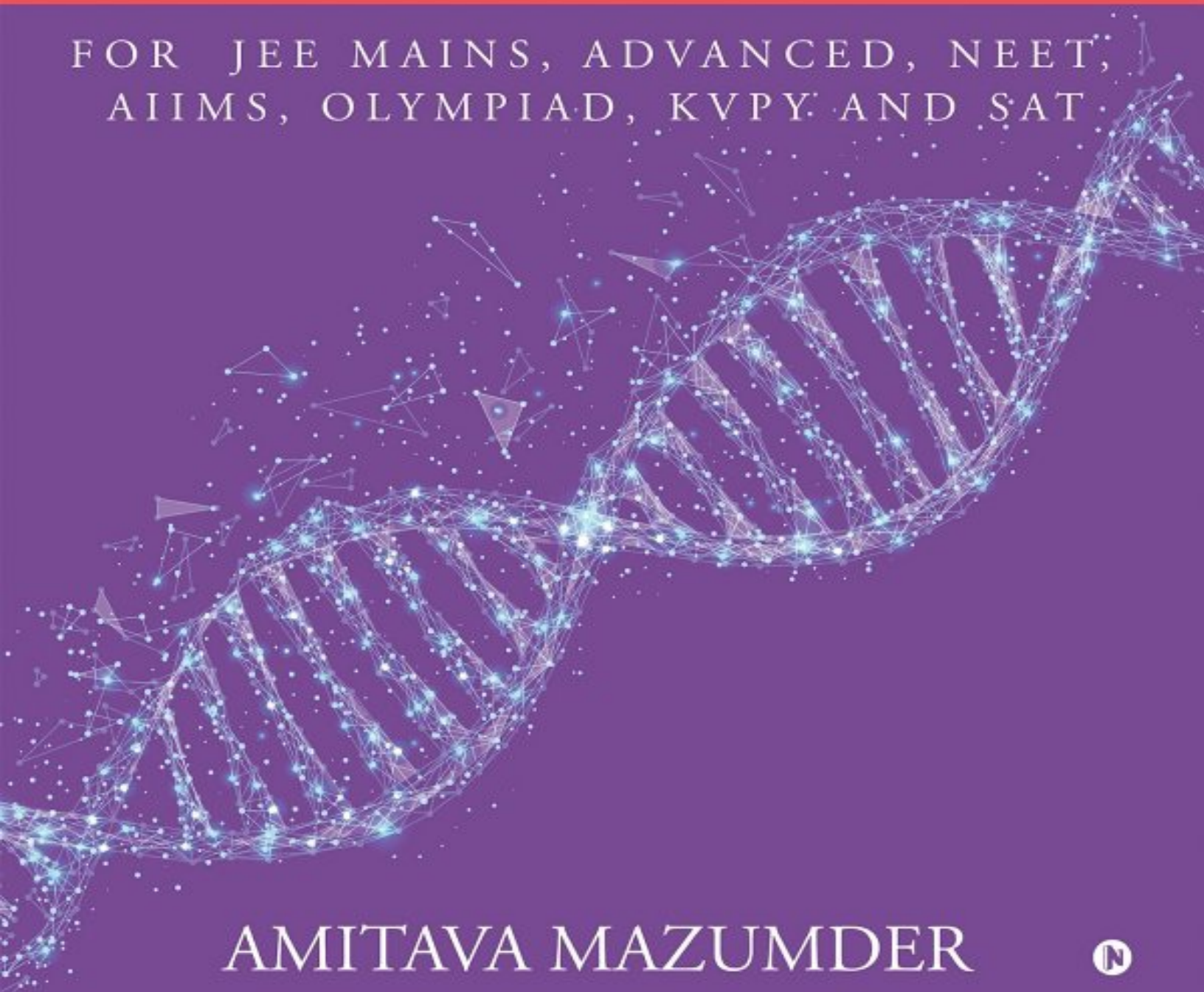
COMPREHENSIVE ORGANIC CHEMISTRY

FOR JEE MAINS, ADVANCED, NEET, AIIMS, OLYMPIAD, KVPY AND SAT



AMITAVA MAZUMDER

COMPRENSIVE ORGANIC CHEMISTRY

FOR JEE MAINS, ADVANCED, NEET,
AIIMS, OLYMPAID, KVPY AND SAT

AMITAVA MAZUMDER

notionpress.com



Notion Press

Old No. 38, New No. 6
McNichols Road, Chetpet
Chennai – 600 031

First Published by Notion Press 2017
Copyright © Amitava Mazumder 2017
All Rights Reserved.

eISBN 978-1-948352-50-5

This book has been published with all reasonable efforts taken to make the material error-free after the consent of the author. No part of this book shall be used, reproduced in any manner whatsoever without written permission from the author, except in the case of brief quotations embodied in critical articles and reviews.

The Author of this book is solely responsible and liable for its content including but not limited to the views, representations, descriptions, statements, information, opinions and references [“Content”] . The Content of this book shall not constitute or be construed or deemed to reflect the opinion or expression of the Publisher or Editor. Neither the Publisher nor Editor endorse or approve the Content of this book or guarantee the reliability, accuracy or completeness of the Content published herein and do not make any representations or warranties of any kind, express or implied, including but not limited to the implied warranties of merchantability, fitness for a particular purpose. The Publisher and Editor shall not be liable whatsoever for any errors, omissions, whether such errors or omissions result from negligence, accident, or any other cause or claims for loss or damages of any kind, including without limitation, indirect or consequential loss or damage arising out of use, inability to use, or about the reliability, accuracy or sufficiency of the information contained in this book.

Preface

Purpose and mission

This book is intended to become a useful companion for the Engineering Test Aspirants of India in areas of accuracy, usability, relevance for the examination, flexibility, and connection with their needs. This text would evolve over the years and should eliminate much of the cost for owning several costly top-quality college-level organic chemistry texts, by putting together the relevant material in one book, and, we hope would contribute eventually to the building of our nation by creating top quality minds.

Author

The author of this book, Amitava Mazumder, had finished his graduation in Engineering from N.I.T. – Durgapur and his Post Graduation in Industrial Metallurgy from Jadavpur University-Kolkata, and has more than ten years experience of teaching Chemistry to the Engineering Entrance Test aspirants in Delhi, Kota and Dubai. He presented his thesis for International Conference for Manufacturing in Dhaka, Bangladesh in 2000 and published his paper in the proceedings of the same conference.

Amitava intends that this book should keep on evolving by contributions from all in the student and teaching community and therefore welcome comments and suggestions so that he can better serve his dream of creating well informed and thoroughly prepared engineering aspirants.

About this book

One of the main difficulties students have with organic chemistry is organizing the information in their minds. An engineering entrance aspirant very quickly will learn over hundreds of chemical reactions. Consequently, it is vital that students take time to not only organize the information, but also to understand it. Indeed, excellent organic chemistry professors will tell, contrary to popular belief, one do not really need to memorize anything for organic chemistry, instead, one simply needs to understand it. By truly learning something, rather than memorizing it, the students will be able to apply concepts beyond what they are memorizing. This book intends to help

the students in getting into the core concepts of Organic Chemistry and encourage them to always ask why something is the case. This book would direct them to inquire, and find out the answer. By taking this approach the student will enrich the learning experience, and the information will be "locked" in their mind so that they are able to face the challenging problems of entrance examinations.

Contributions

Amitava has always endeavored to research facts and interpretations available in the best Organic Chemistry books, and, present it to the students of India in a form that they would understand thoroughly. He has freely learned from the writings of eminent authors in this field and for this book he has drawn from this knowledge so that the students can get a comprehensive source of organic chemistry for entrance examinations in this book. Amitava therefore thanks all those authors, and would always be indebted to them for enrichingAmitava's knowledge of the very vast field of organic chemistry.

Specifically he is thankful to his parents who have always nurtured and motivated him to follow his dream, his wife Swati & siblings Sudip, Swagata, Sudeshna, nephew Rishi who have stood by him in the most difficult times. A special thanks to Mr.R.K. Verma, founder director of Resonance Institute of Kota, who has always motivated Amitava to selflessly contribute to the welfare of the students. Amitava is also deeply indebted to Mr. Arijit Das, who has motivated from the beginning itself and who has designed the front and back cover of the book as well as the preface, Prof. U. C. Ghosh, Prof. K. L. Ghatak (Presidency College, Kolkata), who were his teachers, Dr. R.C. Sharma, Mr. Lokesh Khandelwal, Dr. Bikramjit Basu (IIT-Kanpur), Mr.R.K. Bandopadhyaya, Dr.V. P. Mittal, Mr. Pramod Rana, Mr.Ramashish Paul for always encouraging Amitava to author this book, and for guiding his vision of serving the ambitions of the students of India.

Finally .. ...

In spite of our best efforts this first edition may contain several inadvertent errors and misprints. I hope that you would sincerely pardon the author for the same andAmitava looks forward to your sincere contributions to keep on improving this effort.

After all a knowledgeable Indian student is a pride for all ofus.

-Amitava Mazumder
May 2006

Acknowledgement

My mom Mrs Kalyani Mazumder, dad Late Mr. Suprasanna Kumar Mazumder, wife Swati. and kids Anuska and Aayush; Mr. Mahesh Patil (IPS), Mrs. Archana Patil, Mr. Pratap Singh (Commisioner, IRS), my sibling Sudip, Swagata, Dr. Sudeshna, Prof. Bikramjit Basu (Prof. IISc, Bangalore), Isha Sethi, Mr. Sanjeev Sethi (cfo, Star TV), Prof. Asish Arora (Physics), Mr. R.K. Verma (MD, Resonance), Mr. Jitendra Panda (MD, Peerless, Kolkata). Mrs. Sumi, Pratik, and Projwal; thanks to Ms. Gabriela Caster and Ms. Preethi.K of Notion Press and their team as a whole.

Contents

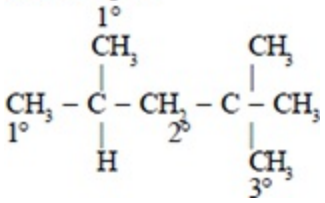
1) IUPAC Nomenclature
2) General Organic Chemistry
3) Isomerism
4) Nucleophilic substitution and elimination
5) Alkane
6) Alkenes
7) Alkynes
8) Alkyl halide, Grignard's reagent
9) Alcohol
10) Ether (cyclic, acyclic), thioether
11) Aromatic electrophilic substitution
12) Aromatic hydrocarbons
13) Aromatic halides
14) Phenol
15) Carbonyl compounds
16) Carboxylic acids
17) Carboxylic acid derivatives
18) Aliphatic and aromatic nitro compounds
19) Amines
20) Carbohydrate
21) Amino acid
22) Polymer
23) Practical organic chemistry
24) Reagent list
Exercises

IUPAC Nomenclature

In the early days an organic compound was named as per their origin or their characteristic property. These names are called as common name or trivial name. Take an example like formic acid (HCOOH). It originates from ant & the latin name of ant is formicium and also it behaves like an acid. Thus the name formic acid is given. But with increasing number of organic compounds & complexities name, scientific tools were developed by an international body, famously called as International Union of Pure and Applied Chemists in the year 1947. Since then this IUPAC system has been followed to name the compound. We will observe while naming the organic compounds that in some cases trivial names or common name's have been retained by IUPAC.

Paraffins or alkanes (general formula C_nH_{2n+2}) : First look that there can be several types of C and H in the simplest alkane There are the compounds made up single bond between C–atoms (due to its catenation property)

For example,



1° C means that C, which is attached to only one C. Like wise 2°, 3°, 4° and 1°, 2°, 3° H means that corresponding H-atoms are attached to 1° C, 2° C, 3° C respectively. There cannot be any 4° H.

Let us introduce the functional groups & their names available in organic chemistry in table-1.

Table-1 Names and formulae of functions and classification of acyclic compounds with examples(G=general, I=IUPAC name)

Name of the function	Graphic formula	Class name of the acyclic compound		Example
X	$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$	Paraffin (G) Alkane (I)	$CH_3 - CH_3$	Ethane Ethane
Carbon-carbon double bond	$-\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}-$	Olefin (G) Alkene (I)	$CH_2 = CH_2$	Ethylene Ethene
Carbon-carbon triple bond	$-C \equiv C-$	Acetylene (G)	$HC \equiv CH$	Acetylene
Halo	–X(F, Cl, Br, I)	Alkyl halide (G) Haloalkane (I)	CH_3Cl	Methyl chloride Chloromethane
Hydroxyl	–OH	Alcohol (G) Alkanol (I)	CH_3OH	Methyl alcohol Methanol
Ether linkage	– O –	Ether (G)	$(CH_3)_2O$	Dimethyl ether Methoxymethane

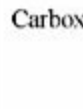
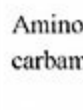
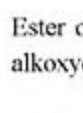
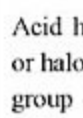
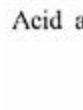
Aldehyde, oxo or formyl		Aldehyde (G) Alkanal (I)	$HCHO$	Formaldehyde Mehtanal
Keto or oxo		Ketone (G) Alkanone (I)	$(CH_3)_2CO$	Acetone Propanone
Carboxyl		Carboxylic acid (G) Alkanoic acid (I)	$HCOOH$	Formic acid Methanoic acid
Amino or carbamoyl		Acid amide (G) Alkanamide (I)	$HCONH_2$	Formamide Methanamide
Ester or alkoxycarbonyl		Ester (G) Alkyl alkanoate (I)	$HCOOCH_3$	Methyl formate Methyl methanoate
Acid halide group or haloformyl group or carbonyl halide group		Acid halide (G) Alkanoyl halide (I)	CH_3COCl	Acetyl chloride Ethanoylchloride
Acid anhydride		Acid anhydride (G) Alkanoic anhydride (I)	$(CH_3CO_2)O$	Acetic anhydride Ethanoic anhydide
Cyano		Alkyl cyanide (G) Alkanenitrile (I)	CH_3CN	Methyl cyanide Ethanenitirle
Isocyano		Alkyl isocyanide (G) Alkylcarbylamine (I)	CH_3NC	Methyl cyanide Methylcarbylamine
Nitro		Nitroalkane (G & I)	CH_3NO_2	Nitromethane
Amino		Alkylamine (G) Alkanamine (I)	CH_3NH_2	Methylamine Methanamine
Nitroso		Nitrosoalkane (G & I)	CH_3NO	Nitrosomethane
Sulphonic acid		Alkanesulphonic acid (G & I)	CH_3SO_3H	Methanesulphonic acid
Mercapto		Thioalcohol (G) Alkanethiols (I)	CH_3SH	Methyl mercaptan Methanethiol

Table-2
Some simple alkanes or paraffins

Molecular formula	Condensed structural formula	Common name	IUPAC name
CH_4	CH_4	Methane	Methane
C_2H_6	$CH_3.CH_3$	Ethane	Ethane
C_3H_8	$CH_3.CH_2.CH_3$	Propane	Propane
C_4H_{10}	$CH_3.CH_2.CH_2.CH_3$	n-Butane	Butane
C_4H_{10}	$(CH_3)_2CH.CH_3$	Isobutane	1-Methylpropane
C_5H_{12}	$CH_3.CH_2.CH_2.CH_2.CH_3$	n-Pentane	Pentane
C_5H_{12}	$(CH_3)_2CH.CH_2.CH_3$	Isopentane	2-Methylbutane
C_5H_{12}	$(CH_3)_4C$	Neopentane	2.2-Dimethylpropane

Olefins or alkenes (General formula C_nH_{2n}) :

Table-3 Some simple alkenes or olefins

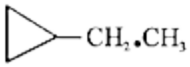
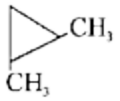
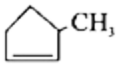
Molecular formula	Condensed structural formula	Common name	IUPAC name
C_2H_4	$CH_2.CH_2$	Ethylene	Ethene
C_3H_6	$CH_3.CH = CH_2$	Propylene	Propene
C_4H_8	$CH_2 = CH.CH_2.CH_3$	α-Butylene	1-Butene
C_4H_8	$CH_3CH = CH.CH_3$	β-Butylene	2-Butene
C_4H_8	$(CH_3)_2C = CH_2$	Isobutylene	2-Methylpropene
C_5H_{10}	$CH_2 = CH.CH_2.CH_2.CH_3$	α-Pentylene or β-amylene	1-Pentene
C_5H_{10}	$CH_3.CH = CH.CH_2.CH_3$	β-Pentylene or β-amylene	2-Pentene
C_5H_{10}	$(CH_3)_2C = CH.CH_3$	Isopentylene Isoamylene	2-Methyl 2-butene

Alkynes (General Formula C_nH_{2n-2}) :

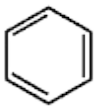
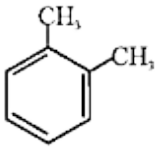
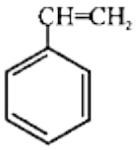
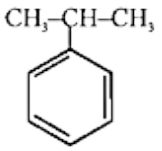
Some alkynes or acetylenes

Molecular formula	Condensed structural formula	Common name	IUPAC name
C_2H_2	$HC \equiv CH$	Acetylene	Ethyne
C_3H_4	$CH_3.C \equiv CH$	×	Propyne
C_4H_6	$CH_3.CH_2.C \equiv CH$	×	1- Butyne
C_4H_6	$CH_3. C \equiv C.CH_3$	×	2- Butyne
C_5H_8	$CH_3.CH_2. CH_2. C \equiv CH$	×	1- Pentyne
C_5H_8	$CH_3.CH_2.C \equiv CCH_3$	×	2- Pentyne
C_5H_8	$(CH_3)_2CH.C \equiv CH$	×	3- Methyl-1-butyne

Some simple alicyclic hydrocarbons

Molecular Formula	Structural formula	IUPAC Name
C_5H_{10}		Ethylcyclopropane
C_5H_{10}		1, 2- Dimethylcycloprapane
C_5H_{10}		1,1-Dimethylcyclopropane
C_6H_{10}		3-Methyl Cyclopentene

Some common benzenoid aromatic hydrocarbons (Arenes)

Molecular formula	Structural formula	Common name	IUPAC name
C_6H_6		Benzol	Benzene
C_8H_{10}		o-xylene (ortho xylene)	1,2–dimethylbenzene
C_8H_8		Styrene	Phenylethene
C_9H_{12}		Cumene	Isopropylbenzene

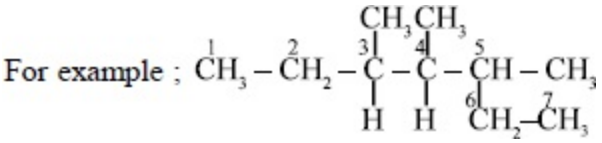
IUPAC System of nomenclature

1. Unsaturated hydrocarbons

Case-1 **Unbranched alkane :** Count the number of C–atoms and write the name depending on number of C–atoms as mentioned in table-2) i.e. for 1–Carbon methane, for 2-carbons ethane etc.

Case-2 **Branched alkane :** Count the C–atoms in the longest chain and consider the other radicals as the substituents.

For example ;

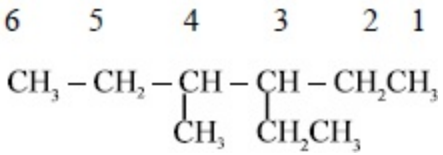


The longest chain contains 7-C atoms in the above.
∴ Base name is heptane.

Now 3 methyl group are in branches so, they are called as substituents. To name them follow the rule that (a) lowest locant rule, in which the alkyl substituent should get minimum locant which ever comes first. So, the name of the compound is 3, 4, 5-trimethylpentane.

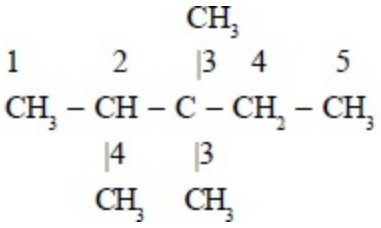
Use hyphen and no gap between number & substituent. If there are two different alkyl groups then the seniority will be according to the alphabetical order and listing of name also will be according to the alphabetical order.

For example ;



So, the name is 3-ethyl 4-methylhexane.

There is another rule called as lowest sum rule popularly used for the organic compounds having functional groups, also can be applied here.

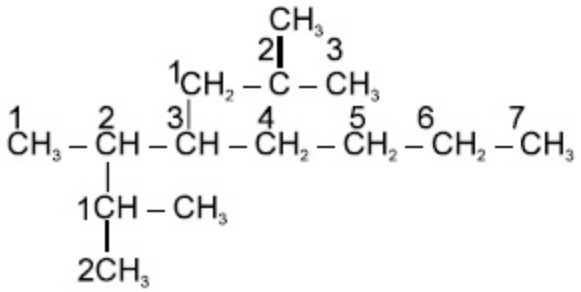


Sum of locants = 2 + 3 + 3 = 8
Sum of locants = 3 + 3 + 4 = 10

So, lowest sum in the way shown at the top can give us the right numbering. The rule tells us that the sum of the locants should be minimum to write the correct name.

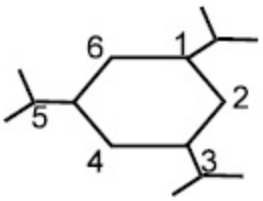
Case-3 : **Complex branching with compound substituent :** In this case d of di, t of tri, c of cyclo, i of iso, n of neo has to be considered as the part of alphabets but not the s of sec, t of tert (i.e. tertiary) etc. are

considered while determining the alphabetical serniority. If a compound possess two or more identical compound substituents then we use bis, tris, tetrakis, pentakis instead of di, tri, tetra, penta etc. respectively. Look at the following examples;

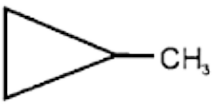


2-(1-methyl ethyl)-3-(2-methyl propyl) heptane

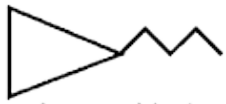
Name of the first substituent | (Name of the second substituent) | ↑ Base name



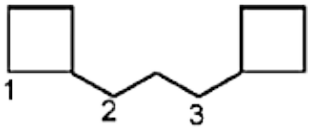
The name is 1, 3, 5 tris (isopropyl) cyclohexane. tris (name of the radical) pattern has been followed with the specification of position. We can also write 1, 3, 5 tris (1-methyl ethyl)cycloclohexane. For cyclic molecules (also acyclic molecules) most substituted part is taken as the base chain. If number of C–atoms is less outisde then the base name used for cyclic compound.Forexamples ;



Methylcyclopropane

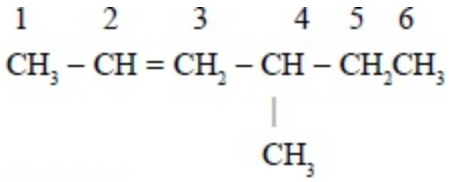


1-cyclopropyl-butane



Like groups should get similar treatments, so base name is propane and the name is 1, 3 dicyclo-butylpropane for the last figure.

Alkenes, Cyclo alkenes : Priority of double bond is given in a chain. With the branching of alkyl groups, the priority goes to double bond. It has no prefix and only shown as suffix (ene) used after the root name.

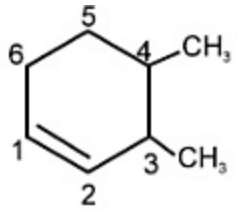
For example : 

4-methylhex -2-ene (suffix)

(prefix) (Root)

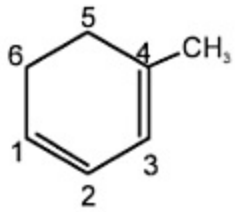
Same rule for cyclealkene also.

For example ;



3,4 dimethylcyclohex-1-ene

donot wirte 'xa'



5 methylcyclohexa-1, 3-diene

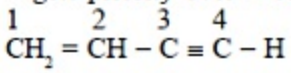
Use 'a' after x because here 'd' of diene is not vowel (a, e, i, o, u, y is also grouped into this).

Alkyne : 'yne' is used after the base name and the rule is name as that of alkene.

For example : $CH_3 - C \equiv CH$ (prop-1-yne)

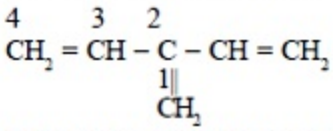
Combination of =, ≡ ;

= gets priority over ≡ but while listing the name ene comes first and yne comes later.



But-1-en-3-yne

(Donot write ene as 'y' is considered as vowel in IUPAC)

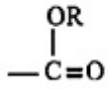
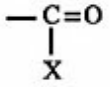
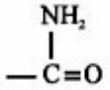
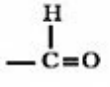
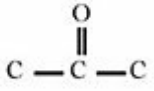


2-Ethenyl-1, 3-butadiene or 2-Ethenyl buta-1, 3-diene

For the other functional groups the name of the functional groups (common, IUPAC), prefix, suffix in the priority order has been shown in the following table. The priority order is followed upto $-\overset{|}{N}-$ group. I

List of some functions with prefixes and suffixes in order to precedence

(the order is followed upto —N— group)

Graphic formula of the function	Name of the function	Prefix	Suffix	The process of forming base names of acyclic compounds
$\overset{+}{N}R_3$, $\overset{+}{S}R_2$, etc.	Ammonium Sulphonium		– onium (halide, sulphide)	Tryalkyl ammonium
–COOH	Carboxyl	Carboxy	oic acid	Alkonic acid or alkanecarboxylic acid
SO_2OH	Sulphonic acid	Sulpho	Sulphonic acid	Alkanesulphonic acid
	Ester	Alkoxy- -carbonyl	 ...oate	 Alkyl alkanoate
	Carbonyl halide	Haloformyl	oyl halide carbonyl halide	Alkanoyl halide Alkanecarbonyl halide
	Amido	Carbamoyl	amide carboxamide	Alkanamide Alkanecarboxamide
– C ≡ N	Carbonitrile/Cyano	nitrile	Alkanenitrile	
$-\overset{+}{N}\equiv\overset{-}{C}$	Isonitrile	Isocyanide	carbylamine	Alkylcarbylamine
	Formyl	Formyl, oxo, aldo	al carboxaldehyde	Alkanal Alkanecarboxaldehyde
	Keto	Oxo or Keto	one	Alkanone
– OH	Hydroxyl	Hydroxy	ol	Alkanol
– SH	Mercapto	Mercapto	thiol	Alkanethiol
$-NH_2$	Amino	Amino	amine	Alkanamine Alkylamine
RO–	Ether linkage	Alkoxy	alkane	Alkoxyalkane

RSO_2–	Alkyl sulphonyl	Alkyl sulphonyl	sulphone	Alkanesulphone
C = C	double bond	.....	ene	Alkene
C ≡ C	triple bond	.....	yne	Alkyne
– Cl	Chloro	Chloro	.....	Chloroalkane
–Br	Bromo	Bromo	.....	Bromoalkane
–I	Iodo	Iodo	.....	Iodoalkane
–N = N–	Azo	Azo	.....	Azoalkane
– NO_2	Nitro	Nitro	.....	Nitroalkane
– NO	Nitroso	Nitroso	.....	Nitrosoalkane

After $-\overset{|}{N}-$ (amino) group the groups with only prefix are given preference according to their seniority and according to the alphabetical order and listing of the same is also according to the alphabetical order.

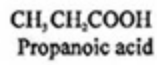
-CO_2 H (carboxylic acid) :

1- Count the C of – CO_2 H and put it in the longest chain (look this is a terminal group).

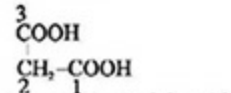
2- Find the base name i.e. rest name and add 'oic acid' at last and follow seniority. Take for example;



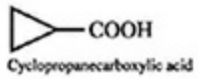
Ethanoic acid



Propanoic acid



Propane–1, 3- dioic acid



Cyclopropanecarboxylic acid

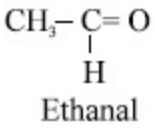
With cyclic compounds C of CO_2 H is not counted in the main chain, therefore use carboxylic acid.

- CHO (aldehyde) :

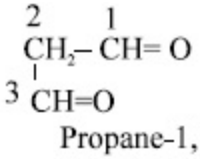
This is also a terminal group, rule 1 is followed as above. At the end we use 'al'

For the cyclic compounds we use carboxaldehyde.

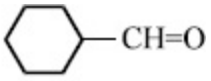
For example;



Ethanal



Propane-1, 3- dial

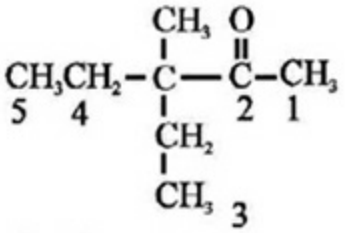


Cyclohexane carboxaldehyde

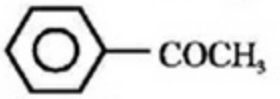
–C=O (Ketone) :

It is a non terminal group. Count the C– in the main chain at minimum locant in simple ketones. Otherwise follow the seniority table.

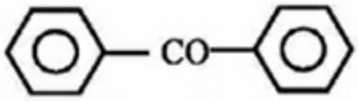
For example ;



3 - Ethyl -3- methylpentan-2- one

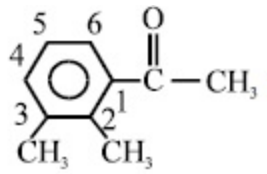


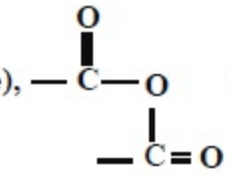
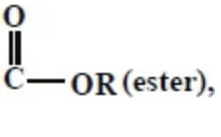
Acetophenone



Benzophenone

The above names are retained. So derivatives of these compounds will get the base names of the above compounds.

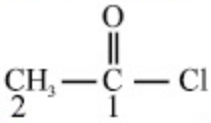

2, 3- dimethylacetophenone

–COX (acid halide) , – $CONH_2$ (amide),  **(anhydride),**  **OR (ester),**

– C ■ N (nitrilies or cyanide) , – NC (isocyanide) :

We will take one example from each to understand the writing technique.

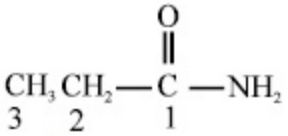
For example ;



Root name : ethan

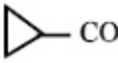
Suffix or name of the functional group : oyl chloride.

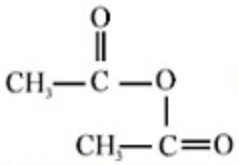
Therefore ethanoylchloride is the IUPAC name.



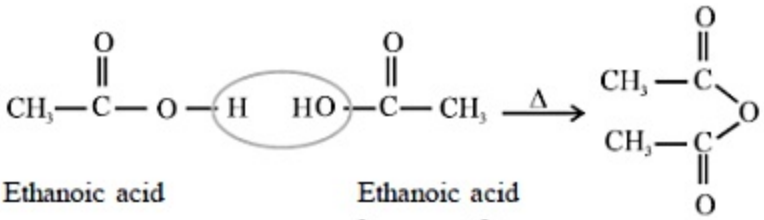
Root name : Propan

Suffix or name of the functional group : amide

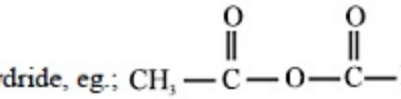
Therefore name is propanamide. Similarly for  $CONH_2$, cycloprapanecarboxamide.

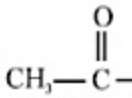
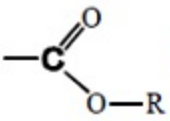


ethanoic anhydride is the IUPAC name. As we can think of the formation of this compound as follows;

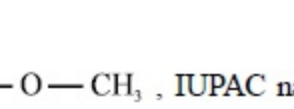


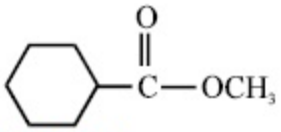
Ethanoic acid Ethanoic acid

For mixed anhydride, eg.;  , ethanoic methanoic anhydride is the IUPAC name.

In case of  , write the alkyl group (R) of  first. Give space then write the parent acid's root name and add 'oate' finally.

Methyl ethanoate

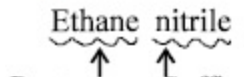
For  , IUPAC name is methyl methonate .



Prefix : Methyl Suffix : Carboxylate

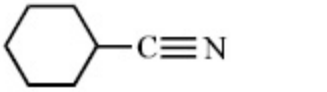
Root name : cyclohexane, therefore name is methyl cyclohexancarboxylate.

space



Ethane nitrile

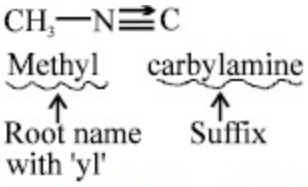
Root name Suffix



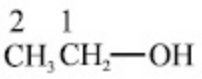
Cyclohexanecarbonitrile

Root name Suffix

No space

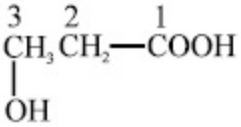


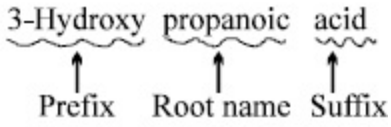
–OH (alcohol), – SH (thiol)



Root name : Ethane
Suffix : ol

Therefore Ethanol is the IUPAC name



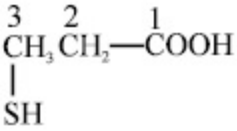


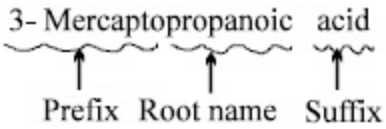
$CH_3CH_2 - SH$

Root Name : ethane

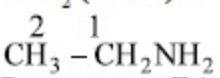
Suffix : thiol

Therefore, ethane thiol is the IUPAC name of the above compound.

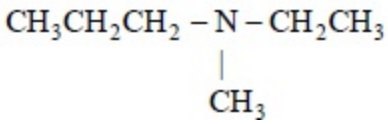




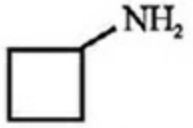
–NH_2 (amine) :



Root name : Ethan
Suffix : amine
Therefore IUPAC name is ethanamine.



N-Ethyl–N –methylpropanamine. Here we count number of carbon atoms along the chain having maximum C as the root name (i. e. alkanamine part comes from the alkane with longest chain)

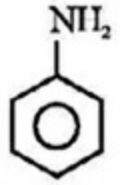


Cyclobutanamine

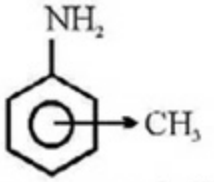


Cyclopropylethanamine

Aromatic amines have common names and are used as their base names while writing the names of their derivtives.

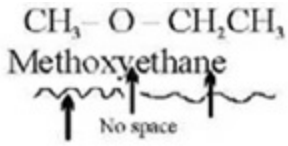


aniline



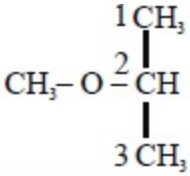
o. m, p toluidine

IUPAC has retained the common names for aromatic amine like aniline etc. The other groups Cl, Br, I, NO_2 etc. are used as prefix and seniority depends on alphabetical seniority of their names. Examples ;

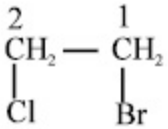


(Smaller alkyl group) (Larger alkyl group)

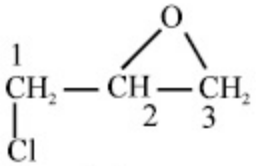
Likewise , considering the smaller alkyl group in the alkoxy part and larger alkyl group as alkane, the name of the following compound is ;



Methoxyisopropane
or
2-Methoxypropane



1-Bromo-2-Chloro ethane
(alphabetical seniority)

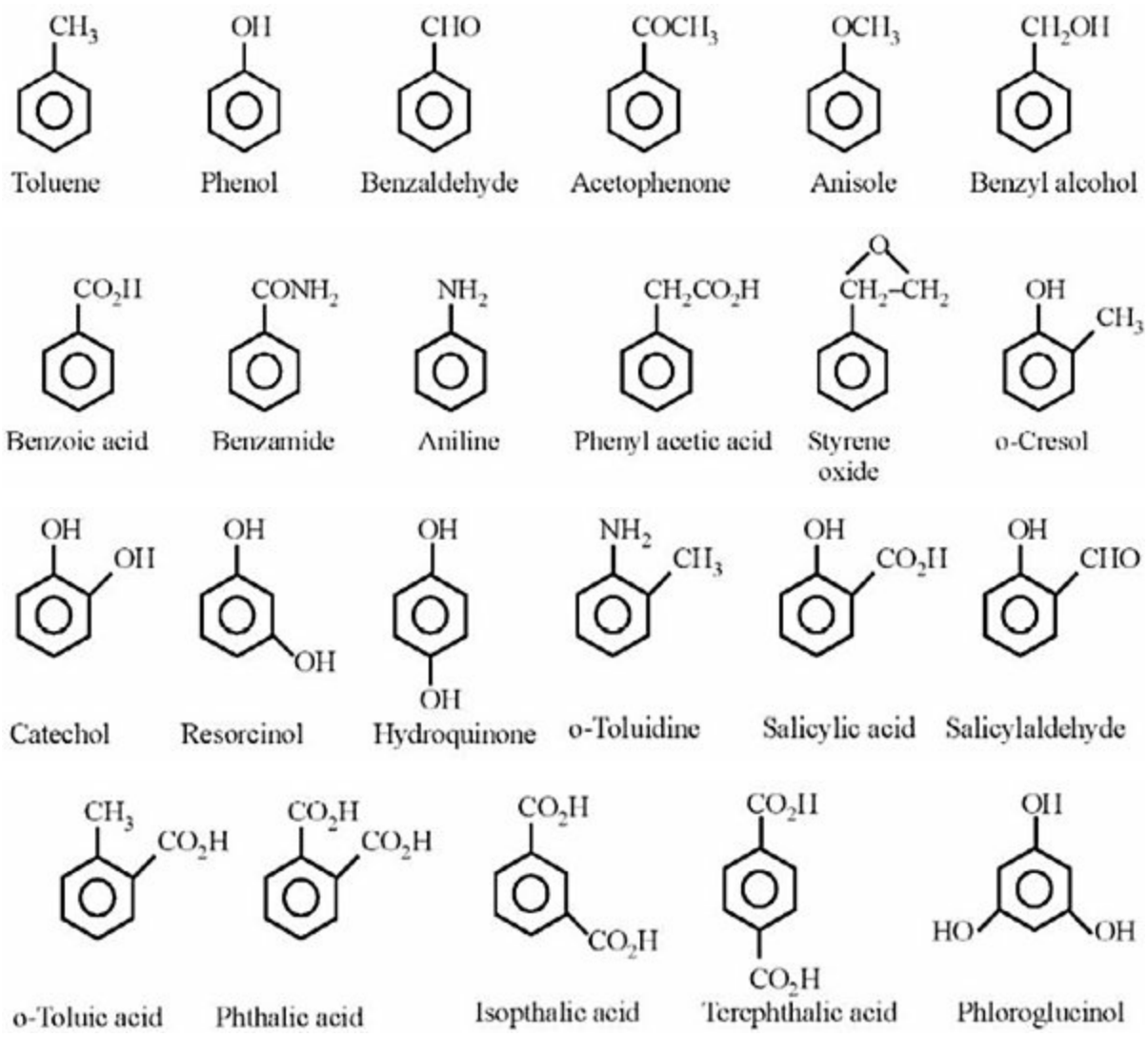


1-chloro-2, 3 epoxy propane

If we understand the naming then we can derive structural formula of the

organic compounds.

Some common as well as IUPAC names of benzene derivatives



General Organic Chemistry

Introduction :

Before going into the chemistry of organic compounds, we will briefly understand the concept of orbitals in a very brief manner and then gradually go into the depth. For this we need to have knowledge in physical chemistry where atomic structure is taught.

Concept of orbital :

The mathematical form of the movement of electrons round the nucleus considering wave particle duality of electron was given by Schrodinger, which was

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h}(E-V)\ \psi=0$$

Where, ψ = wave function, (x, y, z) are the variable coordinate positions of the electron, m= mass of the electron, h= Planck's constant, E, V are total energy and potential energy of the electron respectively.

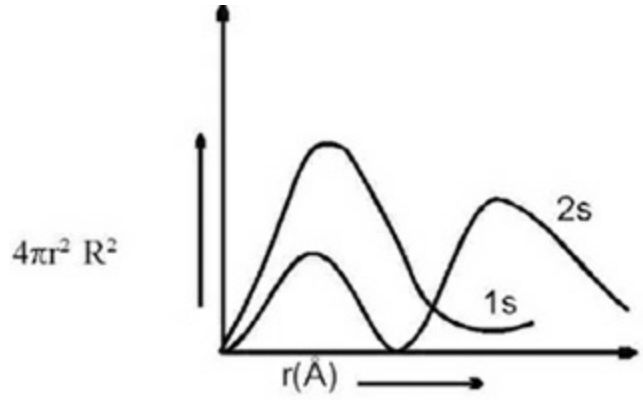
Solving for radial wave functions, we obtain,

For 1s, ($n=1, \ell=0$)
$$R=\left[2\left(\frac{Z}{a_0}\right)^{3/2}e^{-Zr/a_0}\right]$$

For 2s, ($n=2, \ell=0$)
$$R=\left[\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{\frac{-Zr}{2a_0}}\right]$$

For 2p ($n=2, \ell=1$)
$$R=\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0}e^{\frac{-Zr}{2a_0}}$$

where Z = no. of protons, a_0 = first Bohr's radius, r = radial distance of the electron from the nucleus. Therefore radial probability will be R^2 and characteristic graphs are ,



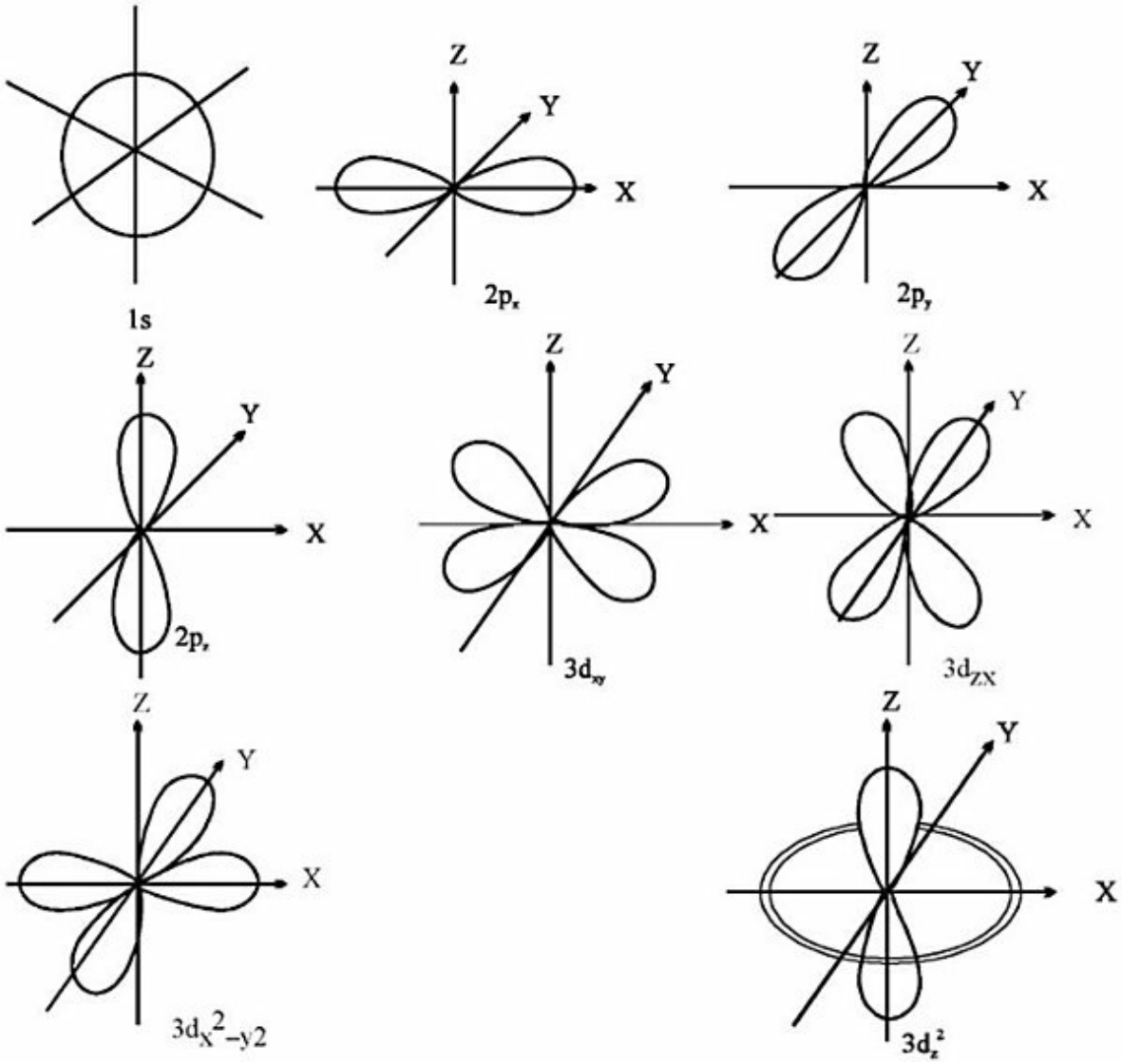
Similarly angular wave functions are,

$$\text{for s orbital ; } \Theta\phi = \left(\frac{1}{4\pi}\right)^{1/2}$$

$$\text{for } p_z \text{ orbital ; } \Theta\phi = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta;$$

$$\text{for } d_{Z^2} \text{ ; } \Theta\phi = \left(\frac{5}{16}\pi\right)^{1/2} (3\cos^2\theta - 1)$$

where θ = angle by the radius with the z- axis in polar coordinate. Therefore combination of $R^2\ \Theta^2\phi^2$ gives overall probability of finding an electron around the nucleus. As many properties of atom match with the mathematical domain of the orbitals (i.e. maximum probability of finding an electron), therefore we can draw the following pictures of the orbitals.



From the above diagrams, we should have the following understandings;

(1) The orbitals are where we can have maximum probability to find an electron.

(2) Energywise, 1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d etc. according to Aufbau principle.

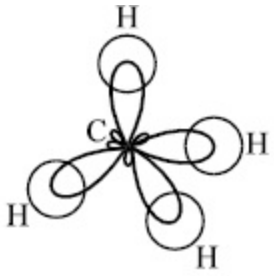
(3) These orbitals house the electrons.

(4) When a bond forms of the nature σ - bond, then pure orbitals with one electron unpaired in each comes and make the bond by overlapping of orbitals and probability of electron density in between these two nuclei is maximum.

(5) σ - bond can be formed by the participation of hybridised orbitals instead of pure orbitals.

For example C–H bond in CH_4 forms by sp^3 orbital of C and pure 1s orbital of H. The advantage is to explain the bond length, bond angle etc. within the molecules.

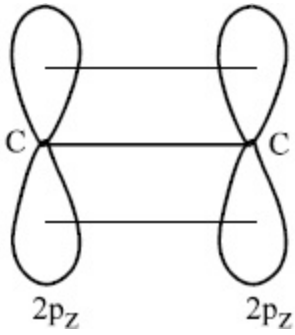
For example



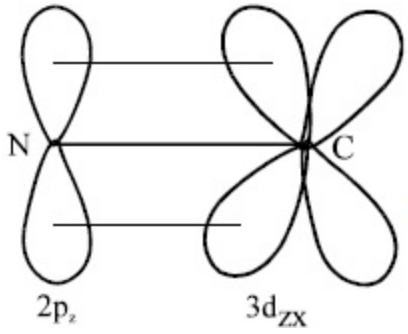
In the above diagram sp^3 orbital of C overlaps with 1s orbital of H.

(6) π - bonds form by lateral overlap of orbitals, which are parallel and also lying in the same plane.

For example ;



or,

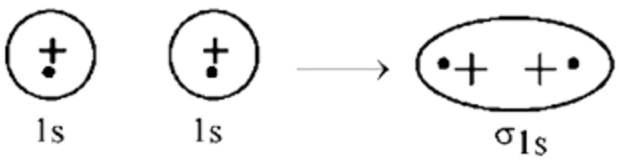


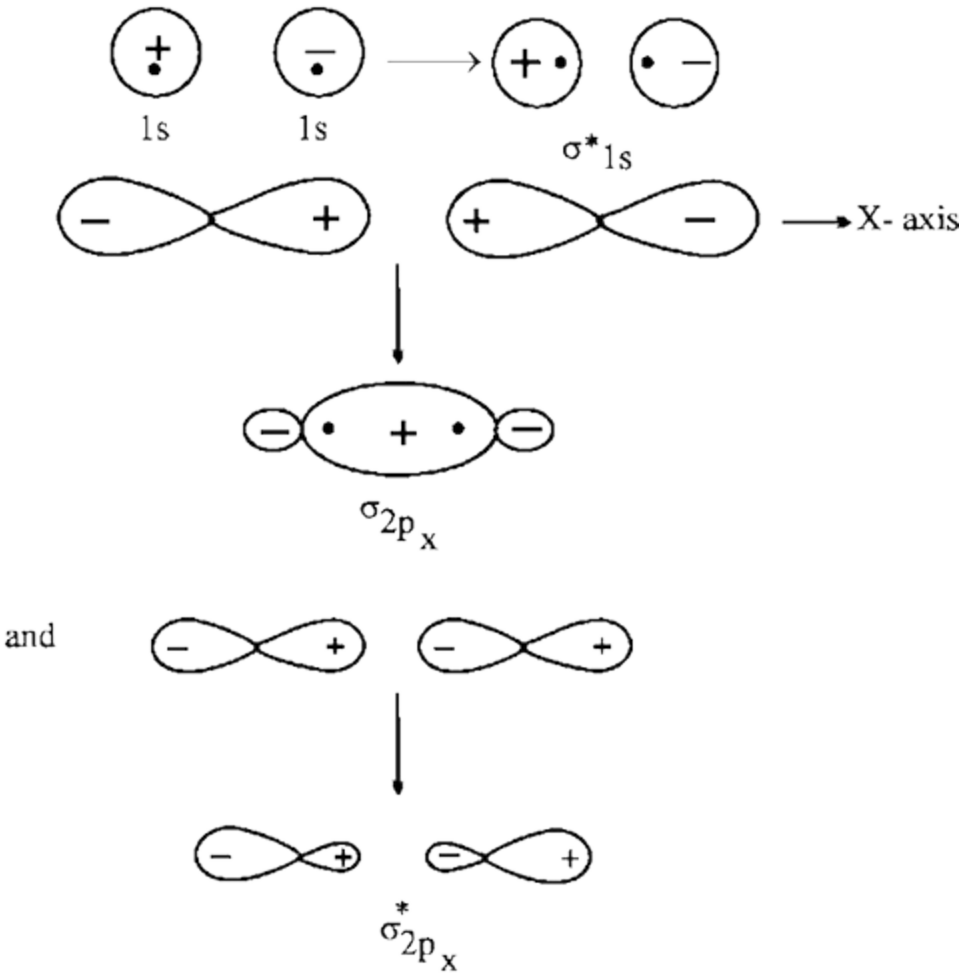
etc.

(7) Atoms generally undergo hybridisation and then overlap to make σ - bond or coordinate covalent bond. They accomodate the unpaired electrons in pure orbital/s and π - bond forms by lateral overlap of pure orbitals.

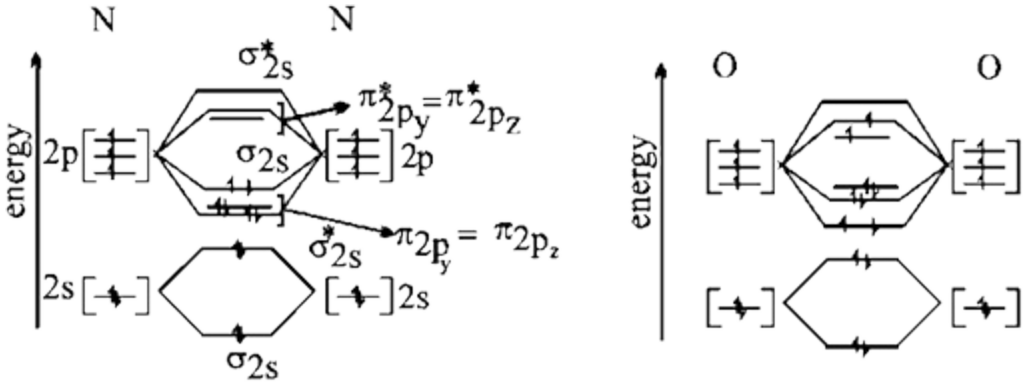
(8) To remove certain complexities e.g. colour of the molecule/s, LCAOMO theory came into picture. It consider number of atomic orbitals taken part in linear combination = total number of molecular orbitals.

Diagramatically the formation of bonding and anti bonding molecular orbitals can be shown as follows;

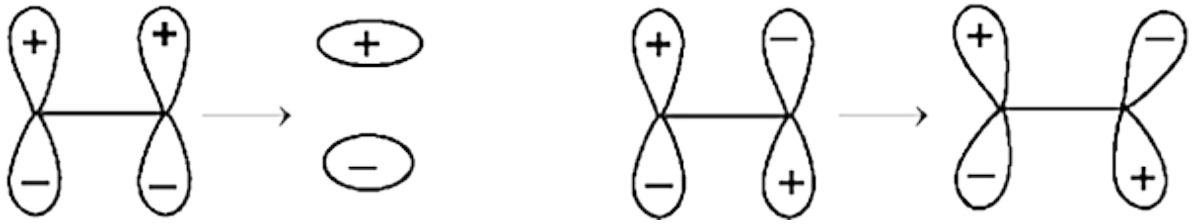




Therefore, to explain the formation of Li_2 – N_2 we consider the following diagrams.

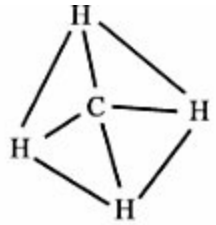


For π BMO, π ABMO diagrams the overlapping can be shown as follows ;

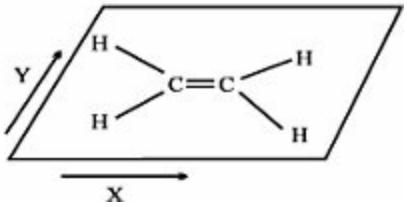


Structure of molecules of importance and the hybridisation of atoms.

1- CH_4 (Methane) — C, sp^3 ($s + p_x + p_y + p_z$)



2- C_2H_4 (Ethylene) — C, sp^2 ($s + p_x + p_z$)

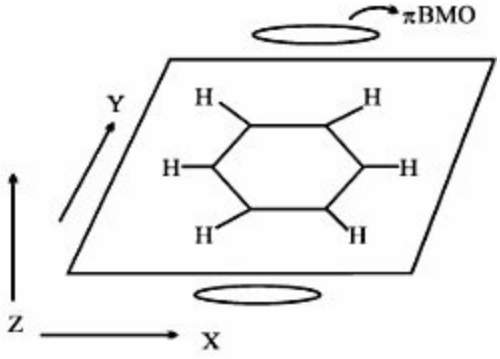


3- C_2H_2 (Acetylene) — C, sp ($s + p_x$)

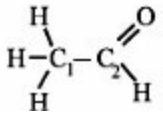
linear

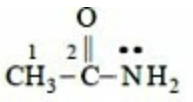
H– C ≡ C – H

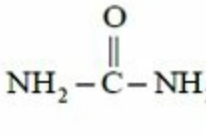
4- C_6H_6 (Benzene) — C, sp^2



(5) $CH_3CH=O$ — (C^1, sp^2) (C^2, sp)

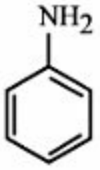


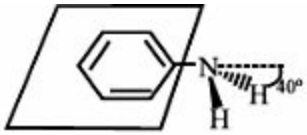
(6)  C_1, sp^2, $C_2 sp^2$; N, sp^2

(7)  N sp^2, C sp^2

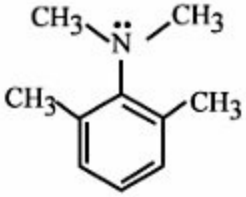


(lp of N participates in resonance with C = O bond)

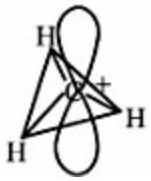
(8)  N; in between sp^2, sp^3 hybridisation



NH_2 group is 40° away from the plane of the benzene ring

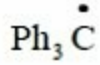
(9)  N; sp^3 ; Due to steric inhibition of resonance

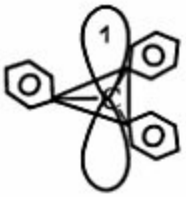
(10) C; sp^2



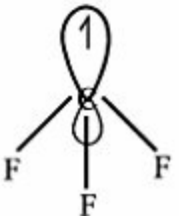
(11)  C; sp^2

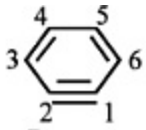


(12)  C, sp^2



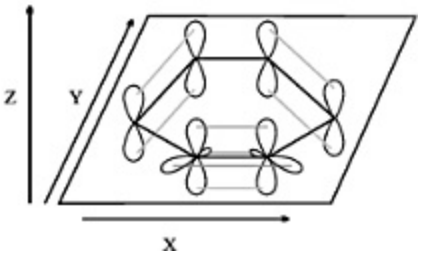
(13)  C, sp^3

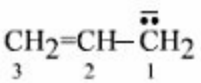


(14) 

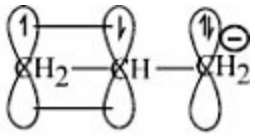
Benzyne

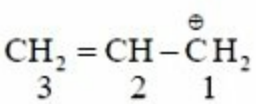
C_1, C_6 are sp^2 and π- bond between sp^2 hybridised orbitals



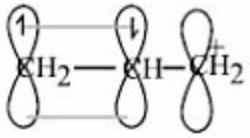
(15) 

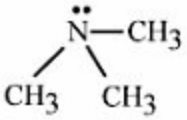
C_1 ,C_2 , C_3 are sp^2



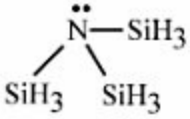
(16) 

C_1 ,C_2, C_3 are sp^2



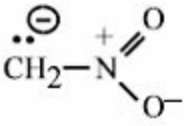
(17) 

N is sp^3

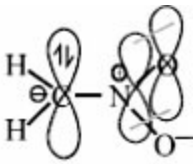
(18) 

N is sp^2 as lp goes into resonance with 3d orbital of Si



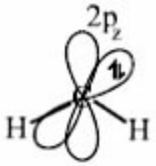
(19) 

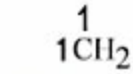
(C, sp^2) ; (N, sp^2)



(20) 

C, sp^3



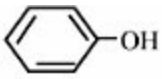
(21) 

(Triplet Carbene)
C, sp



(22) 

(Singlet)
C, sp^2

(23) 

(C, sp^2)

(O, sp^2 due to lp of O resonates with benzene ring)

(24) $\overset{1}{C}H_2 = \overset{2}{C} = \overset{3}{C}H_2$

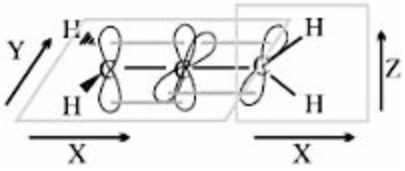
Allene

(C_1,C_3 are sp^2), (C_2,sp)

C_1 involves ($s + p_x + p_y$)

C_2 involves $s + p_x$

C_3 involves $s + p_x + p_z$

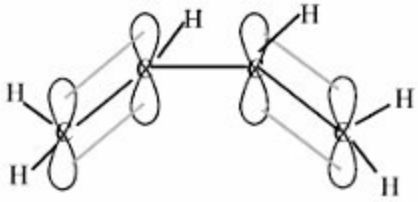


(25) $\overset{1}{CH_2} = \overset{2}{CH} - \overset{3}{CH} = \overset{4}{CH_2}$

C_1 –C_4 are sp^2

all involves

($s + p_x + p_y$)



(26) $\overset{1}{CH_2} = \overset{2}{C} = \overset{3}{C} = \overset{4}{CH_2}$

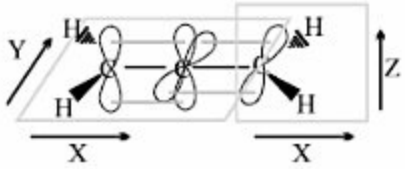
C_1, sp^2 ($s + p_x + p_y$);

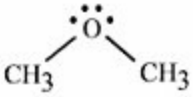
C_2, sp ($s + p_x$)

C_3, sp ($s + p_x$)

C_4, sp^2

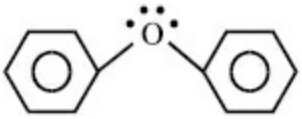
($s + p_x + p_y$)



(27) 

(C, sp^3);

(O, sp^3)

(28) 

(All carbons are sp^2);

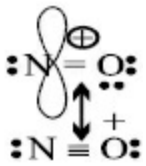
(O, sp^2), O-lps are highly involved in resonance with two benzene rings.

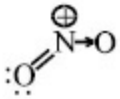
(29) 

(C, sp) ; (O, sp)

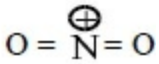
(30) $\overset{+}{N} = O$

(N, sp) ; (O, sp)



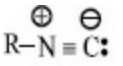
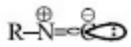
(31) 

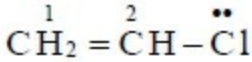
(N, sp); (O, sp)

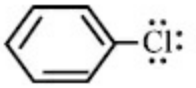


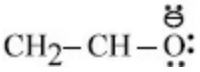
(32) $R - C \equiv N :$

(C, sp) ; (N, sp)

(33)  (N, sp), (C, sp) 

(34)  (C_1, sp^2), (C_2, sp^2) (Cl, sp^2)

(35)  (C atoms are sp^2); (Cl, sp^2)

(36)  (C, sp^2); (O, sp^2)

Electronegativity : This is defined as the tendency of an atom in a molecule to attract towards itself, the electrons in a chemical bond (actually σ - bond) e.g. inwhere B is more electronegative than A. $\overset{\delta+}{A}\!\!-\!\!\div\!\!-\overset{\delta-}{B}$ Pauling suggested that, $X_A - X_B = 0.208\sqrt{E_{A-B} - (E_{A-A}.E_{B-B})^{1/2}}$ where X_A, X_B are electronegativities of A and B. E_{A-E}, E_{A-A} E_{B-B} are the bond dissociation energies in kcal/ mole (1 eV= 23.06 kcal/mole = 96.5 kJ/mole).

Also, $X_A - X_B = 0.102\sqrt{\Delta}$ when Δ is expressed in kJ/ mole which is $E_{AB} - \sqrt{E_{A-A}.E_{B-B}}$. He assumed that $X_H = 2.1$ and then $X_F = 4.0$, $X_{Cl} = 3.0$, $X_O = 3.5$, $X_N = 3.0$, $X_{Li} = 1.0$, $X_{Na} = 0.9$, $X_S = 2.5$, X_C=2.5, $X_{Br} = 2.8$, $X_I = 2.5$, $X_{Si} = 2.8$, $X_{Al} = 1.5$, $X_{sp^3(C)} = 2.5$, $X_{sp^2(C)} = 2.75$, $X_{sp\ (C)} = 3.3$, $X_{sp^3(N)} = 3.7$, $X_{sp^2(N)} = 3.9$, $X_{sp(N)} = 4.7$ etc.

Mulliken suggested $X = \dfrac{\text{I.P.} + \text{E.A.}}{3}$ Here energy values are in eV.

Allred and Rochow stated that $X = \dfrac{0.359}{r^2}Z_{eff} + 0.744$ (where r is in A and Zeff = effective nuclear charge)

Dipole moment of a bond (i.e. bond moment)

If we observe that $\overset{\delta q^+}{A}\!\!-\!\!\div\!\!\rightarrow\overset{\delta q^-}{B}$, then A –B bond will have a dipole moment from A towards B. $\mu = \delta q \times d$, where δq = fractional charge on the atoms and d= distance between two nuclei. Unit is Debye. 1 Debye= 10^{-18}esu. cm.

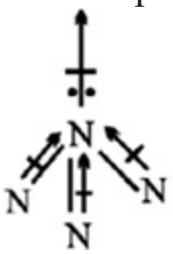
Some individual moments are, $\mu_{C-H} = 0.5$, $\mu_{C-O} = 0.8$, $\mu_{C-Cl} = 1.6$, $\mu_{O-H} = 1.7$, $\mu_{C=O} = 2.1$, $\mu_{H-Cl} = 1.1$

% ionic character in σ - B bond $= \left(\dfrac{\mu_{obs.}}{\mu_{theo.}}\right) \times 100$

Also, by Pauling,

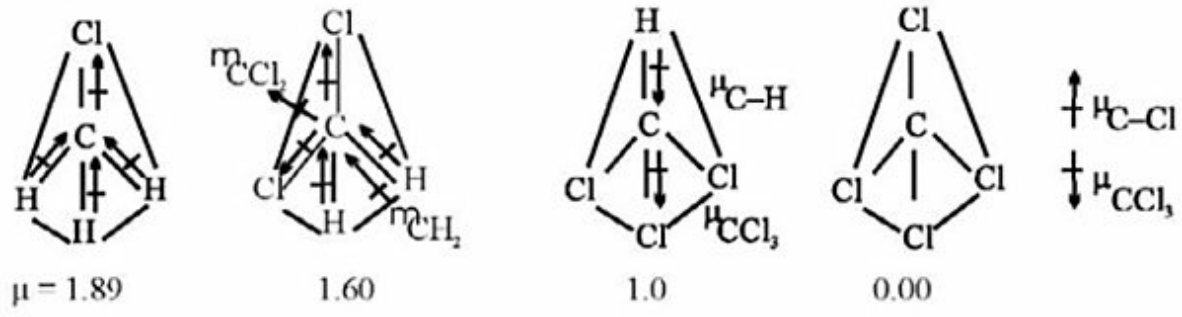
% ionic character $= [0.16\,(X_A - X_B) + 0.035(X_A - X_B)^2] \times 100$

Some dipole moment values and directions;





$\therefore \mu_{net}$ for NH_3 = 1.5 D and μ_{NF_3} = 0.2 D by vectorial addition and considering the lp, bp moments. Dipole moment studies shows that $\mu_{H\text{-}F}$ = 1.90 D, μ_{H_2O}=1.88 D, $\mu_{H_2O_2}$ = 2.3 D, μ_{HCl} =1.0 D, $\mu_{H\text{-}Br}$ = 0.8 D, μ_{HI} = 0.40 D.



To calculate, $\mu_{CHCl_3} = \mu_{C-H} + \mu_{C-Cl}$

$\because$ 3 μ_{C-H} individually working at 109° 28′ to each other and the resultant vector μ_{C-H} acts in the same direction of μ_{C-Cl} and they are collinear vectors.

$\therefore \mu_{CHCl_3} = \mu_{CH_3} + \mu_{C-Cl} = \mu_{C-H} + \mu_{C-Cl} = 0.3 + 1.5 = 1.8$ D

For $\mu_{CH_2Cl_2}$, two Cl atoms repel each other, therefore $\angle Cl-C-Cl > 109° 28'$.

$\therefore \mu_{C-Cl} > \mu_{CCl_2}$ ignoring the bond moments of C-H bond.

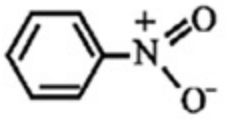
$\therefore \mu_{CH_2Cl_2} = (\mu_{CH_2} + \mu_{CCl_2})$ and which is clearly less than μ_{CH_3-Cl}

For, μ_{CHCl_3}, due to bigger size of Cl atoms more repulsion and $\angle Cl-C-Cl$ also increases compared to CH_2Cl_2. Therefore net resultant $|\vec{\mu}_{CCl_3}| = |\vec{\mu}_{C-Cl} + \vec{\mu}_{C-Cl} + \vec{\mu}_{C-Cl}|$ reduces compared to even $|\vec{\mu}_{CCl_2}|$

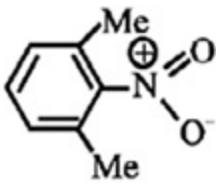
$\therefore$ Net $\mu_{CHCl_3} = \vec{\mu}_{CCl_3} + \vec{\mu}_{C-H} < \vec{\mu}_{CCl} + \mu_{C-H}$ i.e. $\mu_{CHCl_3} < \mu_{CH_2Cl_2} < \mu_{CH_3Cl}$

Quite obviously $\vec{\mu}_{CCl_4} = \vec{\mu}_{CCl_3} + \vec{\mu}_{C-Cl} = 0$

Some more examples are;

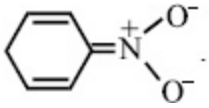


μ = 3.9 D

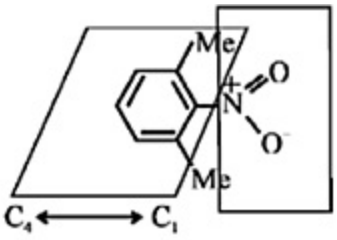


3.6 D

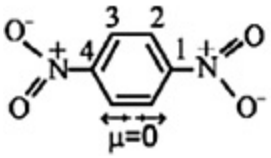
The above result is due to the fact that resonance (discussed later) causes benzene ring more positive and O atoms of – NO_2 more negative.



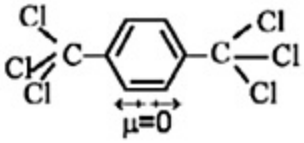
∴ Large charge separation causes more μ But when there is steric repulsion between O atoms and ortho methyl groups then C– N rotation causes non planarity of – NO_2 group with benzene ring and resonance stops, ie. electron cannot go out side from benzene ring to – NO_2. For example,



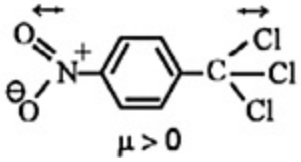
Therefore μ reduces as shown in the diagram.



μ=0

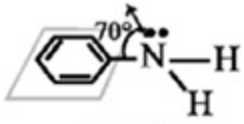


μ=0



μ > 0

Here we must understand that the net resultant moment due to the group moments lie in the same plane with that of benzene ring and collinear with C1–C4 axis. Let us see the other cases below ;

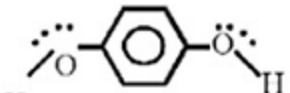


μ=1.52 D

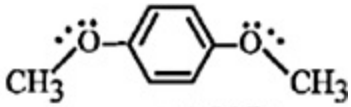
μ_{NH_2} not along C_1 –C_4 axis. It is at an angle of 70° with the plane of the benzene ring. Therefore, If unsymmetrical groups are present at para, μ can never be zero.



μ=2.5 D



m=1.7 D

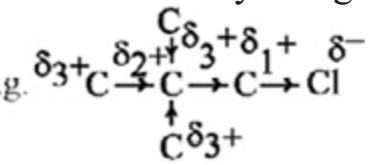
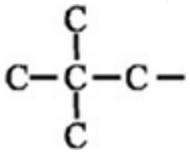


μ=1.75 D

In organic chemistry, we must understand some effects which govern the

mechanisms and reactions in organic chemistry.

(1) Inductive effect (+I, – I) :

As we know that two different elements if connected by a bond there is always a pull of the σ -bp electrons towards one of those two atoms and thereby polarisation occurs at that bond. Due to this permanent dipole induced in a bond by another bond directly along a chain within a molecule is called inductive effect. e.g.  . Cl pulls the bond pair towards itself, so it is called – I (electron pair withdrawing) group and other i.e.  is supplying the C–Cl electron pair towards Cl, therefore it is called +I (electron pair repelling) group. Magnitude wise, $\delta_1 + > \delta_2 + >> \delta_3 +$. It is found that inductive effect operates upto C_2 strongly from the source and dies down at C_4. ∴ +I groups which always supply electron pair can make happy those which are in need of electrons (to be octet for example)

Decreasing order of +I effect,

$$-O^- > -COO^- > R_3C- > R_2CH- > RCH_2- > CH_3- > D- > H-$$

Increasing order of – I effect,

$$H < R_2C=CH- < Ph- < R-C\equiv C- < -OH < -SH < -OR < -COOR < -I < -Br < -Cl < F$$
$$< -COOH < -CN < -NO_2 < \overset{+}{N}H_3 < -\overset{+}{N}R_3$$

Here the measurement of I effect is done on the basis of Ingold's view. Any group R_3C of R_CG if decreases electron density in R_3C part compared to R_3CH then G is called as + I group, else it is called as – I group

Application of inductive effect will be seen in different sections.

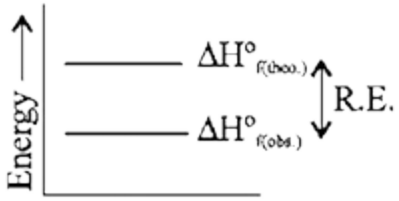
2- Field effect :

This effect operates through space or solvent molecules. Inductive effect and field effect are almost the same. Field effect still can be identified as it depends on the geometry of the molecule but inductive effect depends on the nature of bonds.

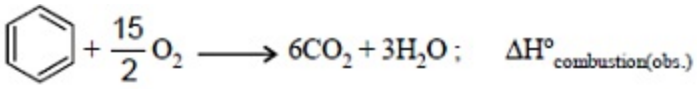
Resonance and Mesomeric effect :

To explain the stability of many compounds the concept of resonance and or mesomeric effect brought into the picture by scientists. Inglold called this phenomenon as mesomeric effect and Heisenberg termed this as resonance effect from the perspective of quantum mechanics. Basically both these were to explain why CO_2, benzene (C_6H_6) etc are stabler than expected.

But truely speaking there are differences between these two phenomena which we will see later on. Thermodynamically, the extra energy by which a molecule is stable, is called as resonance energy and which is, $R.E. = \Delta H^0_{f(obs.)} - \Delta H^\circ_{f\,(theoretical)}$, where $\Delta H^\circ_{f(obs)}$ = observed heat of formation (standard) and $\Delta H^\circ_{f(theo)}$ = theoretical heat of formation (standard). With the help of energy diagram,



For example if we burn benzene, we obtain, $\Delta H^\circ_{combustion(obs.)}$

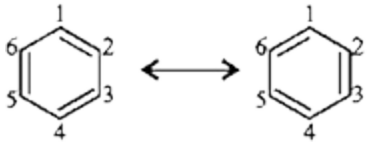


and theoretically, $\Delta H^\circ_{f(theo.)} = [3 \times (BDE_{C-C} + BDE_{C=C}) + 6BDE_{C-H} + \frac{15}{2} BDE_{O=O}] - [6(2BDE_{C=O}) + 3(2BDE_{O-H})]$.

We find that there is a difference of energy and which is called as resonance energy ;

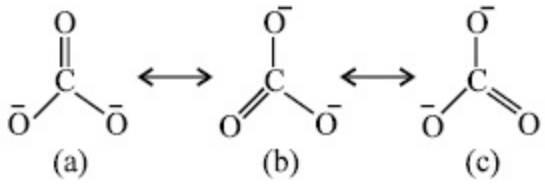
$$R.E. = \Delta H^\circ_{comb(obs.)} - \Delta H^\circ_{comb(theo)}$$

So, there are certain things must be operative. To explain that we can draw two meaningful resonating structures (also called as cannonical forms) as shown below;

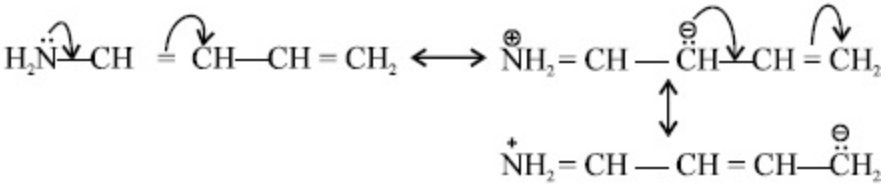


The above change over of the μ -bonds not only explain the extra stability but also explain equal bond length between all carboN–Carbon atoms. Actually, the more such kinds of structures we can draw more stability appears for the compound.

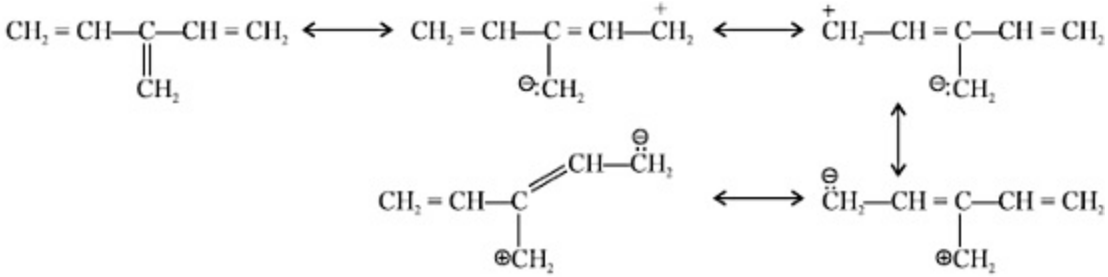
Examples are ;

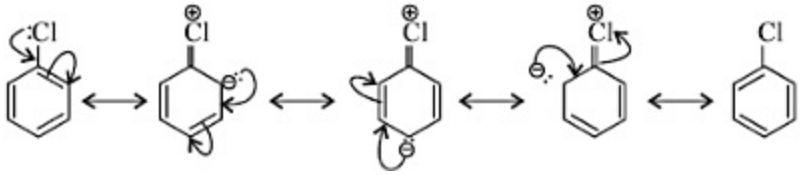
(1) 

(2)

(3) 

(4) 

(5) 

(6) 

Same structures also can be drawn for many aromatic compounds of the type : :Z 

Now we are in a position to understand that a molecule is stable if it has π-σ-π or lp-σ-π etc. type of arrangements. In that case we can easily draw many resonating structures which make it stable. Frankly speaking none is the actual representations of actual molecule and only we are presenting the molecule on paper. Therefore nothing is resonating as such and actual molecule's structure is hybrid of all the the resonating structures.

So, to draw resonating structures we must follow the **rules** mentioned below;

(1) All the cannonical or resonating sturdcure must be Lewis structures, we

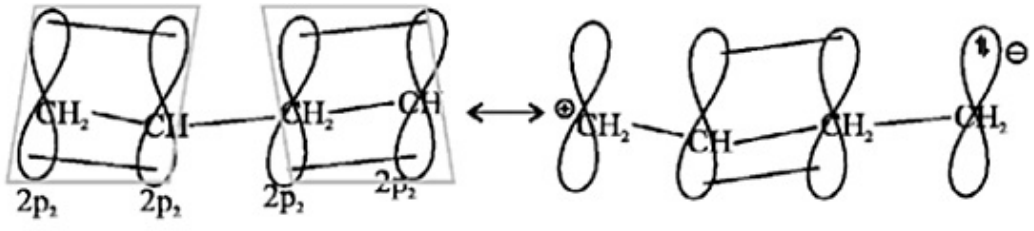
can not write the structures in which C, N has five bonds etc. Between two structures we shall use ↔ sign.

