonic acid.



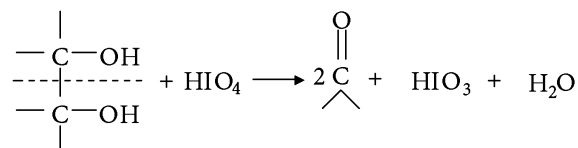
(b) With strong oxidizing agents

Vigorous or strong oxidation of aldose using nitric acid gives an aldaric acid. In the case of glucose, the product of oxidation is saccharic acid. Under strong oxidative conditions, both the end groups namely the aldehyde group in the first carbon atom and the primary alcohol group in the end carbon atom are oxidized to acids.



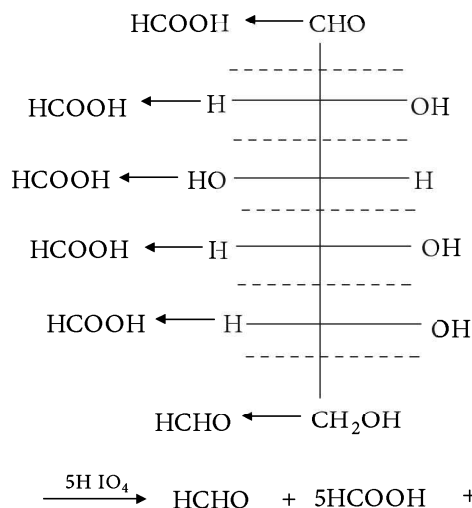
(c) Oxidative cleavage with HIO_4

Treatment of monosaccharides like glucose with periodic acid (HIO_4) results in oxidative cleavages, breaks the carbon-carbon bonds and produces aldehydes, ketones or acids. The stoichiometry of general reaction of the cleavage of a vicinal diol is



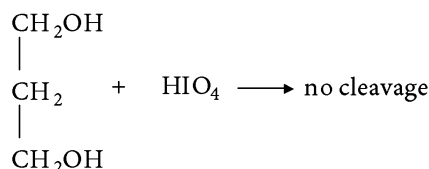
When there are three or more continuous $-\text{OH}$ groups, the internal ones are converted as formic acid.

When glucose is treated with HIO_4 , the following reaction occurs.



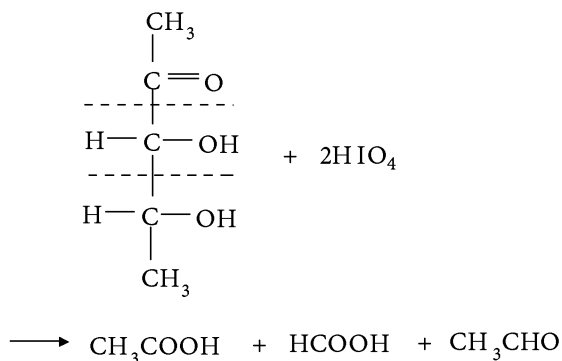
So one mole of glucose consumes five moles of periodic acid forming one mole of HCHO and five moles of HCOOH .

Periodic acid does not cleave compounds in which the hydroxy groups are separated by intervening $-\text{CH}_2-$ groups.



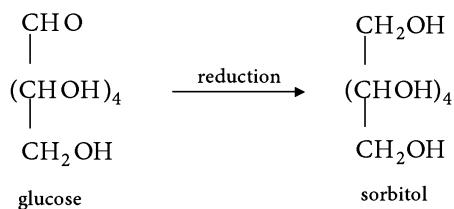
Oxidative cleavage occurs when an -OH group is adjacent to the carbonyl group of an aldehyde or ketone, but not that of an ester or an acid.

For example

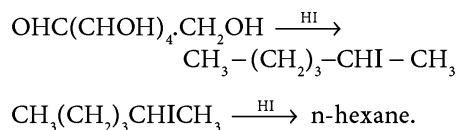


Reduction

- (a) When glucose is reduced with sodium amalgam, sodium borohydride (NaBH_4), high pressure catalytic hydrogenation, or electrolytic reduction in acid medium, the product obtained is an alcohol (sorbitol).

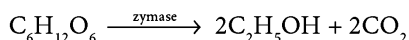


- (b) Under strong reducing conditions using hydroiodic acid (HI) and red phosphorus at about 100°C , glucose gives 2-iodohexane. Continuous heating with the reducing agent gives n-hexane.



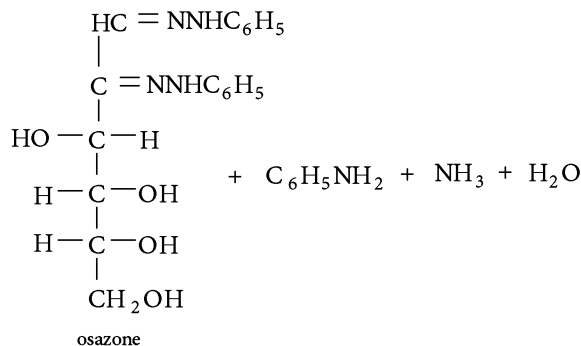
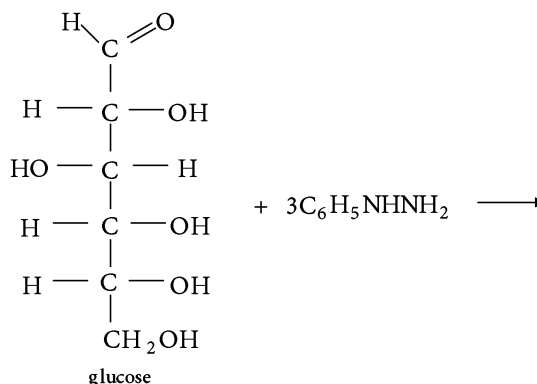
Fermentation reaction

Dilute solution of glucose undergoes fermentation by yeast to give ethanol.

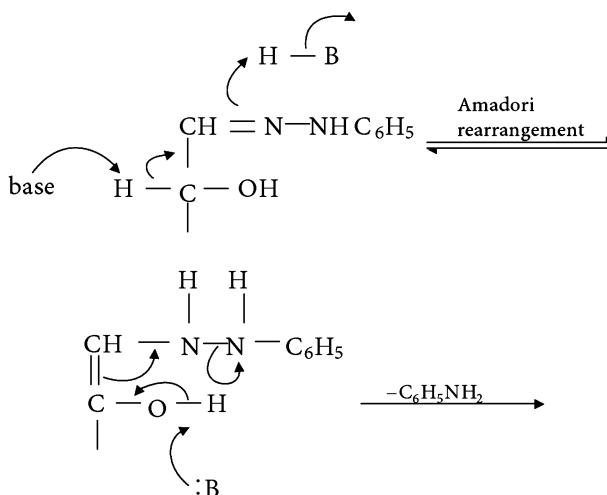


Reaction with phenylhydrazine

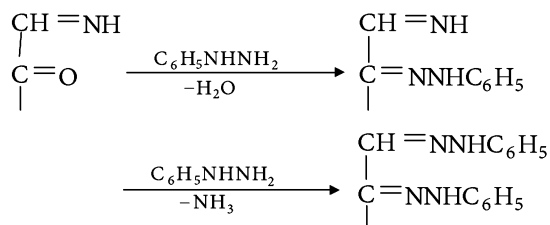
Glucose reacts with phenylhydrazine to form phenylhydrazone. The aldehyde group of glucose forms the phenylhydrazone. If excess phenylhydrazine is used, further reaction occurs to give an osazone, which contains two phenylhydrazine units per molecule of glucose.



Mechanism of osazone formation

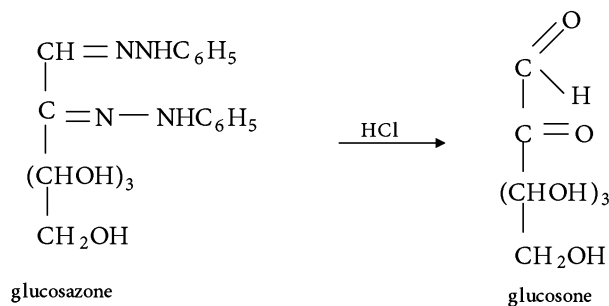


7.6 Carbohydrates, Polymers and Practical Organic Chemistry



According to the mechanism, the first step is the formation of glucose phenylhydrazone which then undergoes Ama-dori rearrangement. Osazone formation results in the loss of the stereocentre at carbon-2, but it does not affect the other stereo centres.

Removal of the phenylhydrazino groups by hydrolysis with hydrochloric acid yields a dicarbonyl compound (an aldehyde and a ketone) known as osone.



Reduction of glucosone with zinc and acetic acid reduces only the aldehyde group giving fructose.

Osazone formation destroys the configuration of the C-2 of glucose but does not affect the configuration of the rest of the molecule. Therefore, osazone formation is useful in identifying the configuration of the carbohydrates.

Mutarotation

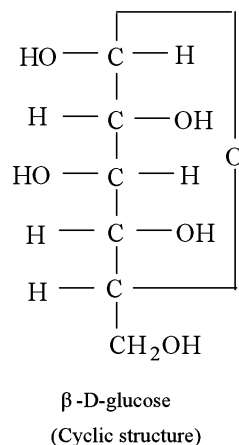
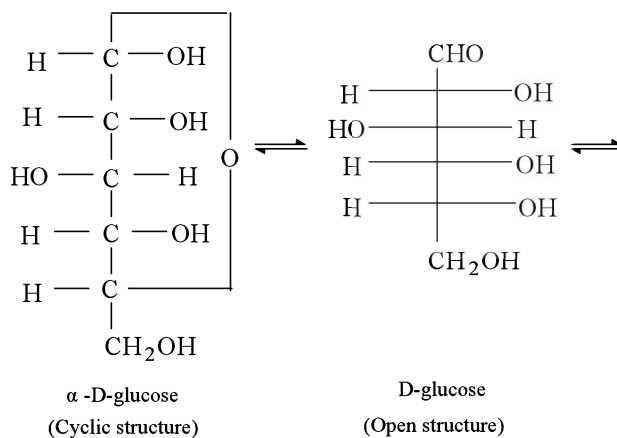
When D-glucose is crystallized from a concentrated solution at 30°C, it gives a form of glucose called α-D-glucose. A freshly prepared solution of α-D-glucose has a specific rotation of +111°. When this solution is allowed to stand, the specific rotation gradually falls to +52.5°. However, if D-glucose is crystallized from a saturated solution at a temperature above 98°C, another form of glucose called β-D-glucose is obtained. Fresh solution of β-D-glucose has a specific rotation of +19.2° and it gradually rises to +52.5° on keeping.

The two forms of glucose are known as anomers of glucose as these two forms differ in their stereochemistry

at carbon-1. The specific rotations of the two solutions change slowly and reach a constant value. The equilibrium is reached faster if a trace of acid or base catalyst is present.

The change in specific rotation of an optically active compound due to the interconversion of one anomer to the other (like two forms of glucose), on standing, is called mutarotation.

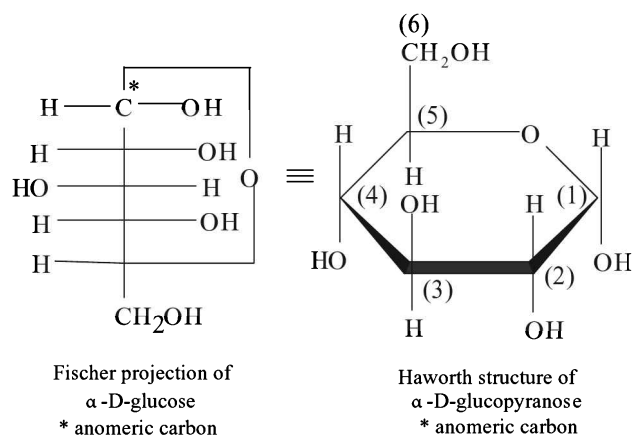
To explain mutarotation and the existence of two crystalline forms, a cyclic hemiacetal structure is assigned to glucose. Glucose forms a six membered ring by the interaction between the aldehyde group and the hydroxyl group at C-5



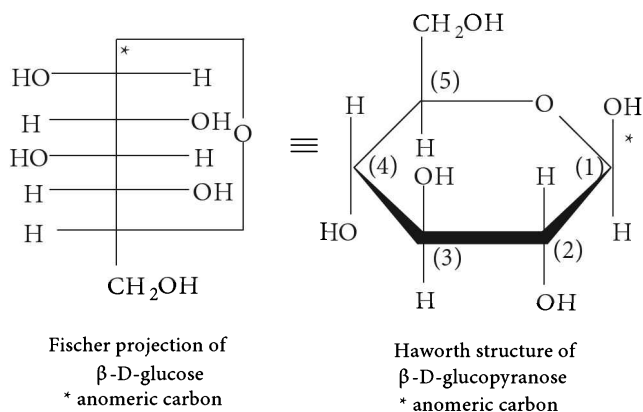
As a result of cyclization, the anomeric carbon (the first carbon from the top) (C1) becomes asymmetric and the newly formed -OH group can be either to the left or to the right in the projection formula, thereby resulting in two anomers.

A pair of diastereomers which differ in their configuration only at carbon-(1) are known as anomers and such a carbon is known as anomeric carbon.

The structure in which the hydroxyl group on carbon C-1, is to the right is designated as α -D-glucose while the structure with -OH group on carbon C-1 to the left is designated as β -D-glucose. These two forms are not mirror images and therefore they are not enantiomers. Fischer projection and Haworth projection of α -D-glucose and β -D-glucose are given below.

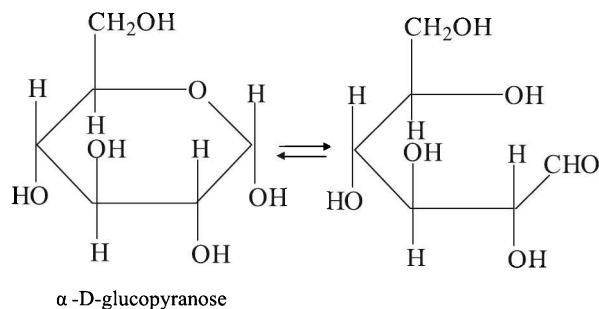


The lower thickened lines covering carbons 1 to 4 in Haworth structure are close to the observer.



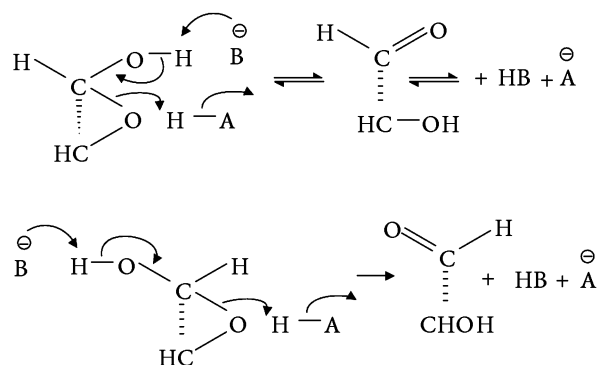
Explanation of mutarotation

The two crystalline forms of glucose are quite stable in the solid state. However, when either form is placed in solution, it slowly forms the other via the open chain aldehyde form. The final value of $+52.5^\circ$ corresponds to the equilibrium mixture of the two forms.



Mechanism of mutarotation

The generally accepted mechanism involves a simultaneous attack by an acid and a base to yield the open chain aldehyde form, which then recloses to the other form. Water, being amphoteric, can behave both as acid and base.

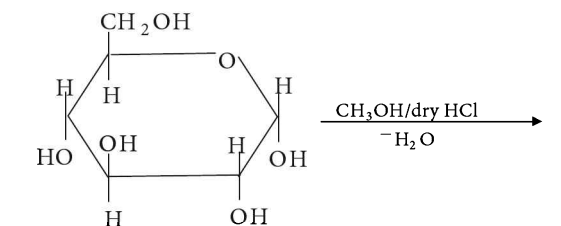


Methyl glucoside formation

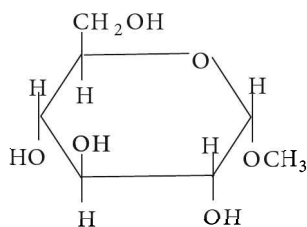
When D-glucose is treated with methanol in the presence of anhydrous hydrogen chloride, two isomers of methyl-D-glucoside are formed. This reaction results in the formation of anomeric methyl acetals. Anomeric carbon is the

7.8 Carbohydrates, Polymers and Practical Organic Chemistry

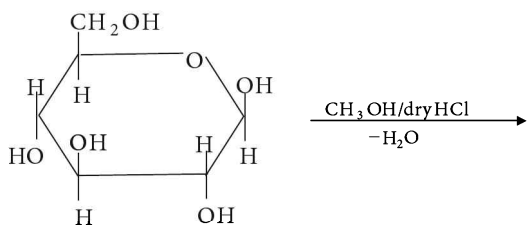
first chiral centre in the molecule when carbon atoms are arranged in a vertical row.



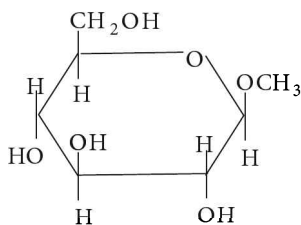
α -D-glucopyranose



methyl- α -D-glucopyranoside



β -D-glucopyranose



methyl- β -D-glucopyranoside

The methyl D-glucosides have been shown to have six membered ring structures and there are two forms namely methyl α -D-glucopyranoside and methyl β -D-glucopyranoside.

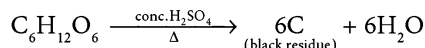
Formation of penta acetate

When glucose is treated with acetic anhydride or acetyl chloride in the presence of zinc chloride as catalyst, it forms glucose pentaacetate.

This experiment proves the presence of five free hydroxy groups in a molecule of glucose.

Dehydration

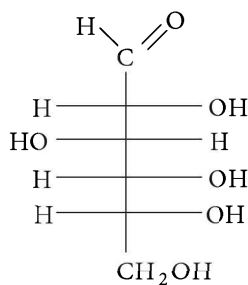
Glucose undergoes dehydration (loss of water) to give a black mass of carbon on treatment with conc. H_2SO_4 under warm conditions.



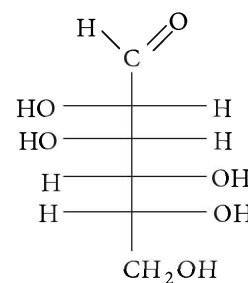
Epimerization

Aldoses which produce the same osazones must have the same configuration on all their asymmetric carbon atoms except the anomeric or first carbon atom. This is because only the aldehydic group and the α -carbon atom are involved in osazone formation. Such type of sugars are known as epimers. The change of configuration of one asymmetric carbon in one compound containing two or more asymmetric carbons is known as epimerization. A pair of diastereomeric aldoses that differ only in configuration about C-2 are called epimers.

Epimers will form same osazone when treated with excess phenyl hydrazine. For example, D-glucose and D-mannose are epimers.



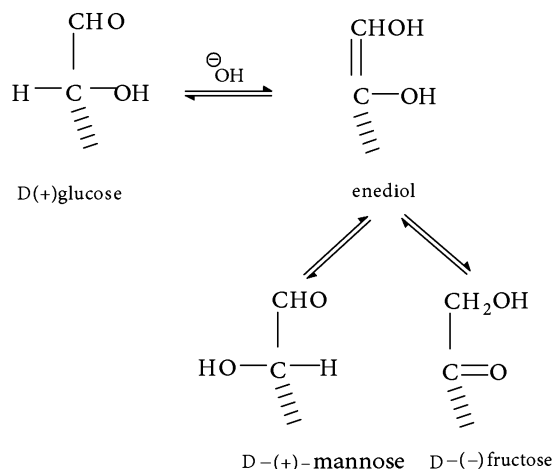
D-glucose



D-mannose

Lobry de Bruyn-van Ekenstein rearrangement

When glucose is treated with a dilute solution of an alkali, it undergoes reversible isomerisation to form an equilibrium mixture of D-glucose, D-fructose and D-mannose. This is called Lobry de Bruyn-van Ekenstein rearrangement. The rearrangement occurs through an enediol.



Cyclic structure

Ring formation of glucose is hemiacetal formation, one alcohol group of the sugar forming a hemiacetal with the

aldehyde group of the same molecule, thereby forming a cyclic structure.

The carbon atoms in the chain tends to form a loop. C_1 can be linked with C_4 to form a five membered ring known as furanose structure or C_1 can be linked with C_5 to form a six membered ring known as pyranose structure.

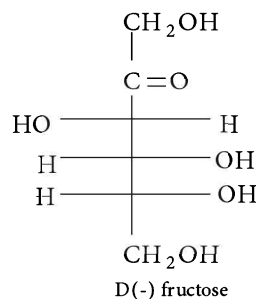
Later work has shown that glucose exists not as a five membered ring but as a six membered ring in two forms, α and β pyranose forms. Such pairs of stereoisomeric ring forms are known as anomers.

The cyclic structure of glucose accounts for the following facts.

- (i) The existence of two isomers of glucose, α and β -glucose.
- (ii) The existence of two isomers of methyl glucosides.
- (iii) Mutarotation
- (iv) The failure of glucose (and other aldoses) to give certain characteristic reactions of aldehydes like reaction with NH_3 , NaHSO_3 , Schiff's reagent, etc.

STRUCTURE OF FRUCTOSE

Fructose is an important ketohexose. Naturally occurring fructose is laevorotatory. It is D-(-)-fructose. Fructose also has a cyclic structure. Free fructose has a six membered ring structure and it exists in two forms just like glucose. Fructose is a reducing sugar and it shows mutarotation. In the combined state such as in sucrose, fructose exists in the furanose form (i.e., as five membered ring) D-glucose and D-fructose give the same osazone when treated with excess phenyl hydrazine because they have identical configurations on C-3, C-4 and C-5 carbon atoms.



SUCROSE

Sucrose is the common sugar. The molecular formula is $\text{C}_{12}\text{H}_{22}\text{O}_{11}$. It is a non-reducing sugar and does not reduce Tollen's or Fehlings solution. (+)-sucrose does not form an osazone, does not exist in anomeric forms and does not show mutarotation in solution. (+)-sucrose does not contain a free carbonyl group.

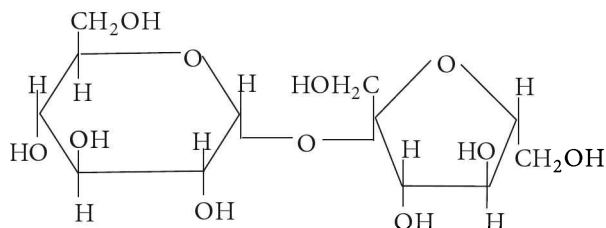
When (+)-sucrose is hydrolyzed by dil.aqueous acid, or under the influence of an enzyme invertase (obtained

from yeast), it yields equal amounts of D-(+)-glucose and D-(-)-fructose. As this hydrolysis is accompanied by a change of sign of rotation from $+66.5^\circ$ to -19.9° , it is called the inversion of (+)-sucrose, and the laevorotatory mixture of D-(+)-glucose and D-(-)-fructose obtained is called the invert sugar. Since D-(-) fructose has a greater specific rotation than D-(+) glucose, the resulting mixture is laevorotatory.

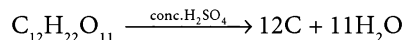
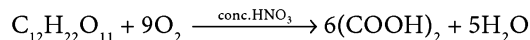
7.10 Carbohydrates, Polymers and Practical Organic Chemistry

(+)-sucrose is made up of D-glucose and D-fructose. There is no free carbonyl group in the form of an aldehyde or ketone in a molecule of sucrose. So sucrose must be a D-glucoside or a D-fructoside. The hexose (six carbon sugar) units are joined by a glycosidic linkage between C-1 of α -glucose and C-2 of β -fructose.

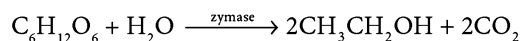
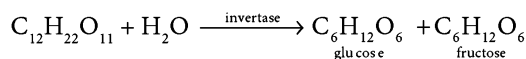
Sucrose is α -D-glucopyranosyl- β -D-fructofuranoside.



Concentrated nitric acid converts sucrose to oxalic acid whereas concentrated sulphuric acid chars sugar.