(2) The positions of the nuclei must be the same in all structures and we are only allowed to move electrons (unshared or π bond pairs)

For example ; $CH_2=CH_2 \nleftrightarrow CH_3-\ddot{C}H$

(4) All atoms taking part in resonance, must lie in the same plane or nearly in the same plane. The reason for for this is to gain maximum lateral overlap of p-orbitals.

eg;



$CH_2=CH-CH=CH_2 \longleftrightarrow {}^{+}CH_2-CH=CH-{}^{\ominus}CH_2$

From the above picture individually all C–atoms lie in X-Y plane and therefore resonance can take place.

(5) All cannonical forms must have the same number of unparied electrons. Therefore,

$CH_2=CH-CH=CH_2 \longleftrightarrow \dot{C}H_2-CH=CH-\dot{C}H_2$

(6) Contributing resonating structures: (a) All resonanting structures do not **contribute** equally to the true (hybrid) molecule. Contribution by one structure is a function of its own stability

Hence $\underset{I}{CH_2=CH_2} \nleftrightarrow {}^{+}CH_2-{}^{-}CH_2$

or, $\underset{II}{CH_2=CH-CH=CH_2} \nleftrightarrow {}^{+}CH_2-{}^{-}CH-CH=CH_2 \leftrightarrow {}^{-}CH_2-{}^{+}CH-CH=CH_2$

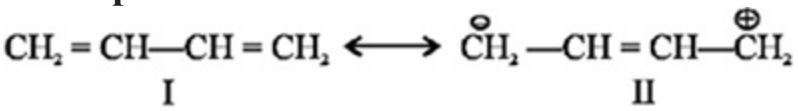
As in the above cases opposite charge separation only by π -bond cleavage requires high energy compared to I or II which are uncharged.

(b) Equivalent cannonical forms such as 1(a), 1(b), 1(c) contirbute equally to

the resonance energy hybrid. actually these cause greater resonance energy.

(c) The more covalent bonds a structre has, the more stable it is. As more the covalent bonds form more the amount of energy will be released.

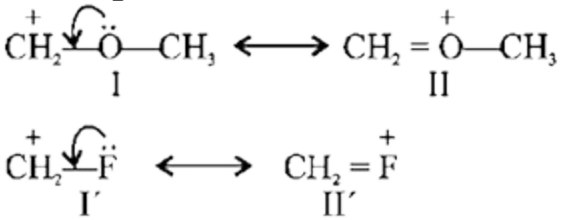
For example :



I is stabler than II

(d) Structures in which all of the atoms have complete valence shell of electrons are especially stable and make large contribution to the hybrid.

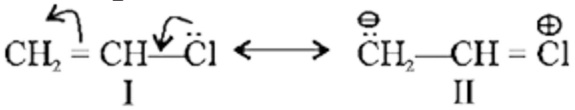
For example :



II, II' will have more contribution to the stability of the hybrids.

(e) Charge separation brings instability to the molecule and therefore oppositely charge separated structured are less stable and therefore less contributing.

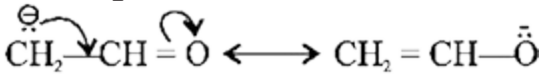
For example :



II is less stable than I, we can also think this way that charge separation considers electron affinity of C which is less negative and I.P. of Cl which is highly energy requiring process.

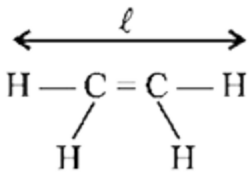
(f) Structures that carry a negative charge or more electronegative atom are more stable than those in which negative charge is on less electronegative element and positive charge is on more electronegative elements.

For example ;

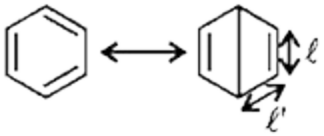


(g) Structures with distorted bond angle, bond length are unstable.

For example;



also,

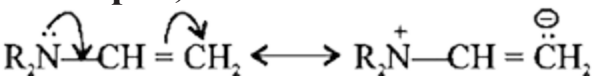


When $\ell \neq \ell'$ and ℓ is much bigger than which C–C bond length should be.

As we were discussing that resonance is not the same as mesomeric effect therefore let us see now that how they actually differ.

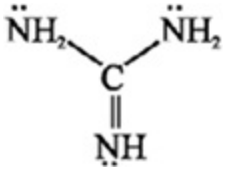
Mesomerism involves π -bond to operat but resonance does not always need to have n bond to occur.

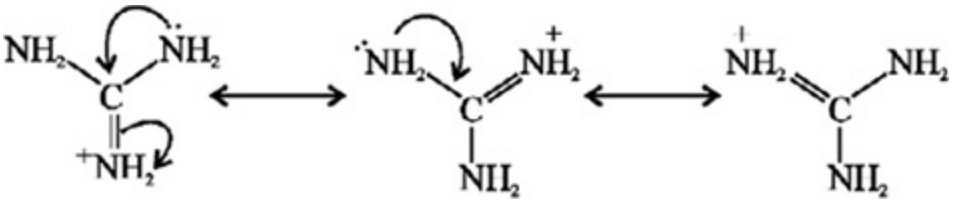
For example ;



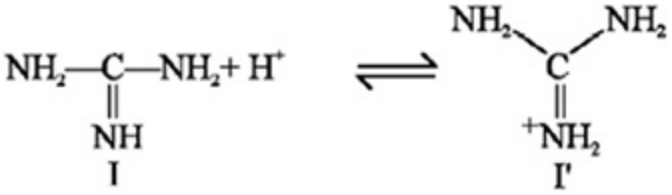
but $H-Cl \longleftrightarrow H^+ \ \ddot{C}l^-$ So, first example is due to resonance/mesomeric effect but second one is only the example of resonance. So, theoretically resonance involves all permanent displacement of electrons but mesomerism involves permanent displacement through π -bond. Therefore it is worth mentioning that resonance or mesomerism is polarisation (permanent) effect. Taking mesomeric or resonance effect in conjugated system along with electromeric effect is called as conjugative effect. In this book we have used the term resonance and the groups which take part in resonance by donating their lp electrons have been identified as +R groups and which accept the lp electrons in their vacant orbits are termed as –R groups.

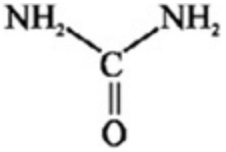
Application of resonance are lot many.

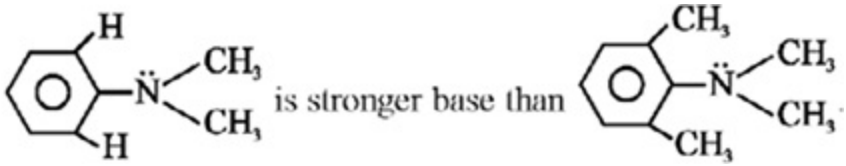
For example; (1)  is a very strong base. This is because of following resonating structures of the conjugate acid.



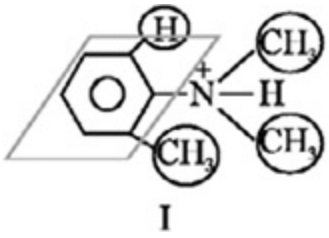
So, the above isovalent resonanting structures are also equivalent structures and by the rule 6(b) the hybride will be very stable.

Therefore in, 

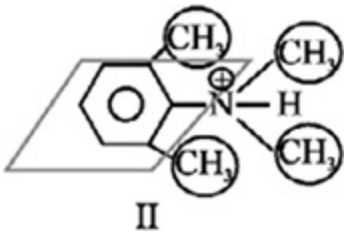
Conjugate acid I' is very stable than I. Hence I is a very strong base even stronger than (Explain on your own) 

(2) 

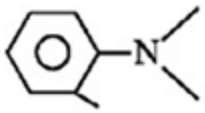
The answer again lies with the fact that steric inhibition of resonace occur in both the cases due to which lps are very much donable to protons but look at one stability of conjugate acids below.

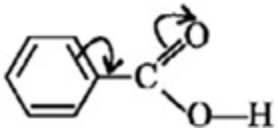
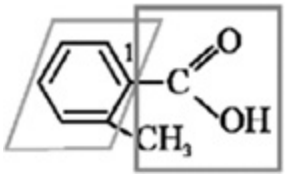


I

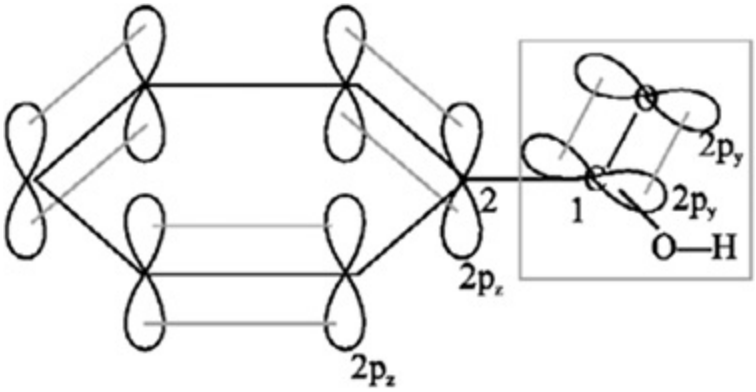


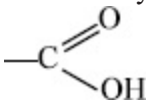
II

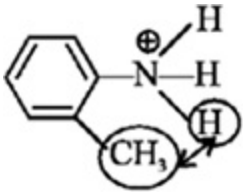
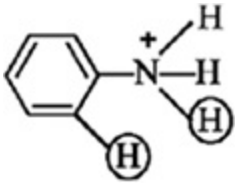
Steric repulsion is more in II than in I. Therefore base  is stronger. As we know the basic fact that more the stability of conugate acid, stronger is the base and more the stability of conjugate base stronger is the acid.

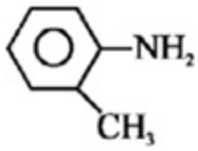
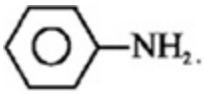
(3)  is weaker than  according to their acid strength.

This is due to, π -bond pair of benzene takes part in conjugation with C = O bond (π - σ - π) and thereby π -electron clouding takes place on carbon of –COOH and no more pulling of the sort $\overset{\delta'+}{C} \leftarrow O \leftarrow H$ takes place strongly as δ'^{+} is less. But in the second one $–CH_3$, –OH repels each other if they lie on the same plane and therefore actually $C^1 – C^2$ rotation takes place causing loss of planarity of CH_3, OH groups and as well as participating π bonding orbitals. See below;



So, as $2p_z$ cannot form n bond with $2p_y$ orbital, therefore no movement of n electron pair from benzene to  part. Therefore C of CO_2H is more partially positively charged and expected $—C \leftarrow O \leftarrow H$ pulling takes place and therefore more acidic strength. CH_3 has little effect. This above phenomenon is called as "ortho effect" and which is used to explain more acidic strength in case of o-substituted benzoic acids apart from polar effect of the groups (ie. +I, –I).

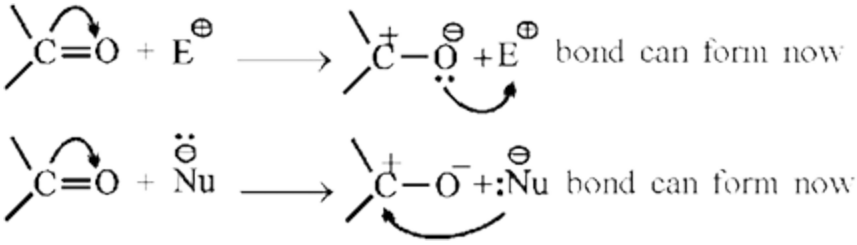
Likewise  is less stable than  due to steric repulsion between CH_3, H.

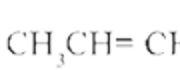
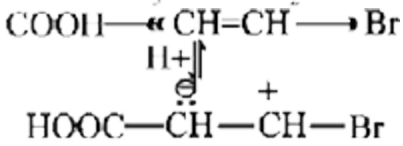
Therefore  is less basic than  .

This is called as the "ortho effect" applied to explain stability of conjugated acids of aniline derivatives. Therefore ortho effect is a base weakening effect.

(4) Electromeric effect (+E, – E) :

The temporary or time variable effect involving the complete transfers of shared π – electrons to one of the atoms joined by a multiple bond at the requirement of an attacking reagent is called as electromeric effect. As soon as the attacking reagent is removed the π – bond again forms. Therefore it is a temporary effect it can be shown as

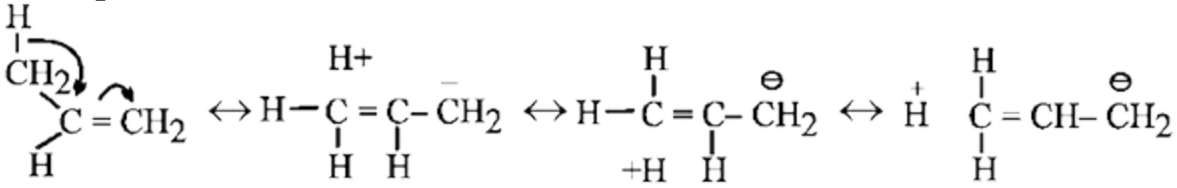


But in both the cases if we remove E^+ or $\ddot{N}u$ reformation of C = O π – bond takes place. It is to be understood that inductive effect acts in the same direction. e.g.  It may change also, for example, 

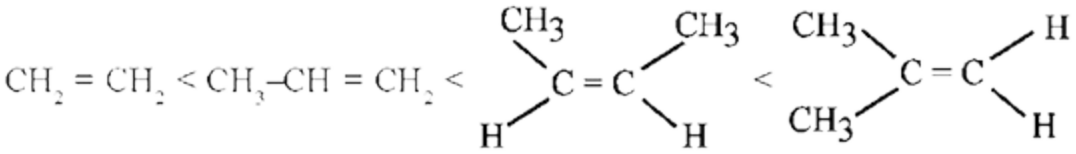
(5) Hyperconjugation :

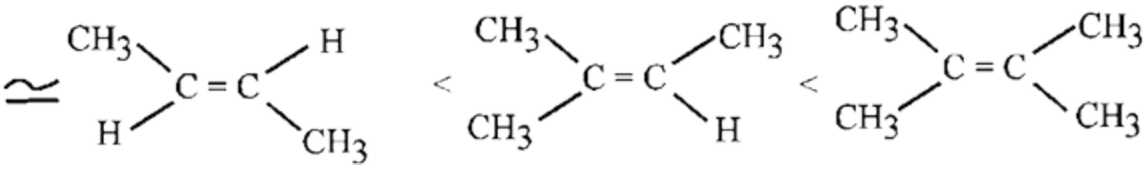
Conjugation involves the π – bond for delocalisation which brings stability to the system. Another type of stability called as hyperconjugation, which involves σ - bond pair electrons for the delocalisation (i.e. stability). C– H, C– X (X = Cl) σ - bond pair electrons generally involves into conjugation with π -bond or vacant orbital.

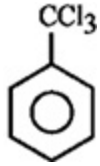
Example –

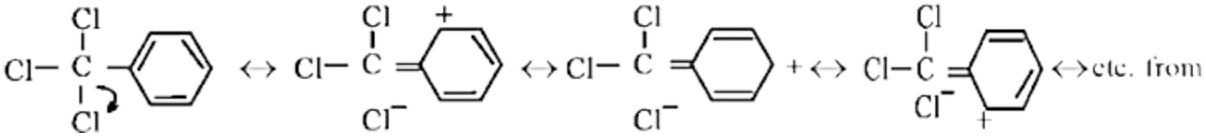


This is also called as no bond resonance, as when resonance or conjugation takes place then C– H does not have any bond. Therefore H atoms at α – C with respect to double bonded C is very important. Effect of hyperconjugation is mainly observed in the stability of alkenes.
For example ;

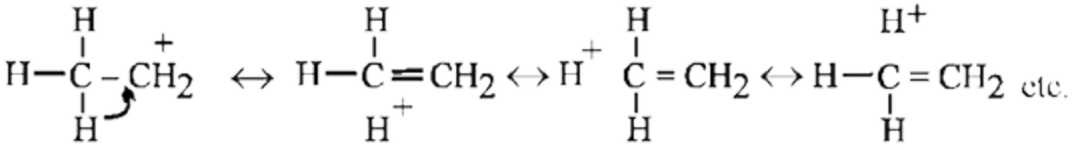




Therefore to speak about the stability of alkene, count only number of α –H atoms  ihows very slow ArSE reactions which is due to C– Cl σ - bond which takes part in hyperconjugation. For example-

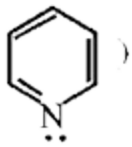


which we can easily observe that ⊖ charge comes into o, p positions w.r.t – CCl_3 group causing the incoming electrophiles attack with difficulty and also attack at meta position is not very much easy. Stability of alkyl carbocation and free radical also depends on hyperconjugation. It occurs in the following way;



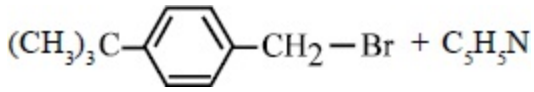
See, that too many no bond resonating structures are appearing and as we know more the resonating

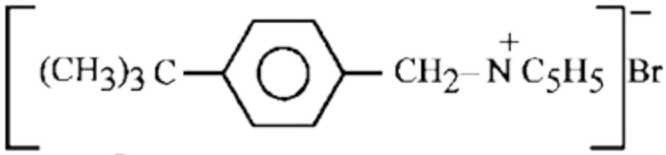
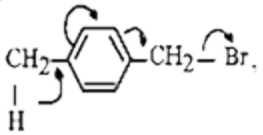
structures more the stability. Bond length of C^2– C^3 in $\overset{3}{C}H_3-\overset{2}{C}H=\overset{1}{C}H_2$ is less than C– C σ - bond length and the explanation is based on the double bond

character between $C_2 - C_3$ bond by hyperconjugation. Baker and Nathan found that the rate of reaction with pyridine  of p-substituted benzyl bromides and the result was opposite to the expectation.

It was found that



reaction rate as the fastest and 

 is the slowest. The reason being,  where CH_3 supplies electron cloud by hyperconjugation by which $Br^{\ominus}$ can easily leave the bromide when C_5H_5N attack. tert – butyl (group can only supply the electron cloud by +I effect and which is very small at p- position.

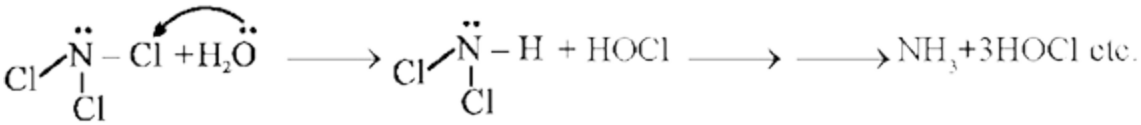
(6) Inductometric effect :

The electron distribution in a σ - bond may change by the approach of a charged species and thus partial polarisation occurs; the temporary effect, a polarisability effect and is known as inductometric effect.

For example, look at N– Cl bond which is non polar as N, Cl both have same electronegativity but it is found to hydrolyse as

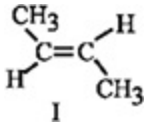
$$NCl_3 + H_2O \longrightarrow NH_3 + HOCl$$

To initiate hydrolysis, N–Cl bond polarises as $\overset{\delta-}{N}-\overset{\delta+}{Cl}$ by the approach of δ^- pole of H_2O molecule and which is the requirement.



But if we remove H2O, N–Cl σ - bond becomes again non- polar.

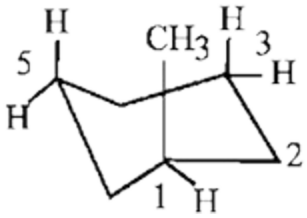
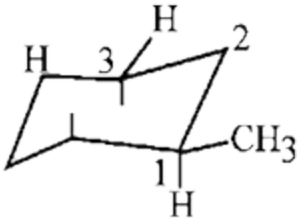
Steric effect :

This factor completely depends on the bulk or volume of the atoms or groups which can make a compound stable. For example,  is stabler than 

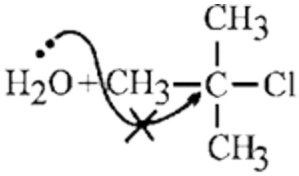
.This is due to repulsion

between two CH_3 –groups in the same side of the double bond (compound II). This factor can increase acid strength, basic strength, can make way to delocalise electron or restricts the delocalisation of electron etc., formation of p- substituted product in larger amount compared to o- substituted product are all the phenomena governed by steric effect.

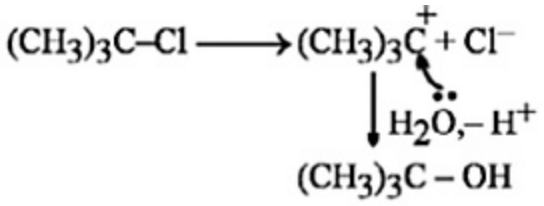
Examples :

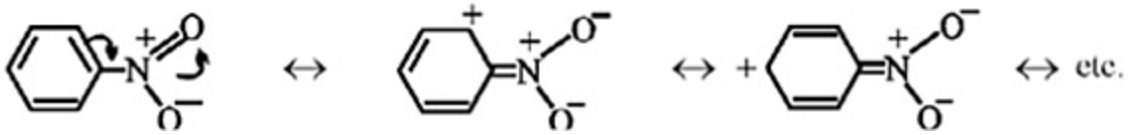
(1)  is less stable than 

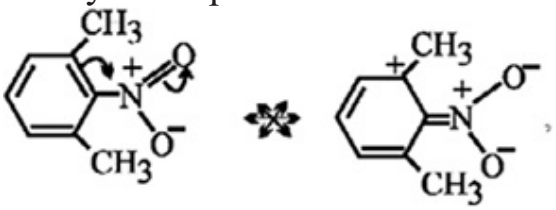
Here CH_3 at C_1 and H at C_3 (also H at C_5) face steric repulsion which is called as 1, 3 transannular strain and it is only due to bigger size of CH_3 which comes within the van der Wall's diameter of CH_3 & H.

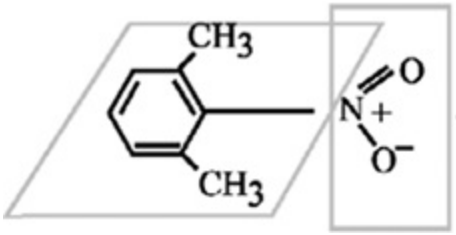
(2)  i.e. H_2O cannot attack due to bulky groups are surrounding

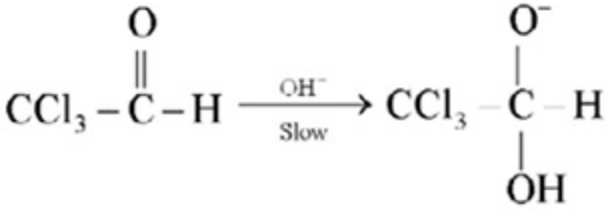
C–atom. Therefore reaction takes place through carbocation formation as shown below.

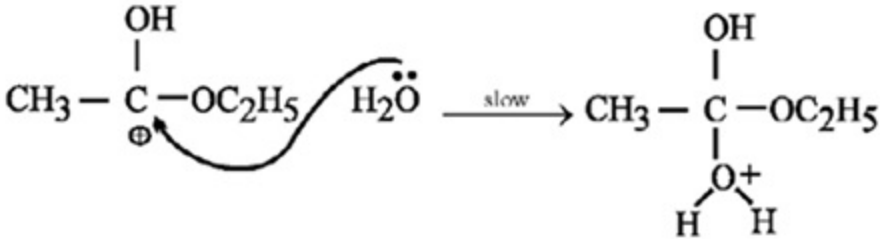


(3) 

Here π – bond pair of benzene ring can easily take part in resonance or conjugation with – NO_2 group, where as in 

resonance never takes place due to repulsion between CH_3 and O atoms of – NO_2 group which cause rotation around C– N σ - bond axis and therefore – NO_2 lies in the perpendicular plane to the plane of the benzene ring. See in the adjacent diagram  . This phenomenon is called as steric inhibition of resonance.

(4) 



The above reactions/mechanisms show that these are slow due to the steric crowding arising at the tetrahdral intermediates. Other applications we will see in foregoing sections.

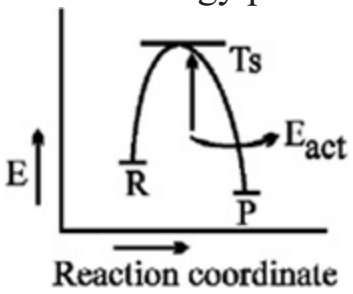
Concept of Transition State : For any reaction, $\begin{matrix} A-B+C-D \\ \downarrow \\ A-D+B-C \end{matrix}$

We consider the reaction occurs through a possible condition where rearrangement of atoms or groups take place and which will have threshold energy or minimum energy. This state is unstable and where bond making and bond breaking takes place. Above reaction can be written as,

$$A-B+C-D \rightarrow \begin{bmatrix} A & \cdots & D \\ \vdots & & \vdots \\ B & \cdots & C \end{bmatrix} \rightarrow \begin{matrix} A-D \\ + \\ B-C \end{matrix}$$

Any reaction always go through the condition where reactants loose individual identity and assume most unstable state. To go to the T.S.reactant needs to have minimum energy, which is called as E_{act} (i.e. activation energy). Between any two reactants or reactant and intermediates or between two intermediates T.S. must form.

The energy profile for the above process is

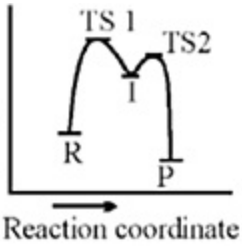


Concept of intermediates and different intermediates :

Intermediates are formed by breaking of bonds homolytically $(A \curvearrowright B \rightarrow A\bullet + B\bullet)$ or heterolytically $(R_3C \rightarrow R_3C^+ + X^-)$ etc. The species which is short lived, highly reactive but less energised than T.S. is called as an intermediate. Sometimes they can be isolated if relative stability is high. Take an example,

$$R_3C-\overset{\curvearrowright}{X} \longrightarrow \underset{I}{R_3C^+} + X^- \xrightarrow{\overset{\curvearrowleft}{:\!Nu}} R_3C-Nu$$

The energy profile is,



$\therefore$ TS1 is $R_3C^{\delta+}\cdots X^{\delta-}$, TS2 is $R_3C^{\delta\oplus}\cdots X^{\delta\ominus}$

$\therefore$ TS1 is $R_3C^{\delta+}\cdots X^{\delta-}$, TS2 is $R_3C^{\delta\oplus}\cdots X^{\delta\ominus}$

Carbocation (C+) or Carbenium ions : This is that species in which C atom has three bonds and having a positive charge and 6 electrons in its outer most shell. This has 2 electrons less than an octet.

Formation :

(1) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-X \longrightarrow CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}\oplus + X^-$ (X = Cl, Br, I)

(2) $CH_3-Br \overset{Ag^+}{\rightleftharpoons} CH_3^{\oplus} + AgBr\downarrow$, other than Ag^+ , Zn^{+2}, Hg^{+2} etc. also can take part in carbocation formation.

(3) $CH_3=CH_2 \xrightarrow{H^+} CH_3-\overset{+}{C}H_2$

(4) $CH_3-C\equiv N: \xrightarrow{ZnCl_2} CH_3-C\equiv \overset{+}{N}-\overset{\ominus}{Z}nCl_2 \leftrightarrow CH_3-\overset{+}{C}=N-\overset{\ominus}{Z}nCl_2$

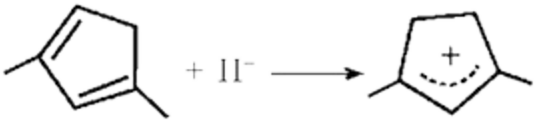
(5) $CH_3-\underset{\displaystyle O}{\overset{\displaystyle \|}{C}}-CH_3 + H^+ \longrightarrow CH_3-\underset{\displaystyle +O-H}{\overset{\displaystyle \|}{C}}-CH_3 \leftrightarrow CH_3-\underset{\displaystyle OH}{\overset{\displaystyle +}{\overset{|}{\underset{|}{C}}}}-CH_3$

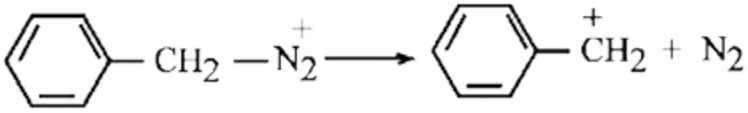
(6) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-\ddot{O}-H + H^+ \longrightarrow CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-\overset{+}{O}H_2 \xrightarrow{-H_2O} CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle +}{\overset{|}{\underset{|}{C}}}}-CH_3$

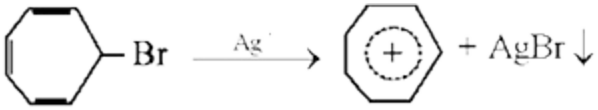
(7) $(CH_3)_2CHCl$ (or R– Cl) + $SbCl_5$ $\longrightarrow$ $\left[(CH_3)_2CH\right]\left[SbCl_6\right]$

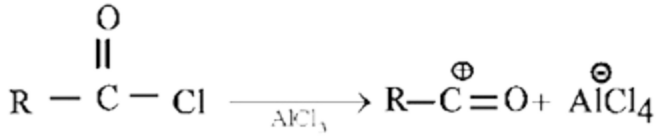
(8) $CH_3CH_2-N\equiv N^{+} \longrightarrow CH_3-\overset{\oplus}{C}H_2 + N_2$

(9) $CH_3-\underset{H}{CH}-\overset{\oplus}{C}H_2 \longrightarrow CH_3-\overset{+}{C}H-CH_3$ (By rearrangement or 1, 2 shift of $H^{\ominus}$ group).
(1°) (2°)

(10)  + H^-

(11) 

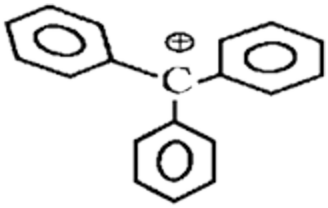
(12) 

(13) 

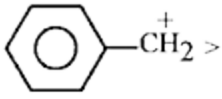
(14) $Ph_3C-Cl \longrightarrow Ph_3C^{+} + Cl^{-}$ etc.

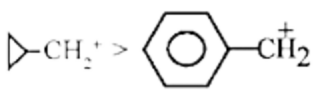
Structure and stability :

Structure has already been discussed. C^+ is sp^2 hybridised and shape is planar triangular. Ph_3C^+ is propeller shaped, though the central carbon and carbon atoms of three phenyl rings are connected to it in the same plane.



Experiment shows that stability order of carbocations is,

$(CH_3)_3\overset{+}{C} >$  $> (CH_3)_2\overset{+}{C}H > CH_2=CH-\overset{+}{C}H_2 > \overset{\oplus}{C}_2H_5 > CH_2=\overset{+}{C}H > \overset{+}{C}H_3$. Also,

it has been found that $(CH_3)_3C^+ > (CD_3)_3C^+$ and 

The above fact, can be explained on the basis that +I, hyperconjugation of 9-H atoms lead to tert –butyl cation more stable than benzylic cation. Although resonance dominates over inductive effect, hyperconjugation, individually but the experimental result is to given the importance. More +I groups and groups attached, which can take part in hyperconjugation to C+ or delocalises positive charge by resonance always bring stability to C+. Solvation to a large extent also stabilises cation. – I groups destabilises carbocation.

Carbanion $(\overset{\ominus}{C}:)$: These are negatively charged C atoms having three bond pairs and a lone pair of electrons which is $-\overset{|}{\underset{|}{C}}:^{\ominus}$

Formation, Stability :

(1) $CH_2 \rightarrow CH=O + \overset{\ominus}{O}H \rightleftharpoons \overset{\ominus}{C}H_2-CH=O \longleftrightarrow CH_2=CH-\overset{\ominus}{O}$

Carbanion + H_2O ; enolate ion

(2) $CO_2Et \leftarrow CH-CO_2Et \overset{\overset{\ominus}{:}OEt}{\rightleftharpoons} CO_2^{\ominus}Et-\overset{\ominus}{C}H-CH_2COOEt$

(3) $Ph_3C-Cl \xrightarrow[Na]{Na} Ph_3\overset{\ominus}{C}: + NaCl + Na^+$

(4) $R-C(=O)-\overset{\ominus}{O}: \xrightarrow{\Delta} \overset{\ominus}{R}: + CO_2$

(5) $Ar-\overset{O}{\overset{\|}{C}}-CH(H)-CH(Cl)-CH_3 \xrightarrow{\overset{\ominus}{:}OEt} Ar-\overset{\ominus}{C}(=O)-CH(Cl)-CH_3 \longleftrightarrow Ar-C(O^-)=CH-CH(Cl)-CH_3$

It occurs during E1CB reaction, which will be discussed later.

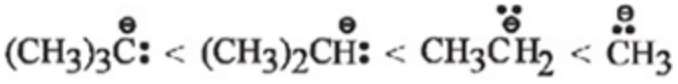
(8) $R-X \xrightarrow[Ether]{Mg} \overset{\ominus}{R}\ \overset{\oplus}{MgX}$

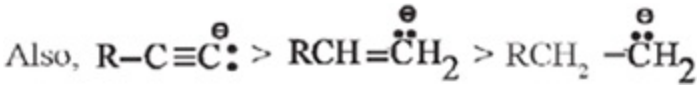
Also in $\overset{\ominus}{R}Li^{+}$, $\overset{\ominus}{R}_2Cd$, $\overset{\ominus}{R}_2CuLi$ alkyl groups(R) bear negative charge. Stability of carbanion occurs

due to the presence of – I, –R group at α - position. The functional groups which can stabilise from α - position and the order of stabilising carbanion are;



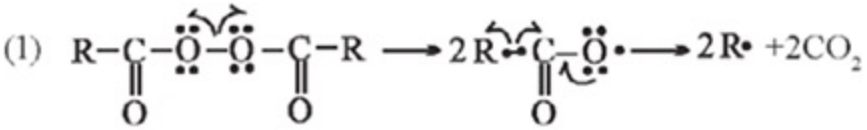
Similarly, + I group at α - position destabilises the carbanion. For example ;





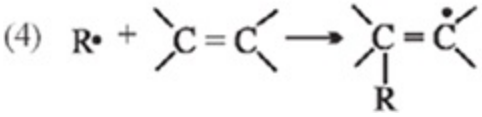
As electronegativity decreases negative charge holding capacity also decreases.

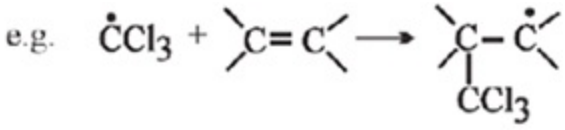
Free radical (alkyl, allyl, aryl etc.) formation, stability :

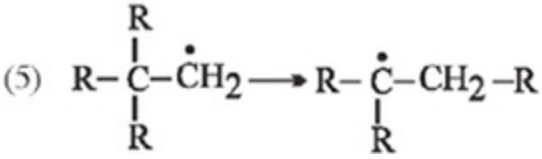








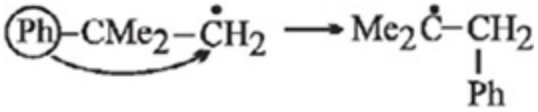




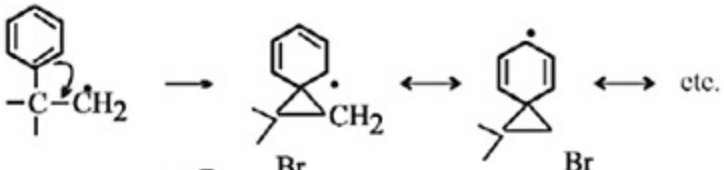
The rearrangement is not at all common as occured in carbocation. The above

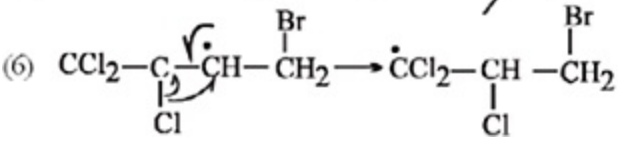
rearrangement take place when R ≠ alkyl or hydrogen. Aryl group migrates easily.

For example ;



and the migration of phenyl radical may be due to low energy requirement to attain T.S. The migration of phenyl radical can be shown as follows;





; Cl generally migrates but it is not easy for Br.

Migrating order in $RCMe_2\dot{C}H_2$, is R; $Me_3CCO >$ Ph . The rearrangements told above is always to

give more stable radical. Stability wise,

$$CH_2=CH-\dot{C}H_2 > H-\dot{C}=O > Ph\dot{C}H_2 > Me_3\dot{C} > Me_2\dot{C}H > Me_3C\dot{C}H_2 \simeq \dot{E}t \simeq \dot{M}e > CH_2=\dot{C}H > Ph\bullet$$

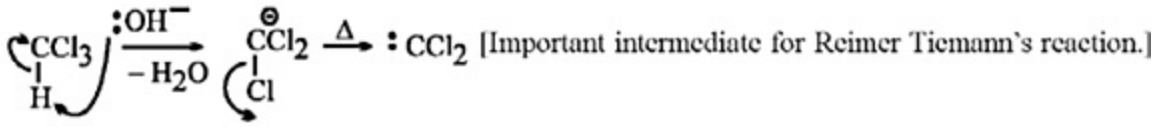
Less the bond energy to form the radical higher is the stability. From the above informations inductive, hyperconjugation, resonance all these can help stabilising the free radical. Therefore we should not forget to apply the above effects to explain the stability of free radical.

Carbene, Nitrene :

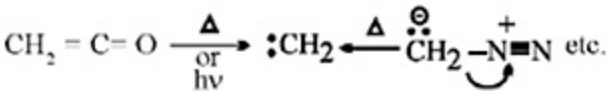
Carbene is basically electron deficient species in which C has two bonds and two electrons (may be paired or unpaired). For example, $:CH_2$, $:CCl_2$, $CH_2=C=C:$ etc.

Formation, Stability :

(1) $CCl_3-\overset{\overset{O}{\|}}{C}-O^{\ominus} \xrightarrow{\Delta} :CCl_2 + CO_2 + Cl^-$

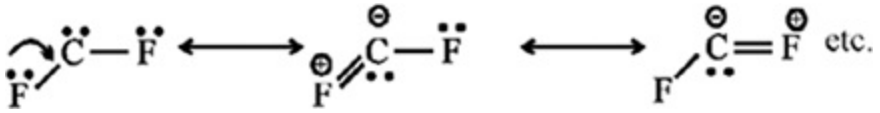
(2) 

[Important intermediate for Reimer Tiemann's reaction.]

(3) 

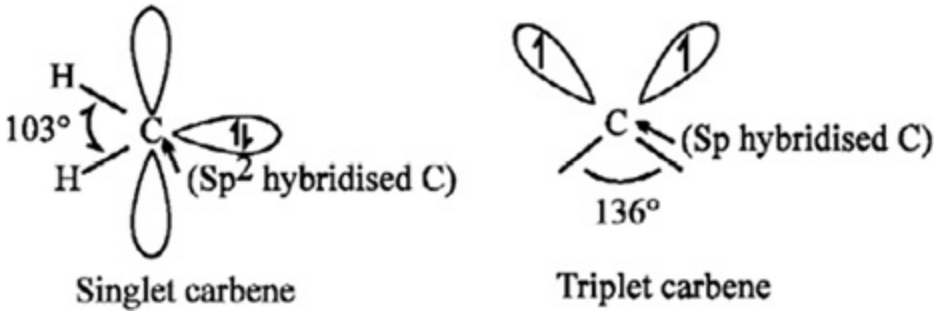
As carbene is electron deficient species therefore +I, +R groups can stabilise carbene to some extent. Carbenes are of two types.

(a) Singlet carbene : In this state electrons are paired up. Stability is less compared to the other variety < H- CH = 103° and it is bent shape. Stabilisation by σ - atom which can show +R effect as shown below can stabilise carbene.



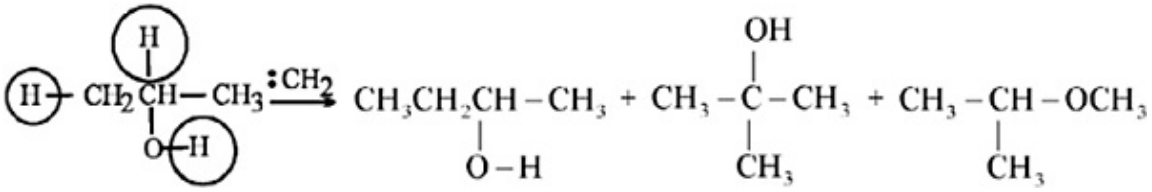
Triplet Carbene : It is relatively stabler and found in gas phase decomposition in presence of inert gas etc. This is more stable and it may be due to two electrons in two different orbitals. Carbenes have stability of less than a second.

Types of reactions for singlet carbene :



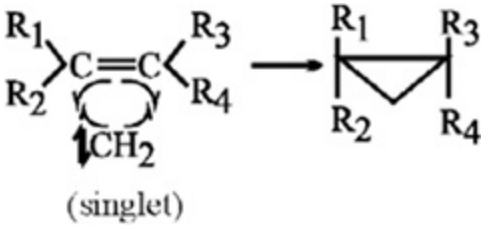
a) Insertion between C – H, O – H, C – Cl bond but not between C – C bond occur.

eg.

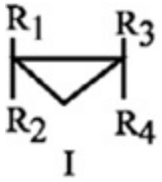
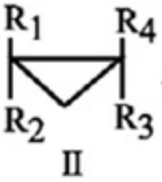


$:CCl_2$ does not show above kind of insertion reaction.

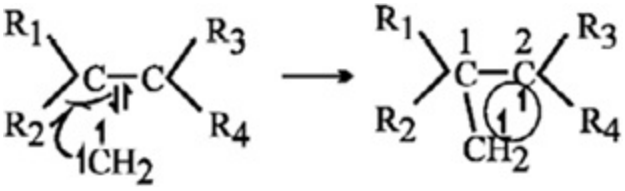
b) Addition between C– atoms in a double bond :



(singlet)

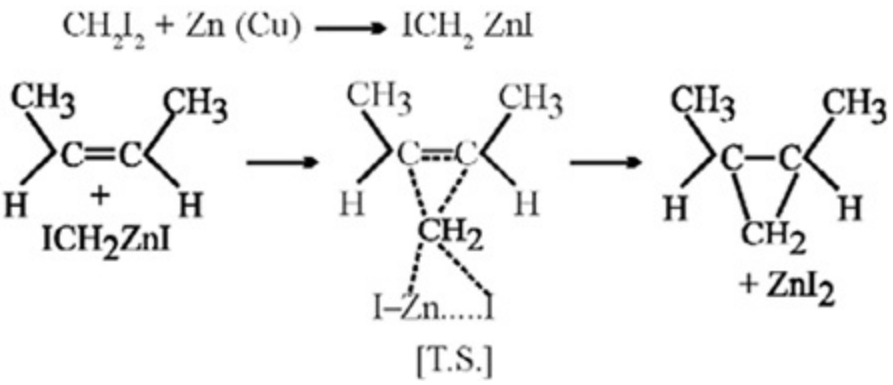
Note : Triplet give two products  ,  . If spin inversion takes place faster than the rotation w.r.t. C –C σ - bond axis then 1 form. But if spin inversion is slower than rotation with respect to C – C σ - bond axis then II form.

Look,

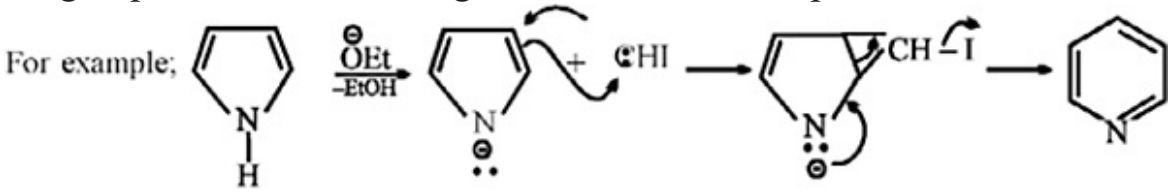


Two parallel spins as shown above can not make a bond. Spin inversion takes place at that temperature, simultaneously rotation with respect to $C^1 – C^2$ σ - bond axis can also take place. Therefore if spin inversion is faster then the product I forms and in case of slower rotation with respect to $C^1 – C^2$ σ - bond axis, product II results.

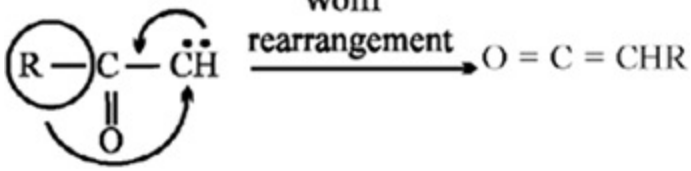
In Simmon Smith reaction not the free carbene but similar kind of species carbenoid form and the reaction is



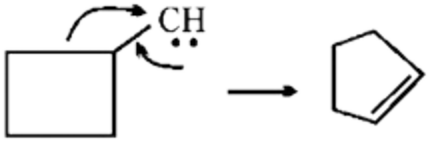
(c) Ring expansion and rearrangement also can take place as shown below.



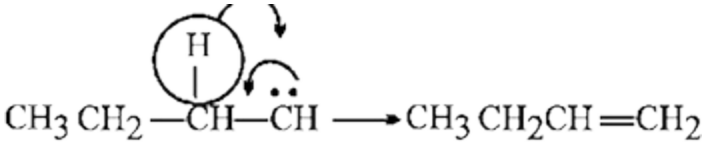
(2)



(3)

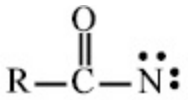


(4)

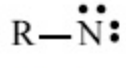


i.e. 1, 2 hydride shift takes place. Similarly alkyl group can migrate also.

Nitrene : A very short lived species similar to carbene is nitrene. These are,

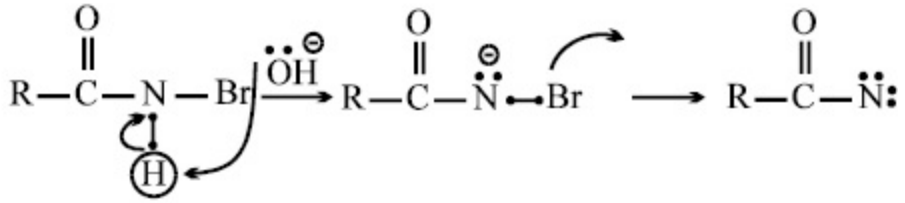


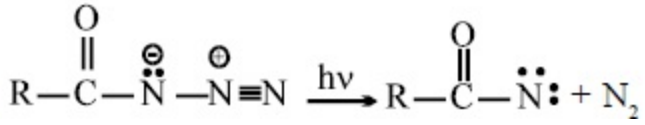
Acyl nitrene



Alkyl nitrene

Formation :

(i) 

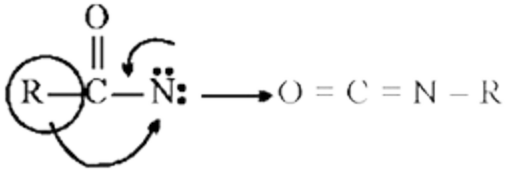
(ii) 

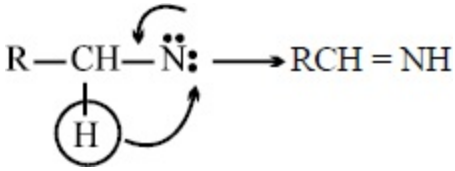
Between two types of nitrene triplet is stabler than singlet as we observed in case of carbene.

Types of reactions :

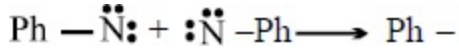
(1) Rearrangement reactions :

This is a very rapid step, therefore it is difficult to isolate nitrene.

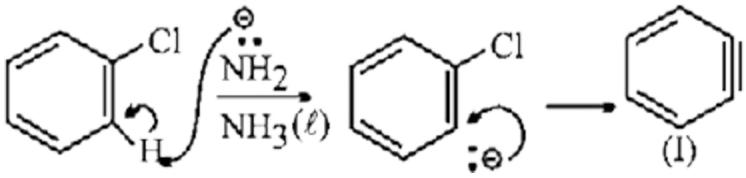
(a) 

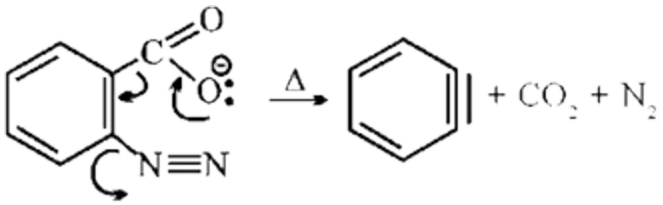
(b) 

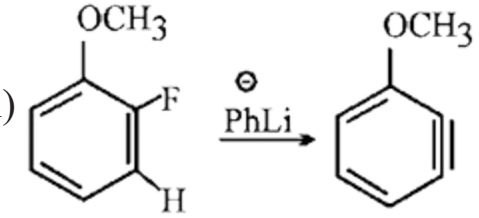
(2) Dimerisation :



Benzyne : This is basically 1, 2 dehydrobenzene (I). See below only the formation of benzyne and later on we will discuss the reaction of this unstable intermediate in aryl halide chapter.

(i) 

(ii) 

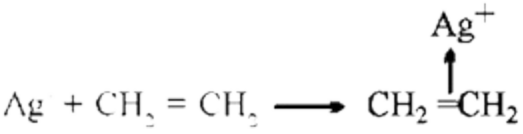
(iii) 

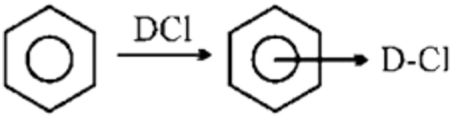
Mechanism of benzyne formation and reaction will be discussed in the aryl halide chapter.

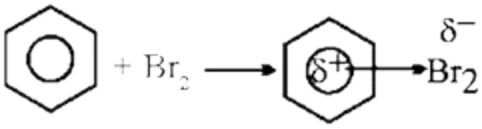
π - **Complex** : A weakly bonded charge transfer complex which exist in solution and formed by

π - electron pair participation with a polarising cation or electron deficient species.

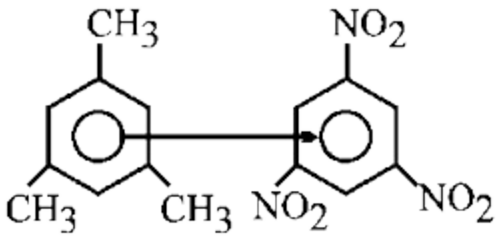
For example :

(1) 

(2) 

(3) 

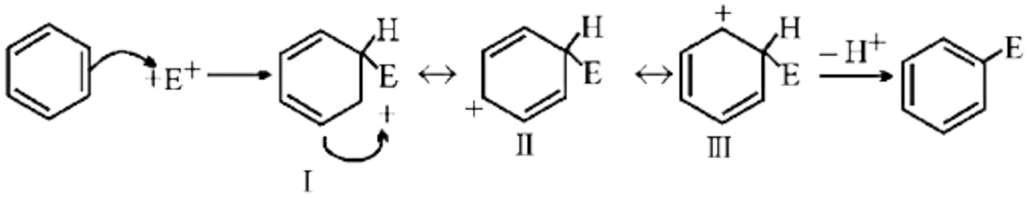
π - complex between two neutral species is non ionic (eg., 2, 3)

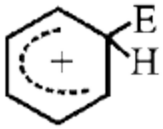


The above is a charge transfer complex, which is also a π – complex as

shown above. π – complex basically forms by the interaction of polarisable π – electron cloud and polarising species (a kind of soft acid, soft base interaction).

σ - **complex** : It is a stable intermediate and ionic in nature. It occurs when benzene reacts with electrophiles.

For example, 

Resonance hybrid of I, II, III is,  and it is called σ - complex.

Later on we will see how a σ - complex is stabilised in the chapter dealing with aromatic electrophilic substitution reactions.

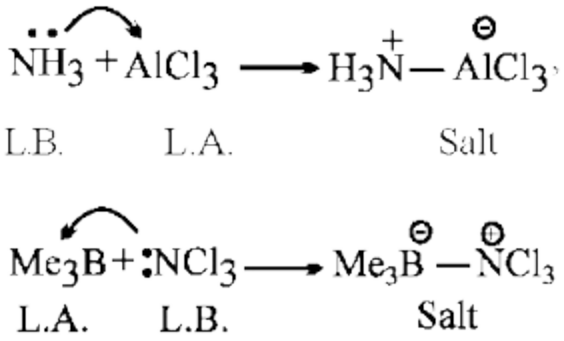
Acid strength and basic strength :

According to Arrhenius the acids are those which produce H^+ ion and bases are more which produce OH^- ion eg. $HCl \rightarrow H^+ + Cl^-$ and $NaOH \rightarrow Na^+ + OH^-$ are respectively acid and base. According to Bronsted, proton donors are acids and proton acceptors are bases. For example,

$NH_3 + HCl \rightarrow \overset{\oplus}{N}H_4 + \overset{-}{Cl}$; or, $HCl + H_2O \rightarrow H_3O^+ + Cl^-$

B–2 A–1 CA–2 CB–1 A-1 B-2 CA-2 CB-1

Where A= acid, CA = conjugate acid, B = base and CB = conjugate base According to Lewis, lp acceptors are acids and lp donors are bases. For example;



In organic chemistry, we mainly see the acidic behaviour of O – H, C– H,N – H bonds. Most important is that the acidity of C– H bond, by which we can join many C– atoms (as it shows excellent catenation property).

Measurement of acid strength :

$$HA \rightleftharpoons H^+ + A^- \; ; \; \therefore K_a = \frac{[H^+][A^-]}{[HA]}, \; \{\text{where } K_a = K \times [\text{solvent}]\}$$

measuring the $[H^+] = [A^-]$ and $[HA]$ = remaining undissociated acid concentration, we can have standard K_a values, for each acid. We also use another term pK_a which is $-\log K_a$. If K_a increases, stronger will be the acidic strength.

Measurement of base strength :

$$\ddot{B} + H_2O \text{ (or any solvent)} \rightleftharpoons \overset{+}{B}H + OH^-$$

$$\therefore K_b = \frac{[BH^+][OH^-]}{[B]}$$

More the $[OH^-]$ or extent of H^+ acceptance by $\ddot{B}$, stronger is the basic strength of B. Similarly sometimes, we use, $pK_b = -\log K_b$. K_b increase means pK_b is less i.e. basicity is higher. Thermodynamically, for any equilibrium reaction,

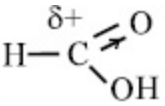
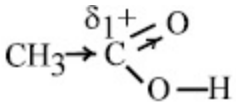
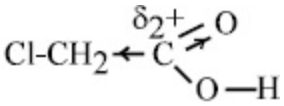
$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT\ \ell n\ K_a$ [or $= -RT\ \ell n\ K_b$ for base dissociation.]

$$\therefore\ K_a = \exp.\left(-\frac{\Delta H^\circ - T\Delta S^\circ}{RT}\right)$$

$$\text{or, } K_b = \exp.\left(-\frac{\Delta H^\circ - T\Delta S^\circ}{RT}\right)$$

We would discuss some approach to predict the acidic strength obeying the experimental results.

Case-1 : If we consider the acidic strength of $-C(=O)-O-H$ then we will observe how much $\delta+$ charge is accumulated on C of $-CO_2H$.

For example,   

I II III

CH_3 has +I effect which reduce $\delta\oplus$ produced by pulling of O from $C \rightleftharpoons O$ σ-bond. H does not have any I effect but $ClCH_2$ – will have – I effect. Moreover more the $\delta\oplus$ on C of $-C(=O)-O-H$ more pulling of the σ - bp of O – H towards O, and resulting more acidic strength. So, always focus on $\delta\oplus$ on C of $-C(=O)-O-H$

Look now,

Case – 1 (a) : $HCOOH > CH_3COOH > CH_3CH_2{-}COOH > CH_3{-}C(CH_3)_2{-}COOH$

pKa	3.75	4.76	4.9	5.0
		$\longrightarrow$ +I increases	rightward	

Case – 1 (b) : $F{\leftarrow}CH_2COOH > Cl{\leftarrow}CH_2COOH > Br{\leftarrow}CH_2COOH > I{\leftarrow}CH_2COOH$

pKa	2.70	2.90	2.90	3.40

⟶ –I decreases rightward

Case – 1 (c) : $Cl(CH_2)_3–COOH < CH_3\underset{Cl}{CH}–CH_2COOH < CH_3CH_2–\underset{Cl}{CH}–COOH$

pKa	4.50	4.00	29

⟶ δ ⊕ on C of $–CO_2H$ increases because Cl is coming closer to –COOH group

Case – 1 (d) : $ClCH_2 \leftarrow COOH < Cl_2CH \twoheadleftarrow COOH < Cl_3C \threeheadleftarrow COOH$

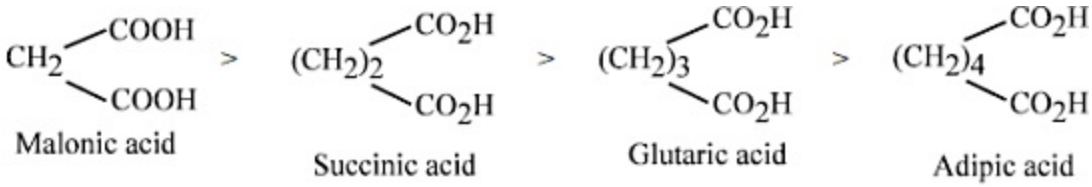
pKa	2.90	1.20	0.50

⟶ δ ⊕ on C of $–CO_2H$ increases because number of Cl atoms increase adjacent to –COOH group

Case – 2 : Stronger the base, stabler is the conjugate acid and therefore it will be a weaker acid.
For example,

	$\overset{+}{N}H_4$ >	$(CH_3)_3\overset{+}{N}H$ >	$CH_3\overset{+}{N}H_3$ >	$(CH_3)_2\overset{+}{N}H_2$
pKa	9.20	9.80	10.60	10.86

Case –3 : For dicarboxylic acids K_{a1}, is high when both the $–CO_2$ H groups are closer. For example,



Malonic acid > Succinic acid > Glutaric acid > Adipic acid

pK_1	2.90	4.25	4.30	4.50
pK_2	6.00	5.60	5.30	5.50

⟶ δ ⊕ on C reduces as –COOH (–I) goes away from each other

If we compare all pK_a values then we can conclude that more – I due to proximity of –COOH, stronger is the acidity. It is always observed that $pK_{a_1} < pK_{a_2}$ due to monoanion to dianion formation is difficultas $H_2A \rightleftharpoons H^+ + HA^-$ is easier, than $HA^{-1} \rightleftharpoons H^+ + A^{-2}$. This may be negative charge accumulation takes place on conjugate base (monoanion).

Case –4 : As the electronegativity of atom bonded to H increases, acidic strength increases

	$H_3C – H$	$H_2N – H$	$HO – H$	$F – H$
pK_a	48.5	38.2	15.7	3.3

Case – 5 : Weaker the overlap of the atoms halogen with 1s orbital of H, stronger is the acidity.

	HF	< HCl	< HBr	< HI
pK_a	32	–7.2	–9.1	–10.0

⟶ acidic strength increases in the right.

Also, $H_2O < H_2S < H_2Se$

pK_a	+15.7	+7.3	+4.5

⟶ acidic strength increases in the right.

Case –6 : Effect of hybridisation is also observed as we know $sp_{(c)}$ is the most electronegative and $sp^3{}_{(c)}$ is the least electronegative,

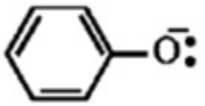
So,

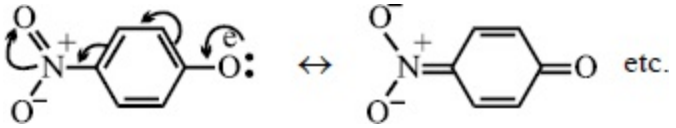
	$HC \equiv C \leftarrow H$	$H_2C = CH - H$	$CH_3 - CH_2 - H$
pK_a	25	44	50

Very strong pulling of C – H bp towards $sp_{(c)}$ due to high % s- character of C on C– H a -bond cause greater acidity of acetylene. **Case – 7 :** Among alcohols ;

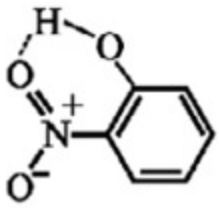
	$CH_3 \rightarrow O \rightarrow H >$	$CH_3CH_2 \twoheadrightarrow O \twoheadrightarrow H >$	$(CH_3)_2CH \twoheadrightarrow O \twoheadrightarrow H >$	$(CH_3)_2CH \twoheadrightarrow O \twoheadrightarrow H$
pK_a	15.4	15.9	16.8	17.8

⟶ More +I causes more shifting of σ-bp towards H, therefore less acidic strength is observed from left to right.

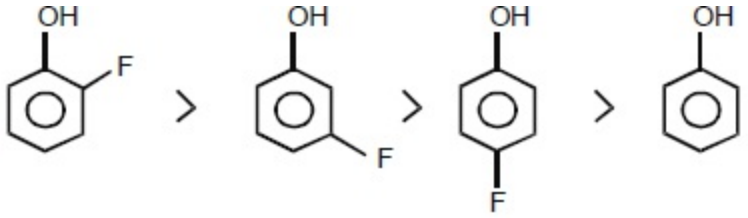
Case –8 : Among Phenols, only + I, – I effect operates for different groups, CH_3 by hyperconjugation reduces acidic strength as it put negative charge on C of C– OH bond by +I, hyperconjugation/ +R. We understand more δ + on C of C–OH bond, stronger will be the acidic strength. $–NO_2$ or other –I ,–R groups work in the same direction. Also they stabilise  by – R effect.

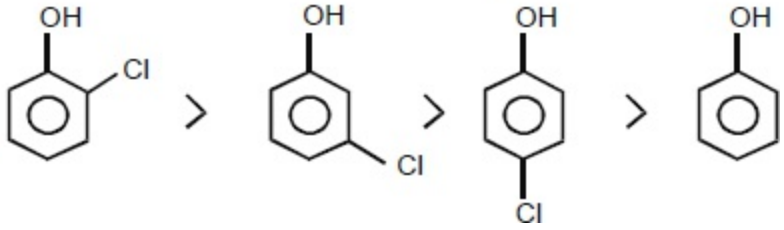
For example,  etc.

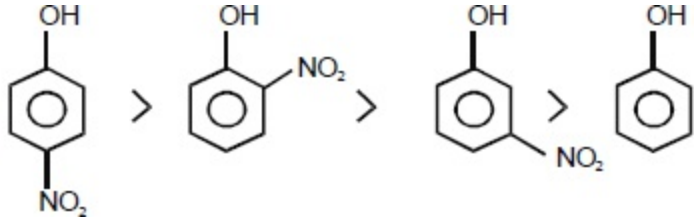
In o- nitro phenol, intramolecular H- bonding reduces its acidity as shown below ;

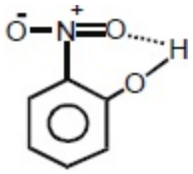


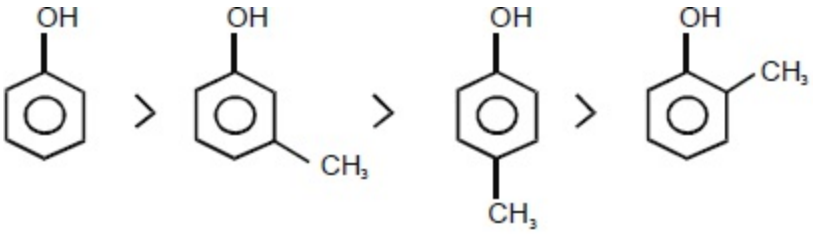
In case of acidic strength of phenols only –I effect of halogens play the roles in halophenols. For examples ;

(1) 

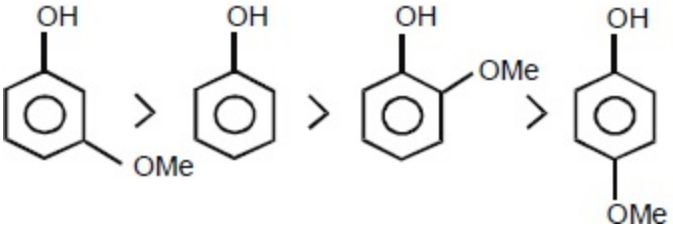
(2) 

(3) 

p > o is due to the fact that in ortho,  H-bonding takes place intramolecularly, therefore it reduces acidity. For, para – R effect of $–NO_2$ in nitro phenoxide ion stablises the conjugate base by extensive resonance. Quite obviously –I effect of NO_2 at meta will increase acidity compared to phenol. Similarly +R, +I and groups which show hyperconjugation reduce the acidic strength of phenol derivatives. For examples;



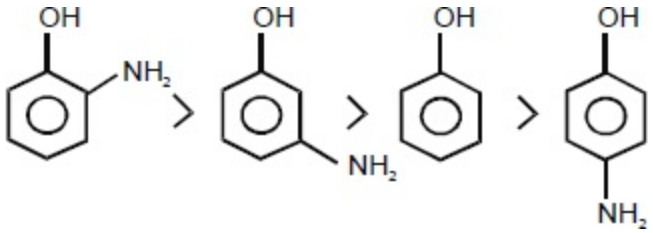
(pKa = 10.32)



Here –OMe shows + R > – I effect from o, p positions therefore less acidic but from meta position it shows only –I effect which increases acidity.

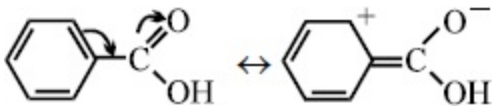
Astonishingly $–NH_2$ only shows –I effect from o, m but +R from para not to a large extent.

Therefore,

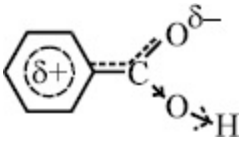


Case –9 : Among aromatic carboxylic acids, we must take care of ortho effect, which cause stronger acidity irrespective of the polar nature of the group when it is at ortho position with respect to –COOH.

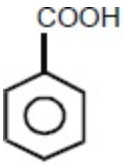
What happens in benzoic acid is



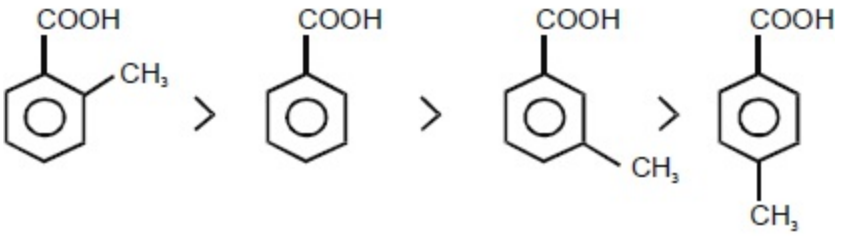
Due to the above resonating structures C becomes π - electron clouded as we can show the resonance hybrid as

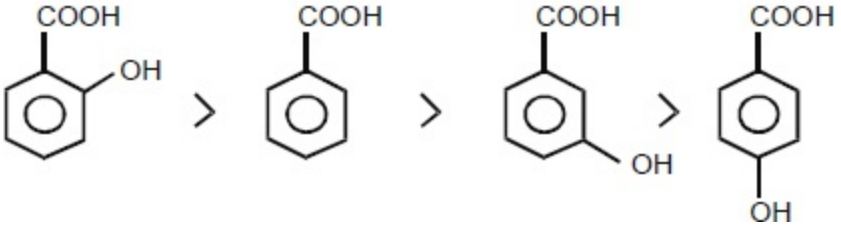


It means O does not pull σ - bp from hydrogen and therefore less acidity is observed. But when any group at ortho to – COOH come, then due to rotation with respect to C – C σ - bond – CO_2H loose planarity with the plane of benzene ring. Resonance cuts off from benzene to –COOH, therefore stronger acidity is observed.Let us look at following examples and reasoning;



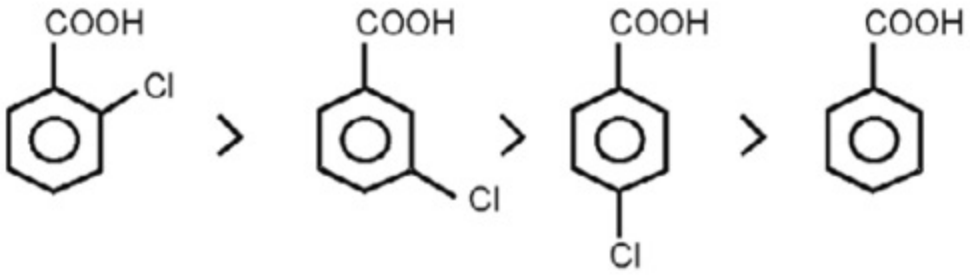
pKa = 4.2



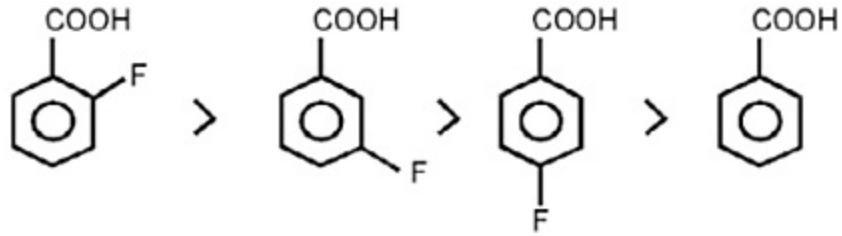


The reason being that CH_3 has +I, hyperconjugation effect and which can act from ortho, para to reduce δ + on COOH very strongly. But due to ortho effect, ortho methyl bengic acid is stronge than bengoic acid. m > p is also due to the same reason mentioned above. Similar situation arises for salicylic acid (i.e., ortho effect) and p < m due to the +R effect of –OH group which increases –ive charge with in benzene ring.

If we look at haloacids,

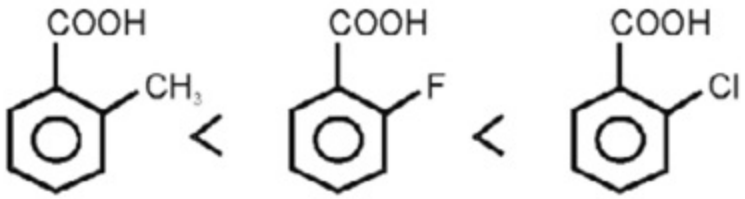


as well as,



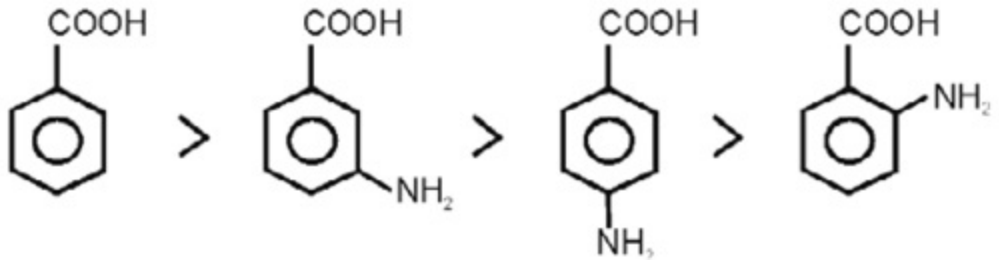
Here in all cases – I > +R effect of halogen determines the acidic strength

order. If the compare the followings

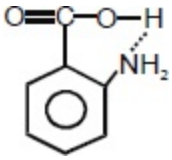


Due to larger size of Cl and as well as CH_3 group increases electron density in the benzene ring along with inductive effect are the reasons for the above order.

Example :



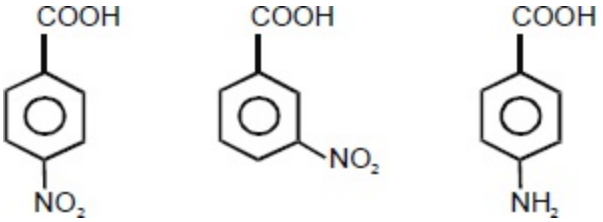
Explain the above order.

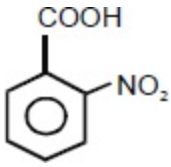
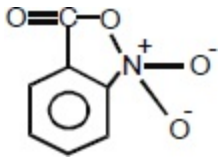
Solution : This may be due to the possible H-bonding 

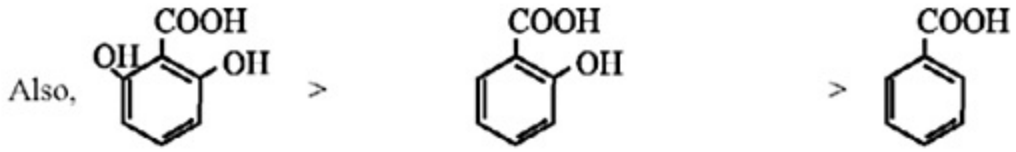
which suppresses the acidic character of H of COOH group and rest can be explained on the basis of +R effect of $-NH_2$ group, which increases electron density in the benzene ring.

Unsolved example :

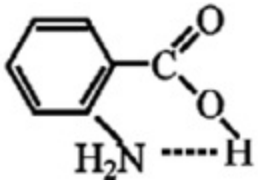
Explain the acidic strength order of the followings.



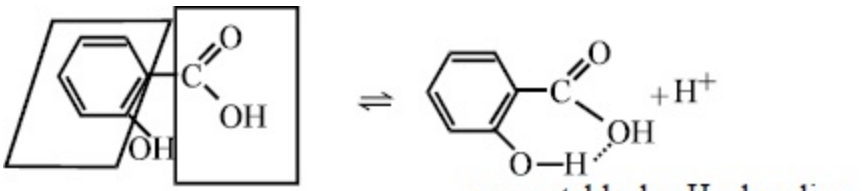
2. Do you think that  is stronger acid due to  formation when it converts to its conjugate base ?



The electron withdrawing groups at ortho always increase the acidic strength compared to the +I groups present at ortho position. Again we must consider that $\delta+$ reduce due to +I group at closer position. (Look at ortho- Me, ortho – NO_2/F/Cl/OH/OMe etc. follow the above explanation excepting $-NH_2$, where may be possibly H- bonding takes place, which reduces acidic strength, as shown below, otherwise – NH_2 should have behaved like other groups i.e. OH, OMe etc.



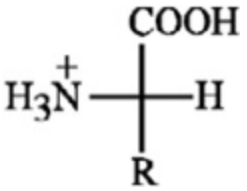
For o- hydroxy benzoic acid intramolecular H- bonding stabilise the conjugate base anion, as shown below;

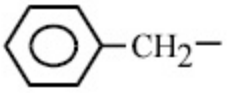
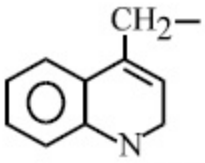
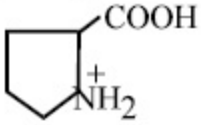


very stable by H– bonding,
6-membered ring formation.

Therefore coupled with the fact – I of OH groups and H- bonding increase acidic strength considerably.

Case – 10 : Amino acids in its conjugate acid form show acidic strength from its two sites. One is COOH groups and another is $-\overset{+}{N}H_3$. Let us look at the

acidic strength of two groups by the following table 

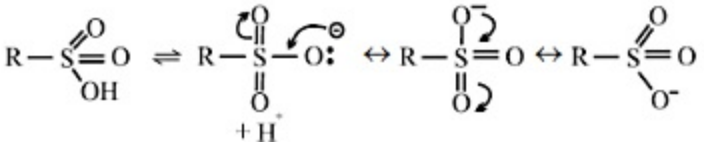
R	Name	pKa_1	pKa_2	pKa_2	pI
H–	Glycine	2.3	9.6		6
CH_3–	Alanine	2.3	9.7		6
$(CH_3)_2CHCH_2$–	Leucine	2.4	9.6		6
	Phenyl alanine	1.8 (Rise due to –I of phenyl)	9.1		5.5
	Tryptophan	2.4	9.4		5.9
 (Complete structure)	Proline	2.0	10.6		6.3

$CH_2(OH)-CH(NH_3^+)-COOH$	Serine	2.2	9.2		5.7
$CH_2(SH)-CH(NH_3^+)-COOH$	Cysteine	1.7	10.8	8.3	5.0
$NH_3^+-(CH_2)_4-CH(+NH_3)-COOH$		2.2	9.0	10.5	9.8

(Dicationic form of lysine)

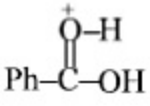
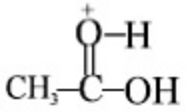
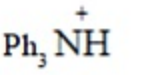
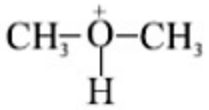
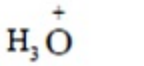
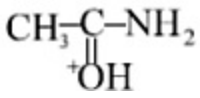
So everywhere we observe that – COOH is stronger acidic than – $\overset{+}{N}H_3$ group.

Case- 11 : SO_3H group also shows stronger acidity compared to – COOH due to the resonance stabilisation as shown below,



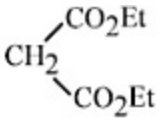
i.e. 3- resonating structures of conjugate base make the acid stronger. More the stability of CB stronger is the acid.

Case – 12: Protonated species also show acidity.

Acid	pK_a	Acid	pK_a
	– 7.1		– 6.7
	– 4.9		– 3.6
	– 1.8		– 0.8

Therefore from the pK_a values we can arrange the above protonated bases in the increasing order of acidic strength.

For more informations the increasing order of acidic strength is given as follows ;

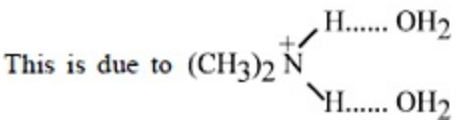
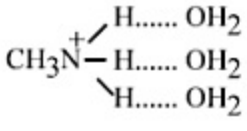
$HF > H_2S > PhSH > PhOH > CH_3SH > CH_2(CN)_2 > CH_3COCH_2CO_2Et >$  > 

$\approx CH_3CH_2CHO > CH_3COOC_2H_5$ ($pK_a = 24.7$)

Basic Strength :

We understand when $\ddot{N}:$ donates the ℓp . So more +I groups attached to N, more donability of N ℓp , therefore more basic strength is observed. Therefore $(CH_3)_3N > (CH_3)_2NH > CH_3CH_2NH_2 > CH_3NH_2 > NH_3$ is the basic strength order of amines in gas phase. But in aqueous solution, hydration of conjugate acids non-substituted/substituted ammonium ions play an important role in the basic strength order is as follows ;

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

This is due to  .  formation, where very good solvation by H_2O molecules take place. Whereas in case of 3°, $(CH_3)_3\overset{+}{N}-H.....OH_2$ solvation is very less. Also 2° > 1° because of more +I groups make ℓp of N available to proton.NH_3 dose not have any group which has +I effect. Therefore it is least basic.

Here we will consider K_b or pK_b or pK_a of conjugate acids. K_b increase means pK_b decrease which means pK_a(conjugate acid) increase and all these mean basic strength to be more.

For example,

$$NH_3 + H_2O \overset{K_b}{\rightleftharpoons} \overset{+}{N}H_4 + OH^-$$

$$\overset{+}{N}H_4 + H_2O \overset{K_a}{\rightleftharpoons} NH_4OH + H^+$$

$K_aK_b = K_w$ or $pK_a + pK_b = pK_w$ or, $pK_a = pK_w - pK_b$

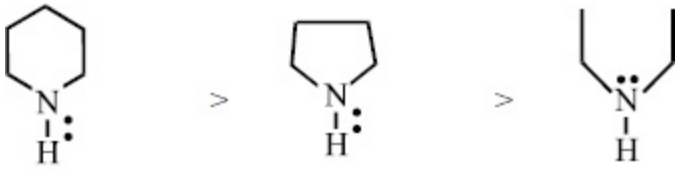
$\therefore$ pK_b decrease means pKa of conjugate acids of the corresponding bases increase.

Case – 1: Aliphatic amines thus have been discussed above. Also, $(CH_3CH_2)_3N > (CH_3)_3N$ due to +I effect of the alkyl groups.

Case –2 : More is the electronegativity less the basicity.

$CH_3CH_2\ddot{N}H_2 > CH_3CH=\ddot{N}H > CH_3-C\equiv N:$

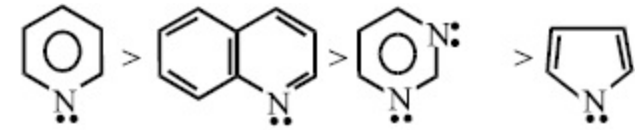
Case – 3 : Basicity of heterocyclic amines which are no π - aromatic are almost same as that of acyclic aliphatic amines. According to their decreasing pK_a values the following bases can be arranged as follows;



I > II > III

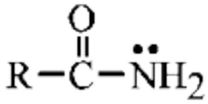
I > III may be due to statistical availability of lp which is less due to pyramidal inversion of amines towards external proton.

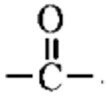
Case – 4: Heterocyclic aromatic amines are far more weaker bases than heterocyclic nonaromatic amines, NH_3. According to their decreasing pK_a values the following bases can be arranged as follows;

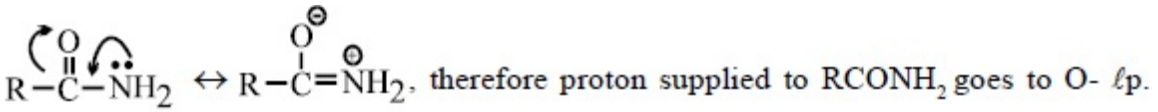


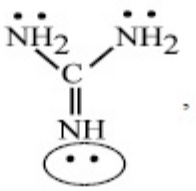
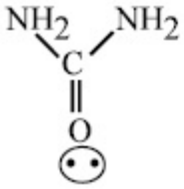
Pyridine > Quinoline > Pyrimidine > Pyrrole

In the gas phase however, pyridine, pyrrole are more basic than NH_3 . Pyridine is more basic than pyrrole is due to the participation of N ℓp of pyrrole into aromaticity[(4n + 2) nelectron rule given by Hückel **].**

Case- 5 :  is less basic than NH_3 due to of N resonates with

 For example

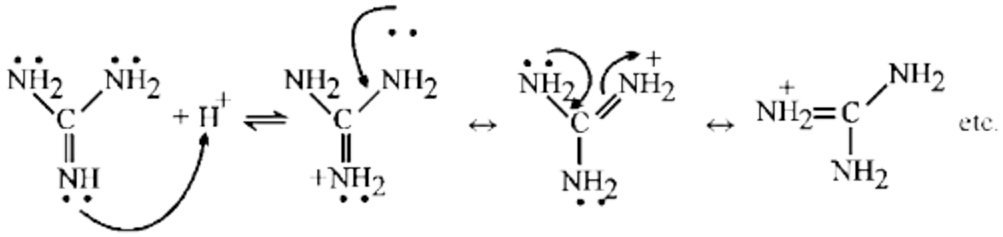


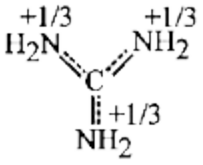
In  , 

Guanidine Urea

sp^2 N, sp^2 O ℓp (marked) accept the proton so that they can give very stable conjugate acids by resonance.

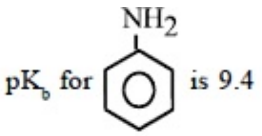
For example -



So, resonance hybrid of the above structures of the conjugate acid is 

It has been found that guanidine is the strongest organic base.

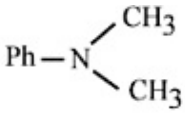
Case – 6: For aromatic amines i.e. aniline and its derivatives ortho effect operate in their conjugate acids irrespecitve of their polar effect. van der Waal's repulsion cause less stability of the conjugate acids and therefore less basic are their counterparts.

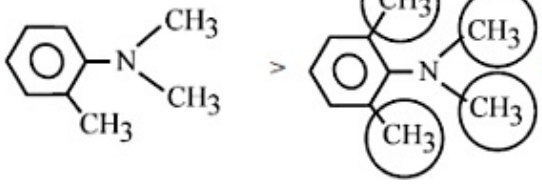


Substituents	pK_b		
	o	m	p
NH_2	7.8	9	9.5
OCH_3	8.7	9.7	9.5
CH_3	8.9	9.3	9.6
Cl	10	10.5	11
NO_2	13.1	11.5	4

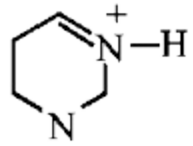
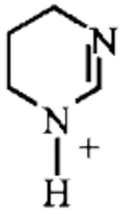
Therefore from all aspects considering ortho effect, – I, + I, hyperconjugation (in case of CH_3), resonance (+R, – R), we conclude that more the δΘ on C of C – N bond, more the basicity.

Case- 7 : Steric inhibition of resonance sometimes causes more basicity. Basic strength order :

(i)  > $PhNHCH_3$ > $PhNH_2$

(ii)  Here the repulsion between the methyl groups

cause large steric inhibition of resonance, therefore $\ddot{N}$ ℓp doesnot go inside the benzene ring. So both donate the lp to the proton easily. In the conjugate acid of II the number of repelling methyl groups is more compare to that of the conjugate acid of I. Thus the basicity order is I > II. To conclude acid strength and basic strength first look at all aspects of the acid and base molecules and after that consider the stability of conjugate base (may be by inductive, resonance etc. e.g. $RCOO^-$) for the acid and stability of the conjugate acid for the base (may be by inductive, resonance etc. e.g.;

 is less stable than  and in solution also consider the solvation of the (acid, conjugate base) and (base, conjugate acid pairs respectively).

Kinetics & thermodynamics of a reaction .

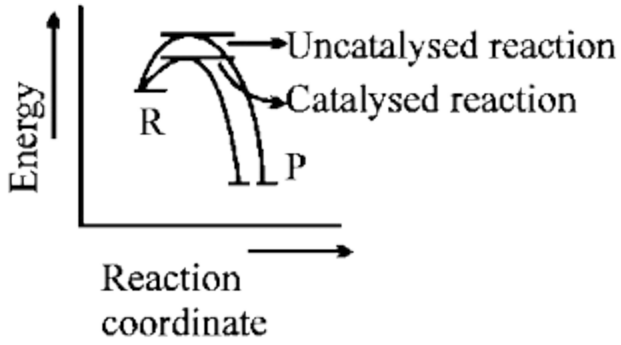
To understand the mechanism of reaction study of kinetics is very important. For a reaction mA + mB $\rightarrow$ xP , we can measure the rate of reaction as $-\frac{1}{m}\frac{d[A]}{dt} = -\frac{1}{n}\frac{d[B]}{dt} = \frac{1}{x}d\frac{[P]}{dt}$ and the expression can be written as, $-\frac{1}{m}\frac{d[A]}{dt} = -\frac{1}{n}\frac{d[B]}{dt} = +\frac{1}{x}d\frac{[P]}{dt} = K[A]^{\alpha}[B]^{\beta}$

where α, β are the order with respect to A, B and $(\alpha + \beta)$ is the overall order of the reaction. There is another term called molecularity. This is the number of molecules or species involved in the slowest (or rate determining step i.e. rds) step in a multistep rection. This is a theoritical prediction considered to satisfy the experimental fact and it cannot be fraction or negative. It is always an integer unlike the order a, b which are experimental quantities and may be fraction, integer , –ive , + ive.

Above, we defined k = rate constant =A. $e^{-Ea/RT}$

Where, A = Arrehenius constant, E_a = activation energy, R = universal gas constant, T = temp. in absolute scale. The above equation is called Arrhenius equation.

Also, we must know that in presence of a catalyst a reaction always take place faster due to reduction of the E_a (activation energy)



Mechanism of a reaction is explained by (a) collision theory, which is two or more molecules may collide to give activated species and then they decompose into the products.

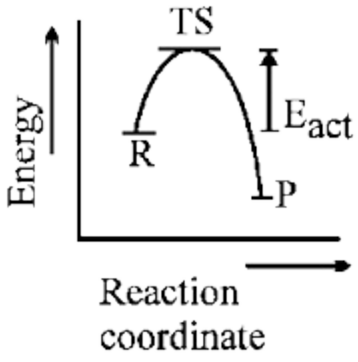
e.g.
$$\begin{array}{ccccc} A & A & A.....A & & A_2 \\ | & | & | \quad\quad | & & + \\ B & B & B.....B & & B_2 \\ \rightarrow & & \leftarrow & & \end{array}$$
(Activated state)

(b) Transition state theory : It states that gradual change of reactants into products via a very unstable state called as transition state.

$$A - B + C - D \rightarrow \begin{bmatrix} A & \cdots & D \\ \vdots & & \vdots \\ B & \cdots & C \end{bmatrix} \rightarrow A - D + B - C$$

T.S.

Energy profile is :



The discussion of these theories is beyond the scope of this book. To understand whether a reaction will occur spontaneously or not, we calculate Δ G (i.e. Gibb's free Energy) which is (Δ H – T Δ S). If Δ G is negative then the reaction is feasible. Here Δ H = change in enthalpy ,
Δ S = change in entropy, T = temperature(K).

At equilibrium,

$\Delta G = 0 = \Delta G^\circ + RT \ell n\, K_{eq}$.

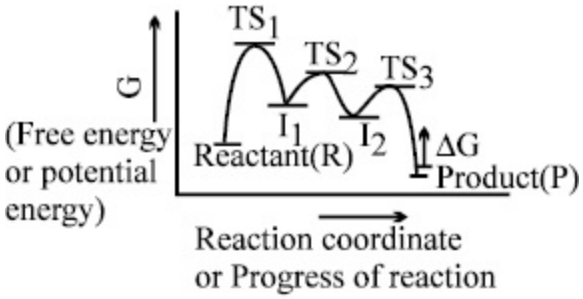
$\therefore\ \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT\ \ell n\, K_{eq}$

From the above equation we can measure K_{eq}. Also, we must remember that

K_{eq} is a function of temperature in absolute scale. The temperature dependence of K_{eq} can be mathematically expressed by van't Hoff's equation which is,

$$\ell n\left(\frac{K_2}{K_1}\right) = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Lastly, energy profile for a reaction having intermediates and transition states is shown as follows;



(I_1, I_2 are the instermediates)

We can also plot enthalpy or internal energy along the ordinate and reaction coordinate along abscissae.

Application of thermodynamics and kinetics :

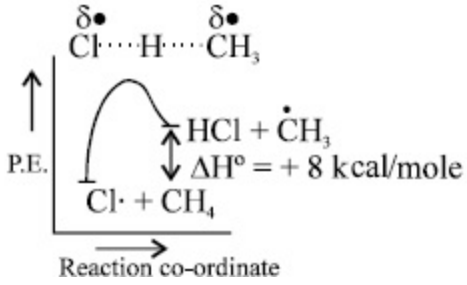
To understand the rds/slowest step the E_{act} (i.e. activation energy values) here to be observed. By the following ways we can find out activation energies.

(1) When bonds are broken then it will have Eact > 0.

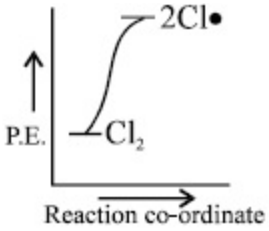
(2) Activation energies of endothermic reactions that involve both bond formation and bond rupture will be greater than the heat of reaction **A**H°.

eg., $Cl\cdot + CH_4 \longrightarrow \dot{C}H_3 + HCl$; $\Delta H^\circ = 2$ kcal/mole but $E_{act} = +4$ kcal/mole

$Br\cdot + CH_4 \longrightarrow HBr + \dot{C}H_3$; $\Delta H^\circ = 18$ kcal/mole but $E_{act} = +18$ kcal/mole



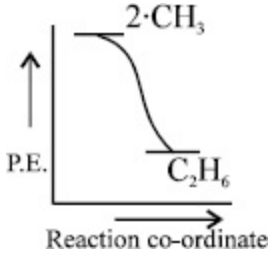
3. The energy of activation of a gas phase reaction where bonds are broken homolytically but no bonds are formed, is equal to Δ H°.



eg., $Cl \longrightarrow 2Cl\cdot$ $\Delta H^\circ = E_{act} = +68$ kcal/mole ;

4. The energy of activation for a gas phase reaction in which small radicals combine to form molecules is zero.

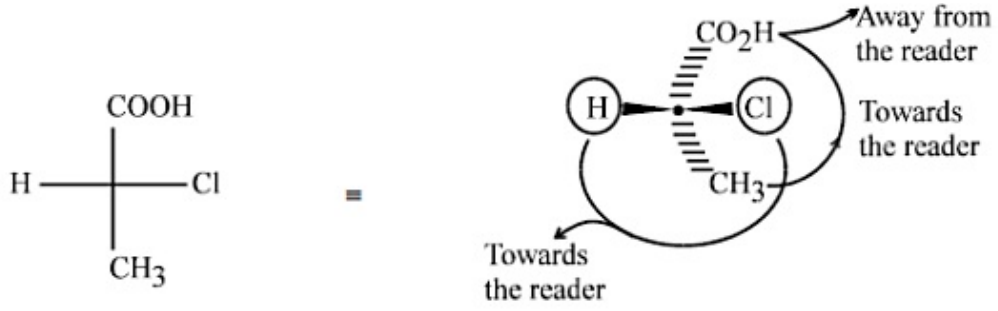
$2CH_3\cdot \longrightarrow C_2H_6$; $\Delta H^\circ = -92$ kcal/mole ; $E_{act} = 0$ kcal/mole



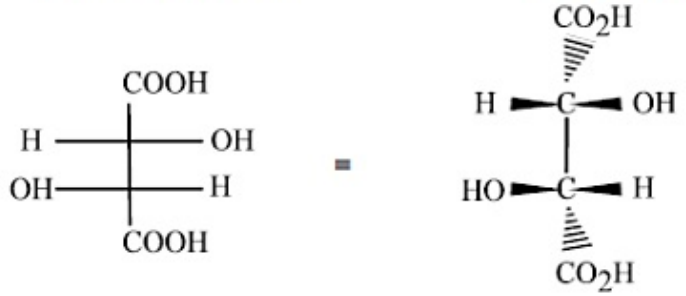
Projection formulae : (Fischer's , Flying Wedge, Wedge-dash, bond line, Sawhorse, Newmann's & interconvertibility of the projections):

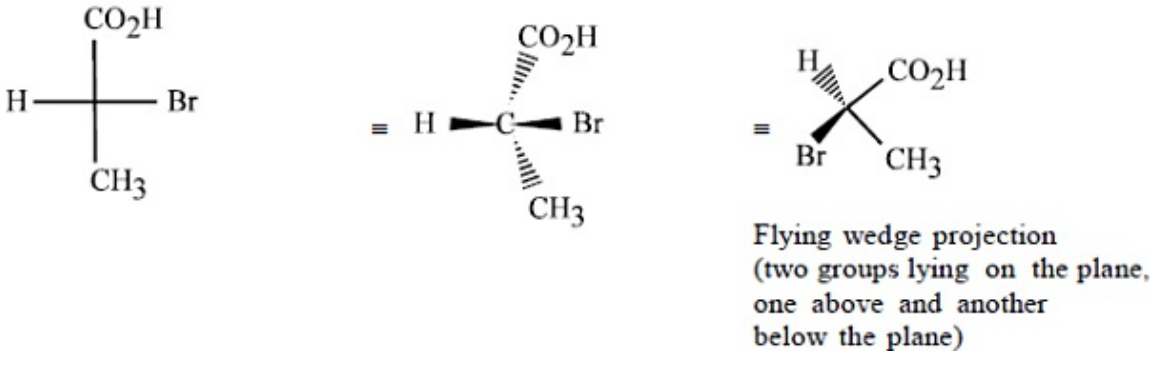
Fischer's projection ; In this projection crossing of horizontal and vertical lines indicate the position of chiral –C which lies on the plane of the paper. The two groups along horizontal lines are actually above the plane and two groups situated vertically are below the plane. Usually the C– atom directly bonded to chiral C and bearing the lowest locant in IUPAC system of nomenclature is placed at the top of the vertical line while that having the

lower locant is placed at the bottom. Let us look now,



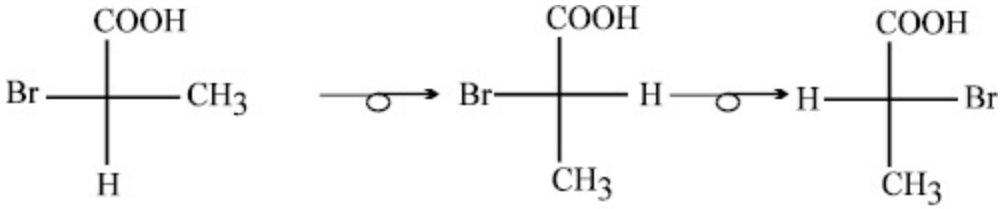
Fischer's projection Wedge dash presentation





Flying wedge projection (two groups lying on the plane, one above and another below the plane)

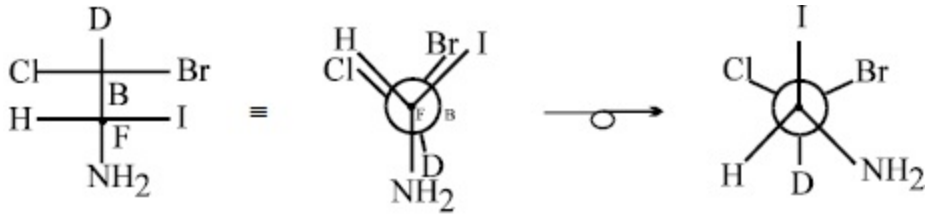
Whatever projection given in Fischer's projection, applying even number of interchanges between the groups at 90° or 180°, we get the same compound.
For example ;



(I) (II) (III)

I, III are same due to even interchange of the groups in configuration I lead to configuration III but II is the enantionmer of I (later on we will see).

Newmann's projection :

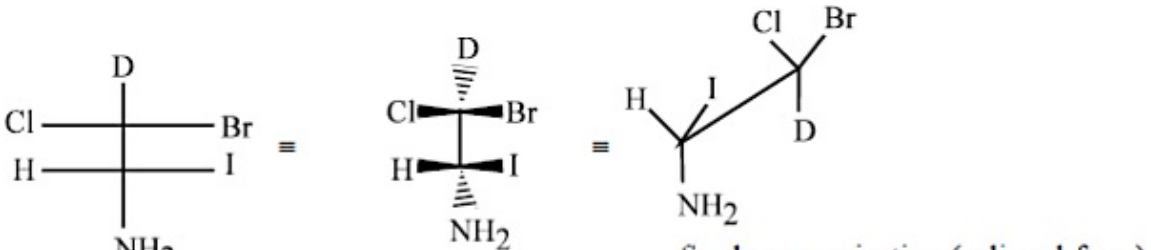


F= Front (Eclipsed conformation) Staggered

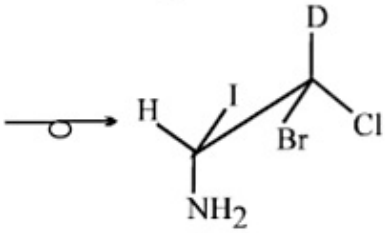
B= Black

Here centre represent front carbon and larger circle represent back carbon. Applying the concept of Fischer's projection vertical bonds indicate the groups which are down the plane and groups which are placed horizontally are above the plane (as shown in Newmann's projection formula).

Sawhorse projection : Look the molecule at an angle.



Sawhorse projection (eclipsed form)



Staggered form

Intermolecular forces : The forces which are responsible to hold several molecules together are called as intermolecular forces. The forces are –

(a) dipole- dipole interaction : The magnitude of this force $\propto \frac{1}{r^3}$ where r = internuclear separation of opposite partial charges. Opposite poles attract each other and responsible for solubility, b.p.m.p. etc.

(b) ion-dipole attraction : Hydration or solvation of cations mainly due to this force and to some extent applicable for anions.

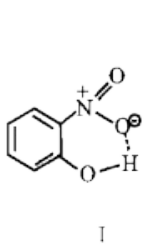
(c) induced dipole interaction : Some non polar molecules dissolve in polar solvents due to this force. Actually opposite charge is induced first and

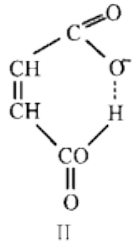
then attraction take place.

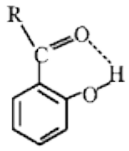
(d) instantaneous dipole induced interaction (London's dispersion force) : This is the force which operate among alkane molecules, solid iodine etc. For this to happen, dipole is induced first due toimbalancement of electron cloud between two atoms and which then induce opposite charge in the next and this way clustering of molecules take place. The magnitude of the force $\propto \left(\frac{1}{r^7}\right)$

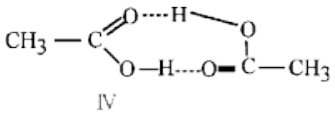
(e) Hydrogen bonding : When H is bonded to O, N, F covalently and O, N, F come closer to the H from another molecule then H-bonding take place. Nature of the bond has been found to be dipole- dipole interaction and probably the strongest one (i.e. electrostatic forces). In some cases Cl has also been found to show H- bond but not always.

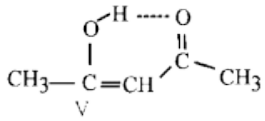
Examples are;

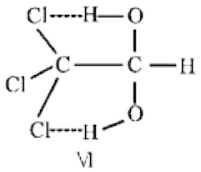

I

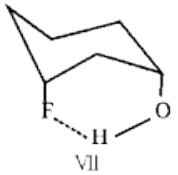

II

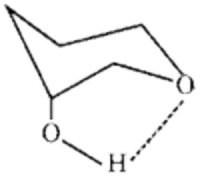

III

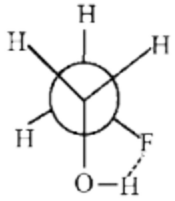

IV

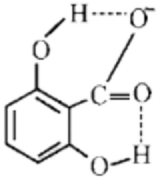

V

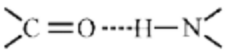

VI

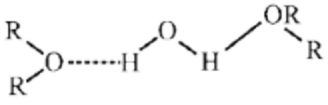

VII


VIII


IX


X


XI (H- bonding in protein)


XII

In the examples (I to X) intermolecular H- bonding has taken place. IV is the

example of intermolecular H-bonding. I, II, III show less acidity as H is internally locked by O– atoms comparatively. IV is a dimer therefore n, ΔT_b, ΔT_f measurement register the molar mass to be twice of molar mass of CH_3COOH. In V, H-bonding give 6- membered ring, therefore it is very stable (and also does not undergo MPV reduction, later on we will see. VI is a stable hydrate which is isolable. VII, VIII, IX are stable in the diaxial or skew conformations

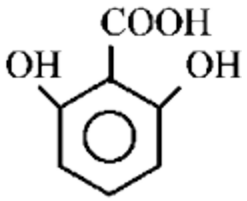
X is very stable, therefore  is strongly acidic.

Fig. XII, show the intermolecular H- bonding of ether in water, due to which ether is soluble in water. Therefore, whenever b.p., m.p. and high solubility etc.are observed then the phenomenon of H-bonding should come into our mind alongwith other intermolecular forces.

Types of reagents :

Reagents can be of the following types –

1- oxidising $Cr_2O_7^{-2}/ H^+$, MnO_4^-/ H^+, SeO_2 etc._

2- reducing (eg. Pt or Pd or Ni/ H_2, $LiAlH_4$ etc.)

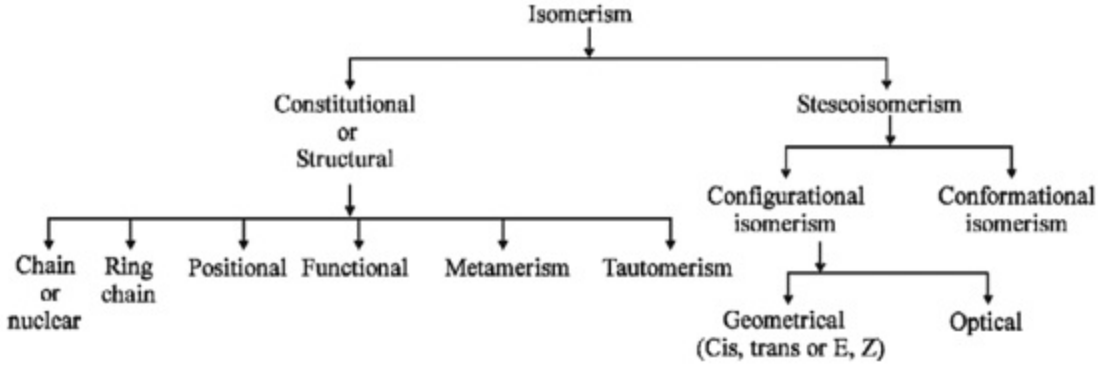
3- nucleophilic (eg. $\ddot{C}N$, $\ddot{C}H_2CHO$ etc.)

4- electrophilic (eg. $(CH_3)_3\ C^+$, $AlCL_3$etc.)

We will broadly discuss (3,4) in the next to next section to come and (1,2) in many reactions in the foregoing chapters.

Isomerism

Chemical entities having same molecular formula in the covalent molecular or formula unit (in the case of ionic compounds) but differ in structure and are separated by energy barriers. This phenomenon of existence of isomers is called isomerism. The following is the classification of isomerism.

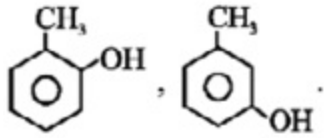


Constitutional isomerism :

These isomers are different compounds that have the same molecular formula but differ in connectivity i.e., in sequence in which the atoms of those compounds are bonded. To write these kind of isomers we must rearrange the positions of nuclei of the atoms.

For example $CH_3CH_2CH_2CH_3$, $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$ are the chain or nuclear isomers.

Structural isomerism of constitutional isomerism

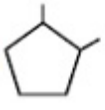
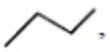
The phenomenon of existence of two or more compounds with the same molecular formula but different structural formula is called as structural or consititutional isomerism. For example 

Look that the position of OH group is different with respect to CH_3 group in two different compounds but their molecular formulae is same

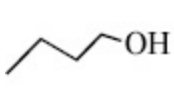
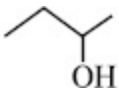
i.e. C_7H_8O.

(1) Chain isomerism : These isomers differ in the variation of the carbon chain, which is the base chain. The molecule with straight chain can be converted into branch .

For example ;

(1)  ;  ; (2)  ,  ; (3)  ,  etc.

(2) Position isomerism : If the compounds have the same functional group but differ in the position with respect to the base chain, then they are called as position isomers to each other.

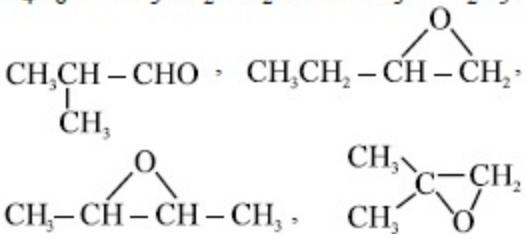
 ;  are position isomers

(3) Functional isomerism : If compounds with the same molecular formula but differ only in the nature of functional group present, is called as functional isomers to each other and the phenomenon is called as functional isomerism . For example :

(i) C_2H_4O; CH_3CHO, $CH_2=CH-OH$, 

(ii) C_3H_6O ; CH_3CH_2CHO, CH_3COCH_3, $CH_2=CH-CH_2-OH$

(iii) C_4H_8O ; $CH_3CH_2CH_2CHO$, $CH_3COC_2H_5$, $CH_3-CH=CH-CH_2OH$



Therefore aldelydes, ketones, unsaturated alcohols, alkene oxides are functional isomers to each other. Similarly, acids, esters are also functional isomers.

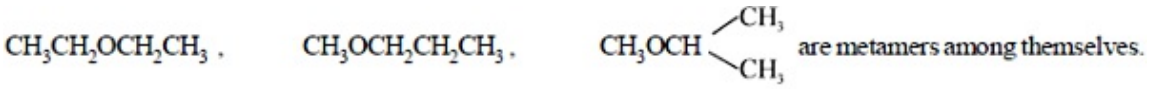
For example ; CH_3CH_2 COOH, CH_3COOCH_3

Among amines, primary, secondary and tertiary amines can also be functional isomers.

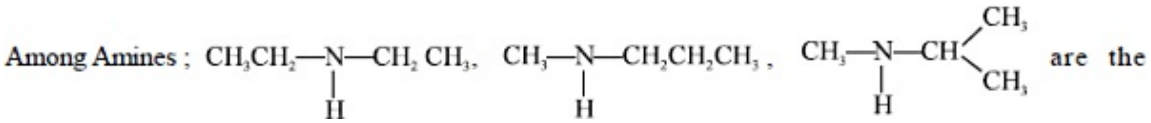
For example; $CH_3CH_2CH_2NH_2$, $CH_3NHCH_2CH_3$, $(CH_3)_3N$.

(4) Metamersim : It is a type of constitutional isomerism exhibited by the organic compounds of the same class (i.e. functional group) but are joined by different alkyl groups with the central atom.

For example :

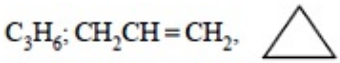


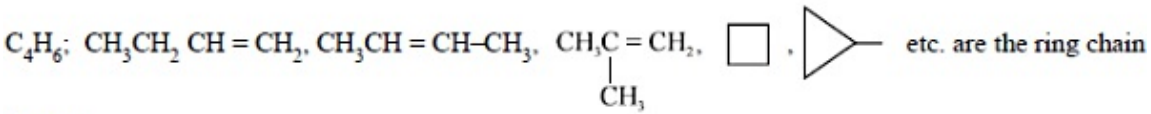
Among esters ; $CH_3CH_2COOCH=CH_3$ $CH_3COOCH_2CH_2CH_3$, $CH_3COOCH(CH_3)_2$ are considered to be metamers.



metamers. Therefore change of the alkyl groups in two valencies of the central atoms leads to metamerism.

Note : There is another kind of isomerism, called as ring chain isomersim. Ring when opened becomes a chain. For example :

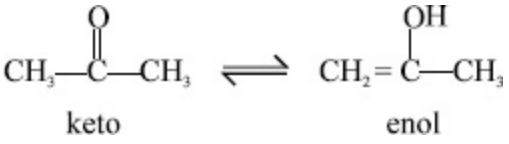




isomers.

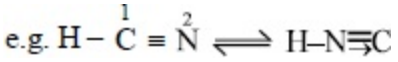
(5) Tautomerism: Lastly, the most important structural isomerism is tautomerism. The tautomerim exist in rapid equlibrium in the pure liquid state or in solution. Tautomers are therefore a kind of functional isomers, which exist in dynamic equilibrium.

For Example :



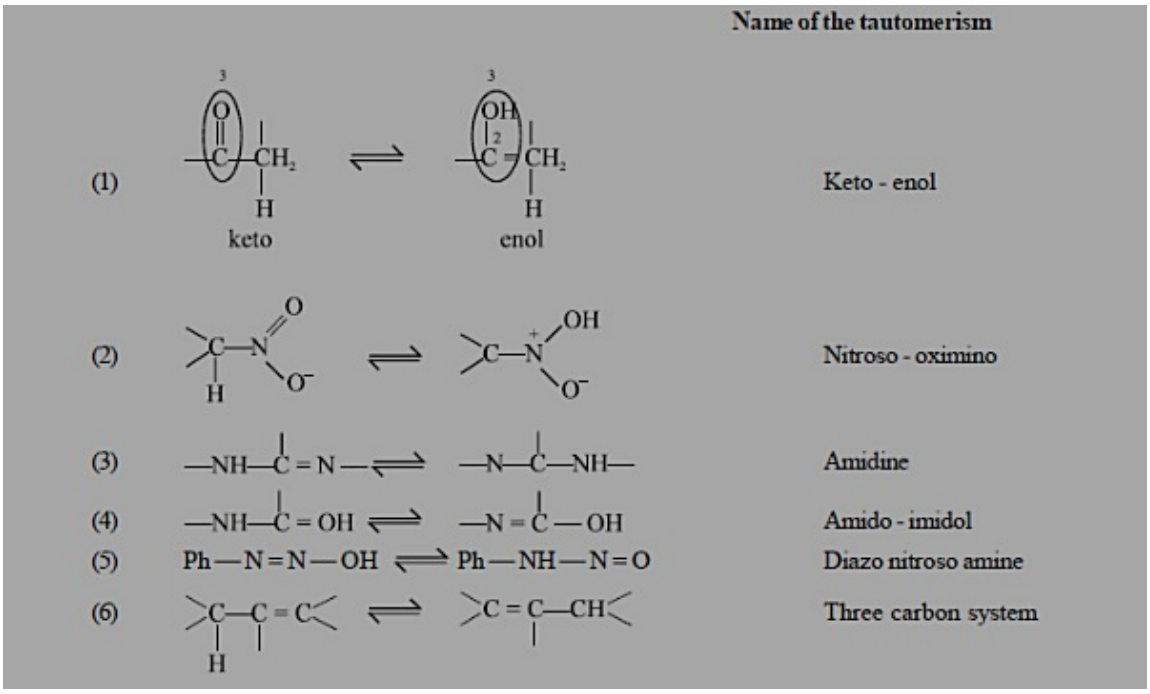
Tautomerism (desmotropism) is of several types given as follows ;

(a) Dyad system : It involves oscillation of H atom between two polyvalent atoms



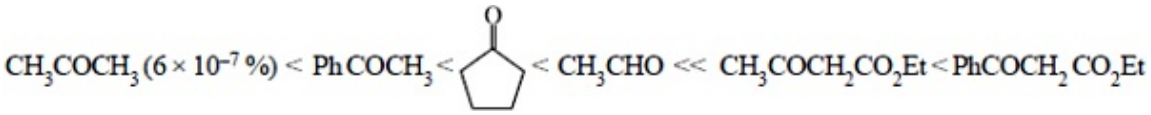
Look, H is oscillating between C,N atoms numbered as 1, 2 regarding there position and therefore this is also called as 1,2 or dyad system.

(b) Triad system : In this type H-atom oscillates between three polyvalent atoms and as H-oscillates between two polyvalent elements at 1,3 positions, therefore, this is called as 1, 3 system or triad system. For example ;



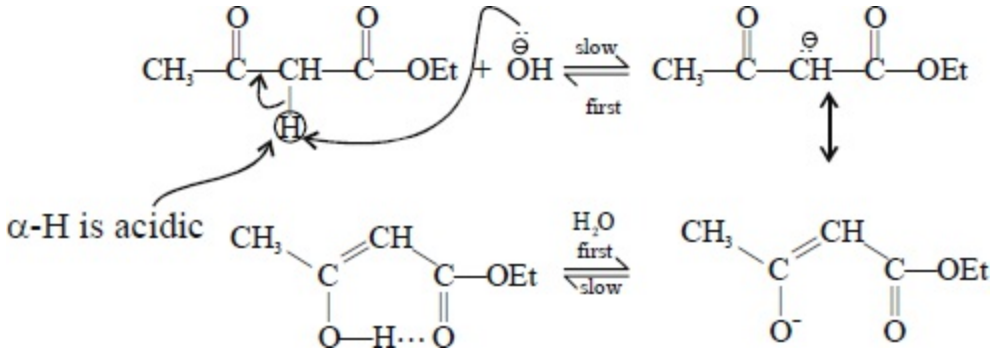
Now a days tautomerism is divided into two classes. Those are (i) cationotropy, where cation moves (for example prototropy i.e., proton moves) and (ii) anionotropy, where anion moves. Above examples belong to cationotropy.

Example of anionotropy is $CH_3\underset{\displaystyle Cl}{\underset{|}{C}}H—CH=CH_2 \rightleftharpoons CH_3CH=CH-CH_2Cl$. Here Cl^- ion migrates from one carbon atom to other carbon atom at equilibrium. Let us now concentrate on the keto-enol tautomerism in this book mainly i.e. $—\underset{\displaystyle H}{\underset{|}{C}}—\underset{\displaystyle O}{\underset{||}{C}}— \rightleftharpoons —C=\underset{\displaystyle OH}{\underset{|}{C}}—$. This keto – enol co-existence has been found in the pure liquid state as well as in the solution also. Percentage keto and enol form varies from one compound to the other. Some of the compound show very large percentage enol content and according to their increasing percentage enol content we can write the following order.



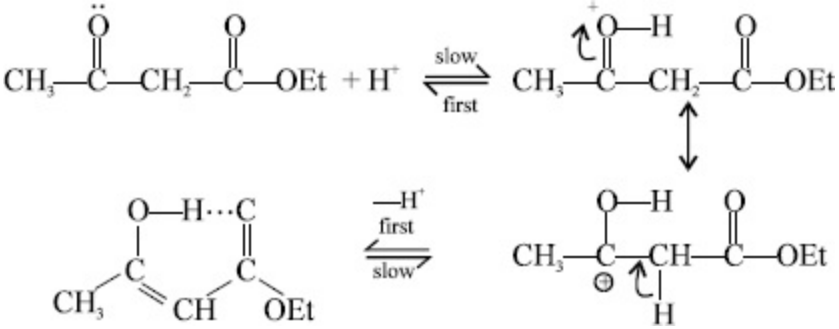
Let us discuss the base and acid catalysed mechanism as follows ;

Mechanism with base catalyst :

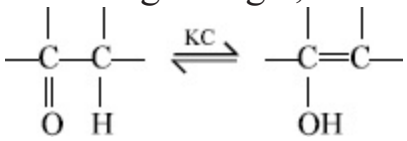


In the above reaction mechanism all the steps are reversible and the first step is rate determining step.

Mechanism with acid catalyst :



Now let us consider the thermodynamics as to why % enol content becomes very low or very high for some compounds. Look at the following change ;



Actually in the above conversion process

$$\Delta H^{\circ} = \left[\underset{(C-H)}{B.D.E} + \underset{(C=O)}{BDE} + \underset{(C-C)}{BDE}\right] - \left[\underset{(C-O)}{BDE} + \underset{(O-H)}{BDE} + \underset{(C=C)}{BDE}\right]$$

= 12 Kcal/mole (approx. by standard data). It means keto → enol conversion is an endothermic process, i.e. keto form is stabler than enol

form and if no other forces like H-bonding, solvation of enol etc. are taking place.

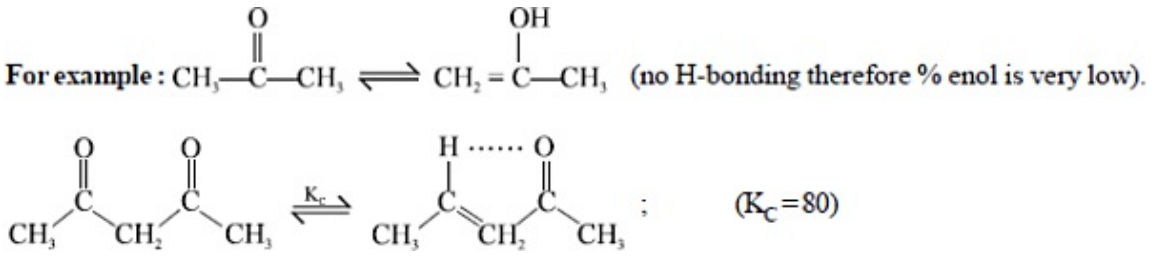
Therefore, $\Delta G^\circ = -RT \ln K_C = \Delta H^\circ - T\Delta S^\circ$

or, $$K_C = \exp\left[-\left(\frac{\Delta H^\circ - T\Delta S^\circ}{RT}\right)\right]$$

From the above equation K_C becomes very low (around 10^{-5}-10^{-6}). Here we can consider Δ S°equal to zero. But % enol content increases whenever there are ;

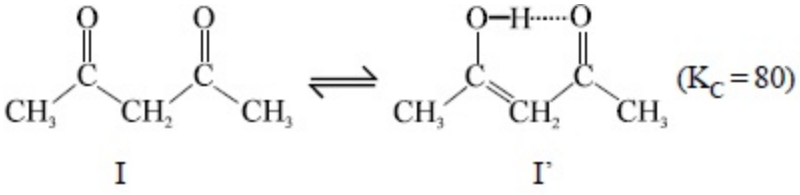
(1) H-bond in the enol , (2) conjugation in the enol, (3) steric effect , (4) solvation effect, (5) inductive effect (6) hyperconjugation etc.

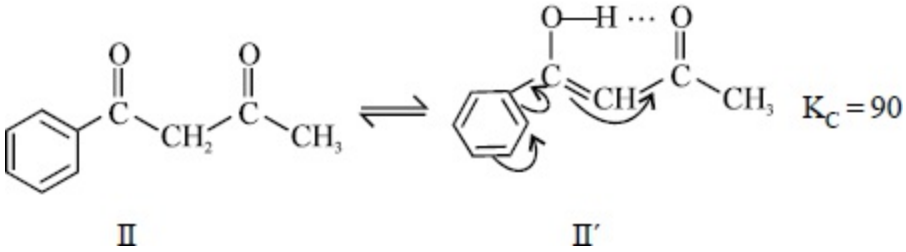
Case-1 : H-bonding (intramolecular) stabilise enol.



So, H-bonding (intromoleculon) makes 6-membered ring (i.e. chelation) causing the product enol very stable.

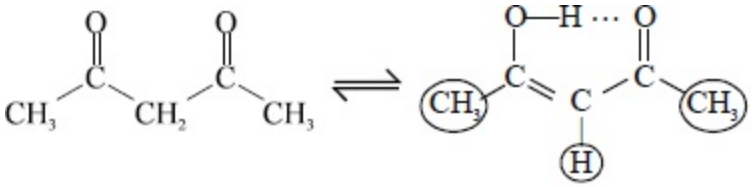
Case-2 :



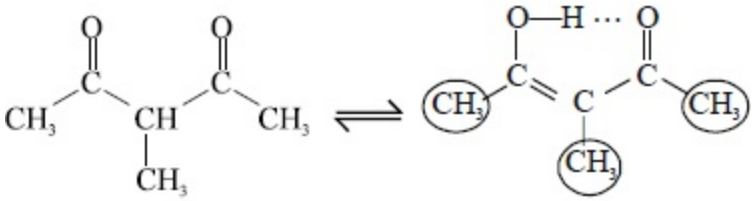


In II'(enol) phenyl ring can take part in conjugation with the newly formed double bond of the enol. Therefore increase in % enol content is found to increase.

Case – 3 :



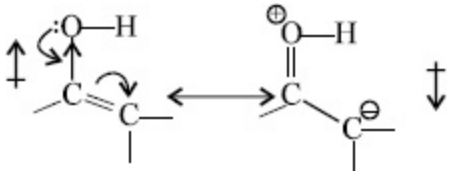
I



II

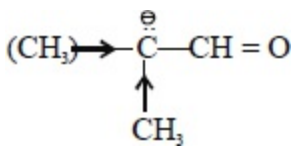
% I is much more than % II due to steric reason. In II all CH_3 groups (which are bulky) falling in the same side of the 6-membered ring therefore they undergo steric repulsion and therefore %II is less in the gas phase.

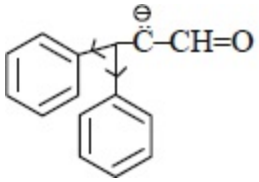
Case – 4 :



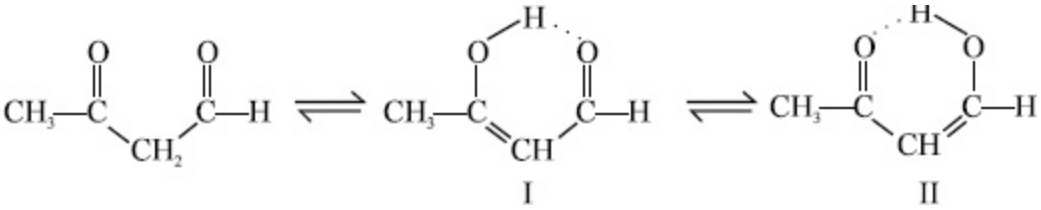
In case of enol, one dipole moment (due –I effect of OH) as if opposes the another, which arises due to +R effect of –OH. So, keto is more polar than enol. Hence by like dissolves like principle, keto is liked by polar solvent like water but enol is liked by less polar solvents or nonpolar solvent. Look at the following decreasing % enol content of acetyl acetone ($CH_3COCH_2COCH_3$) in different solvents. % enol (gas phase) >> % enol (MeCN) >> % enol (H_2O).

Case-5, 6 : % enol of $(CH_3)_2$ CH CH = O < % enol of $Ph_2CHCH = O$. This is due to +I effect and carbanion formed



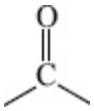
is less stable than the carbanion  In the later carbanion, phe- nyl groups show electron pair withdrawing (-I) effect and therefore carbanion stability is more resulting into more %

enol. Similar case occurs in the following ;

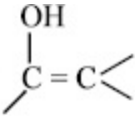


I II

For the above β -keto aldehyde, I is stabler than II and therefore I forms in major amount. The reason being I has ene (C = C) stabilised by H atoms of the CH_3 group due to hyperconjugation, which is absent in II .

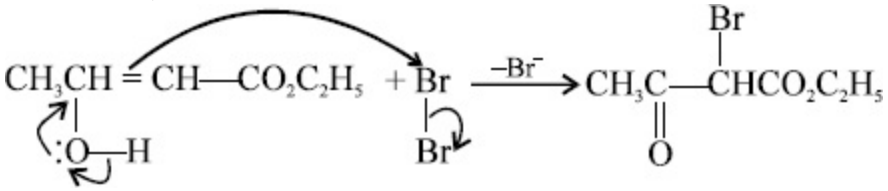
Detection of  **(keto) form in the equilibrium mixture :**

(1) $NaHSO_3$ test gives a bisulphite compound , **(2)** cyanohydrin with HCN etc.

Detection of  **(enol) form in the equilibrium mixture :**

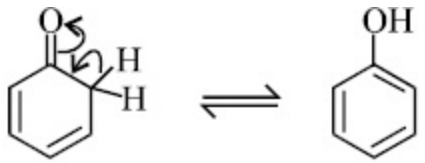
(1) Addition of Na gives H_2 gas (due to O – H is acidic here, i.e. active–H is present)

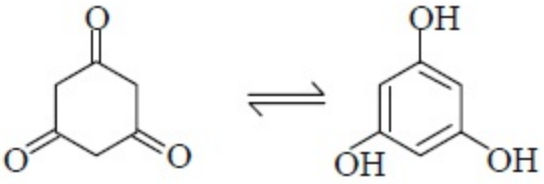
(2) (Br_2 + C_2H_5OH) when added, red colour discharges due to the following reaction ;

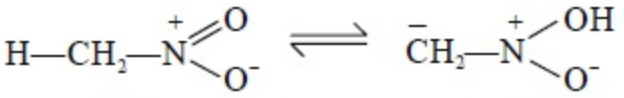


(3) FeCl3 solution test gives violet colour (as enol is present).

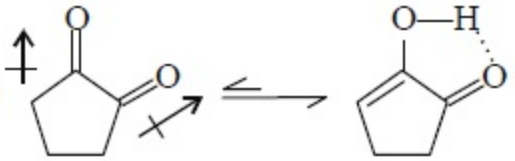
Some more examples (even with trace or large enol) and other systems are :

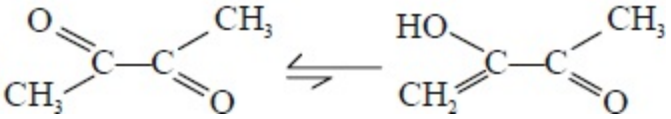
(1) 

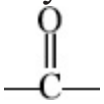
(2) 

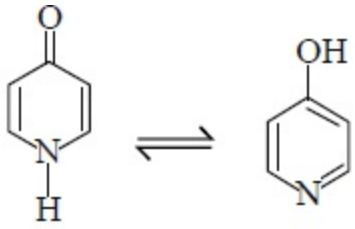
(3) 

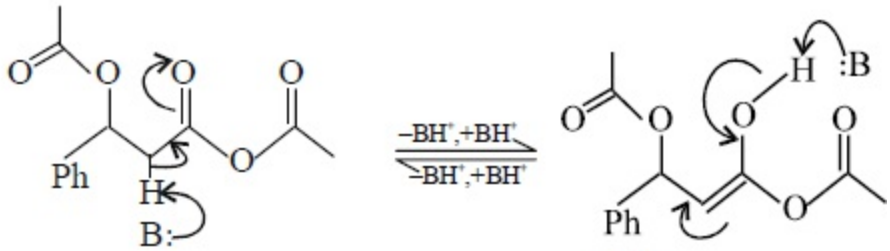
nitro acinitro

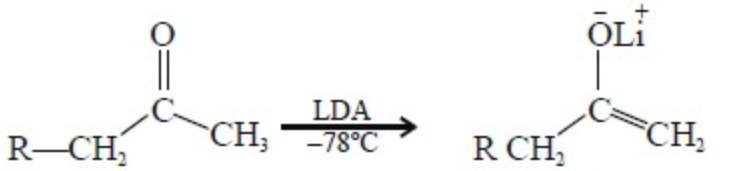
(4) (a) 

(b) 

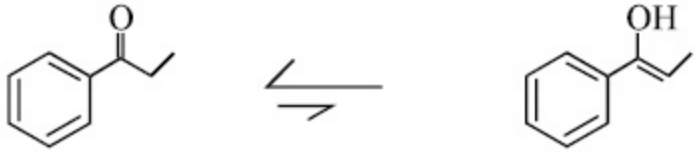
In case (a) mainly it exists in enol form as the C = O dipoles repel each other very strongly. But in (b) in biacetyl free rotation with respect to C–C bond axis takes place in which  bond moments oppose each other. Therefore no such dipole-dipole repulsion arises in di keto form. Hence the above result.

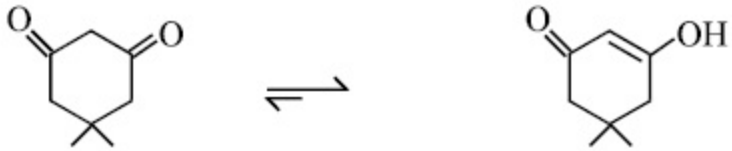
(5)  (example of 1, 5 system)

(6) 

(7) 

only one enolate is obtained not the other one due to strong acidic character of α-H in CH_3.

(8) 

(9) 

Dimedone

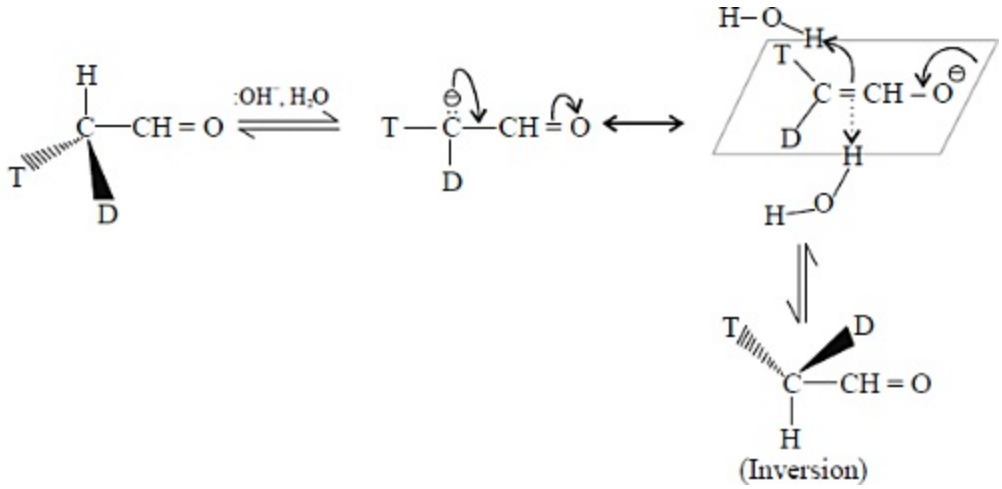
Applications of tautomerism are too many . Few examples are given as follows ;

(1) Acid catalysed aldol condensation from carbonyl compounds.

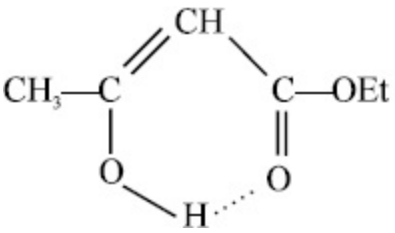
(2) Enol formation during HVZ reaction.

(3) Racemisation of an optically active compound

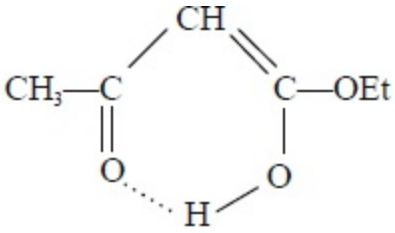
For example;

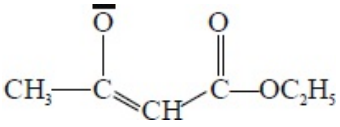


Note : During prototropy, acidic α –H moves from one atom to the other as we have seen % enolisation is a function of the pKa values of the compounds.Less the pKa values more the % enol content is well understood. Another important feature is that cross conjugation, when appears registers less acceptable route to stabilise carbanion which leads to less formation of enol. Therefore we write,

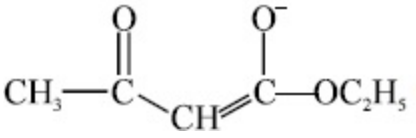
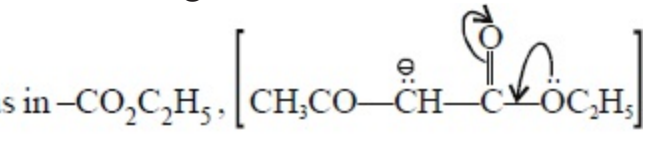


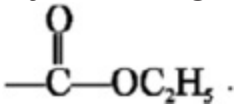
not



Because carbanion stabilisation takes place through 

not through

 , as in $-CO_2C_2H_5$, 

cross conujugation appears as shown in the adjacent diagram.Therefore ⊖ ive charge on  cannot delocalise through  .

Stereoisomerism :

These isomerism involves 3D arrangement of groups or atoms (from the Greek word ‘Stereos’ means 3-dimensionality) of the compounds having same molecular formula (i.e.; identical structural or constitutional

differing only in the arrangement in space for the groups or atoms) are called stereoisomers. The position of groups or atoms are interchangeable in space. The above isomerism is due to the following reasons ;

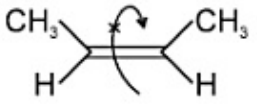
(a) restricted rotation of a molecule about a C – C single bond, which leads to rotational isomerism or conformational isomerism.

(b) restricted rotation of a part of the molecule about a double bond or σ-bond also in a ring or asymmetric carbon. This leads to configurational isomerism. Usually configurational isomers are known as steseoisomers.

We first discuss geometrical isomerism which is basically cis and trans type (also called as Z and E respectively).

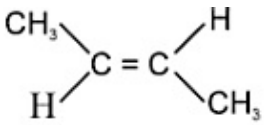
Case – I :

Acyclic molecule



cis

(Same groups in the same side)

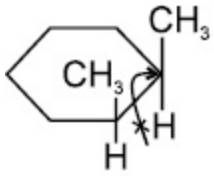


trans

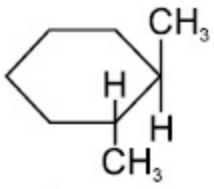
(Same groups in the opposite side)

Case – II :

Cyclic molecule :

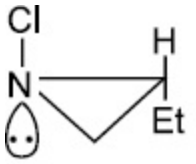


cis

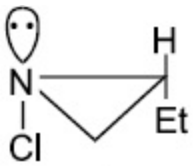


trans

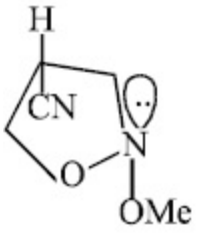
In the above cases restriction in rotation is shown. The following are the cases where cis, trans isomerism also may occur. Look at the following examples.



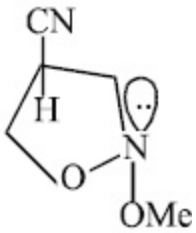
trans



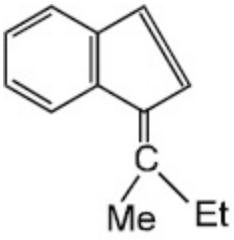
cis



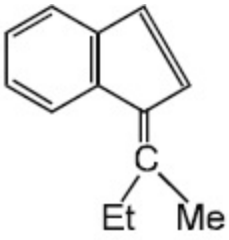
cis



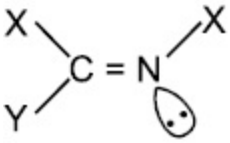
trans



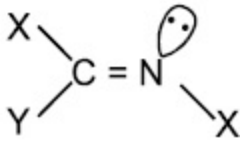
E



Z

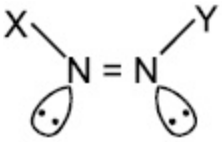


Syn

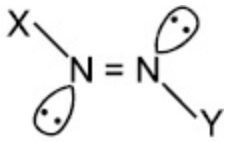


Anti

Here syn or anti may be called as Z, E respectively.



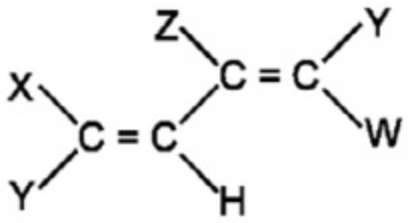
syn/Z



Anit/E

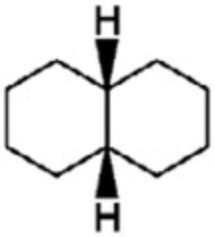
Case – III

With two or more double bonds in conjugation or isolation but not cumulative ;

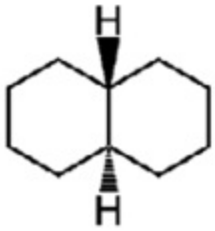
e.g.  etc. in different rigid parts cis, trans or E/Z arises.

Case – IV

Fused and bridged ring systems :



cis-decalin

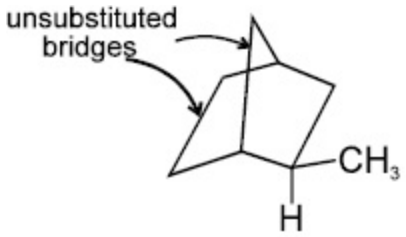


trans-decalin

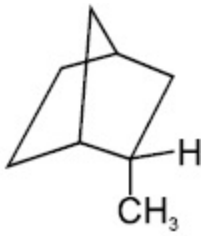
For small fused rings trans configuration is impossible. In smallest junction with 3, 6 or 4, 5 etc. where trans fusion is observed. But for 4, 4 junction only cis isomer is observed.

Case – V

Unsubstitued bridges :



exo



endo

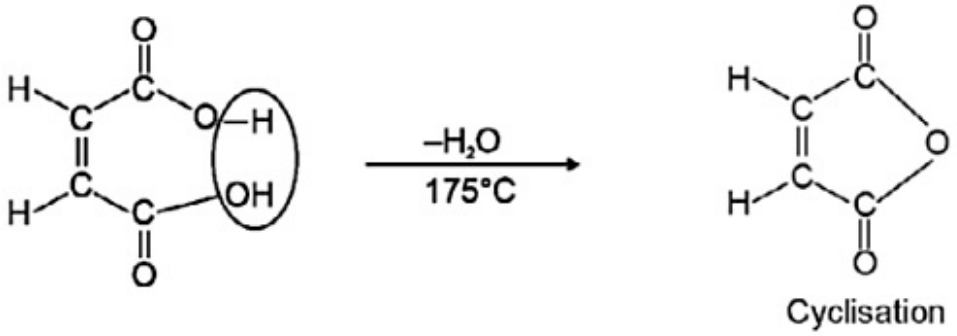
Here exo is called when substituent CH_3 is closer to the shorter bridge and endo is called when substituent is closer to the longer of the two unsubstituted bridges.

Properties of geometrical isomers (i.e., cis, trans, etc). :

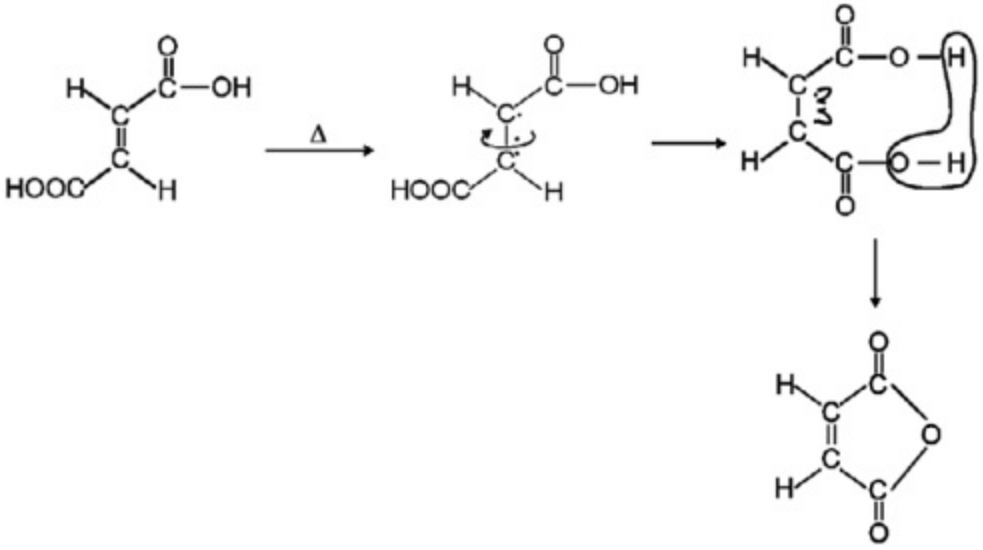
(1) They are diasteseomers as they are nonsuperimposable or not related to each other as mirror image. Therefore all the physical and chemical properties are different. e.g., Easy cyclization of cis compound as shown

below.

Example 1 :

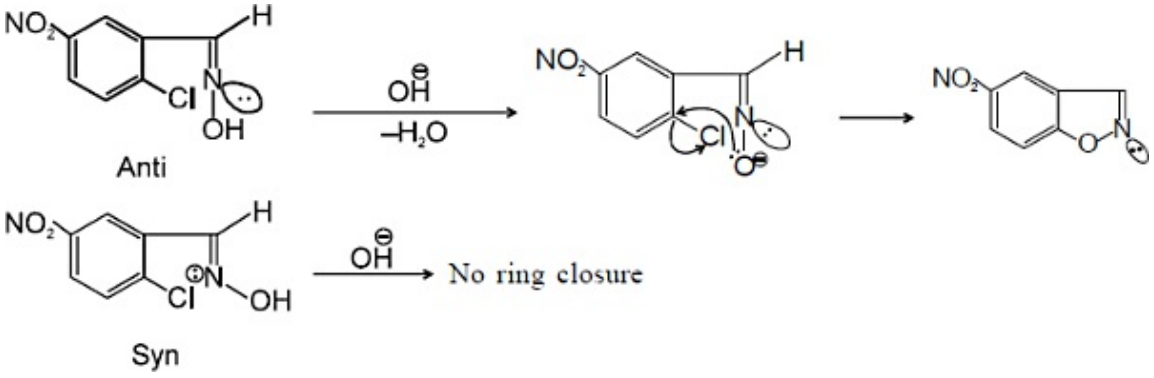


But fumaric acid cyclises at 240°C and not at 175°C. Mechanism may be

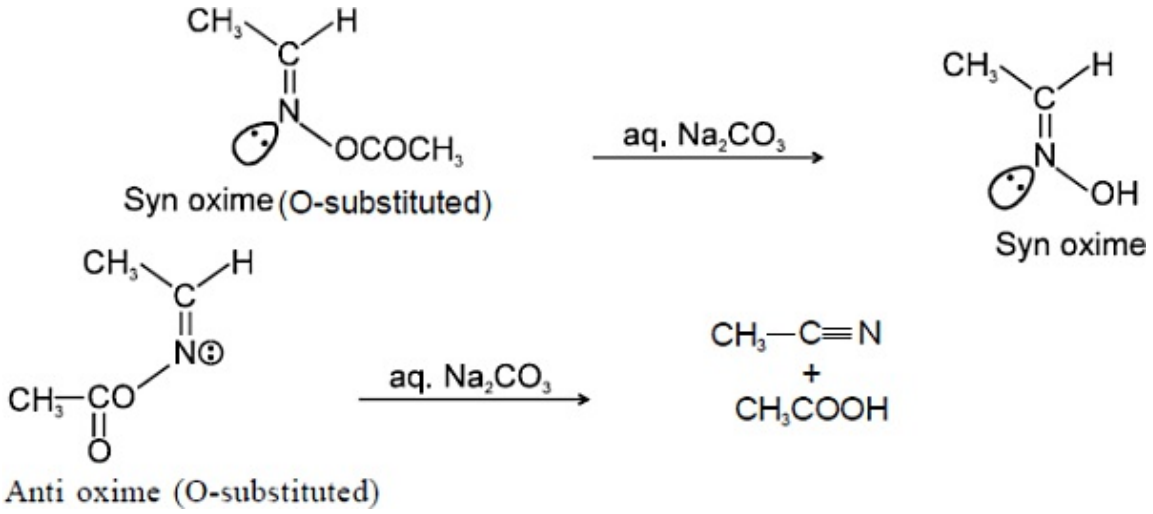


that is free rotation in σ -bond takes place easily which is not possible in case of rigid double bond.

Example 2 :



Example 3 : Other than cyclisation the following hydrolysis reactions show difference in behaviour of the geometrical isomers.



2. More symmetry in trans isomers, have higher melting points than cis isomers.

3. Lower solubilities of trans in inert solvents.

4. cis has higher heat of combustion due to less stability compared to trans isomer.

5. Acidic strength (Ka, ie first dissociation constant) of maleic acid is higher than fumaric acid.

6. Boiling point is a function of dipole moment, H-bonding and other intermolecular forces, molecular mass. Therefore if cis isomer has more dipole moment then it will have higher bp.

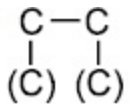
E/Z specification (as it is configurational isomers) :
CIP (Cahn Ingold Prelog) method ;

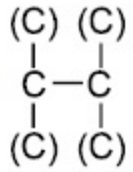
1. Structural formula is drawn on the paper.

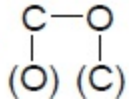
2. Priority rule : The atom with higher atomic number bonded to double bonded carbon atoms is marked as 1, 2 (i.e. higher, lower).

3. If same atom is encountered then navigate to the next element etc. and when atom with higher atomic number is found then it is prioritized as 1.

4. Phantom atom rule is followed. By that,

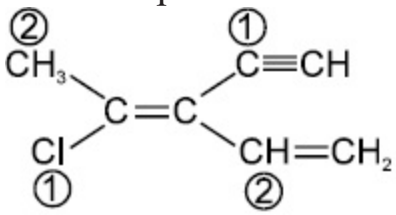
C = C is considered as 

C ≡ C is considered as 

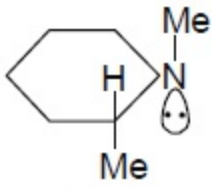
C = O is considered as  etc.

Finally if it is observed that both the higher priority groups (1) are on the same side of the double bond/ σ -bond in the ring/ π -bond in the C = N etc. then we call it as Z, otherwise we call it as E.

For example :



E



E

Lone pair (lp) is less prior group to any atom or group.

Calculation of total number of geometrical isomers (TNGI) :

Case – 1

Number of double bonds = n, in a isolated polyene compound and end or terminal groups are different.

$TNGI = 2^n$

e.g., $PhCH = CH - CH = CHCl$

$TNGI = 2^n = 2^2 = 4$

Case – 2

If terminal groups are same of the polyene and n = even.

$TNGI = 2^{n-1} + 2^{n/2-1}$

e.g., $CHCl = CH - CH = CH - CH = CH - CH = CHCl$

$TNGI = 2^{4-1} + 2^{4/2-1} = 8 + 2 = 10$

The above equation is not valid for n = 2

Case – 3

n = odd and terminal groups of the polyene are same.

$TNGI = 2^{n-1} + 2^{(n+1)/2 - 1}$

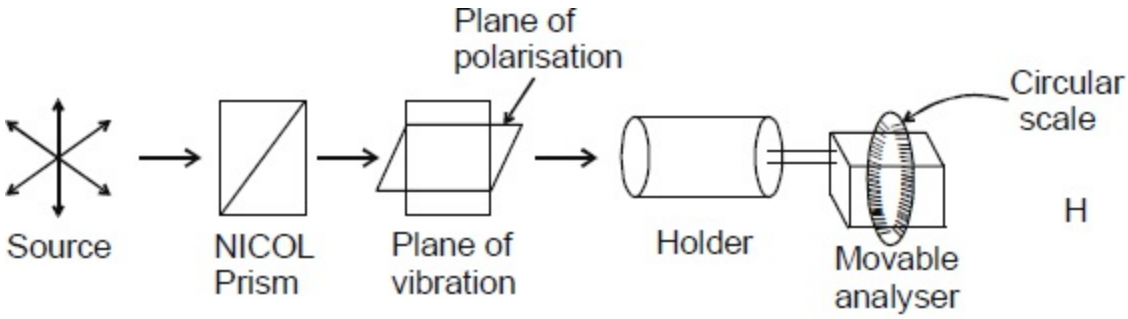
e.g., $CHCl = CH - CH = CH - CH = CHCl$

$\therefore \quad TNGI = 2^{3-1} + 2^{(3+1)/2 - 1}$

$= 2^2 + 2 = 6$

Optical isomerism :

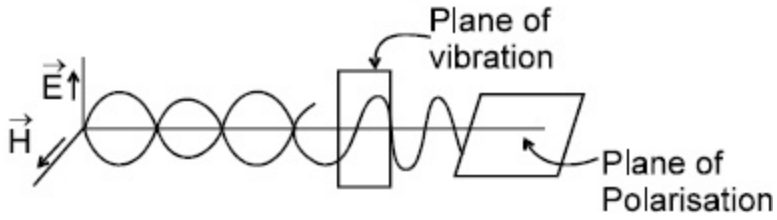
This isomerism is due to restriction in rotation of groups bonded to chiral atoms. (i.e., optically active atom). Let us first see the experimental findings then we will see why such kinds of optical activity arises.



POLARIMETER

Plane of vibration :

This is the plane in which electrical vector $(\vec{E})$ oscillates.



Plane of polarization:

This is the plane perpendicular to the plane of vibration. Actually $\vec{E}$, $\vec{H}$ for the light are mutually perpendicular, when $(\vec{E})$ oscillates on a straight line ( ) is called as polarised light.

Dextrorotatory Compounds (d) :

The compounds in solution when rotates the plane of polarisation of plane polarised light is called as dextrorotatory compound and designated as d.

Levorotatory Compounds (l):

The compound in solution when rotates plane of polarisation in left or anticlockwise is called as levorotary (ℓ) .

It should be remembered that d, ℓ are experimental findings.

Reason to show optical activity by molecules :

If a molecule do not have the following symmetry elements then molecule shows optical activity.

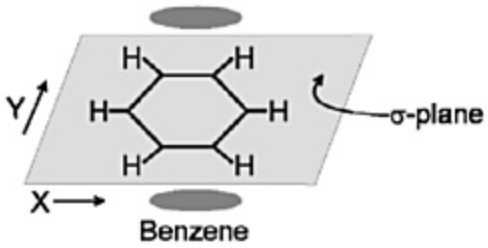
1. σ - plane of symmetry or simply plane of symmetry.
2. Centre of symmetry.
3. Alternating axis or rotation reflection axis of symmetry (S_n axis)
4. Simple axis (Cn axis) of symmetry.

If a compound doesn't have S_n, σ -plane and centre of symmetry then molecule is called as dissymmetric and if it does not have Sn axis (i.e. S_n , σ Plane, centre of symmetry) and C_n axis also then molecule is called as asymmetric. Therefore all asymmetric molecules are dissymmetric but all dissymmetric molecules are not asymmetric.

Plane (σ -Plane) of symmetry :

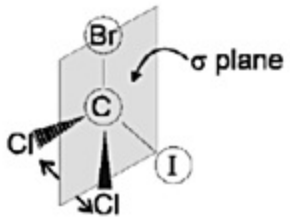
Any plane passing through the molecule & bisecting in such way that one part is mirror image of the other.

The plane of symetry can be shown as follows ;



Benzene

σ plane is XY plane itself



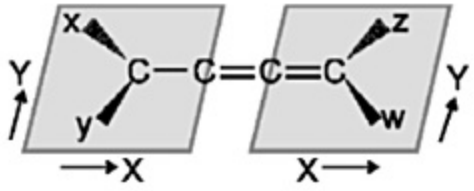
Rounded atoms are divisible by the imaginary plane (i.e. plane of mirror)



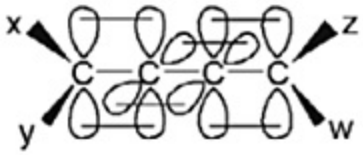
XZ is σ-plane here

For biphenyls having bulky ortho substituents, rotation with respect to $C_1 - C_2$ bond axis take place so that two rings assume perpendicular plane to each other to minimise repulsion between the bulky ortho substituents.

From the above diagram of allene, it is clear that neither XY not XZ is plane of symmetry. For cummulenes with odd number of double bonds (3, 5 etc) molecule possess plane of symmetry but for even number of double bonds (2, 4, 6 etc) if the terminal groups are same then molecule possess plane of symmetry but for different terminal groups (i.e. A ≠ B and D ≠ E) molecule does not possess plane of symmetry.



≡



∴ XY plane is the plane of symmetry.

Similarly for spiranes,

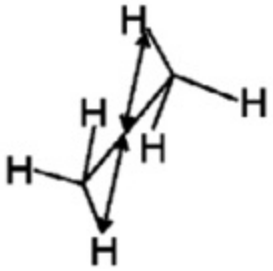


XY, XZ are the planes at which the molecule has its different parts. Two distinct planes XY, XZ have evolved and no one is a-plane.

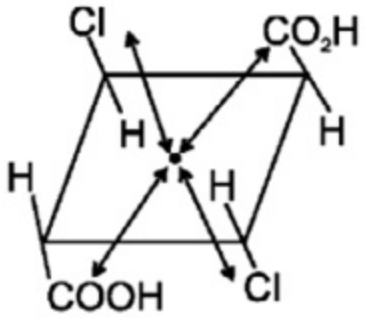
Centre of symmetry :

It is a point or centre such that if a line is drawn from any atom or group and extend through this centre to reach at the same distance to obtain the same group or atom (i.e. present diametrically opposite position).

For example ;



See all the H atoms are equidistant from the centre and diametrically opposite to each other.

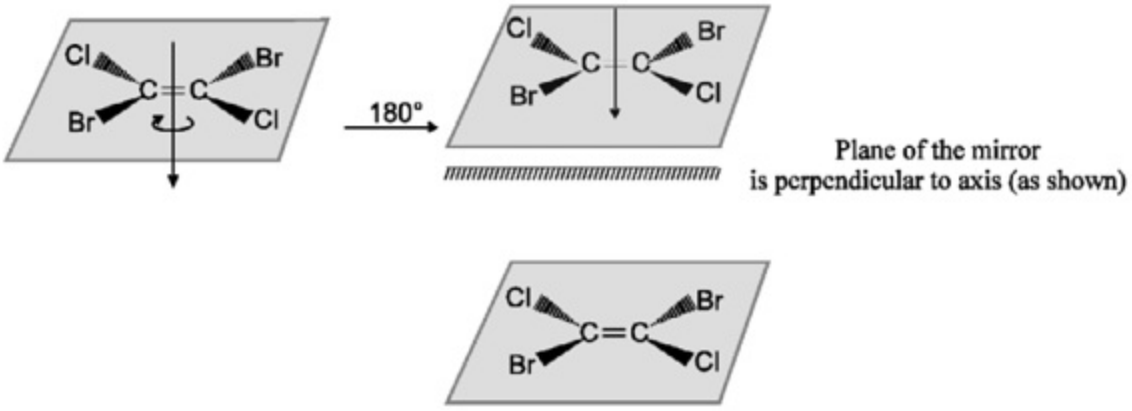


In the above example centre of symmetry is present.