Sucrose on fermentation with yeast gives ethanol and carbon dioxide.



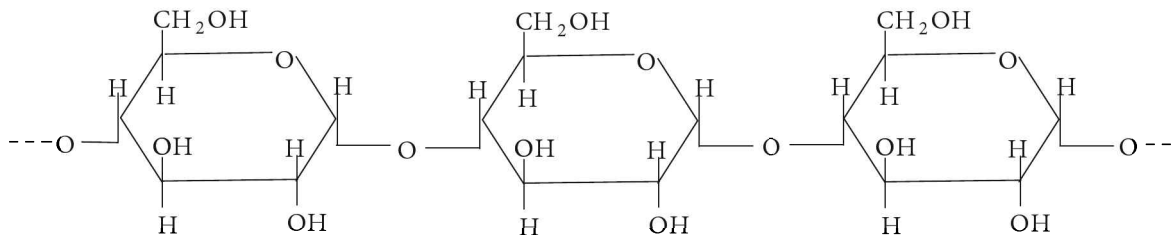
STARCH

Starch, $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ occurs in all green plants. The common sources of starch are wheat, barley, rice, potatoes, maize, etc. Starch is a polymer of α -D-glucose. It consists of two components: amylose and amylopectin.

Amylose

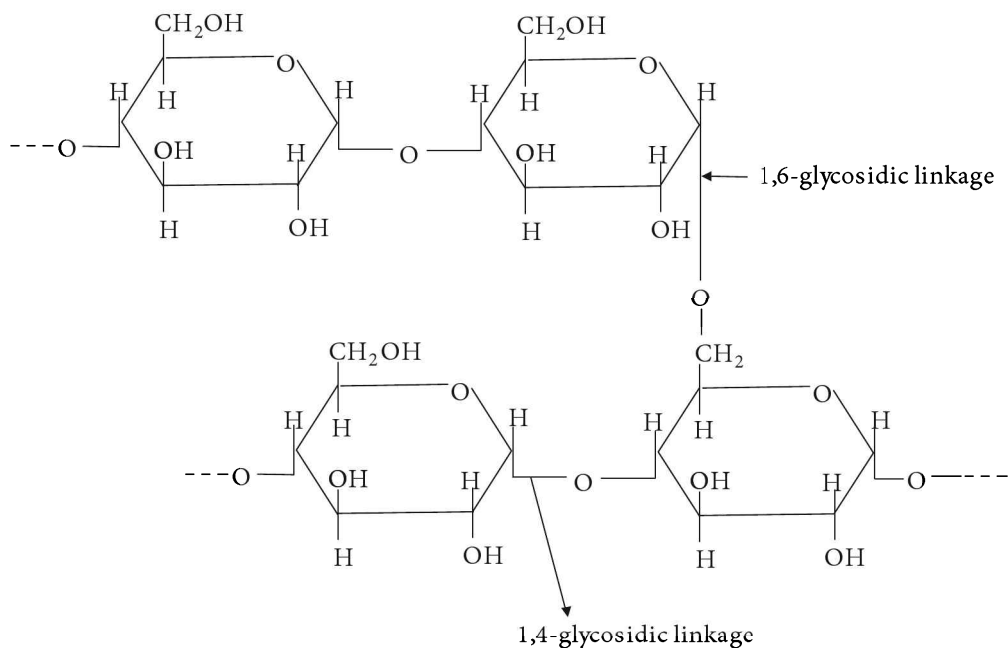
It is the water soluble component of starch and constitutes about 15-20% of it.

Amylose is a straight chain polymer where C-1 of glucose unit and C-4 of the neighbouring one are involved in the formation of α -1,4-glycosidic linkage. It gives blue colour with iodine.



Amylopectin

Amylopectin is water insoluble and contains branched chains; the branching occurs through 1,6-linkages and the length of the unbranched sections being about 24-30 glucose units. First amylose write-up followed by amylopectin.



Mild hydrolysis of starch with dilute acids results in dextrin, which is a mixture of maltose, D-glucose and a few other oligosaccharides. Glycogen found in muscle and liver is similar to starch. The 1,4 and 1,6 poly glucoside structure found in glycogen is similar to that of amylopectin. Glycogen allows ready formation of glucose,

by hydrolytic enzyme, when needed by the body. Important application of starch includes its consumption as a source of carbohydrate. In addition, they are used in foods as thickening and jelling agents. Starch is also used to improve the strength of fabrics and the writing qualities of paper.

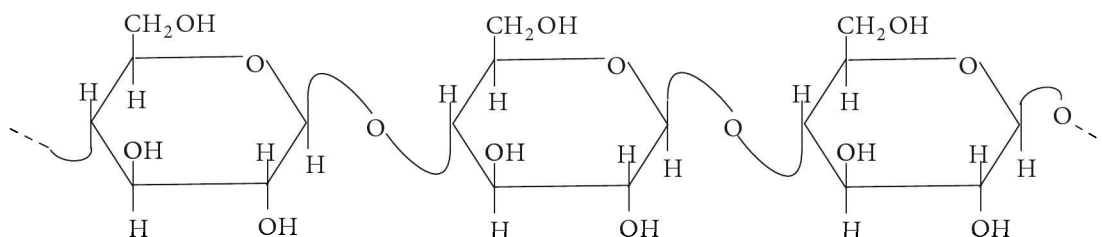
CELLULOSE

Cellulose is the main constituent of the cell wall of the plants. It has the composition $(C_6H_{10}O_5)_n$. The most important sources of cellulose are cotton and wood.

Cellulose is insoluble in water. It is soluble in ammoniacal cuprous hydroxide solution which is known as Schweitzer's reagent. It is a non reducing carbohydrate.

Hydrolysis of cellulose gives cellobiose. Complete hydrolysis gives D(+) glucose.

The molecular weight of cellulose varies from 20,000 to 500,000. Cellulose is different from starch in the configuration of the glycosidic linkage. All the glycosidic linkages in cellulose are β -linkages. Cellulose is made up of linear chains of D-glucose units joined by β -glycoside linkages to C-4 of the next unit.



structure of cellulose

7.12 Carbohydrates, Polymers and Practical Organic Chemistry

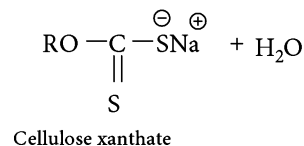
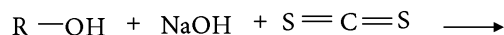
When cellulose reacts with acids, the glycosidic linkages are broken and each cellulose molecule yields large number of units of glucose.

In each glucose unit of cellulose there are three free $-OH$ groups.

Reactions of cellulose where the chain of glucose units are not broken are decided by the three free $-OH$ groups. Like any alcohol, cellulose also forms esters. When cellulose is treated with a mixture of nitric acid and sulphuric acid, cellulose nitrate is formed. Gun cotton is cellulose trinitrate. It is used as explosive.

Cellulose triacetate is formed from cellulose by treatment with acetic anhydride, acetic acid and catalytic amounts of sulphuric acid. When the reaction is complete, required quantity of water is added to decompose the triacetate to the diacetate. Cellulose diacetate in the presence of suitable solvents can be converted into fine threads or filaments. This is known as acetate rayon. It is used in making fibres. Cellulose acetate is also used for making non inflammable photographic and motion picture films, non-shatterable glass, lacquers and varnishes.

Cellulose is broken down with $NaOH$ and then allowed to react with carbondisulphide to form a xanthate derivative. The solution so obtained is known as viscose.



Viscose is a viscous colloidal suspension which is cellulose xanthate. When viscose is forced through a spinnerette into an acid bath, cellulose is regenerated in the form of fine filaments which results in threads known as rayon. Rayon is used as a fabric for clothing. Rayon is also used as the cord of tyres.

If viscose is forced through a narrow slit, cellulose is regenerated as thin sheets which are then softened by means of glycerol. They are known as cellophane which are used as protective films.

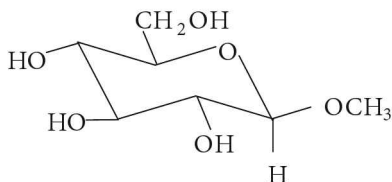
Some cellulose ethers are used in the manufacture of plastics. For example the ethyl ether of cellulose is used.

Cellulose is oxidized by nitrogen dioxide, in which half of the $-CH_2OH$ groups are oxidized to carboxyl groups. This increases the solubility in $NaOH$ solution. The oxidized cellulose is very useful in medicine.

CONCEPT STRANDS

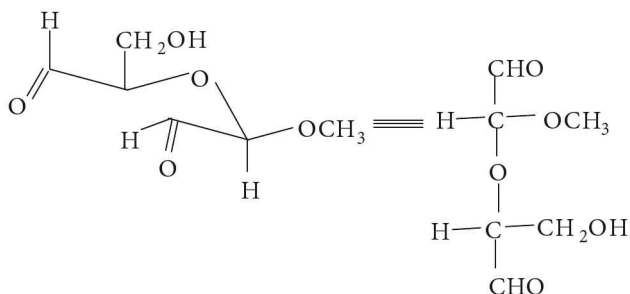
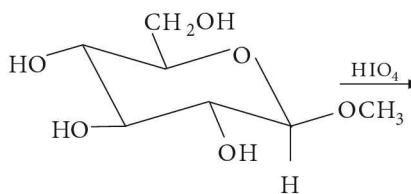
Concept Strand 1

Methyl- β -D-glucopyranoside is represented as



What happens when this is treated with HIO_4 ?

Solution

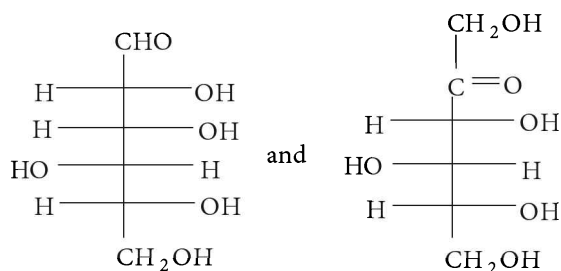


Concept Strand 2

D-sorbose is a ketohexose that gives the same osazone as the aldohexose D-gulose. What is the structure of D-sorbose?

Solution

The structures of D-gulose and D-sorbose are respectively

**POLYMERS**

Polymers are macromolecular sized substances of high molecular weight. A number of small molecules are joined together to obtain a polymer. *A large number of some simple molecules known as monomers undergo repeated addition or condensation to form a very high molecular weight species known as polymer. The process of formation of polymers from simpler units is known as polymerization. The simpler units are known as monomers.*

Classification of polymers based on structure**1. Linear polymers**

These are polymers in which monomers are joined together in a linear arrangement. Because of close packing of polymer chains, linear polymers have high melting points, high density and high tensile strength. Examples: nylon, PVC, high density polyethylene (HDPE), etc.

2. Branched chain polymers

These are polymers in which the monomer units are joined to form long chains with side chains or branches of different lengths. They have lower densities, melting point and tensile strength as compared to linear polymers. E.g., amylopectin, glycogen, low density polyethylene(LDPE), etc.

3. Cross linked polymers

In these polymers, cross links are formed among the initially formed linear polymer chains resulting in three

dimensional network structure. Such polymers are hard, rigid and brittle, e.g., bakelite, urea-formaldehyde polymer, melamine-formaldehyde, etc.

Classification based on the mode of polymerization**1. Addition polymers**

These are polymers formed by the repeated addition of monomer units and the reaction is known as addition polymerization. For example, vinyl chloride undergoes addition polymerization to form polyvinyl chloride (PVC). Polyethylene, polypropylene, polystyrene, Teflon, etc. are other examples.

2. Condensation polymers

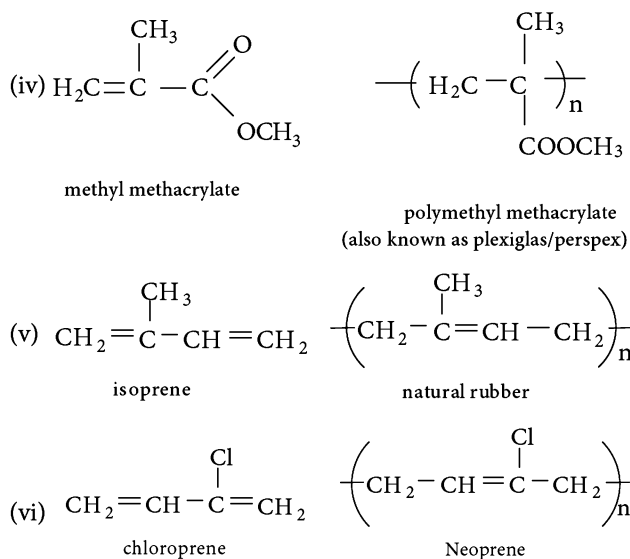
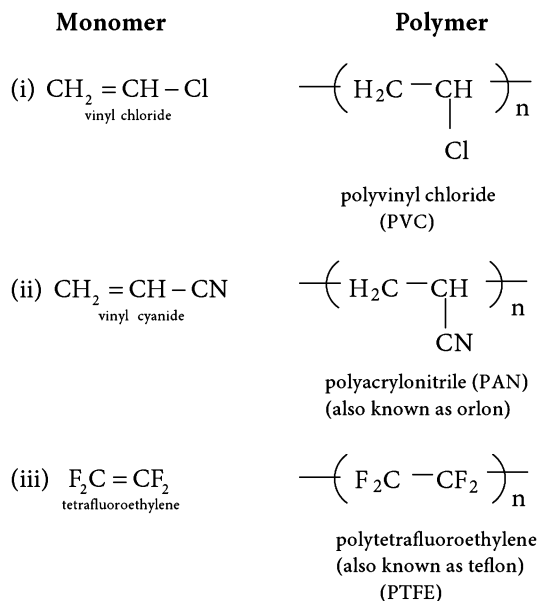
These are polymers formed by a series of condensation reactions between monomer units. The monomers are generally polyfunctional compounds and during condensation simple molecules like water, HCl, NH₃, etc. are eliminated. e.g., Nylon - 66, terylene

Chain growth and step growth polymers

Successive addition of monomer units to a growing chain by a chain reaction is called chain growth polymerization and the product is called chain growth polymer or addition polymer

7.14 Carbohydrates, Polymers and Practical Organic Chemistry

A few examples of chain growth polymers are given below.



A polymerization process which takes place by individual reactions of the functional groups of the monomer units in a stepwise manner is called step growth polymerization and the product is called a step growth polymer. The condensation polymers like dacron, nylon, bakelite, etc. are step growth polymers.

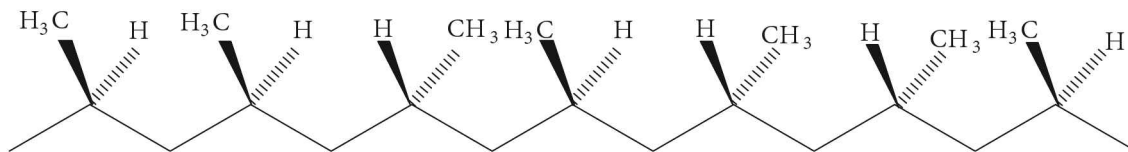
Homopolymers and copolymers

Polymers which are formed from only one type of monomer are called homopolymers. e.g., starch, cellulose, polyethylene, PVC, Teflon, polystyrene, etc.

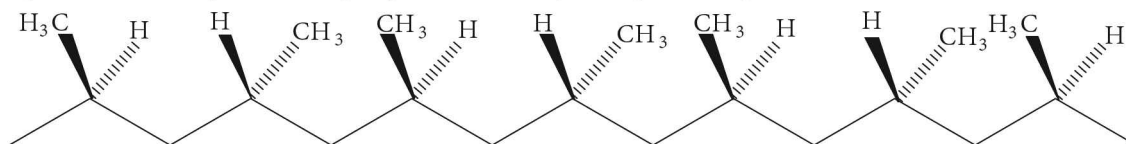
Polymers which are formed by the polymerization of more than one type of monomer are known as copolymers. e.g., nylon-66, terylene, Buna-S, etc.

There are three general arrangements of the groups and hydrogen along the polymeric chain. For example, the three arrangements possible in polypropylene are shown below.

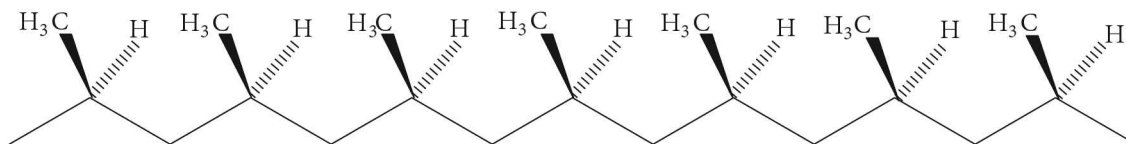
(i) Atactic is the arrangement where the stereochemistry is random.



(ii) In syndiotactic arrangement, the groups are alternately arranged in a regular fashion.



(iii) In isotactic arrangement, all the similar type of groups are on the same side.

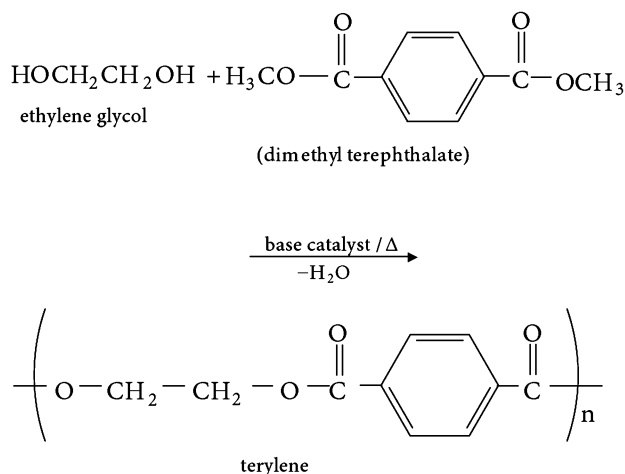


CONDENSATION POLYMERS

In the condensation polymerization, monomeric units are formed by the combination of two smaller units with the elimination of a simple unit like water, alcohol, hydrogen chloride, ammonia, etc.

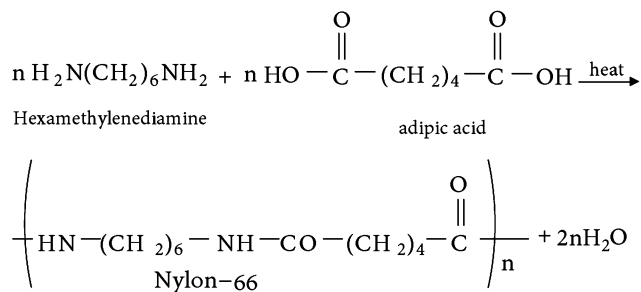
Polyesters

Terylene or Dacron is a polyester and is formed from ethylene glycol and terephthalic acid or its ester.



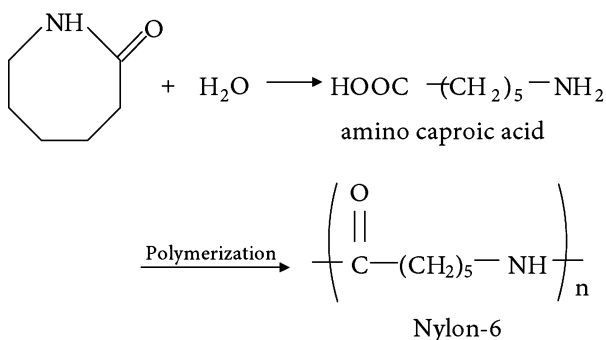
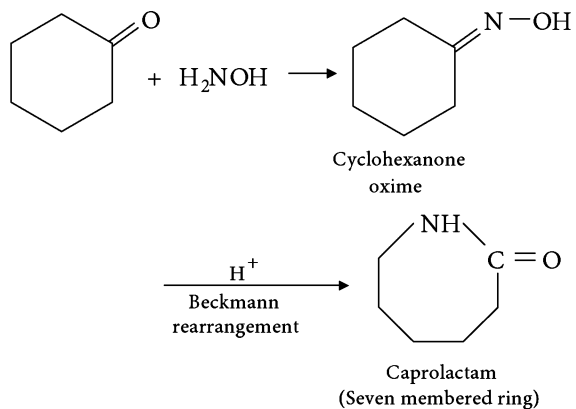
Polyamides

The polymer formed by the copolymerization of hexamethylenediamine and adipic acid is called nylon-66.



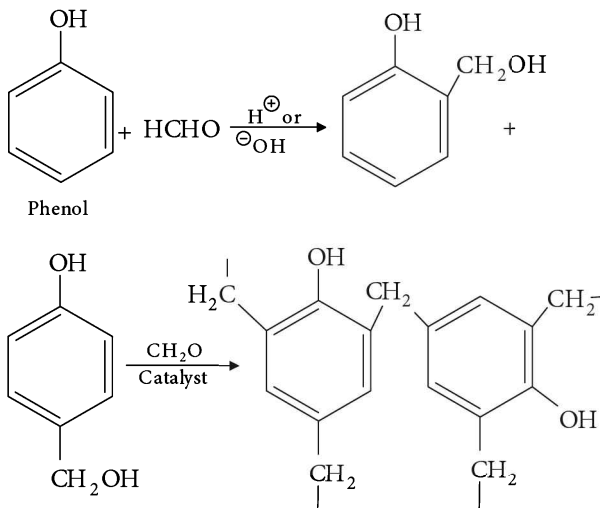
Nylon-66 is used to make brushes, synthetic fibres, ropes, carpets etc.

Nylon-6 is an amide polymer obtained from caprolactam, which, in turn, is obtained from cyclohexanone.



Nylon-6 is insoluble in common solvents, has good strength and absorbs little moisture. Nylon-6 is used for making fibres, plastics, tyre, cords, and ropes.

Phenol-formaldehyde resins



7.16 Carbohydrates, Polymers and Practical Organic Chemistry

The reaction between phenol and formaldehyde is known as *Lederer-Manasse reaction*.

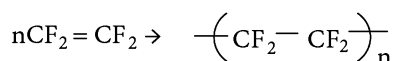
Zeigler-Natta catalysts are employed in the polymerization reaction where no radicals are observed.

Zeigler-Natta catalysts are prepared from transition metal halides; they have the composition $\text{TiCl}_4\text{-R}_3\text{Al}$ (trialkylaluminium).

ADDITION POLYMERS

Polytetrafluoroethylene (Teflon)

Teflon is PTFE which is polytetrafluoroethylene. The monomer is tetrafluoroethylene, $\text{CF}_2 = \text{CF}_2$.

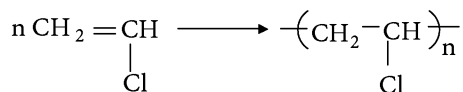


Teflon is used as a lubricant, insulator and for making cooking wares. It is also used for making chemically resistant pipes, pumps, valves and for making fibres.

Teflon melts around 320°C , density around $2.1\text{-}2.3 \text{ g cc}^{-1}$. The properties of teflon do not change in the temperature interval from -100°C to 250°C . It is not easily soluble and is highly resistant to common mineral acids and other organic solvents. In dielectric properties, it is similar to that of polyethylene and polystyrene.

Poly vinyl chloride (PVC)

Vinyl chloride undergoes polymerization to give polyvinyl chloride.



Polyvinyl chloride is a solid at room temperature and becomes elastic on heating. PVC is used in the manufacture of raincoats, hand bags, vinyl floorings and leather clothes.

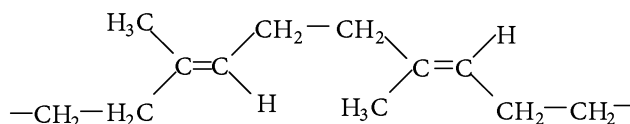
Natural rubber

It is a natural polymer and is highly elastic. Natural rubber undergoes long range reversible extension when a relatively small force is applied. This elasticity makes natural rubber very valuable for variety of uses. In the structure of rubber, there are no polar substituents. Rubber has weak van

der Waals forces of attraction. The cis-polyisoprene which is natural rubber is not a straight chain but has a coiled structure.

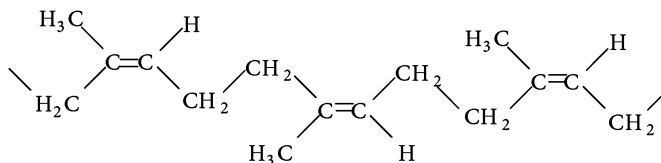
Natural rubber and Gutta-percha (trans-1,4-polyisoprene) are three dimensional isomers of polyisoprene. Rubber is an elastic substance, molecular mass is around 200,000 to 400,000 with density of 0.9 g cc^{-1} . Rubber is soluble in petrol, carbondisulphide and chlorinated hydrocarbons.

Gutta-percha is a coloured solid with a molecular mass around 23,000 and a slightly higher density. Dissolves in petrol when heated and comes out of the solution when cooled. Gutta-percha has the structure stereo isomeric to natural rubber.



trans-polyisoprene (Gutta-percha)

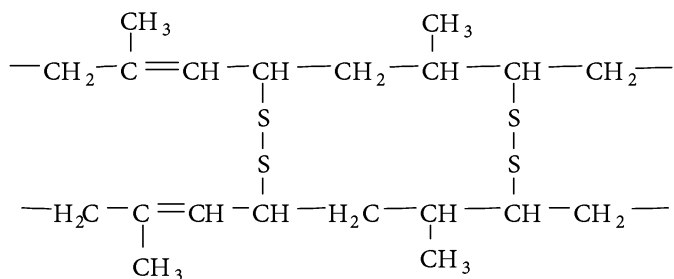
Natural rubber consists mainly of polymer of isoprene units (C_5H_8)_n in which the double bonds are in cis geometry.



cis-1,4-polyisoprene (natural rubber)

Natural rubber is a 1,4-addition polymer of isoprene. When natural rubber is subjected to pyrolysis, it is broken to isoprene. The isoprene units of rubber are linked in a head to tail fashion.

Zeigler-Natta catalyst makes it possible for isoprene to polymerize as a synthetic product which is identical with rubber from latex.



Vulcanized form of rubber

Pure natural rubber is soft and elastic. To make useful rubber products, natural rubber has to be vulcanized. In vulcanization, natural rubber is heated with sulphur. Cross links are formed between isoprene chains with sulphur, thereby making rubber a harder substance. Sulphur reacts both at the double bonds and at allylic positions.

Natural rubber is used as tyre tubes and for making erasers. Natural rubber is obtained from latex of the rubber tree which is known as *hevea brasiliensis*.

CONCEPT STRANDS

Concept Strand 3

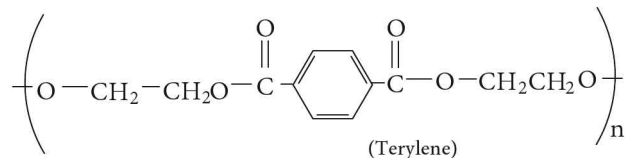
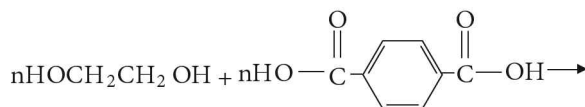
Give one example each of a

- polyester
- polyamide

Solution

- Polyester

Terylene or Dacron are classical examples of polyester resins.



- Polyamide

Nylon-6,6 is an example of polyamide polymer



Concept Strand 4

What is PDI? Explain.

Solution

PDI = Poly Dispersity Index.

In general, there are two different types of polymers.

- Polymers whose molecules have the same or narrow range of molecular weights, such polymers are known as monodisperse.
- Polymers which have a wide range of molecular weights. Such polymers are called polydisperse. PDI is the ratio of the mass average molecular mass to the number average molecular mass

$$\text{PDI} = \frac{\overline{M}_w}{\overline{M}_n}$$

For natural polymers PDI is equal to one which means they are monodisperse. Such polymers are more homogenous. Synthetic polymers have $\text{PDI} > 1$, which means they are less homogenous.

Mathematically,

$$\overline{M}_n = \frac{\sum N_x M_x}{\sum N_x} \quad \overline{M}_w = \frac{\sum N_x M_x^2}{\sum N_x M_x}$$

PRACTICAL ORGANIC CHEMISTRY

All organic compounds, derived from plants and animal origin, contain necessarily the two elements namely carbon and hydrogen. In addition, some other elements such as nitrogen, oxygen, sulphur, phosphorus and halogens are also present in some organic compounds.

Organic compounds are isolated from natural sources or synthesized in the laboratories. An organic compound thus obtained is subjected to qualitative and quantitative analysis after being purified by specific methods.

Practical organic chemistry deals with the preparation, purification and analysis of organic compounds.

The following methods of purification of organic compounds are in practice.

- (i) Simple crystallization
- (ii) Fractional crystallization
- (iii) Sublimation
- (iv) Simple distillation
- (v) Fractional distillation
- (vi) Vacuum distillation
- (vii) Steam distillation
- (viii) Chromatography
- (ix) Chemical methods

Activated charcoal is used to remove coloured impurities by a process of selective adsorption. Solvents of generally low boiling point are used for crystallization procedures.

The purity of an organic substance is tested by determining its melting point or boiling point as the case may be. Each and every pure organic solid compound has a characteristic melting point and therefore melting point is taken as a criterion of purity.

Analysis

When a pure sample of an organic compound is available, the various elements contained in the compound have to be detected and identified. Carbon and hydrogen are found in almost all organic compounds.

There is no direct test for the detection of oxygen in organic compounds. Hence the presence of oxygen in an organic compound is detected indirectly from the presence of various functional groups like $-OH$, $-CO-$, $-COOH$, $-CHO$, $-NO_2$, etc.

Once the presence of various elements are established, then the compound is subjected to quantitative analysis. By quantitative analysis, the exact elemental composition of a compound can be ascertained.

DETECTION OF ELEMENTS-QUALITATIVE ANALYSIS

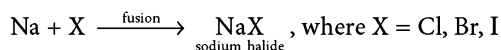
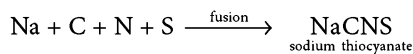
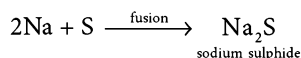
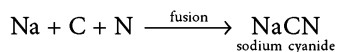
The detection of elements constitutes an important part of qualitative analysis. Lassaigne's test is used for the detection of nitrogen, halogens and sulphur in an organic compound. The first step in Lassaigne's test is the preparation of Lassaigne's extract or sodium fusion extract.

Preparation of sodium fusion extract

A small piece of sodium metal is heated gently in a fusion tube till it melts and a small amount of the organic substance is added to the melt and heated strongly to red heat. The hot tube is suddenly plunged into a small beaker containing about 10 mL of pure distilled water. The fusion tube cracks and the contents dissolve in water. It is boiled and filtered. This clear filtrate is known as sodium fusion extract or Lassaigne's extract. Sodium fusion extract is generally

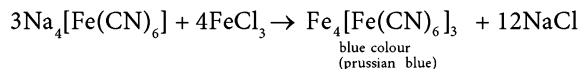
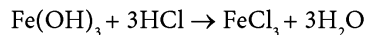
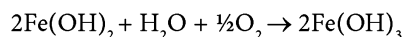
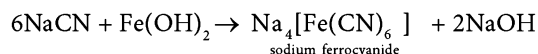
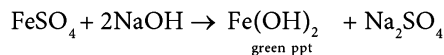
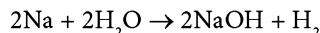
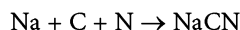
alkaline due to the reaction of excess sodium with water to form sodium hydroxide.

In this process, nitrogen in the organic compound is converted to $NaCN$, sulphur to Na_2S , halogen to NaX . If both nitrogen and sulphur are present, then $NaCNS$ is formed.



Test for nitrogen: Lassaigne's test

To the alkaline filtrate, a freshly prepared saturated solution of ferrous sulphate (FeSO_4) is added and then gently boiled. On cooling, one or two drops of conc. HCl are added. The appearance of a pale green or deep blue coloured solution or precipitate of ferri ferrocyanide or prussian blue indicates the presence of nitrogen.



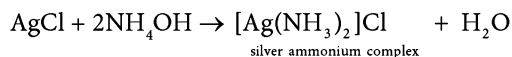
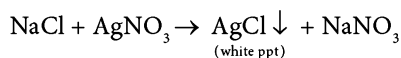
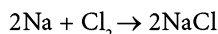
Lassaigne's test is not answered by diazo compounds, as nitrogen is eliminated from these compounds by heating. Lassaigne's test is also not answered by compounds like $\text{H}_2\text{N}-\text{NH}_2$, (hydrazine) or H_2NOH (hydroxylamine) NH_4Cl , NaNO_3 , etc. because they do not contain carbon.

Test for halogens

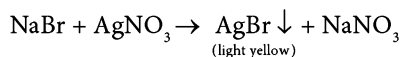
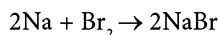
(a) Lassaigne's test

A small part of the sodium fusion extract is neutralized with dil. HNO_3 until it is slightly acidic and boiled. To the acid solution a few drops of AgNO_3 solution is added.

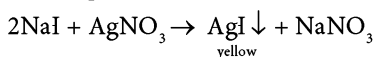
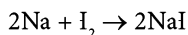
A white precipitate of AgCl soluble in NH_4OH shows the presence of chlorine.



A light yellow precipitate of AgBr , sparingly soluble in NH_4OH solution indicates the presence of bromine.



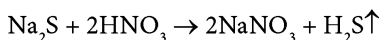
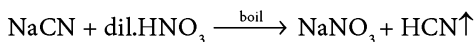
A deep yellow precipitate of AgI , insoluble in NH_4OH shows the presence of iodine.



If nitrogen or sulphur is also present in an organic compound containing a halogen, an interference is observed. Nitrogen and sulphur combine with carbon and sodium to form NaCN and Na_2S , respectively. Halogen combines with sodium to form sodium halide NaX .

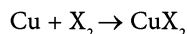
The NaCN or Na_2S present in the sodium fusion extract will react with AgNO_3 solution giving precipitate of AgCN or Ag_2S , respectively.

In order to prevent this, sodium fusion extract is first boiled with dil. HNO_3 when the NaCN or Na_2S is converted to HCN or H_2S , respectively which are volatile and escape.



(b) Beilstein test

This is another simple test for the halogens. A small piece of copper strip is heated strongly in an oxidizing flame of the burner until it no longer imparts a green colour. To the preheated strip, a small pinch of the organic compound suspected to contain the halogen is introduced. The strip is heated again with the substance. A green or bluish green colour is imparted if the compound contains the halogen.

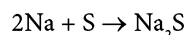


Copper halides impart a green or bluish green colour to the flame. Copper halides are volatile and the colour is due to the vaporization of the cupric halides. However, a few compounds like urea (NH_2CONH_2), thiourea ($\text{H}_2\text{NC-SNH}_2$) and pyridine give a green colour in the Beilstein test, although these compounds do not contain any halogen.

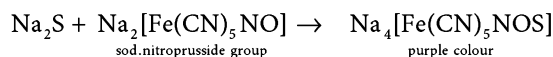
Hence it is often considered that Beilstein test for halogens is not a dependable test and a negative Beilstein test is more useful than a positive one.

Test for sulphur

Sulphur present in the organic compound gets converted to the form of soluble sodium sulphide (Na_2S) in the sodium fusion extract.

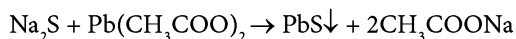


When sodium nitroprusside solution is added to a few drops of the sodium fusion extract, a purple or violet colour is observed, if sulphur is present.



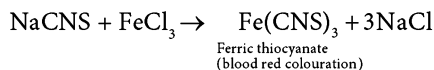
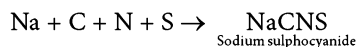
7.20 Carbohydrates, Polymers and Practical Organic Chemistry

To a few drops of sodium fusion extract, lead acetate solution is added. A black precipitate of lead sulphide is formed if sulphur is present.



If the organic compound contains both nitrogen and sulphur, sodium sulphocyanide (sodium thiocyanate) is

formed in the sodium fusion extract. When FeCl_3 solution is added to the sodium fusion extract a deep red or blood red colouration of ferric thiocyanate is observed.



DETECTION AND IDENTIFICATION OF THE FUNCTIONAL GROUPS

In order to identify various functional groups in an organic substance, the reactions of the functional groups are necessary to be known.

For example when elements like nitrogen and halogens are absent in an organic compound, it can be concluded that the groups like amines, amides, halides, nitro compounds, acid chlorides, anilides are absent. Only those functional groups, which do not contain nitrogen or halogens have to be looked for.

Test for alcohols

Alcohols are neutral in nature. Chemically alcohols do not react with mineral acids like dil.HCl , $\text{dil.H}_2\text{SO}_4$, nor do they react with NaOH solution. Although lower alcohols are miscible with these reagents to form homogeneous solution, there is no chemical reaction with acids or alkalis.

(a) Lucas test

Lucas reagent is a mixture of anhydrous ZnCl_2 and conc. HCl . When Lucas reagent is added to a primary alcohol, no turbidity is observed at room temperature.

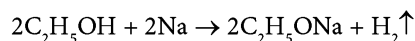
When Lucas reagent is added to a secondary alcohol, turbidity is observed in about 5-10 minutes, after mixing at room temperature.

When Lucas reagent is added to a tertiary alcohol, immediate turbidity appears at room temperature.

(b) Reaction with metallic sodium

When a small freshly cut piece of sodium is added to alcohol, it reacts vigorously and produces hydrogen. Primary alcohols react vigorously while tertiary alcohols react sluggishly with sodium.

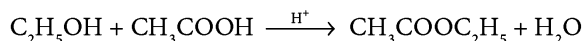
For example, ethyl alcohol reacts vigorously with sodium to produce sodium ethoxide, liberating hydrogen.



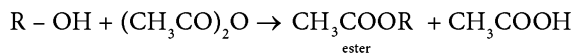
(c) Reaction with carboxylic acids, acid chlorides and anhydrides

Alcohols react with carboxylic acids to form esters with fruity odour or with some pleasant smell. The reaction of an alcohol with acid chloride will be more vigorous.

For example, ethyl alcohol reacts with acetic acid in the presence of catalytic amounts of dil.HCl to form an ester, ethyl acetate.



Alcohols can be identified by esterification reaction with acetic anhydride.



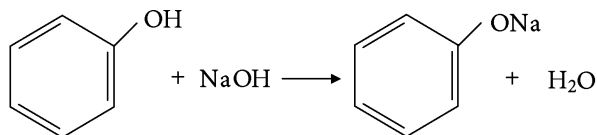
(d) Ceric ammonium nitrate test

Alcohols form a red colour with ceric ammonium nitrate.

Test for phenols

(a) Reaction with sodium hydroxide

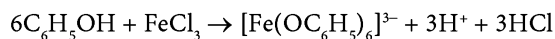
Phenols are more acidic than alcohols. Phenols react with NaOH solution to form phenoxides.



Phenol dissolves in dil. NaOH solution (10 %) forming a clear homogeneous solution and gets regenerated on the addition of acid forming a turbid solution.

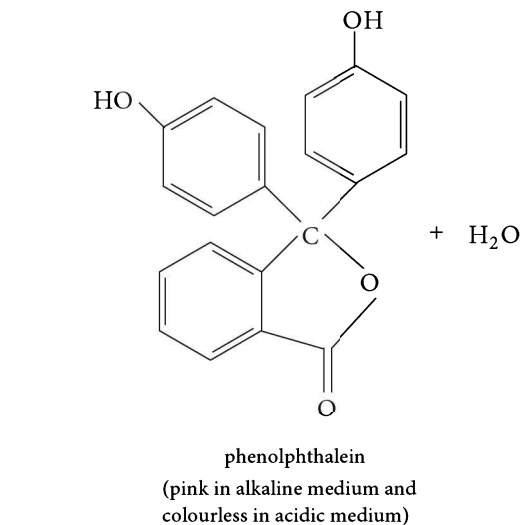
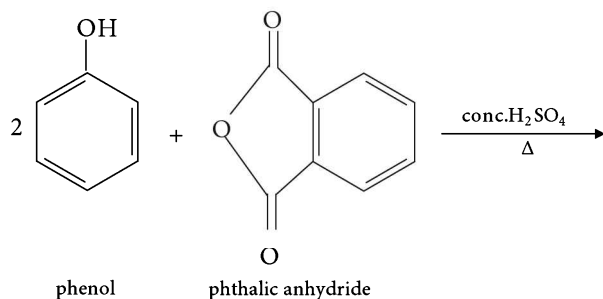
(b) Neutral ferric chloride test

To a few drops of phenol, 2 mL of neutral FeCl_3 solution is added and shaken. The formation of a violet colour shows the presence of phenol. The colour varies with the substituents in phenols.



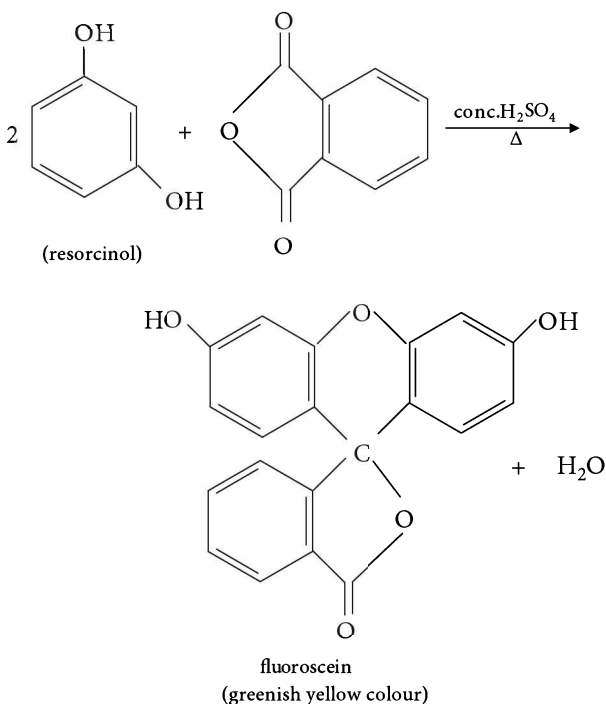
(c) Phthalein fusion test

To a small quantity of a phenol, 0.5 g of phthalic anhydride, and 2-3 drops of conc. H_2SO_4 is added. The mixture is heated gently and poured into a beaker containing 20 mL of dil. NaOH solution. The formation of a pink colour shows the presence of a phenol. The pink colour is due to the formation of phenolphthalein.



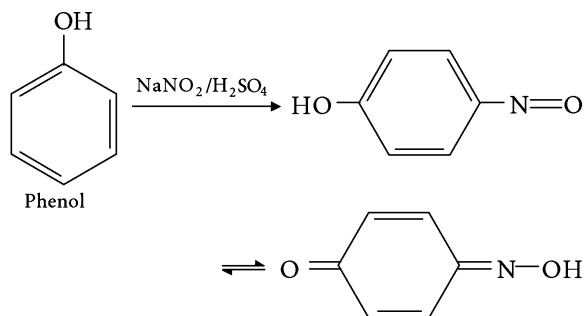
The same reaction can be carried out with resorcinol as follows.

Resorcinol is 1,3-dihydroxybenzene. To a small quantity of resorcinol, about 0.5 g of phthalic anhydride is added, followed by a few drops of conc. H_2SO_4 . The mixture is heated gently and poured into a dilute solution of NaOH. A greenish-yellow fluorescence appears.

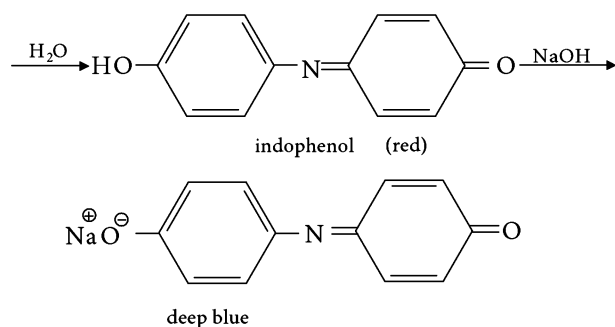
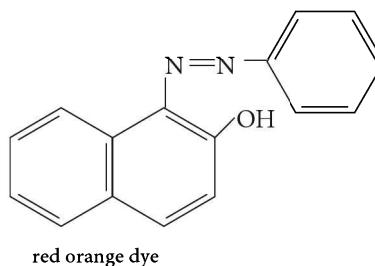
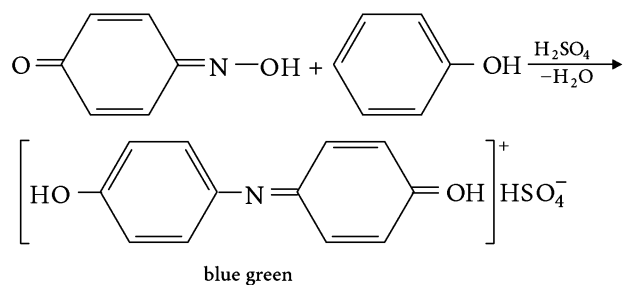


(d) Liebermann's nitroso reaction

A small quantity of phenol is taken. A freshly prepared solution of NaNO_2 in water is added. Few drops of conc. H_2SO_4 is then added. A blue coloured solution will be obtained. The mixture is poured into about 30 mL of water in a beaker and dilute NaOH solution is added in excess. A red solution is obtained first, which in excess NaOH changes to deep blue.

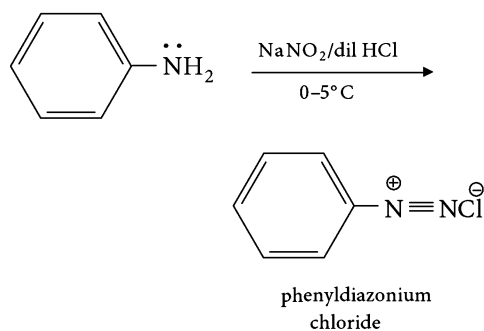


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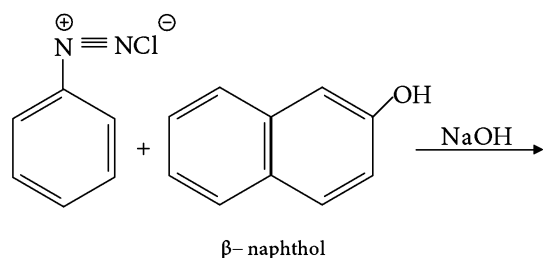


(e) Dye test

Aniline is converted into phenyl diazonium chloride under ice cold conditions as follows.



To this ice cold solution, an alkaline solution of phenol is added. A red orange azo dye is obtained.



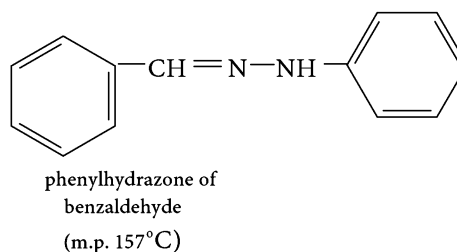
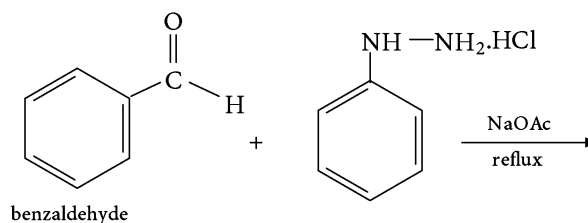
Test for aldehydes and ketones

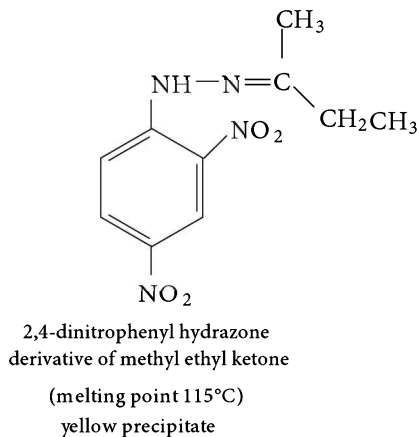
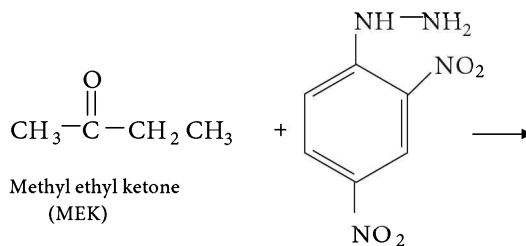
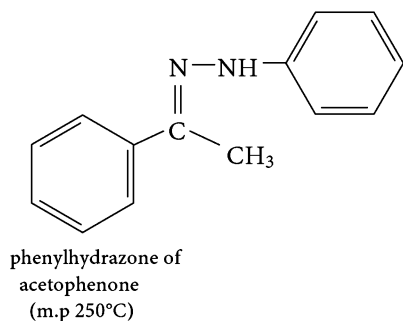
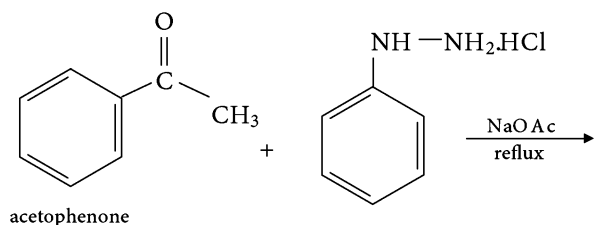
Reactions of aldehydes and ketones are classified into two groups, namely the reactions which are common to aldehydes and ketones and those which are answered only by the aldehydes and not by ketones.