Alternating axis of symmetry (S_n) :

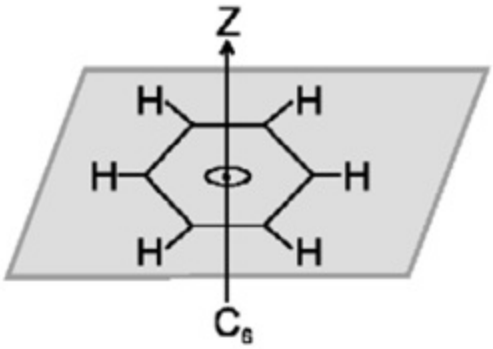
A molecule or species is said to have S_n axis if after rotation by $2\pi/n$ about an axis passing through it and followed by reflection through a plane perpendicular to this axis produce the structure in which the species is superimposable.

For example ;

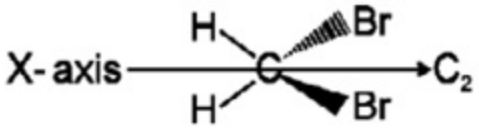


4. Simple axis of symmetry (C_n) :

If a species rotating about an axis through 360° and coincides with itself by n times then the axis is called as the n-fold axis of symmetry.



As benzene molecule on rotation wrt Z axis produce the same structure 6 times, therefore Z axis is the simple axis of symmetry.



Dibromo methane show the
C_2-axis of symmetry as shown

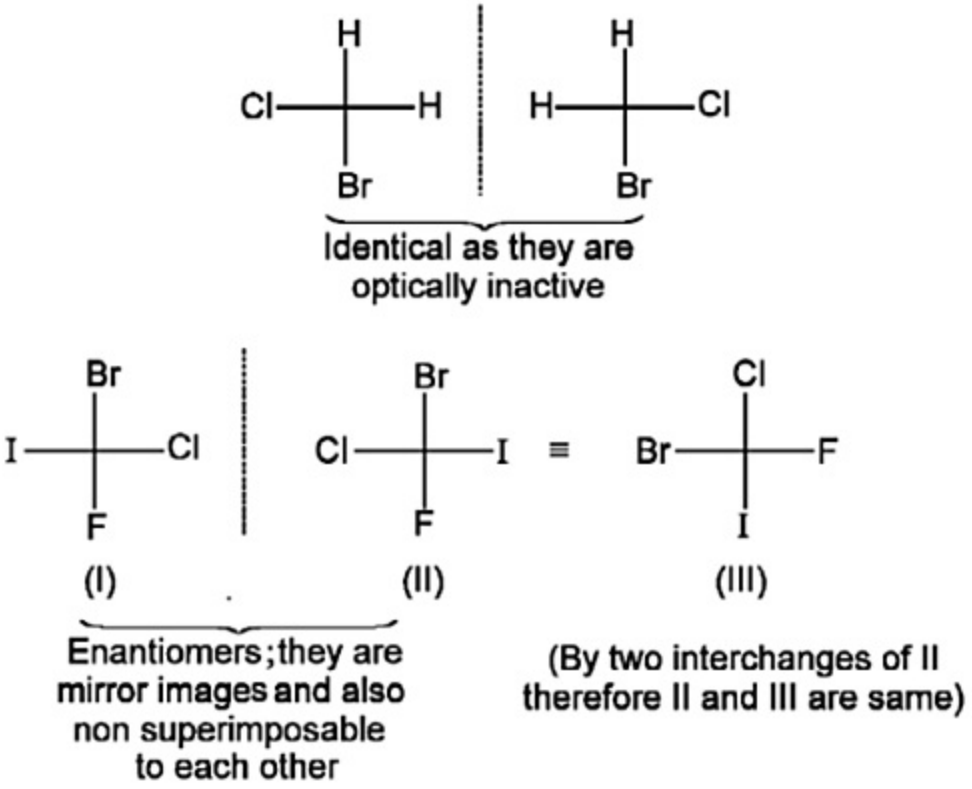
Note :

Truely speaking if a molecule lacks σ - plane of symmetry and centre of

symmetry the molecule will be optically active. Do check only the first two elements of symmetry to find the optical activity of a molecule.

Chiral centre of optically active centre: It is the centre due to which molecule is non-superimposable on its mirror image. Optically inactive species are called achiral molecule.

Enantiomers : The optically active entity which is non superimposable on its mirror image is called as enantiomer to each other .



Enatiomers are also called as optical antipodes.

Properties :

Physical properties (mp, bp., solubility in optically inactive solvent) are same for enantiomers. Behaviour with achiral reagent, solvent etc is same but with chiral reagent, solvent or catalyst etc. the enantiomers react at different rate.

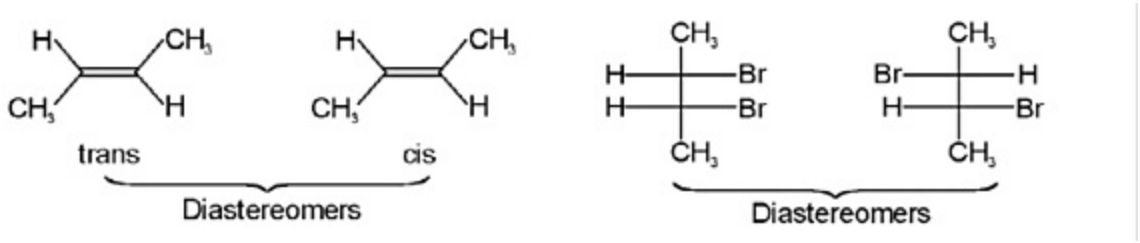
e.g., $R-COOH + R-OH \overset{H^+}{\rightleftharpoons} R-\overset{O}{\overset{\|}{C}}-OR$

(d) and (ℓ) acid will have different rate of esterification with same d or ℓ alcohol.

Diastereomers :

If two stereoisomers donot have mirror image relation between them they are called as diastereomers.

e.g.,



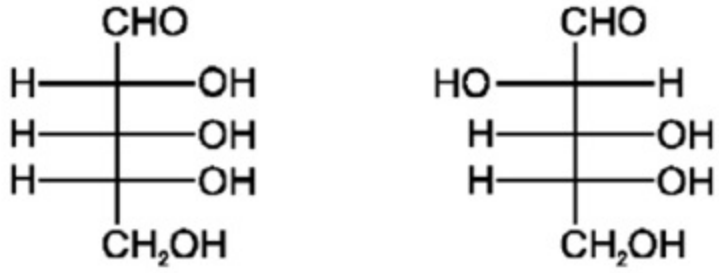
Properties :

They have different physical, chemical and spectral properties etc. d/ ℓ tartaric acid which has m p. 170°C but meso tartaric acid has mp 206°C. They have different solubilities also.

Epimers :

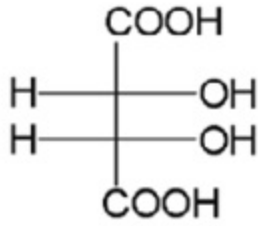
These are also diastereomers containing more, than one chiral carbon atoms but differing at only one C atom.

For example;

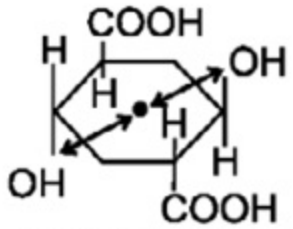


Meso Compounds :

If an optical isomer having more than one optically active carbon atoms but inactive due to the presence of σ -plane or centre of symmetry within the molecule is called as meso compound.
For example ;



meso tartaric acid



meso compound as centre of symmetry is present

Meso compounds are optically inactive by internal compensation.

Optical purity (Enantiomeric excess) :

This is basically the presence of excess entantiomer in a sample containing recemic mixture and extra quantity of one enantiomer (+/–). This is meausred by percentage quantity.

Percentage optical purity or percent entantiomeric excess = $\frac{[\alpha]_{obs.}}{[\alpha]_{max.}} \times 100$

where α_{obs} = observed rotation of the contaminated sample i.e., with one of the d/ ℓ in excess. $[\alpha]_{max}$ = specific rotation of the corresponding enantiomer. Specific rotation is the degree of rotation of the plane of polarisation of a plane polarised light of specific wave length caused by a solution or pure liquid of 1 dm (i.e. the thickness of the container) containing 1 gram of the substance /ml solution at a particular temperature (°C). The expression of sp. rotation is,

Sp. rotation = $[\alpha]^T_D = \frac{\alpha_{obs.}}{\ell \times C}$ (C = g/100 ml, name of the solvent of the solution);

α_{obs}. depend on the number of optically active molecules interact with the polarised light. Clearly, $\alpha_{obs.} = f(T, \lambda, \ell, C)$. More the ℓ or C more will be the α_{obs} i.e. α_{sp} . It is found that association, dissociation causes α_{obs} more and less respectively. Kinetic energy of the molecules is a function of temperature. Therefore α_{obs} change with temperature and lastly λ of the plane polarised light. α can be written also as $\alpha \pm 180°n$ where n = 0, 1, 2, etc.

Molecular rotation = $[M]^T_D = \frac{[\alpha]^T_D \times M}{100}$; M = Molecular weight.

Determination of specification of configuration (R/S) for optically active molecules with chiral 'C' :

To write the absolute configuration (R/S) we follow the principles given below;

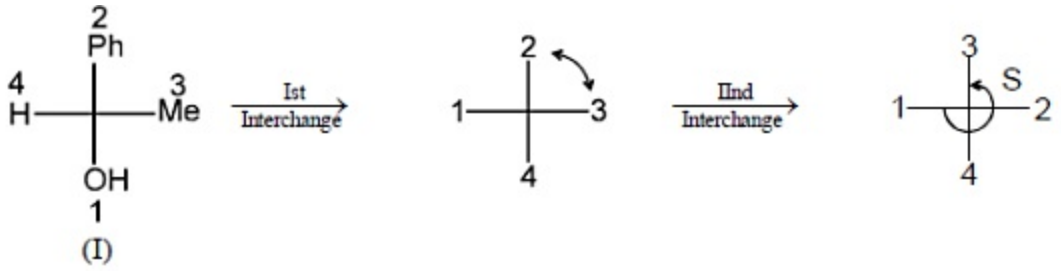
1. Fischer projection of the molecule is drawn.

2. Priority rule applied (as was in E/Z) and groups are numbered as 1, 2, 3, 4 according to the seniority. 1 = highest priority etc.

3. Bring the lowest priority group in the vertically down (i.e., to make the lowest priority group away from the viewer's eye) and then travel from $1 \rightarrow 2 \rightarrow 3$ If it travels in clockwise direction then the configuration is 'R' otherwise if it travels in anitclocwise direction then it is called as 'S'.

4. The extension of the priority rule is (heavier isotope) 'D' > 'H', 'Z' > 'E', 'R' > 'S'

e.g.,

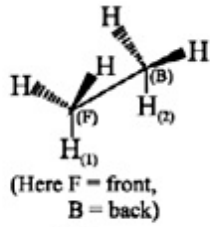


Therefore (I) has S configuration as shown above which can also be shown as follows ;



Conformation of Molecules

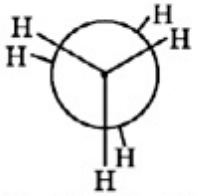
Conformation of any molecule arises due to free rotation around C – C σ - bond. Conformations of minimum energy are termed as conformational isomers or conformers or rotamers. The phenomenon due to which conformers arises is called as conformational isomerism. Let us consider ethane molecule $CH_3 – CH_3$.



(Here F = front, B = back)

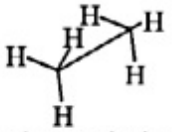
(I)

or,



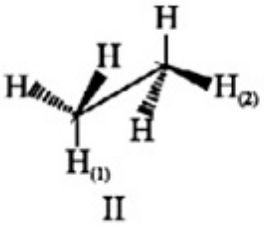
Centre is front -C and bigger circle is back carbon (Newton's projection)

or,



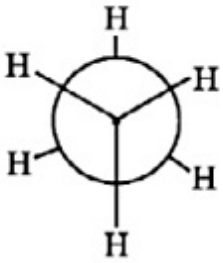
Sawhorse projection

The three dimensional view will look like as one of the conformations as shown above. Actually this is called as eclipsed conformation, where all H-atoms of the front – C shields or eclipses the H-atoms with the other – C. New if we rotate back C by 60° then it will look like as given in the following.

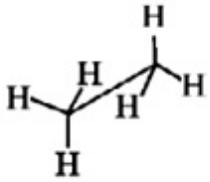


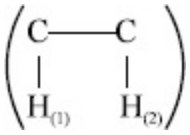
II

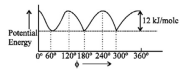
or,



or,



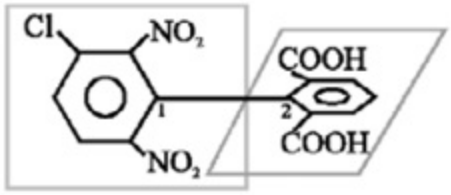
Conformation II is called as staggered or anti conformation. In the eclipsed conformation 

H_1 – C and H_2 – C makes an angle, which is called as dihedral angle or angle of (ϕ) and $\phi = 0$ here. But in II, $H_{(1)} - C{-}C{-}H_{(2)}$ angle (ϕ) is $60°$. In II actually H-atoms of $C_{(F)}$ is at maximum separation from H-atoms of $C_{(B)}$ and thus this conformation is of minimum energy and is called as staggered or anti conformation. If we plot the energy barrier for staggered changing to eclipse or eclipse changing to staggered then it will be as the following ; 

Eclipsed conformations thus arise in ethane when $\phi = 0°, 120°, 240°, 360°$ and anti or staggered conformations arise at $\phi = 60°, 180°, 300°$. . The interchange of eclipsed to staggered or vice versa is very fast even at room temperature because the energy amounting to reach the energy barrier is present. Therefore its very difficult to isolate eclipsed from staggered, though it spend most of its time close to minimum energy. It is to be remembered that if any conformation is frozen that is no change in the conformation by rotation with

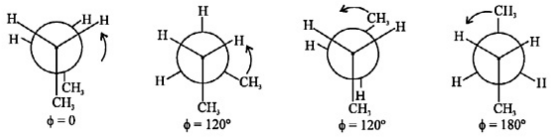
respect to σ -bond occurs then that is called as configuration.

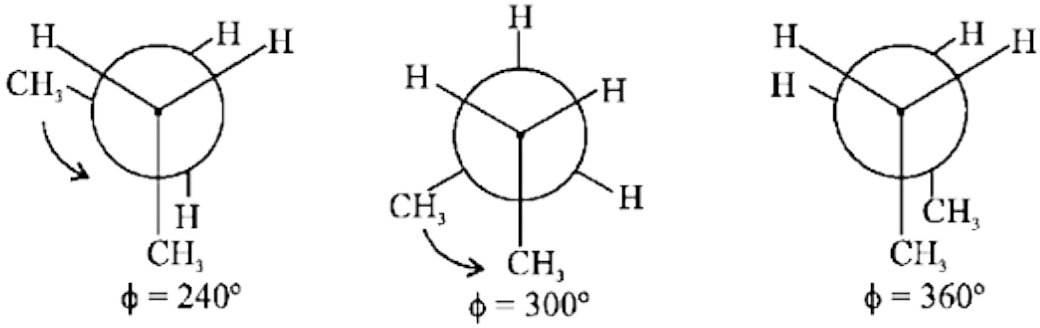
For example ;



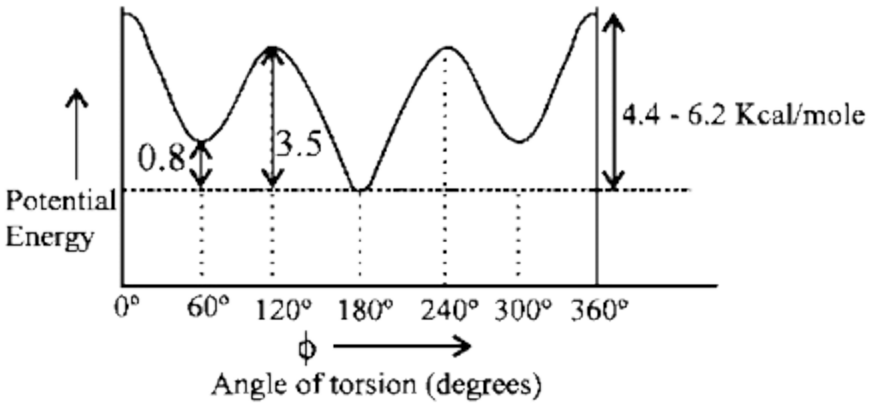
No rotation with respect to $C_1 - C_2$ occurs, therefore it is called as configuration.

In case of n-butane we can draw several conformations with the help of Newmann's projection as shown below;





Few points to be remembered now for n-butane. At ϕ = 0°, 360° the conformations are called as eclipsed or fully eclipsed or syn periplanar conformation. At ϕ = 180° the conformation is called as anti or staggered or anti periplanar conformation. At ϕ = 60°, 300° the conformations are called as gauche or syn clinal or skewed conformation. At ϕ = 120°, 240° the conformations are called as partly eclipsed conformation.



Stabilitywise anti > gauche (or skewed) > partly eclipsed > eclipsed. In the conformations CH_3 goups are at 180° apart. So minimum van der Waal's or steric repulsion between the groups arises. Maximum repulsion arises at ϕ = 0° or 360°. Hence n-butane normally spends time mainly in anti along with little time in gauche conformation (which are conformers by definition).

Actually gauche forms are optically active in a single but change from ϕ = 60° to 300° is so rapid that equal percentage of them make the composition optically inactive.

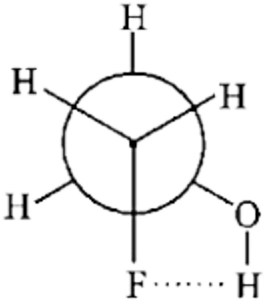
Few cases with the informations regarding the stable conformations are;

(1) $\begin{matrix}CH_2—CH_2\\ |\quad\ |\\ Cl\quad Cl\end{matrix}$ in CCl_4 ; % anti = 70% ; % gauche = 30%.

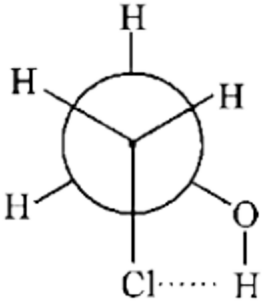
(2) $\begin{matrix}CH_2—CH_2\\ |\quad\ |\\ Br\quad Br\end{matrix}$ in CCl_4 ; % anti = 90%; % gauche = 10%.

(3) For $\begin{matrix}CH_2—CH_2\\ |\quad\ |\\ Y\quad X\end{matrix}$ or $\begin{matrix}CH_2—CH_2\\ |\quad\ |\\ Y\quad X\end{matrix}$ if there is possiblity of formation of H-bonding then gauche conformaton is generally stabler than anti.

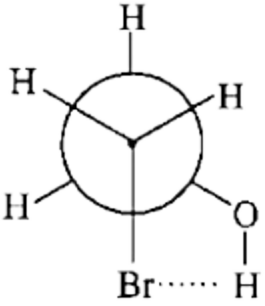
For example ;



(2-Fluro ethanol)

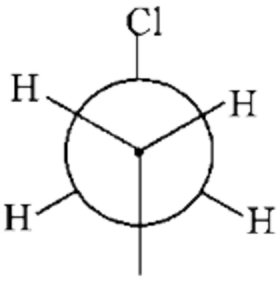


(2-chloro ethanol)

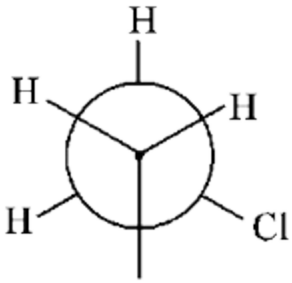


(2-Bromo ethanol)

$CHCl_2 – CHCl_2$, $CHBr_2 – CHBr_2$ also prefer gauche conformation, but $CHF_2 – CHF_2$ prefer anti. With 1–Chloropropane,



(Stable in the solid state)



(Stable in the liquid)

In liquid state larger interaction among molecules may arise due to dipole-dipole attraction which is large in II and less in I.

For any conformational analysis we must analyse the followings as to state which conformation is stable.

(1) van der Waal's strain or steric strain

(2) Torsional stain ie. bp – bp repulsion

(3) Angle strain (i.e. any state of deviation from the theortical angle)

(4) Hydrogen boding

(5) Dipole-Dipole repulsion.

Conformation of cyclobutane, cyclopentane, cyclohexane

In 3-D space cyclobutane is non coplanar, and carbon atoms remain on two planes with an angle of 20° between them.

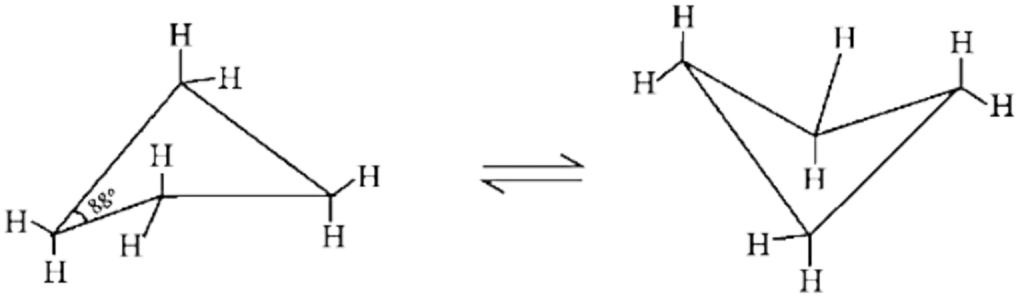


Fig. Puckered ring structure

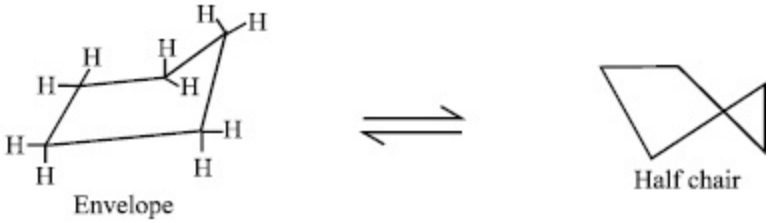
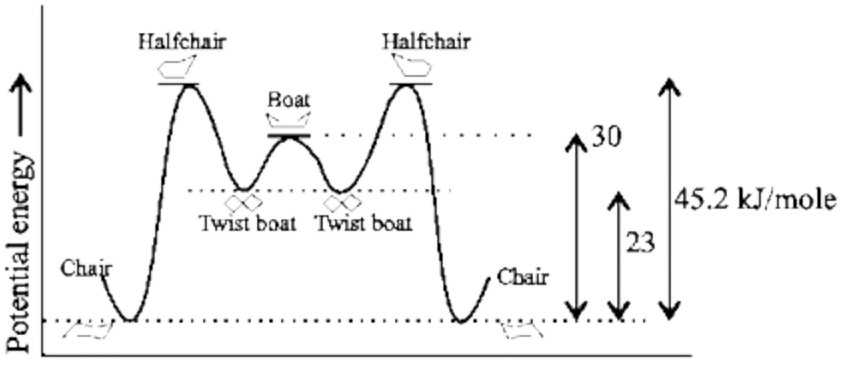


Fig. Puckered ring structure of C_5H_{10}

Cyclopentane mainly exists in envelope from as well as half chair form. In envelope form four carbon atoms lie on one plane and one out of the plane only. Substituted cyclopentane exists in envelope form.

For the cyclohexane, four types of conformations have been found. These are chair, half chair, twist boat, boat. The following figure will show the position and energy wise plot.



Among all the conformations of cyclohexane chair conformation is maximum stable as there is no

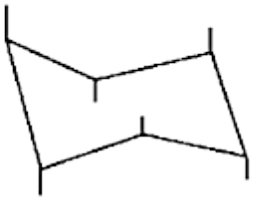
(1) van der Waal's strain or steric strain,

(2) torsional strain,

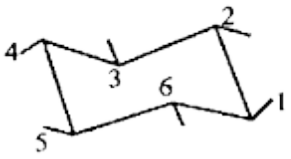
(3) angle strain,

(4) dipole-dipole repulsion.

To draw chair conformation we will draw in the following way and put the groups or atoms at equatorial or axial bonds.

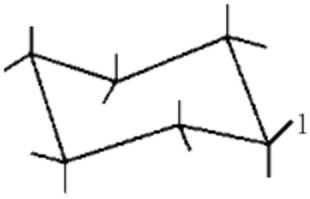


Axial bonds are drawn vertically up and down alternatively

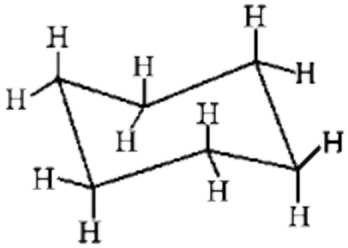


Equatarial bonds are shown in which $C_1(eq) \parallel C_2 - C_3$, $C_2(eq) \parallel C_3 - C_4$ etc.

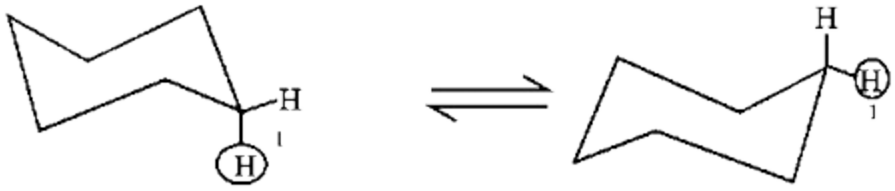
So, taking both axial and equatorial bonds we get



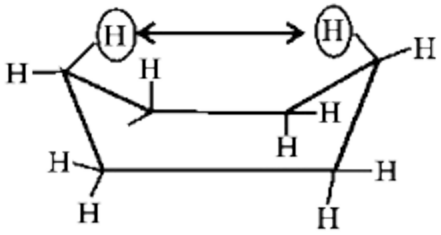
So cyclohexane  should be expressed as,



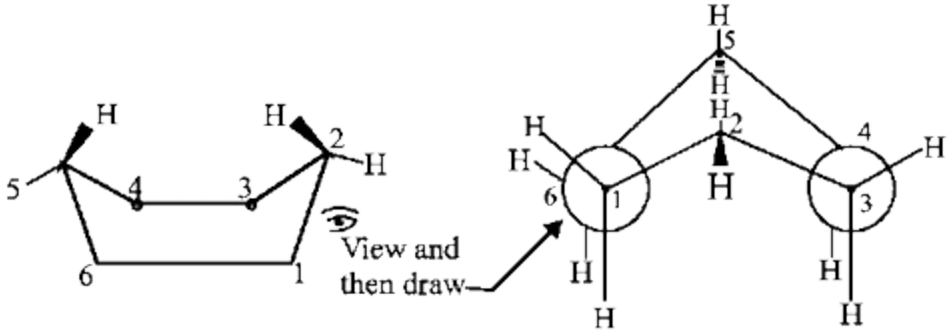
and it remains in equilibrium with its another form which is called as flipped form as shown below;



Rounded Ⓗ atom initially was axial but after flipping it will be equatorial. Likewise all groups will behave in the same fashion. In the boat form the rounded H atoms repel strongly and are called as flagpole hydrogen atoms and has flagpole interation between them. Therefore van der Waal's repulsion, torsional strain due to bp-bp repulsion etc. exists and therefore it is of high energy.

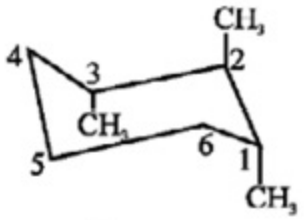


Newmann's projection of cyclohexane in its chair form is as the following ;
It is clear that chair form represents staggered conformation of cyclohexane.

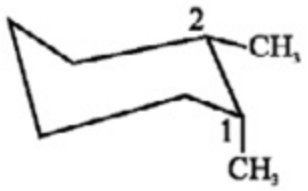


Newmann's projection shows the eclipsed conformation of cyclohexane when itamunes boat from ;

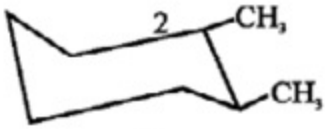
Geometrical isomerism in cyclohexane :



trans



cis



trans



cis

Therefore (1a, 2a) is trans along with (1a, 2a) etc as shown. So,(1a, 3a), (1a, 4e), (1a, 5a), (1a, 6e) etc. are cis isomers. Cis in the sense that the groups are in the same direction but trans means the groups are in the opposite direction (may be directly diametrically or in tilted mamer).

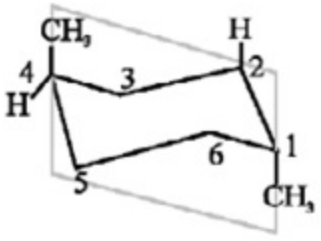
Stereoisomerism in disubtituted cyclohexane using chair conformation :

Case : 1

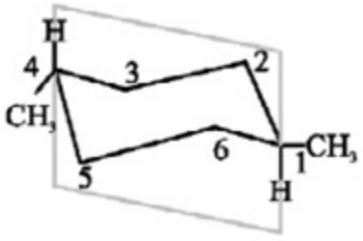
For 1, 4 dimethyl cyclohexane ;



Plane passing through $C_1 - C_4$ vertically, cuts the molecule into two idential halves, therefore it is σ -plane and no optical activity therefore arises. For, trans(1, 4) dimethyl cyclehexane, the plane passing through $C_1 - C_4$ is the σ -plane.

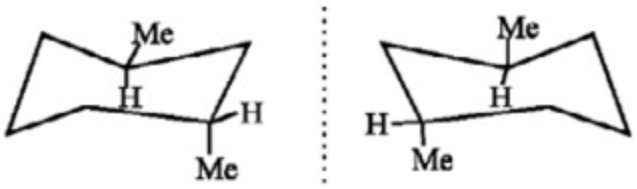


or

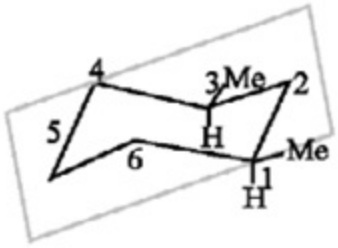


Case : 2

For 1, 3 dimethyl cyclohexane ;



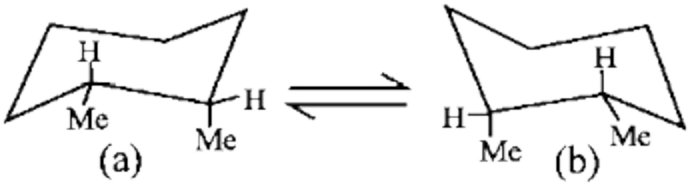
Therefore trans–1, 3–dimethyl cyclohexane does not posess plane of symmetry. Thus d, l will appear (i.e. 2 optical isomers). For cis (1, 3) dimethyl cyclohexane, there is a plane of symmetry and therefore it is optically inactive.



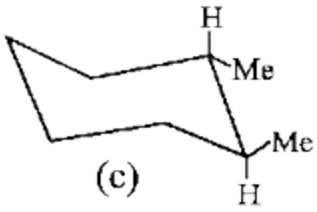
Case : 3

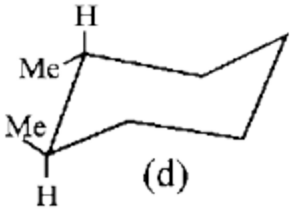
For 1, 2 dimethyl cyclohexane ;

Like wise cis will not have plane of symmetry but the mirror images are nothing but interconvertible from one to the other by flippling. Therefore they cannot be separated and they act as the optically inactive mixture.



With trans 1, 2 dimethyl cyclohexane clearly there is no plane of symetry so, two optical isomers (d, l) exists.





Therefore (c, d) are called configurational stereoisomers and (a, b) are called conformational enantiomers or stereoisomers.

So, in total three isolable stereoisomers are present for 1, 2 dimethyl cyclohexane molecule.

Resolution of Racemic Mixture

The mixture of d, *l* forms in equal proportion (50% each) is called racemic mixture. Many chemical compounds occuring in animals are in pure enantiomeric form. But while synthesis of the same compound is carried out in laboratory often we come across the racemic mixture. Therefore it becomes necessary to separate the mixture into pure d and pure *l* .

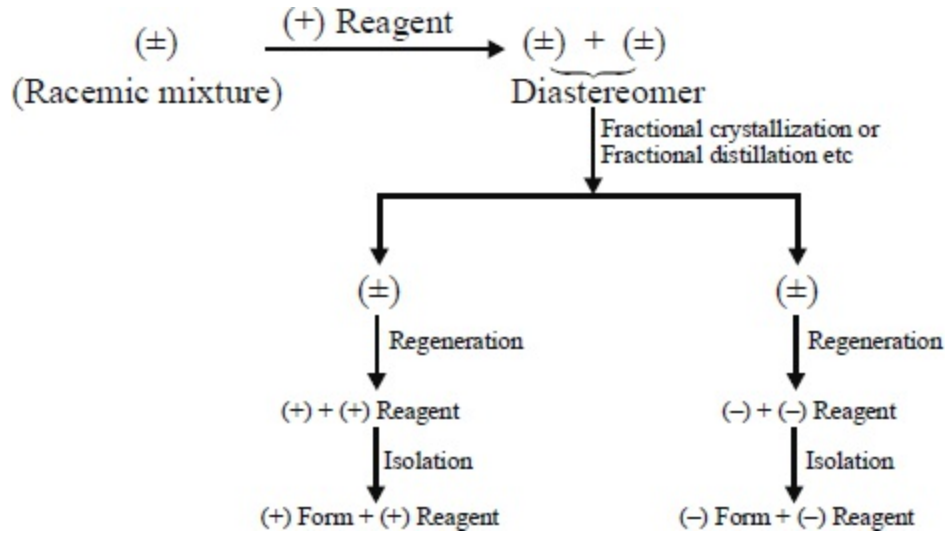
(a) Mechanical separation : +, – forms have different crystallive shapes. These are seen under a microscope and using tweezer we separate (+) and (–) form (i.e. d, *l* form). The process is tedious and it was carried out by Pasteur to separate (±) tartaric acid.

(b) Preferential crystalisation by inoculation :
(d) In a saturated solution of (±) compound, a crystal of either (+) form or (–) form is hold in the solution.(+) or (–) forms deposit on the crystal and thereby pure (+)/(–) gets separated. This is called inoculation technique and it is used in purification of (+) and (–) mostly.

(c) Chromotographic separation : (+), (–) reacts at different rate with an optically active compound (as we know rates, optical properties are different for the enantioness only) . Actually the column is made up of an optically active reagent & (±) racemic mixture is allowed to fall through the bed. As they have differential rate of reaction (i.e. adsorption), so one is adsorbed first compare to other isomer. After the column is eluted (method) with suitable reagent, one comes first which forms unstable diastereomer and comes later and colleted in two different containers.

(d) Biochemical separation : Living organisms have enzyme which are optically active and react at different rates with a pair of enantiomers. Actually this process is called as biochemical separation and it has limited use as to find the proper organism and we lose one set of enantiomer to get another. Living organism eats up one in preference to the other.

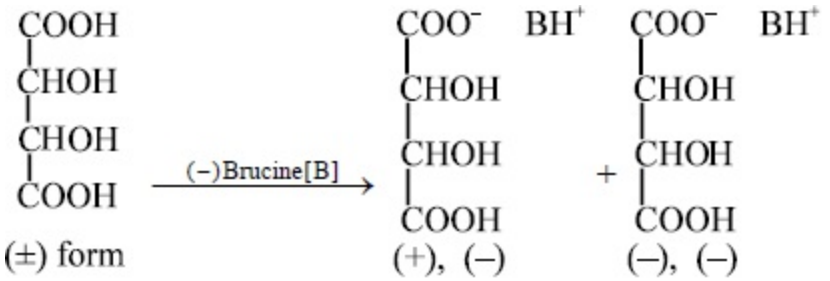
(e) **By diastereomer formation :** This is the mostly applied technique. Diasteromers have different physical and chemical properties. Therefore once we make the diastereomer from (±) form, immediately we separate the diastereomer by fractional distillation or fractional crystallisation. Finally required treatment yields pure(+), (–) separated. The technique is very simple and look at the flow chart given below ;

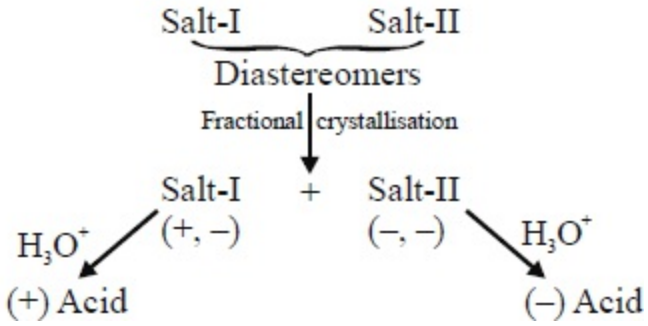


For acid :

Let us separate (±) tartaric acid i.e.  using an optically active base

(–) brucine no doubt we can use any other base (+) or (–) morphine, ephedrine etc. alkaloids.

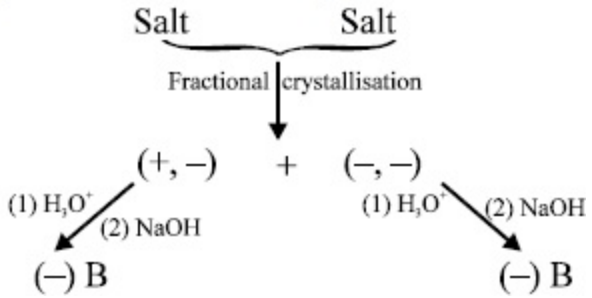




By bases :

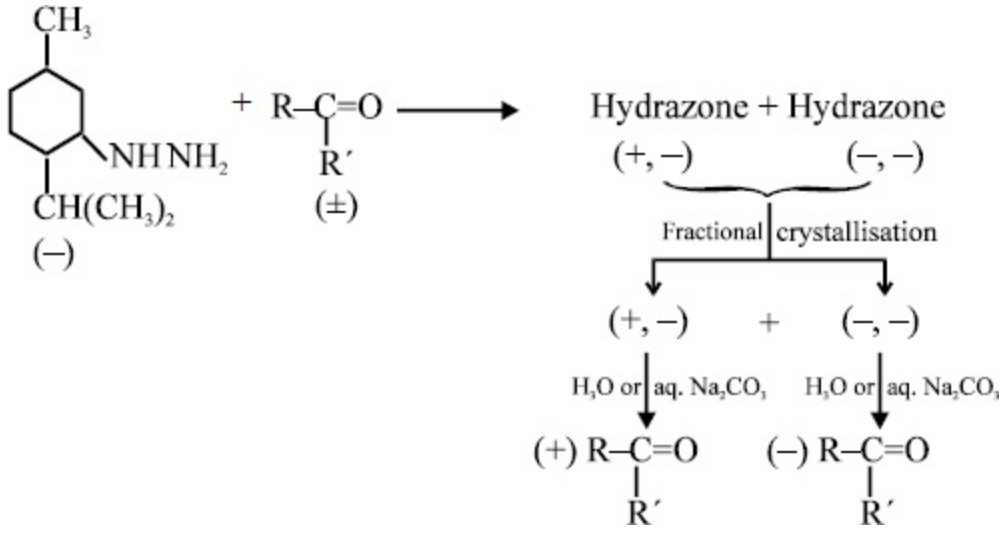
Simlarly we use optically active acids to isolate optically active bases from their racemic mixture. We use malic acid, tartaric acids etc.

$\therefore$ (±) Base + (–) acid → (±) + (=)

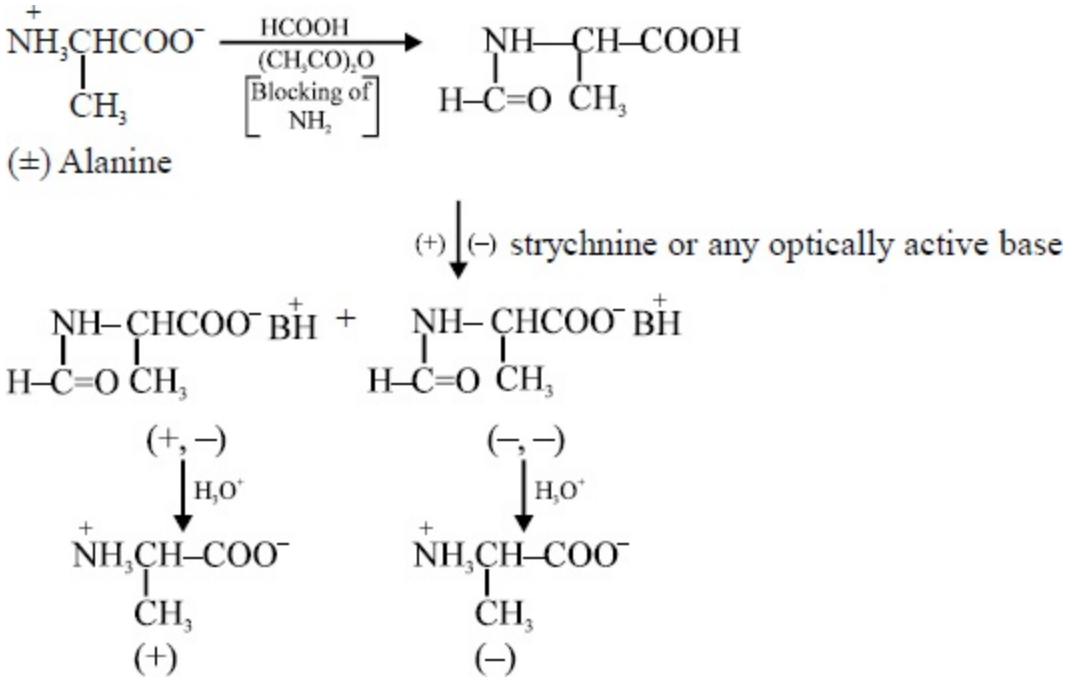


Aldehyde and Ketones :

Follow the loop given below ;

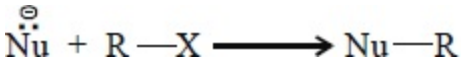

CH3
NHNH2
CH(CH3)2
(–)
+ R–C=O
R′
(±)
Hydrazone + Hydrazone
(+, –)
(–, –)
Fractional crystallisation
(+, –)
+
(–, –)
H2O or aq. Na2CO3
H2O or aq. Na2CO3
(+) R–C=O
R′
(–) R–C=O
R′

Amino Acids :


+
NH3CHCOO–
CH3
HCOOH
(CH3CO)2O
Blocking of NH2
NH—CH–COOH
H–C=O CH3
(±) Alanine
(+) (–) strychnine or any optically active base
NH– CHCOO– BH+
H–C=O CH3
+
NH– CHCOO– BH+
H–C=O CH3
(+, –)
(–, –)
H3O+
H3O+
+
NH3CH–COO–
CH3
(+)
+
NH3CH–COO–
CH3
(–)

Nucleophilic substitution and elimination

Nucleophilic substitution (S_N) means a nucleophile replaces another nucleophile. For example,


(Both charge and mass balanced equation). S_N reactions can be of several types. Following are the classifications of S_N reaction.

(1) S_N1 (Nucleophilic substitution unimolecular)

(2) S_N2 (Nucleophilic substitution bimolecular)

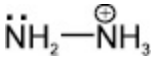
(3) S_N1' (Nucleophilic substitution unimolecular with π – bond rearrangement)

(4) SN2' (Nucleophilic substitution bimolecular with π – bond rearrangement)

(5) S_Ni (Nucleophilic substitution internal)

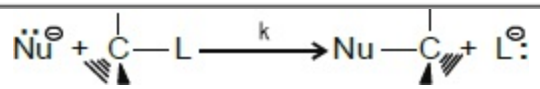
(6) S_N Th (bimolecular), which is neucleophilic substitution through tetrahedral intermediate.

These above methods are applied to aliphatic halides, alcohals etc. But ArS_N1, ArS_N2 are applied to compounds having aromatic ring.

Before going to the several ways of nucleophilic substitution we must understand what a nucleophile is. A nucleophile is primarily a Lewis base (may be negatively charged eg :  , neutral e.g.  positively charged eg:  (hydrazinium cation) etc. So lone pair donating substance (Lewis base) is called as

nucleophile and by this way we understand it is a base too. But there are differences between a base and a nucleophile.

	Nucleophile	Base
1.	These are soft bases and they attack in general $C^{\delta+}$ (i.e. partially positive charged C) which is a soft acid. Soft bases are those which have the following characteristics of the lp donating atom.	These are basically hard bases, which prefer to attack proton (which is a hard acid) and following are the characteristics of lp donating atoms of the hard base.
	(1) low electronegativity	(1) high electronegativity.
	(2) high polarisability of the electron cloud.	(2) very low polarisable eletron cloud
	(3) larger size	(3) smaller size relativity
	(4) easy to oxidise	(4) difficult to oxidise
	eg : I, Br, S, P are the donating sites of good nucleophiles.	eg : F, O, N etc. are the donating sites of good bases.
2.	To be a good nucleophile it should show large rate constant (k) of the following reaction	To be a good base the equilibrium constant (K_{eq}) should be high $B: + HA \overset{K_{eq}}{\rightleftharpoons} \overset{\oplus}{B}H + \overset{\ominus}{A}$



Nucleophiles generally show the following behaviours.

1. Nucleophile with –ive charge is always a better and powerful nucleophile than its conjugate acid (HA). Therefore $OH^{\ominus} > H_2O$, $\overset{\ominus}{N}H_2 > NH_3$, $CH_3O^{\ominus} > CH_3OH$ CH_3OH etc. It may be due to large lp-lp repulsion.
2. Keeping attacking atom in the same row of the periodic table same, nucleophilicity parallels basicity. Therefore the observed order of nucleophilicity, which has been found out $\overset{\ominus}{N}H_2 > RO^- > OH^- > R_2NH > PhO^- > NH_3 > F^- > H_2O$ and also,(all lp donat- ing atoms are sp^3 hybridised). $R_3C^- > R_2N^- > RO^- > R^-$
3. Down the group of the periodic table nucleophilicity increases but basicity decreases.For example $I^- > Br^- > Cl^- > F^-$ (nucleophilicity order) but reverse is the basicity order. Similarly $\overset{\ominus}{S}H > OH^-$
4. Adjacent to the lp donating atom if there is an atom containing unshared electron pair, the nucleophilicity is increased (This is called α –effect) eg : $H-O-\overset{\ominus}{O} > H\overset{\ominus}{O}$, $\dot{N}H_2-\dot{N}H_2 > \dot{N}H_3$ and it may be due to lp-lp repulsion between the unshared pair of electrons on adjacent atoms. But it is astonishing that the basic strength is observed to be reverse! Another

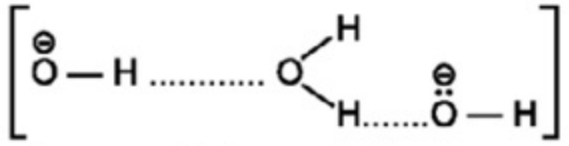
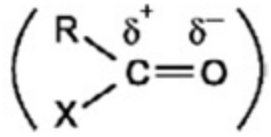
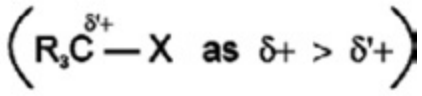
explanation can be that less solvation of the lp donating atom due to the presence of lp on the adjacent atom.

5. Also it is understood that more free the nucleophilic is, faster is the rate of reaction and therefore better is the nucleophile.

Effect of solvent on nucleophilicity :

Polar solvents like to dissolve nucleophiles. More the enveloping of the nucleophiles by the solvent, weaker will be the nucleophilicity as it loose the chance to attack the electrophilic $C^{\delta\oplus}$ site. H-bonding ion/dipole-dipole attraction are the reasons for solvation.

eg : In polar protic solvent , $\overset{\ominus}{RS} > \overset{\ominus}{I} > \overset{\ominus}{CN} > \overset{\ominus}{OH} > \overset{\ominus}{Br} > \overset{\ominus}{Cl} > \overset{\ominus}{OAc} > H_2O$. In the gas phase (no solvent is present), $\overset{\ominus}{OH} > \overset{\ominus}{F} > \overset{\ominus}{OMe} > \overset{\ominus}{Cl} > \overset{\ominus}{Br}$

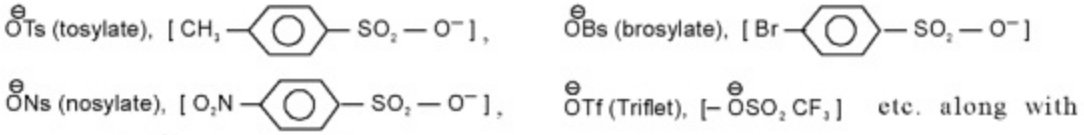
Apparent anomaly of OH– being the better nucleophile than $\overset{\ominus}{RS}$ in gas phase may be due to high lp-lp repulsion on small sized O-atom. In aq-solution H-bonding as shown on  reduces the lp donating ability of O. For substitution at carbonyl carbon, as it is much harder acid  than the alkyl –C as alkyl halide  , the following order is observed in which basicity order is almost the nucleophilicity order.

$EtO^- > MeO^- > OH^- > F^- > H_2O > Br^- \sim I^-$ [Compare pK_a values.]

Leaving group :

The groups (also leaving nucleophiles) which leave after the nucleophilic attack are called as leaving groups. Very good leaving groups are those of which conjugate acids are very strongly acidic. eg : $I^- > Br^- > Cl^- > F^-$ is the leaving ability as I $HI > HBr > HCl > HF$ is the order of acidic strength. [Actually later on we will see that best leaving groups are very much the requirement of S_N1 and they mostly take place under acidic conditions and

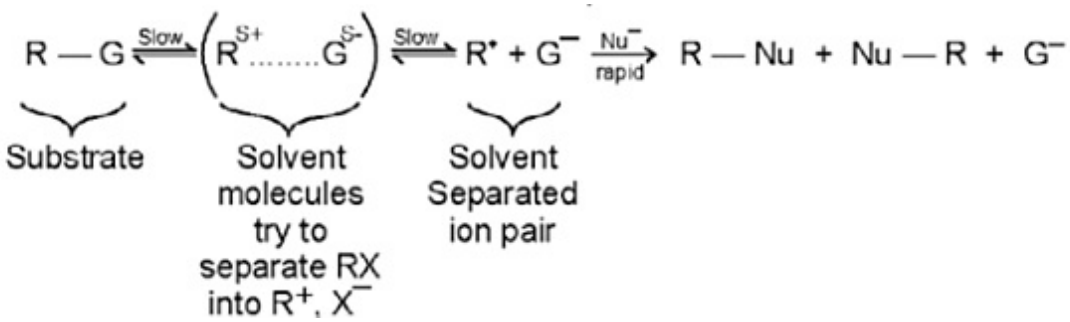
S_N2 as it requires good nucleophiles, there fore it take place under neutral or basic condition.] The good leaving groups are;



I^-, Br^-, Cl^-, H_2O, N_2, $-\overset{+}{N}R_3$, SO_4^{-2}, KSO_3^-, $RCOO^-$, NO_3^- etc. Poor leaving groups are NH_2^-, NHR^-, NR_2^-, OH^-, OR^-, H^- etc. The above concept is applied to S_N reactions at sp^3C (i.e. for $R_3C — X$). For the S_N reactions at sp^2C in $R—\underset{\underset{X}{|}}{C}=O$, the δ+ character of carbonyl-C determines the reactivity order. As such it does not reflect the actual characteristics of leaving groups still the reactivity other is, RCOCl > RCOOCOR' > RCOOR' > RCONH$_2$ > RCONR$_2$

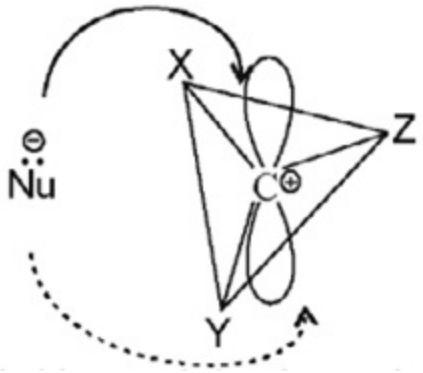
The commonly occurred SN reactions are as described below;

S_N1 : The reaction can be described as follows;

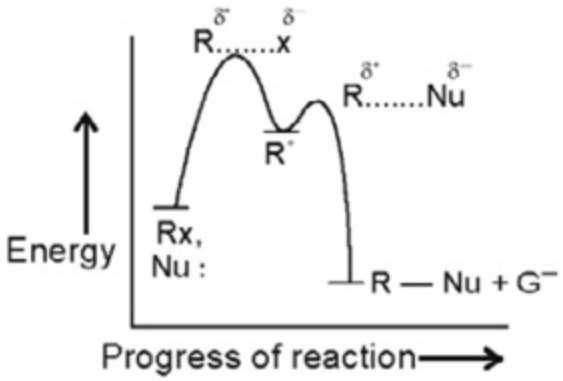


Process : Polar solvent by dipole-dipole attraction tries to separate the poles into cations and anions. Initially they form ion pairs i.e. R^+X^- and then solvent separated ion pairs.

Result : Solvent starts attacking from the back side of the cation to the leaving group and result into products. With the large stabilisation of cation both side attack increases, resulting into the equal percentage of +, – forms that is enantiomers (if the substrate is optically active)



The above figure shows the equally probable attack by the nucleophile to the free carbocation.Therefore theoretically 100% racemisation is favoured but practically more inversion and less retention occur (i.e. 5-20% inversion and 80-95% racemisation occur). Energy profile of S_N1 is,



Rate equation for S_N1, rate = k[RX].

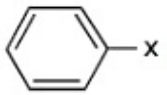
Factors on which S_N1 depends :

1. more polarisation of R—X bond,
2. more concentration of R—X,
3. polar solvent,
4. good leaving groups etc. support S_N1. Generally S_N1 reactions are carried out in polar protic solvents which act as nucleophile.

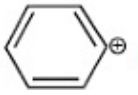
(A) Reactivity order of the substrate during S_N1 is as follows;

(Ph = phenyl) Ph_3C-X > Ph_2CH-X > ($RO-CH_2-X$, $RS-CH_2-X$, R_2N-CH_2X) >

R_3C >>> X > $PhCH_2-X$ > $-\overset{|}{C}=\overset{|}{C}-CH_2-X$ > R_2CH >>> X > (RCH_2 >>> X ≅ $R_3C\,CH_2-X$) >

$-\overset{|}{C}=\overset{|}{C}-X$ > $RCO-CH_2-X$ >  and the corresponding cations are ; Ph_3C^+,

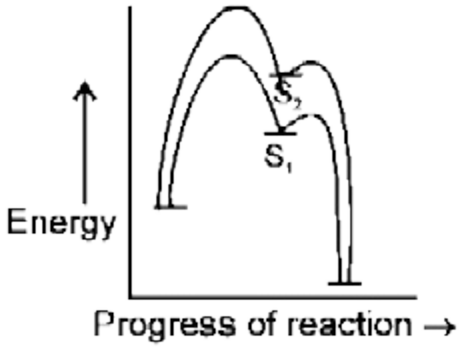
Ph_2CH^-, ($RO-CH_2^+$ $RSCH_2^+$, $R_2NCH_2^+$), R_3C^+, $PhCH_2^+$, $-\overset{|}{C}=\overset{|}{C}-CH_2^+$, R_2CH^+, (RCH_2^+, $R_3C\,CH_2^+$)

$-\overset{|}{C}=\overset{|}{C}^+$, $RCOCH_2^+$,  respectively.

The reason of Ph_3C — X being at the top is the stability of Ph_3C^+ is due to extensive resonance of +ive charge in three benzene rings. The above

reactivity also tells us the order of stability of cations in solution and down the table, the stability of cation decrease and therefore the S_N1 reactivity also decrease for the substrates respectively.

2. We can also observe that more the reactant polarity S_N1 will be more favoured as stabilisation of C^+ take place more in S_1. S_1 is having more dielectric constant (more useful term) than S_2 .

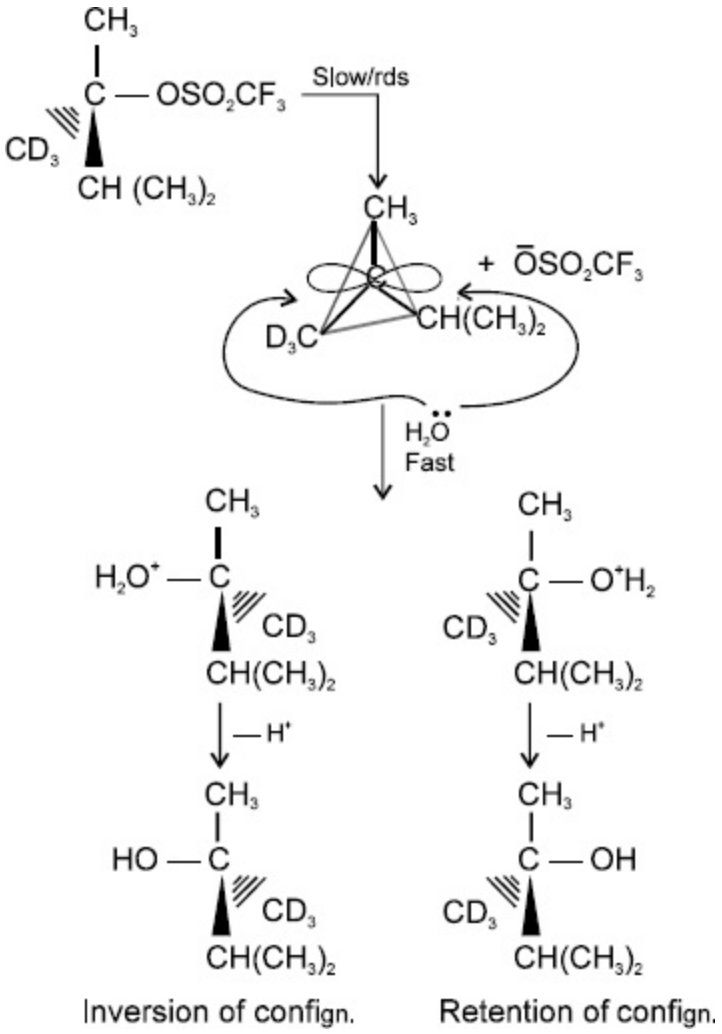


Look at the following useful dielectric constant (approximate) values for various solvents below.

According to the dielectric constant values the solvents can be arranged in the increasing order given as follows –

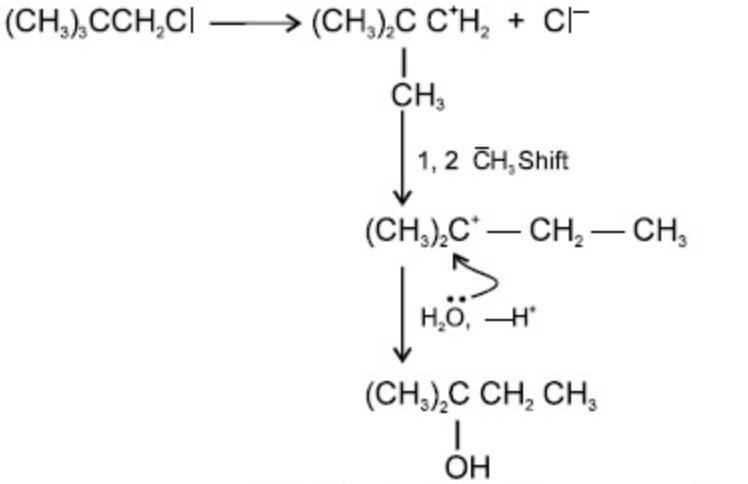
$CH_3COOH(5) < CH_3COCH_3 < CH_3OH < HCONMe_2$ (DMF) $< (CH_3)_2S = O$ (DMSO) $< HCO_2H < H_2O$ (81) For S_N1 ($C_2H_5OH + H_2O$) or ($CH_3OH + H_2O$) are good solvents as most halide does not dissolve in pure water.

Example 1 :



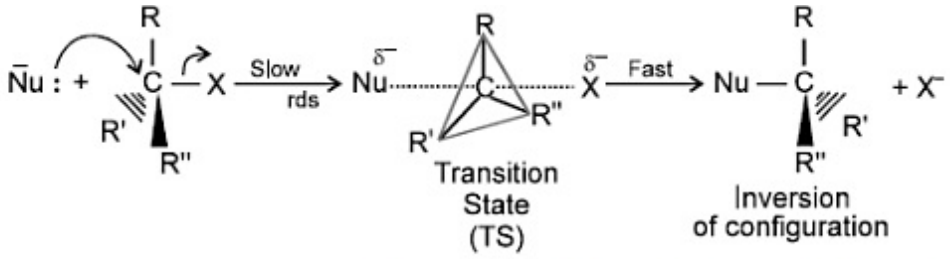
Inversion of config. Retention of config.

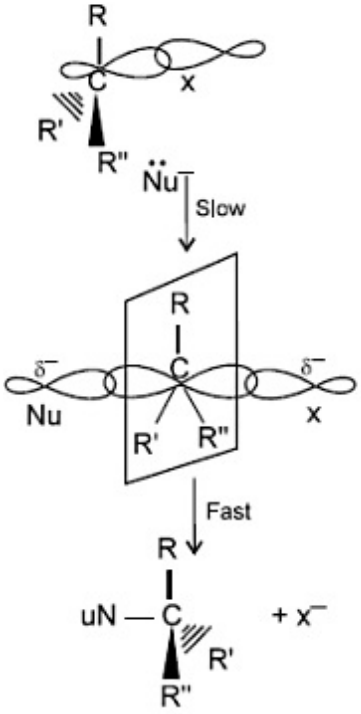
Example 2 :



3° cation is stabler than neopentyl cation therefore first step is very slow.

S_N2 : The process can be shown diagrametically as follows ;

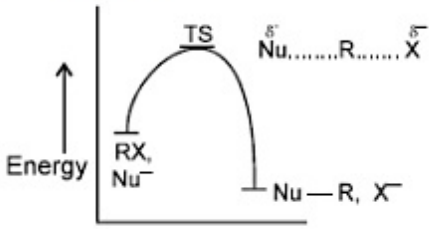




S_N2 reaction with the orbital diagram has been shown in the adja cent diagram. Here bond breaking and bond making take place at a time (which is called as transition state) and C- has 5 valency, 3 are full and 2 are partial. Leaving group and incoming nucleophile are at 180° to each other and crowding is observed. From the characteristics of T.S. we understand that excessive crowding at α–C reduces the S_N2 rate of reactivity as groups interact with $\overset{-\delta}{Nu}$, $\overset{-\delta}{X}$ at 90° to each other. But it is true that more $\delta+$ charge on C more the Nu^- is attracted towards the electrophilic centre and faster is S_N2 .

Result : 100% inverted product results (i.e. R → S or vice versa)

Energy profile of S_N2 is given as follows ;



Progress of reaction

Factors influencing S_N2 :

1. The effect of substrate structure :

As it is evident that less the $\delta+$ charge and α – branching S_N2 rate will decrease. Therefore $(CH_3)_3C-X$ will show least S_N2 rate and CH_3X will show maximum S_N2 rate. Also, T.S. with 3° halide will be of high energy as small sized —C atom will be highly sterically crowded. Similarly —I group at α – C increase S_N2 rate. There fore the reactivity rate is,

$PhCH_2X > G\text{–}CH_2X > -\overset{|}{C}=\overset{|}{C}-CH_2-X$ $(sp^2) > R\,CH_2-X \cong RCHO\text{–}CH_2X > R_2CHX > R_3C-X > -\overset{|}{C}=\overset{|}{C}-X$ (vinylic halides) > Ph—X, Where G = RCO—, HCO—, $ROC(=O)-$ etc.

— I (i.e. electron withdrawing) groups.

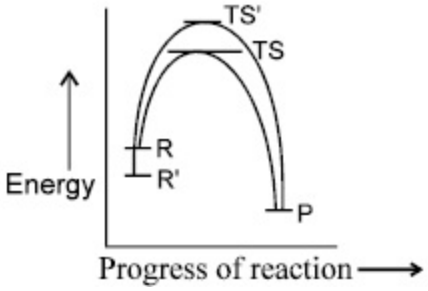
2. Better the leaving groups, faster will be the

S_N2. eg : $I^- > Br^- > Cl^- > F^-$ and $H_2O > R{-}OH > OH^-$ which are conjugate bases of weak acids and they are weak leaving groups. Leaving ability of the groups generally is, $OTf > OTs > I > Br > Cl > H_2O^+ > F > OAc > N^+R_3 > OR > NR_2$ and that way S_N2 will also be favoured as faster the leaving group leaves it assitst the nucleophile to make bond with electrophilic carbon (as can be observed in S_N1 reaction).

3. Especially less polar protic solvents assist S_N2 reactivity For example,

Case - I ; $\bar{N}u + \overset{\delta+}{R}{-}\overset{\delta-}{X} \longrightarrow \overset{\delta-}{Nu} \ldots\ldots R \ldots\ldots \overset{\delta-}{X} \longrightarrow Nu{-}R + X^-$

Energy profile is :

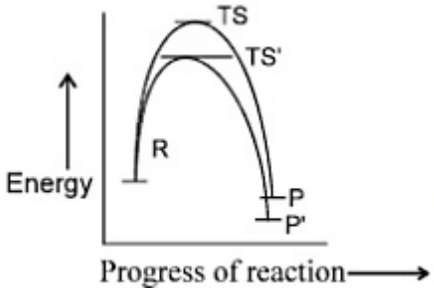


In polar solvent (like protic solvents) stabilisation of reactants at R' and T.S. will be at TS' position. So, E_{act} will be higher. Therefore the polar aprotic solvent which will solvet the Nu^- ($^-$ charge) less and TS will be of lower energy causing S_N2 rate faster . Case – 2 :

$\ddot{N}u + R{-}X \longrightarrow \overset{\delta+}{Nu} \ldots\ldots R \ldots\ldots \overset{\delta-}{X} \longrightarrow Nu^+{-}R + X^-$

(Neutral)

Energy Profile is :

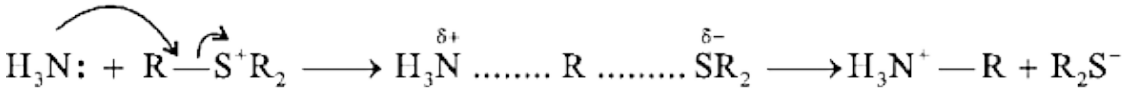


(TS', P') for polar protic solvent

Polar protic, aprotic solvents both will not stabilise the reactants and TS at large difference but obviously product will be stabilised much by the polar protic solvents. Therefore as far as the rate is concerned, it will not be affected much but definitely rate will be increased for polar solvent as TS' is

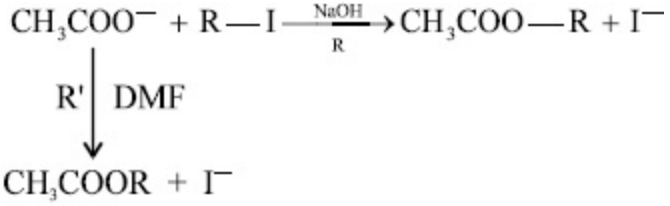
nothing but the opposite charge separated species and will be liked by polar protic solvents.

Case – 3 :



Here also, charged species (R_3S^+ , R_4N^+) etc. will be much stablised by polar protic solvents (like dissolves like) and automatically the S_N2 rate will reduce. In conclusion if the H_2O or $C_2H_5OH + H_2O$ etc. polar protic solvents then OH^- , NH_2^-, F^-, Cl^-, N_3^- etc. nucleophile react slowly due to H-bonding with the solvent and greater solvation of the anions reduced S_N2 . But if we change the solvents to DMF, DMSO (polar aprotic), the S_N2 rate jumps, For

example ;



$R' \cong 10^7 R$

Therefore preferably less polar aprotic solvents are very good solvents for S_N2 .(eg : CH_3COCH_3, DMF, DMSO etc., see the list of solvent given earlier).

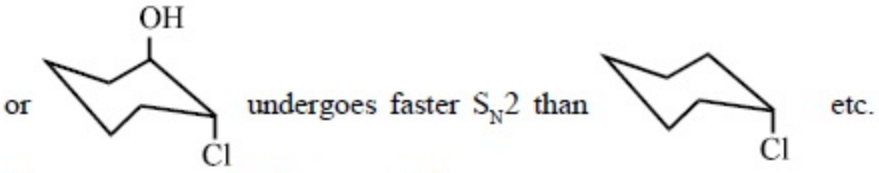
4. Nucleophiles should also have high nucleophilic activity, i.e. they should be good soft bases. $C^{-}: > N^{-}: > O^{-}:$ or $I^- > Br^- > Cl^- > F^-$ etc. are the nucleophilicity order.

Overall S_N2 reactivity order of nucleophiles in polar solvent has been found to be $RS^- > I^- > CN^- > OH^- > Br^- > Cl^- > AcO^- > H_2O$

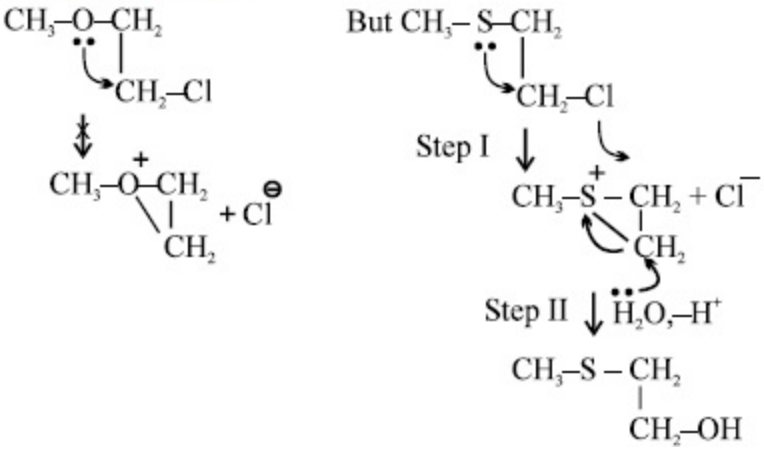
RS^- to CN^- we can well explain on the basis of soft centre. OH^- on the basis of electron density (lp-lp) repulsion sitting on small sized atoms want to be donated (exception). Again Br^-, Cl^- from the point of view of solvation and lastly low electron density can well explain $AcO^- > H_2O$.

5. NGP or anchimeric assistance support S_N2 rate.

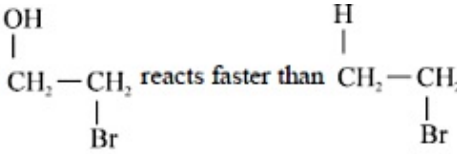
Neighbouring group participate as or anchimeric assitance is observed when some compounds are found to react faster than expected for example; $CH_3SCH_2CH_2$–Cl hydrolyses slower than $CH_3SCH_2CH_2Cl$

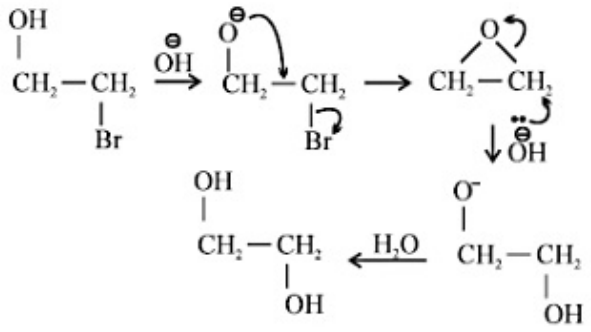


The reason may be shown as follows ;



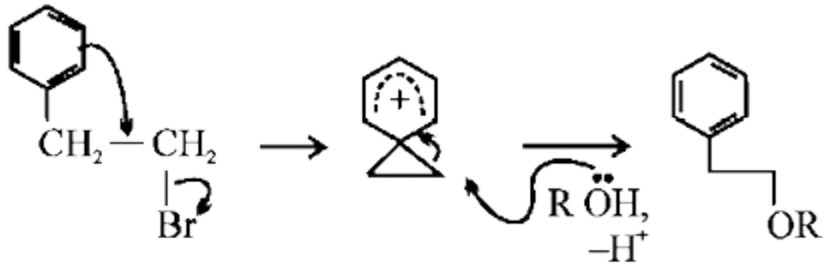
As 'O' cannot hold positive charge, therefore it cannot internally replace $\overset{\ominus}{Cl}$, whereas 'S' being less electromagnative, it can easily hold positive charge so it easily replaces Cl by S_N2. Another S_N2 reaction takes place by H_2O molecule to open up the strained ring, which leads to the product. Therefore two consecutive S_N2 processes lead to retention of configuration. The rate has been found to be first order that is step I is the slowest step.

Some more examples are ;  reacts faster than with aq. KOH due to the following reason ;



i.e.clearly not the OH but the $\overset{\ominus}{O}$ from antiperiplanar arrangement knocking out Br. By NGP when 3/ 5/6 membered ring forms, the reaction has been found to occur rapidly.

The following are the neighbouring groups $-COO^-$, $-\bar{O}H$, $-\bar{O}-$, $-\ddot{N}H_2$, $\ddot{N}R_2$, I, Br, Cl etc. Other than those phenyl ring or activated phenyl rings also can take part in anchimeric assitance.
For example;

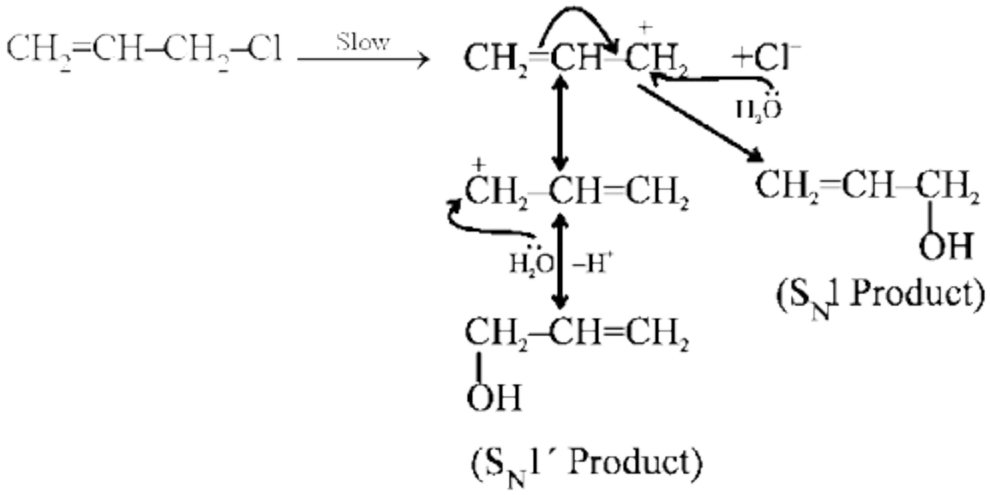


It is found that (ROH < CH_3CO_2H) more less the nucleophilicity of the solvent e.g.; is NGP and more the activating group at the para to the benzene ring, faster will be the reaction.

S_N1':

Sometimes S_N1 reaction occurs with π -bond rearrangement. With allylic halides this type of mechanism operates and this is called as S_N1' reaction.

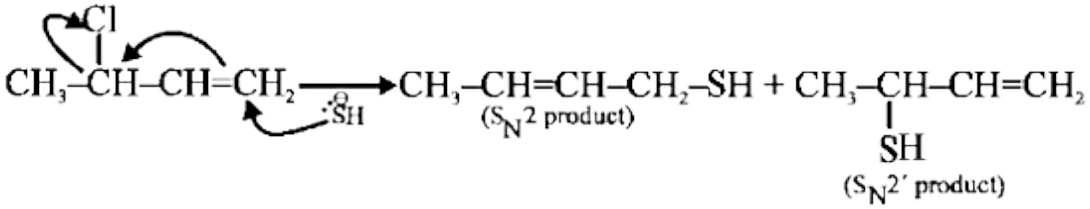
Mechanism :



Conditions of S_N1, S_N1' are the same other than the nature of alkyl halides.

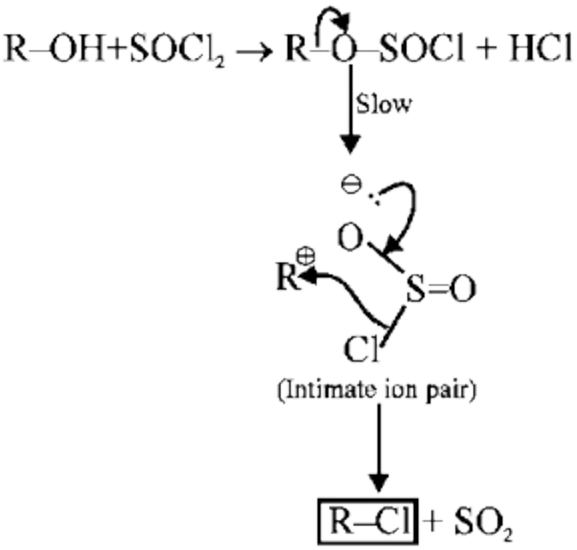
S_N2':

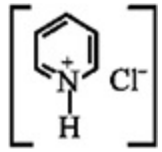
When the α -C is sterically crowded then instead of S_N2, S_N2' takes place. Else they can be competitor to eachother and π -bond shift takes place for S_N2'. For example ;

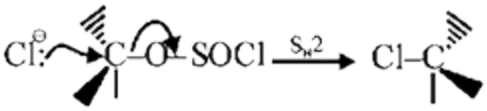


S_Ni:

In this mechanism nucleophile is supplied by the leaving group itself and attacks the C from the same side of that of the leaving group. This is called as nucleophilic substitution internal .