(a) Phenylhydrazine test

To a small quantity of the aldehyde or ketone, about 0.5 g of phenylhydrazine hydrochloride is added. A small quantity of sodium acetate is also added followed by a few drops of water. The mixture is gently heated. The formation of a crystalline white solid of the corresponding phenylhydrazone indicates the presence of an aldehyde or ketone.

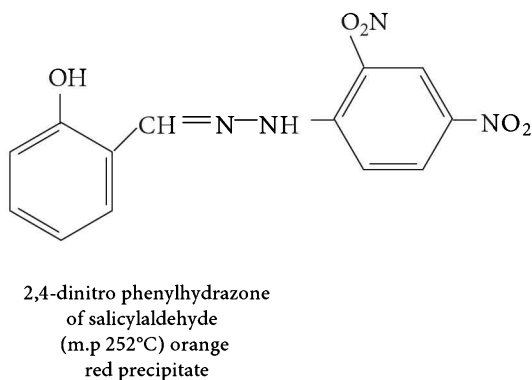
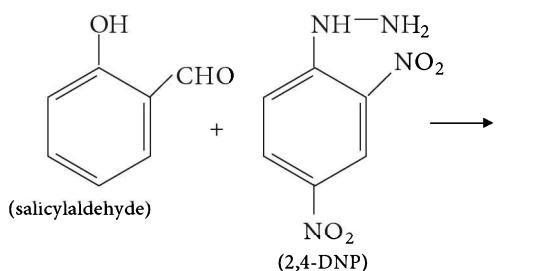
Phenylhydrazine is a corrosive and toxic liquid. Generally, direct use of phenylhydrazine is avoided and instead its salt namely phenylhydrazine hydrochloride is used along with sodium acetate which will liberate free phenylhydrazine during the reaction.





(b) Borsche's test (Brady's reagent)

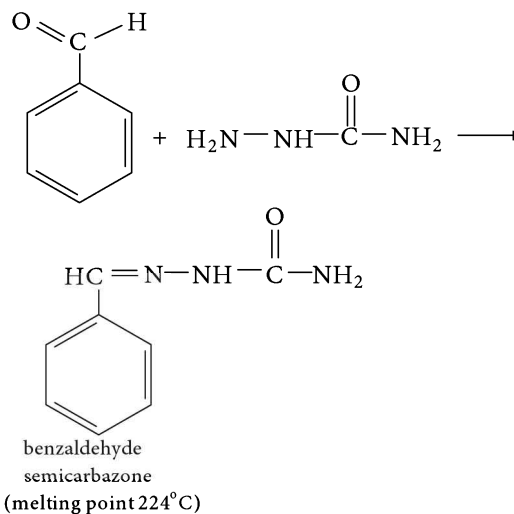
Borsche's reagent is 2,4-dinitrophenylhydrazine (2,4-DNP). The reagent is dissolved in a mixture of water and methanol and used for testing aldehydes and ketones. To about 1 g of the aldehyde or ketone, few mL of a solution of Borsche's reagent is added. The mixture is gently heated on a water bath. A bright yellow or orange coloured solution or precipitate is obtained.



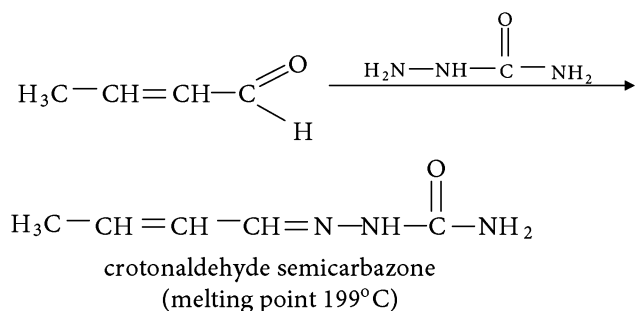
These derivatives are known as Borsche's derivatives of the aldehydes or ketones.

(c) Semicarbazide test

Semicarbazide hydrochloride is another reagent which on reaction with aldehydes and ketones gives solid derivatives. To a small quantity of the aldehyde or ketone, about 1 g of semicarbazide hydrochloride is added, followed by a small quantity of sodium acetate and 5 mL of water. Heat for about 2 minutes. Crystals of semicarbazone of the aldehyde or ketone will separate out.

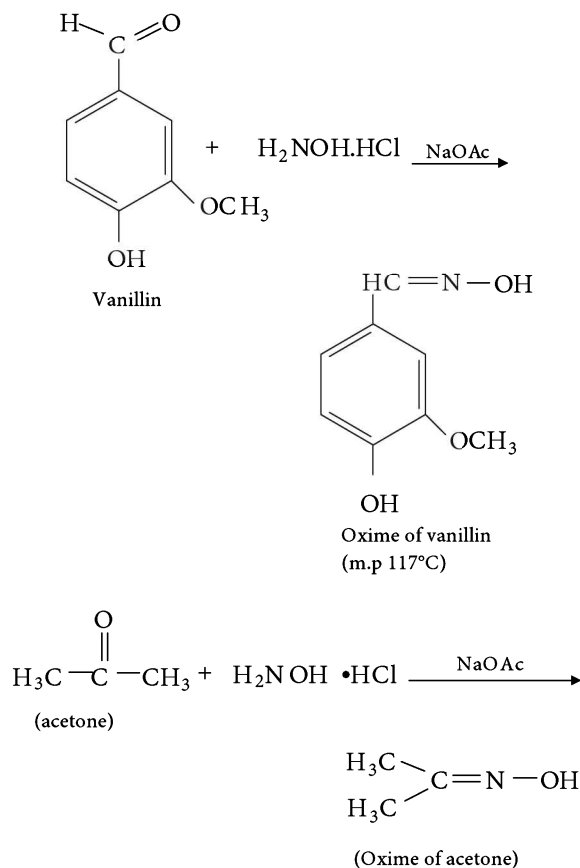


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(d) Formation of oximes

Hydroxylamine reacts with carbonyl compounds to give oxime. To a small quantity of the aldehyde or ketone, about 1 g of hydroxylamine hydrochloride ($\text{H}_2\text{NOH} \cdot \text{HCl}$), NaOAc solid (a small quantity) and 2–3 mL water are added and gently heated. A solid derivative of the oxime of the aldehyde or ketone is obtained.



(e) Reactions characteristic of the aldehydes

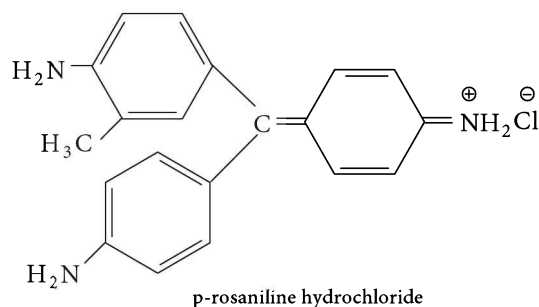
Aldehydes are more reactive than ketones. Aldehydes exhibit reducing properties. Hence there are a few reactions

which are answered by the aldehydes only and not responded by the ketones. Ketones do not show reducing properties.

Schiff's reagent test

Schiff's reagent is magenta solution of p-rosaniline hydrochloride decolourized by SO_2 . Schiff's reagent is a colourless liquid. Aldehydes restore the pink colour to the colourless reagent.

Schiff's reagent is prepared from p-rosaniline hydrochloride. It is a triphenyl methane dye.



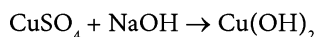
p-rosaniline hydrochloride is dissolved in water to make a dilute (1%) aqueous solution. The solution has a violet colour; SO_2 gas is passed through the solution until it turns completely colourless. This colourless solution is known as Schiff's reagent.

To a small quantity of a dilute solution of aldehyde, 1 mL of Schiff's reagent is added. Pink or violet colour is restored. Aldehydes restore the quinonoid structure of the reagent to give back the magenta colour.

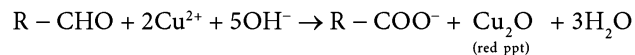
Fehling's test

Fehling's reagent is made use of in this test. Fehling's solution is made up of 1 : 1 mixture of two solutions Fehling's (A) and Fehling's (B). Fehling's (A) is prepared by dissolving 40 g of pure $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (copper sulphate) crystals in a litre of water. Fehling's solution (B) is prepared by dissolving Rochelle's salt (sodium potassium tartarate) in sodium hydroxide solution.

Mixing equal quantities – 20 mL of Fehling's (A) and 20 mL of Fehling's (B) – of Fehling's solution results in Fehling's reagent. The colour of the solution is blue. Fehling's solution mixture consists of cupric ions in basic medium. When a small quantity of the aldehyde is boiled with 2 mL of Fehling's solution, a red precipitate of cuprous oxide (Cu_2O) is obtained. Aldehyde reduces the cupric ions in solution in alkaline medium to cuprous oxide, which is a red precipitate.

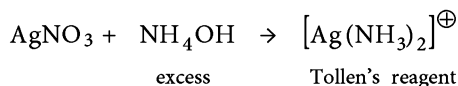


$\text{Cu}(\text{OH})_2$ + sodium potassium tartarate $\rightarrow$ Cupric Cu^{2+} ions in alkaline medium

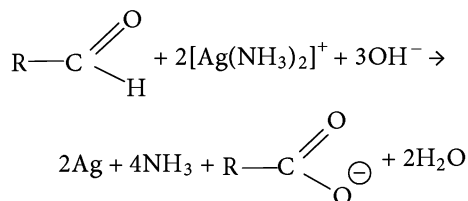


Tollens' reagent test

Tollens' reagent is ammoniacal silver nitrate solution. To 2 mL of AgNO_3 solution, few drops of NH_4OH solution is added. A dark brown precipitate appears which dissolves on the addition of excess of NH_3 solution to form a clear and colourless solution. This solution is known as Tollens' reagent. This solution contains Ag^+ ions in the form of a complex.



When Tollens' reagent is added to aldehyde and warmed, a bright silver mirror is obtained on the inside surface of the test tube in which the reaction is carried out. In some cases, a black precipitate of silver is obtained instead of the silver mirror.



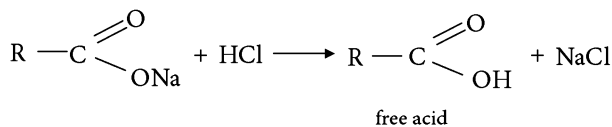
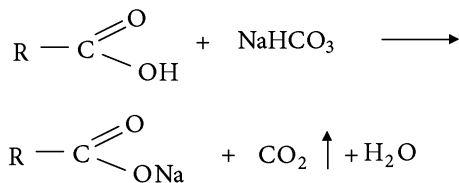
Test for carboxylic group

Carboxylic compounds are acidic in nature.

(a) Reaction with NaHCO_3

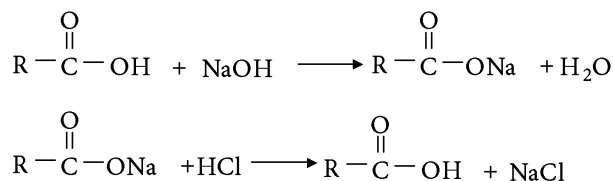
An organic acid is soluble in saturated solution of NaHCO_3 due to the formation of sodium salt and gets free as a solid on the addition of dil.HCl.

To a small quantity of the carboxylic acid, few mL of a saturated solution of NaHCO_3 is added. Brisk effervescence with liberation of CO_2 is observed. The solid acid dissolves in bicarbonate solution forming a clear solution. To the clear solution, if dil.HCl is added, the dissolved acid reappears.



(b) Sodium hydroxide test

All carboxylic acids are soluble in NaOH solution. If a dilute solution of NaOH is added to a small quantity of the carboxylic acid taken in a test tube, upon shaking the acid dissolves forming a clear solution. The free organic acid gets liberated on the addition of dil.HCl.

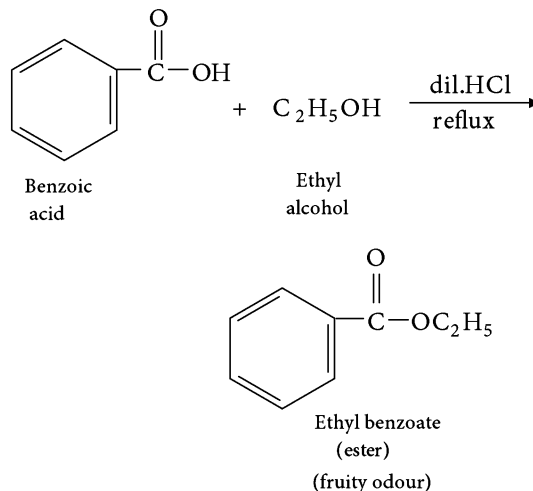


(c) Litmus test

An aqueous solution of the acid (if the acid is soluble in water) will change the colour of blue litmus paper to red.

(d) Esterification test

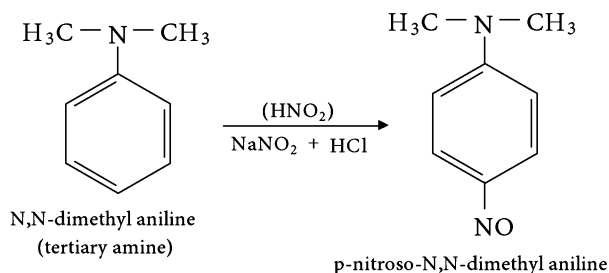
To about 1 g of the acid, 5 mL of ethyl alcohol and few drops of dil.HCl are added. The mixture is gently refluxed in a boiling tube. The mixture after cooling is poured into a beaker containing 10 mL of dilute Na_2CO_3 solution. A pleasant fruity odour of an ester indicates the presence of an acid.



CAUTION: All N-nitrosoamines are carcinogenic in nature and to be handled carefully.

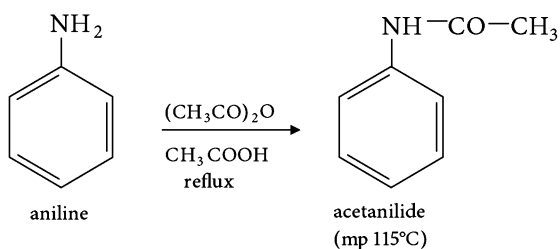
(e) Test for tertiary amines

Aromatic tertiary amines on reaction with nitrous acid gives p-nitroso derivatives, which is green in colour.



(f) Acetylation

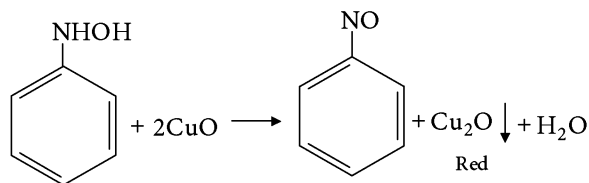
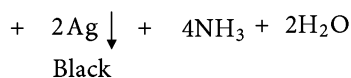
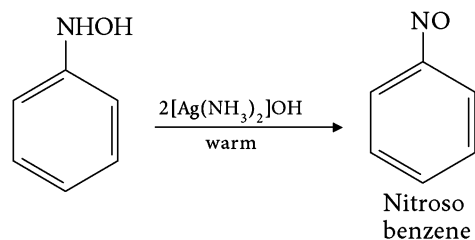
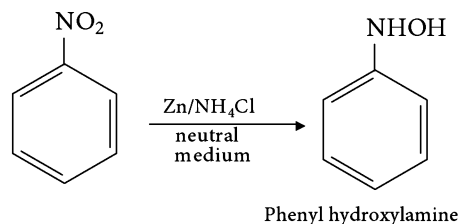
Primary and secondary amines undergo acetylation when heated with acetic anhydride or acetyl chloride. About 1 mL of aniline is taken and treated with 2 mL of acetic anhydride and 2 mL of glacial acetic acid. The mixture is refluxed for 2 minutes and poured into a beaker containing ice cold water. Bright shining crystals of acetanilide (an acetyl derivative of aniline) is formed.



Test for nitro group

(a) Mulliken and Barker's Test

About 0.5 g of the nitro compound is mixed with few drops of ethanol (solvent) to form a homogeneous solution. NH_4Cl (0.5 g) and Zn dust (0.5 g) are added and heated carefully for 2 minutes. The mixture is allowed to stand for 3 minutes. Then filtered and the filtrate is divided into two parts. To one part, 2 mL of Tollens' reagent is added and warmed in a water bath. A black precipitate of silver shows the presence of the nitro group. To another part, Fehling's solution is added and boiled. A red precipitate of Cu_2O shows the presence of nitro group.



CHEMICAL METHODS OF SEPARATION OF MONO FUNCTIONAL ORGANIC COMPOUNDS FROM BINARY MIXTURES

When a mixture of two organic compounds is to be separated and analyzed for their identification, certain special procedures have to be followed depending on their nature.

Pilot separation

Before the mixture of two components is subjected to a large scale separation, a pilot separation is conducted by

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making use of a small quantity of the mixture. In the pilot separation, about 1.0 g of the binary mixture is taken (the mixture may be a solid-solid mixture, solid-liquid mixture or a liquid-liquid mixture) and 10 mL of ether (solvent) is added to the mixture. This is to test whether both the components are soluble in ether.

If a clear solution, either coloured or colourless, is formed, then both the components are soluble. Generally most of the organic compounds are soluble in ether. If one of the components is not soluble in ether, then it is separated by decantation and washed with ether. Very few substances are insoluble in ether, like carbohydrates, phthalic acid, oxalic acid and some strongly polar compounds. These ether insoluble compounds are separated and analysed separately. The ether soluble portion is further treated with other reagents to identify them.

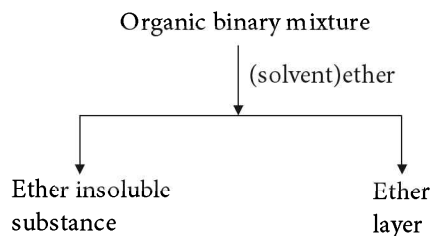
The ether soluble portion is transferred to a separating funnel. 5 mL of a saturated aqueous solution of sodium bicarbonate is added to the ether solution and shaken well. The two layers are allowed to separate. The lower aqueous layer consisting of NaHCO_3 layer is drained into a test tube, and neutralized with dil.HCl until just acidic. The formation of a solid indicates the presence of a carboxylic acid or an acidic substance.

The ether layer is retained in the separating funnel. To the remaining ether solution in the separating funnel, about 5 mL of NaOH solution (10 %) is added and shaken well. The two layers are allowed to separate. The lower aqueous

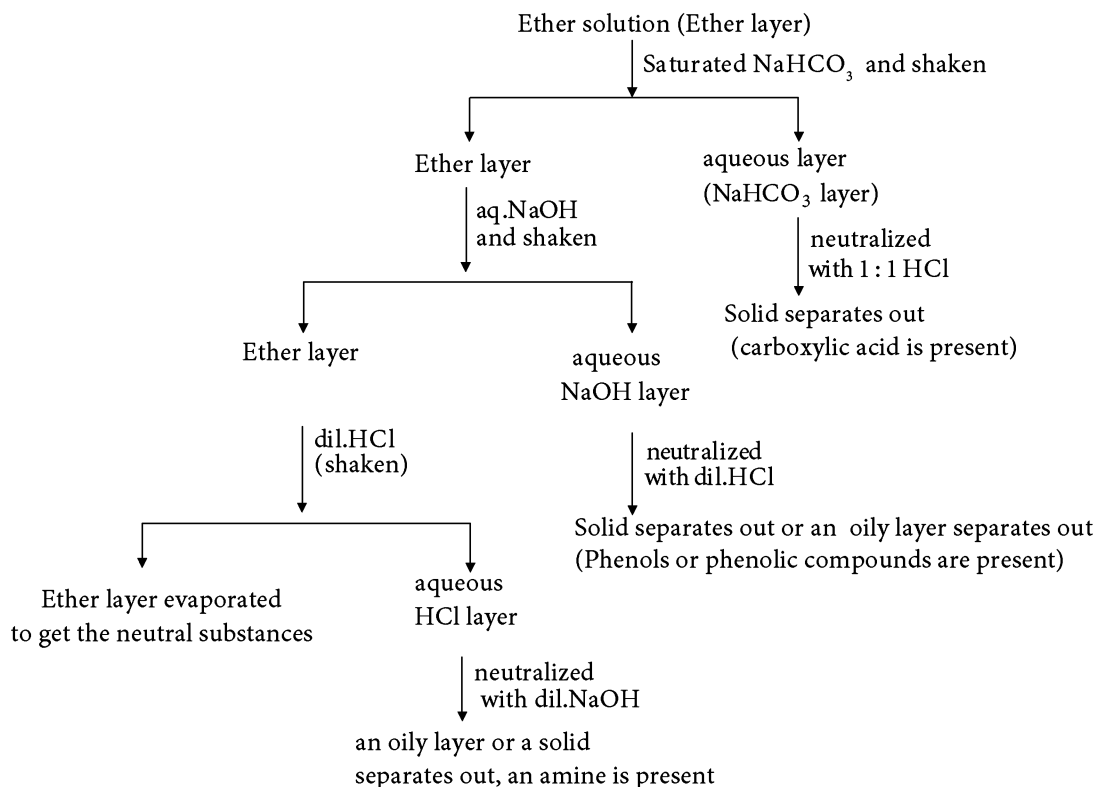
layer which consists of NaOH solution, is transferred to a test tube, leaving the ether layer with the separating funnel. On neutralization of the aqueous NaOH solution with dil. HCl, if a solid separates out or an oily layer separates out, it indicates the presence of a phenolic component.

To the remaining part of the ether solution in the separating funnel, about 5 mL of dil.HCl is added and shaken well. The two layers are allowed to separate. The lower aqueous acid layer is collected in a test tube and neutralized with dil.NaOH solution. If turbidity appears, an oily layer separates out or a solid separates out, then it indicates the presence of a basic substance like an amine.

The ether layer remaining in the separating funnel is removed and evaporated in a china dish to get any neutral component if present.



Ether insoluble substances are separated, washed with ether and ether portions are added to the original ether layer.



On the basis of the above pattern, a pilot separation is carried out to ascertain whether an acidic or a basic or a neutral component is/are present in the mixture.

For example, if it is found that an acid component and a neutral component are the constituents of the mixture, based on pilot separation, the bulk separation is carried out by dissolving the mixture in ether and extracting the acid component with saturated aqueous NaHCO_3 solution and evaporating the remaining ether to get the neutral component.

If, on the other hand, the mixture is made up of a basic and neutral component, then the basic component is separated in the bulk separation by extracting the basic component in the ether medium with conc. HCl . The remaining ether is evaporated to get the neutral component.

In another case, if the mixture is made up of a neutral component and a phenolic component, the phenol is

directly recovered from the ether layer by extraction with dil. NaOH and the remaining ether portion is evaporated to get the neutral part.

The individual components are separated and analyzed individually. The isolated component is purified either by recrystallization or by distillation if it is a liquid and subjected to further analysis. The exact melting point if it is a solid and the boiling point if it is a liquid are determined by suitable methods. Then each component is subjected to the detection of elements. The isolated, purified components further are subjected to individual analysis for detection of various functional groups.

ANALYSIS OF ORGANIC MIXTURES

Mixture I (Mixture of salicylic acid and acetophenone)

Salicylic acid is an acid component and it is a solid. Acetophenone is a neutral component and it is a liquid. A pilot separation is initially carried out. The major components are identified from the pilot separation as a carboxylic acid and a neutral component.

Analysis of the acid component

Melting point is 155°C . The solid is subjected to elemental analysis. No elements like nitrogen, halogen or sulphur are present. The solid is then subjected to functional group analysis.

To a small quantity of the solid, few mL of saturated NaHCO_3 solution is added. A brisk effervescence accompanied by the evolution of CO_2 is observed. This confirms the presence of an acid group.

To a small quantity of the acid, few mL of neutral ferric chloride solution is added. A violet colouration shows the presence of a phenolic group. Hence the solid component is a phenolic acid.

Acetyl derivative of the phenolic acid is prepared by taking 1 g of the acid, mixed with acetic anhydride and a few drops of conc. H_2SO_4 . Heating the mixture for few minutes and pouring the hot contents over a beaker containing cold water, results in the acetyl derivative of the phenolic acid in the form of a crystalline white solid. The solid

obtained is filtered off, washed repeatedly with ice cold water, and the solid is dried and the melting point is determined. Melting point was found to be 136°C .

Analysis of the neutral liquid component

The compound is subjected to distillation and the boiling point was found to be 202°C . The liquid component is subjected to elemental analysis. No elements like nitrogen, halogen or sulphur was found.

Test for functional groups

(a) Borsche's test

To a small quantity of the sample, 2 mL of Borsche's reagent is added. A yellow or orange red precipitate is obtained, which indicates the presence of an aldehyde or a ketone.

(b) Fehling's test

To a small portion of the liquid, 2 mL of Fehling's solution (A and B) is added and boiled for a few minutes. No red precipitate was obtained. This proves that the sample contains a ketone and not an aldehyde.

(c) Iodoform test

To a small portion of the ketone, 0.5 g of iodine crystals and 3 mL of dil. NaOH solution are added. The mixture

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is gently refluxed for few minutes and on cooling shining yellow crystals of iodoform are observed. This shows that the ketone is a methyl ketone.

(d) Test for an aromatic substance

The given sample is taken in a spatula and burnt in a flame. The substance burns with a sooty flame showing that the compound is aromatic.

The solid acid component was also burnt in a spatula and was found to burn with a sooty flame. The acid is also an aromatic acid.

Final report

Component I (Solid)

It is an aromatic carboxylic acid with a phenolic group having a melting point of 155°C. Acetyl derivative has a melting point of 136°C.

Component II (liquid)

It is an aromatic methyl ketone with boiling point of 202°C. Borsche's derivative has a melting point of 250°C

Mixture II (Phenol and chlorobenzene)

The two major components are identified by pilot separation. They are identified to be a phenolic compound and a neutral compound. The two components are separated in the bulk separation by taking the ether solution and extracting the phenol by NaOH. The neutral component is obtained by the evaporation of ether after the separation of phenol.

Tests for the phenolic component

Boiling point was determined to be 180°C. On treating with neutral FeCl_3 solution, a violet colouration was observed. When treated with benzoyl chloride, a benzoyl derivative with melting point of 69°C was obtained. Elements like nitrogen, sulphur or halogens were absent.

Report

The component I is a phenol. It is a liquid with boiling point of 180°C.

Analysis of component II

The neutral component was distilled and the boiling point was found to be 132°C. The compound was tested for the

presence of elements nitrogen and sulphur and found to be absent. The compound was found to contain a halogen. The halogen has to be a nuclear halogen. A side chain halogen gives a precipitate with alcoholic silver nitrate solution, whereas the nuclear halogen does not give a white precipitate with alcoholic silver nitrate solution.

Report

The given compound is a neutral aromatic compound with chlorine in the nucleus with a boiling point of 132°C. Nitro derivative of the compound is prepared with a melting point of 52°C.

Mixture III (Aniline and benzamide)

The mixture is dissolved in ether. From the pilot separation, the presence of a basic component is found out. The basic component is separated by extraction of the ether extract with dil.HCl. The remaining part of the ether solution is evaporated to get the neutral component.

Analysis of component I

This is obtained by the HCl extraction. Hence this is an amine. The compound is purified by distillation. Boiling point is 181°C. The compound is tested for the elements and nitrogen was found to be present.

Test for an amine

Dissolves in dil.HCl and regenerated by adding alkali shows the presence of an amine. Carbylamine reaction was carried out. From the pungent smell of isocyanide, the presence of a primary amine is established. A small portion of the compound is burnt in a spatula and was found to be burning with a sooty flame. Shows the presence of an aromatic compound.

Report

The basic compound is an aromatic primary amine with a boiling point of 181°C. Acetyl derivative of the compound has a melting point of 114°C.

Analysis of component II

This is a solid neutral component with a melting point of 121°C. Tested for the elements and nitrogen was found to be present. Since the compound is neutral, an amide could be present.

Test for the amide

To a small portion of the solid, NaOH solution was added and boiled for few minutes. Strong smell of NH_3 was observed and the liberated gas turned red litmus paper blue. The residue on dilution with water and acidification with dil.HCl gave a solid, which gave effervescence with NaHCO_3 . This proves the presence of an amide.

Report

The mixture consists of a solid neutral compound which is an aromatic primary amide with a melting point of 121°C . The solid derivative of the amide is obtained by hydrolyzing the amide with NaOH. The melting point of the acid obtained is 121°C . The other component of the mixture is a liquid, aromatic primary amine with a boiling point of 181°C . Its acetyl derivative has a melting point of 113°C .

CONCEPT STRANDS**Concept Strand 5**

Answer whether following statements are true or false.

- Fractional distillation cannot be carried out for a liquid mixture which form azeotropic mixture.
- Steam distillation is applied for liquids which are steam volatile and insoluble in water.
- $\text{H}_2\text{N}-\text{NH}_2$ gives a prussian blue colour for nitrogen in Lassaigne's test.
- $\text{C}_6\text{H}_5\text{SO}_3\text{H}$ on Lassaigne's test gives a blood red colour on the addition of NaCNS to the sodium fusion extract.
- All compounds containing an odd number of nitrogen atoms (1, 3, 5, 7, etc.) will have odd number of molecular weights and those having even number of nitrogen atoms will have even number of molecular weights.
- Chloroform and benzene are miscible with each other.

Solution

- True.
- True.
- False, there is no carbon in hydrazine and it does not form NaCN.
- False, a blood red colour is observed only if both nitrogen and sulphur are present in the organic compound.
- True, this is known as nitrogen rule.
- True.

Concept Strand 6

An organic compound contains sulphur and bromine. How is bromine tested?

Solution

In the sodium fusion extract, sulphur is converted as Na_2S . If sulphur is not removed, then it will interfere with the

testing of bromine. So the sodium fusion extract is treated with dil. HNO_3 and boiled. So any sulphur present is removed as volatile H_2S . The remaining solution contains bromine as NaBr. To the acidified solution, when AgNO_3 is added, a pale yellow precipitate of AgBr is obtained, which is sparingly soluble in NH_4OH solution.

The presence of bromine can be confirmed by adding CS_2 to the sodium fusion extract, followed by Cl_2 water and shaking. The CS_2 layer turns orange red indicating the presence of bromine. Chlorine displaces bromine from bromide and iodine from iodide.

Concept Strand 7

A sample of p-chlorobenzoic acid is given. How would you proceed to identify the sample?

Solution

- A portion of the sample is burnt in a spatula. It burns with a luminous flame. It shows that the sample is aromatic.
- A small portion of the sample is tested with saturated NaHCO_3 solution. A brisk effervescence is observed which shows that the given compound is an aromatic carboxylic acid.
- The given sample is tested with dil.HCl. Substance is not soluble in HCl. This shows that no basic components are present.
- The sample is tested for other neutral functional groups like aldehydes, ketones and amides. They are answered negatively.
- The given sample is tested for the elements. Absence of nitrogen indicates absence of amines, or nitro compounds. To a portion of the sodium fusion extract, dil. HNO_3 is added, followed by AgNO_3 solution. A white precipitate soluble in NH_4OH is observed. This confirms the presence of a halogen (chlorine).

SUMMARY

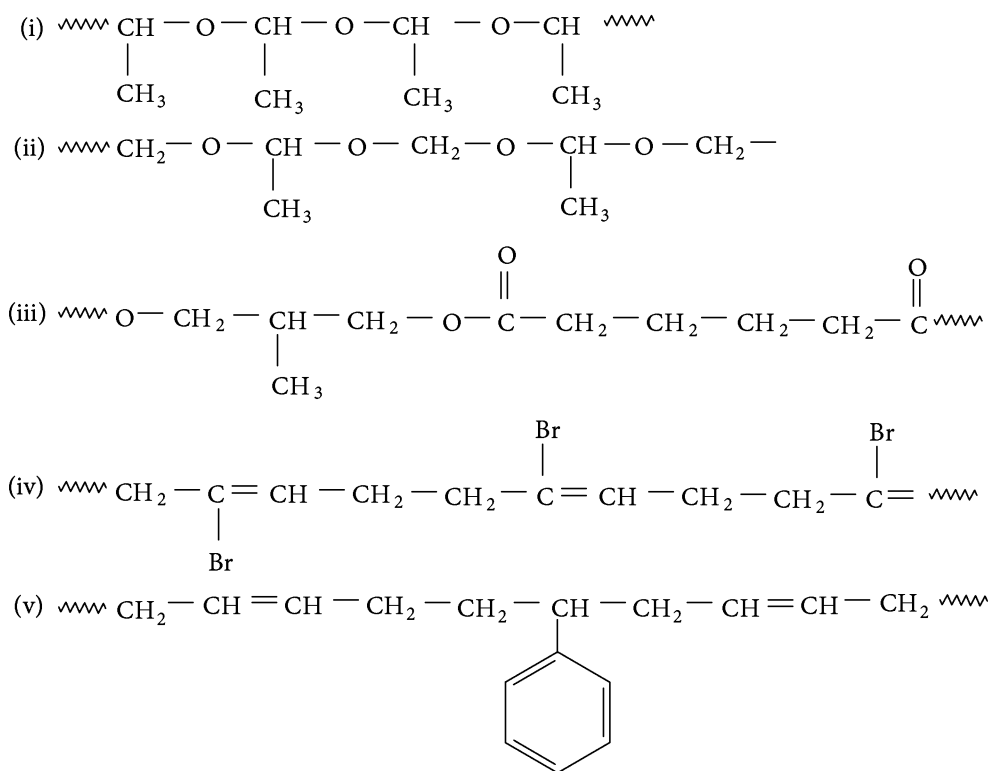
Introduction to carbohydrates	Definition, general formula
Classification of carbohydrates	Monosaccharides, oligosaccharides and polysaccharides. Examples for each class
Glucose	D and L designation. Oxidation of glucose with mild and strong oxidizing agents, reduction, fermentation reaction, reaction with phenyl hydrazine, mutarotation, methyl glucoside formation, formation of pentaacetate, dehydration, epimerization, Lobry de Bruyn van Ekenstein rearrangement, cyclic structure of glucose
Fructose	Structure, formation of same osazone as glucose
Sucrose	Structure, oxidation with con. HNO_3 , fermentation reaction
Starch	Structure of amylose and amylopectin
Cellulose	Structure, hydrolysis reaction preparation of gun cotton, cellulose rayon and viscose rayon
Classification of polymers	Classification based on structure: linear polymers, branched chain polymers and cross linked polymers. Classification based on the mode of polymerisation: addition polymers and condensation polymers. Chain growth and step growth polymers—examples, Homopolymers and copolymers.
Preparation of important polymer	Polyesters, polyamides, phenol—formaldehyde resins, Teflon and PVC
Natural rubber	Structural aspects, vulcanization of rubber.
Detection of elements in organic compounds	Lassaigne's test for the detection of N, S and halogens, Beilsteins's test.
Identification of functional group in organic compounds	Tests for alcohols, phenols, aldehydes and ketones, carboxylic acids, amines and nitro compounds.
Separation of binary mixtures of organic compounds	Separation using aqueous NaHCO_3 , NaOH and HCl . Separation using ether solvent.

TOPIC GRIP



Subjective Questions

1. What type of linkage is known as glycosidic linkage?
2. What is the basic structural difference between starch and cellulose?
3. Glucose forms an oxime when treated with hydroxylamine, but glucose pentaacetate does not. why?
4. Give the sequence of reactions when D-glucose reacts with excess of $C_6H_5NHNH_2$ in the presence of acetic acid?
5. Give the main points of differences between glucose and fructose.
6. Illustrate Ziegler-Natta polymerization.
7. Indicate which of the following polymers are homopolymers, and which are copolymers. Mark the bonds that connect the monomer units.



8. Give reasons for the following statements.
 - (i) o- and p-nitrophenols can be separated by steam distillation.
 - (ii) Sodium fusion extract has to be neutralized with dil. HNO_3 before testing for the halogen with $AgNO_3$.
 - (iii) Benzene does not decolourise bromine water though it contains three double bonds.
 - (iv) Lassaigne's test for nitrogen is not given by diazonium compound.
 - (v) Sodium fusion extract is boiled with HNO_3 for testing for halogen, if nitrogen and sulphur are present.

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9. How will you distinguish between chlorobenzene and benzyl chloride?
10. Discuss the main purpose of vulcanization of rubber.



Straight Objective Type Questions

Directions: This section contains multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

11. Glucose, fructose and mannose form the same osazone because they have the same configurations at all carbon atoms except
(a) C_1 and C_2 (b) C_2 and C_3 (c) C_3 and C_4 (d) C_4 and C_5
12. Pairs of isomeric polyhydroxy aldehydes differing only in the configuration at first carbon are called
(a) anomers (b) enantiomers (c) mesomers (d) epimers
13. Percentage of α -D-glucose in the equilibrium mixture with its anomer in aqueous solution is
(a) 64 (b) 52.5 (c) 36 (d) 32
14. A fibre, which does not contain nitrogen, is
(a) Nylon-6 (b) Dacron (c) Orlon (d) Buna-N
15. A mixture of aniline and paranitrobenzoic acid can be separated by using
(a) only con. HCl (b) only NaHCO_3 solution
(c) only con. HNO_3 (d) either conc.HCl or NaHCO_3



Assertion–Reason Type Questions

Directions: Each question contains Statement-1 and Statement-2 and has the following 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

16. Statement 1

Tollen's test can be used to distinguish between glucose and fructose.

and

Statement 2

Glucose is an aldose while fructose is a ketose.

17. Statement 1

D-glucose does not undergo addition reaction with NH_3 and NaHSO_3 .

and

Statement 2

NH_3 and NaHSO_3 are unable to break the cyclic hemiacetal structure of D-glucopyranose.

18. Statement 1

Low density polyethylene (LDPE) is a branched chain polymer.
and

Statement 2

LDPE is prepared by coordination polymerization of ethylene using Ziegler-Natta catalyst.

19. Statement 1

An aqueous solution of sucrose is dextrorotatory but on hydrolysis in presence dilute acid it becomes laevorotatory.
and

Statement 2

Hydrolysis of sucrose gives more of laevorotatory fructose than dextrorotatory glucose.

20. Statement 1

Mulliken and Barker's test is used to detect nitro group in an organic compound.
and

Statement 2

Nitro compounds are reducing agents and they reduce Tollen's reagent in the test.

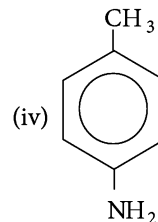
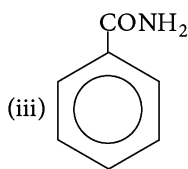
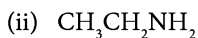
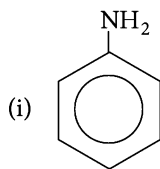
**Linked Comprehension Type Questions**

Directions: This section contains 2 paragraphs. Based upon the paragraph, 3 multiple choice questions have to be answered. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

Passage I

In order to identify and characterize the various functional groups present in an organic compound (or a mixture of organic compounds), a complete knowledge of the tests answered by these functional groups is essential.

21. An organic compound of the formula $C_4H_{10}O$, gives a blue coloured solution when Victor-Meyer's test is performed. The organic compound could be
 (a) $CH_3CH_2CH_2CH_2OH$ (b) $CH_3CH_2\underset{\substack{| \\ OH}}{CH}-CH_3$ (c) $(CH_3)_2CHCH_2OH$ (d) $(CH_3)_3OH$
22. An organic compound burns with a sooty flame and gives a violet colouration with neutral $FeCl_3$ solution. It gives effervescence when treated with metallic sodium and also with sodium bicarbonate solution. The compound could be
 (a) phenol (b) benzoic acid (c) salicylic acid (d) toluic acid
23. An organic compound burns with a sooty flame and dissolves in dilute acids. The compound gives a product with foul smell when heated with alkaline chloroform. The organic compound could be



- (a) (i), (iii) and (iv) (b) (ii) only (c) (i) and (iv) only (d) (i), (ii) and (iv)

7.36 Carbohydrates, Polymers and Practical Organic Chemistry

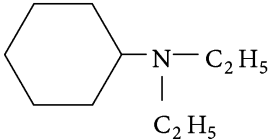
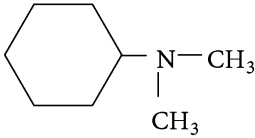
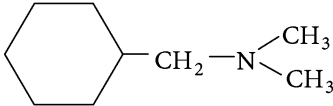
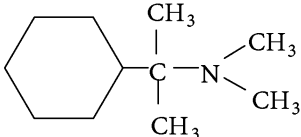
Passage II

An organic compound (A) gives violet colour with neutral FeCl_3 . It answers Liebermann's test. This compound on catalytic reduction gives (B). The saturated compound (B) on oxidation with CrO_3 gives (C) of molecular formula $\text{C}_6\text{H}_{10}\text{O}$. (C) gives precipitate with 2,4-dinitrophenylhydrazine. (C) can be obtained by reductive ozonolysis of (D). The other product of reductive ozonolysis, (E), undergoes Cannizzaro reaction with benzaldehyde to give (F) and HCOONa . Answer the following questions.

24. Arrange in order of increasing acidity of

(i) (A)	(ii) p-nitrophenol	(iii) p-methylphenol	(iv) $\text{C}_2\text{H}_5\text{OH}$
(a) (iv) < (iii) < (i) < (ii)	(b) (iv) < (iii) < (ii) < (i)		
(c) (i) < (iv) < (iii) < (ii)	(d) (ii) < (iv) < (iii) < (i)		

25. (D) can be obtained by heating the amine oxide formed from

- (a) 
- (b) 
- (c) 
- (d) 

26. Which of the statements about (F) is wrong?

- (a) (F) can have intermolecular hydrogen bonding.
 (b) (F) is produced by $\text{S}_{\text{N}}1$ reaction of $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ with $\text{OH}^\ominus$.
 (c) (F) undergoes facile dehydration.
 (d) (F) reacts with acetic anhydride to form a compound used in perfumery.



Multiple Correct Objective Type Questions

Directions: Each question in this section has four suggested answers of which ONE OR MORE answers will be correct.

27. Linear Polymer(s) among the following is/are

- (a) Terylene (b) amylopectin (c) cellulose (d) Nylon

28. Which of the following pairs contain only reducing carbohydrates?

- (a) maltose, sucrose (b) fructose, maltose (c) starch, ribose (d) glucose, galactose

29. The polymer(s) which contain 1, 3-butadiene as one of the monomers is/are

- (a) SBR (b) PAN (c) neoprene (d) nitrile rubber



Matrix-Match Type Question

Directions: Match the elements of Column I to elements of Column II. There can be single or multiple matches.

30.

Column I

- (a) Glucose
(b) Sucrose
(c) Mannose
(d) Glycogen

Column II

- (p) Reduces Tollens' reagent
(q) Gives the same osazone as fructose
(r) Presence of glycosidic linkage
(s) Aldohexose
(t) Polysaccharide

IIT ASSIGNMENT EXERCISE

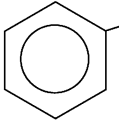


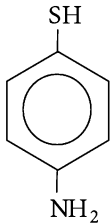
Straight Objective Type Questions

Directions: This section contains multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

31. Ester linkages are present in
 (a) teflon (b) orlon (c) nylon (d) terylene
32. A material resistant to heat and chemical attack is
 (a) polythene (b) PTFE (c) PAN (d) PVC
33. Zeigler-Natta catalyst is
 (a) $(C_6H_5)_3Al$ and $TiCl_4$ (b) $(CH_3)_3Al$ and $ZnCl_2$ (c) $(C_2H_5)_3Al$ and $TiCl_4$ (d) Cu_2Cl_2 and $TiCl_4$
34. Orlon is
 (a) PAN (b) PVC (c) PMMA (d) SBR
35. Which of the following carbohydrates is a non-sugar?
 (a) Galactose (b) Glycogen (c) Fructose (d) Lactose
36. Interconversion of glucose, fructose and mannose when warmed with dilute alkali or amine is called
 (a) Fries rearrangement (b) Lobry de Bruyn-van Ekenstein rearrangement
 (c) Beckman's rearrangement (d) Hoffmann's rearrangement
37. Interchange between α -D-glucose and β -D-glucose in aqueous solution to form an equilibrium mixture is called
 (a) isomerization (b) molecular rearrangement
 (c) mutarotation (d) tautomerism
38. In starch and maltose, the glucose units are linked between
 (a) C_1 and C_1 (b) C_1 and C_2 (c) C_1 and C_4 (d) C_4 and C_4
39. The sweetest natural sugar is
 (a) cane sugar (b) glucose (c) fructose (d) galactose
40. Lassaigne's solution gives violet colouration with sodium nitroprusside. This indicates presence of
 (a) nitrogen (b) fluorine (c) chlorine (d) sulphur
41. When Lassaigne's solution is treated with $dil.HNO_3$ and $AgNO_3$, a white precipitate soluble in ammonium hydroxide shows the presence of
 (a) chlorine (b) bromine (c) sulphur (d) nitrogen
42. Glucose on prolonged heating with HI and red phosphorus at 373K gives
 (a) sorbose (b) sorbitol (c) hexane (d) hexan-1-ol
43. The products of oxidation of glucose by bromine water and $conc.HNO_3$ are respectively
 (a) gluconic acid and glucaric acid (b) oxalic acid and saccharic acid
 (c) glucaric acid and gluconic acid (d) saccharic acid and oxalic acid
44. Which of the following statements about starch is false?
 (a) Starch is a polymer of α -D-glucose.
 (b) It consists of 20% amylose and 80% amylopectin.