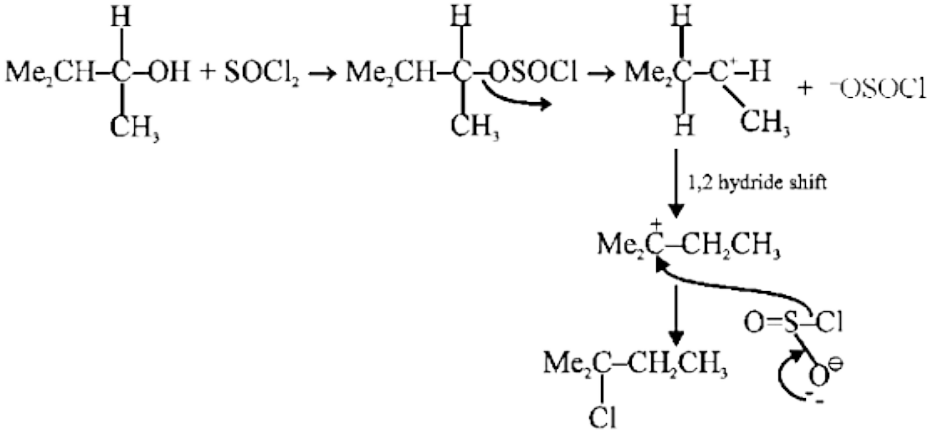


Rate of the overall reaction has been found to be , Rate = k[R–OH] [$SOCl_2$] and it is very important that retention of configuration takes place in the product . In presence of pyridine, sal  pyridimim chloride forms and therefore $Cl^{\ominus}$ becomes free and attacks the chiral-C from the diametrically opposite side of the leaving group in which S_N2 reaction takes place

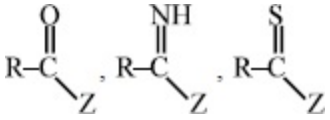


Inversion of configuration)

Note : It has been found that migration in carbenium ion is also possible as shown below ;

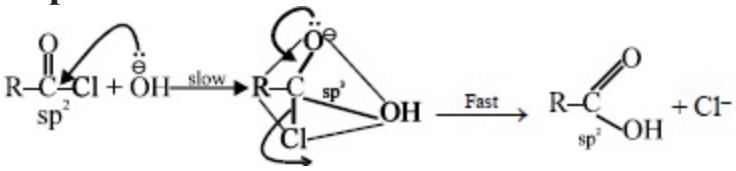


S_N reaction at sp2 hybridised aliphatic C atom :



etc. can undergo S_N2(Th) i.e. nucleophilic substitution bimolecular through tetrahedral intermediate, when treated with neuclophiles like OH^-, $R^{\ominus}$ etc. Here Z is –Cl, –OH, –OR, –OCOR, $-\bar{O}Ns$, $-\bar{O}Bs$, $-\bar{O}Ts$, $-\bar{O}Tf$, $-\bar{N}H_2$ etc.

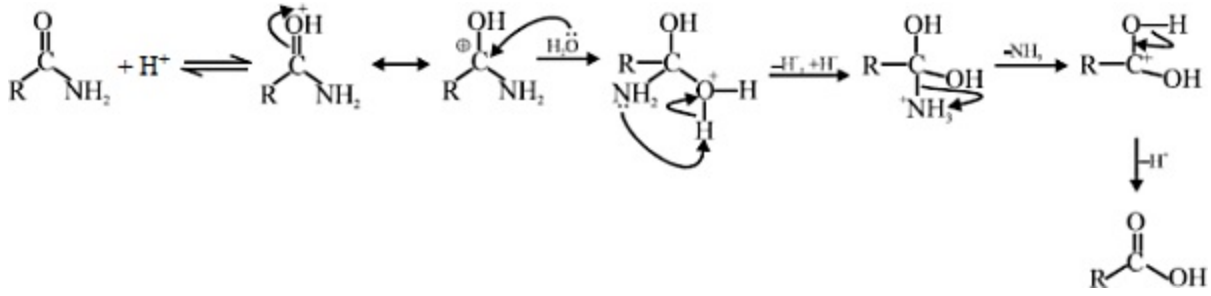
Example with mechanism:



Rate has been found to be, Rate $= k\,[\overset{\ominus}{Nu}]\left[R–C(=X)–Z\right]$, where X = O/N/S

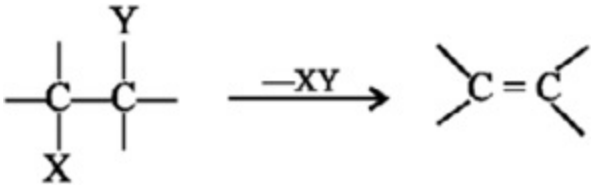
Acid catalysed SN reaction on an aliphatic sp2 C atom also takes place through this S_N2 (Th) process.

Mechanism :

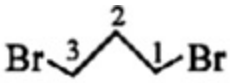

+ H+
H2O
-H+, +H+
-NH3
-H+

Elimination

If a compound loose two groups from two adjacent carbon atoms, then the process is called elimination. In simple manner we can understand that ,



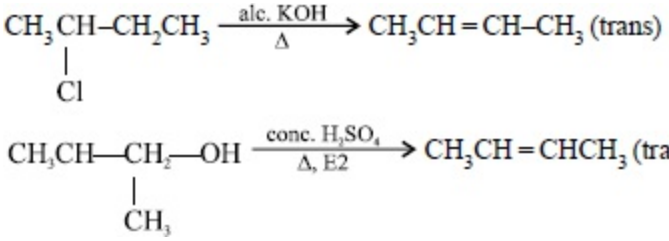
Therefore by the loss of two groups a double bond or unsaturation comes in.Very rarely 1, 1 and 1, 3 eliminations are also observed.

eg., $CHCl_3 \xrightarrow[\Delta]{\bar{O}H} :CCl_2$,  $\xrightarrow[\Delta]{Zn}$ △ + $ZnBr_2$

Elimination can be of several types E1, E2, $E_{1C}B$, Ei. By 1, 2 elimination we can create C = N, C = O, C = S, N = N – etc. There can be two kinds of elimination modes, as far as the product formation is concerned.

(1) Sayetzeff's elimination, in which product alkene attains stability by hyperconjugation only. With smaller base (i.e. unhindered) or in the substate if Cl, Br, I like leaving groups are present then the product becomes Sayetzeff's product. Also dehydration of 1° alcohol by concentrated sulphuric acid and 2°, 3° alcohol by dilute sulphuric acid upon heating leads to predominantly Sayetyeff's product. There can be rerrangment
possible in some cases also.

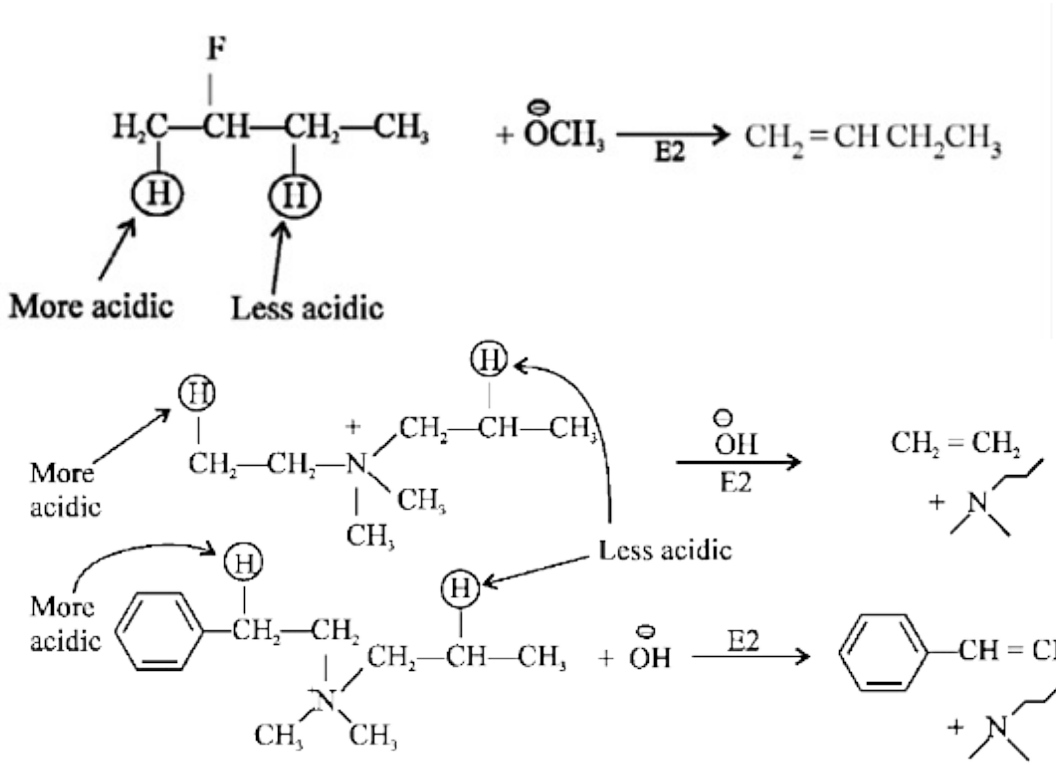
For example ;



(2) Hofmann's elimination in which, compounds containing leaving groups like F, NR_3^+, $–SR_2^+$, $–PR_3^+$ etc. upon action with base (smaller) leads to

Hofmann's product. In Hofmann's product we do not consider the double bond stability by hyperconjugation. With bulkier bases like $t\text{-BuO}^{\ominus}$ etc. even for chloro, bromo, iodo alkanes Hofmann's products result .

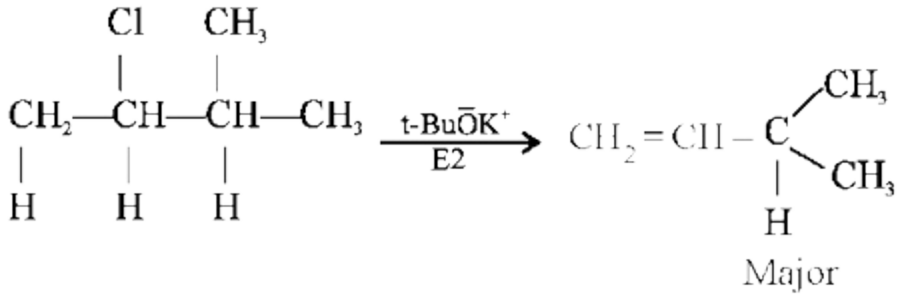
We should know how Hofmann's elimination occur?



So, in every cases we find that base has only choice to pick up that H which is

(a) more acidic – H , (b) least hindered –H and (c) which accounts for the stability of the product by conjugation, not the hyperconjugation.

Also,

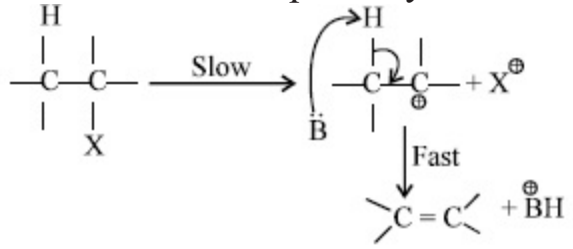


i.e., base can approach that acidic H which is less crowded when the base is bulky. With increasing size of base as well as good leaving group Hoffman's

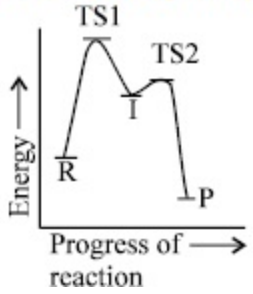
product is found to dominate over Sayetzeff's product experimentally.

E1 (Elimination unimolecular);

The mechanism folows the pathway as shown below;



Rate has been found to be Rate = k[R – X]. Energy profile is given as the following;



By the nature of the reaction pathway we can conclude that

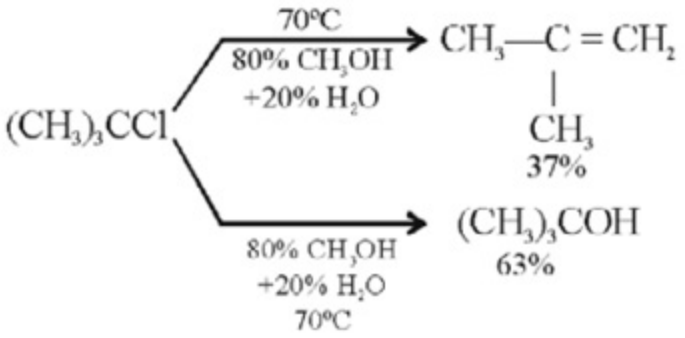
(1) 3° >2° > 1° should be the reactivity order of alkyl halide which is just like S_N1 as carbocation stability is the important issue. Halogen at bridgehead carbon do not undergo E1.

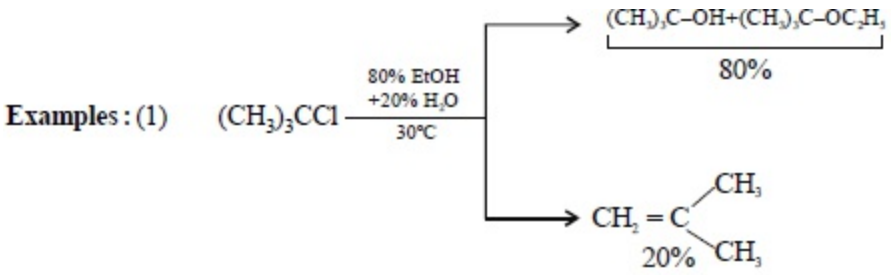
(2) Protic polar solvents act as a base. Generally we do not add base from outside and bases therefore are weak, which is the reason why S_N1 product becomes more than the competitive E1 product.

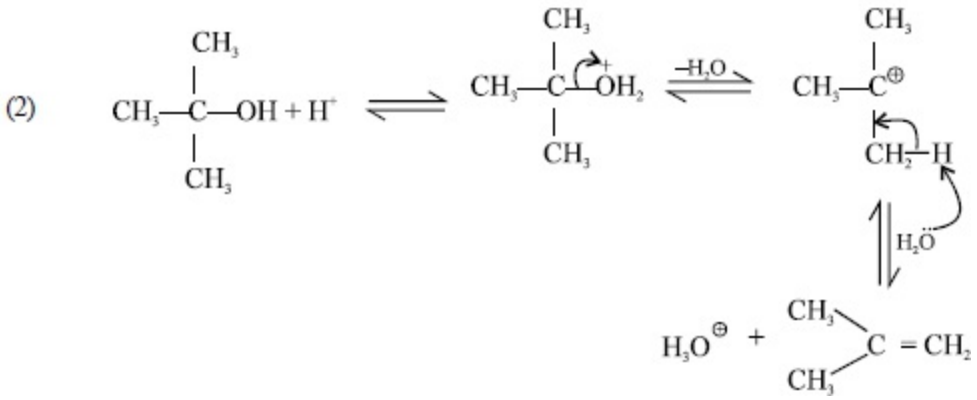
(3) Better the leaving group, easier the departure to form carbenium ion. Therefore H_2O> ROH>CH_3COO^->OH^- and I^- > Br^- > Cl^- > F^- are the leaving trend.

(4) Solvent should be polar proptic to stabilise ions. Low polar and poor nucleophilic solvents favour E1 over S_N1.

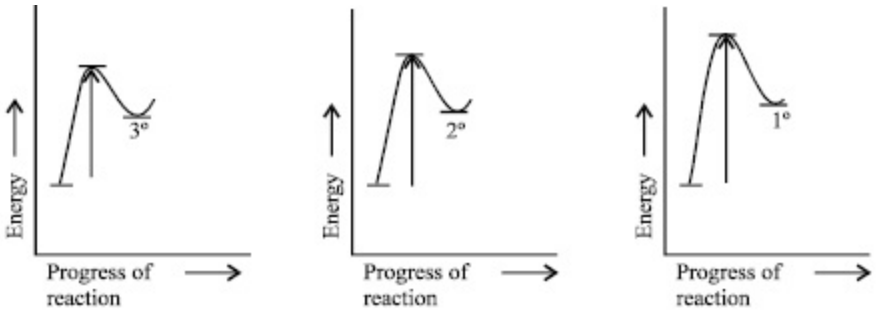
(5) With rise in temperature E1/S_N1 ratio rises as in the elimination process $\Delta S^\circ = \oplus ive$, therfore ifwe increase the temperature, Δ G° becomes highly – ive., favouring the E1 process.



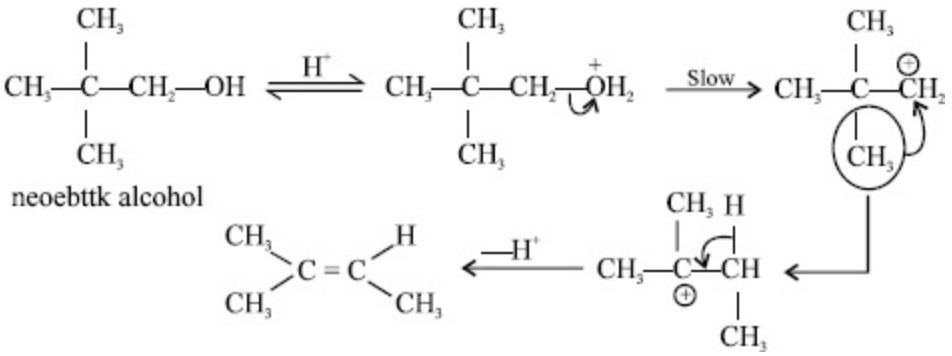




Therefore 2°, 3° alcohol always dehydrates reversibly and through E1 method. We will see later on that 1° alcohol dehydrates by E2 mnechanism. Activation energy required for 3° < 2° < 1° as shown in the following diagrams.



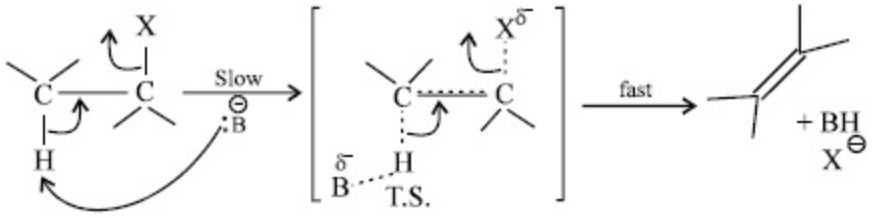
(3)



Therefore neopentyl alcohol produces Sayetzeff's product with rearrangement in presence of conc. H_2SO_4 and heating.

E2 (Elimination bimolecular)

This process takes place in a concerted step that is both the leaving groups eliminate at the same time.



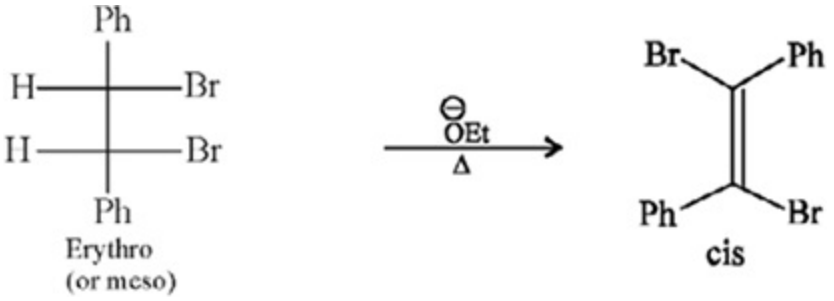
Leaving groups X can be –F, –Cl, –Br, I, $-NR_3^+$, $-SR_2^+$, $-PR_3^+$, OTs, etc.

Used bases: $\overset{\ominus}{O}R$, $\overset{\ominus}{N}H_2$, $\overset{\ominus}{O}H$ etc.

Stereochemical features for E2 to occur

(1) The leaving groups α –H and X should be anticoplanar to each other before departure as it is found that thero form gives trans olefin and erytho form gives cis olefin respectively as shown below;

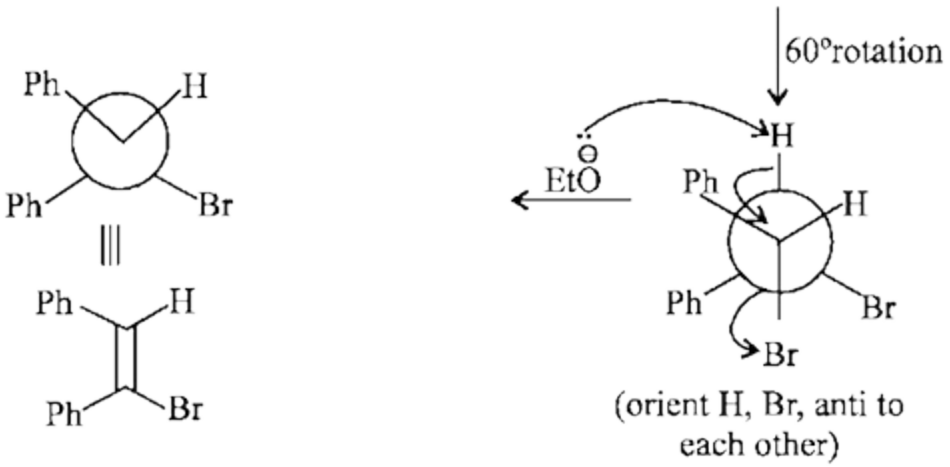
For example ;



Erythro, thero means the same groups in the same side or in the opposite side of the vertical bond i Fischer's proj ection.

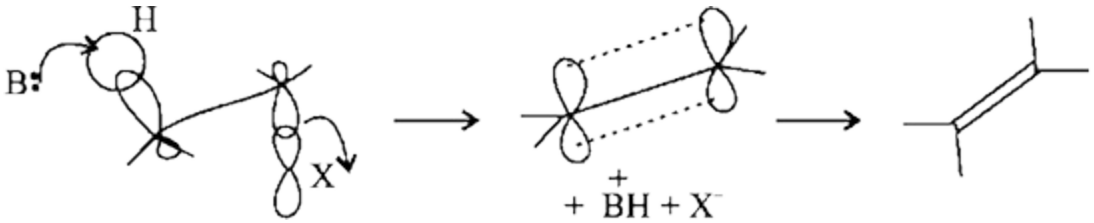
Let us see how this is possible through stereochemistry below;





So, do on your own for threo form.

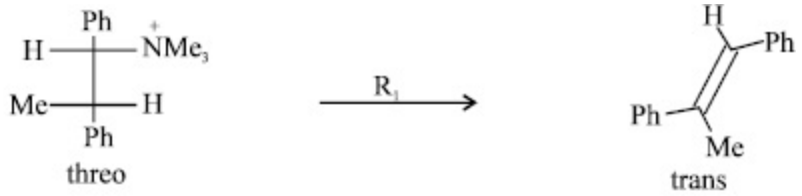
Actually why this anti orientation is required can be explained easily by looking at the orbital picture.

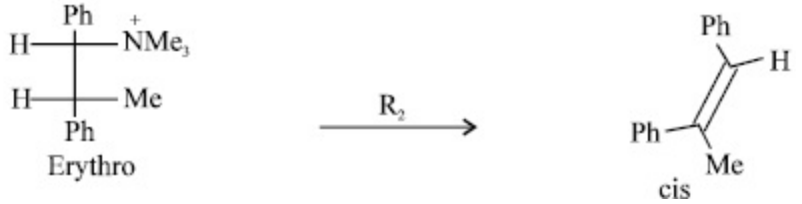


As the two orbitals are going to be free and tne parallel, they can easily make

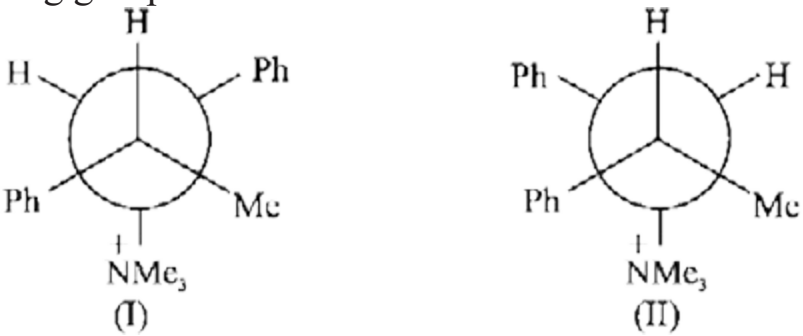
the π -bond.

Example : (1)





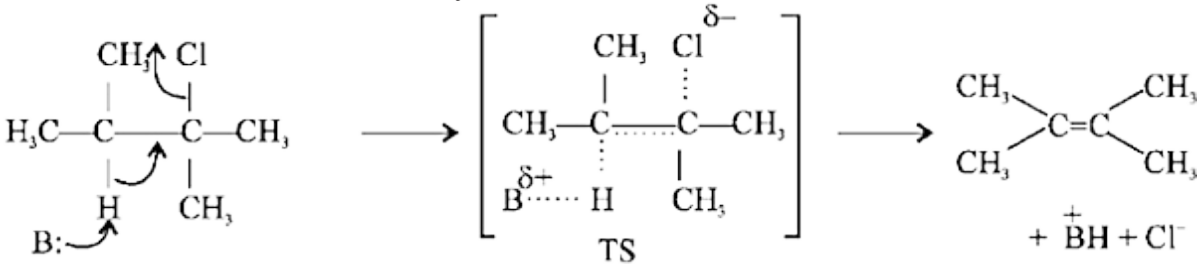
$R_2 < R_1$ as there will be Ph, Ph repulsive interaction in case of eryturo from at 60° (II) which is absent in threo form (I) while they take the anti orientaion of leaving groups.

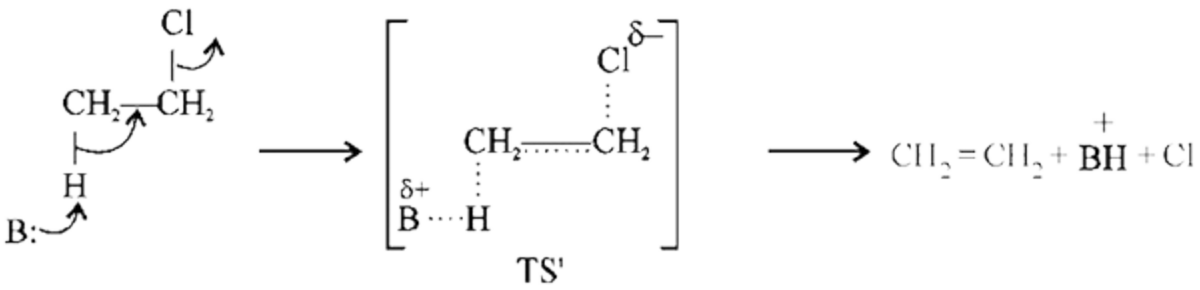


(2) Substrate Structure

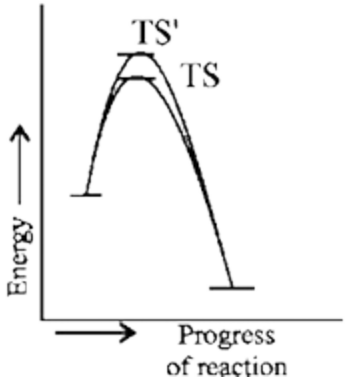
E2 reactivity is high for 3° and least for 1° (and which is not like S_N2) under the base condition. Other things are same for both E2, S_N2.

We can understand that T.S. stabilisation of E2 takes place through partially formed double bond stabilisation. More the stability of partially formed double bond more is the stability of the T.S.





Here TS from 3° halide is much more stable than that from 1° due to hyperconjugation. Therefore more branching at α , β carbon atoms more will be E2. See the following energy profile.



(3) Better the leaving groups, higher is the rate of E2 reaction, with higher polarisability, leaving ability rises

eg., eg., $I^- > Br^- > Cl^- > F^-$

(4) More the concentraion and strength of the base faster will be the elimination.

eg. $\bar{N}H_2 > \bar{O}Et > O\bar{H}$

E2/S_N2 ratio increases when basic strength increases and decreases if nucleophilicily increase of the added base.

(5) More the solvent polarity, lower is E2/S_N2.

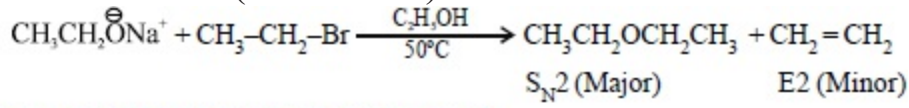
(6) With rise in temperature E2/S_N2 ratio increases.

Elimination versus substitution :

At this point we should observe that conditions of S_N1 and E1 are the same as in S_N2 and E2. Already regrading S_N1 vs. E1 it is told that high temperature and low polar poor nucleophilic solvents prefer E1 over S_N1, but percentage

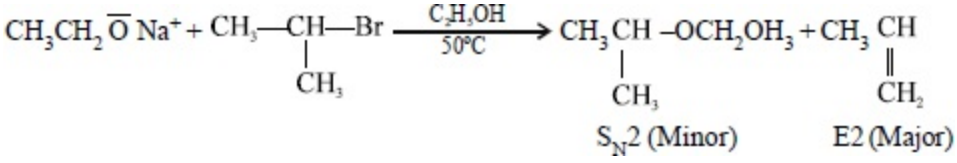
S_N1 is always higher as solvent used as a base is a poor base. For S_N2 and E2 let us have a case study,

Case I : With 1° halide (unhindered)



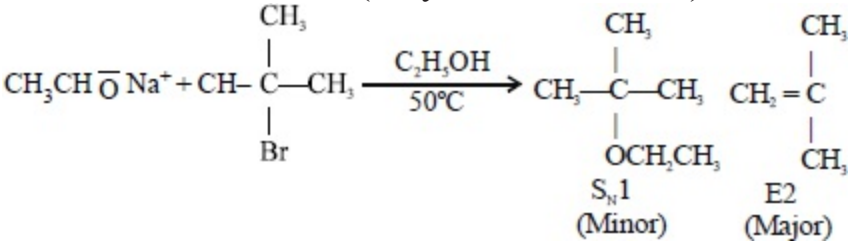
Here both the base and alkyl halide are unhindered .

Case – 2: With 2° halide (hindered)



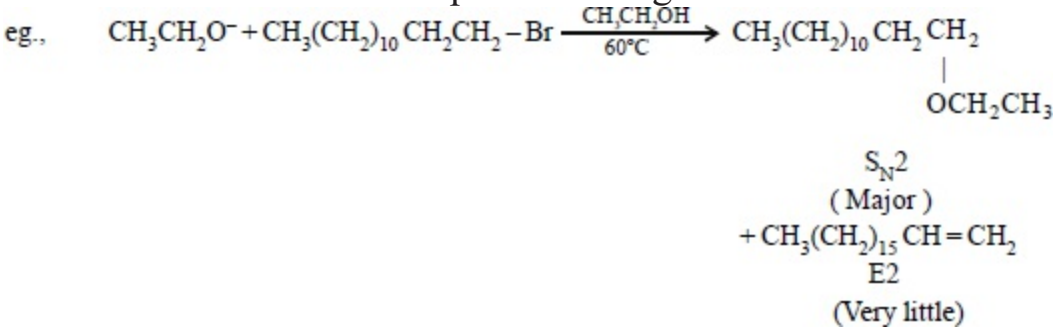
Here the base is unhindered but the substrate alkyl halide is hindered. Therefore E2 will be major as we understand that base to attacke α – C face steric crowding therefore β –H (having δ + charge) will be picked up by the base easily leading to more E2 product.

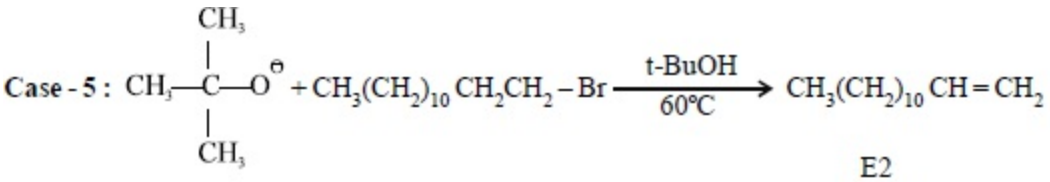
Case – 3: Wtih 3° halide (very much hindered)

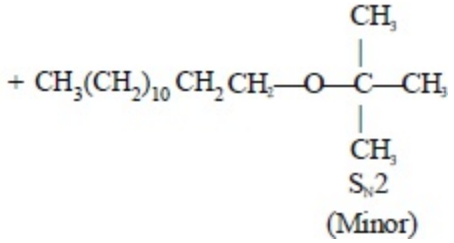


Here 3° halide is so hindered S_N2 doesnot take place at all and S_N1 takes place instead leading to only 6-8% S_N1 and 92-94% E2 product.

Case – 4 : Size of the base or nucleoophile is changed







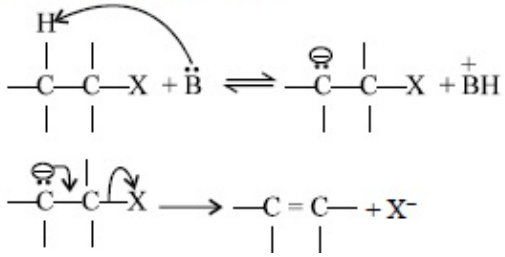
So we can understand that,

hindered base + unhindered substrate ⟶ Alkene (Major) i.e. E2 product + Minor S_N2 product
hindered base + hindered substrate ⟶ Alkene (Major) i.e. E2 product + Minor S_N2 product
unhindered base + hindered substrate ⟶ Alkene (Major) i.e. E2 product + Minor S_N2 product
unhindered base + unhindered substrate ⟶ Alkene (Minor) i.e. E2 product + Ether Major S_N2 product.

Hindrance starts from 2° substrate or 2° alkoxide base. With weaker bases like Cl^-, CH_3COO^-, or weakly basic and highly polarisable anions like Br^-, I^-, RS^- etc. $\%S_N2$ product increases but with hindered alkoxide, NH_2^- like strong bases %E2 product increases.

E_1CB (Elimination unimolecular through conjugate base)

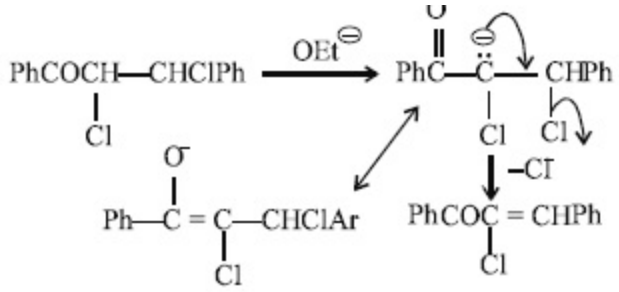
In E1, X leaves before H leaves, whereas in E2 X and H leaves simultaneously. But in E_1CB, H goes first as proton then carbanion forms reversibly (which is stable by resonance) and then X leaves. The mechanism of carbanion formation by E_1CB is,

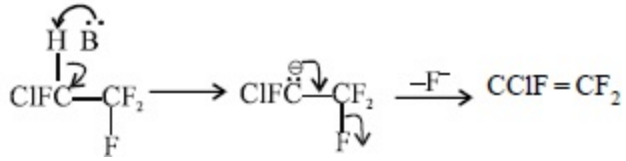


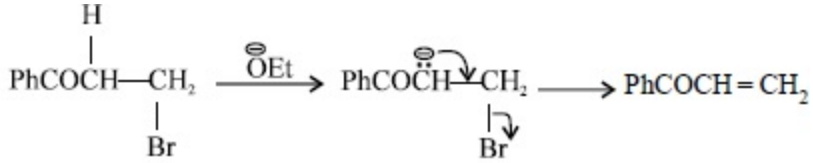
Therefore clearly carbanion stabilising groups at β-C can only support this E_1 CB mechanism.

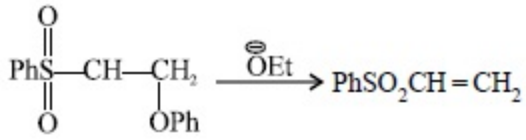
eg; $—NO_2$, , $ArSO_2—$, —CN, —CO etc. alongwith the fact the substrate should have poor leaving groups like —OPh , —SPh , $PhSO_2—$, MeO— etc.

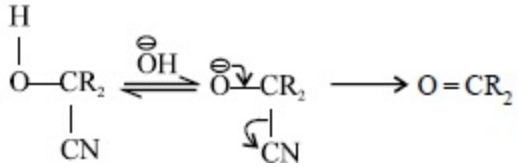
Examples are:

(1) 

(2) 

(3) 

(4) 

(5) 

In this mechanism first step is the fast step and second step is slow step and rate has been found to be rate = k [CB]. VMth increasing concentration and strength of base E_1CB increases. Polar solvents (nonhydroxylic) like DMSO increases the rate.

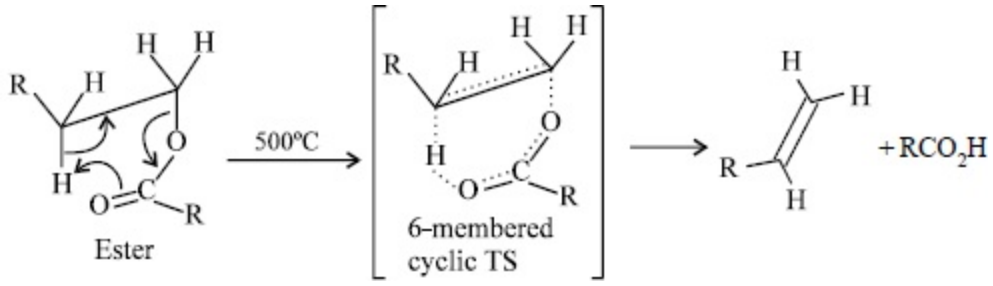
Experimentally found that there can be change over of the first step to be the rds, which is beyond the scope of this book. Hofmann's product dominates if E_1CB happens. With increase in temperature E_1CB rate rises. It is to be worth mentioning that this mechanism is very rare.

Ei (Elimination intramolecular):

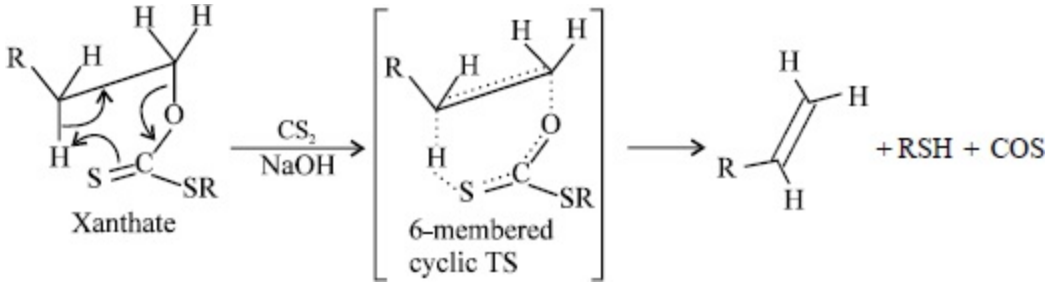
This is popularly known as syn pyrolytic elimination. Xanthates, esters, quartenary ammonium oxides undergo elimination upon heating through this mechanism only. The mechanism is given as follows with all the possible compounds.

Examples :

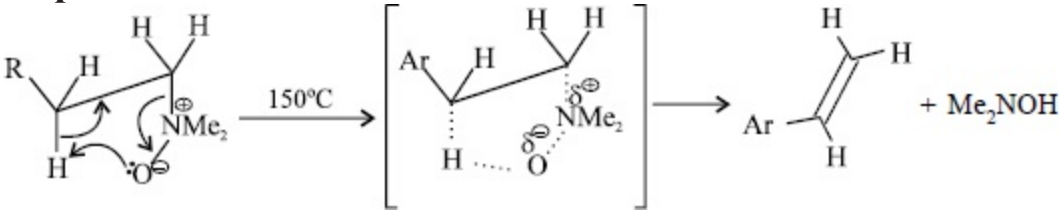
(1)



(2) Chugaev's reaction :



(3) Cope's reaction :



All types of reactions mentioned above take place through 5/6 membered cyclic TS and rate is found to be Rate = k[Substrate]. The reactions are possible because of cyclic TS formation and in all cases elimination of those groups are taking place, which are lying in the same plane and same side. The elimination process have synthetic utility in producing terminal unrearranged alkene. The above elimination is thus stereoselectively cis.

Alkane

General formula is C_nH_{2n+2} where n = 1, 2 etc. but n ≠ 0.

Preparation:

(1) Reduction of alkene, alkyne in presence of metal, hydrogen.

$$C_2H_4 + H_2 \xrightarrow[200\text{–}300^\circ C]{Ni} C_2H_6$$ **(Sabatier-Senderen's reduction)**

(2) Reduction of R—X;

(a) $R—X + Zn \xrightarrow{C_2H_5OH} R—H$

Mechanism :

$$Zn - 2e \longrightarrow Zn^{+2}$$

$$R—X + e \longrightarrow R^{\cdot} + \overset{\ominus}{X}\ ; \quad \overset{\ominus}{R} \xrightarrow{C_2H_5OH} R—H + C_2H_5\bar{O}$$

(+e)

(b) $1^\circ, 2^\circ \quad R\,X \xrightarrow{LiAlH_4} R—H$

$2^\circ, 3^\circ \quad R\,X \xrightarrow{NaBH_4} R—H$

$1^\circ, 2^\circ, 3^\circ \quad R\,X \xrightarrow{Ph_3SnH} R—H$

where 'X' is halogen and mechanism is possibly by $\overset{\ominus}{H}$ tansfer.

(c) $R—COR' \xrightarrow[HCl]{Zn—Hg} RCH_2R'$

Clemensen's reduction

$NH_2–NH_2 + C_2H_5ONa + Heat$

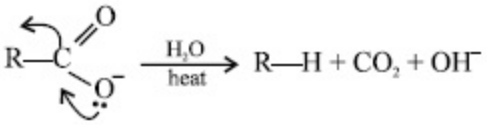
Wolff Kischner reduction

(d) R—OH, RCHO, RCOR', RCOOH all gives alkanes with red P, HI.

(3) Form Grignard's reagent:

$$R—MgI \xrightarrow{H_3O^+} R—H$$

(4) $RCO_2Na \xrightarrow[CaO + heat]{NaOH,} R—H + Na_2CO_3$



[Here R may be alkyl or phenyl or aryl group]

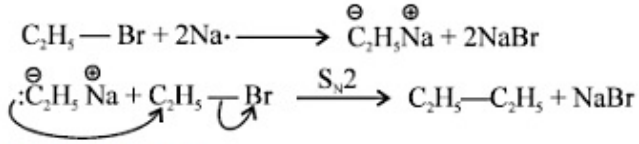
(5) Wurtz reaction:

$R'X + RX \xrightarrow[Ether]{2Na} R—R' + 2NaX$

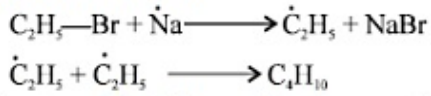
Wurtz reaction gives good yield for the alkanes with even number of C- atoms i.e., symmetrical alkane.

Mechanism

(a) Polar mechanism:

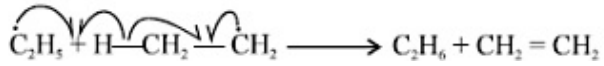


(b) Free radical mechanism :

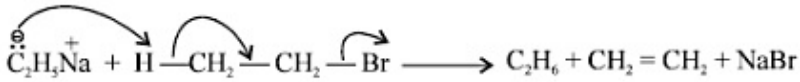


In addition to product alkanes also disproportionation products result as shown below;

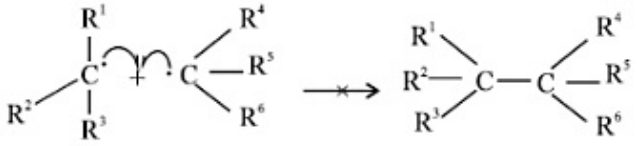
Free radical pathway :



Polar pathway :



Wurtz reaction fails with 3° halide may be because of steric crowding, which appears when two bulky free radicals collide. Therefore alkenes result as the products.



Kolbe's electrolysis method :

$R^1CO_2K + R^2CO_2K + 2H_2O \longrightarrow R^1—R^2 + 2CO_2 + H_2 + R^1—R^1 + R^2—R^2 + 2KOH$

This is an electrolysis process in which electrolytic oxidation of $RC\overset{\ominus}{O}_2$ takes place and in the anode chamber two radicals R· combine to give R — R. By products obtained are alkenes, alcohols, esters. In solvent DMF ($HCONMe_2$) the yield of alkane is very high.

Mechanism :

$$RCO_2K \longrightarrow RCO_2^- + K^+$$

Anode reaction :

$$RCO_2^- - e \longrightarrow R\text{—}C(=O)\text{—}\ddot{O}\cdot \longrightarrow R\cdot + CO_2$$

$$R\cdot + R\cdot \longrightarrow R\text{—}R$$

Also, $R\cdot + RC\dot{O}_2 \longrightarrow RCO_2R$ etc.

$\dot{C}_2H_5$ or higher radicals undergo disproportionation reaction in the following way

$$\underset{\text{reduction}}{\dot{C}_2H_5} + H\text{—}\underset{\text{oxidation}}{CH_2}\text{—}\dot{C}H_2 \longrightarrow C_2H_6 + C_2H_4$$

7. $3RCH = CH_2 \xrightarrow{BH_3.THF} \left[RCH_2\text{—}CH_2\right]_3 B \xrightarrow{CH_3COOH} RCH_2\text{—}CH_3$

8. Hydrolysis:

$$Al_4C_3 + 12H_2O \longrightarrow 3CH_4 + 4Al(OH)_3$$

9. Corey House synthesis :

When methyl or 1° alkyl halide is treated with lithium dialkyl cuprate, an alkane results.

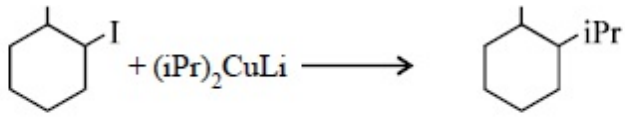
$$2RX \xrightarrow[\text{Ether}]{Li} \underset{+\ LiX}{RLi} \xrightarrow[RLi]{CuI} \underset{\text{(Reagent)}}{R_2CuLi} + LiI$$

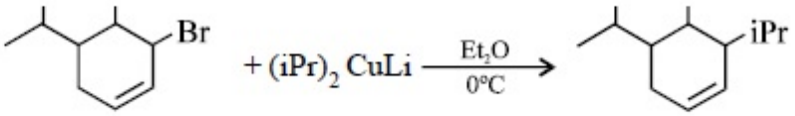
Next,

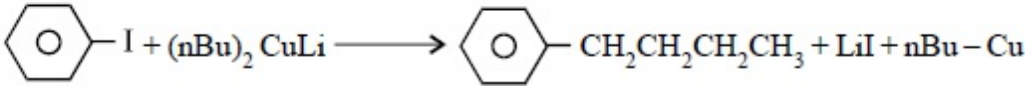
$$\overset{\ominus}{R}_2\overset{+1\ +1}{Cu}Li \xrightarrow[R'\text{—}X]{S_N2} R\text{—}R' + R\text{—}Cu + LiX$$

The following alkenes, cycloalkanes, arenes may also be prepared by the following reactions;

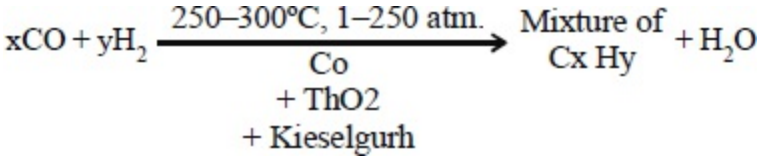
(1) $CH_3CH_2CH_2\text{—}C(H)=C(H)\text{—}I \xrightarrow[-95°C]{(nBu)_2CuLi,\ Et_2O} CH_3CH_2CH_2\text{—}C(H)=C(I)\text{—}nBu$

(2) 

(3) 

(4) 

Fischer TroDsch Synthesis:



The produced Fischer Tropsch oil is used as valuable chemical raw material rather than being used as fuels.

Physical properties:

The normal alkanes C_1 – C_4 are odourless gases, C_5 – C_{17} colourless liquids, C_{18} and above are solids. The bps of normal alkanes are more than the branched alkanes. The reason is London's dispersion force which acts on the large surface area in case of normal alkanes. Melting point has been found to be more for alkanes with even number of C–atoms compared to the alkanes with odd number of C–atoms. Alkanes are insoluble in water but soluble in alcohol and ether. Solubility also decreases with increase in molar mass. Heat of combustion has also been studied in case of normal as well as branched alkanes.

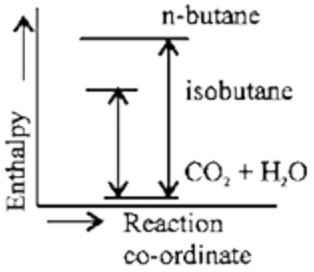
$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O;\ \Delta H^\circ = -21 \text{ kcal/mole.}$$

$$CH_3CH_2CH_2CH_3 + \frac{13}{2} O_2 \longrightarrow 4CO_2 + 5H_2O;\ \Delta H^\circ = -719 \text{ kcal/mole}$$

$$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_3 + \frac{13}{2} O_2 \longrightarrow 4CO_2 + 5H_2O;\ \Delta H^\circ = -717 \text{ kcal/mole}$$

From last two equations isobutane is found to be stabler than butane, as it liberates less heat on combustion. Therefore it can be understood that reltaive stability of branched alkane is more. For cyclo alkanes let us

follow the given data.



Cydoalkane (homologues)	ΔH° (kcal/mole) approx.	ΔH° per CH_2 group (kcal/mole) approx.	Ring strain (kcal/mole) approx.
	500	166	27
	656	164	26
	794	158	6
	945	157	0
	1109	158	6

Here ring strain means $[\Delta H^\circ - 157 \times n]$, where n = number of CH_2 groups and we consider cyclohexane is strain free as we find in n–Hexane. More the strain in the molecule, less will be the stability. So, stability order is 3-memberd < 4-membered < 5-membered < 6-memberd > 7 > 8 etc.

Chemical reactions:

Halogenation of alkanes:

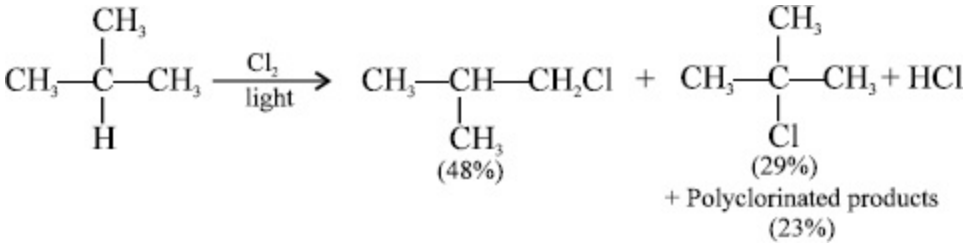
Halogenation of alkanes depend on the homolytic bond dissociation energy values of different alkanes.

eg, $CH_3CH_2CH_2 - H \longrightarrow CH_3CH_2\dot{C}H_2 + \dot{H}$; $\Delta H^\circ = +105$ kcal/mole.

$(CH_3)_2CH - H \longrightarrow (CH_3)_2\dot{C}H + \dot{H}$; $\Delta H^\circ = +103$kcal/mole.

$(CH_3)_3C - H \longrightarrow (CH_3)_3\dot{C} + \dot{H}$; $\Delta H^\circ = +100$ kcal/mole.

From the above data it can also be inferred that $3^\circ > 2^\circ > 1^\circ > \dot{C}H_3$ is the radical stability order as least energy is required for 3° and maximum energy is required for 1°. Therefore,



Polychlorination can be minimised by the use of excess alkane. The reaction is promoted by heat or light. (UV at a wavelength absorbed by Cl_2). Regarding the photochemical reactions and to determine the mechanism we must know the definition of quantum yield. It is the fraction of absorbed light that goes to produce a particular result. Thus product quantum yield for a product P, which forms by a photochemical reaction is shown as,

$$\phi = \frac{\text{number of molecules of P formed}}{\text{number of quanta absorbed by initially excited molecules R}}$$

Actionemeter is used to determine ϕ .

Mechanism of chlorination of CH_4

Chain initiation:

$$Cl_2 \xrightarrow{h\nu} 2\dot{C}l; \quad \Delta H^\circ = +60 \text{ kcal/mole}$$

Chain propagation :

$$\dot{C}l + CH_4 \longrightarrow \dot{C}H_3 + HCl \quad ; \; DH^\circ = +2 \text{ kcal/mole}$$
$$\dot{C}H_3 + Cl_2 \longrightarrow CH_3 - Cl + \dot{C}l \quad ; \; DH^\circ = -27 \text{ kcal/mole}$$

Effective radical Cl· forms, therefore chain propagates.

Chain termination :

$$\dot{C}H_3 + \dot{C}l \longrightarrow CH_3Cl \; ; \qquad \Delta H^\circ = -88\text{kcal/mole.}$$
$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow C_2H_6 \; ; \qquad \Delta H^\circ = -94 \text{ kcal/mole.}$$
$$Cl\cdot + Cl\cdot \longrightarrow Cl_2 \text{ (least frequent); } \Delta H^\circ = -61 \text{ kcal/mole.}$$

Here all the effective radicals combine. CH_3Cl thus forms can give rise to CH_2Cl_2, $CHCl_3$, CCl_4.

eg; $CH_3Cl + Cl\cdot \longrightarrow \dot{C}H_2Cl + HCl$

$\dot{C}H_2Cl + Cl_2 \longrightarrow CH_2Cl_2 + Cl\cdot$ etc.

Reaction of CH_4 with other halogens

Among F, Cl, Br, I the most reactive is F and CH_4 explodes and the reactivity order is F > Cl > Br > I. I is very unreactive and undergoes iodination at

equlibrium. Therefore in presence of HI03 or HgO or FfN03 iodination reaction takes place. [$CH_4 + I_2 \rightleftharpoons CH_3I + HI + HIO_3$; $5HI + HIO_3 \longrightarrow 3H_2O + 3I_2$] By some informations regarding the energy parameter we can explain the reaction and rate of reactivity of different halogens.

Case : 1

Chain initiation :

$F_2 \longrightarrow 2F\cdot$ $\quad \Delta H_1° = +40$ kcal/mole $\quad E_{act} = +40$ kcal/mole

Chain propagation :

$F\cdot + CH_4 \longrightarrow \dot{C}H_3 + HF$; $\quad \Delta H_2° = -32$ kcal/mole ; $\quad E_{act} = +1.2$ kcal/mole

$\dot{C}H_3 + F_2 \longrightarrow CH_3F + F\cdot$; $\quad \Delta H_3° = -75$ kcal/mole ; $\quad E_{act}$ = Very small

So, in chain propagation $\Delta H°_{total} = \Delta H_2° + \Delta H_3° = -107$ kcal/mole

Case : 2

Chain initiation :

$Cl_2 \longrightarrow 2Cl\cdot$ $\quad \Delta H_1° = +61$ kcal/mole $\quad E_{act} = +61$ kcal/mole

Chain propagation :

$Cl\cdot + CH_4 \longrightarrow \dot{C}H_3 + HCl$; $\quad \Delta H_2° = +2$ kcal/mole ; $\quad E_{act} = +4$ kcal/moles

$\dot{C}H_3 + Cl_2 \longrightarrow CH_3Cl + Cl\cdot$; $\quad \Delta H_3° = -27$ kcal/mole ; $\quad E_{act}$ = Small

So, in chain propagation $\Delta H°_{total} = \Delta H_2° + \Delta H_3° = -29$ kcal/mole

Similarly for the chain propagation steps for bromination and iodination $AH°_{total}$ = – 16 kcal and +13 kcal respectively, activation energy for the step (1) in chain propagation step are 20 kcal and 35 kcal respectively.

From the above results due to high evolution of energy in the chain propagation step for F_2 causes explosion as well as little E in both the steps cause largest reactivity of F_2. Therefore dilution by inert gas of the reaction mixture may reduce rate of reactivity.

We can look that gradually higher E_{act} from F to I causes the least reactivity of I and the first step of chain propagation actually determines the rate of reactivity of different halogens, as hydrogen abstraction step requires (E_{act}) least energy during fluorination and maximum during iodination. Combination of the two facts 3°>2°>1°–H and E_{act} for chlorination at3°,2°, 1°H tells us that rate of reactivity must be different and during thermal chlorination at less than 300°C the rate of reactivity

has been found to be 10 : 2° : 3° H is 1 : 3.25 : 4.43 and above 300°C it becomes 1:1:1. Substitution of halogen atom also reduces the reactivity at β-C atom and increases the halo substituion at α -C atom.

During bromination, the reactivity order of 1°: 2°: 3°H is 1 : 82 : 1600 i.e. 3°H is much reactive than 2° and 1°.

Look at the following results :

$$(CH_3)_3CH \xrightarrow[130°C]{Br_2,\ light} \underset{(\sim 100\%)}{(CH_3)_3C\text{–}Br} + \underset{(trace)}{(CH_3)_2CHCH_2Br}$$

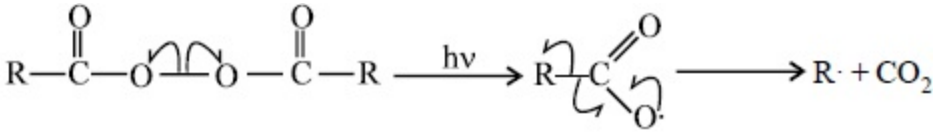
$$(CH_3)_3CH \xrightarrow[30°C]{Cl_2,\ light} \underset{(35\%)}{(CH_3)_3C\text{–}Cl} + \underset{(65\%)}{(CH_3)_2CHCH_2Cl}$$

Therefore Cl is less selective than Br. Similarly least selective is F and most selective is Br.

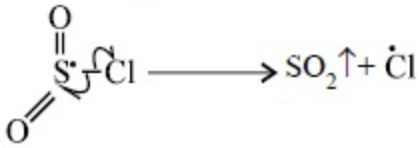
Other ways of chlorination of alkanes are

$$CH_4 \xrightarrow[(RCO)_2O_2,\ h\nu]{SO_2Cl_2} CH_3Cl$$

Mechanism:



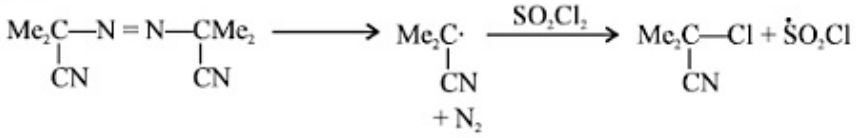
$$R\cdot + SO_2Cl_2 \longrightarrow RCl + \dot{S}O_2Cl$$



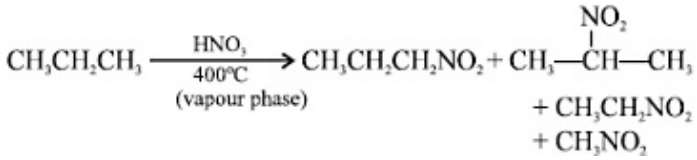
$$CH_4 + Cl\cdot \longrightarrow \dot{C}H_3 + HCl$$

$$\dot{C}H_3 + SO_2Cl_2 \longrightarrow CH_3Cl + \dot{S}O_2Cl$$

In presence of $Me_2C(CN)-N=N-C(CN)Me_2$ the chlorination by SO_2Cl_2 is best carried out as it directly produces free radicals.



Nitration :



Therefore we get mixture of nitroalkanes so, synthetically this is not a good synthetic route.

Sulphonation:

This is carried out by H2S04 but reactivity order is 3° > 2° > 1°.

eg.; $(CH_3)_3CH + H_2SO_4 \longrightarrow (CH_3)_3CSO_3H + H_2SO_4$

Mechanism of hydrogen exchange :

$$(CH_3)_3CH + 2H_2SO_4 \longrightarrow (CH_3)_3C^+ + HSO_4^- + SO_2 + 2H_2O$$
$$(CH_3)_3C^+ + (C_2H_5)_3CH \longrightarrow (CH_3)_3CH + (C_2H_5)_3C^+$$

i.e., H– exchange takes place in presence of H2S04.

Oxidation:

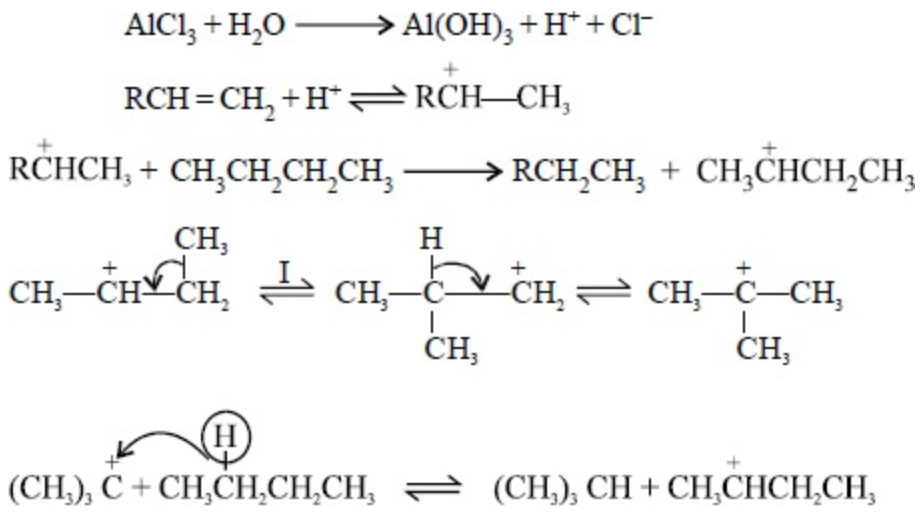
$KMnO_4$ oxidation 3° –H into 3° alcohol.

$$(CH_3)_3C-H \xrightarrow{KMnO_4} (CH_3)_3C-OH$$

Isomerisation :

n-Alkanes convert into branched alkanes in presence of $A1C1_3$ at 300°C. Trace amount of H_2O together with R – X or $RCH = CH_2$ helps in isomerisation.

Mechanism:



Although step I is not favourable where 2° cation converts to 10 cation, may be due to high temperature which compensates the required activation energy in the process, $CH_3CH_2CH_2CH_3$ converts to $(CH_3)_3CH$ and whole the reaction is in equilibrium.

Alkenes

The molecular formula of alkene is C_nH_{2n}, when we consider only one double bond in the hydrocarbon. This is also the general formula of cyclo alkane.

Preparation : (a) Generally elimination reaction of alkyl halides by base leads to alkene.

Examples are;

1) $CH_3CH(Br)-CH_3 \xrightarrow[C_2H_5OH,\ 60°C]{C_2H_5O^-Na^+} CH_3CH=CH_2$ Major

2) $(CH_3)_3CBr \xrightarrow[C_2H_5OH,\ 60°C]{C_2H_5O^-Na^+} CH_2=C(CH_3)_2$ (100%)

3) $CH_3(CH_2)_{15}CH_2CH_2-Br \xrightarrow[(CH_3)_3COH,\ 40°C]{(CH_3)_3CO^-K^+} CH_3(CH_2)_{13}CH=CH_2$ Major

4) $CH_3CH_2O^{\ominus} + CH_3CH_2-C(CH_3)(Br)-CH_3 \xrightarrow[CH_3CH_2OH]{70°C} CH_3CH=C(CH_3)_2$ Major (more stable, Sayetzeff's product) $+ CH_3CH_2-C(CH_3)=CH_2$ (Minor) (less stable, Hoffmann's product)

5) $CH_3)_3CO^{\Theta}$ (Bulkybase) $+ CH_3CH_2-C(CH_3)(Br)-CH_3 \xrightarrow[(CH_3)_3COH]{75°C} CH_3CH=C(CH_3)_2$ (Minor) $+ CH_3CH_2=C(CH_2)(CH_3)$ (Major) (Hoffmann's product)

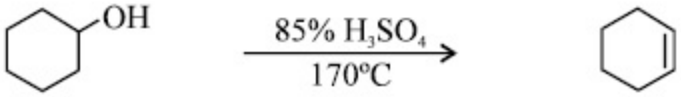
(6) $RC\equiv C^{\ominus}$ (Alkynyl anion) $+ H-CHR-CH(Br)-R' \xrightarrow{E2} RCH=CHR'$(trans)

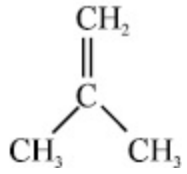
2° halide

Actually when 2°, 3° halides are used, instead of S_N reaction β - elimination (1, 2) takes place but with 1° halide S_N product forms.

(B) Acid catalysed dehydration of alcohol

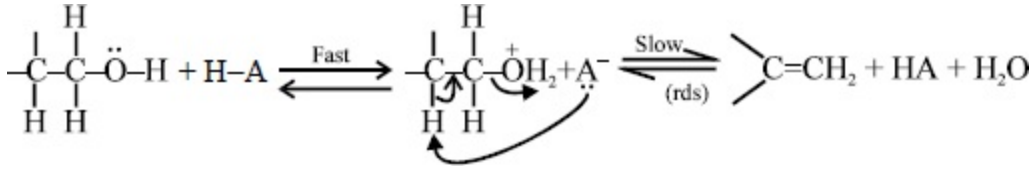
1) $CH_3CH_2OH \xrightarrow[180°C]{conc.H_2SO_4} CH_2=CH_2$

2) 

3) $(CH_3)_3COH \xrightarrow[85°C]{dil.\ H_2SO_4(20\%)}$ 

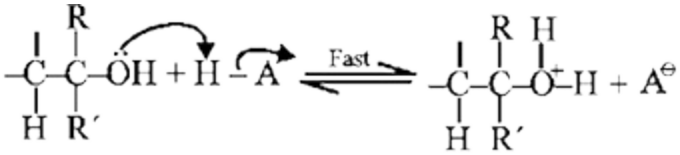
As the concentrated H_2SO_4 is being replaced by dil. H_2SO_4 here, therefore relative rate of delydration is 3° alcohol > 2° alcohl > 10 alcohol. Also we can understand that $3°\ C^+ > 2°\ C^+ > 1°\ C^+$ from the stability point of view, which already we have discused.

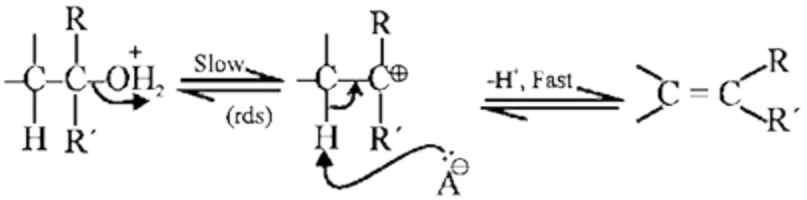
Case–1 : Acid catalysed dehydration of 1° primary alcohol is an example of E2 reaction.



Acid HA normally used is cone. H_2SO_4 ($H.HS0_4$)

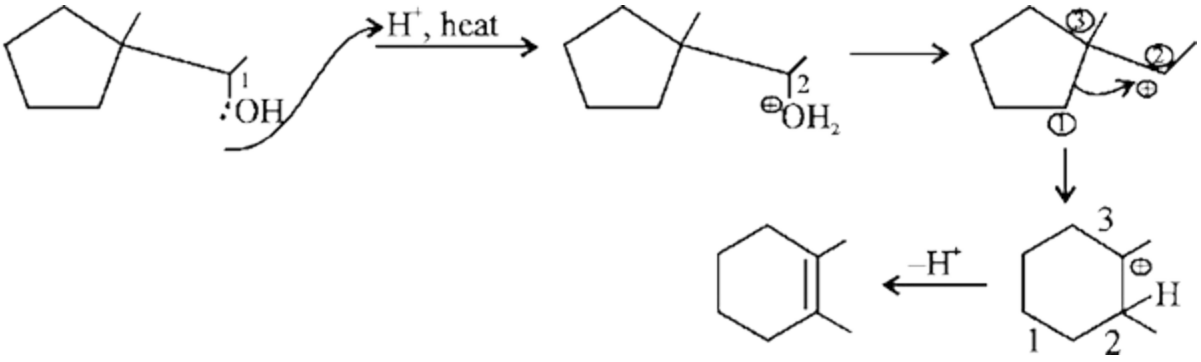
Case–2 : Dehydration of 2° (secondary), 3° (tertiary alcohol) are examples of El reaction.





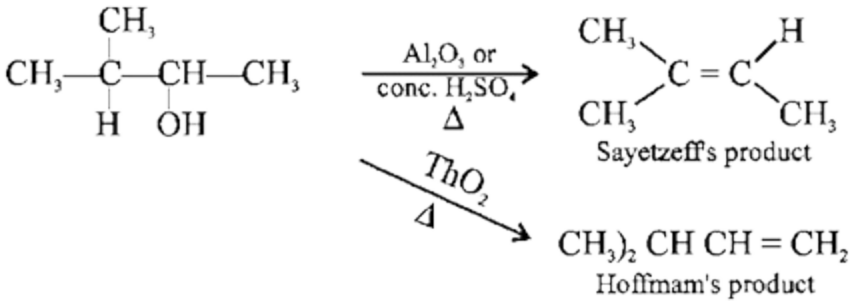
In this case $A^{\ominus}$ can be H_2O, ROH, conjugate base of the acid HSO^-_4 etc . In all these reactions rearrangement is possible if any.

4)



Ring expansion occurs from 5 to 6, 4 to 5 etc for the stability of the product alkene when exocyclic carbocation forms, (i.e. outside the ring carbocation forms).

(5)

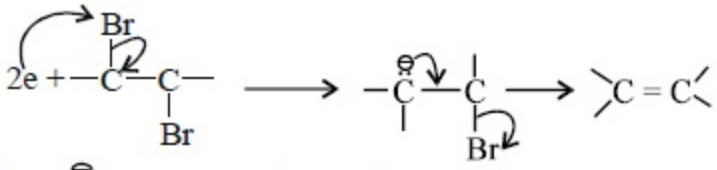


C. Dehalogenation:

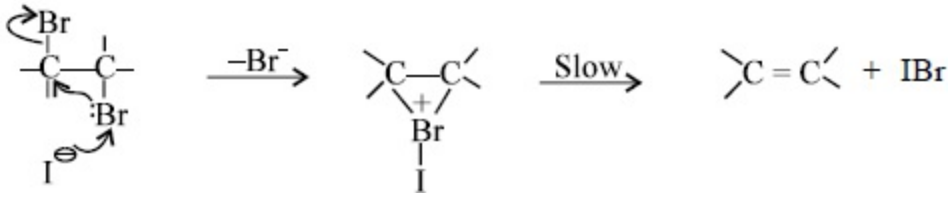
(1)

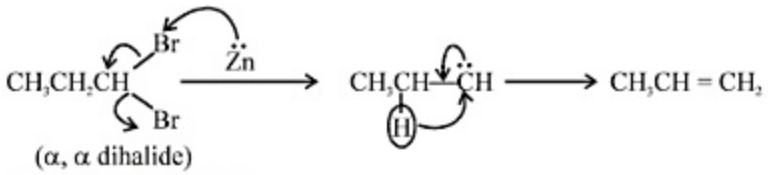


Mechanism : $Zn - 2e \longrightarrow Zn^{+2}$



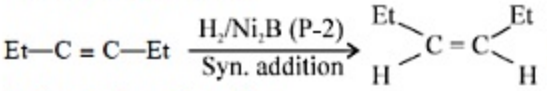
(2) For $I^{\ominus}$ as a reagent, the machanism is,



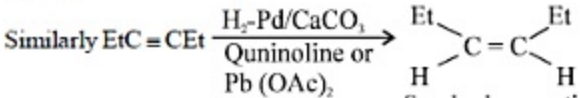
(3) 

(α, α dihalide)

D. By Hydrogenation :

(1) 

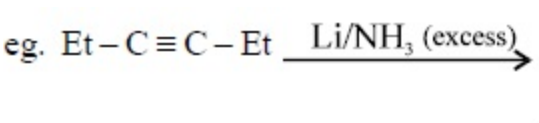
: i.e. in presence of catalyst P-2 (nickel boride) syn hydrogenation takes place.



Syn hydrogenation by 1 mole
(So, streoselective as well as
streospecific reaction)

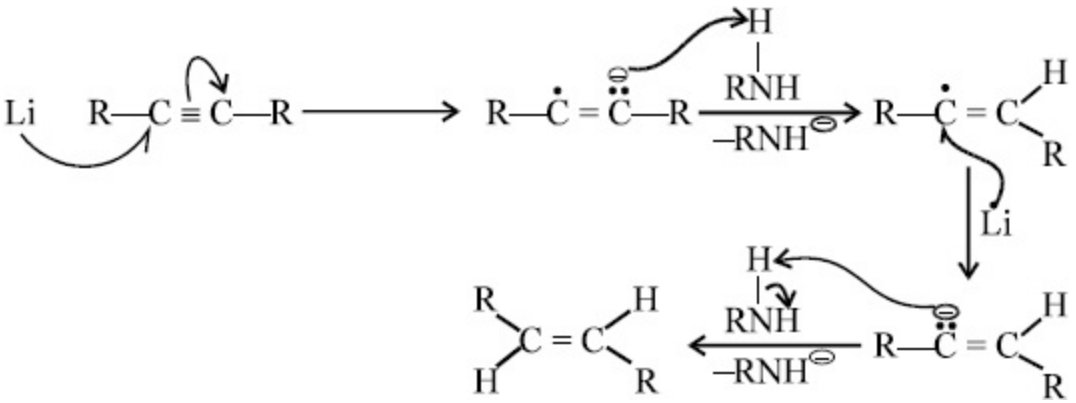
Stereoselective reactions are those reactions in which one set of stereoisomeric products result. Stereo specific reactions are those in which stereo isomeric reactants only yield one set of stereoisomeric products. All stereospecific reactions are stereoselective but reverse is not true.

(2) Alkali metals like Li, Na etc. in presence of solvent like amonia or amine causes trans streoselective addition of hydrogen to produce alkene from alkyne.



trans hydrogenation by 1 mole
(So, streoselective as well as
streospecific reaction)

Mechanism:



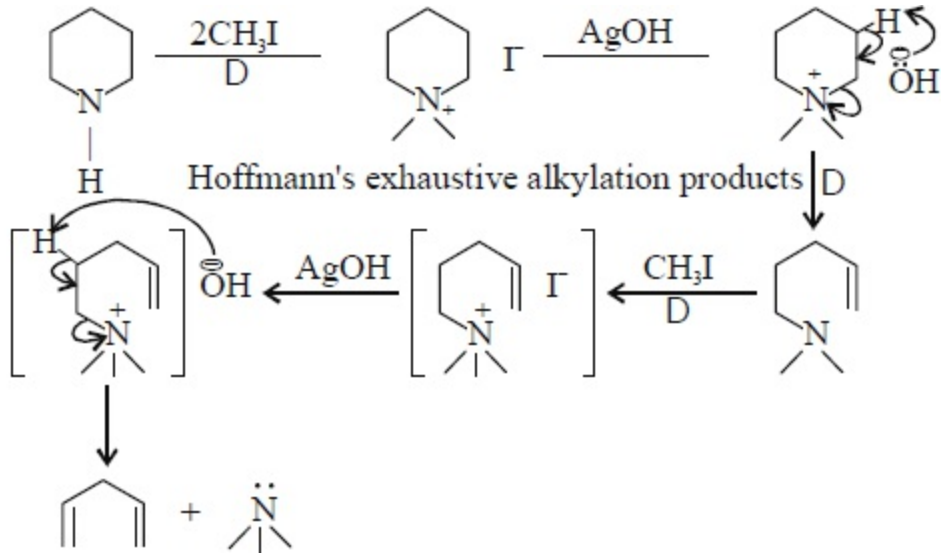
E Syn pyrolytic elimination of ester, xanthates etc. which already have been

discussed produce alkene.

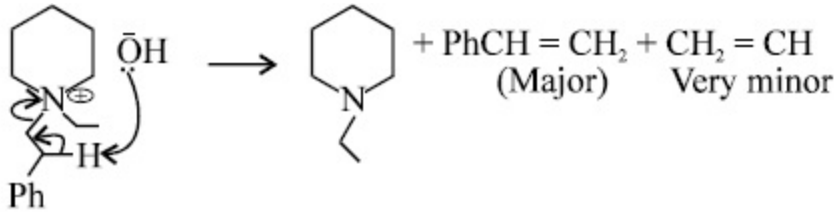
F Quarternary ammonium, sulphomum, phosphonium salts also yield Hoffmann's elimination products. The nature of elimination is 1, 2 i.e. β - elimination which occurs by E2 method.

Few examples:

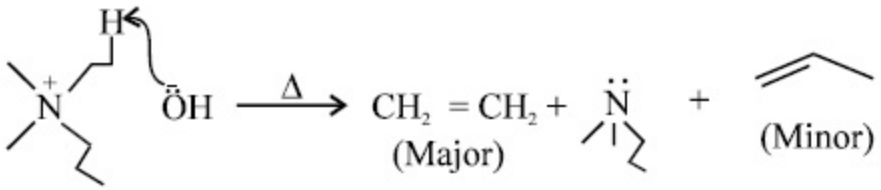
1.



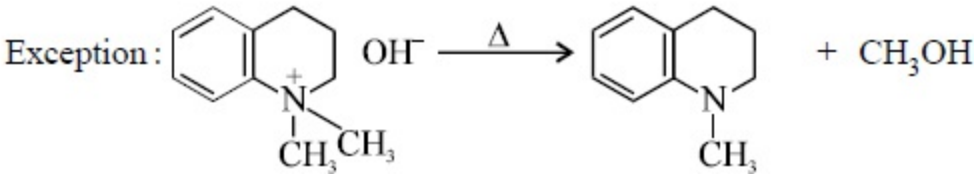
2.



3.



4.

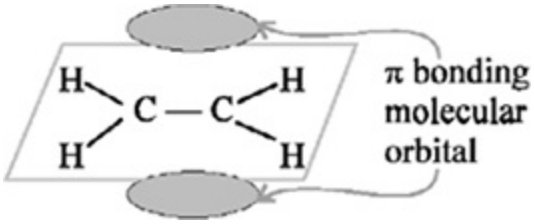


Physical properties structure and stability:

They have similar physical properties similar to alkanes. Upto C_4 are gases at room temperature. It dissolves in low polar solvent or nonpolar solvent.

Density is lower than that of water.

Structure:



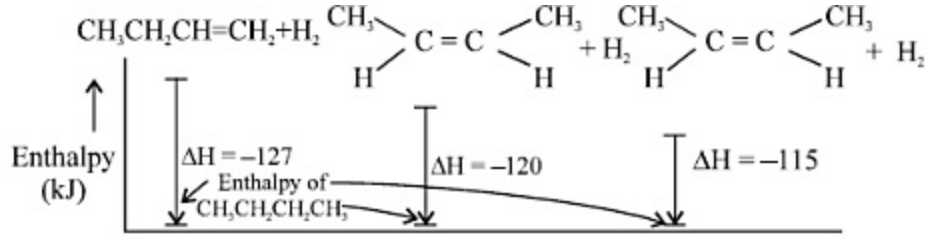
π -electron could below and above the plane is shown in above figure where sp^2 hybridised C–atoms lie in the plane XY Therefore the electron cloud only likes the electrophile and alkenes showmostly electrophilic addition, where E^+ attacks first in slow/rds and after that nucleophile adds up. For polarised double bond

by –I, –R group, can facilitate nucleophilic addition (Michael addition eg; $\overset{\delta\ominus}{CH_2} = \overset{\delta\ominus}{CH} \rightarrow CN$)

Stability of alkene is measured by,
(a) heat of hydrogenation

Reaction : $>C=C< + H_2 \xrightarrow{Pt} -\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}- \quad \Delta H° = -119\ kJ/mole$

More the heat of hydrogenation (exothermic process) less will be the stability. See the diagram below;



Similarly heat of hydrogenation data for others are $CH_2=CH_2$; –32.82 kcal/mole; $CH_3CH=CH_2$ (–30.12) kcal/mole

∴ The stability order is

$$R_2C=CR_2 > R_2C=CHR > \begin{matrix} R \\ R \end{matrix}\!\!>C-C<\!\!\begin{matrix} H \\ H \end{matrix} \simeq RCH=CHR\ (trans) > RCH=CHR\ (cis) > RCH=CH_2 > CH_2=CH_2$$

∴ More the substitution at double bonded carbon atoms more the stability is observed due to hyper conjugation.

There is another way of determining the stability of alkene that is by considering heat of combustion.

eg; $MeCH_2CH=CH_2 \xrightarrow{6O_2} 4CO_2 + 4H_2O$ $\Delta H = -650.7$ kcal/mole

$MeCH=CH-Me\ (cis) \xrightarrow{6O_2} 4CO_2 + 4H_2O$ $\Delta H = -649$ kcal/mole

$MeCH=CHMe\ (trans) \xrightarrow{6O_2} 4CO_2 + 4H_2O$ $\Delta H = -648$ kcal/mole

$Me_2C-CH_2 \xrightarrow{6O_2} 4CO_2 + 4H_2O$ $\Delta H = -647$ kcal/mole

$\therefore \quad |\Delta H_{hydrogenation}|_{MeCH=CHMe(trans)} > |\Delta H_{hydrogenation}|_{Me_2C=CH_2}$

But $|\Delta H_{combustion}|_{MeCH=CHMe(trans)} < |\Delta H_{combustion}|_{Me_2C=CH_2}$

Therefore their stability is considered to be almost same.

Chemical reactions:

(1) Hydrogenation:

(a) Alkene when reacted with H_2 produces alkane in presence of catalysts like Pd, Pt, raney Ni etc.

$$>C-C< + H_2 \rightleftharpoons >\underset{H}{C}-\underset{H}{C}<$$

(cis addition)

The mechanism is uncertain but assumed that H_2 gas and the define is chemisorbed on the metal surface as shown below and consequently new C–H bond formation takes place.

$$H_2 + CH_2=CH_2 \rightleftharpoons \underset{*}{H}\ \underset{*}{H} + \underset{*}{CH_2}-\underset{*}{CH_2} \rightleftharpoons \underset{*}{H} + \underset{*}{CH_2}-CH_3 \rightleftharpoons CH_3-CH_3$$

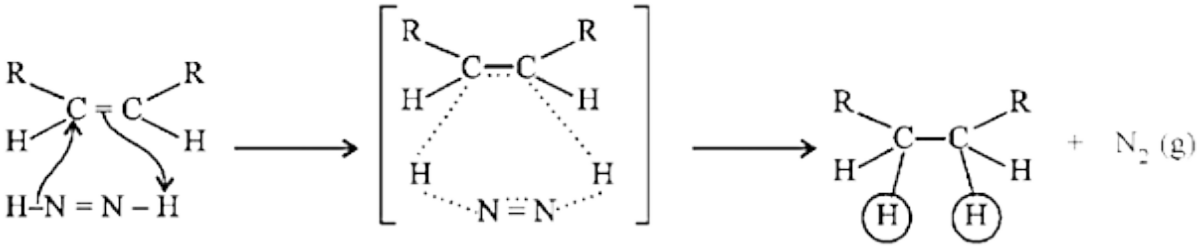
The asterisks indicate the metallic sites. The reversibility is assumed to prove isomerisation of alkene and deuterium exchange withH. (i.e., also to prove adsorption of one H occurs at a time).

Uncatalysed reactions are highly energy (activation energy) requiring process even though thermodynamics says that K i.e., equlibrium constant $\left(K = \exp\left(-\frac{\Delta G^\circ}{RT}\right)\right.$ is very high, but the rate of hydrogenation

is very very slow. In presence of catalyst the rate of hydrogenation is fast. C = O, C ≡ N, COOR etc. also get reduced along with C = C, C ≡ C etc.

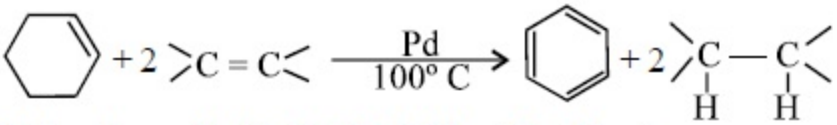
Other hydrogen suppliers:

b) N_2H_2(Diimide)



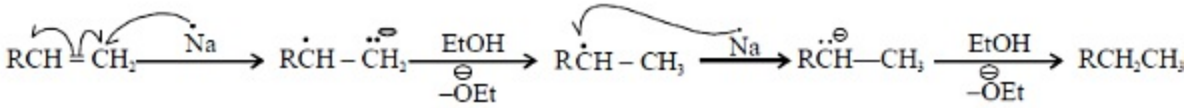
100% cis addition of one mole of hydrogen takes place and therefore this is a stereoselective and ste–Reospecific reaction. Here the driving force of the reaction is N_2 formation. C = O, NOz, C ≡ N donot reduce but C – C, N – N multiple bonds easily reduces by N_2H_2.

c)  i.e., cyclohexene ;



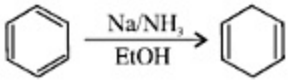
This reduces C = C, C ≡ C, $–NO_2$, –N = N – etc.

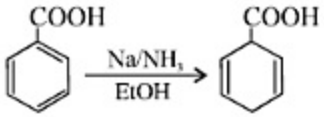
d) Li or Na in NH_3 in presence of alcohol (CH_3OH or C_2H_5OH etc).

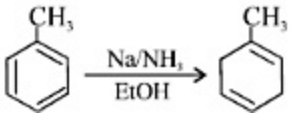


This reagent is called as Birch reducing reagent. Birch reduction is also found in benzene ring.

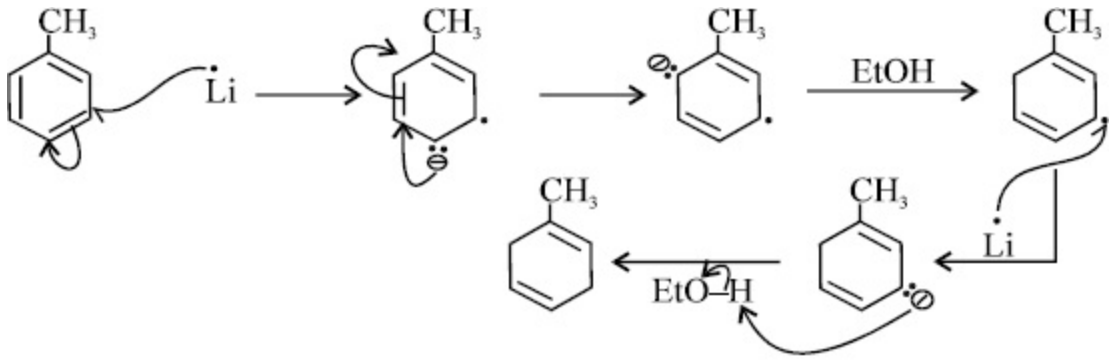
For example ;

(1) 

(3) 

(2) 

Mechanism:



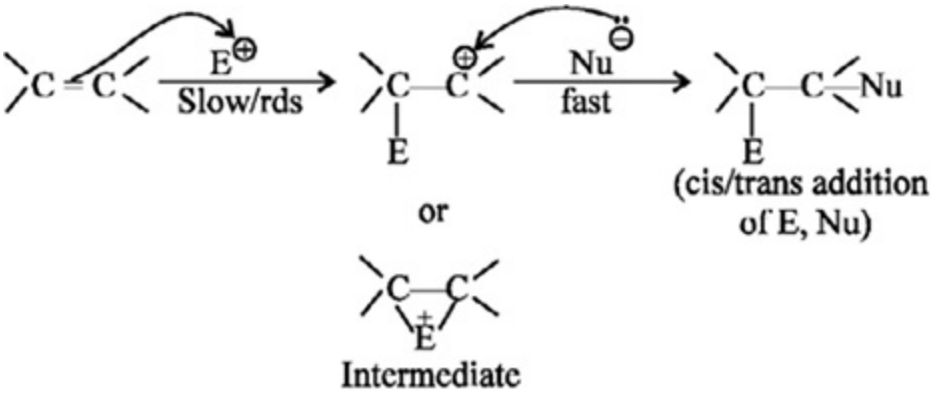
Conjugation of double

By Birch reduction, conjugation of double bond in the benzene ring vanishes.

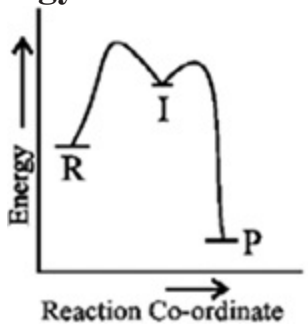
Electrophilic addition:

Because of the negative charge density in olefins, electrophiles are attacked by the π-bond pair of electrons first and then nucleophile adds.

Mechanism:



Energy Profile is:

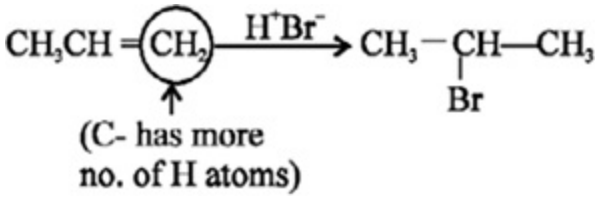


Intermediate I may be free carbocation or cyclic cation.

Rate has been found to be, Rate = k [Substrate] [Reagent] i.e., second order overall. For an electrophile, where to go initially in an unsymmetical alkene,

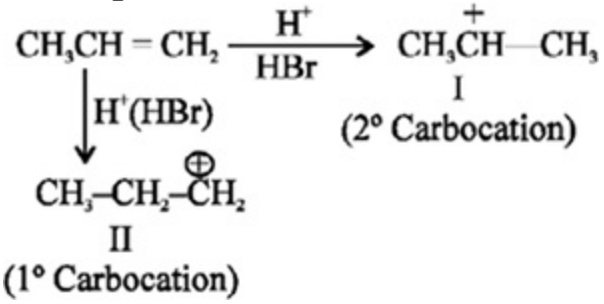
has been governed by **Markownikoff's rule.** This rule states that positive part of the unsymmetrical addendum (eg, HC1) atttaches to that multiple bonded carbon atom which has more H atoms. It means that its negative part goes to the multiple bonded C atom which bears less H-atoms.

By this rule,

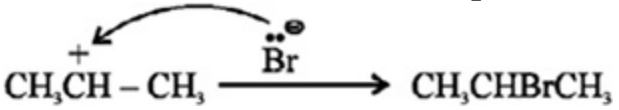


Actually speaking, stability of C^+ determines the mode of addition of the addendum.

For example;

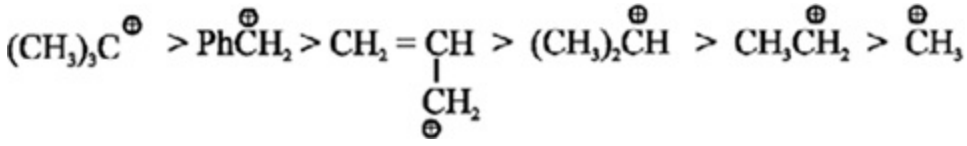


Which one is more stable I or II? Surely it is I. So, II will not form at all. Therefore I will lead to the final products as,



Try out with $CF_3CH=CH_2+HBr \longrightarrow CF_3CH_2-CH_2Br$.

Therefore following the stability order electrophihc addition can be worked out;



(Note : There is a dispute in the stability order with respect to 3° cation and benzylic cation. But the above order is more acceptable as far as the energy to form the carbocations are concerned.)

Therefore following above stability order we must decide the addition

product. At this point we should also learn that HBr (not HF, HC1, HI) in presence of organic peroxides adds up in the opposite manner (which just we have seen) and this is called **anti Markownikoff's addition** or **Kharasch effect.**

i.e., $CH_3CH=CH_2 \xrightarrow[H_2O_2]{HBr} CH_3CH_2-\underset{Br}{CH_2}$

We will study this later on.

As form as the **stereochemistry** of the addition is concerned, it is found that,

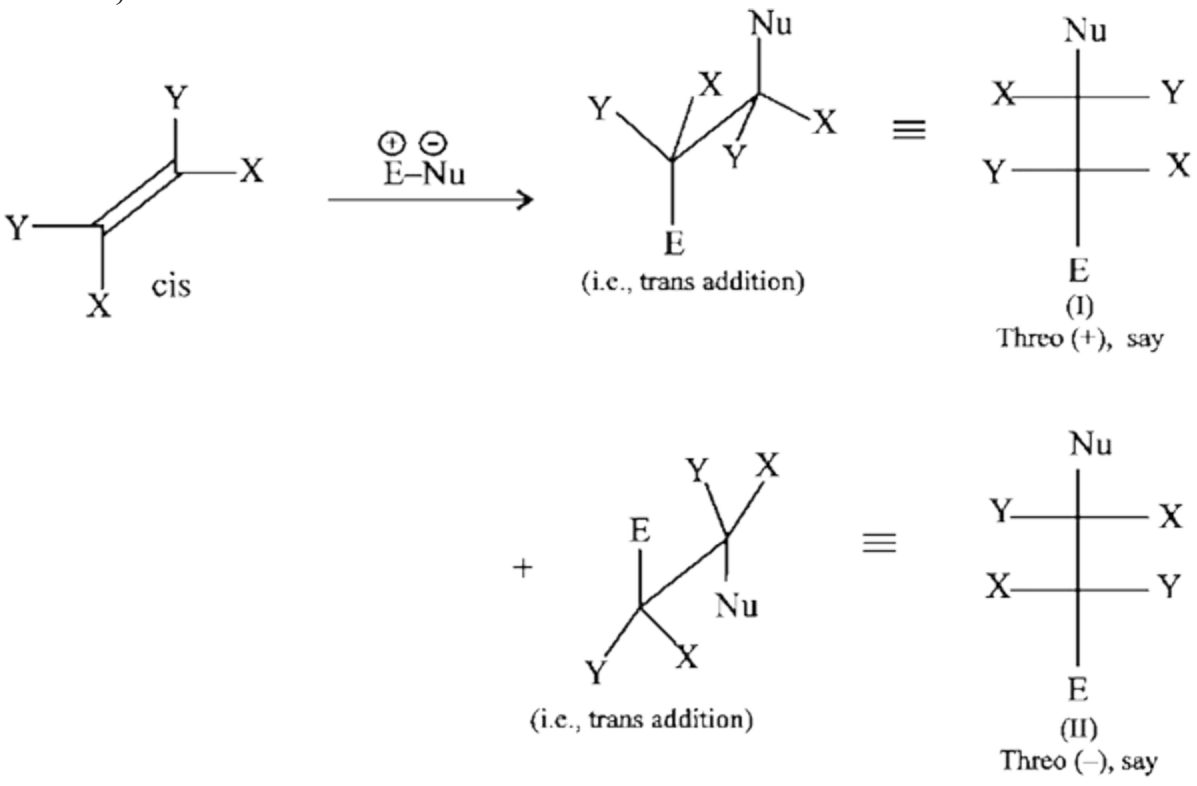
cis (alkene) + cis addition ⟶ (±) erythro (also meso may be the product)

trans (alkene) + trans addition ⟶ (±) erythro (also meso may be the product)

cis (alkene) + trans addition ⟶ (±) threo (also d,l that is racemic mixture may be the product)

trans (alkene) + cis addition ⟶ (±) threo (also d,l that is racemic mixture may be the product)

Let us see,



I, II both form equally therefore I or threo or racemic mixture form. Similarly try out with other combinations.. As we know the rate of reactivity of E^+ to the double bond is rate determining step therefor more supply of electrons to the multiple bonded carbon atoms faster will be the reaction. So, the order of

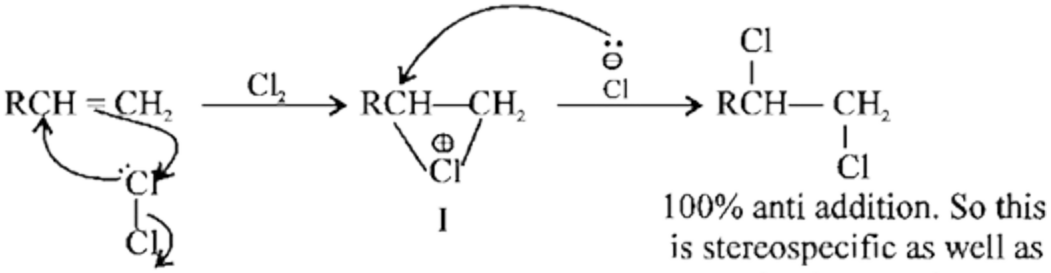
addition is, $CCl_3CH=CH_2 < Cl_2CHCH=CH_2 < ClCH_2CH=ClH_2 < CH_3CH=CH_2$. Also, it is observed that, reactivity towards electrophilic addition reaction is,

$Me_2C=CMe_2 > Me_2C=CHMe > Me_2C=CH_2 > MeCH=CH_2 > PhCH=CH_2 > CH_2=CH_2 > CH_2=CHBr$

Here we will discuss some importatnt electrophylic addition reactions.

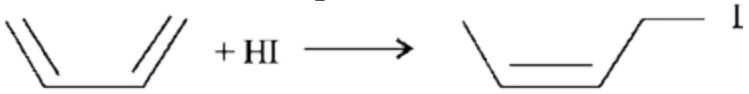
(1) Addition of

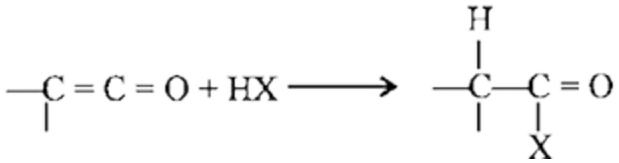
WhenX = Cl,Br.



3-centre halonim ion I can form also through π -comlex formation $\left[RCH \overset{X_2}{=} CH_2\right]$ route. Red colour of Br_2 decolourises at room temperature due to vie dibromide formation. The reaction with I_2 is reversible and addition mechanism is same as that of Cl_2, Br_2. IF, I Cl, INCO addition are also trans. Size of F is small, therefor it can't show the NGP, by which it could have formed 3 centred halonium ion but Cl, Br, I form 3-centre halonium ion.

Addition of HX: HF, HI, HBr adds up at room temperature but addition of HC1 requires heating as it is difficult. Regioselectivity (when a reaction that can preferentialy yield two or more constitutional isomers actually produces only one may be predominantly, the reaction is said to be regionselective) is Markownikoff's addition. Addition can be cis, trans both. Mechanism already has been shown. Examples of few 1, 4 addition reactions.

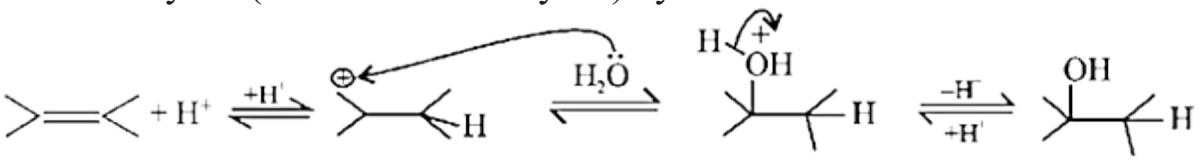




Reactivity order is HI > HC1 > HBr > HF in aqueous medium.

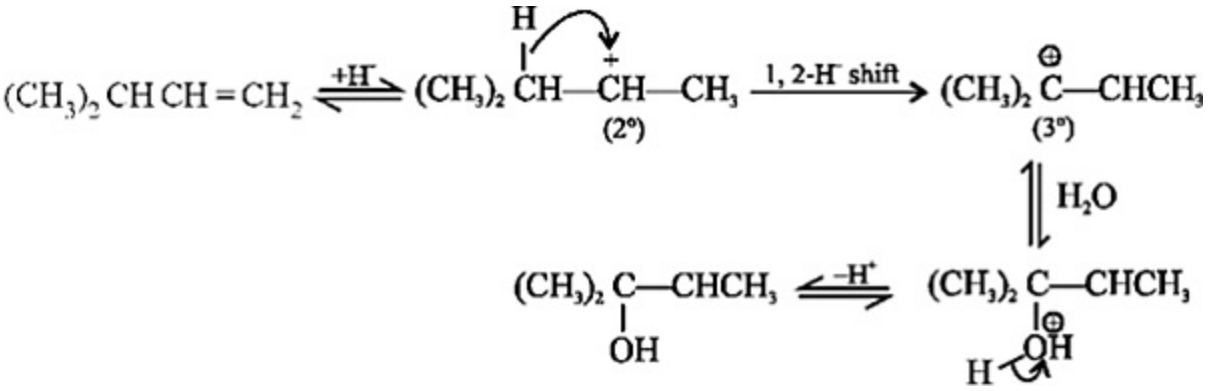
Addition of H_2O : Three cases are there for hydration of olefin,

(a) Acid catalysed (not the base catalysed) hydration.

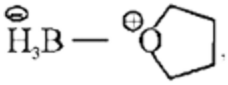


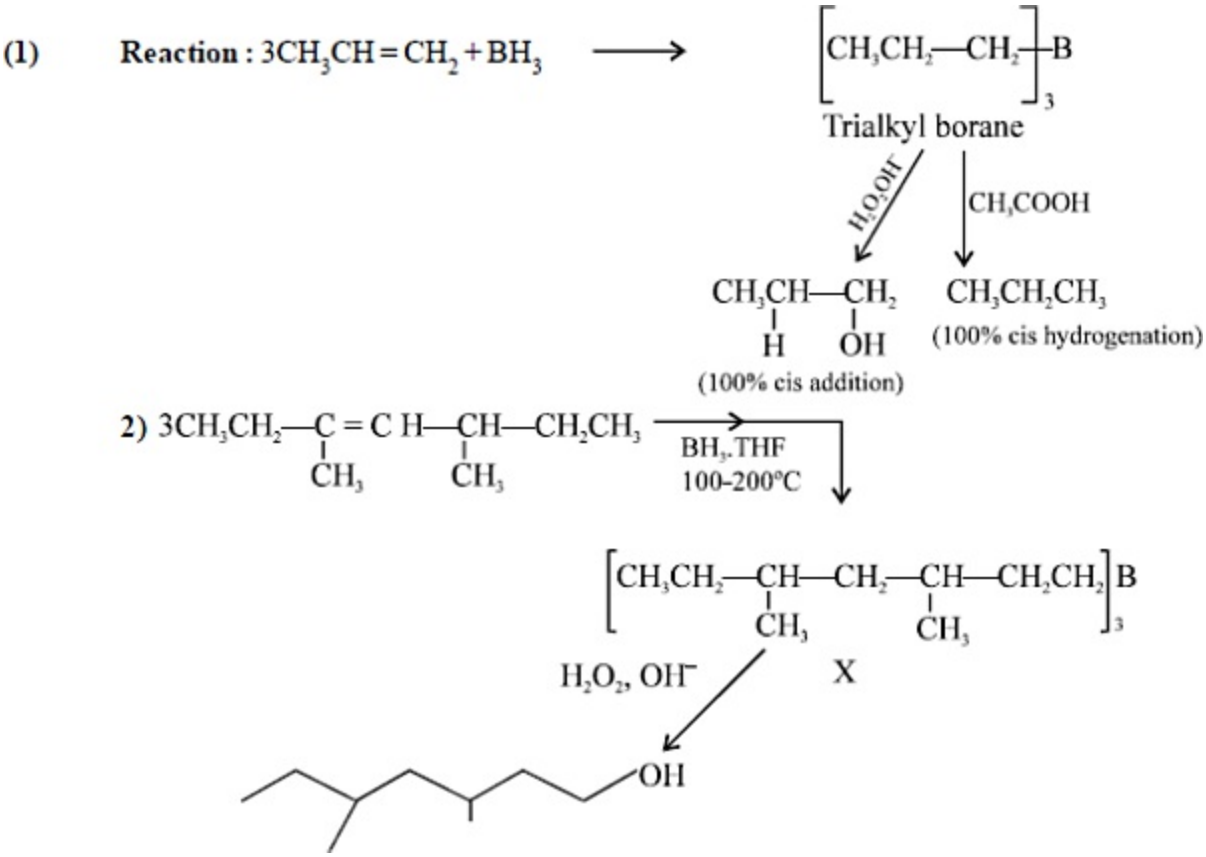
If possible then rearrangment can take place.

For examole:

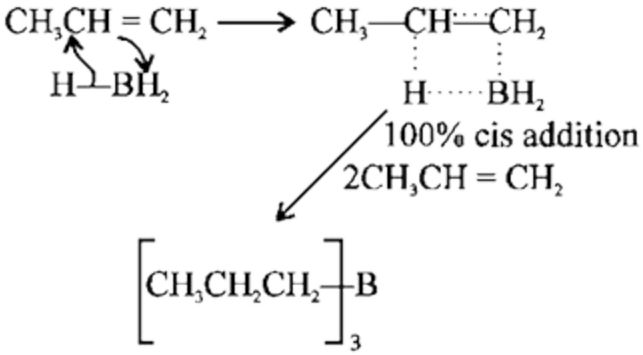


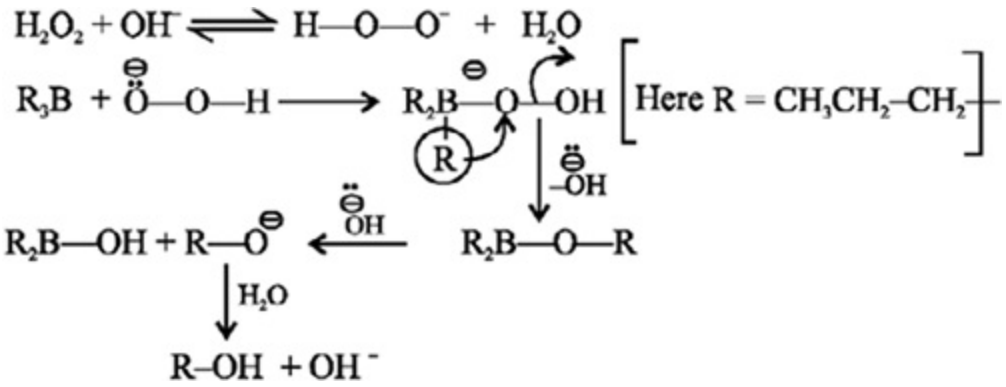
(b) Hydroboration oxidation:

 i.e., BH_3 in THF and finally H_2O_2 inNaOH is the set of reagent.

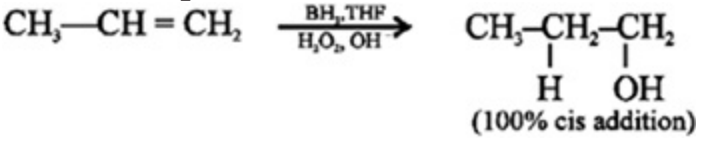


In this reaction a normal alkyl boranes isomerises to an 1° alkyl borane at 100-200ºC 'X' as shown above. Logic of BH_3 addtion is that 'B' end goes to less sterically crowded C atom, due to large size of B and H goes to more sterically crowded atom through a cylic T.S.





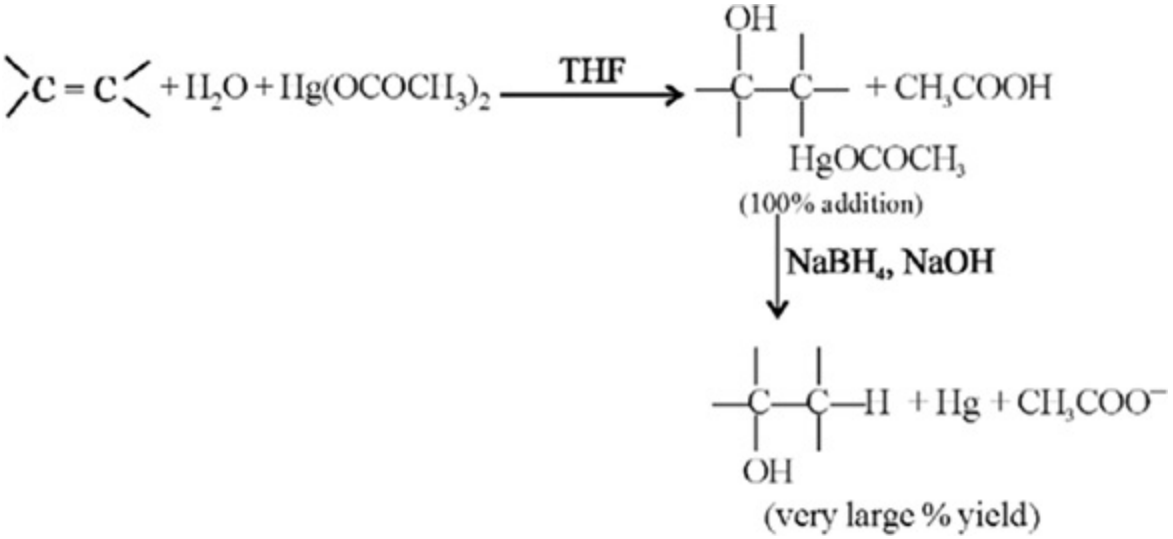
R_2BOH will successively goes to produce 2 more moles of ROH by. Therfore net result is anti Markownikoff's addition of H_2O and it is a stereoselective as well as stereospecific reaction and occurs at 25°C.



C. Oxymercuration – demercuration :

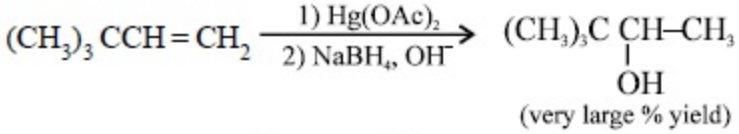
It is an useful laboratory method to produce alcohol. $Hg(OCOCH_3)_2$ in THF and water are first treated with the alkene and then (hydroxylalkyl) mercurry compound is then reduced to alcohol with $NaBH_4$ and NaOH mixture.

Reaction:

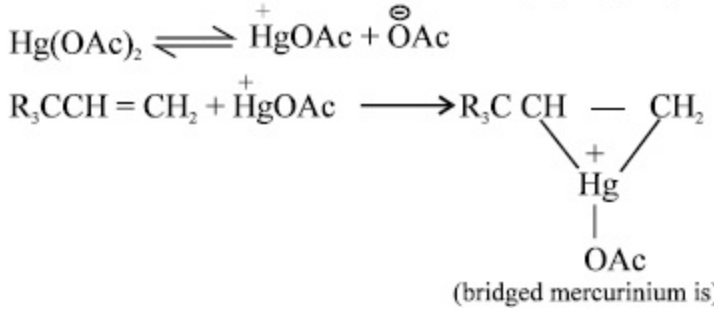


Regioselectivity is Markownikoff's addition of H_2O. No rearrangement takes place during this process.

For example ;

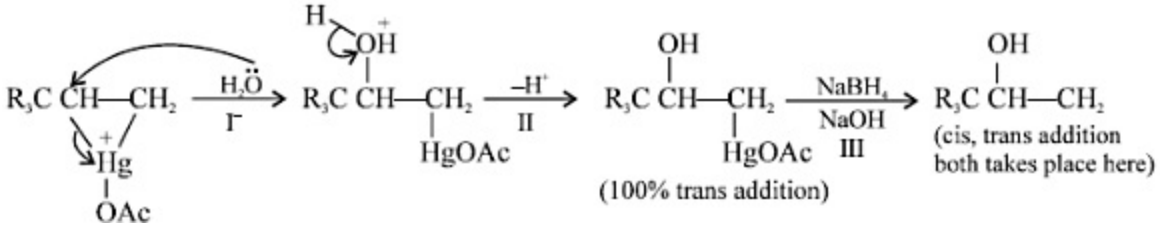


Mechanism :



3-centred cation forms, therefore a nucleophile (H_2O) attacks to that 'C' which can hold $\delta\oplus$ easily

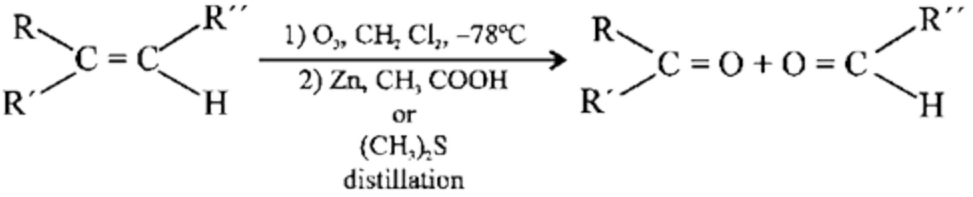
$\overset{\delta+}{(C}\cdots\overset{\delta+}{Ag}\ OAC)$

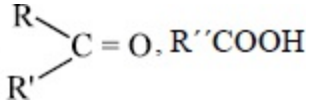


In step (III) scramble of the overall strechochemistry occurs and net resuslt is syn, anti (or cis, trans) addition of H, OH of H_2O takes place and which involves free radical reaction.

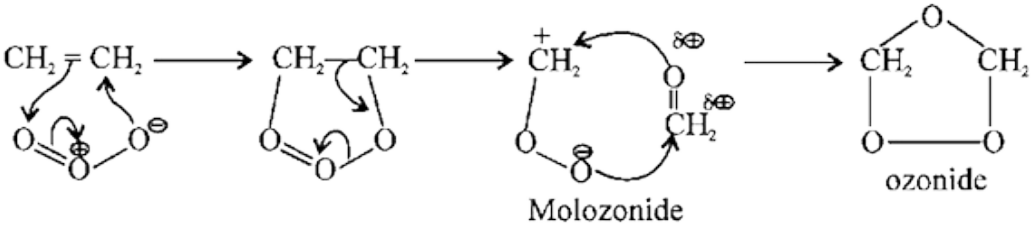
Ozonolysis :

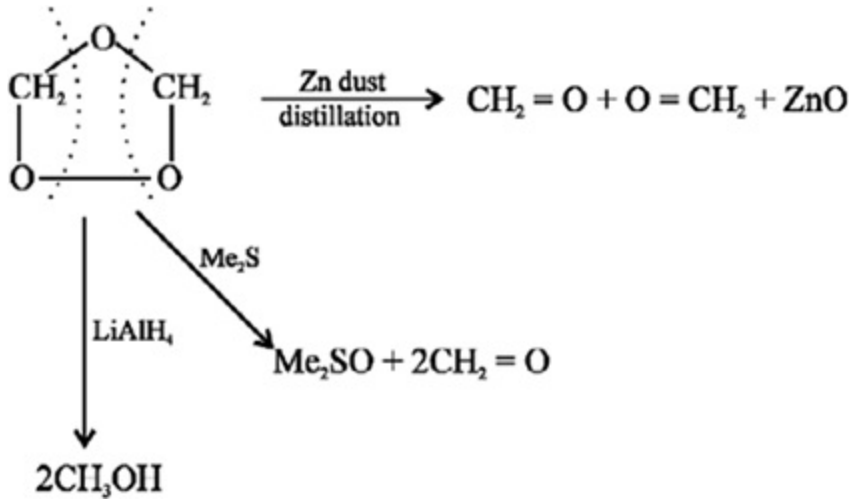
Reaction:

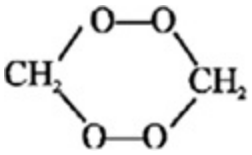


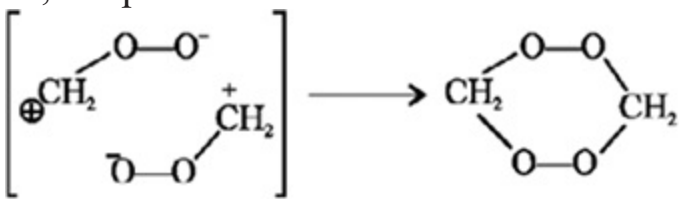
Here clearly C = C breaks down and the nrocess is called as reductive ozonolysis. If it is carried out with H_2O distillation ther  would result and the process is called oxidative ozonolysis.

Mechanism:





Proof behind molozonide formation and decomposition is the experimental detection of diperoxide  , formed by the following union of two 1, 3 dipolar ions

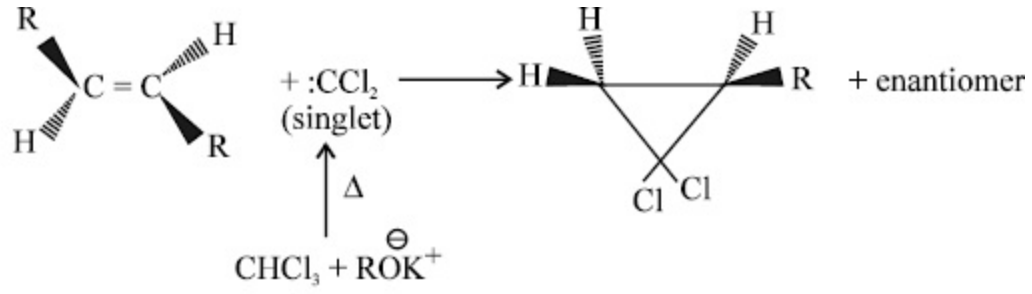


This is very important process to locate the position of double bond in a compound.

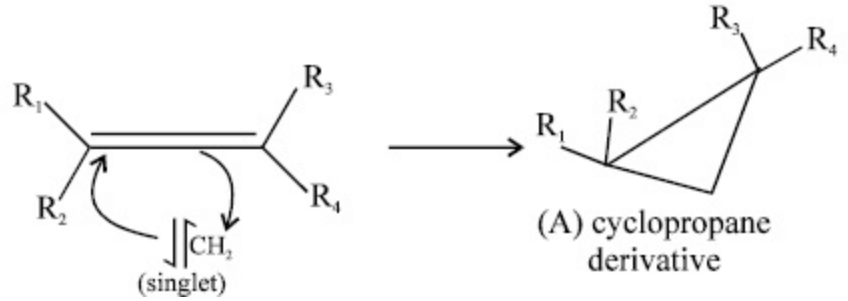
Addition of carbene

Reaction:

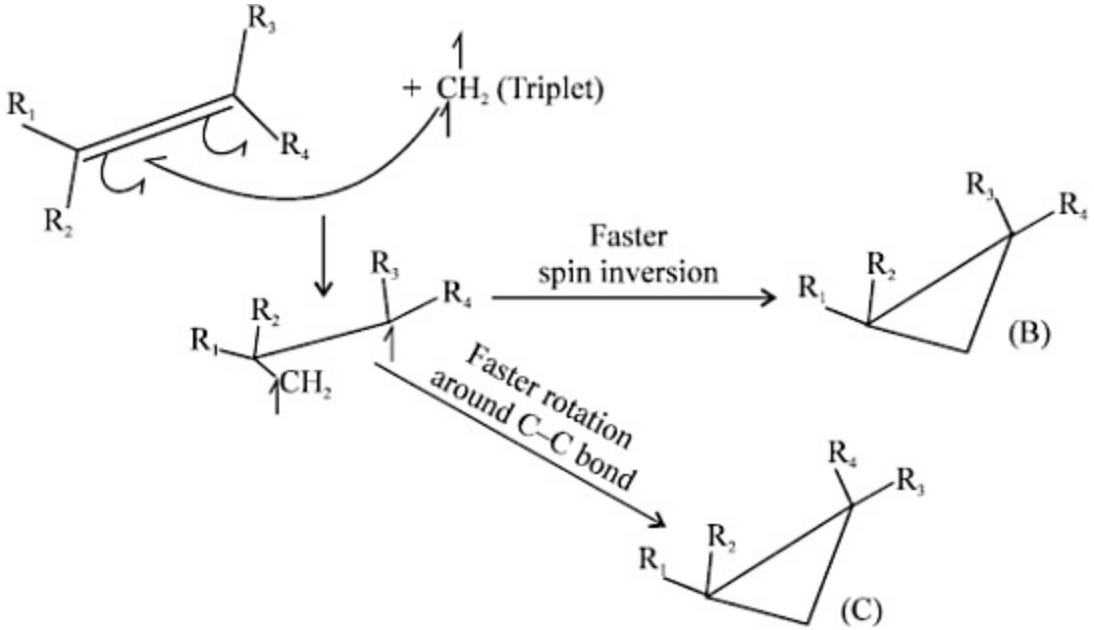
(1)



(2)



(3)

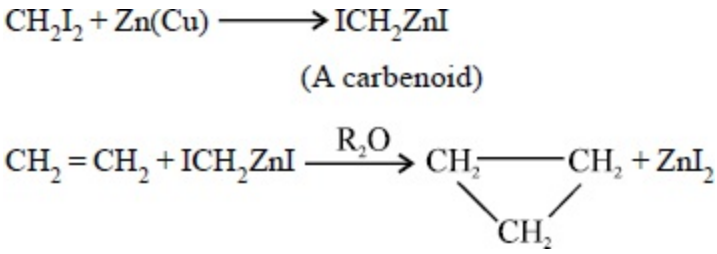


Carbene as we know, can be of two types, singlet and triplet. When singlet reacts with alkene then 100% product (A) result. But with triplet carbene two products result (B), (C). If spin inversion is faster than the rotation with respect to C–C σ -bond axis then (B) results.But if rotation with respect to C–C σ -bond axis is fater than the spin inversion then (C) results.

Carbenoids:

Simmons, Smith formulate the following synthesis of cyclopropane from

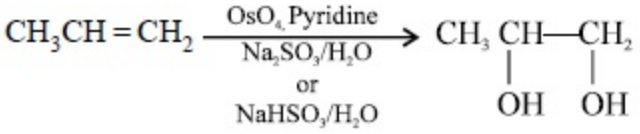
alkene.



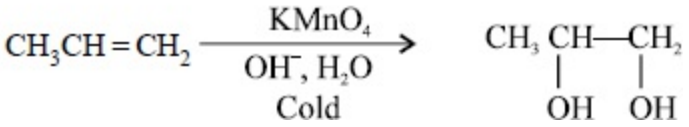
Oxidation of alkenes

(A) In the following reactions 1, 2 dihydroxylation (syn) formation takes place, which are stereoselective as well as stereospecific reactions.

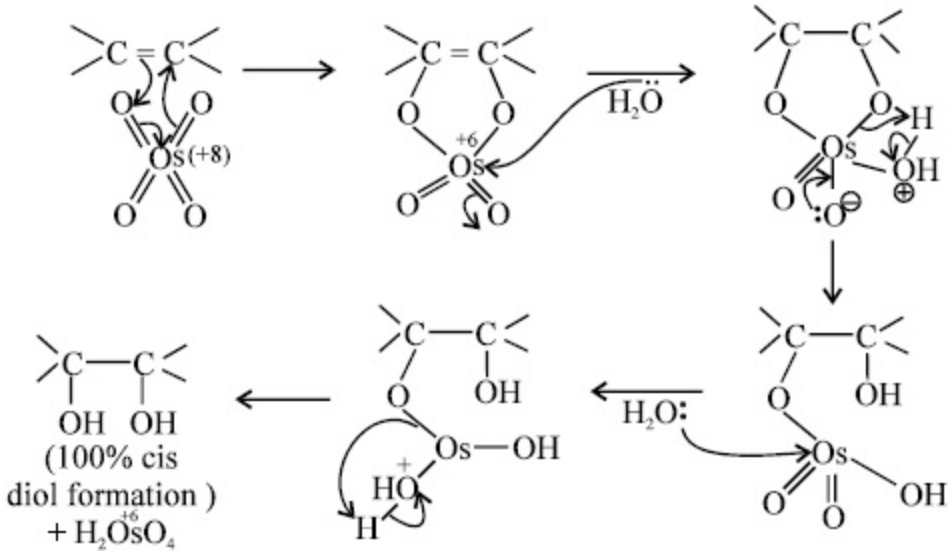
Reactions are ; (1)



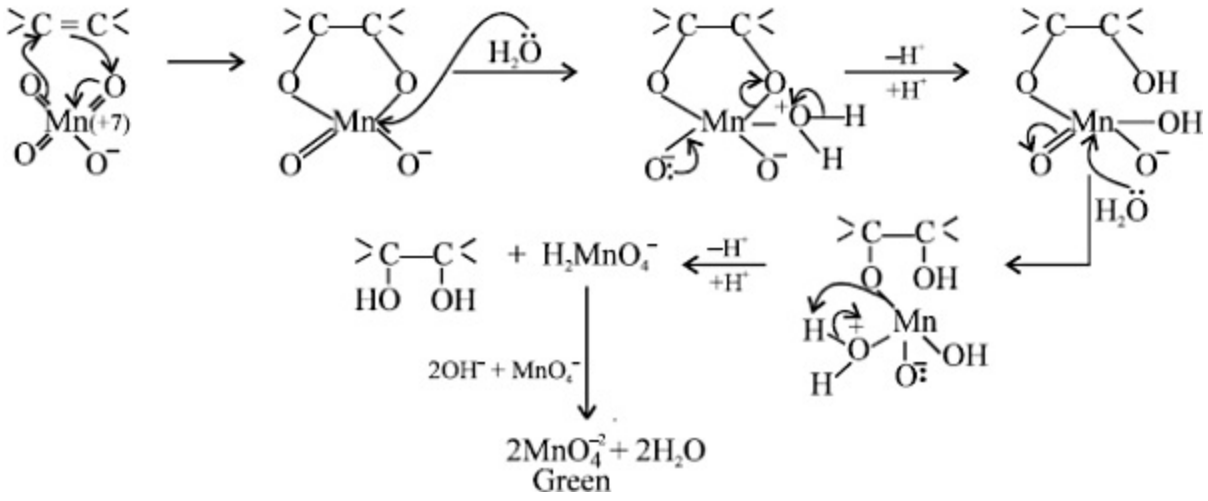
(2)



Mechanism with OsO_4 :



Mechanism with $KMnO_4$:

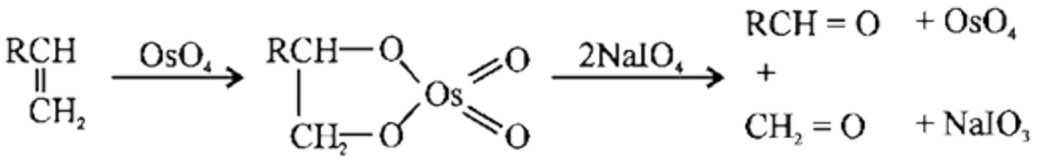


∴ Alkaline $KMnO_4$ solution (purple) leads to green manganate (MnO_4^{-2}) solution (which is the test for unsaturation). But in neutral condition brown MnO_2 separates out. Watch that the oxygen transfer from $KMnO_4$, OsO_4 towards the double bond takes place through cyclic intermediate formation.

Lemiux reagent:

The reagent is $NaIO_4 + KMnO_4$ or OsO_4 and by which we determine the position of double bond at room temperature.

Reaction:



With hot basic $KMnO_4$ cleavage takes place at the double bond.

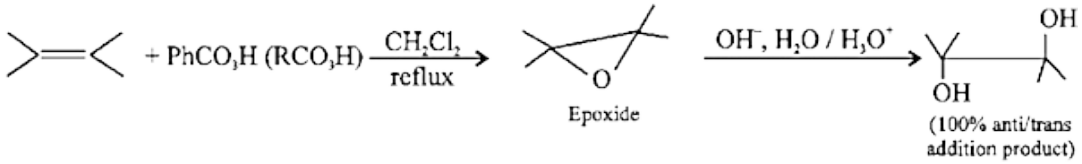
For example;

(1) $CH_3—CH=CH—CH_3$ (cis/trans) $\xrightarrow[H_2O,\ heat]{KMnO_4,\ OH^-}$ $2CH_3COO^- \xrightarrow{H_3O^+}$ $2CH_3COOH$

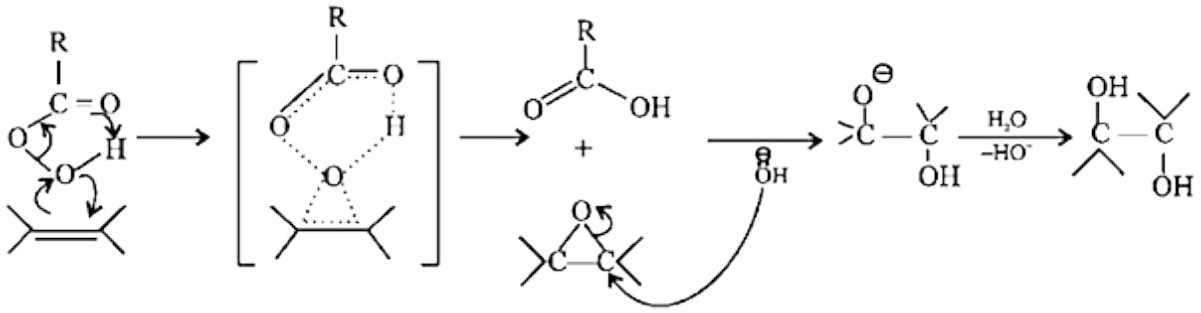
(2) $CH_3—CH_2—\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=CH_2 \xrightarrow[H_2O,\ heat]{Hot\ KMnO_4} CH_3CH_2—\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=O + CO_2 + H_2O$

B. In the following reactions 1,2 dihydroxylation (anti/trans) formation takes

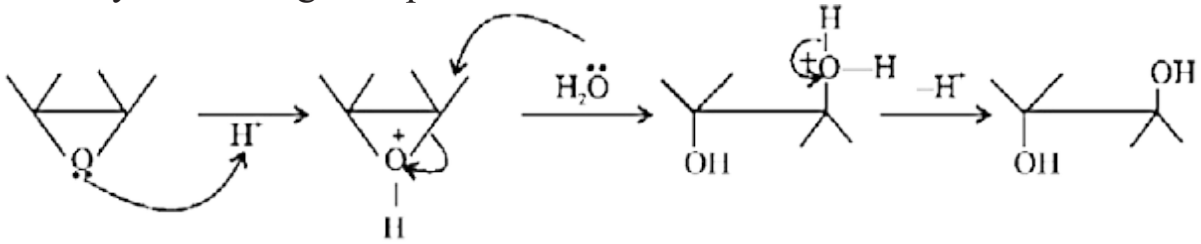
place, which are stereoselective as well as stereospecific reactions. The reaction takes place by epoxide formation initially and then acid or base catalysed cleavage leads to the trans-1, 2-diol formation.

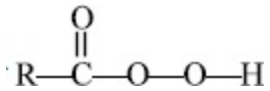
Reaction: 

Mechanism:



Acid catalysed cleavage of epoxide results into trans diol formation.

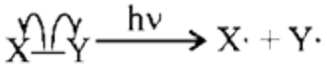


Look at that (O) of OH bond of  goes to make epoxide linkage.

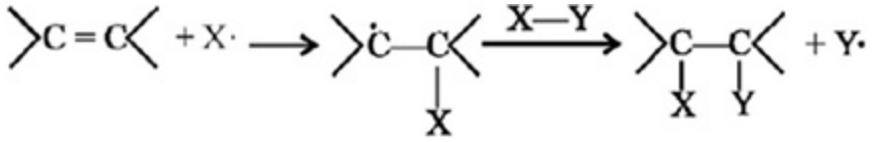
Free radical addition of HBr in presence of peroxide (Kharasch effect) and other radical addition like X_2, HOXetc.)

The radical addition reactions to double bond follows the following procedure.

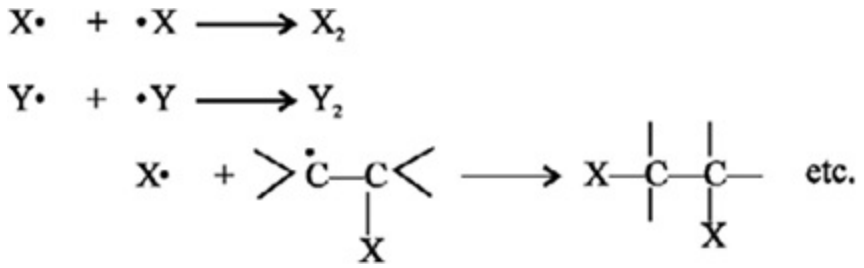
Chain initiation: –



Chain propagation:

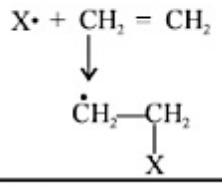
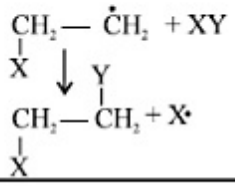


Chain teramination:



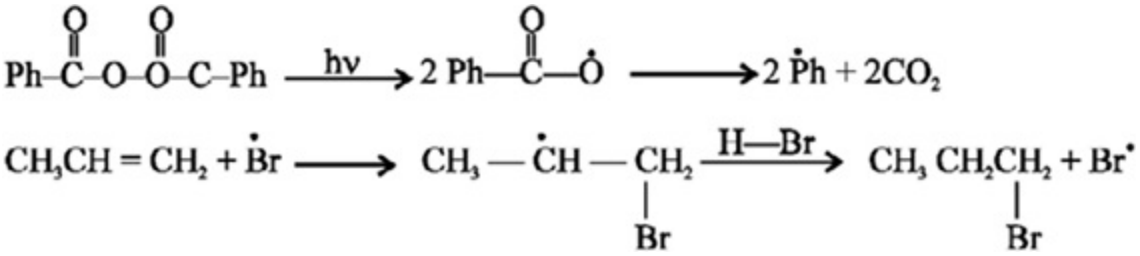
Therefore we should always keep in mind that initial free radical which forms from the double bond has to be stabler.

∴ Radical stability order $Ph\dot{C}H_2 \simeq$ allyl $> 3° > 2° > 1°$ should be remembered.

X-Y	ΔH (kcal) (approx.) 	ΔH (kcal) (approx.) 
H – F	–40	+6
H–Cl	–19	+5
*H–Br	– 5	– 11
H–I	+9	– 27
*HO–Cl	– 32	– 17

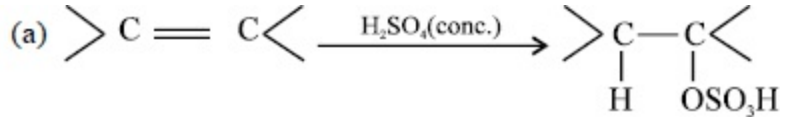
For only all the asterisked species the free radical addition (stepwise) will be favoured as ΔH is Θive (also $\Delta G = \Theta$ive) both the steps. Therefore clearly by thermodynamical requirement HF, HC1, HI addition is always polar and Markownikoff's addition is followed even in presence of peroxide.

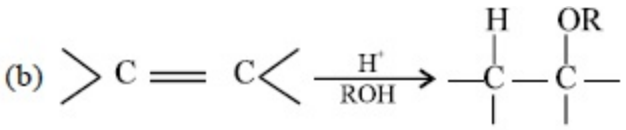
Mechanism for HBr / $(PhCO)_2O_2$ (Benzoyl peroxide) :

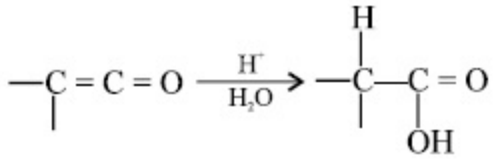


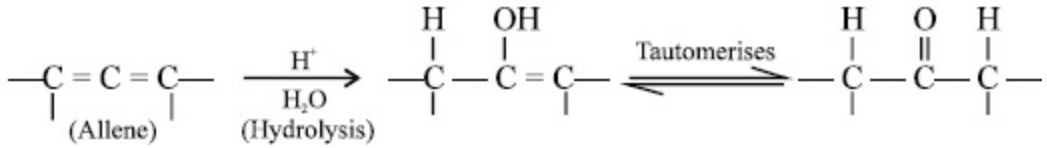
During the above reaction presence of O_2, hydroquinone, heat etc. stops the reaction.

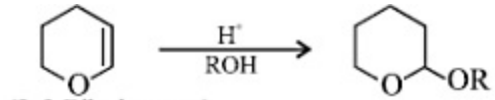
Other reactions with C = C double bond:

1. (a) 

(b) 

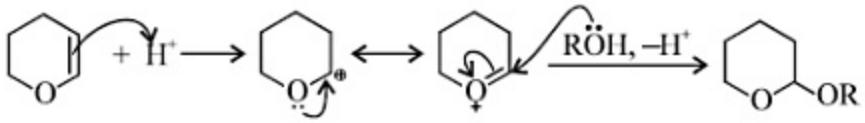
2. 

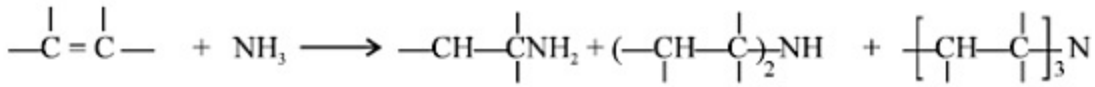
3. 

4. 

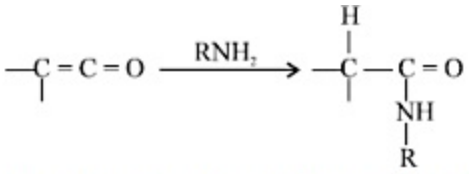
(2, 3-Dihydropyran)

Mechanism :



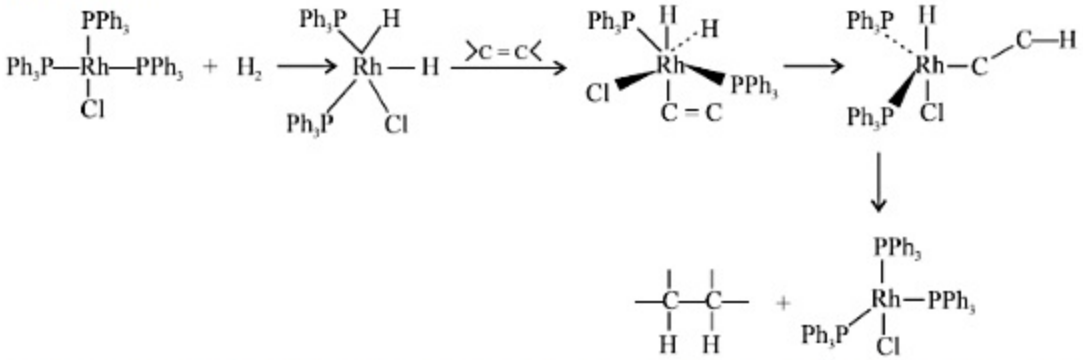
5. 

But for 1°, 2° amines two and one products form respectively.

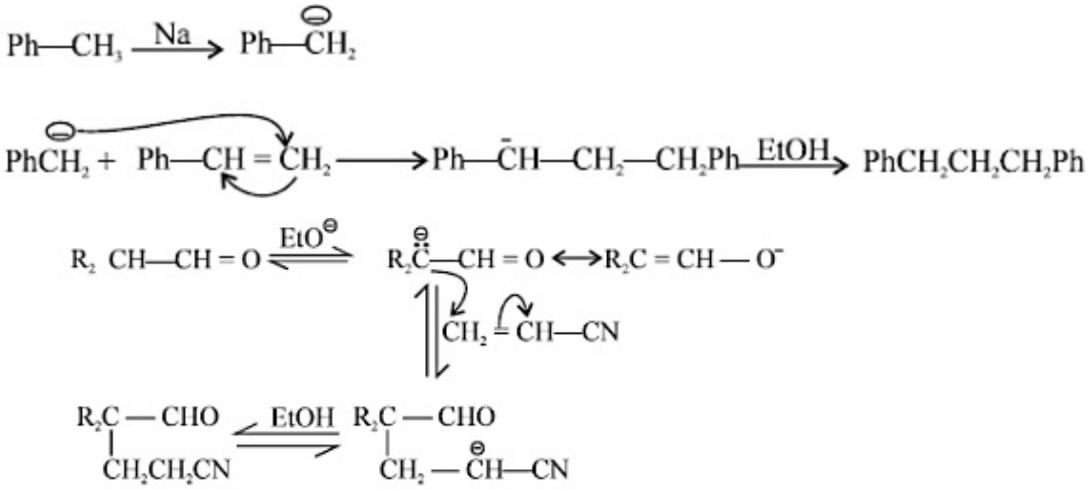
6. 

7. Homogeneous catalysis by Wilkinson's catalyst :

Mechanism :

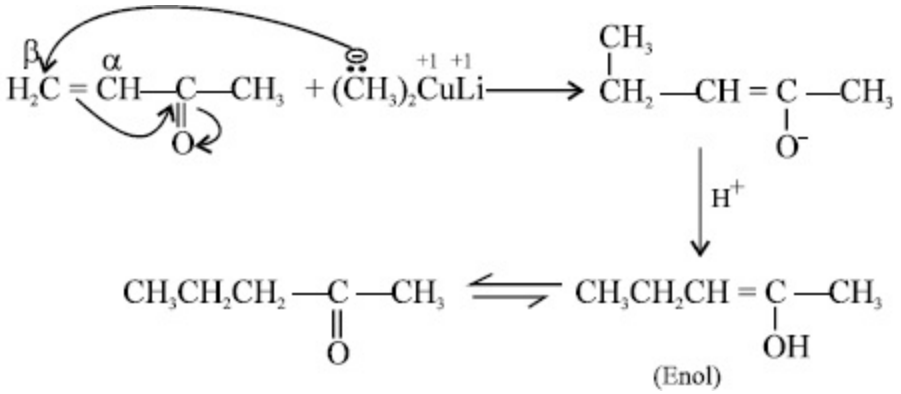


Here homogeneous catalysis means catalyst is soluble in the reaction medim. It does not affect —COOR, $—NO_2$, —CN, —COR present in the same molecule and addition of hydrogen is cis or syn.

8. 

In has synthetic utility also. Carbanions normally are obtained form $CH_2(CO_2Et)_2$ (DEM), $CH_3COCH_2CO_2Et$(EAA), $\begin{matrix}CH_2CO_2Et\\|\\CN\end{matrix}$ etc. Addition of R_2CuLi, RMgBr etc. to α, β unsaturated carbonyl compounds are the examples of Michael addition reactions.

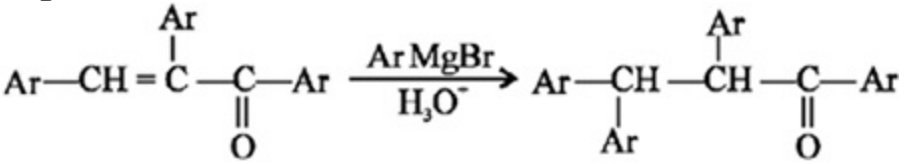
10.



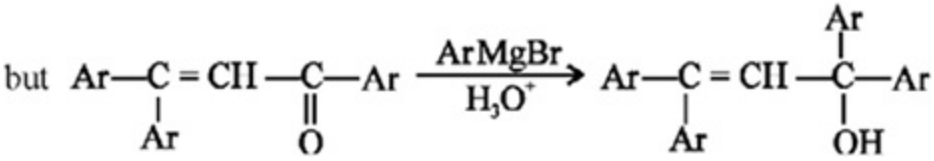
α , β unsaturated carbonyl or ester compounds can show conjugate addition with R_2 CuLi. With α , β unsaturated acid the reaction fails in R_2 CuLi, R can be vinyl, aryl, alkyl radical.

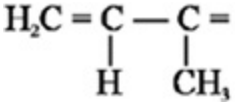
11. Grignard's reagent add in 1, 2 as well as 1, 4 fashion to the conjugated double bonds.

For example;

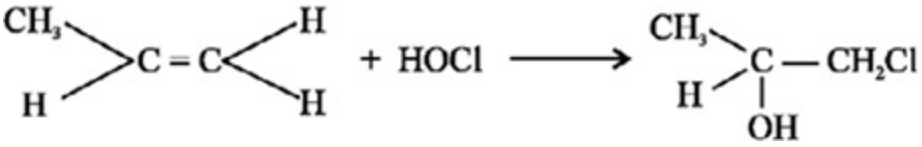


but

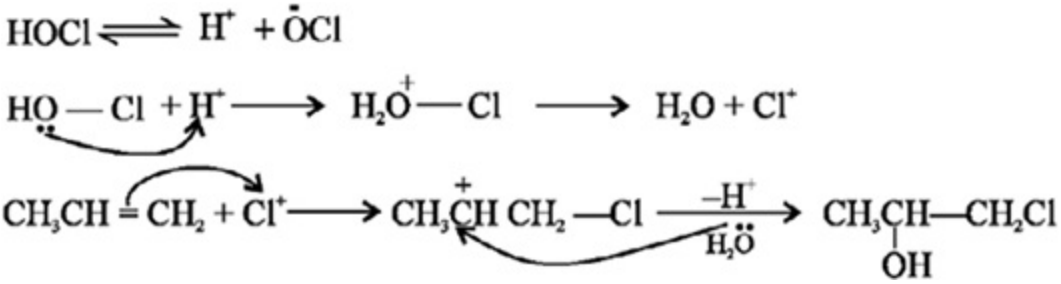


It may be due to less steric crowding in the first case at the β -C 1,4 addition takes place but due to more steric crowding at β -C and in second case 1, 2 addition takes place. In both the cases nucleophilic attack by Ph^- has taken place to the less sterically crowded, partially positive charge carbon atoms. In general substitution at carbonyl carbon leads to 1, 4 addition or use of CuCl etc. increase 1, 4 addition. Otherwise α , β unsturated aldehydes gives mainly 1, 2 addition product. R – Li always gives 1, 2 addition product with  , $CH_2=CH-COOR, CH_2=CH-COOH$ etc. But with CH_2 = CH – COOAr it gives 1, 4 addition product.

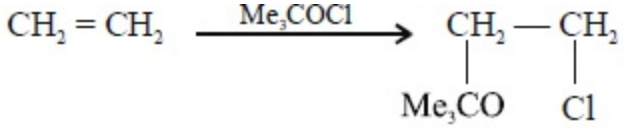
12. Addition of HOCl/HOBr/HOI



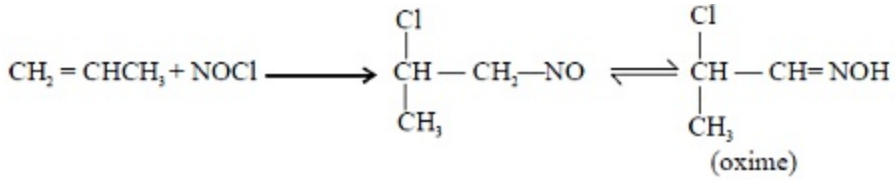
Mechanism:



With HOBr, HOI mechanism remain same.

13. 

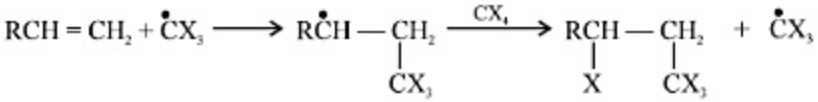
i.e., hypochlorite addition which contains Me_3CO^+, Cl^-.

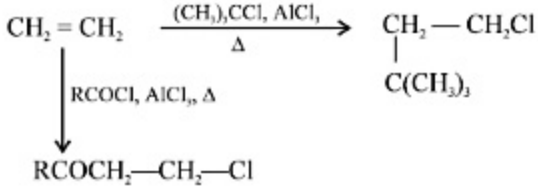
14. 

Markownikoff's rule is followed in reactions 13, 14.

15. CCl_4, $BrCCl_3$, ICF_3 etc. polyhalides add to olefines in large yield. Reactions are initiated by peroxides.

For example ;



16. 

Good yield appears for 2°, 3° halides. For 1°, CH_3–, CH_3CH_2– etc. no reaction at all takes place during alkylation.

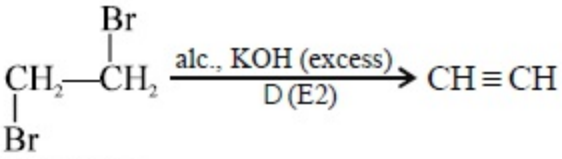
Alkynes

The general formula of alkyne is C_nH_{2n-2} and the functional group we mean –C ≡ C –. Same molecular formula also appears for cycloalkenes.

Preparation :

(1) **Hydrolysis :** $CaC_2 + H_2O \longrightarrow Ca(OH)_2 + C_2H_2$

(2) $3CH_4 + 3O_2 \xrightarrow{1500^\circ C} CO + C_2H_2 + 5H_2O$

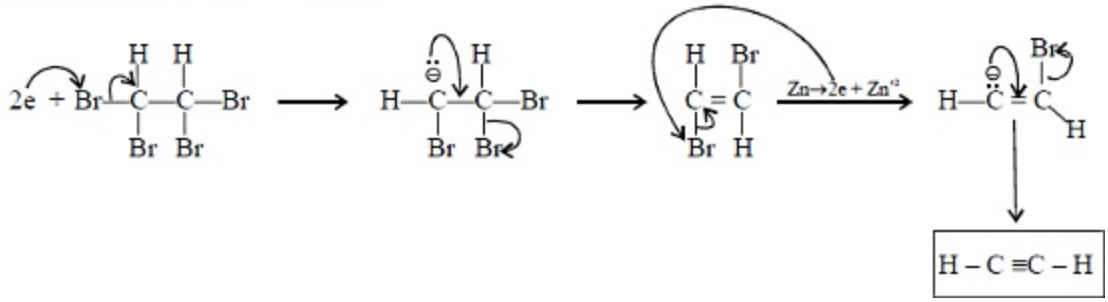
(3) 

(vic dihalide)

(4) $CHBr_2 - CHBr_2 \xrightarrow{Zn,\ heat} HC \equiv C{-}H$

(α, α, β, β tetrabromo alkane)

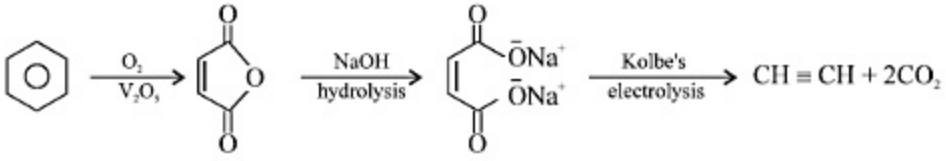
Mechanism : $Zn - 2e \longrightarrow Zn^{+2}$



(5) $RCH_2CHCl_2 \xrightarrow[\Delta]{alc.,\ KOH} RC \equiv CH$

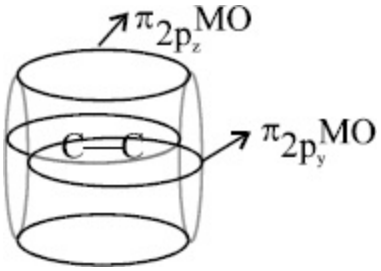
(gem dihalide) $(NaNH_2/\ KNH_2)$

(6) $2CHX_3 \xrightarrow[\Delta]{Ag\text{-}Powder} HC \equiv CH + 6AgX$

(7) 

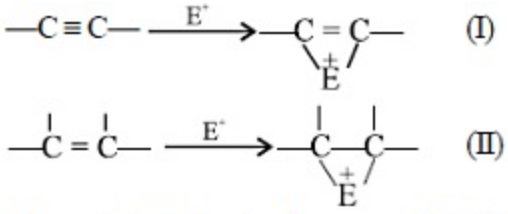
Structure and physical properties : C atoms in the C ≡ C bond are sp hybridised. It consists of one σ and two π-bonds and is linear in shape H–C ≡ C – H.

C ≡ C bond length < C = C bond < C – C bond length. In C ≡ C the charge density is cylindrically symmetrical which can be shown as,



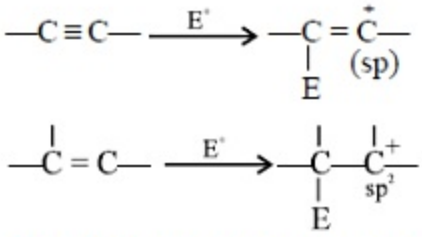
Therefore C ≡ C only can be attacked by an electrophile easily (E^+) not by a negative charge of nucleophile. Because of high electrtonegativity sp C compared to sp^2, sp^3 C C_2H_2 is slightly soluble in water may be due to somewhat dipole-dipole attraction but C_2H_2 is readily soluble in acetone (like dissolves like). It is used in oxyacetylene flame (temperature is above 3000°C). C_2H_2 is less reactive towards E^+ compared to C_2H_4 which it may seem opposite to the expectation as there is much more electron cloud in between C ≡ C. But actually the reverse happens. It may be due to the following two facts.

1.



More strain in the ring I compared to II.

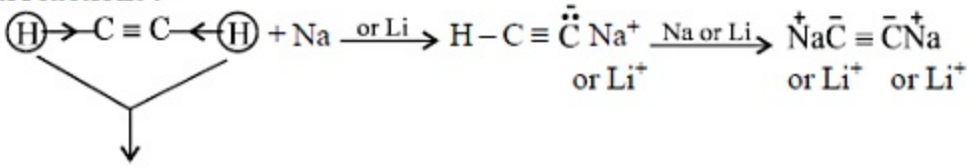
2.



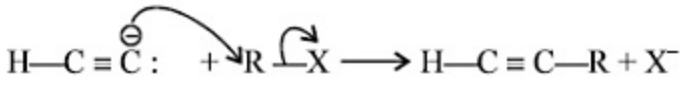
As sp (C) is more electronegative than sp^2(C), so ⊕ive charge can easily sit on sp^2 C.

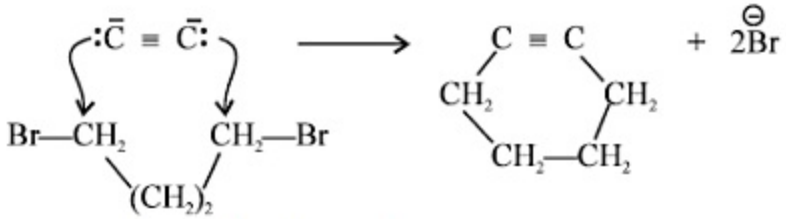
Chemical reactions :

(1)



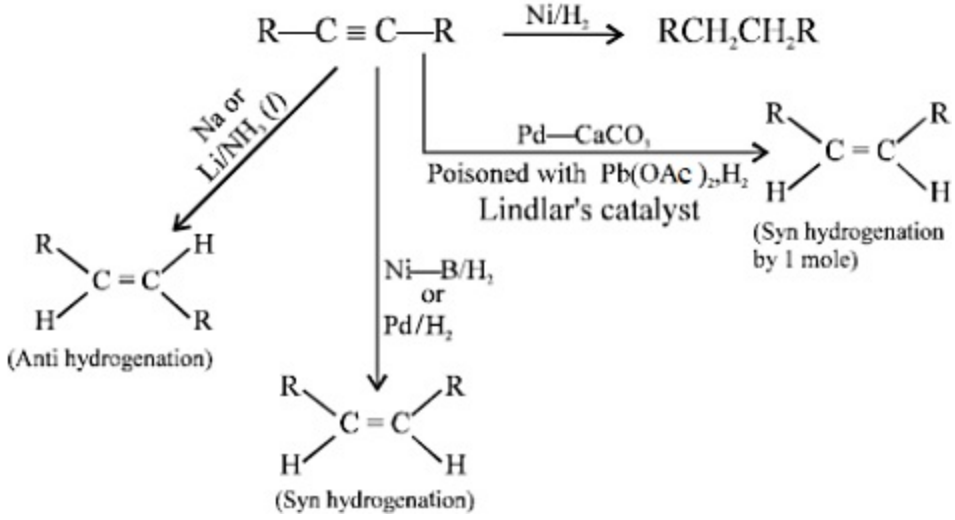
These two H' s are very much
acidic due to higher electronegativity of sp (C).
So,

(a) 

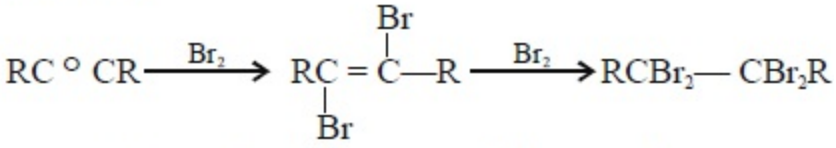
(b) 

etc. reactions can be observed.

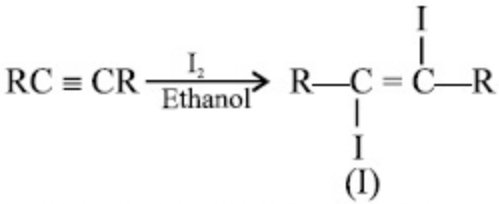
(2) Reduction :



(3) Halogen addition :



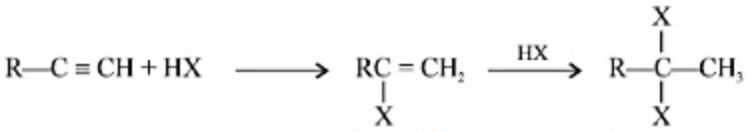
(Stereoselectively trans addition product)



(I)

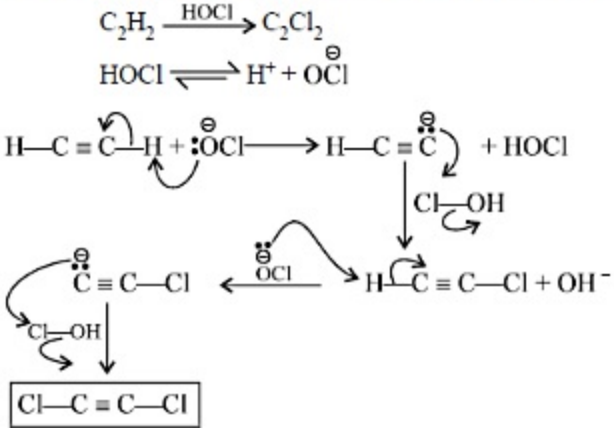
No further iodination is observed of (I).