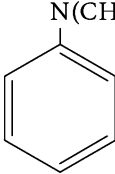
- (c) Glycosidic linkages between glucose units are always formed only between C_1 and C_4 .
 (d) Amylose is water soluble and amylopectin is insoluble.
45. Number of $-OH$ group(s) that can be methylated by treating glucose with CH_3OH is/are
 (a) 4 (b) 1 (c) 5 (d) 3
46. One mole of glucose can react with how many moles of phenyl hydrazine to form osazone?
 (a) 1 (b) 2 (c) 3 (d) 4
47. Which of the following is used in making nylon-6,6?
 (a) Caprolactam (b) Adipic acid (c) Terephthalic acid (d) Ethylene glycol
48. Which among the following is a polymer?
 (a) Teflon (b) Pyrene (c) acrolein (d) Freon
49. Which of the following monomers may not undergo step growth polymerization?
 (a) Adipic acid (b) Hexamethylene diamine (c) Vinyl chloride (d) Phenol
50. An organic compound is treated with $NaNO_2$ and HCl under ice cold conditions and the resulting solution is treated with 2-naphthol solution. A brilliant red colour indicates that the organic compound contains
 (a) aliphatic $-NH_2$ group (b) aromatic $-NH_2$ group (c) $-CONH_2$ group (d) $-NO_2$ group
51. Natural rubber is a polymer of
 (a) chloroprene (b) isoprene (c) butadiene (d) styrene
52. Which of the following is an example of phenol-formaldehyde resin?
 (a) Perlon (b) Nylon-6,6 (c) Bakelite (d) Dacron
53. The sodium fusion extract of an organic compound gave blue colour when heated with acidified ferric chloride solution. The organic compound could be
- (a) $C_6H_5 - N = N - C_6H_5$

(b) 

(c) 

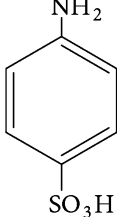
(d) NH_2NH_2
54. A compound (A) reacts with phenyl hydrazine to give a crystalline yellow precipitate. When (A) is added to a solution of rosaniline—hydrochloride decolourized by SO_2 gas, the solution remains colourless. (A) is reduced with $LiAlH_4$ to give (B). (B) is a
 (a) phenol (b) primary alcohol
 (c) aromatic polyhydric alcohol (d) secondary alcohol
55. A compound containing a conjugated double bond, decolourises bromine water. On heating with I_2 and $NaOH$, a yellow precipitate is formed. If the compound contains five carbons including a methyl substituent, the compound may be
 (a) 3-methyl but-3-en-2-one. (b) 3-methyl but-3-enal
 (c) 3-methyl but-2-enal (d) 2-methyl but-2-enal
56. Arrange the following in the increasing order of their intermolecular forces nylon, PVC, rubber, cellulose nitrate
 (A) (B) (C) (D)
- (a) $(C) < (A) < (B) < (D)$ (b) $(C) < (B) < (A) < (D)$ (c) $(D) < (C) < (B) < (A)$ (d) $(D) < (C) < (A) < (B)$
57. Polyurethane is a polymerisation product of ethylene glycol and
 (a) vinyl chloride (b) terephthalic acid
 (c) acrylonitrile (d) toluene-2,4-diisocyanate

7.40 Carbohydrates, Polymers and Practical Organic Chemistry

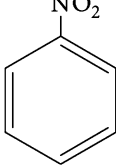
58. The enzyme, which decomposes glucose to alcohol and CO_2 is
 (a) Invertase (b) Zymase (c) Diastase (d) Maltase
59. Which among the following is a non-reducing sugar?
 (a) Maltose (b) Glucose (c) Cellulose (d) Cellobiose
60. An ice cold solution of aniline in HCl is treated with NaNO_2 . The compound (A) thereby formed is tested for nitrogen using Lassaigne's test. The result would be
 (a) a Prussian blue colour confirming the presence nitrogen in aniline.
 (b) a green colour confirming the presence of nitrogen in aniline
 (c) an absence of any coloured solution to confirm the presence of nitrogen
 (d) evolution of ammonia which gives a colour with Nessler's reagent.
61. A monomer unit on ozonolysis produced two molecules of formaldehyde and one molecule of $\text{O}=\text{C}-\underset{\text{Cl}}{\underset{|}{\text{C}}}-\text{H}$. The monomer unit will form the polymer
 (a) nylon (b) neoprene (c) buna -S (d) polyvinyl chloride.
62. An organic compound on elemental analysis is found to contain two chlorine atoms. This compound is treated with caustic soda and subsequently with $[\text{Ag}(\text{NH}_3)_2]\text{OH}$ to get a silver deposit. Then we can say that
 (a) The two Cl atoms are attached to an aromatic ring.
 (b) The two Cl atoms are on adjacent carbons of an aliphatic chain.
 (c) The two Cl atoms are on the same carbons of an aliphatic chain.
 (d) One chlorine is on a tertiary carbon atom.
63. A compound gives white precipitate with Tollen's reagent and answers Lucas test in about five minutes. The compound may be
 (a) $\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_2\text{OH}$ (b) $\text{CH}_3 - \underset{\text{OH}}{\underset{|}{\text{C}}} = \text{CH} - \text{CH}_3$
 (c) $\text{CH}_3 - \underset{\text{OH}}{\underset{|}{\text{CH}}} - \text{CH} = \text{CH}_2$ (d) $\text{CH} \equiv \text{C} - \underset{\text{OH}}{\underset{|}{\text{CH}}} - \text{CH}_3$
64. Which of the following compounds will give deep blue colour on boiling their Lassaigne's extract with ferrous sulphate solution followed by acidification and addition of a drop of aqueous ferric chloride?
- 

(i)

(ii) $\text{H}_2\text{N} - \text{NH}_2$

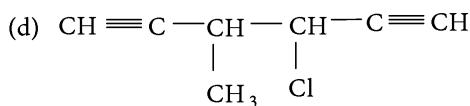
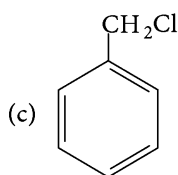
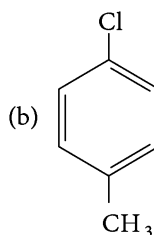
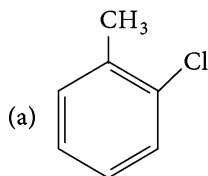


(iii)

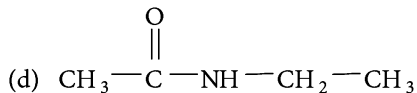
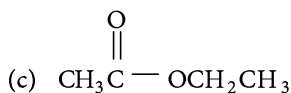
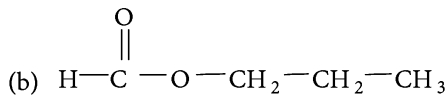
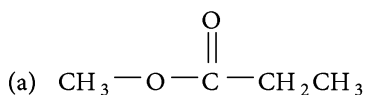


(iv)
- (a) (i) and (iv) only (b) (i), (ii) and (iv) (c) (i), (iii) and (iv) (d) (i) only
65. A compound (A) gives red colour with ceric ammonium nitrate. (A) on mild oxidation gives (B) which restores the pink colour of Schiff's reagent. (A) is
 (a) aldehyde (b) primary alcohol (c) secondary alcohol (d) alkyl bromide
66. The oxidation of monosaccharides using periodic acid, will work well
 (a) in aqueous medium (b) in organic solvent
 (c) in the presence of a catalyst (d) in the presence of base

67. Cellulose on treatment with sodium hydroxide gives
 (a) mercerised cotton (b) D-(+)-glucose (c) pyroxylin (d) xanthate
68. The intermolecular forces of attraction are expected to be greatest in
 (a) linear chain polymers (b) branched chain polymers
 (c) cross linked polymers (d) elastomers.
69. An organic compound was fused with sodium and the water extract was treated with silver nitrate solution when a black precipitate was obtained. The test suggests
 (a) absence of halogen (b) presence of sulphur (c) presence of nitrogen (d) presence of halogen
70. An organic compound of empirical formula C_7H_7Cl , gives sooty flame on burning. It gives white precipitate with $AgNO_3$. The compound is



71. A compound (A) reduces $[Ag(NH_3)_2]OH$ and $HgCl_2$. On warming (A) with (B) in presence of conc. H_2SO_4 gives a product with pleasant fruity smell. When (B), containing two carbons, is heated with conc. H_2SO_4 to $180^\circ C$, (C) is obtained. Identify correct statement regarding (C).
 (a) It decolourizes bromine water (b) It is oxidized to (B) by hot acidified $KMnO_4$
 (c) It is oxidized to (A) by cold alkaline dil. $KMnO_4$ (d) It is unaffected by H_2 and Pt
72. A liquid (A) with fruity smell gives (B) and (C) on hydrolysis. (B) on oxidation with potassium dichromate gives (C). The molecular formula of (A) is



73. Which of the following have α -glycosidic linkages?
 (i) starch (ii) cellobiose (iii) lactose
 (iv) maltose (v) cellulose
 (a) (i), (ii) and (iv) (b) (ii), (iii) and (v) (c) (i) and (iv) (d) (i), (iv) and (v)
74. Which of the following pairs contain only reducing carbohydrates?
 (i) glucose, fructose (ii) maltose, lactose
 (iii) sucrose, cellulose (iv) starch, cellobiose
 (a) (i), (ii) and (iii) (b) (i), (ii) and (iv) (c) (i) and (ii) (d) (i), (ii), (iii) and (iv)

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75. Which of the following will exhibit mutarotation?

(i) Fructose	(ii) Glucose	(iii) Maltose	(iv) Galactose
(v) Lactose	(vi) Sucrose		
(a) (i), (ii), (iii), (iv) and (v)	(b) (i), (ii), (iii), (iv), (v) and (vi)		
(c) (i), (ii), (iv), and (vi)	(d) (i), (ii), (iii) and (vi)		

76. Two chiral centres are present in

(a) aldotetrose	(b) aldohexose	(c) aldotriose	(d) ketotriose

77. Which of the following does not have any chiral centre?

(a) glyceraldehydes	(b) dihydroxyacetone	(c) aldopentose	(d) ketopentose

78. When treated with ammoniacal silver nitrate, glucose forms

(a) saccharic acid	(b) glucuronic acid	(c) meso tartaric acid	(d) gluconic acid

79. Which of the following compounds on reduction will give a mixture of two diastereomers?

(a) Glucose	(b) Mannose	(c) Fructose	(d) Galactose

80. Identify the correct statements among the following

- (a) Cellulose has alpha 1, 4-glycosidic linkage while amylose has beta 1, 4-glycosidic linkage.
 (b) Cellulose has alpha 1, 6-glycosidic linkage and amylose has alpha 1, 4-linkage.
 (c) Cellulose has beta 1, 6-glycosidic linkage and amylose has alpha 1, 6-linkage.
 (d) Cellulose has beta 1, 4-glycosidic linkage and amylose has alpha 1, 4-glycosidic linkage.

81. Cellulose $\xrightarrow[\text{(ii) dil HCl}]{\text{(i) CS}_2 / \text{NaOH(aq)}} \text{(A)}$

(A) obtained in the above treatment of cellulose is known as

(a) Cellulose xanthate	(b) Cellulose sulphide	(c) viscose rayon	(d) Gun cotton

82. The reaction of glucose with methanol and a small amount of HCl to form methyl glucoside shows that

(a) it is a pentahydroxy compound.	(b) it is a polyhydroxy aldehyde.
(c) it contains six carbon atoms in a straight chain.	(d) it exists as cyclic hemiacetal.

83. Which of the following statement is correct with respect to two epimeric hexoses?

- (a) C-1 and C-2 of both have the same configuration.
 (b) C-3, C-4 and C-5 of both have the same configuration
 (c) C-2, C-3 and C-4 of both have the same configuration
 (d) one of them must be an aldose and the other must be a ketose

84. Number of optical isomers possible for a ketohexose is

(a) 8	(b) 4	(c) 16	(d) 2

85. The number of moles of periodic acid (HIO_4) required to oxidize completely one mole of D(+) glucose is

(a) 3	(b) 4	(c) 5	(d) 6

86. The number of moles of periodic acid required to oxidize one mole of methyl glucoside is

(a) 2	(b) 3	(c) 4	(d) 5

87. (+) Sucrose is

(a) α -D-glucopyranosyl- β -D-fructopyranoside	(b) α -D-glucopyranosyl- β -D-fructofuranoside
(c) α -D-glucopyranosyl- β -D-fructofuranoside	(d) α -D-glucopyranosyl- α -D-fructopyranoside

88. The reagent that can be used to distinguish between glucose and fructose is

(a) Fehling's solution	(b) Schiff's reagent	(c) Bromine water	(d) both (a) and (b)

89. Intermolecular forces present in nylon-66 are mainly
 (a) hydrogen bonding (b) dipole-dipole interactions
 (c) van der Waal's forces (d) cross linking
90. A step growth polymer among the following is
 (a) Buna – S (b) neoprene (c) Teflon (d) Dacron



Assertion–Reason Type Questions

Directions: Each question contains Statement-1 and Statement-2 and has the following 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

91. Statement 1

Glucose reduces Tollens' reagent and hence used in silvering of mirrors.

and

Statement 2

Glucose is less acidic than monohydric alcohols such as ethanol.

92. Statement 1

Millons test is a test used to identify carbohydrates in organic qualitative analysis.

and

Statement 2

Millon's reagent is a solution of mercurous nitrate and mercuric nitrate in nitric acid.

93. Statement 1

Liebermann's nitroso reaction is used as a test for phenol as well as for secondary amines.

and

Statement 2

Indophenol is formed in the reaction.



Linked Comprehension Type Questions

Directions: This section contains 1 paragraph. Based upon the paragraph, 3 multiple choice questions have to be answered. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

Passage I

Carbohydrates are classified as monosaccharides, oligosaccharides and polysaccharides depending on their behaviour towards hydrolysis. All monosaccharides containing five or six carbon atoms can have two cyclic structures namely furanose and pyranose form. Oligosaccharides are further classified as di, tri, tetra etc saccharides depending upon the number of monosaccharide units actually obtained on hydrolysis. In oligosaccharides and polysaccharides, the different monomer units are joined together by glycosidic linkages.

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94. Mutarotation involves
- (a) conformational inversion (b) racemisation
(c) diastereoisomerisation (d) epimerization
95. The incorrect statement about sucrose is
- (a) It does not reduce Tollen's reagent for Fehling's solution.
(b) It is not optically active.
(c) It is an α -D-glucoside.
(d) It does not form osazone with phenyl hydrazine.
96. The wrong statement relating to carbohydrates is
- (a) Monosaccharides, whether aldose or ketose, are reducing sugars.
(b) Most naturally occurring monosaccharides are pentoses or hexoses.
(c) Most disaccharides are reducing sugars, only exception is sucrose which is non reducing.
(d)
$$\begin{array}{c} \text{CH}_2\text{OH} \xrightarrow{5\text{HIO}_4} 4\text{HCOOH} + 2\text{HCHO} \\ | \\ (\text{CHOH})_4 \\ | \\ \text{COOH} \\ \text{gluconic acid} \end{array}$$



Multiple Correct Objective Type Questions

Directions: Each question in this section has four suggested answers of which ONE OR MORE answers will be correct.

97. Identify the correct statement(s) about thermoplastics from among the following
- (a) They can be remelted and remoulded many times by heating and cooling.
(b) The intermolecular forces in thermoplastics are weaker than those present in elastomers.
(c) There are no cross links between polymeric chain.
(d) Neoprene is a thermoplastics polymer.
98. Which of the following carbohydrates undergo mutarotation?
- (a) Maltose (b) Sucrose (c) Cellulose (d) Fructose
99. The wrong statement(s) among the following is/are
- (a) Glucose does not react with Grignard reagents. (b) Hydrolysis of maltose can be called inversion of sugar.
(c) Amylopectin gives blue colour with iodine. (d) Ribose is an aldopentose.



Matrix-Match Type Question Questions

Directions: Match the elements of Column I to elements of Column II. There can be single or multiple matches.

100.

Column I

- (a) Nylon-66
(b) Teflon
(c) Galactose
(d) Cellulose

Column II

- (p) Addition polymer
(q) Condensation polymer
(r) Linear polymer
(s) Thermoplastic polymer
(t) Reducing carbohydrate

ADDITIONAL PRACTICE EXERCISE



Subjective Questions

101. Write the steps involved in the conversion of D-glucose to D-fructose.
102. What are the main differences between thermoplastic polymers and thermosetting polymers?
103. Give the properties of glucose which cannot be explained by its open chain structure.
104. State whether the following statements are true or false?
 - (i) Glucose is the only aldose that shows mutarotation.
 - (ii) The smallest aldose to form a hemiacetal is a tetrose.
 - (iii) α -D-glucose $\rightleftharpoons$ aldehyde form $\rightleftharpoons$ β -D-glucose. This conversion is known as mutarotation.
 - (iv) The anomers of D-glucose have specific rotations of same magnitude but opposite sign.
 - (v) Sucrose is a 1,4'-glycoside.
 - (vi) In alkaline medium, fructose is a reducing sugar.
 - (vii) Cellobiose is a polysaccharide.
 - (viii) Natural sugar has D-configuration.
105. Explain the products obtained when
 - (i) Fructose is treated with excess phenyl hydrazine
 - (ii) Glucose is heated with concentrated hydrochloric acid
 - (iii) Glucosazone is hydrolysed with dilute hydrochloric acid



Straight Objective Type Questions

Directions: This section contains multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

106. Neoprene, Plexiglas and orlon are all

(a) homopolymers	(b) copolymers	(c) step growth polymers	(d) fibres
107. The test that cannot be used to distinguish between 1-propanol and 2-propanol is

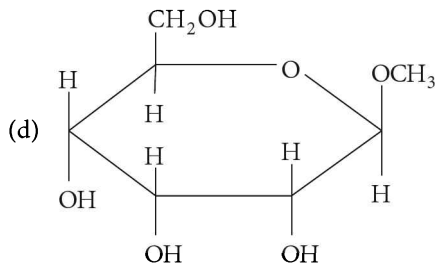
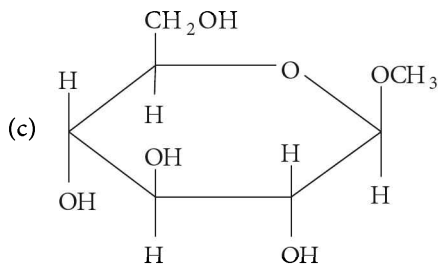
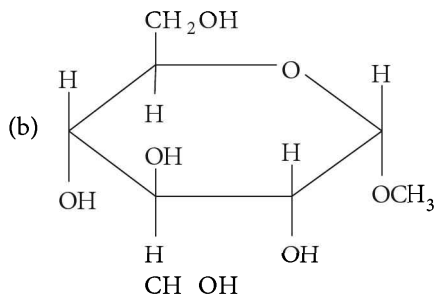
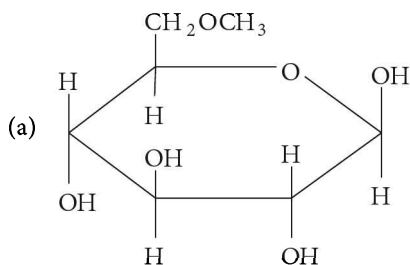
(a) Lucas test	(b) Iodoform test
(c) Reaction with acetic anhydride	(d) Victor Meyer's test
108. A mixture of benzoic acid and phenol can be separated using

(a) Dilute HCl	(b) Aqueous NaOH	(c) aqueous NaHCO_3	(d) both (b) and (c)
109. A chain growth copolymer is

(a) terylene	(b) neoprene	(c) nylon-6	(d) SBR
110. Which of the following is a wrong statement?
 - (a) Cellulose is a biodegradable homopolymer
 - (b) Nylon-6 is a linear homopolymer in which the monomer units are linked through amide linkages
 - (c) Gutta percha is cis-polyisoprene
 - (d) p-benzoquinone acts as a chain inhibitor in free radical polymerization reaction

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111. The polymer which does not contain halogen is
 (a) neoprene (b) glyptal (c) PVC (d) Teflon
112. D(+) glucose $\xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) HCN}}$ (A) $\xrightarrow[\Delta]{\text{HI/P}}$ (B)
 The compound (B) in the above reaction is
 (a) n-heptane (b) n-hexane (c) n-heptanoic acid (d) 7-iodoheptanoic acid
113. Identify the wrong statement among the following
 (a) Molisch's test is used for the identification of carbohydrates.
 (b) Fehling solution A is an aqueous solution of CuSO_4 .
 (c) Fehling solution B is an alkaline solution of Rochelle salt.
 (d) All aldehydes reduce Fehling's solution to a red precipitate of Cu_2O .
114. Methyl- α -D-glucoside and methyl- β -D-glucoside are
 (a) anomers (b) epimers (c) enantiomers (d) functional isomers
115. The correct structure of methyl- β -D-glucoside is



Assertion-Reason Type Questions

Directions: Each question contains Statement-1 and Statement-2 and has the following 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

116. Statement 1

D-glucose on treatment with dilute alkali gives an equilibrium mixture of D-glucose, D-mannose and D-fructose.
and

Statement 2

The rearrangement involves the formation of enediol.

117. Statement 1

Dextro rotatory solution of sucrose on heating with dilute acid becomes laevorotatory.
and

Statement 2

All disaccharides on hydrolysis undergo inversion of rotation.

118. Statement 1

Fructose reduces Tollen's reagent even though it does not contain an aldehyde group.
and

Statement 2

In presence of bases, fructose undergoes Lobry de Bruyn van Ekenstein rearrangement.

119. Statement 1

Maltose is a reducing disaccharide while sucrose is a non-reducing disaccharide.
and

Statement 2

Maltose contains a hemiacetal linkage while sucrose does not contain such a linkage.

120. Statement 1

All reducing sugars undergo mutarotation.
and

Statement 2

α -D-glucose during mutarotation is converted to an equilibrium mixture containing 50% each of α -D-glucose and β -D-glucose.

**Linked Comprehension Type Questions**

Directions: This section contains 2 paragraphs. Based upon the paragraph, 3 multiple choice questions have to be answered. Each question has 4 choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

Passage I

Polymers are classified in a number of ways. On the basis of structures, they are divided into three types: linear polymers, branched chain polymers and cross linked polymers. Depending upon the nature of the repeating structural unit, polymers are classified as homopolymers and copolymers. Based on the magnitude of the intermolecular forces, they are classified into four types namely elastomers, fibres, thermoplastics and thermosetting plastics. Polymers are again classified as addition polymers and condensation polymers depending on the mode of polymerization

121. Which of the following can be considered as a condensation homopolymer?

- (a) Teflon (b) cellulose (c) terylene (d) bakelite

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122. The different linear chains of terylene molecules are held together by
- van der Waals forces
 - covalent bonds
 - hydrogen bonds
 - dipole-dipole interaction
123. The advantage of polymerization using Ziegler–Natta catalyst is
- It takes place by free radical polymerization.
 - It takes place by anion polymerization mechanism.
 - It gives linear polymer permitting stereochemical control.
 - It gives highly branched polymer.

Passage II

Synthetic polymers are classified by their sequence of synthesis as chain growth or step growth polymers. Chain growth polymers are produced by chain reaction polymerization in which an initiator adds to a carbon–carbon double bond of a vinyl monomer to yield a reactive intermediate. The intermediate reacts with a second monomer to yield a new intermediate which reacts with a third unit and so on. The initiator may be a radical or an acid or an anion. Acid catalysed polymerization is effective in case of vinyl monomers having electron donating groups. Anionic polymerization requires the presence of electron withdrawing groups. One of the important catalysts used in polymerization is Ziegler–Natta catalyst (triethyl aluminium and titanium tetrachloride). One of the important aspects of Zeiglar–Natta catalysed polymers is that they are stereo–chemically controllable. Three forms (i) isotactic (ii) syndiotactic and (iii) atactic can be produced.

124. Vinylidene chloride $\text{H}_2\text{C} = \text{CCl}_2$ does not polymerize in isotactic, syndiotactic or atactic forms because
- it contains electronegative chlorine atoms.
 - it has sp^2 hybridized carbon.
 - it is a planar molecule.
 - the polymer formed has no chiral centre
125. Arrange the following monomers in order of increasing reactivity towards cationic polymerization.
- | | | | |
|--|---|---|---|
| (i) $\text{H}_2\text{C} = \text{CHCH}_3$ | (ii) $\text{H}_2\text{C} = \text{CHCl}$ | (iii) $\text{H}_2\text{C} = \text{CHC}_6\text{H}_5$ | (iv) $\text{H}_2\text{C} = \text{CHCO}_2\text{C}_2\text{H}_5$ |
| (a) (i) < (ii) < (iii) < (iv) | (b) (iv) < (i) < (ii) < (iii) | (c) (iv) < (ii) < (i) < (iii) | (d) (iii) < (iv) < (i) < (ii) |
126. Arrange the following monomers towards reactivity in anionic polymerization.
- | | | | |
|-----------------------------------|----------------------------------|--|------------------------|
| (i) $\text{CH}_2 = \text{CHCH}_3$ | (ii) $\text{CH}_2 = \text{CHCN}$ | (iii) $\text{CH}_2 = \text{CHC}_6\text{H}_5$ | |
| (a) (i) < (ii) < (iii) | (b) (i) < (iii) < (ii) | (c) (i) = (ii) < (iii) | (d) (ii) = (iii) < (i) |



Multiple Correct Objective Type Questions

Directions: Each question in this section has four suggested answers of which ONE OR MORE answers will be correct.

127. Which of the following statements are not correct?
- Hydrolysis of lactose gives D-glucose and D-galactose.
 - In sucrose, glucose is present in the furanose form while fructose is present in the pyranose form.
 - Gun cotton is cellulose triacetate.
 - On heating with dilute H_2SO_4 under pressure, cellulose undergoes hydrolysis to give D-glucose.
128. Polyvinyl chloride is a/an
- chain growth polymer
 - thermoplastic polymer
 - cross linked polymer
 - elastomer
129. Glucose is oxidized to gluconic acid or its anion by
- $\text{Br}_2/\text{H}_2\text{O}$
 - I_2/OH^-
 - con. HNO_3
 - Tollen's reagent

**Matrix-Match Type Questions**

Directions: Match the elements of Column I to elements of Column II. There can be single or multiple matches.

130.

Column I

- (a) D(+) glucose
- (b) D(−) fructose
- (c) (+) Maltose
- (d) (+) sucrose

Column II

- (p) Lobry de Bruyn–van Ekenstein rearrangement
- (q) Red precipitate with Fehling's solution
- (r) Exhibits mutarotation
- (s) oxidized by $\text{Br}_2/\text{H}_2\text{O}$
- (t) $\text{C}_1\text{--C}_2$ glycosidic linkage

SOLUTIONS

ANSWER KEYS

Topic Grip

- The C—O—C linkage that joins two or more monosaccharide units in oligo and polysaccharides is known as glycosidic linkage.
- Starch consists of α -D- glucose units joined through glycosidic linkage while cellulose is made up of β -D-glucose units. The major fraction of starch (amylopectin) contains branching while cellulose contains only straight chain.
- Glucose pentaacetate cannot be converted into the open chain form because its anomeric hydroxyl group, i.e, the hydroxyl group at C-1, is acetylated. So it cannot get a free—CHO group and hence cannot form oxime
- Glucosazone is formed
- Glucose is a polyhydroxy aldehyde while fructose is a polyhydroxyketone. Glucose is oxidised by bromine water but fructose is not.
- Polymerisation using zeigler-Natta catalyst $[(C_2H_5)_3Al / TiCl_4]$ can be carried under relatively mild conditions and linear polymers with considerable degree of stereochemical control is generally obtained.
- (i) and (iv) — homopolymers
(ii), (iii) and (v) — copolymers
- (i) o-nitrophenol is steam volatile while p-nitrophenol is not.
(ii) To neutralise the alkali and to decompose NaCN or Na_2S if present.
(iii) Double bonds are delocalised by resonance.
- (iv) Diazonium compounds decompose on heating and give out N_2 gas
- Benzyl chloride gives white precipitate on heating with alcoholic $AgNO_3$ while chlorobenzene does not.
- To improve its elasticity and resistance to oxidation.
- (a) 12. (a) 13. (c)
14. (b) 15. (d) 16. (d)
17. (a) 18. (c) 19. (c)
20. (c) 21. (b) 22. (c)
23. (c) 24. (a) 25. (c)
26. (c)
27. (a), (c), (d)
28. (b), (d)
29. (a), (d)
30. (a) $\rightarrow$ (p), (q), (s)
(b) $\rightarrow$ (r)
(c) $\rightarrow$ (p), (q), (s)
(d) $\rightarrow$ (r), (t)

Straight Objective Type Questions

31. (d)	32. (b)	33. (c)
34. (a)	35. (b)	36. (b)
37. (c)	38. (c)	39. (c)
40. (d)	41. (a)	42. (c)
43. (a)	44. (c)	45. (b)
46. (c)	47. (b)	48. (a)
49. (c)	50. (b)	51. (b)
52. (c)	53. (b)	54. (d)
55. (a)	56. (b)	57. (d)
58. (b)	59. (c)	60. (c)
61. (b)	62. (c)	63. (d)
64. (a)	65. (b)	66. (a)
67. (a)	68. (a)	69. (b)
70. (c)	71. (a)	72. (c)
73. (c)	74. (c)	75. (a)
76. (a)	77. (b)	78. (d)

79. (c)	80. (d)	81. (c)
82. (d)	83. (b)	84. (a)
85. (c)	86. (a)	87. (b)
88. (c)	89. (a)	90. (d)
91. (c)	92. (d)	93. (a)
94. (c)	95. (b)	96. (d)
97. (a), (c)		
98. (a), (d)		
99. (b), (c)		
100. (a) $\rightarrow$ (q), (r)		
(b) $\rightarrow$ (p), (r), (s)		
(c) $\rightarrow$ (t)		
(d) $\rightarrow$ (q), (r)		

Subjective Type Questions

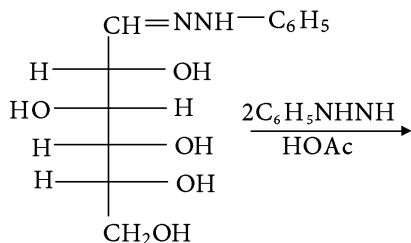
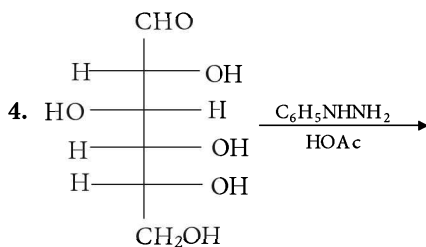
- D-glucose is first converted to glucosazone. It is then hydrolysed with dilute acid to form glucosone and then reduced with zinc and acetic acid.
- The process of heat softening and cooling can be repeated many times on thermoplastics. Thermosetting polymers become infusible and hard on heating and hence cannot be remelted or remoulded.
- Glucose does not undergo certain reactions of aldehydes such as Schiff's test, reaction with $NaHSO_3$ etc. It exists in two crystalline forms and exhibits mutarotation. It gives two isomeric methyl glucosides when treated with CH_3OH and $HCl_{(g)}$
- (ii), (iii), (vi) and (viii) are true
- (i) Fructosazone is formed
(ii) Hydroxymethyl furfural is first formed
(iii) Glucosone is obtained

106. (a)	107. (c)	108. (c)	121. (b)	122. (d)	123. (c)	130. (a) → (p), (q), (r), (s) (b) → (p), (q), (r) (c) → (q), (r), (s) (d) → (t)
109. (d)	110. (c)	111. (b)	124. (d)	125. (c)	126. (b)	
112. (a)	113. (d)	114. (a)	127. (b), (c)			
115. (c)	116. (a)	117. (c)	128. (a), (b)			
118. (a)	119. (a)	120. (c)	129. (a), (b), (d)			

1. The C—O—C linkage that joins two or more monosaccharide units in oligo and polysaccharides is known as glycosidic linkage. It is formed by the interaction of two —OH groups of two monosaccharides with the elimination of a molecule of water. For example, in maltose, the two α -D-glucose units are joined by a 1, 4- α -glucosidic linkage

Cellulose, however, contains straight chains in which β -D-glucose units are joined by 1, 4- β glycosidic linkage

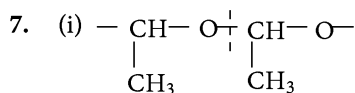
But glucose pentaacetate cannot be converted into the open chain form because its anomeric hydroxyl group, i.e, the hydroxyl group at C-1, is acetylated. So it cannot get a free-CHO group and hence cannot form oxime


$$\begin{array}{c}
 \text{CH}=\text{NNH}-\text{C}_6\text{H}_5 \\
 | \\
 \text{C}=\text{NNH}-\text{C}_6\text{H}_5 \\
 | \\
 \text{HO}-\text{C}-\text{H} \\
 | \\
 \text{H}-\text{C}-\text{OH} \\
 | \\
 \text{H}-\text{C}-\text{OH} \\
 | \\
 \text{CH}_2\text{OH}
 \end{array}
 + \text{C}_6\text{H}_5\text{NH}_2 + \text{NH}_3 + \text{H}_2\text{O}$$

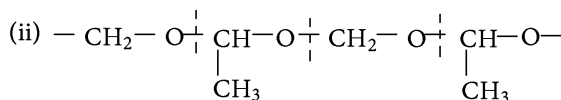
D-Glucose phenyl osazone

6. Vinyl polymerization, using Ziegler–Natta catalysts, is known as coordination polymerisation. The process is carried out in the presence of a complex solid catalyst consisting of TiCl_4 and a trialkyl-aluminium compound. Success of these catalysts depend on the following factors, namely

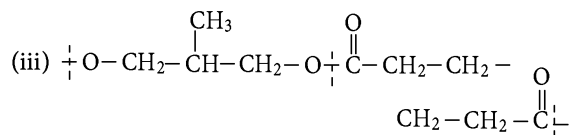
- (i) polymerisation can be effected under relatively mild conditions.
- (ii) linear polymer molecules are obtained.
- (iii) the process permits a considerable degree of stereochemical control.



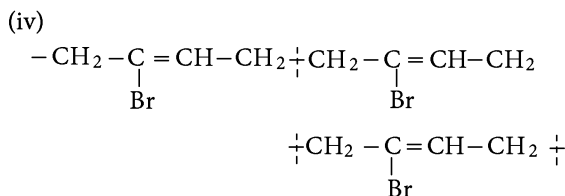
homopolymer



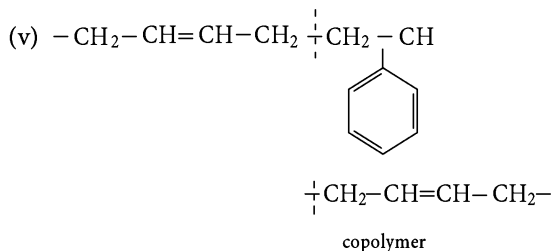
copolymer



copolymer

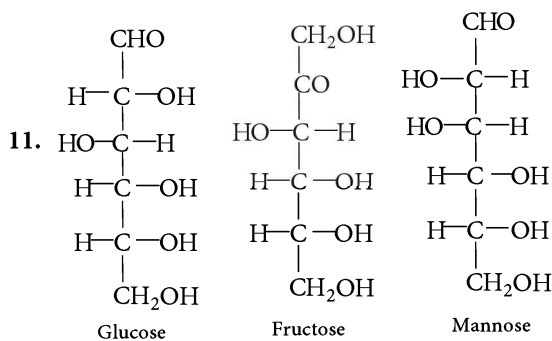


homopolymer



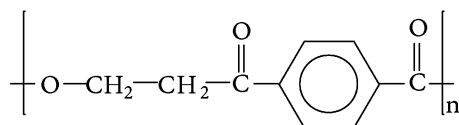
8. (i) o-nitrophenol is steam volatile due to intramolecular hydrogen bonding while p-nitrophenol is not steam volatile due to intermolecular hydrogen bonding.
- (ii) Sodium fusion extract is alkaline in nature. When AgNO_3 is directly added without removing the alkali, Ag_2O is likely to be formed. So the basic solution must be made acidic before adding AgNO_3 . Dilute HNO_3 also decomposes NaCN or Na_2S if present in the extract.
- (iii) The three double bonds of benzene ring constitute the part of the aromatic system and they are resonance stabilised.
- (iv) Diazonium compounds on heating lose nitrogen as N_2 gas before reacting with sodium to form NaCN .
- (v) If nitrogen and sulphur are present in an organic compound, they would interfere with the testing of a halogen, if they (nitrogen and sulphur) are not removed. So when boiled with nitric acid, nitrogen which is present as NaCN is removed as volatile HCN and sulphur is removed as volatile H_2S .
9. Chlorobenzene has a chlorine in the benzene nucleus, while, benzyl chloride has a side chain chlorine. So, compounds having a halogen directly attached to the benzene nucleus, will not answer the test with alcoholic AgNO_3 solution. When chlorobenzene is heated with alcoholic AgNO_3 solution, no white precipitate is observed. Heating benzyl chloride with few drops of alcoholic silver nitrate solution will give a white precipitate of AgCl .
10. Natural rubber is soft and sticky. It becomes more soft at high temperatures. Rubber is readily attacked by oxygen, oxidising agents and organic solvents. Vulcanisation is done by heating rubber with sulphur.

Valcanised rubber has excellent elasticity, low water absorption and good resistance to oxidation and organic solvents. In short, valcanisation improves the qualities of rubber.



They have different configuration only at C_1 and C_2 .

12. Anomers differ only in the configuration at the first carbon. For example, α -glucose and β -glucose are called anomers.
13. An equilibrium mixture of glucose contains 36% of the α -form.
14. Dacron or terylene is a condensation polymer of ethylene glycol and terephthalic acid.



15. Aniline contains an $-\text{NH}_2$ group and paranitrobenzoic acid contains a $-\text{COOH}$ group. If NaHCO_3 is added, p-nitrobenzoic acid goes into solution and aniline is removed. If conc. HCl is added, aniline goes into solution and p-nitrobenzoic acid is removed.
16. Statement 1 is false while statement 2 is correct. Both glucose and fructose are reducing sugars and they reduce Tollen's reagent to metallic silver
17. Both Statements are correct and statement 2 is the reason for statement 1. Those reagents which can convert D-glucopyranose into the open chain form will only react with the aldehyde group of glucose
18. Statement 1 is true while statement 2 is not correct
LDPE has highly branched structure. Hence the molecules cannot be packed well in the solid state and so its density is low.

Statement 2 is wrong because coordination polymerization using Ziegler–Natta catalyst gives linear polymers. HDPE (high density polyethylene) is formed by

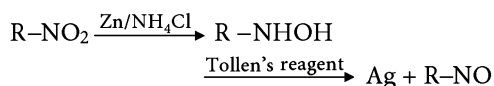
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this method. LDPE is prepared by free radical polymerization of ethylene at high pressure and temperature in presence of a trace of O_2 or peroxide as initiator

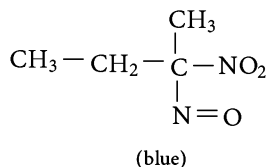
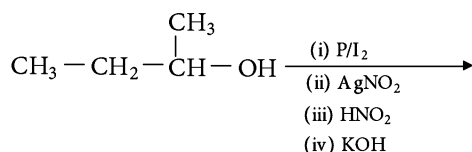
19. Statement 1 is true, but statement 2 is false.

Sucrose on hydrolysis gives equal amounts of glucose and fructose. Since glucose has less positive and fructose has more negative magnitude of specific rotation, the mixture becomes laevorotatory.

20. Statement 1 is correct while statement 2 is false Nitro compounds are not reducing agents and they do not reduce Tollen's reagent to metallic silver. In Mulliken and Barker's test nitrocompounds are reduced in neutral medium (Zn/NH_4Cl) to the corresponding hydroxylamine derivatives which reduce Tollen's reagent to metallic silver



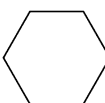
21. Secondary alcohols give a blue coloured solution of pseudonitrole in Victor-Meyer's test.

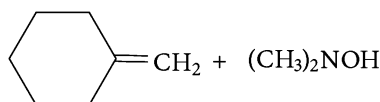
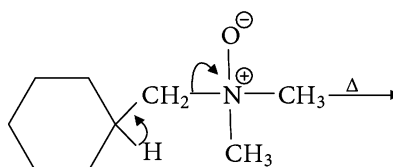
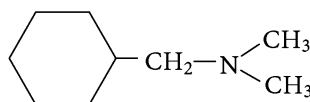


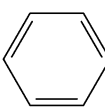
22. The compound has a phenolic group as it burns with a sooty flame (aromatic) and gives violet colour with neutral $FeCl_3$ solution. Phenols and carboxylic acids liberate hydrogen with metallic sodium, but only strong acids evolve CO_2 with $NaHCO_3$. Acid functional groups give esters with alcohol whereas phenolic functional group gives esters with acid anhydride. So the compound could be an (aromatic) phenolic carboxylic acid. The only option is salicylic acid or 2-hydroxy benzoic acid.

23. The compound dissolves in acids, which indicates the presence of basic functional group. Primary amines (aromatic or aliphatic) form foul smelling isocyanide with alkaline $CHCl_3$. Only aromatic compounds burn with a sooty flame. So the organic compound is an aromatic primary amine.

24. (A) is phenol. C_2H_5OH is less acidic than phenols. Presence of electron donating groups reduces acidity while electron withdrawing groups increases acidity. Hence, the order of acidities are $C_2H_5OH < p\text{-methyl phenol} < (A) < p\text{-nitrophenol}$.

25.  is (D). It is obtained by heating amine oxide of

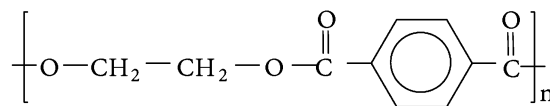


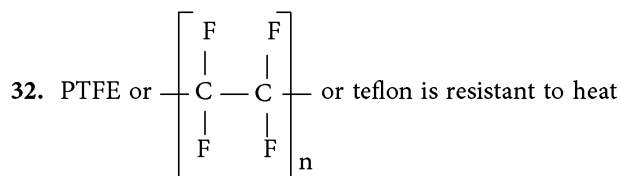
26.  does not have β -hydrogen and cannot undergo dehydration.

27. Terylene, cellulose and nylon are linear polymers while amylopectin is a branched chain polymer
28. Sucrose, starch and cellulose are non-reducing Carbohydrates
29. SBR (styre-butadiene rubber) is prepared by the copolymerization of styre and 1, 3.butadiene. Similarly nitrile rubber (or Buna-N) is obtained by polymerization of butadiene and acrylonitrile
The monomer of PAN is acrylonitrile and that of neoprene is chloroprene

IIT Assignment Exercise

31. Terylene is the polyester formed by copolymerization of ethylene glycol and terephthalic acid.

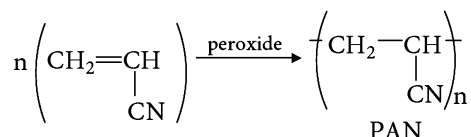




and chemical attack

33. Zeigler-Natta catalyst is triethyl aluminium and TiCl_4 and is used in polymerisation of alkenes.

34. Orlon is polyacrylonitrile (PAN)



35. Glycogen (similar to starch) is a non-sugar.

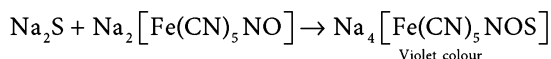
36. Lobry de Bruyn-van Ekenstein rearrangement is the interconversion of glucose, mannose and fructose when warmed with dilute alkali.

37. α -gluco pyranose $\rightleftharpoons$ open structure
 $\rightleftharpoons$ β -gluco pyranose

38. C_1 and C_4 of two glucose units respectively. Maltose and starch contain α -(D)-glucopyranose. Maltose is a disaccharide whereas starch is a polysaccharide.

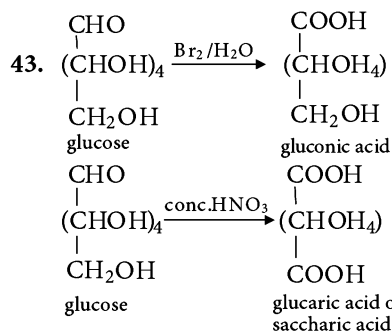
39. Fructose is the sweetest natural sugar.

40. Violet colour indicates the presence of sulphur.



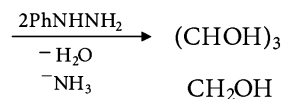
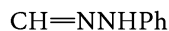
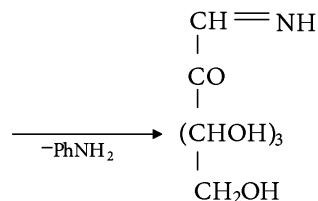
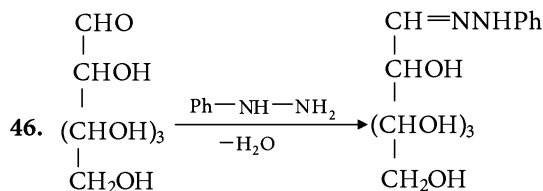
41. The white precipitate of AgCl formed is soluble in NH_4OH due to the formation of soluble $[\text{Ag}(\text{NH}_3)_2]^+$ ion.

42. Total reduction of glucose occurs giving hexane as the final product



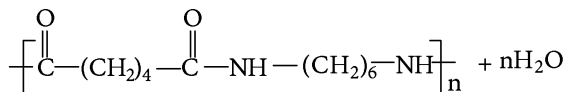
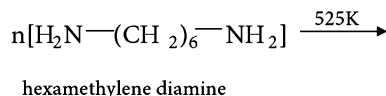
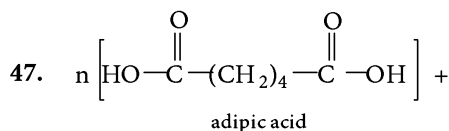
44. Amylopectin contains $\text{C}_1 - \text{C}_6$ linkages at branchings.

45. Only the $-\text{OH}$ group on $\text{C} - 1$ can be methylated.



glucosazone or
glucose diphenylhydrazone

Three moles of phenylhydrazine reacts with one mole of glucose to form osazone.



Nylon-6,6 is obtained from adipic acid and hexamethylene diamine.

48. Teflon $(-\text{CF}_2 - \text{CF}_2 -)_n$ is the polymer of $\text{CF}_2 = \text{CF}_2$

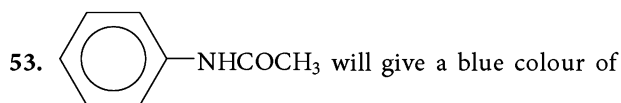
49. Vinyl chloride undergoes chain growth polymerization.

50. Aromatic amines on diazotisation give diazonium chlorides which form coloured azo dyes with phenol or aromatic amines.

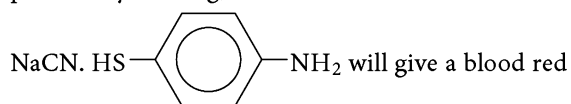
51. Natural rubber is cis-polyisoprene, where all the double bonds have cis stereochemistry.

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52. Perlon or nylon-6 and nylon-6,6 are polyamides, bakelite is phenol-formaldehyde resin, whereas dacron or terylene is a polyester.



prussian blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ when its sodium fusion extract is heated with ferrous sulphate followed by acidification. $\text{C}_6\text{H}_5 - \text{N} = \text{N} - \text{C}_6\text{H}_5$ will not answer this test as nitrogen is eliminated from these compounds by heating, before sodium reacts to form



colour. NH_2NH_2 does not answer due to the absence of carbon.

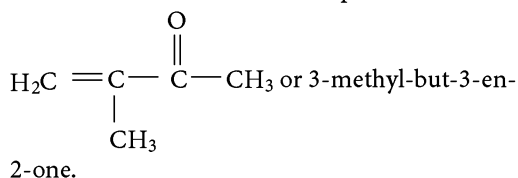
54. With phenyl hydrazine, (A) forms yellow precipitate of phenyl hydrazone which indicates the presence of carbonyl group. Since it does not restore the colour of Schiff's reagent, it is a ketone. Ketones on reduction give secondary alcohol.

55. The compound
(i) contains a conjugate double bond.
(ii) decolourises bromine water. Hence is unsaturated.

(iii) gives haloform reaction. So contains a $-\text{C}(=\text{O})-\text{CH}_3$ group.

(iv) contains a methyl substituent and hence it is a butane system.

From the above details, the compound should be



56. Rubber is an elastomer and are held together by very weak intermolecular forces. That is why it can behave like an elastic. The intermolecular forces in PVC is in between elastomers and fibres. Hence they are thermoplastics. In Nylon, there are strong intermolecular forces like hydrogen bonding. In cellulose, two or more chains make contact, the hydroxyl groups are ideally situated to 'zip' the chains together forming hydrogen bonds.

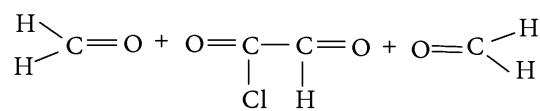
57. Polyurethanes are obtained by the condensation of toluene-2,4-diisocyanate with ethylene glycol. During

the polymerization reaction, low boiling liquids (such as Freon-11) are added to the reaction mixture. The heat of polymerization vapourises the volatile liquid producing bubbles that convert the viscous polymer to a frothy mass of polyurethane foams.

58. Zymase decomposes glucose to ethanol and CO_2 .
59. Maltose, glucose, cellobiose are reducing sugars, cellulose is a non-reducing sugar.
60. (A) is benzene diazonium chloride. On heating (A), with sodium, N_2 gas is lost immediately. So NaCN cannot be formed at all. Hence it will not answer the test for nitrogen.
61. Upon ozonolysis we get two molecules of formaldehyde and one molecule of $\text{O}=\text{C}(\text{Cl})-\text{C}(\text{H})=\text{O}$.