(4) HX addition :



The addition follows Markownikoff's rule (Regioselectivity) Reactivity order is HI > HBr > HCl > HF.

(5) Reaction with HOCl in cold and in absence of light replacement of H of C_2H_2 occurs as shown below ;



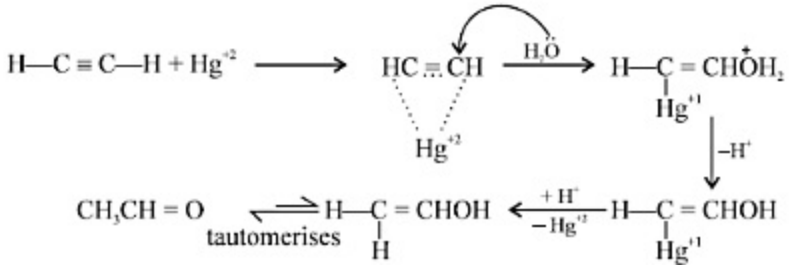
(6) **Hydration :**

$$C_2H_2 \xrightarrow[60^\circ C]{Hg^{+2},\ H_2SO_4\ (20\%)} CH_3CHO$$

It is interesting that C_2H_4 hydrates in presence of H^+ only but C_2H_2 needs metal catalyst like Hg^{+2} (Cu^+ or other as catalyst and this is due to the less reactivity of $C \equiv C$ towards E^+ compared to $C = C$).

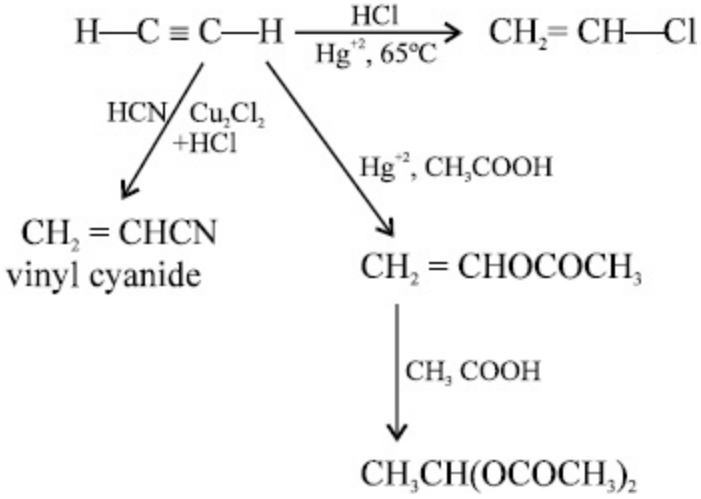
$$R{-}C \equiv CH \xrightarrow[H_2O]{Hg^{+2},\ H^+} RCOCH_3$$

Mechanism :

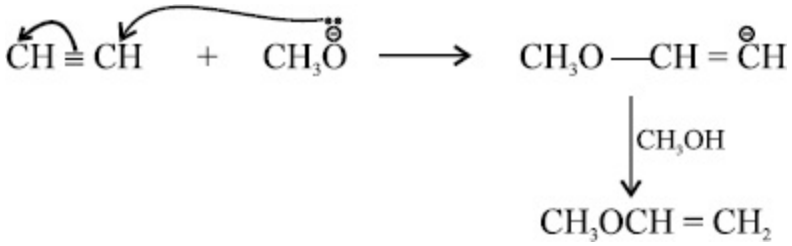


(7) $$CH \equiv CH \xrightarrow[AlCl_3]{RCOCl} RCOCH{=}CH{-}Cl$$

(8)



Nucleophilic addition although is very difficult but at 160° – 200°C and in presence of 1–2% $CH_3O^-K^+$, methyl vinyl ether is formed.



Methyl vinyl ether is a member of the polymoer polynyl ether.

(9) **Additoin of C_2H_2** to unstaurated link is called as ethinylation.

For example;

(a) $CH \equiv CH + CH_2=O \xrightarrow{MeO^-} CH \equiv C—CH_2—OH$

$CH \equiv C—CH_2—OH \xrightarrow{CH_2=O,\ MeO^-} HO—CH_2—CH \equiv C—CH_2OH$

(b) $H—C \equiv C—H \xrightarrow{NaNH_2} H—C \equiv C^{\ominus}\ Na^{\oplus} \xrightarrow{Me_2C=O} Me_2C(O^-Na^+)—C \equiv CH$

(10) **Addition of HOCl**

$H—C \equiv C—H + HO—Cl \xrightarrow{HOCl} [CHCl_2CH(OH)_2] \rightarrow CHCl_2CHO$

Mechanism :

$HOCl \rightleftharpoons H^+ + OCl^-$

$HO—Cl + H^+ \longrightarrow H_2O^+—Cl \longrightarrow H_2O + Cl^{\oplus}$

$H—C \equiv C—H + Cl^{\oplus} \longrightarrow CH(Cl) = CH^+ \xrightarrow{H_2O,\ -H^+} CHCl = CHOH$

$CHCl = CHOH \xrightarrow{Cl^{\oplus}} Cl—CHCl—CHOH$

$Cl—CHCl—CHOH \xrightarrow{H_2O,\ -H^+} CHCl_2—CH(OH)_2 \xrightarrow{-H_2O} CHCl_2CH = O$

(11) **Addition of borane :**

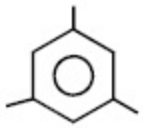
$3RC \equiv CR + BH_3 \longrightarrow [R(H)C = C(R)—B]_3 \xrightarrow[OH^-]{H_2O_2} R(H)C = C(R)OH$

$[R(H)C = C(R)—B]_3 \xrightarrow{CH_3COOH} R(H)C = C(R)H$

$R(H)C = C(R)OH \xrightarrow{\text{Tautomerises}} RCH_2—C(=O)—R$

(12) Polymerisation :

(a) $3CH \equiv CH \xrightarrow[600°C]{\text{Cu-tube}}$ 

(b) $CH_3C \equiv CH \xrightarrow[\Delta]{\text{Cu-tube}}$ 

Mesitylene

(c) $2CH \equiv CH \xrightarrow[Cu_2Cl_2]{\text{Ammonical}} CH_2 = CH - C \equiv CH$

(vinyl acetylene)

$$\xrightarrow[Cu_2Cl_2]{\text{Ammonical}} \overset{CH \equiv CH}{\downarrow}$$

$CH_2 = CH - C \equiv C - CH = CH_2$

(Divinyl acetylene)

$$CH_2 = CH - C \equiv CH + HCl \xrightarrow{[Cu(NH_3)_2Cl]} [CH_2Cl - CH = C = CH_2]$$

(1, 4 addition)

$$\downarrow \text{Isomerises}$$

$$CH_2 = \underset{\displaystyle Cl}{\underset{|}{C}} - CH = CH_2$$

Chloroprene

Chloroprene polymerises to neoprene rubber.

(e) $4C_2H_2 \xrightarrow{\Delta}$ 

(13) $H - C \equiv C - H \xrightarrow{\overset{\ominus}{R}\ \overset{\oplus}{MgX}} RH + H - C \equiv \bar{C}\ \overset{\oplus}{M}gX$

(14) $H - C \equiv C - H + LiNH_2 \longrightarrow NH_3 + H - C \equiv C^-Li^+$

(15) $H - C \equiv C - H \xrightarrow{[Ag(NH_3)_2Cl]} Ag - C \equiv C - Ag \downarrow$

(white ppt.)

(16) $R-C\equiv C-H \xrightarrow{[Cu(NH_3)_2Cl]} R-C\equiv C-Cu\downarrow$ (red ppt.)

(14), (15), (16) reactions are used to detect the presence of terminal alkyne.

(17) Isomerisation :

(a) Shift of terminal ≡ to central position ;

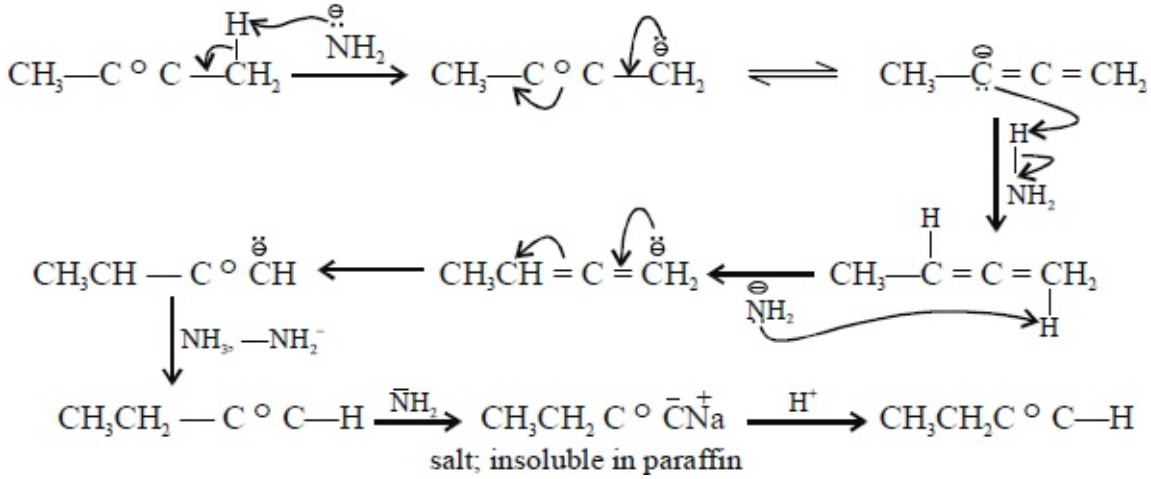
$$CH_3-CH_2C\equiv CH \xrightarrow[\Delta]{\text{alc. KOH}} CH_3-C\equiv C-CH_3$$

(b) Shift of central ≡ to terminal position ;

$$CH_3-C\equiv C-CH_3 \xrightarrow[\text{Paraffin}]{\text{1) } NaNH_2,\ \text{2) } H^+} CH_3CH_2C\equiv C^{\ominus}Na^+$$

Mechanism for (a), (b) are same

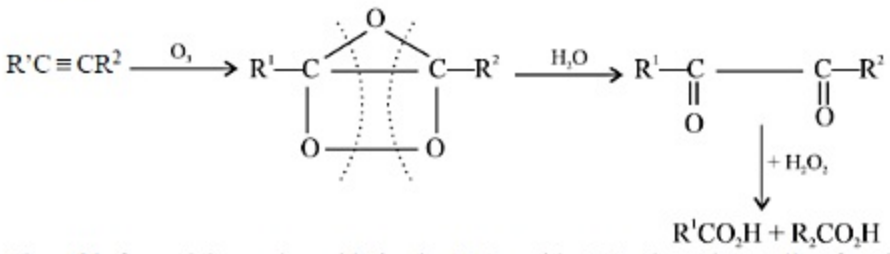
Mechanism for (b) ;



(18) $R-C\equiv C-Cu \xrightarrow[CH_3COOH]{O_2,\ \Delta} R-C\equiv C-C\equiv C-R$

coupling reaction product

(19) Ozynolysis :



The acids formed due to the oxidation by H_2O_2, with C_2H_2 glyoxal as well as formic acid are produced.

Alkyl halide

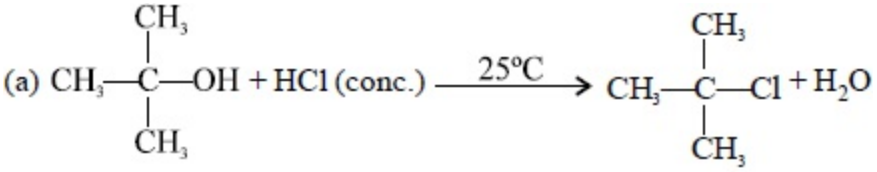
The alkyl halides have general formula $C_nH_{2n+1}X$, where X denotes F, Cl, Br, I.

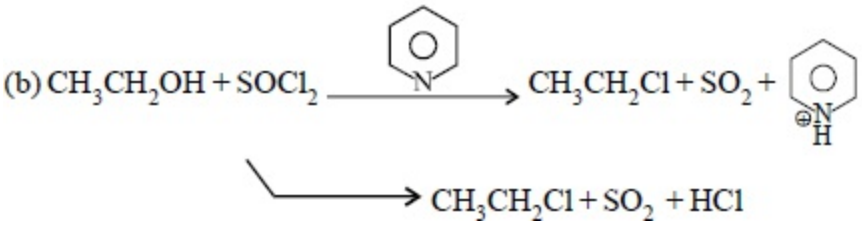
Preperation:

Very good source of alkyl halide is alkane, which we have already discussed in the chapter of alkane. We will discuss other methods of preparations below.

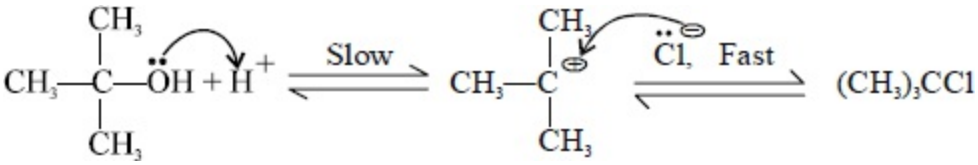
1. From alcohol:

For alcohols –OH is a bad leaving group therefore we first convert it into a good leaving groups like H_2O, $[Zn(OH)Cl_2]$, $-HOPBr_2$, $-OSOCl$, $-OPCl_4$ etc using H^+, $ZnCl_2$ (catalytic amount), PBr_3, $SOCl_2$, PCl_5 etc respectively and the X (halide) attacks to give RX.

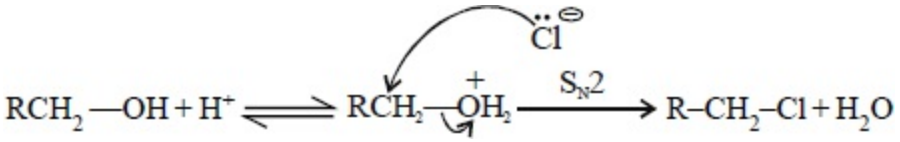




Mechanism for (b) already have been discussed. Mechanism for (a) is,

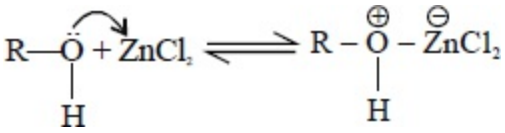


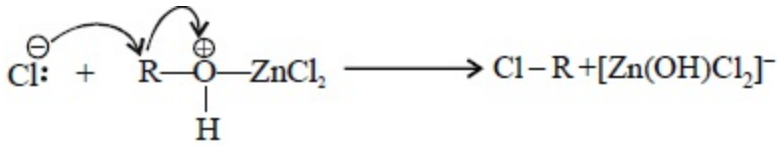
The mechanism is S_N1 where dehydration is slow step and $\ddot{X}^{\ominus}$ is the effective nucleophile at high concentration . For 1 alcohol, CH_3OH proceeds through S_N2 mechanism.



As the Cl^- is a poor nucleophile than Br^-, I^-. Therefore HCl does not react with 1°, 2° alcohol unless $ZnCl_2$ is used and produces a better leaving group than H_2O.

Mechanism:





$$[Zn(OH)Cl_2]^- + H^+ \rightleftharpoons ZnCl_2 + H_2O$$

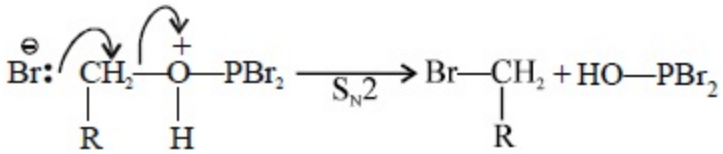
(c) 1°, 2° alcohol react with PBr_3 to give RBr

$$3R\text{–}OH + PBr_3 \longrightarrow R\text{–}Br + H_3PO_3$$

Mechanism:



(Lewis acid)



$$\therefore HOPBr_2 + 2RCH_2OH \longrightarrow H_3PO_3 + 2R\text{–}Br$$

So net 3 moles of R–Br forms.

2. From ether: Ethers can only react with acid not with base or nucleophile.

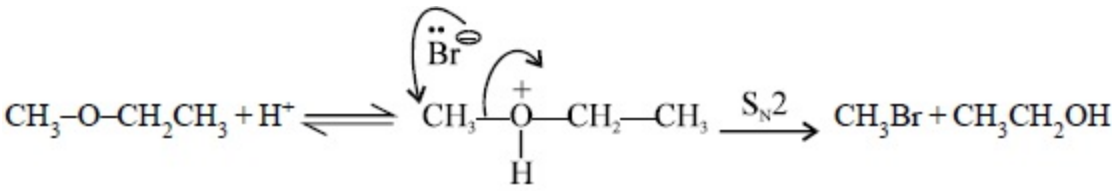
$$R\text{–}O\text{–}R' + HBr \xrightarrow{\Delta} R\text{–}Br + R'OH$$

$$R'OH + HBr \xrightarrow{\Delta} R'\text{–}Br + H_2O$$

For the cleavage of R–O bond and R' – O bond concentrated HI, HBr, H_2SO_4

under heating carry out the change.

Mechanism:



With another mole of HBr, CH_3H_2Br forms by S_N2. With cold conc. HI,

$$R{-}O{-}R + HI \longrightarrow ROH + RI$$

and with concentrated hot HI,

$$ROR + 2HI \longrightarrow 2RI + H_2O$$

This has been discussed vividly in ether chapter.

3. Hunsdicker or Borodine–Hunsdicker reaction:

$$R{-}COOAg + Cl_2/Br_2 \xrightarrow[\Delta]{CCl_4} \underset{\text{or } RBr}{R{-}Cl} + CO_2 + \underset{\text{or } AgBr}{AgCl}$$

Mechanism :

$$RCO_2Ag + Br_2 \longrightarrow RCOOBr + AgBr$$

$$RCOOBr \longrightarrow Br^{\bullet} + RCOO \downarrow R^{\bullet} + CO_2$$

$$R^{\bullet} + Br_2 \longrightarrow R{-}Br + Br^{\bullet}$$

$$R^{\bullet} + RCOOBr \longrightarrow RBr + RCO_2^{\bullet} \quad \text{etc.}$$

4. Birnbaum-Simonini reaction:

Reaction:

$$RCO_2Ag + I_2 \longrightarrow RCO_2R + CO_2 + AgI$$

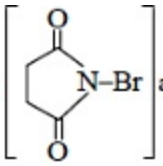
Here instead of R – I, ester results.

5. $$CH_2{=}CH{-}CH_3 \xrightarrow[600^{\circ}C]{Cl_2} CH_2{=}CH{-}\underset{Cl}{CH_2}$$

At high tempertature allylic substitution takes place instead of normal addition to double bond due to formation of Cl.

6. $$CH_2{=}CH{-}CH_3 \xrightarrow{NBS} CH_2{=}CH{-}CH_2{-}Br$$

Mechanism:

In presence of trace amount of water HBr forms from N-bromo succinimide  as shown below;

$$H-Br + NBS \longrightarrow Br_2 + \text{other product}$$

$$Br_2 \xrightarrow{h\nu} 2Br^{\bullet};\ Br^{\bullet} + CH_2{=}CH{-}CH_2 \longrightarrow HBr + CH_2{=}CH{-}\dot{C}H_2$$

$$CH_2{=}CH{-}\dot{C}H_2 \xrightarrow{Br_2} CH_2{=}CH{-}CH_2{-}Br + Br$$

For an enyne, it takes α -C with respect to the triple bond preferab ly. Also trace amount of Br• only picks up allylic–H as the bond dissociation energy is low for allylic C–H.

7. $$CH_3COCH_3 \xrightarrow{X_2/H^+} CH_2(X){-}COCH_3$$

Mechanism will be disscussed in the carbonyl compound chapter.

8. $$RCH_2COOH_3 \xrightarrow{X_2/Red} R{-}CH(X){-}COOH$$

Mechanism wll be disscussed in the carboxylic acid compound chapter.

9. $$(RCO_2)_4Pb + X_2 \longrightarrow 2RX + RCO_2R$$

10. $$R{-}COR' \xrightarrow{PCl_5} RCCl_2R' + POCl_3$$

(Dihalide)

11. $$CH{\equiv}CH \xrightarrow{2HBr} CH_3CHBr_2$$

12. $$CH_3COCH_3 \xrightarrow[OH^-]{3Cl_2} CCl_3COCH_3 \xrightarrow[H_2O]{OH^{\ominus}} CHCl_3 + CH_3COO^-$$

Chloroform

Similarly CHI_3, $CHBr_3$ also can be formed by the above reaction

13. $$CS_2 + Cl_2 \xrightarrow{AlCl_3} CCl_4 + S_2Cl_2 \text{ (sulphur monochloride)}$$

(colourless liquid)

14. Flurocompound can also be prepared in the following ways

(a) $RCH=CH_2 \xrightarrow[\text{Pressure}]{H-F} RCH(F)-CH_3$

(b) $RC\equiv CH \xrightarrow{2HF} RCF_2CH_3$

(c) $R-Cl \xrightarrow{AgF,\ \Delta} R-F$ (Swart's method)

(d) $CHCl_3 \xrightarrow[HF]{SbF_3} CHF_2Cl \xrightarrow{800^\circ C} C_2F_4$ (Tetrafluore ethylene) $+ \ 2HCl +$ Other product

$C_2F_4 \xrightarrow{\text{Polymerisation}} -\left[CF_2-CF_2\right]_n-$

Teflon

(resistant to aquarigia and other chemical reagents)

Physical Properties :

Alkyl halides have only dipole-dipole attraction. Therefore b.p., density has the order R – I > R – Br > R – Cl. For R, 1° > 2° > 3° as b.p. order (among isomers). They burn with green edged flame. Alkyl halides are insoluble in water but soluble in alcohol.

Chemical reactions:

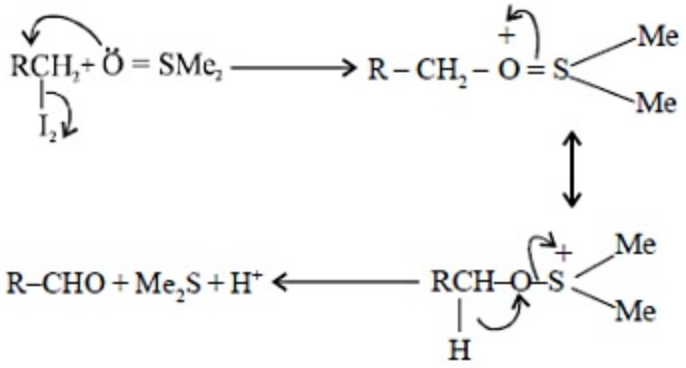
As far as the types of chemical reactions are concerned (S_N, E), those already have been discussed before. Some more reactions are;

1. $R-X \xrightarrow{M/H^+} R-H$ i.e., by dissolving metal in HCl.

2. $R-X+H_2 \xrightarrow{Pd-C} R-H+HX$
(1°, 2°, 3°)

3. $R-CH_2-I+Me_2S=O \longrightarrow RCHO+Me_2S+H^+$

Mechanism :



4. $C_2H_5Cl + 4Na/Pb \longrightarrow (C_2H_5)_4Pb + 4NaCl + 3Pb$

Organometallic compound, called as tetraethyl lead, used as antiknocking agent in petrol.

5. **Isomerisation :**

$$CH_3CH_2CH_2Cl \xrightarrow[\Delta]{AlCl_3} CH_3\underset{\underset{Cl}{|}}{CH}-CH_3$$

6. $RX + NH_3 \xrightarrow[\Delta]{\text{Pressure}} RNH_2$;

$$RNH_2 + R-X \longrightarrow R_2NH \xrightarrow{2RX} R_4\overset{+}{N}\bar{X}$$

This is called ammonolysis of alkyl halides.

7. $R-X \xrightarrow[\Delta]{KCN} R-CN + R-NC + KX$

(Major) (Minor)

8. $R-X \xrightarrow[\Delta]{AgCN} R-NC + R-CN + AgX$

(Major) (Minor)

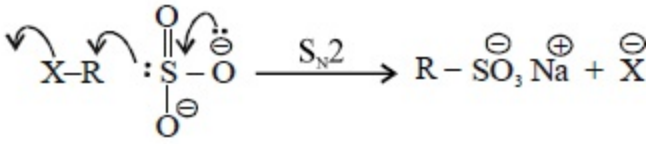
9. $RCO_2Ag + R'-X \longrightarrow RCO_2R' + AgX$

10. $R-X + Ag-O-N=O \xrightarrow{\Delta} R-NO_2 + R-O-N=O + AgX$

11. $RO^-Na^+ + R'-X \longrightarrow R-O-R' + NaX$ (Williamson's synthesis)

12. $R-X + Na_2SO_3 \longrightarrow RSO_3Na + NaX$

Mechanism :



13 $2CHCl_3 + 6Ag \xrightarrow{\Delta} C_2H_2 + 6AgCl$

14. $CHCl_3 + HNO_3\,(conc.) \longrightarrow CCl_3 - NO_2$ (Chloropicrin). It is used as an insectiside.

15. $CHCl_3 + KOH\,(alcoholic) + PhNH_2 \longrightarrow Ph - NC + 3KCl + H_2O$

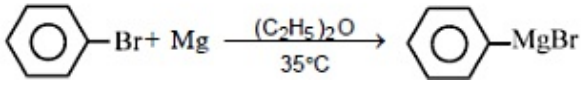
(Poisonous smell)

The above is used as the test for 1° amine.

Grignard's reagent

Preparation :

$$R-X + Mg \xrightarrow[(C_2H_5)_2O]{\text{Anhydrous}} RMgX$$; R = CH_3/ 1°/ 2°/ 3°, alkyl groups or cycloalkyl, alkenyl, aryl group etc.



The order of reactivity of halides are, I > Br > Cl > F and RX > ArX, $CH_2 = CH - X$.

Tetrahydrofuran can also be used as solvent instead of acyclic ether.

Physical properties :

The commonly written structure of Grignard's reagent is RMgX in which R is negatively polarized carbon and can be shown as $\overset{\delta\ominus}{R}-\overset{\delta\ominus}{MgX}$.

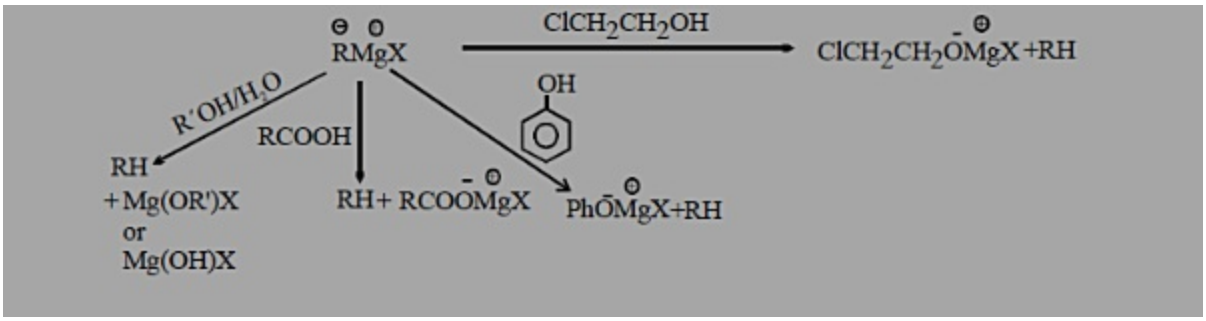
The other experimental data regarding the structure is beyond the scope of this book.

Chemicial reactions:

Generally the alkyl or aryl part acts as the nucleophilic as well as basic site. Therefore it undergoes nucleophilic addition to carbonyl compound or other polarised multiple bond. (eg. – C ≡ N etc.). As it can act as a very strong base (as RH is very weak acid). Therefore whenever it finds acidic – H it picks up and the reactivity order of RMgX is,

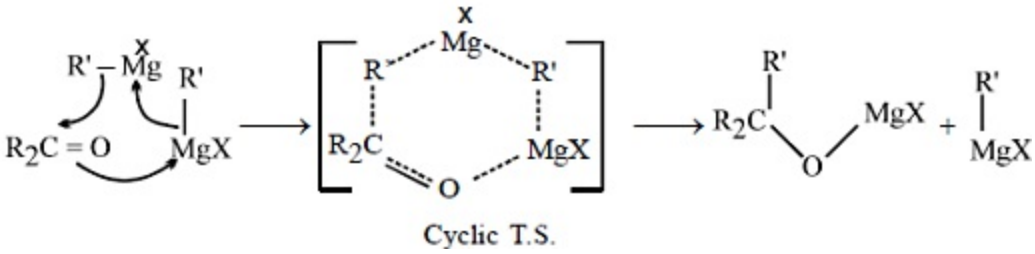
$$\text{Acidic} - H >> -\underset{\underset{H}{|}}{C}=O > -\underset{|}{C}=O > -\overset{\overset{O}{\|}}{C}-Cl > -\underset{\underset{OR}{|}}{C}=O > -CH_2X$$

(1) Grignard's reagent acting as a base;



(2) $R-MgX + R'-\underset{\underset{O}{\|}}{C}-R'' \longrightarrow R-\underset{\underset{R'}{|}}{\overset{\overset{O-MgX}{|}}{C}}-R''$ (1,2, addition)

Mechanism :



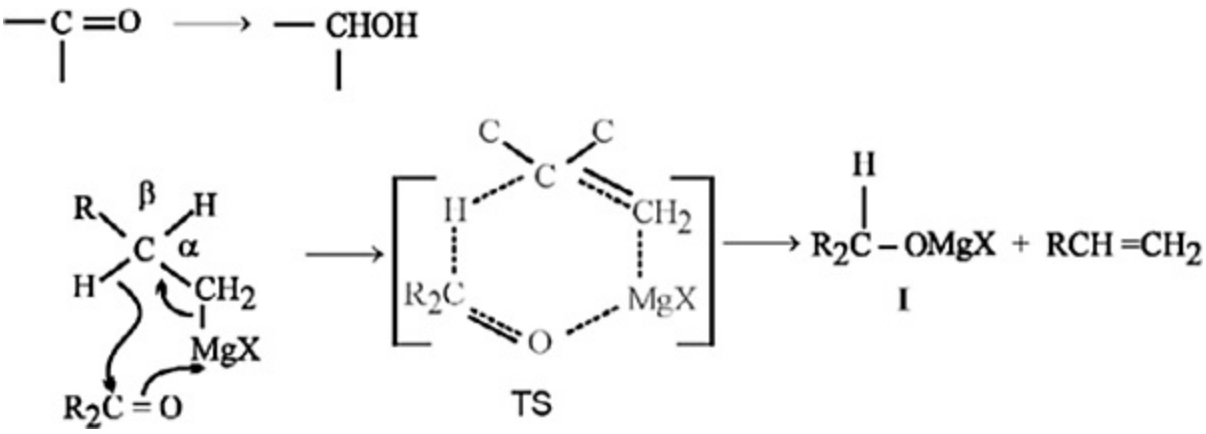
Cyclic T.S.

The mechanism as shown above is predicted because (1) two molecules of Grignard's reagent is involved in which second molecule acts as the Lewis acid and (2) Addition of MgX_2 speeds up the reaction, [Therefore RMgX can be thought of the mixture of $R_2Mg + MgX_2$

As the reactant concentration increases, rate of nucleophilic addition also increases. While reaction to carboxyl compounds shown above always is 1, 2, It can be also 1, 4 addition. Exception to the normal 1,2 addition reactions are also found.

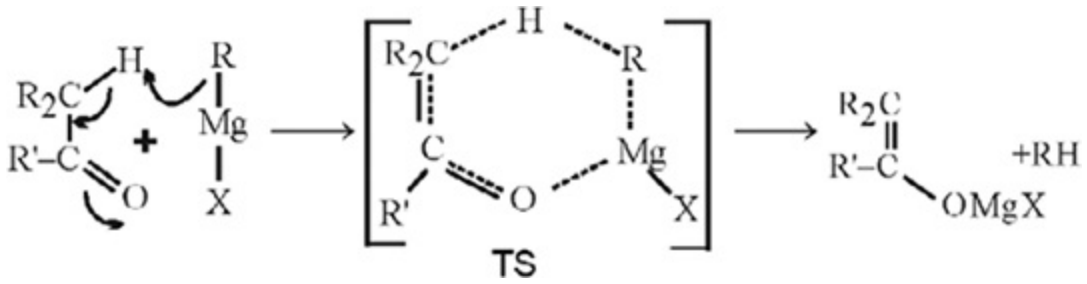
For Example,

Case –1 : GR having H-atoms on their P- carbon atom (RCH_2CH_2MgX) tends to reduce



Look at I, in which instead of alkyl group with bp electrons hydride transfer takes place to the C δ^+ and thereby ketone reduces to 2° alcohol.

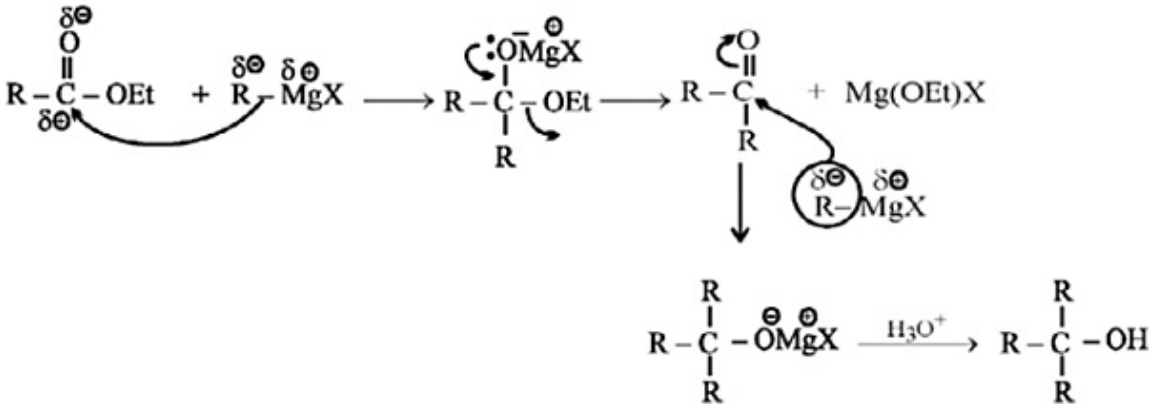
Case- 2 : Sterically hindered ketones having α - H atom tend to be converted to enols and GR converts to R–H.



The above addition reactions are irreversible in nature.

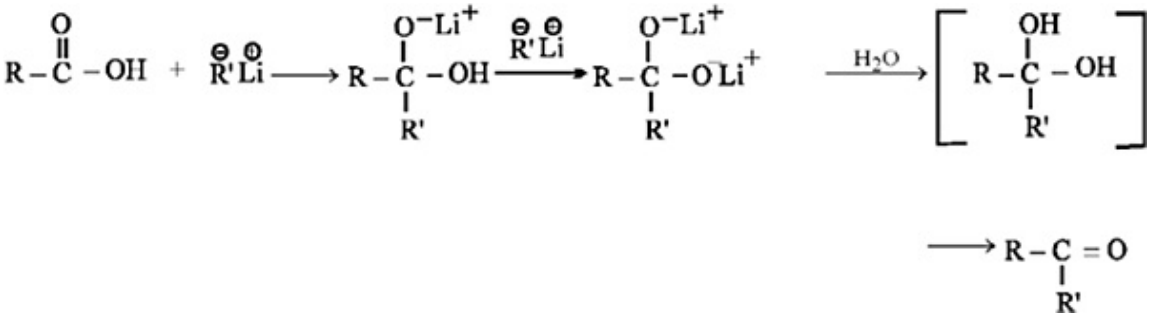
(3) Reactions with $R-\overset{\overset{O}{\|}}{C}-Z$ where Z = Cl, OEt etc.

For example ;



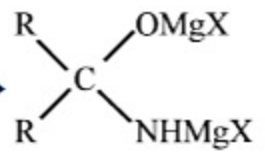
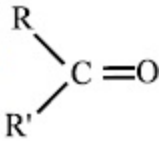
Therefore 2 moles of GR are required for ester, acid halides etc. to produce

3° alcohol upon hydrolysis. Recently GR are replaced by RLi, ArLi etc. as they prefer to give (1, 2) addition product compared to (1, 4) addition product and gives normal addition products with sterically hindered ketones. For example- with acid



(4) $R-C(=O)-NH_2 + R'MgX \longrightarrow R'H + RCONHMgX$

Hence the above hydrogen in amide is acidic.

Further RCONHMgX $\xrightarrow{R'MgX}$  $\xrightarrow[H_3O^+]{\text{Hydrolysis}}$ 

Therefore, $RCONH^{\ominus}$ (conjugate base of $RCONH_2$) is very less acidic.

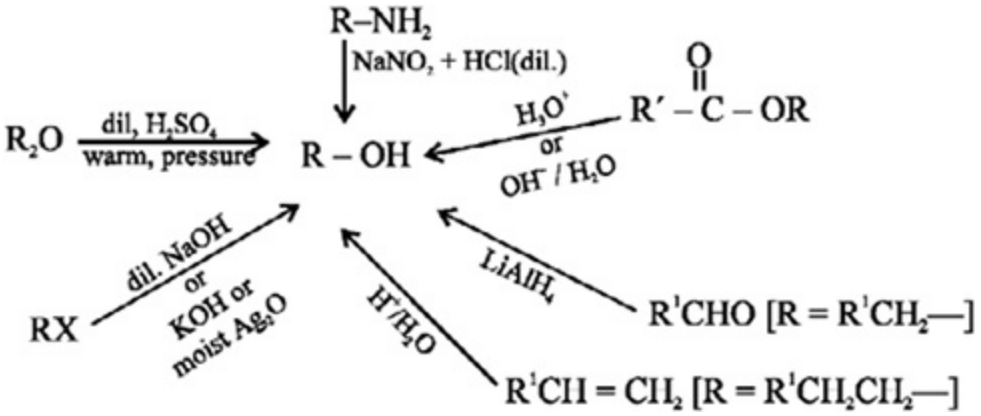
(5) $RMgX + Cl-CN \longrightarrow R-CN + MgXCl$

But, $RMgX + Cl-NH_2 \longrightarrow R-NH_2 + MgXCl$

Alcohol

Alcohol is a compound which contain –OH group. If one –OH group is present then the molecule is called monohydric, if two then dihydric alcohol etc.

Preparation:



Mechanism for the above reactions are :

(1) $R-X + \overset{\ominus}{O}H \xrightarrow[S_N2]{NaOH} R-OH + X^-$

(2) $R-\ddot{N}H_2 + \overset{+}{N}O \xrightarrow[-H^+]{NaNO_2 + HCl} R-NH-N=O \rightleftharpoons R-N=N-\ddot{O}H \xrightleftharpoons{H^+}$

$R-\overset{+}{N}\equiv N \longleftrightarrow R-\ddot{N}=\overset{\oplus}{N} \rightleftharpoons R-N=N-\overset{+}{O}H_2$

$H_2\ddot{O}$, $-H^+$

$HO-R + N_2\uparrow$

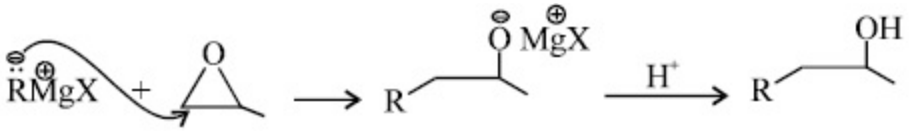
(3) $R_2\ddot{O}: + H^+ \longrightarrow R-\overset{H}{\overset{|}{\overset{+}{O}}}-R + H_2\ddot{O} \longrightarrow R-OH + [R-\overset{+}{\underset{H}{\overset{|}{O}}}-H \xrightarrow{-H^+} R-OH]$.

So, one mole of ether produces two moles of alcohol.

Other mechanisms either we have seen in alkene chapter or we will see in carbonyl and ester chapters.

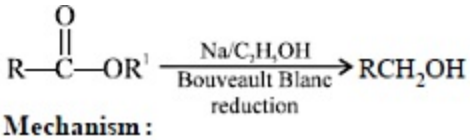
(4) $\overset{\ominus}{R}MgX \xrightarrow{R'CH=O} R-\underset{H}{\overset{R^1}{\overset{|}{C}}}-\vec{O}\,\overset{\oplus}{M}gX \xrightarrow[\delta^+\ \ \delta^-]{H_2O} R-\underset{H}{\overset{R^1}{\overset{|}{C}}}-OH + Mg(OH)X$

H—OH

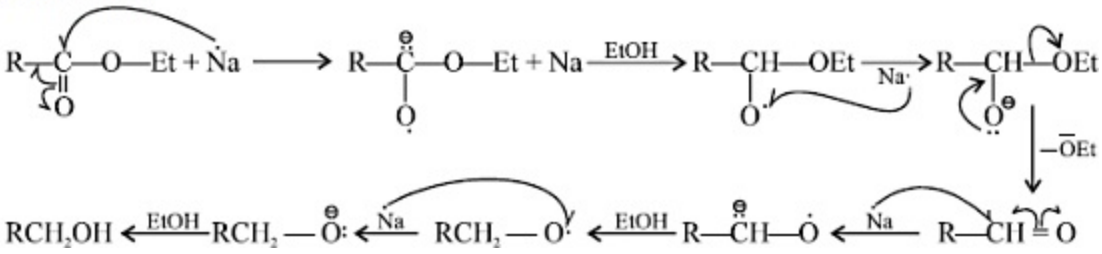
(5) 

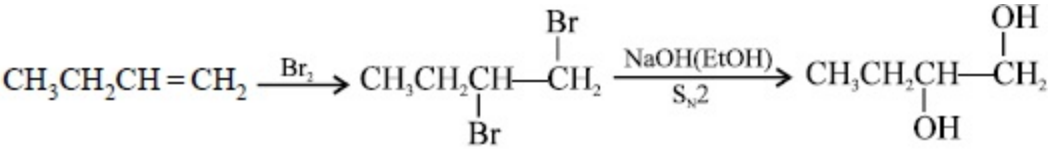
(6) $CO + H_2 \xrightarrow[\text{Zn - Chromite}\\ \text{+ Alkali metal}]{\text{Heat, Pressure}} \text{Mixture of alcohols}$

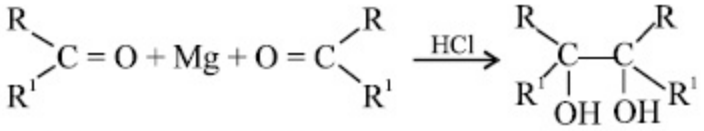
(7) $RCH = CH_2 + CO + H_2 \xrightarrow[\text{Oxo process}]{Co(HCO)_4} \text{Aldehyde} \xrightarrow[H_2]{Zn-Cu} \text{Mixture of Alcohols}$

(8) 

Mechanism :



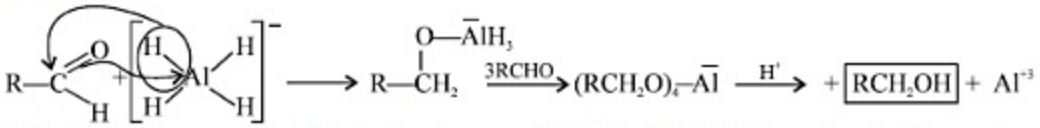
(9) 

(10) 

Mechanism is given later.

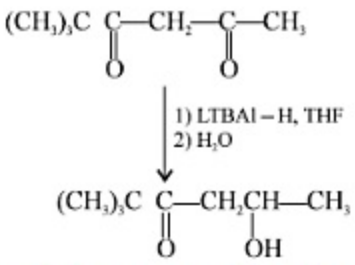
(11) Mechanism of reduction of –CHO, $-\overset{\overset{O}{\|}}{C}-$, $-\overset{\overset{O}{\|}}{C}-OH$ etc. by $LiAlH_4$ or mechanism of reduction of –CHO, $-\overset{\overset{O}{\|}}{C}-$, $-\overset{\overset{O}{\|}}{C}-Cl$ etc. by $NaBH_4$ occurs through hydride ($\overset{\ominus}{H}$:) transfer in ether medium,

For example :



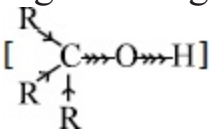
If the size of R increases rate of reduction decreases for $R_2C=O$. With lithium tritertiary butoxy aluminium hydride i.e. $Li[Al(O\text{-}tBu)_3H]$ only sterically unhinderd carbonyl group is reduced.

For example ;



$NaBH_4$ is a weaker reducing reagent and it may be due to strong B – H bond compared to Al – H bond.

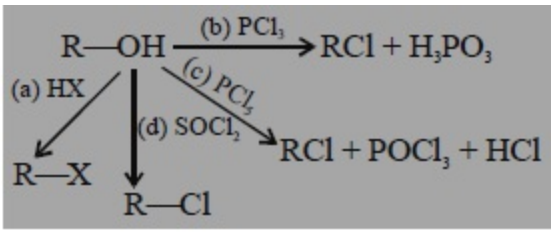
Physical properties :

They can make intermolecular H-bonding due to which they are high boiling, high meltingand low volatile compared to ether. 3° alcohol has least acidity  and CH_3OH has most acidity. Polarity of CH_3OH is less than water. They are acidic and react withNa-metal and produce hydrogen gas. With Grignard's reagent (CH_3MgBr), give alkane. They undergo mainly two types of reactions. (A) C – O bond fission (B) O – H bond fission. These also undergo dehydration in presence of cone. H_2SO_4 and heating strongly.

Chemical reaction:

(A) 'C – O' bond fission reactions :

(1)



(2) $R-OH + NH_3 \xrightarrow[Al_2O_3]{\Delta} RNH_2$

(Excess for 1°, 2°, 3° amine)

(3) $CH_3CH_2OH \xrightarrow{H^+,\ heat} CH_2=CH_2$

(1) **Mechanism with PCl_5 :**

(a) $R\ddot{O}H + PCl_5 \longrightarrow R-\overset{+}{O}(H)-\overset{\ominus}{P}Cl_4(Cl) \xrightarrow{-H^+} R-O-PCl_4 + HCl \xrightarrow[S_N2]{\ddot{Cl}^{\ominus}} Cl-R + \overset{\ominus}{O}PCl_4 \xrightarrow{-Cl^-} O=PCl_3$

(b) $R-OH + H^+ \longrightarrow R-\overset{+}{O}H_2 \xrightarrow{\ddot{Cl}^{\ominus};\ S_N2} R-Cl + H_2O$

(B) **'O – H' bond fission reactions :**

(1) $R-OH + Ph/R\,COCl \longrightarrow R/Ph-\overset{O}{\overset{\|}{C}}-OR$

Mechanism :

$Ph-\overset{O}{\overset{\|}{C}}-Cl + R-\ddot{O}H \longrightarrow Ph-\overset{O^-}{\underset{Cl}{\overset{|}{C}}}-\overset{H}{\overset{|}{O^+}}-R \xrightarrow{-HCl} Ph-\overset{O}{\overset{\|}{C}}-OR$

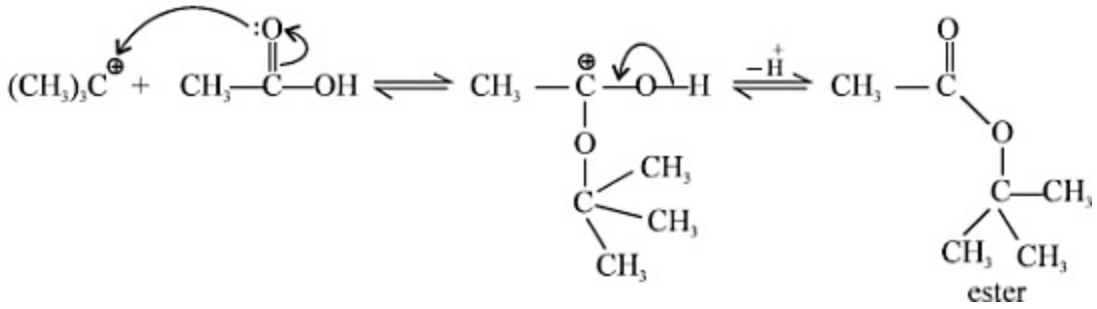
(2) $R-\ddot{O}-H \xrightarrow{\overset{\ominus}{\ddot{C}}H_3MgX} R-\ddot{O}^{\ominus}MgX + CH_4$ [Acidic H is picked up everywhere]

(3) $R-\ddot{O}-H \xrightarrow{\overset{\ominus}{\ddot{C}}H_3Li^+} R\ddot{O}^{\ominus}: Li^+ + CH_4$

(4) $R-OH + D_2O \rightleftharpoons ROD + HOD$ [Deuterium exchange takes place].

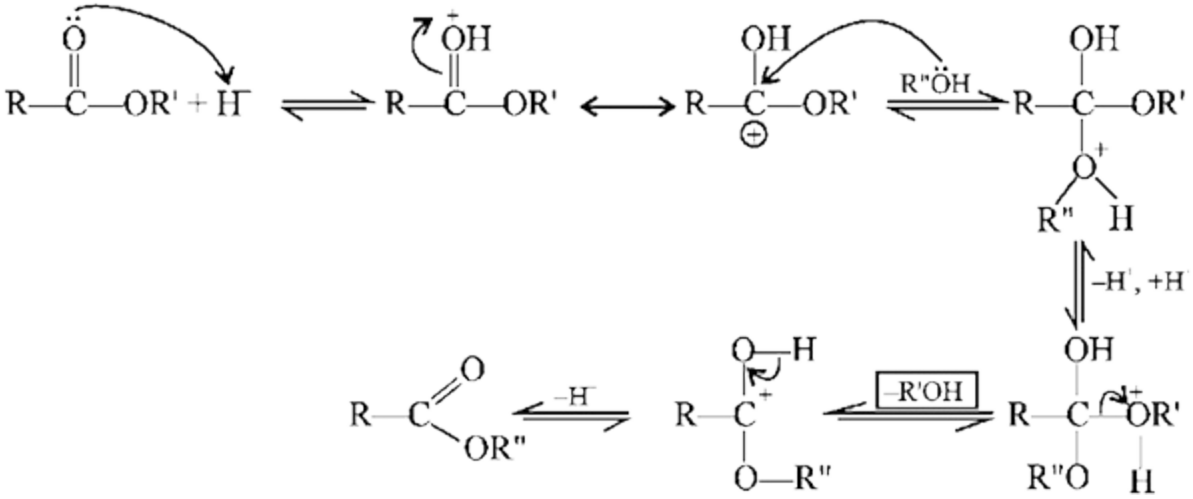
(5) $(CH_3)_3COH + CH_3COOH \overset{H^+}{\rightleftharpoons} CH_3COOC(CH_3)_3$

Mechanism : $(CH_3)_3COH + H^+ \rightleftharpoons (CH_3)_3C\text{—}\overset{+}{O}H_2 \xrightleftharpoons{-H_2O} (CH_3)_3C^+$



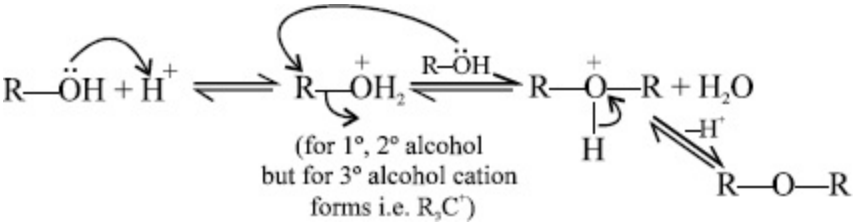
Transesterification is that reaction in which alcohol exchange takes place from the ester. Reaction can be acid or base catalysed.

For example; Mech anism: $RCOOR' + R''OH \overset{H^+}{\rightleftharpoons} RCOOR'' + R'OH$



(9) Alcohols give ether by removal of water and ethers give alcohol by addition of water to ether.

For example;

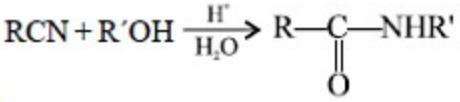


The order of ether formation for alcohols is 3°<2°<l° and it is basically the acidic strength order of 1°, 2°, 3° alcohol.

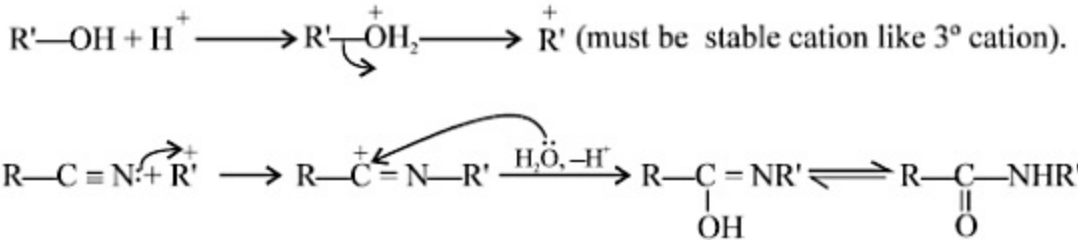
(10) Epoxide ring cleavage also take place which we will see later.

(11) Addition of ROH to polar R'CN molecule is acid catalysed.

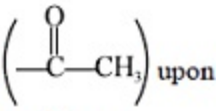
For example ;

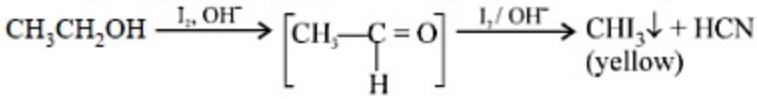


Mechanism :



Haloform reaction :

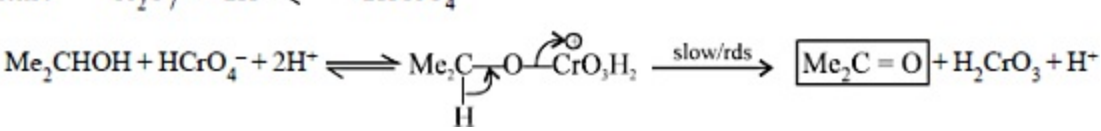
1°, 2° alcohols can respond to haloform reaction provided they give keto methyl group  upon oxidation. eg; CH_3CH_2OH, $CH_3CHOHCH_3$ etc. The mechanism in detail has been discused later.



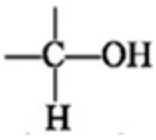
Dehydration : This has already been discused in alkene chapter.

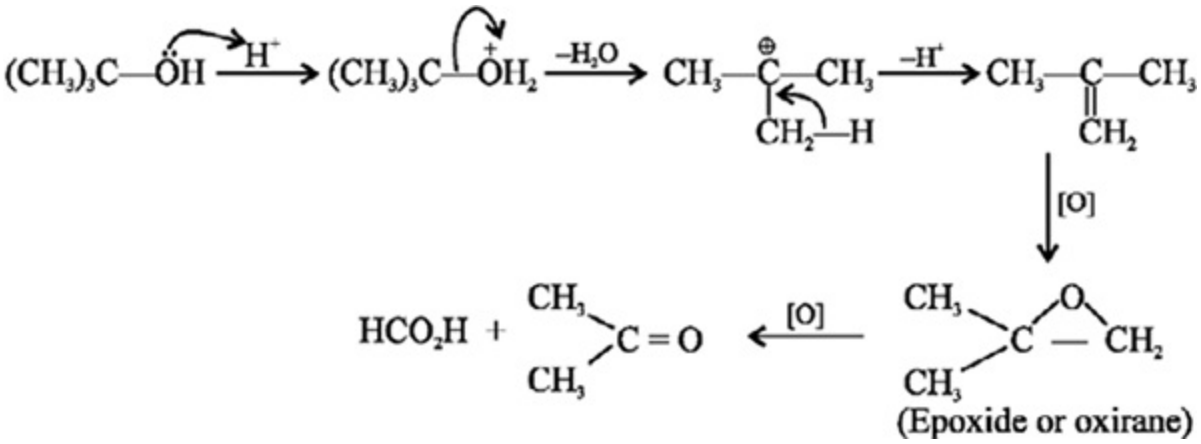
Oxidation by $Cr_2O_7^{-2}$, H^+ or MnO_4^-, H^+

Mechanism :

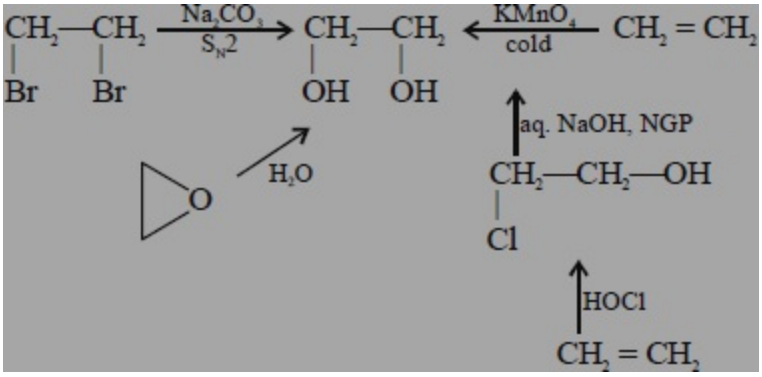


As we understand that the last step is the slowest step or rds, therefore α – C containg D/T atoms will show slow rate of oxidation as we know C—D/C—T bond is stronger than C—H bond. This is called primary kinetic isotope effect as change of isotope decreases the rate of reaction.

When 3° alcohol is oxidised then we donot have  bond, therefore reaction occurs through alkene formation. Look at the mechanism of the reaction and products;



Preparation of diol:

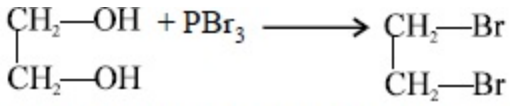


Pinacol (which is also a diol) formation will be seen in the carbonyl chapter.

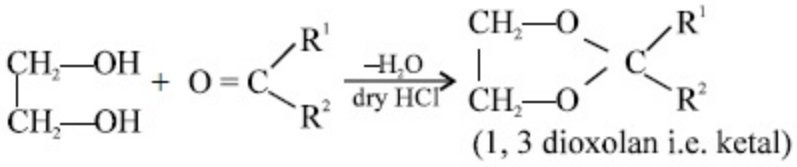
Physical Properties:

These are high boiling, high melting compounds and also highly soluble in water and these are all due to intermolecular H–bonding.

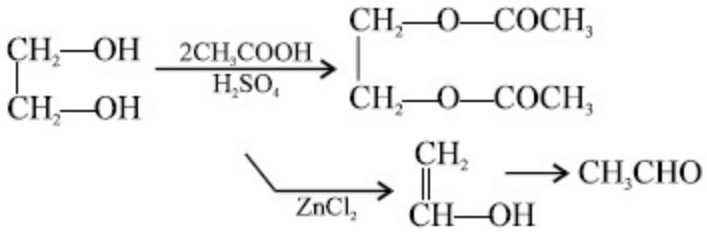
Chamical reaction:

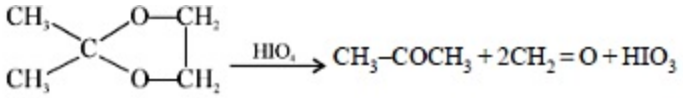
(1) 

Similarly PCl_3, also give the same type of products. With PI_3, $CH_2 \| CH_2$ form.

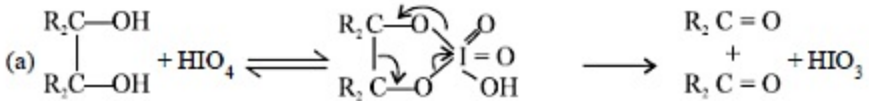
(2) 

(1, 3 dioxolan i.e. ketal)

(3) 

(4) 

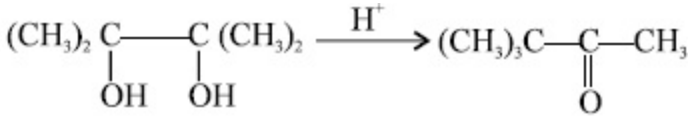
(5) 1, 2 diol cleavage take place by (a) HIO_4 (b) $Pb(OCOCH_3)_4$ and mechanism can be written as the following:

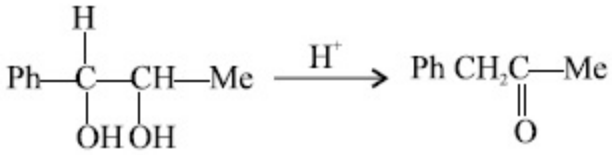
(a) 

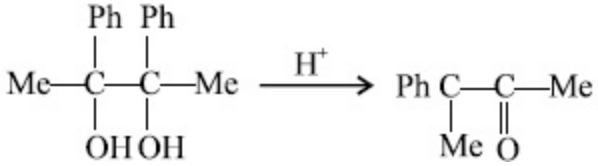
Pinacol – pinacolone rearrangement:

1, 2 diol converts to ketone in presence of dil H_2SO_4 is called as pinacol pinacolone rearrangment.

Reactions:

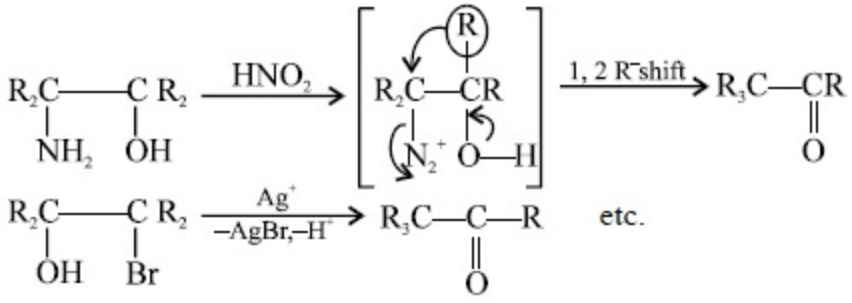
(1) 

(2) 

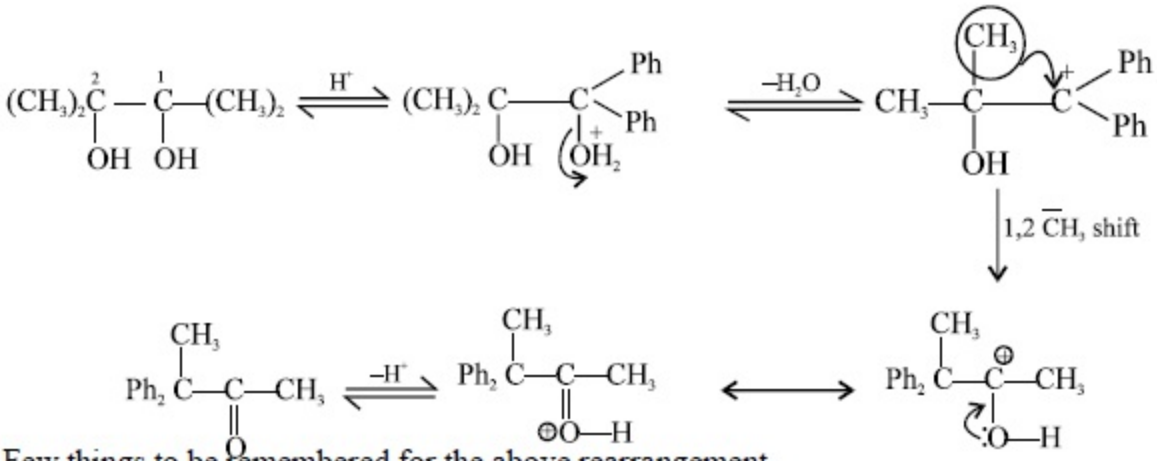
(3) 

Pinacol-pinacolone type rearrangement reactions also have been observed in

the following cases :



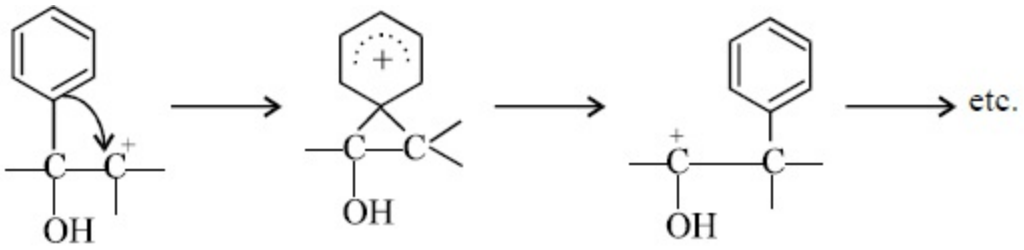
Mechanism :



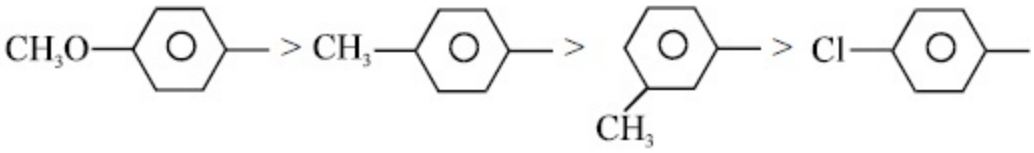
Few things to be remembered for the above rearrangement.

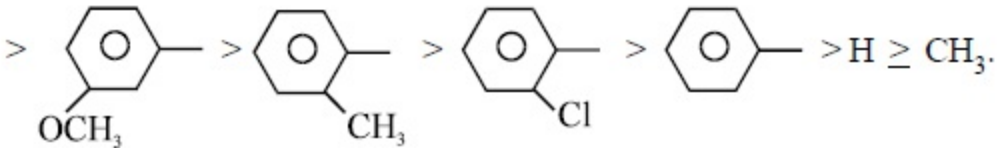
(1) Make the carbocation out of two, C_1, C_2 by protonation at suitable –OH lp.

(2) Mgrate that group after which final $C^{\oplus}$ becomes stabler but as far as phenyl, group with bp electrons migration is concerned it requires low activation energy. The rearrangement can be as shown (through 3 – Centred intermediate) shown below.



Migratory order is,

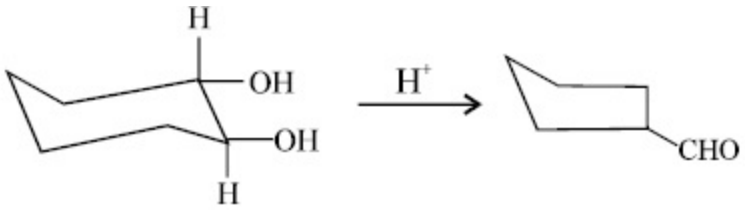




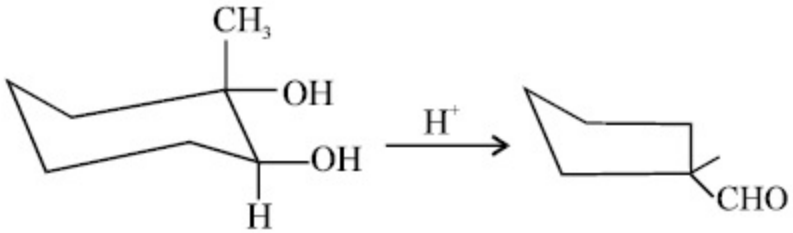
Phenyl with ortho methyl group has less migrating aptitude, may be due to steric crowding it face during the migration.

Some more examples are :

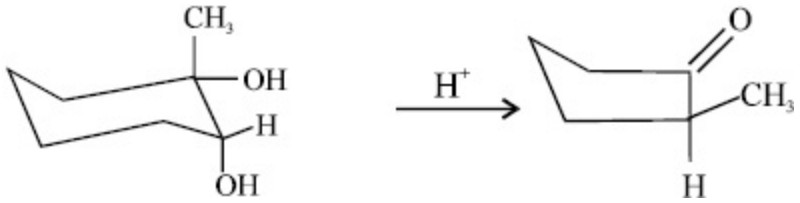
(a)



(b)

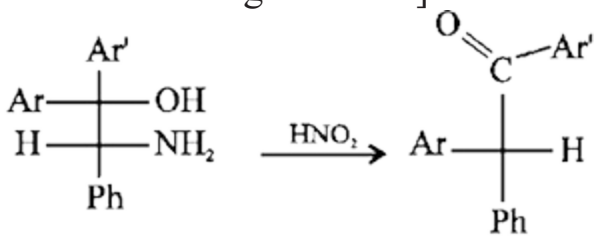


(c)



[Note : lp on axial –OH easily protonates compared to equatorial OH due to

less steric crowding H^+ face.]

(d) 

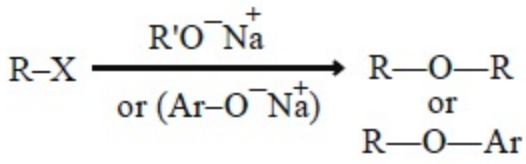
(Here anti group to the leaving group $–N_2$ migrates)

Ether (C—O—C) and thioether (C—S—C)

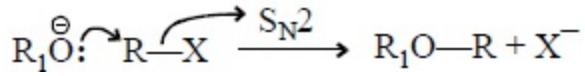
Generally R—O—R' or R-OAr or ArOAr' are called ethers and R-S–R' etc are called thioether, where R= alkyl, allyl, cycloalkyl, vinyl etc. and Ar = Benzyl, phenyl etc.

Preparation:

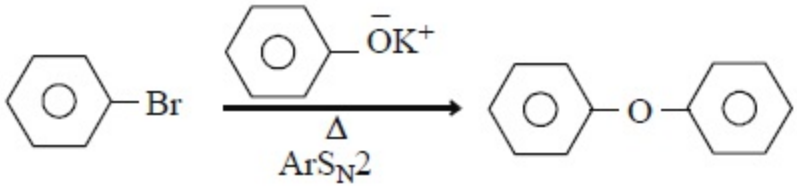
(1) **Williamsons's synthesis:**



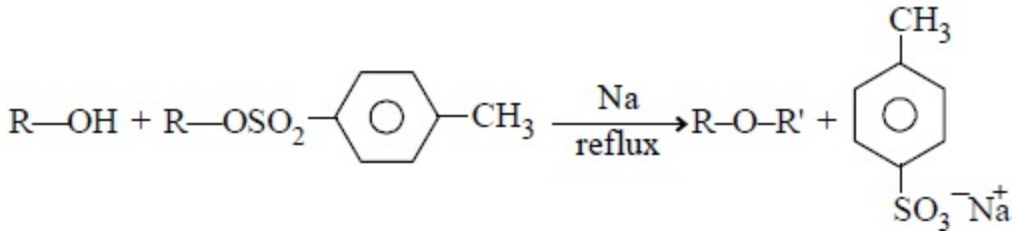
Mechanism:



(2) **Ullmann's synthesis:**

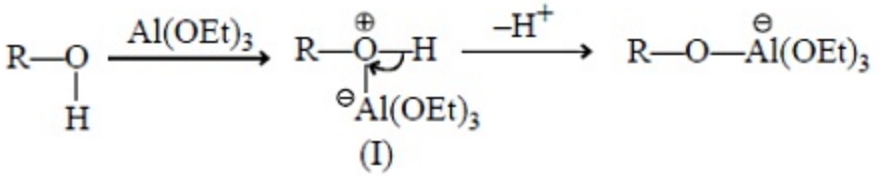


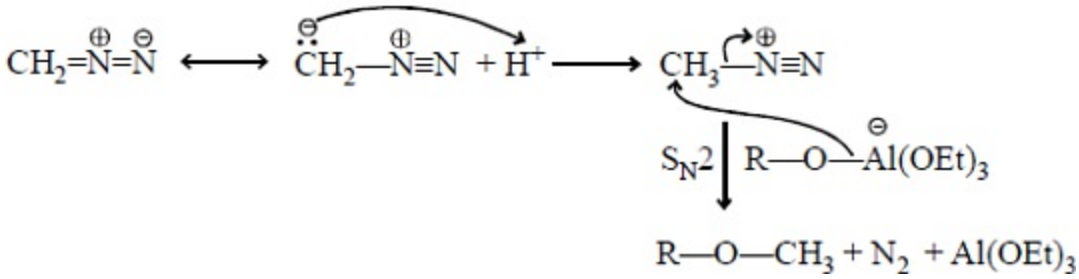
(3)



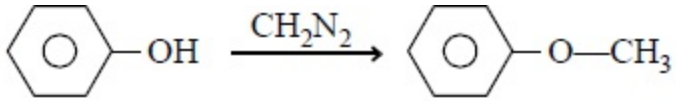
(4) $R—OH + \overset{\ominus}{C}H_2—\overset{\oplus}{N}_2 \xrightarrow[Al(OEt)_3]{BF_3 \text{ or}} R—OCH_3$

Mechanism:





Here Lewis acid increases the acidity and form Lewis acid base salt (I).

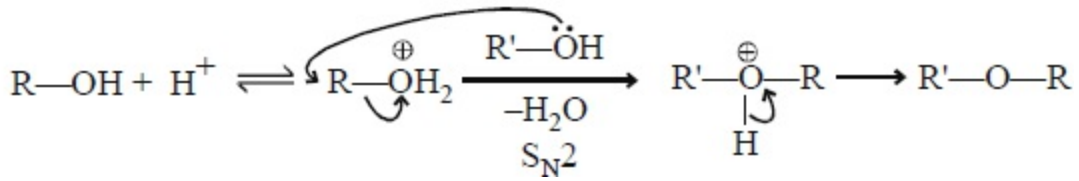
Similarly 

$$R–OH \xrightarrow[heat]{\text{conc. } H_2SO_4} R—O—R$$

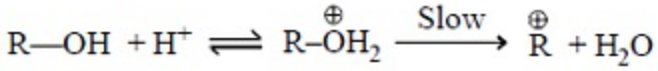
(160°C)

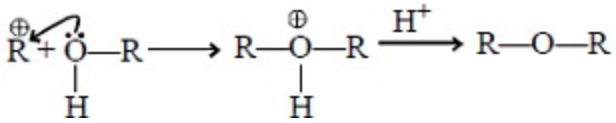
(5) For 1°, 2° alcohol (S_N2) reaction takes place as shown below;

Mechanism:

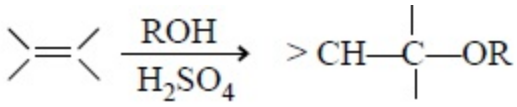


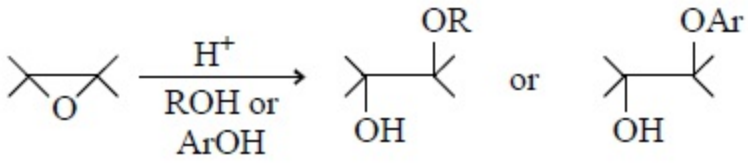
For 3° alcohol S_N1 reaction take place by the obvious reason that 3° cation is stable.



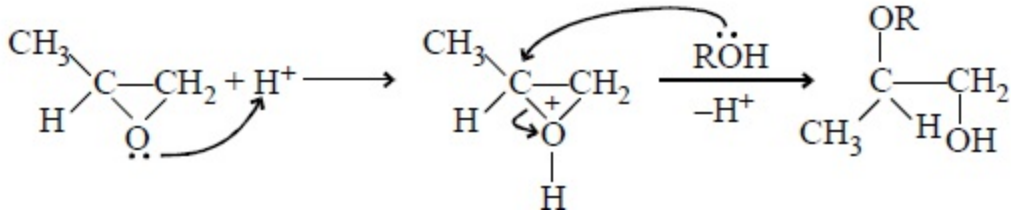


As 3° alcohol mostly leads to alkene, therefore the rate of esterification reaction order is 1° > 2° > 3° alcohol.

(6) 

(7) 

Mechanism:



The nucleophile ROH attack that carbon in the protonated cyclic ether where partially positively charged carbocation is stabler.

Thioether

Preparation:

(1) $2R\text{–}X \xrightarrow{K_2S} R_2S + 2KX$

(2) $5R_2O \xrightarrow{P_2S_5} R_2S + P_2O_5$

(3) $\overset{\ominus}{R}S\overset{\oplus}{N}a + R'\text{—}X \longrightarrow RS\text{—}R' + NaX$

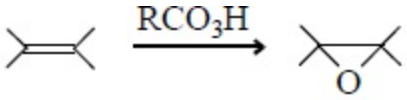
(4) $RMgX \xrightarrow{S} R_2S$

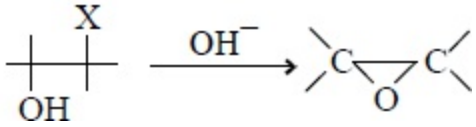
(5) $2Ar\overset{\oplus}{N}_2\overset{\ominus}{X} \xrightarrow{K_2S} Ar_2S$

(6) $RSOR \xrightarrow{LiAlH_4} R\text{—}S\text{—}R$

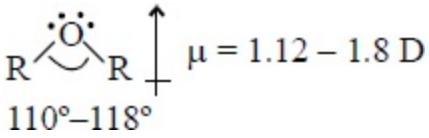
Cyclic ether (oxirane or epoxide)

Preparation:

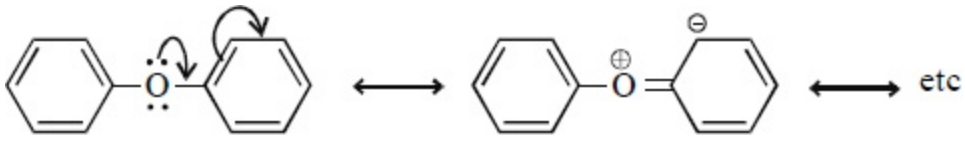
(1) 

(2) 

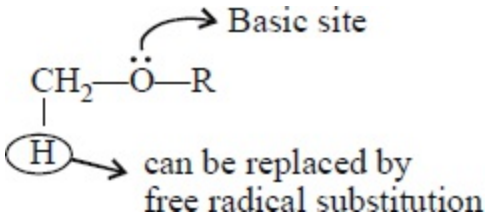
Structure and properties:

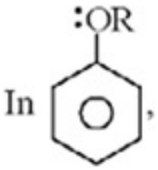


For dialkyl ether hybridisation of O is sp^3 but when O is bonded to aromatic ring it assumes sp^2 hybridisation. Extensive conjugation is present in the diaryl ether as shown below;



Ether is low melting and low boiling due to lack of H-bond and it is highly volatile. However due to H-bond with H_2O it is slightly soluble in water. If we scan the structure then we can see the following facts as shown below;

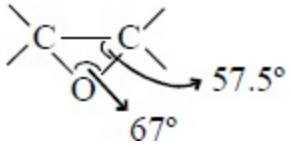


In 

, the OR group is o, p directing during ArSE reactions.