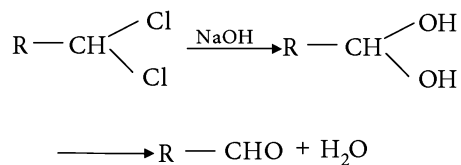


Therefore, formaldehyde should be at the terminal of the molecule.



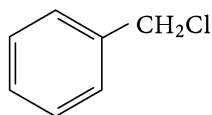
The molecule is thus $\text{CH}_2=\text{C}(\text{Cl})-\text{C}(\text{H})=\text{CH}_2$. This is a chloroprene unit. Hence polymer is polychloroprene i.e., neoprene.

62. When the dichloro compound is treated with caustic soda the product formed is an aldehyde as it gives a silver mirror. Since the chlorine containing compound gives an aldehyde with NaOH , both the chlorine should be attached to the same (aliphatic) carbon.

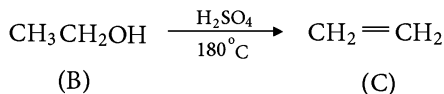


63. Since it gives white precipitate with Tollen's reagent, it has an aldehydic group or a terminal triple bonded carbon. It answers Luca's test in about five minutes which indicates that it is a secondary alcohol. The only structure possible is $\text{CH}_3\text{CH}(\text{OH})\text{C}\equiv\text{CH}$.
64. (i) and (iv) form NaCN when fused with metallic sodium. So they give deep blue colour in the test. (iii) gives blood red colour due to the presence of NaCNS in the extract.

65. (A) gives red colour with ceric ammonium nitrate. So it is an alcohol. (B) restores pink colour of Schiff's reagent so (B) is an aldehyde. (A) on oxidation gives (B) which is an aldehyde. Hence (A) is a primary alcohol.
66. Since both periodic acid and the monosaccharides are soluble in water, it proceeds well in aqueous medium. Periodic acid is a strong oxidising agent in acidic medium as well.
67. On treatment with concentrated sodium hydroxide, cellulose forms a translucent mass, which imparts a silky lustre to cotton. The process is called mercerisation and the cotton so produced is called mercerised cotton.
68. These are linked together to form long straight chains. The polymeric chains are stacked one over the other to form a well packed structure.
69. If sulphur is present it would form Na_2S , with which AgNO_3 will form Ag_2S , a black precipitate. This does not confirm absence of halogen because the white or yellow precipitate may be masked by black Ag_2S . Any NaCN or Na_2S should be removed by boiling with HNO_3 , before conducting the test for halides.
70. Empirical formula is $\text{C}_7\text{H}_7\text{Cl}$. Gives sooty flame means it is aromatic. Since it gives white precipitate with AgNO_3 , chlorine is attached to side chain carbon. $\therefore$ Structure should be



71. (A) reacts with (B) to give a product with fruity smell i.e., an ester so (A) is formic acid as it reacts with Tollen's reagent and (B) is an alcohol. (B) contains 2 carbon atoms only, so (B) is $\text{C}_2\text{H}_5\text{OH}$.

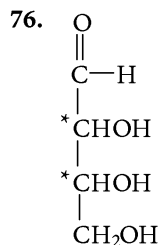


$\text{C}_2\text{H}_5\text{OH}$ on dehydration gives ethene (C). Alkenes decolourise bromine water.

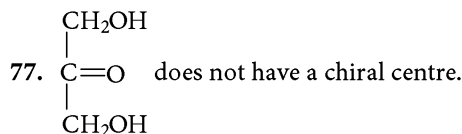
72. (A) has fruity smell, so it is an ester. On hydrolysis, (A) $\longrightarrow$ (B) + (C). Since (B) on oxidation gives (C), (B) is alcohol and (C) is the acid. Both contain two carbon atoms so (B) is $\text{CH}_3\text{CH}_2\text{OH}$ and (C) is CH_3COOH , or (A) is $\text{CH}_3\text{COOCH}_2\text{CH}_3$.
73. Starch and maltose have α -glycosidic linkages between glucose units. Maltose is a disaccharide, whereas starch

is a polysaccharide. Cellobiose (disaccharide) and cellulose (polysaccharide) have β -glycosidic linkages between glucose units. Lactose has β -glycosidic linkage between a galactose and glucose units.

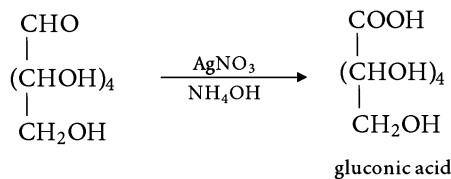
74. Glucose, fructose, maltose, lactose and cellobiose are all reducing sugars whereas sucrose, starch and cellulose are non reducing.
75. (a) All reducing sugars (except some ketose) undergo mutarotation. Fructose, glucose, galactose, maltose and lactose exhibit mutarotation whereas sucrose does not.



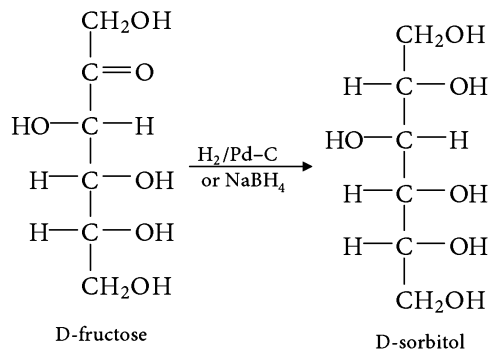
There are two chiral centres in an aldotetrose.



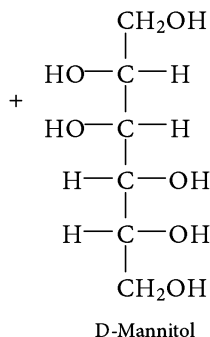
78. Mild oxidising reagents like Tollen's reagent (ammoniacal silver nitrate) oxidizes glucose to gluconic acid. Only the aldehyde group is oxidized.



79. Fructose is a 2-ketohexose. On reduction, it gives a mixture sorbitol and mannitol

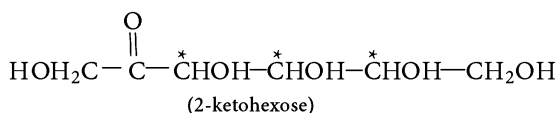


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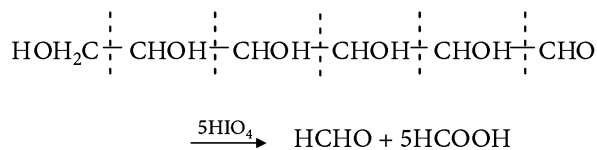


Glucose, mannose and galactose are aldohexoses. Each of them will give only one isomer of the corresponding polyhydric alcohol

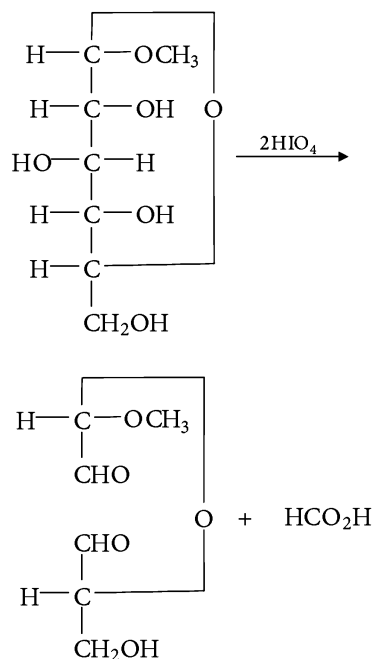
80. Amylose is a component of starch and consists of straight chain of α -D-glucose units joined by 1, 4-glycosidic linkage. Cellulose is a polysaccharide containing β -D-glucose units joined by 1, 4-glycosidic linkage
81. The viscous solution obtained by dissolving cellulose in NaOH solution containing carbon disulphide is known as viscose. It is cellulose xanthate. When it is forced through fine holes into a bath of dilute acid, the fibre regenerated is known as viscose rayon
82. When glucose is heated with CH_3OH in presence of small quantity of HCl, it gives two isomeric methyl glucosides. Ordinary aldehydes react with two molecules of CH_3OH to form stable acetal. But glucose reacts with only one molecule of CH_3OH to form stable methyl glucoside. This confirms that glucose exists as cyclic hemiacetal
83. Aldoses which produce the same osazone when treated with phenyl hydrazine are called eprimers. Osazone formation involves reaction of phenyl hydrazine at C-1 and C-2. Two aldohexoses will give the same osazone if they have identical configuration on C-3, C-4 and C-5 carbon atoms.
For example, glucose and mannose are eprimers and they differ only in configuration at C-2
84. A keto hexose contains 3 different chiral carbon atoms. So the number of optical isomers possible is $2^3 = 8$



85. One mole of D(+) glucose consumes 5 moles of HIO_4 to give 5 moles of HCOOH and 1 mole of HCHO



86. The acetal ring of methyl glucoside is stable in presence of HIO_4 . Hence oxidation of one mole of methyl glucoside consumes only two moles of HIO_4 and produces only one mole of HCOOH



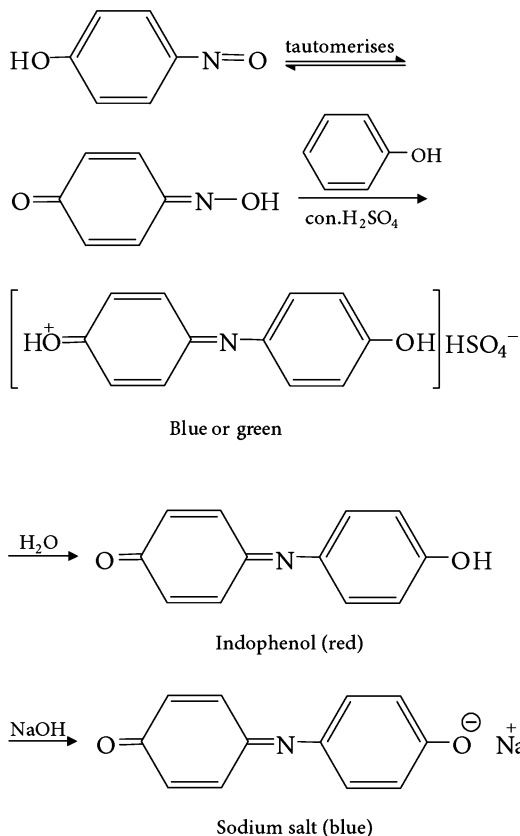
87. Sucrose is α -D-glucopyranosyl- β -D-fructofuranoside
88. Bromine water oxidizes glucose to gluconic acid. But under ordinary conditions fructose does not react with bromine water
89. The intermolecular forces present in nylon-66 is mainly hydrogen bonding
90. Dacron (or terylene) is a step growth or condensation polymer formed from terephthalic acid and ethylene glycol
91. Statement 1 is correct but statement 2 is wrong. Glucose is more acidic than monohydric alcohols such as ethanol due to the presence of aldehyde group which is electron withdrawing
92. Statement 1 is false but statement 2 is correct. Milon's test is the test used for proteins. When a protein

is treated with Millon's reagent, a white precipitate is formed.

93. Both statements are correct and statement 2 is the reason for the characteristic colours obtained Liebermann's nitroso reaction.

For the identification phenol, it is treated with sodium nitrite and few drops of $\text{con. H}_2\text{SO}_4$. Appearance of a green or blue colour which turns red on dilution with water and again blue on adding NaOH confirms the presence of phenol. The final blue colour is due to the formation of sodium salt of indophenol

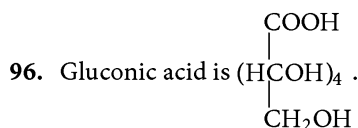
p-nitrosophenol formed by the reaction of phenol with nitrous acid undergoes condensation with excess phenol to form indophenol



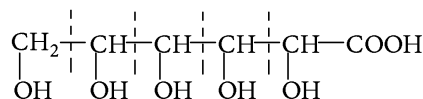
For identification of 2° amine, first it is treated with nitrous acid to form yellow nitrosamine $\text{R}_2\text{N}-\text{N}=\text{O}$. The nitrosoamine is warmed with phenol and a few drops of $\text{con. H}_2\text{SO}_4$ when the same observation is obtained. In this case p-nitroso phenol is formed by the reaction of nitrosamine with phenol. p-nitrosophenol reacts with excess phenol to form indophenol in presence of $\text{con. H}_2\text{SO}_4$

94. Mutarotation involves conversion of one ring form of a sugar to an equilibrium mixture containing the original ring compound and another stereo isomeric ring form of the same sugar which differ only in configuration at C-1 (i.e., anomeric carbon). So it can be considered as diastereo isomerisation

95. Sucrose is optically active and it is dextrorotatory



This can be expressed as



HIO_4 cleaves the C-C bond between the two carbons which contain -OH groups. Hence only four HIO_4 molecules are needed. This results in 3 HCOOH , one HCHO and one $\text{OHC}-\text{COOH}$ units from one unit of gluconic acid

Hence statement (d) is wrong.

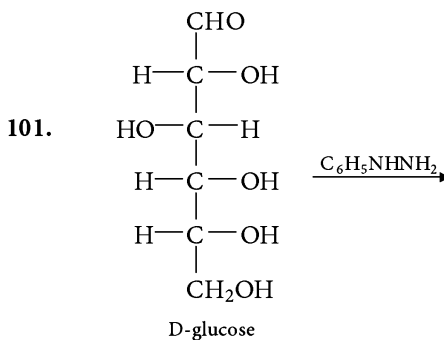
97. Thermoplastic polymers become soft on heating and hard on cooling. Heat treatment can be done any number of times on them. There are no cross links between polymeric chain

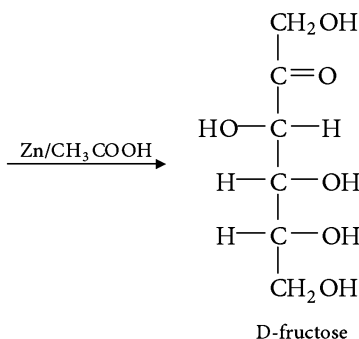
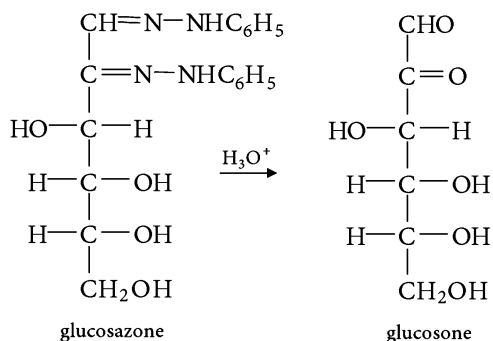
The intermolecular forces in thermoplastic polymers is greater than those present in elastomers. Neoprene is an elastomer and not a thermoplastic

98. All reducing carbohydrates undergo mutarotation in solution

99. Hydrolysis of sucrose is called inversion of sugar. Amylose fraction of starch gives blue colour with iodine.

Additional Practice Exercise





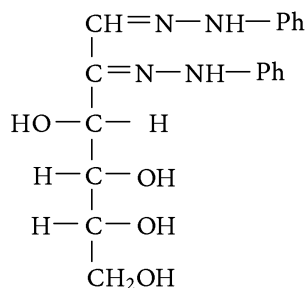
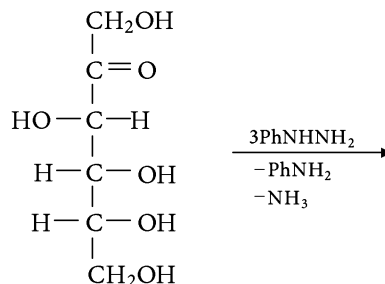
102. Thermoplastics are polymers which can be easily moulded into desired shapes by heating and subsequent cooling. The process of heat softening and cooling can be repeated many times. The intermolecular forces in thermoplastic polymers are intermediate between those of elastomers and fibres

e.g., polythene, polystyrene, pvc etc.,

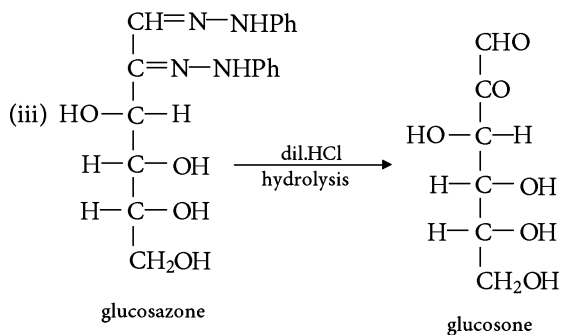
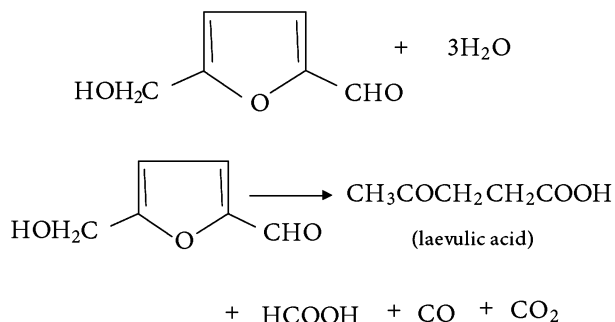
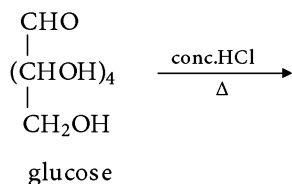
Thermosetting polymers are polymers which become infusible and hard on heating. They cannot be remelted or remoulded. They form cross links on heating e.g., bakelite, melamine-formaldehyde resin etc.,

103. (i) Glucose does not undergo certain reactions of aldehydes such as Schiff's test, reaction with NaHSO_3 etc.,
 (ii) Glucose penta acetate does not react with hydroxylamine indicating the absence $-\text{CHO}$ group
 (iii) Glucose exists in two crystalline forms: α -D-glucose and β -D-glucose. Fresh aqueous solution of α -D-glucose and β -D-glucose exhibit mutarotation
 (iv) D-glucose when heated with CH_3OH in presence of dry HCl gives two isomeric methyl glucosides: methyl α -D-glucoside and methyl- β -D-glucoside

104. (i) False. Mutarotation is shown by any sugar, which can exist as a hemiacetal.
 (ii) True. The aldose should have at least four carbon atoms to form a stable five membered ring.
 (iii) True. The α - and β -forms of D-glucose are in equilibrium with the open chain aldehyde form of glucose.
 (iv) False. Anomers are not enantiomers and could differ in both sign and magnitude of optical rotation. Only enantiomers have the property of having the same magnitude of rotation, but with opposite sign.
 (v) False. Sucrose is 1,2-glycoside.
 (vi) True. Fructose is a reducing sugar in alkaline medium.
 (vii) False. It is a disaccharide (giving two units of D-glucose on hydrolysis).
 (viii) True. All natural sugars have the D-configuration (at the first carbon atom from the bottom).
105. (i) With excess of phenyl hydrazine, fructose gives osazone aniline and ammonia.



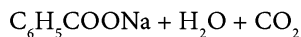
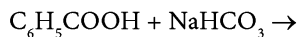
- (ii) Aldohexoses, when heated with con. HCl , first gives hydroxymethyl furfural, which then decomposes into laevulinic acid, formic acid, and oxides of carbon.



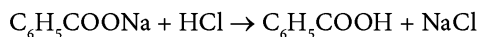
106. The monomer of neoprene is chloroprene. Plexiglas (polymethyl methacrylate) is formed by the polymerization of methyl methacrylate. Orlon (polyacrylonitrile or PAN) is formed by the polymerization of acrylonitrile (or vinyl cyanide)

107. Both 1-propanol and 2-propanol form esters with pleasant smell when heated with acetic anhydride. So it cannot be used to distinguish between the two

108. Benzoic acid alone dissolves in sodium bicarbonate solution forming sodium benzoate



From the aqueous solution benzoic acid is regenerated by acidification

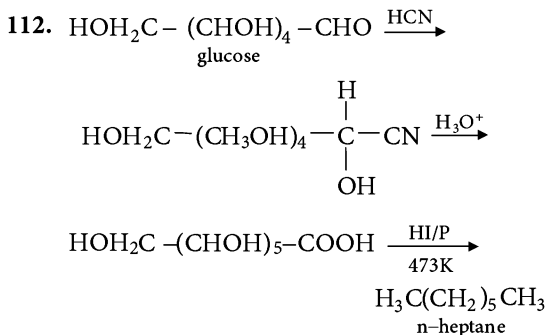


Since both benzoic acid and phenol dissolve in NaOH solution, it cannot be used for the separation.

109. SBR is a copolymer formed from butadiene and styrene and it is an addition (or chain growth) polymer

110. Gutta percha is a naturally occurring isomer of rubber and it is trans-poly isoprene. It is harder and more brittle than rubber

111. Glyptal does not contain halogen. It is a condensation polymer formed from ethylene glycol and phthalic acid. It is used in paints



113. Aromatic aldehydes do not reduce Fehling's solution

114. Methyl- α -D-glucoside and methyl- β -D-glucoside differ only in the configuration at C-1, i.e., anomeric carbon. Hence they are anomers

115. Methyl- β -D-glucoside is formed when β -D-glucose is heated with CH_3OH and HCl (anhydrous)

116. Both statements are correct and statement 2 is the reason for statement 2. The rearrangement is known as Lobry De Bruyn-van Ekenstein rearrangement

117. Statement 1 is true, but statement 2 is not correct. Sucrose shows inversion of rotation on hydrolysis because it is converted into equimolar mixture of glucose and fructose. Since the magnitude of the specific rotation of laevo rotatory fructose is more, the mixture as a whole becomes laevorotatory. This is not true for many other disaccharides. For example, maltose which is made up of only glucose does not show inversion of rotation

118. Both statements are correct and statement 2 is the reason for statement 1. Tollen's reagent and Fehling's solution are alkaline and hence a part of fructose is converted to glucose and mannose by the rearrangement. It may be these compounds which reduce Tollen's reagent and Fehling's solution

119. Both statements are correct and statement 2 is the reason for statement 1

Two glucose units are joined by 1, 4-glycosidic linkage in maltose. So one of the glucose units contain hemiacetal linkage. So maltose is a reducing sugar. But in sucrose, the two monosaccharides are joined by a

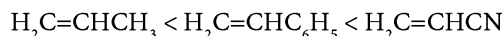
7.62 Carbohydrates, Polymers and Practical Organic Chemistry

glycosidic linkage between C-1 of glucose and C-2 of fructose. Once these two carbon atoms are joined with the elimination of a molecule of water, the linkage at C-1 of glucose and C-2 of fructose actually become acetal linkage. Hence no more hemiacetal linkage is present in sucrose

120. Statement 1 is correct, but statement 2 is not correct
An aqueous solution of α -D-glucose or β -D-glucose undergoes mutarotation to form finally an equilibrium mixture containing 36% of the less stable α -form and 64% of the more stable β -form
121. Cellulose is formed by the condensation polymerization of β -D-glucose units
122. The linear chains of terylene molecules are held together by dipole –dipole interactions
123. Polymerisation using Ziegler–Natta catalyst, $(C_2H_5)_3Al/TiCl_4$, generally give linear stereoregular polymers
124. The polymer formed from $CH_2=C\begin{matrix} \nearrow Cl \\ \searrow Cl \end{matrix}$ has no chiral centre and hence does not polymerize in isotactic, syndiotactic or atactic forms.

125. For cationic polymerisation, electron donating groups if present, stabilize the carbocation intermediate. Hence, greater the electron donating ability, greater will be the ability of polymerisation. Thus the order of increasing reactivity towards cationic polymerisation is $H_2C=CHCO_2C_2H_5 < H_2C=CHCl < H_2C=CHCH_3 < H_2C=CHC_6H_5$

126. The anionic polymerization is favoured by electron withdrawing substituents.



127. In sucrose, glucose is present in the pyranose form and fructose is present in the furanose form Gun cotton is cellulose trinitrate
128. PVC is a chain growth polymer (addition polymer) and it is a thermoplastic polymer
129. Nitric acid oxidizes glucose to saccharic acid