For thioether 'S' assumes sp^3 hybridisation in R_2S but in R–S–Ar or Ar–S–Ar 'S' assumes sp^2 hybridisation. RS–group is o, p directing in benzene ring during ArSE reactions. R_2S experience only dipole-diople attraction as it happens with R_2O. These are insoluble in H_2O.

For cyclic ether the bond angles are shown below;



In the epoxide molecule high small angle strain (I-Strain) is observed. Therefore epoxides are very unstable in acid, basic and under heating but acyclic ethers are very stable in alkaline medium and cleave in acidic medium.

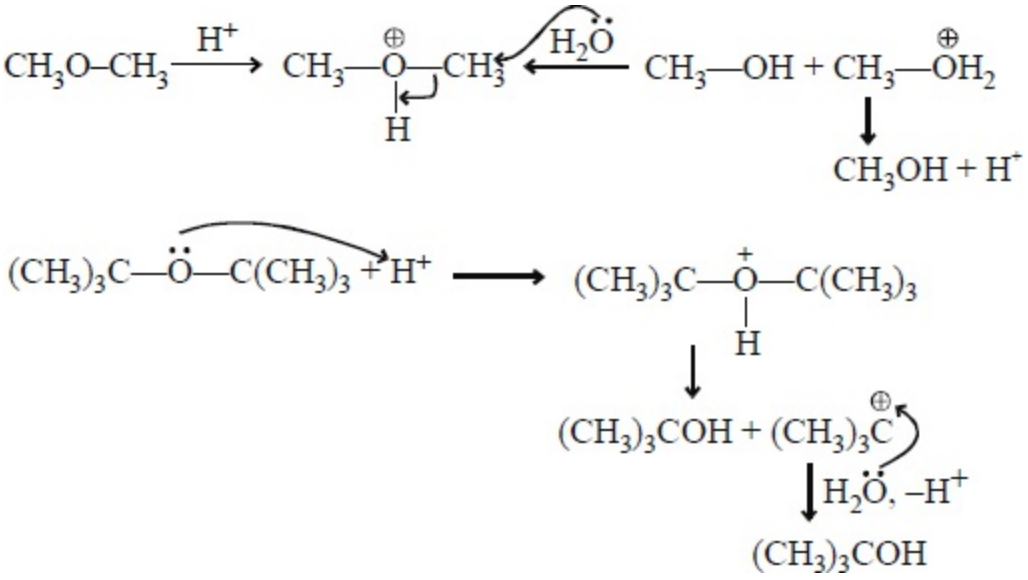
Chemical reactions:

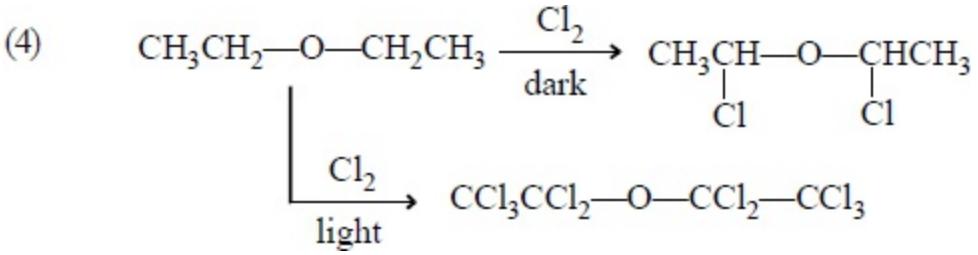
(1) $CH_3OCH_3 + HCl \longrightarrow CH_3-\overset{\overset{H}{|}}{\underset{+}{O}}-CH_3\ Cl^-$ (m.p. –97°C)

(2) $Et_2O + EtBr + AgBF_4 \longrightarrow AgBr\downarrow + [Et_3O^+]\ BF_4^-$

(3) With dil. H_2SO_4 (under pressure) alcohol form as shown below;

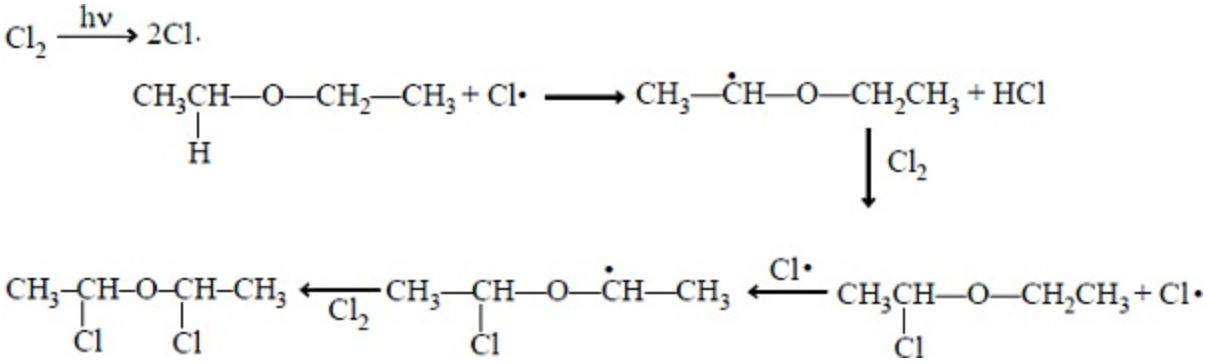
Mechanism:



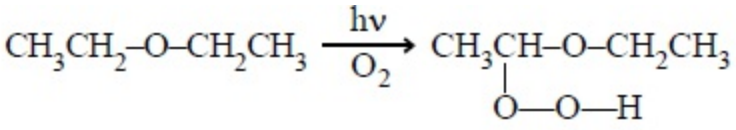


This reaction is also applicable for bromine.

Mechanism:

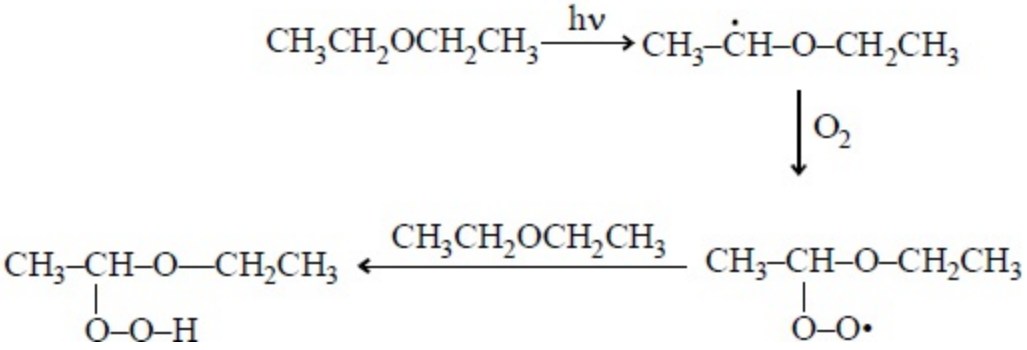


(5) Autooxidation of ether is found when exposed to air. Therefore it is recommended that we should not use ether repeatatively as it form the explosive ether hydroperoxide.

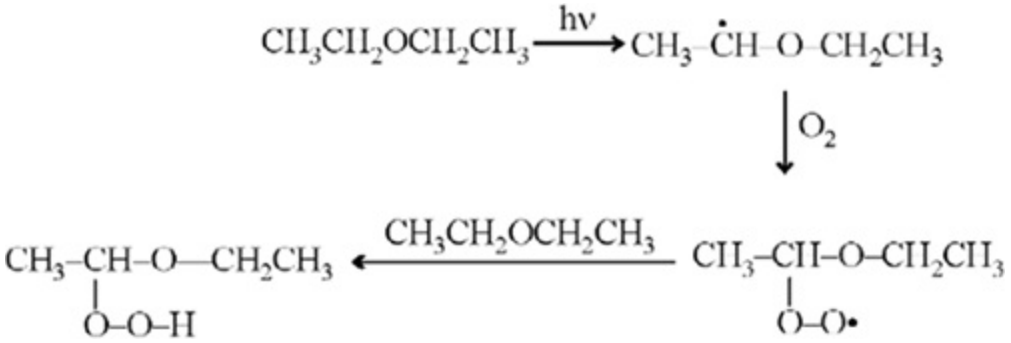


(ether hydroperoxide)

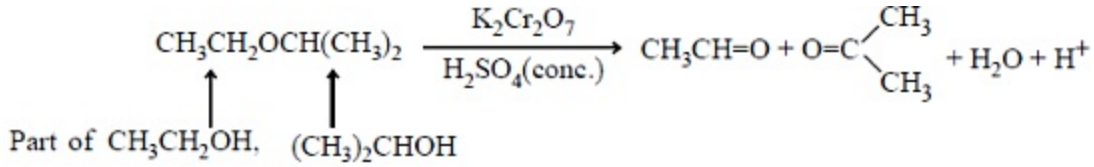
Mechansim:



Mechansim:

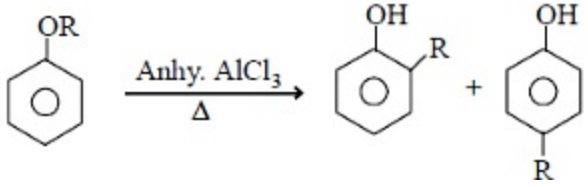


(6)



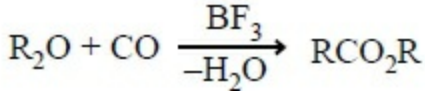
Therefore oxidative cleavage takes place for the corresponding alcohols present.

(7)

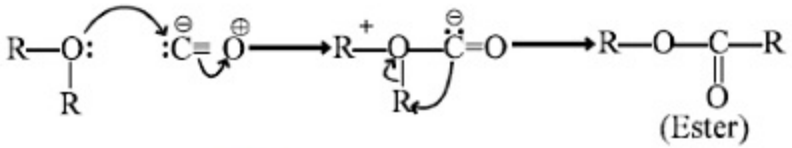


The above reaction is a type of Fire's rearrangement.

(8) Ester formation:

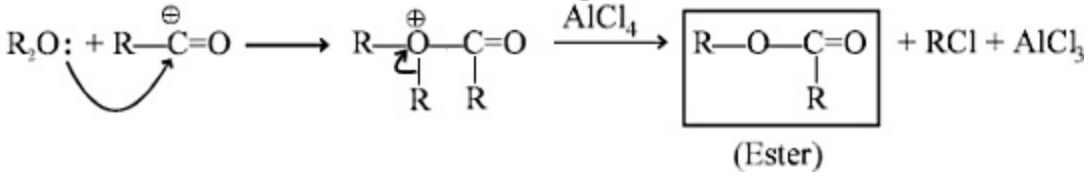


Mechanism:



(9) $R_2O + RCOCl \xrightarrow{AlCl_3} RCO_2R$

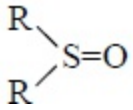
Mechanism: $RCOCl + AlCl_3 \longrightarrow R\text{–}\overset{\oplus}{C}{=}O + \overset{\ominus}{AlCl_4}$



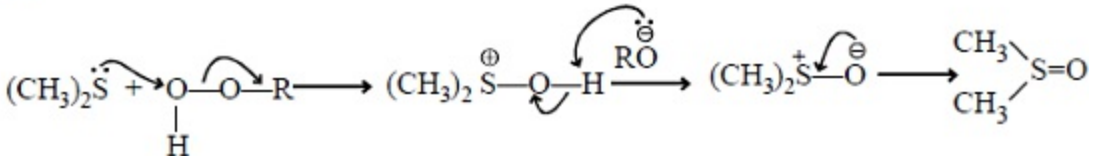
Reactions of thioether:

(1) $Et_2S + H_2SO_4 \xrightarrow{100\%\ HSO_4} (\overset{\oplus}{Et_2SH})\ \ (\overset{\ominus}{HSO_4})$

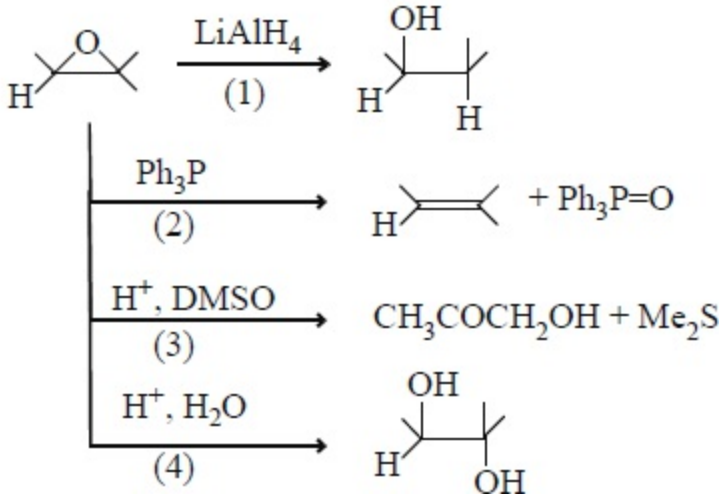
(2) $R\text{–}S\text{–}R' \xrightarrow{Ni/H_2} RH + R'H + NiS$

(3) **Oxidation :** $R_2S + RO_2H \xrightarrow{0°C}$ 

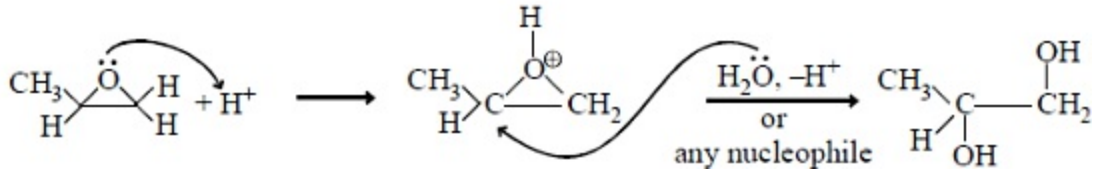
Mechanism:



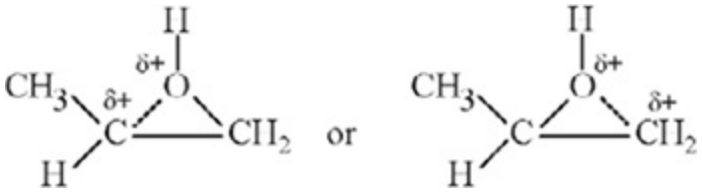
Reaction of oxiranes:

(a) 

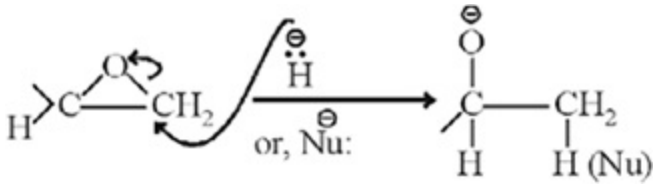
Mechansim:



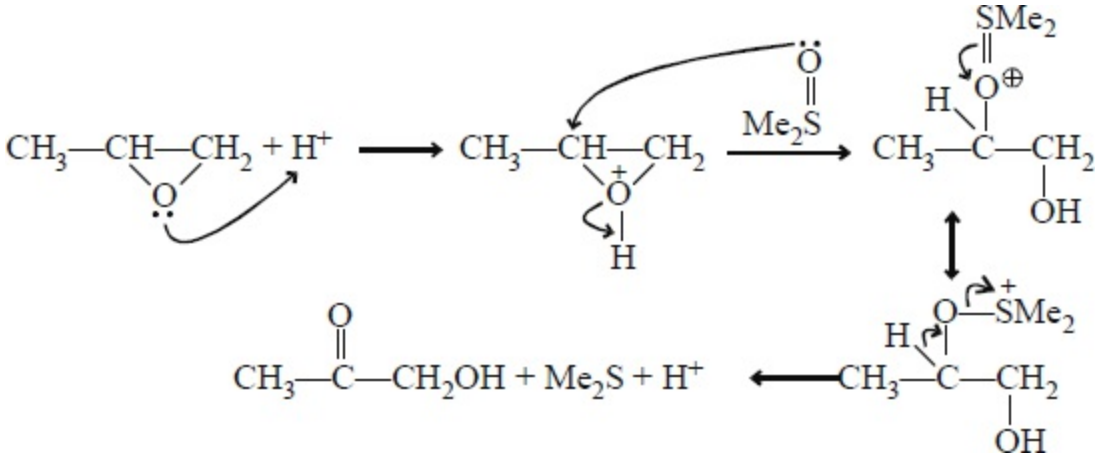
The mechansim is S_N2 with S_N1 character as it is oxonium ion i.e. protonated epoxide. Nucleophile (H_2O) attacks to that 'C' which can hold δ + charge easily.

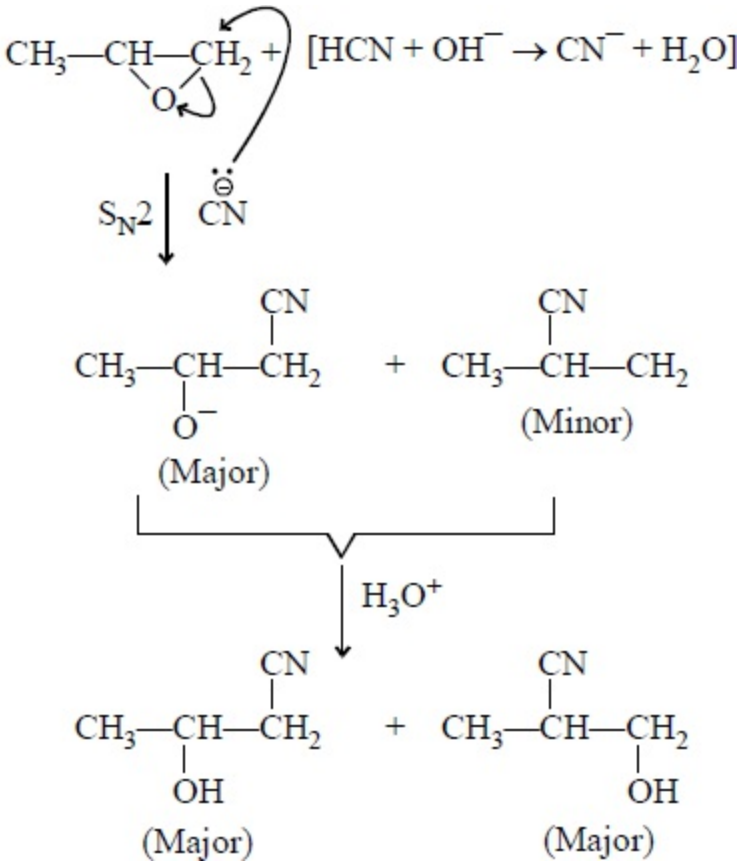


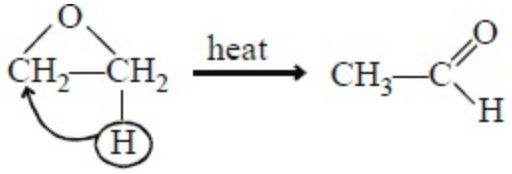
Reaction (4) is of the above type. In reaction (1)

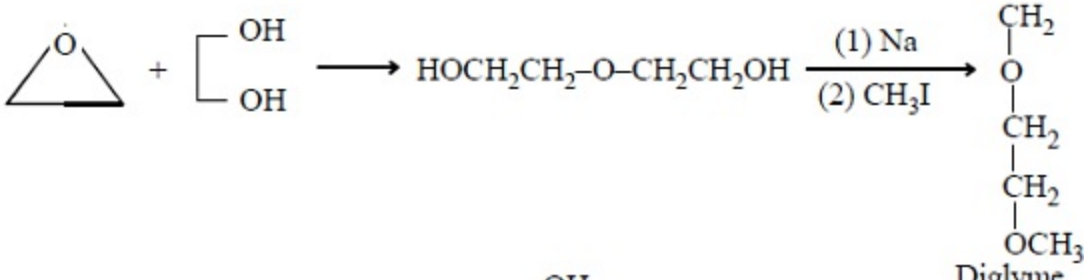


The above mechanism is solely S_N2. Mechnism for reaction(3) is

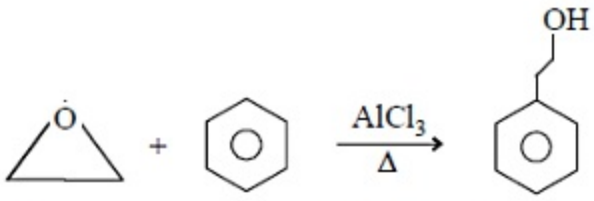


(5) 

(6) 

(7) 

Diglyme

(8) 

This is an example of Friedel Craft's reaction.

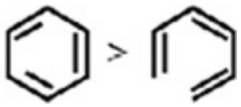
Aromaticity, Non aromaticity and Anti aromaticity

In nineteenth century it was found that a special class of compounds called aromatic largely differ from aliphatic compounds. Aromatic compounds should follow the principles mentioned below.

(a) They should be cyclic, planar (carbocyclic or hetereocyclic) compounds.

(b) They should have $(4n + 2)\pi$ electron system , peripherally situated (Hickel's rule)

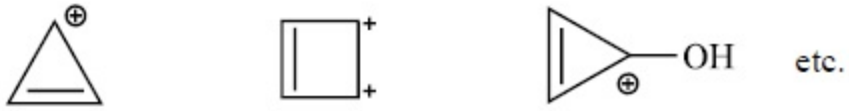
(c) Stability is very high (and may a may not have good smell) and this is stabler than its acyclic conterpart.

e.g.  >

Note :- Aromaticity is understood by nmr spectroscopy which is beyond the scope of this book and most modern technique to understand the aromaticity is that aromatic compounds should be diatropic.

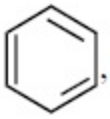
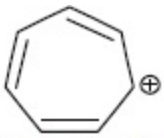
Some examples :

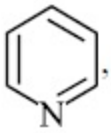
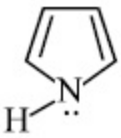
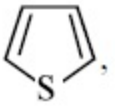
2 π electron systems :



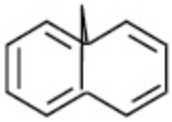
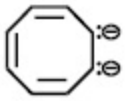
Cyclobutenyl dication

6 π electron systems :


,

,

,
(cyclohaptatrienyl cation)

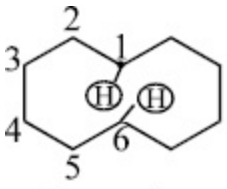

,

,

,

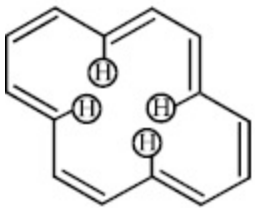
etc.

10π electron systems ;



Cyclooctatrienyl diamion

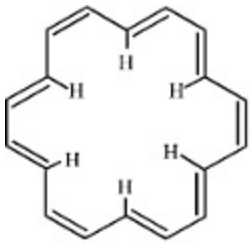
[10] Annulene is not an aromatic species as (C_1 C_6) are nonplanar atoms due to C H repulsion as show below;



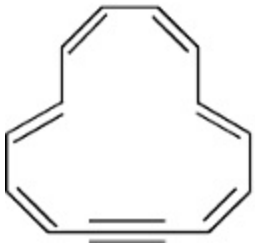


[14] Annulene

In [14] annulene although H atoms shown above cause little repulsion and cause loss of planarity to a very small extent but as it is diatropic therefore this is an aromatic species. Small distrortion from planarity does not prevent aromaticity.

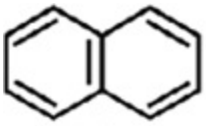


[18] annulene; All H atoms at larger distance therefore plamar and aromatic.

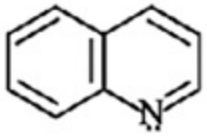


Dehydro [14] annulene

We should not count 2 π bonds ie 4 π electrons at $C_1 - C^2$. Count only 2 π electrons and therefore total 14n electrons are available and it is aromatic.



Naphthalene

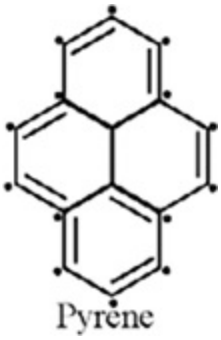


Qminoline



Azulene

Here both the rings are individually aromatic in azulene and quite obviously the compund is aromatic. The direction of dipole moment is from ©ive. ring to Give ring.



Pyrene

Pyrene is aromatic as 14 π electrons are situated peripherally in conjugation as shown. Therefore this is aromatic.

Antiaromaticity :

The compounds are antiaromatic when

(a) they are plamar, carbo or hetero cyclic compounds,

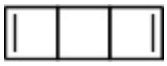
(b) they have 4n π (n = 1, 2... etc. positive integral number) electrons and are destabilised by closedly looped electrons,

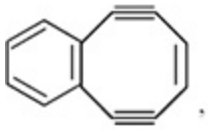
(c) they are less stable compared to noncyclic counterpart and has paramagnetic ring current.



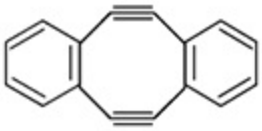
Examples are :



This is so less stable that always it converts to its dimer 



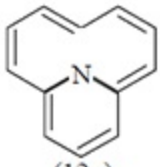
(12π)



(16π)



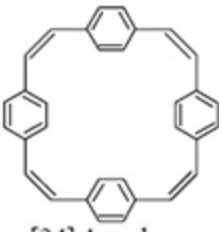
(12π)



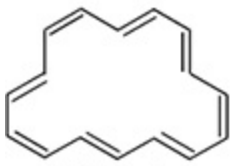
(12π)
cyclo [3.3.3] azine



(16p)
[16] Annulene



[24] Annulene



[16] Annulene



Peracyclene

Peracyclene has 12 π electrons peripherally situated and thus antiaromatic. Nonaromatic compounds are those which are not aromatic or antiaromatic.

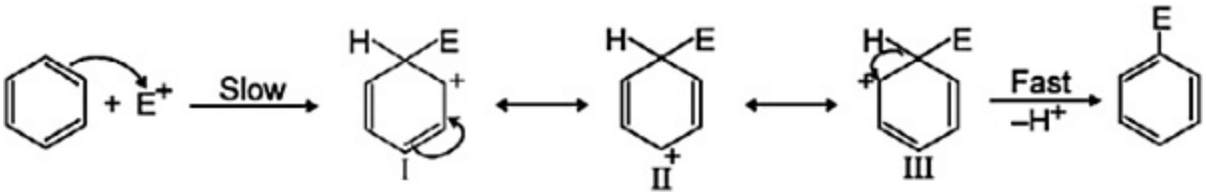
For example;



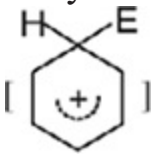
Stabilitywise Aromatic > Nonaromatic > Antiaromatic compounds.

Aromatic Electrophilic Substitution

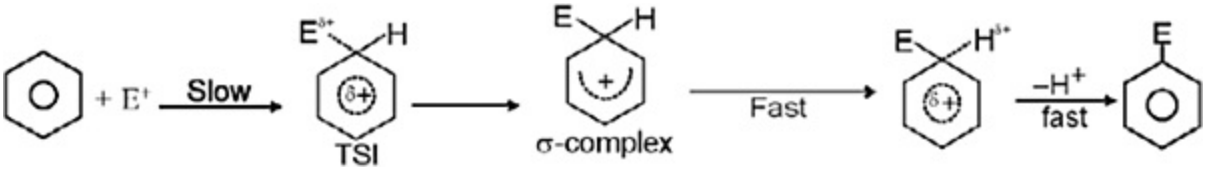
Since aromatic ring has negative charge density therefore it can easily attack electrophile, which is an electron deficient species. Once it attacks the electrophile, it loses its aromaticity in the intermediate and immediately regains the aromatic character by losing proton. Generally ArSE reactions are ArSE 2 type i.e., aromatic electrophilic substitution bimolecular. The mechanism can be written as follows:



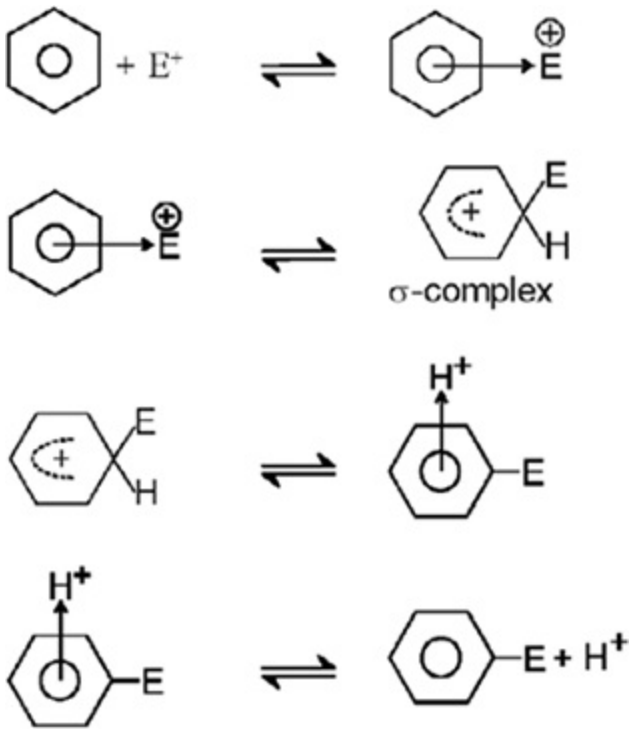
Resonance hybrid of I, II, III is called σ -complex or Whealand intermediate which is



∴ Net reaction is,



Some authors say the π -complexformation with the E^+ and then σ-complex formation happens.. During loss of proton also π -complex formation results and proton thus leaves. This is a four step process.

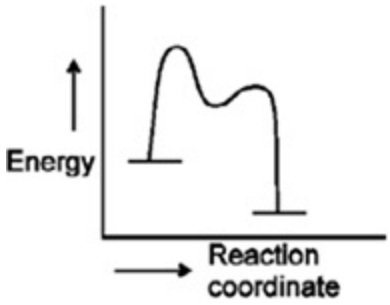


But the widely used mechanism is the initial a-complex formation directly as is being investigated by nmr studies and primary kinetic isotope effect.

The corresponding energy diagrams are ;

Case – 1

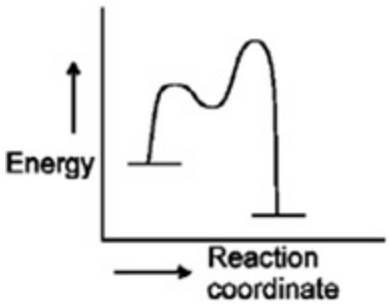
σ -complex formation and first step is slow and second step is fast.



It is found for almost all the cases of ArSE reaction.

Case – 2

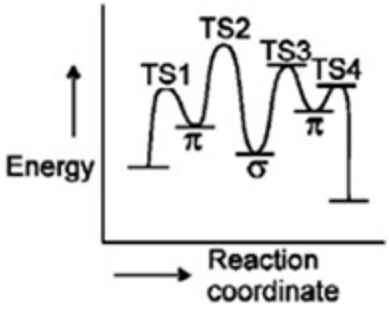
σ -complex formation and first step is fast but the second one is slow.



It is found for sulphonation and iodination of benzene.

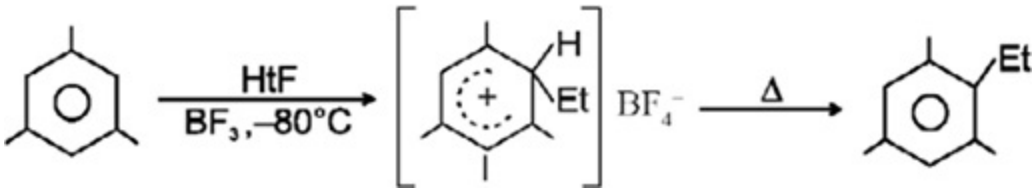
Case – 3

π – complex route ;



It is found for bromination in presence of $Br_2/FeBr_3$

Evidence inform of σ -complex formation :

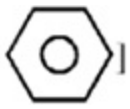


Salt – I was isolated at – 15°C.

Evidence infavour of π -complex formation :

 + HCl → π-complex. Here the π -complex does not conduct electricity and it is colourless,. whereas α -complex forms with HCl, $AlCl_3$. The arenium ion thus formed, is coloured and the solution conducts electricity.

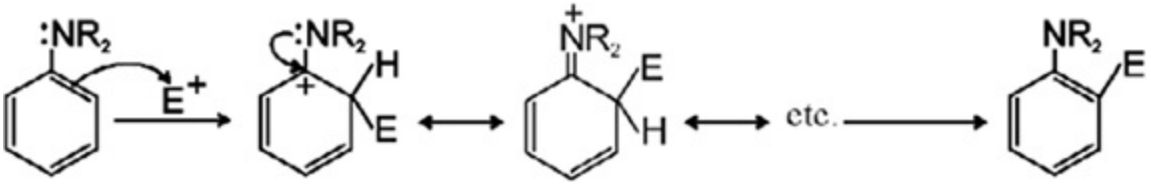
Orientation and reactivity :

As all of us know, benzene ring [] has electron cloud above and below the plane, therefore any group which increases electron density by + R or + I effect enhances the rate of ArSE and – I, – R reduce the rate of ArSE. Activating groups are those that increases rate of ArSE and deactivating groups are those which reduce the rate of ArSE.

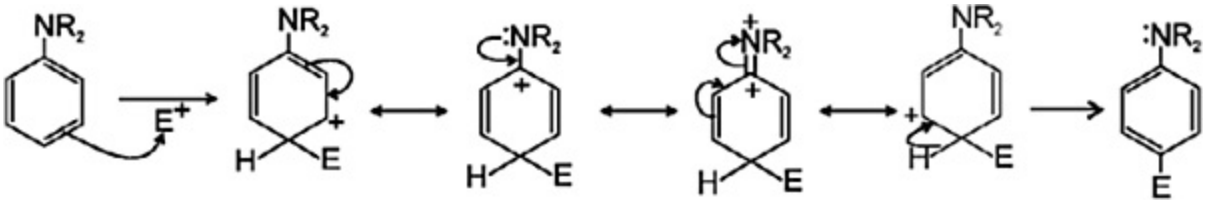
1. Group containing unshared pair of electrons with order are $O^- > NR_2 > NHR > NH_2 > OH >$ OR $\simeq$ NHCOR $>$ OCOR $>$ SR $>$ X (F, Cl, Br, I). Problem with –SH is E^+ attacks at S not at C of the benzene ring. Therefore the above groups are ortho(o), para(p) directing and with X the orientaion is also o, p but with deactivation (i.e. the electrophilic substitution takes place at less rate compared to benzene)

2. Groups containing no unshared electron pair and are –I, – R.
The groups with decreasing deactivating ability, $\overset{+}{N}R_3 > NO_2 > CF_3 > CN > SO_3H > CHO > COR > COOH > CONH_2 > CCl_3 > \overset{+}{N}H_3$

3. Groups may lack unshared pair of electrons which also can be o, p directing. e.g. R, Ar, COO^- groups which also activate the ring.
Let us see why the groups under 1, 3 are o, p directing.

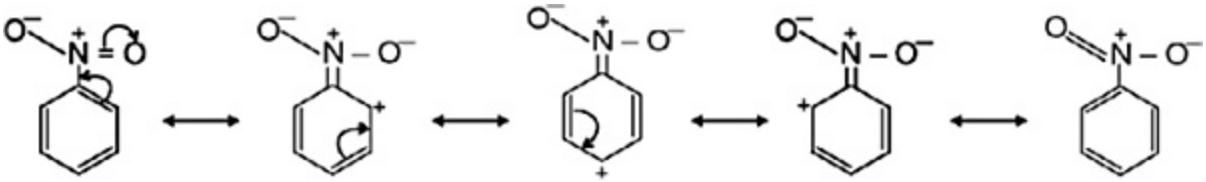


Therefore four resonating structures of the σ -complex account for more stability, that is less activation energy is required to form the σ -complex. Similarly for p-attack,



Therefore in total four resonating structures of the intermidiate brings more stablility to the intermidiate carbocation. When attack by the electrophile takes place at m-position then NR_2 never gets opportunity to stabilise $\oplus$ charge by resonance. Therefore the number of resonating structures will be

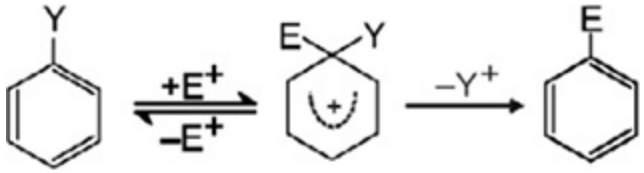
three for the cation. Similarly when there is a withdrawing group, e.g. – NO_2 then $\delta\oplus$ charge resides on the ring itself at o, p.



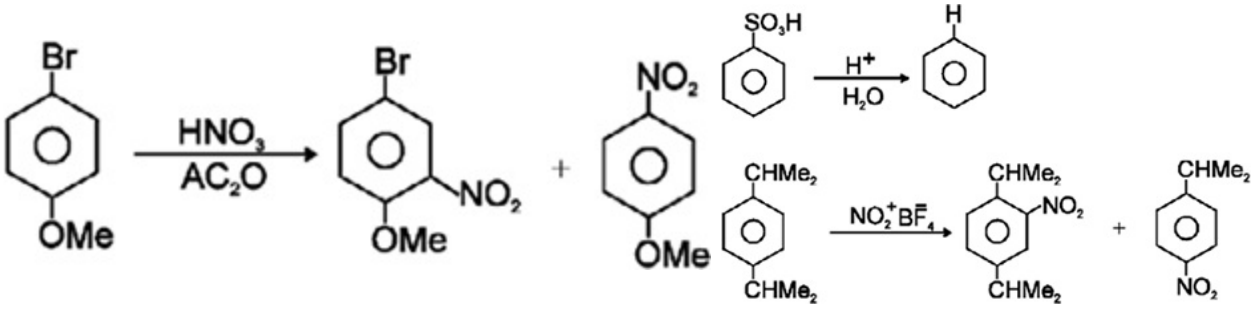
Therefore m-attack is favourable and also due to meta attack positive charge never comes to that C which is bonded to – NO_2 group (you check by writing the mechanism).

Ipso substitution :

Attack of electrophile at the position of substitutent (ipso position as it is called) is also observed.

e.g. 

Some reactions are ;



Generally ipso is favoured by easy formation of Y^+ and also it changes the prediction to o, m, p substitution products. More the stability of Y^+, easier is the ipso substitution.

$Y = (CH_3)_2\overset{\oplus}{C}H$, $(CH_3)_3C^+$ favours ipso substitution reaction. Orientation in benzene ring with more than one substituents can be determined by the following ways.

(a) Activating group dominates over deactivating group.

(b) Stronger activating groups dominate over weaker activating ones.

Decreasing activating order is, NR_2, NHR, NH_2, O^- > OR, OCOR, NHCOR > R > Ar > X > meta directing groups

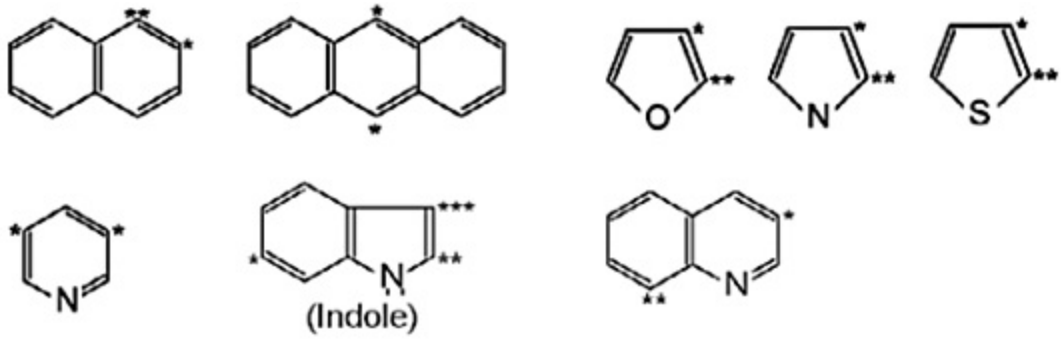
(c) Among deactivating groups the directing order (decreasing) is $^+NMe_3 > NO_2 > CN > SO_3H > CHO > COMe > CO_2H$

(d) All the other things being equal, 3rd group is least likely to enter between two groups in the meta relationship. This is due to steric hindrance.

(e) When a meta directing group is meta to an o, p directing group then the group goes to ortho to the meta group.

Electrophilic substitution in other aromatic systems

Depending upon the stabilities of the carbocatonic intermediates, the positions of electrophilic substitutions are asterisked



Here *** stands for the first preference, ** next preference and * for last choice.

ortho/para ratio and ipso substitution ;

When there is any o/p directing group already present then the substitution product ratio theoretically/statistically should be 2 : 1 but which is practically not possible due to many reasons. Mainly the factors are ;

(a) Steric effect

(b) Electronic effect of the substituents

(c) Interaction between the substituent and the electrophiles

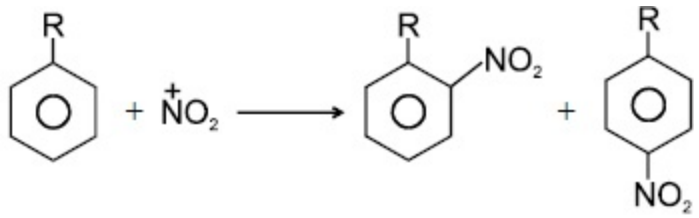
(d) Effect of temperature and solvent.

Larger steric repulsion between the substituent and electrophile increases p-substitution i.e. o/p ratio decreases.

For example :

Case-1

Nitration of alkyl benzene i.e.,



Substituent	% o	% p
Me	Major	Minor
Et	Minor	Major
iPr	Minor	Major
t-Bu	Minor	Major

Case- 2

(a) When volume or size of the attacking electrophile changes

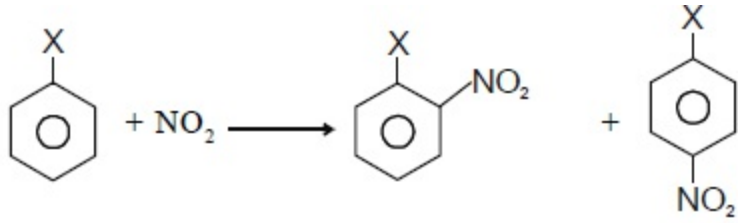
Electrophile	% o
Me	Major
Et	Less (minor)
iPr	Very less
t-Bu	Negligible

(b)

Electrophile	% o	% p
$Cl^{\oplus}$	Minor	Major
Br^{+}	Less	Major
SO_3	Negligible	Very large

The above result is found due to the steric factor. Similarly electronic factor may cause the change in the ratio.

Case- 3



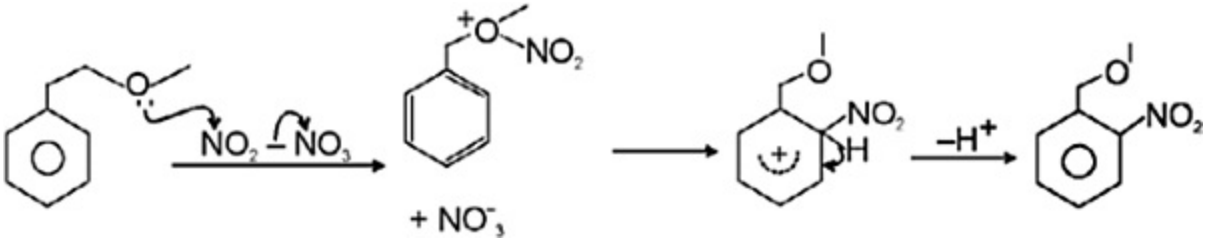
Where X = F, Cl, Br, I

Substituent	% o	% p
F	14	86
Cl	32	64
Br	38	62
I	40	60

Here due to strong – I effect of F, o-position is highly partially electropositive zone. Therefore less % o-product for fluorobenzene, although the steric congestion is very less compared to iodo benzene.

Case – 4

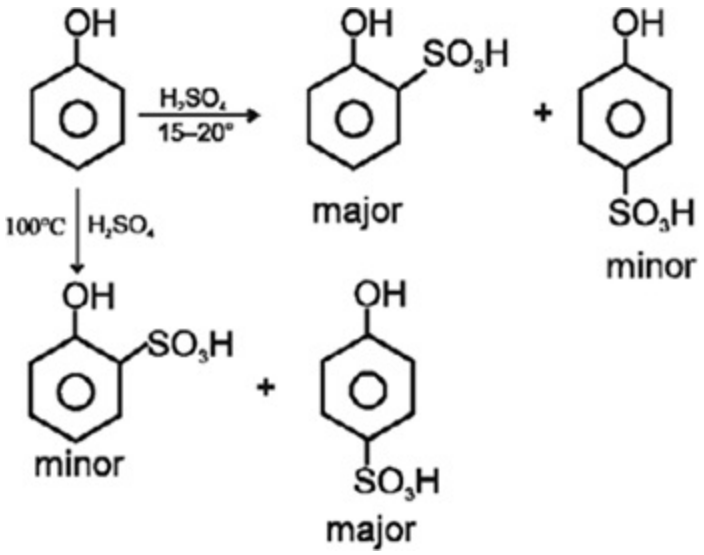
Nitration by N_2O_5 of aryl alkyl ether in methylcyanide solvent, gives ~ 70% o-product but when the nitration is done with mixed acid it results only 32%, o-product (i.e. steric reasons). Actually by the mechanism, N_2O_5 interacts with the ether as shown below.



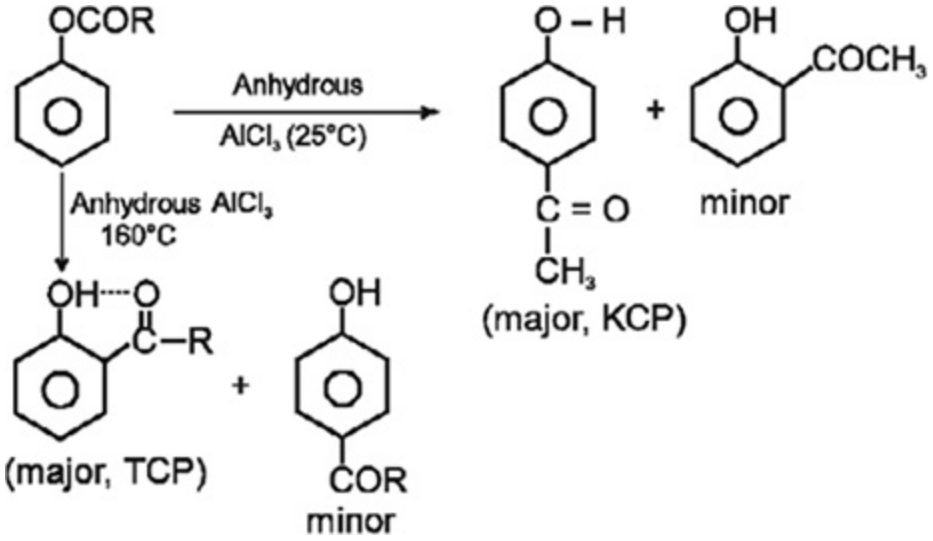
Here the ortho attack occurs due to proximity.

Case – 5

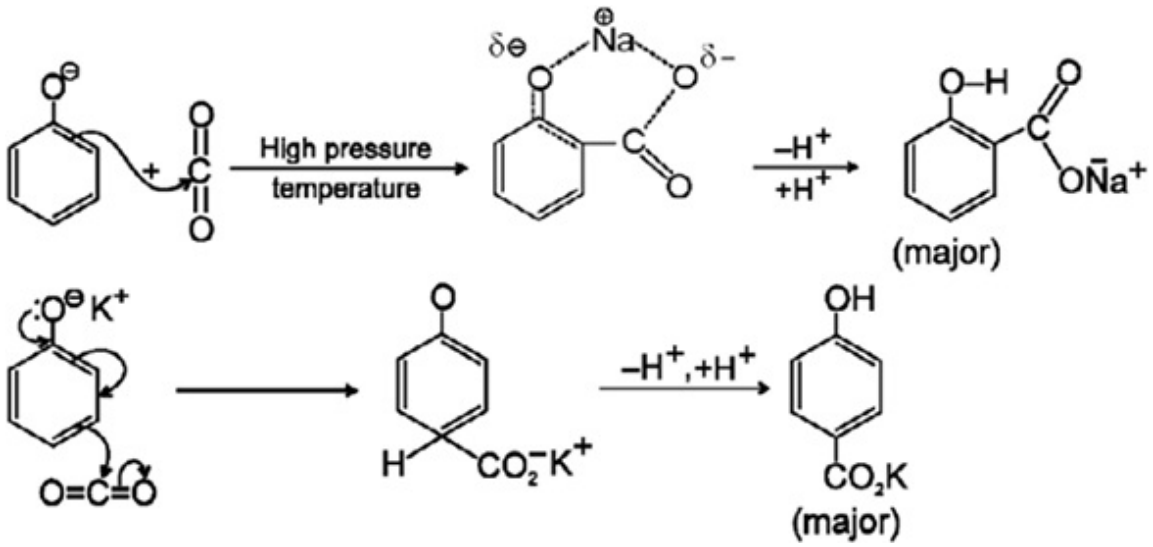
Generally o/p ratio decreases with temperature as o-products are kinetically controlled product (KCP) and p-products are theromodynamically controlled product (TCP).



Similarly in Frie's rearrangement,

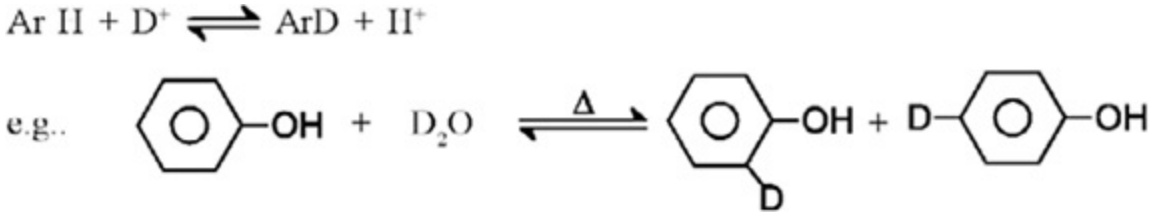


Due to H-bonding o-substituted product becomes thermodynamically stable product. Other kinds of interaction like chelation, e.g., Kolbe Schmidt reaction, Na^+ forms chelate ring (6 membered ring) but K^+ fails, due to which sodium phenoxide gives ortho product and potassium phenoxide gives more p-product.



Electrophilic aromatic substitution reactions and mechanisms :

1. Hydrogen exchange :

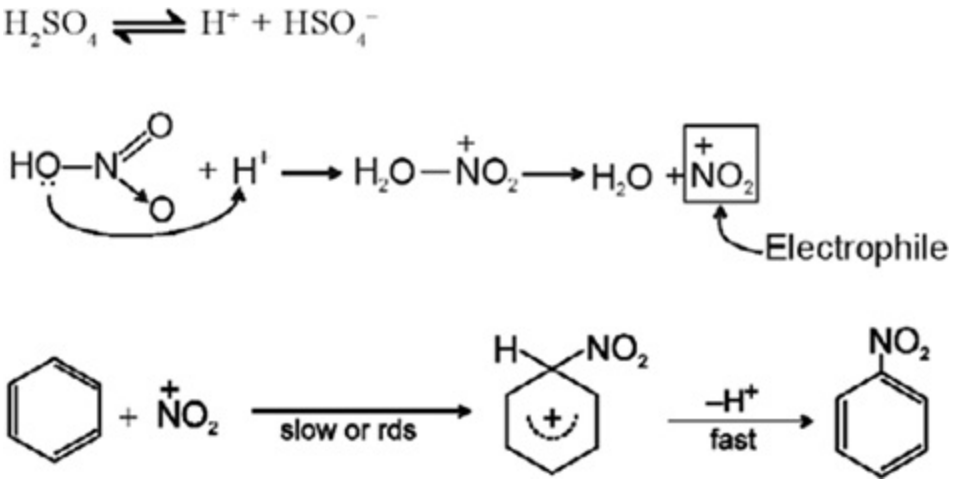


2. Nitration :

Substrate : Most aromatic compounds carbocyclic, heterocyclic compounds.
Reagents : It is variable for various substrates.

Most common reagents are concentrated HNO_3 in concentrated H_2SO_4 (mixed acid), concentrated HNO_3 in glacial acetic acid or in water or in $(CH_3CO)_2O$ i.e. anhydride, nitronium salts $[NO_2^+]$ $[PF_6^-]$, $[NO_2^+]$ $[BF^4]^-$, NO_2O_5 in methyl cyanide etc. For aniline and phenol dilute HNO_3 is used for nitrosation first and then oxidation takes place. We never use mixed acid (MA) otherwise oxidation of the ring takes place.

Mechanism: For mixed acid,



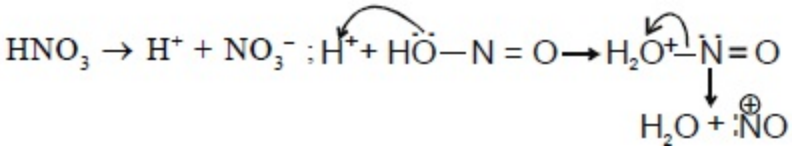
The reaction can be 0, 1st or fractional roder. 0 order when substrates are more reactive than benzene, i.e. NO_2^+ formation is slow step. If substrates are less reactive than benzene then rate = k [substrate] i.e. 1st order. Fractional order possible if the reactivity of the substrates lying in between.

Supply of $\overset{+}{N}O_2$ happens in the following ways.



Supply of $\overset{+}{N}O$ happens by the following way.

HNO_3 (dil.) + organic compound → HNO_2 + oxidised organic compounds.

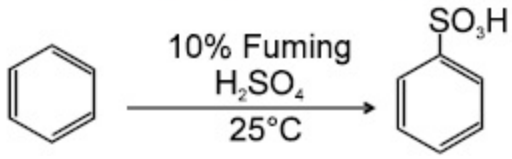


Sulphonation :

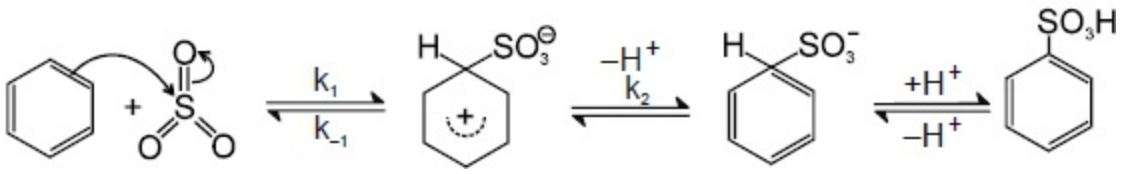
Substrate : All aromatic carbocyclic, heterocyclic & fused ring systems etc.

Reagents : Concentrated H_2SO_4, fuming H_2SO_4, SO_3 or $ClSO_3H$ etc.

Reaction :

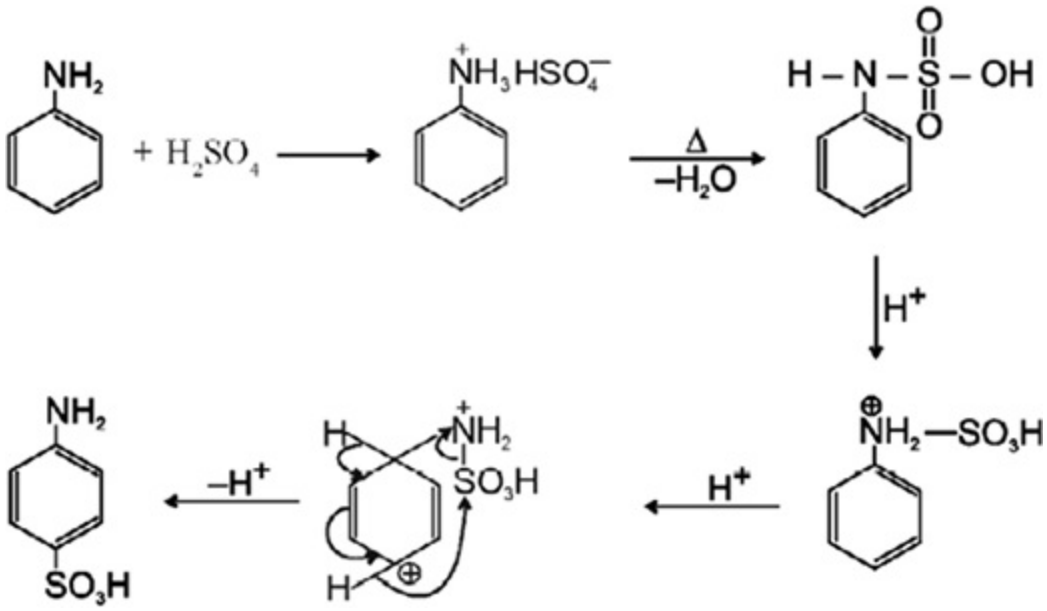


Mechanism : $2H_2SO_4 \rightleftharpoons \underset{\text{(Electrophile)}}{\boxed{SO_3}} + H_2O^+ + HSO_4^-$



Here $k_2 < k_{-1}$ for conc. H_2SO_4 and it has been proved by incorporating D in place of H. Rate of sulphonation of $C_6D_6 < C_6H_6$ and the rate is directly proportional to $[SO_3]$. Advantage of introduction of SO_3H group is easy entry and easy removal by dil. HCl and boiling following the above mechanism.

Mechanism for sulphonation as of aniline :

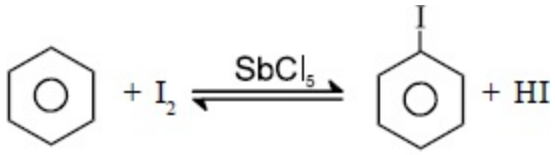


Halogenation :

Substrate : Aromatic compounds (any).

Reagent and catalyst : For chlorination, bromination Cl_2 or Br_2 molecule in presence of Fe or Lewis acid eg; $AlCl_3$, $AlBr_3$, $SbCl_5$, $SbBr_5$ etc. are used. HOCl, HOBr can be used in presence of acid. Br – Cl, can also be used as an interhalogens.

The reactivity of I_2 is very low and it is a reversible reaction. Use of HIO_3, HNO_3 make the reaction forward.

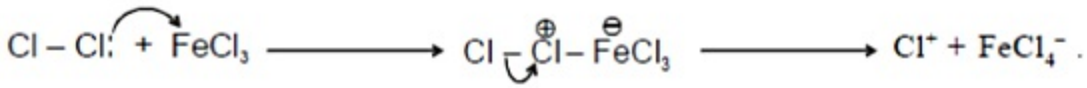


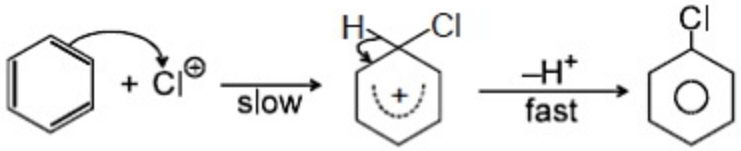
$$HI + HIO_3 \rightarrow I_2 \uparrow + H_2O$$

I – CN, I – Cl, I – Br can also be used as iodinating agents. Fluorination by F_2 is impossible for the explosive nature of the reaction. AgF_2 fluorinate benzene at low temperature.

Mechanism :

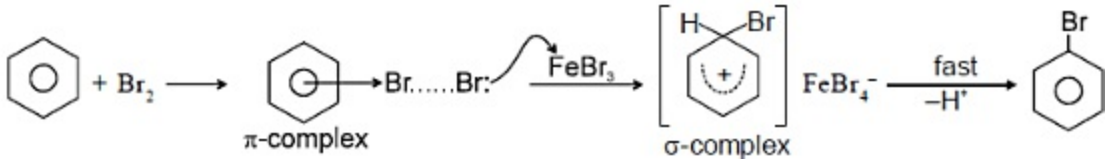
(a) With $Cl_2/FeCl_3$





σ-complex

(b) With $Br_2/FeBr_3$



For bromination, π -complex formation is the difference with that of chlorination where both the cases σ -complex forms. Rate equation is found to be,

Rate = K[Substrate] $[X_2]$ [Lewis acid]

(c) With HOCl, Cl^-

$$2H^+ + OCl^- + Cl^- \longrightarrow H_2O + Cl_2.$$

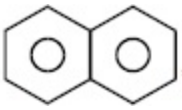
(d) With HOCl and strong acid

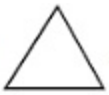
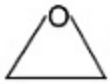
$$H^+ + HO - Cl \longrightarrow H_2O^+ - Cl \longrightarrow Cl^{\oplus} + H_2O$$

From (c), (d) $Cl^{\oplus}$ or any $X^{\oplus}$ we get, reacts, through σ-complex formation and gives the halogenated product.

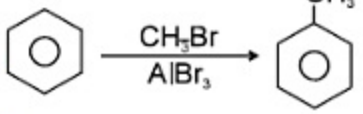
Friedel Craft's reaction :

1. **Substrate :** Aromatic hydrocarbons, haloarenes (Ar- X), Ar – OH etc. With only deactivating groups in benzene ring the reaction fails. e.g., Ph – NO_2.

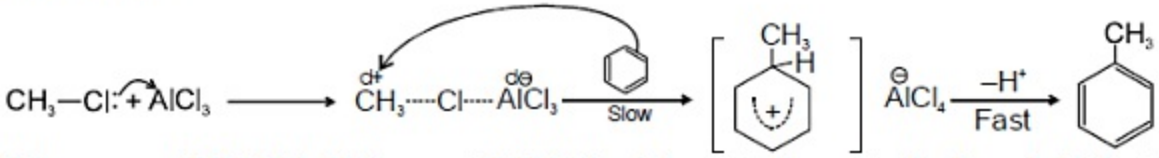
Ph – OH,  , Ph – NH_2, Ph – OMe give less yield. Heterocyclic rings are poor substrates for the reaction.

Reagents : Alkyl halides (R – X), R – OH, RC ≡ CH, R – SH,  ,  . For all types of reagents, the reactivity order is allylic ≃ benzylic > 3° > 2° > 1° carbocation.

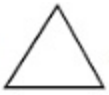
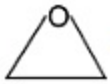
Catalysis : As per the catalytic activity is concerned the order is $AlBr_3$ > $AlCl_3$ > $GaCl_3$ > $FeCl_3$ > $SbCl_5$ > $SnCl_4$ > BCl_3, BF_3, $SbCl_3$ etc. HF or H_2SO_4 can also be used as catalysts for  , R – OH, R – C ≡ CH etc. Anhydrous condition of the catalyst is necessary conditon, otherwise the hydrolysis results into $Al(OH)_3$ and catalytic activity vanishes.

Reaction : 

Mechanism :



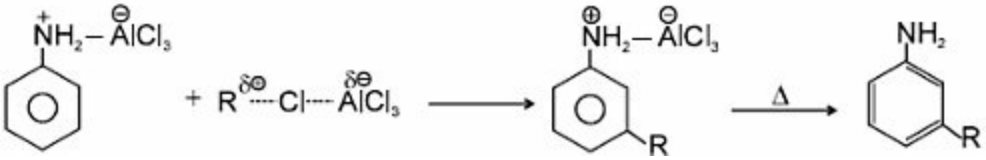
When we use $(CH_3)_3CCl$, $AlCl_3$ we get $(CH_3)_3C^+$ not the partially positively charged alkyl cation.

Reagents : Alkyl halides (R – X), R – OH, RC ≡ CH, R – SH,  ,  . For all types of reagents, the reactivity order is allylic ≃ benzylic > 3° > 2° > 1° carbocation.

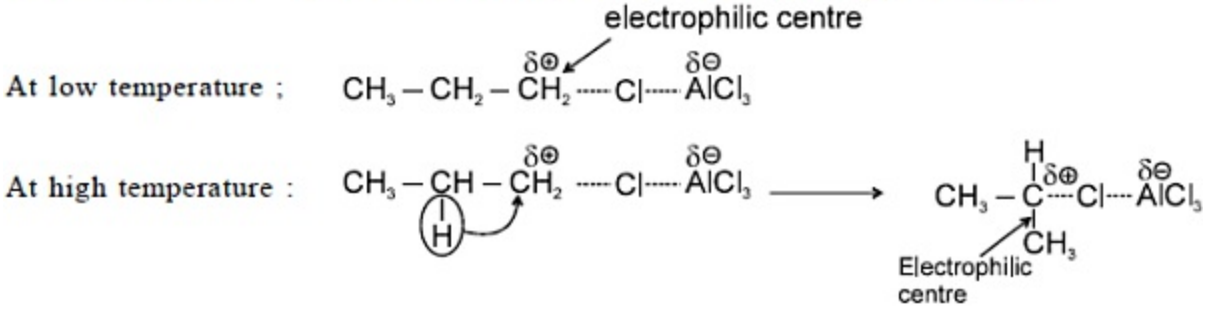
With the substrate – NH_2 (i.e., Ph – NH_2)

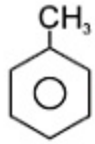
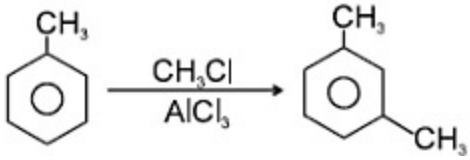
Ph – NH_2 + $AlCl_3$ → Ph – $\overset{\oplus}{N}H_2$ – $\overset{\ominus}{A}lCl_3$ (salt formation. ∴ $AlCl_3$ is trapped).

If we use excess $AlCl_3$, then R – Cl + $AlCl_3$ → $\overset{\delta\oplus}{R}\cdots Cl\cdots\overset{\delta\ominus}{AlCl_3}$ forms and finally unexpected meta product forms.



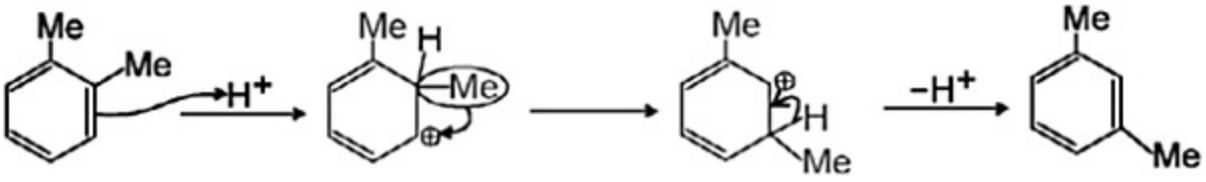
Here – I effect of $\overset{\oplus}{N}$ gives the meta-alkylation. With $CH_3CH_2CH_2Cl + AlCl_3$,



With  as substrate, we get 

Actually initially o, p dimethyl benzene (KCP) form and then subsequent rearrangement gives m-dimethyl benzene (TCP).

Mechanism may be :

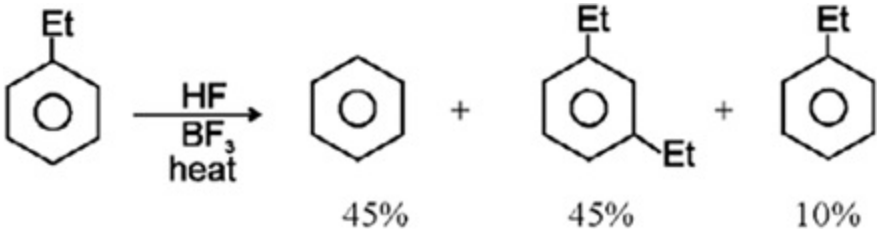


The above reaction can be explained by reactivity selectivity principle :

$\overset{\delta\oplus}{CH_3}$ is highly reactive, so approaches most electron dense ortho position but at high temperature, the steric repulsion with existing – CH_3 group (because of larger amplitude of vibration, radius of rotation) it approaches meta position next and gives the product meta-dimethyl benzene at high temperature.

Dealkylation can also take place under the following condition :

For example;



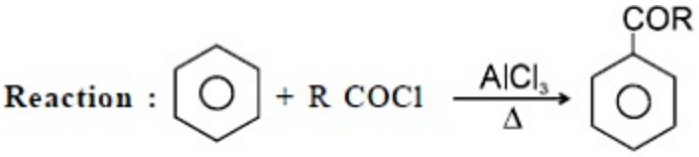
Friedel Craft's acylation :

Substrate : Aromatic hydrocarbons, phenol (i.e., activated ring of any kind) excepting quinoline, pyridine, other heterocyclic aromatic compounds (e.g; pyran, furan, thiophene etc.)

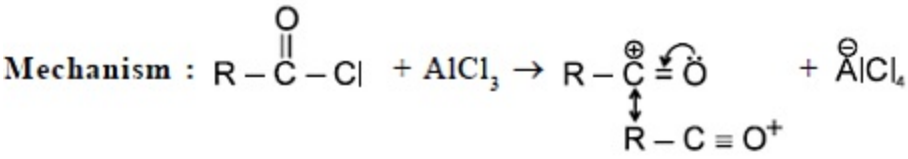
Reagents : R-COCl or Ph COCl or ArCOCl (i.e. acid halides), cyclic or acyclic anhydrides, carboxylic acids.

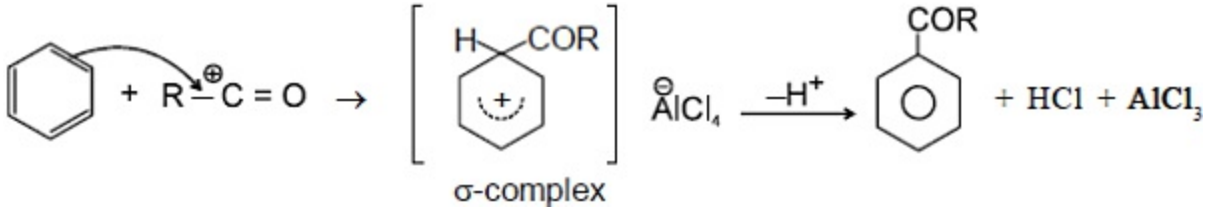
Catalysts : Same is used as in alkylation.

Reaction :

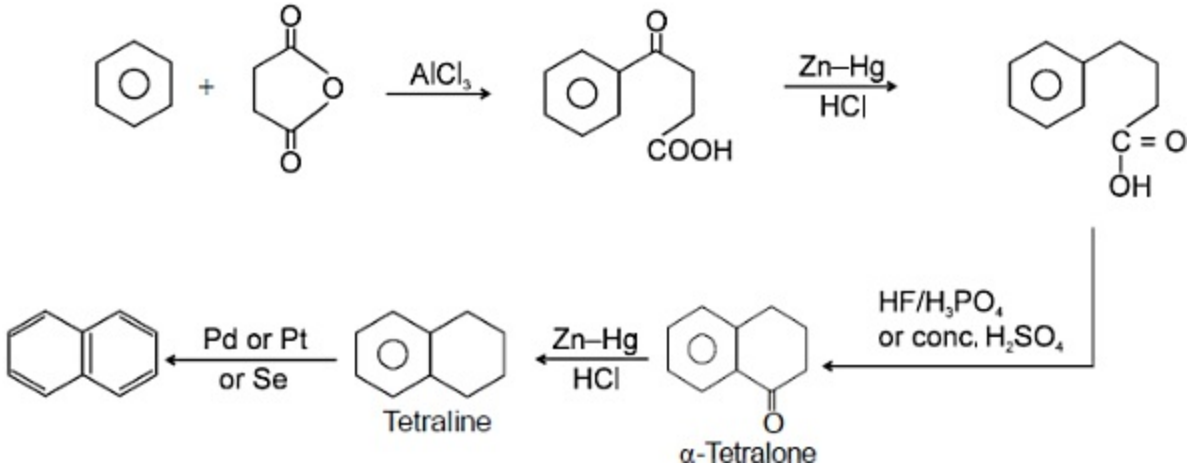


Mechanism :





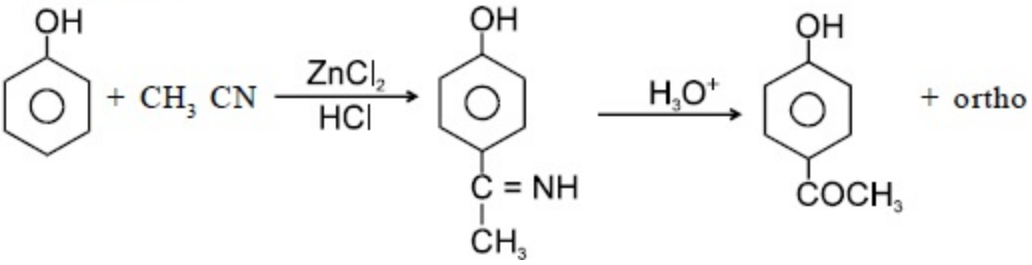
Application :



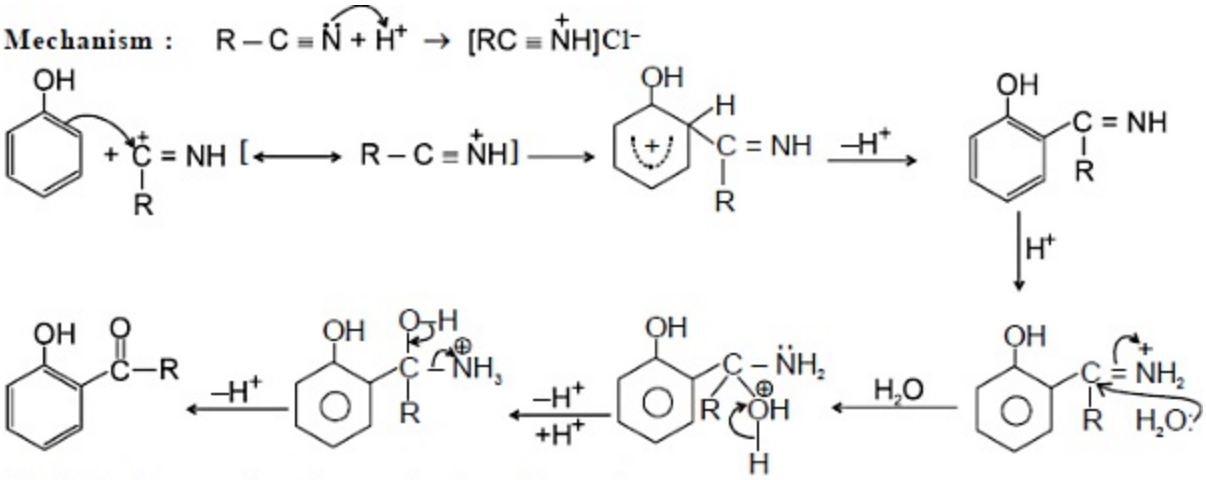
Hauben Hoesch reaction :

Substrate : Phenols, reactive and active to aromatic compounds like pyrrole etc.
Reagent : RCN
Catalyst : $ZnCl_2$, HCl

Reaction :



Mechanism :

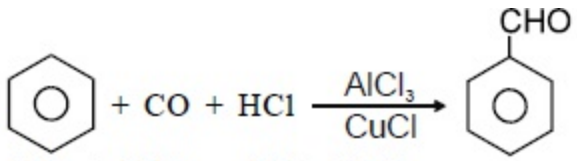


Similarly for p product the mechanism will remain same.

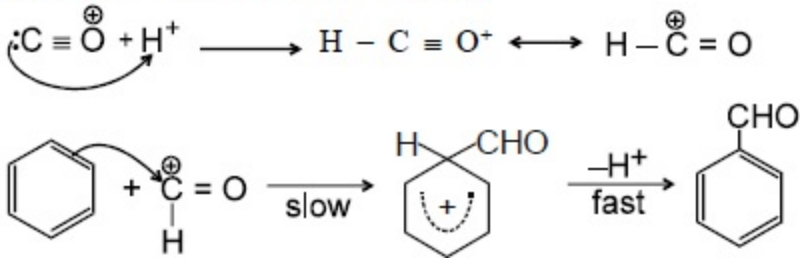
Gattermann Koch aldehyde synthesis :

Substrate : Benzene ring with activating groups. Benzene ring with deactivating groups fails to give yield.
Reagent : CO, HCl,
Catalyst : $AlCl_3$ + CuCl mixture

Reaction :



Mechanism: $HCl + AlCl_3 \rightarrow H^+ + AlCl_4^-$

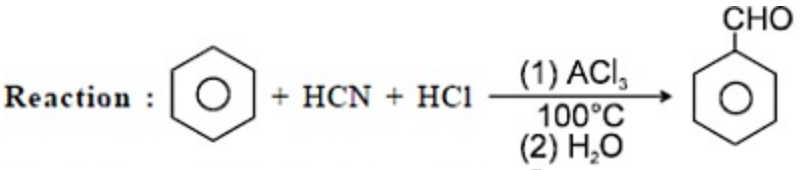


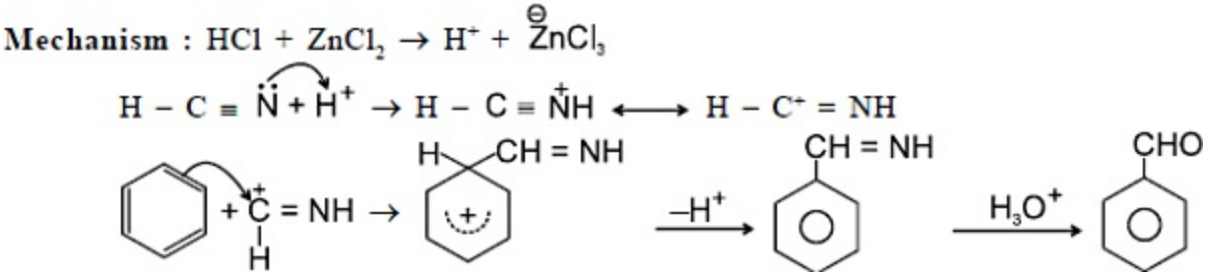
Gatternamm aldehyde synthesis :

Substrate : Aromatic compound (benzene ring with activating as well as

deactivating groups.)

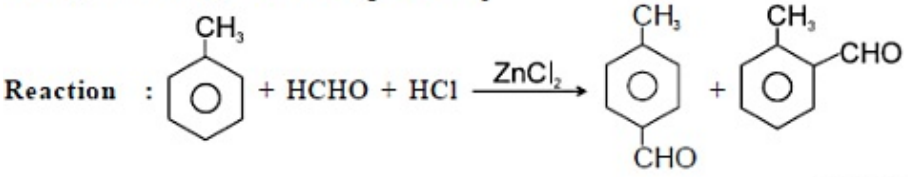
Reagent : HCN, HCl

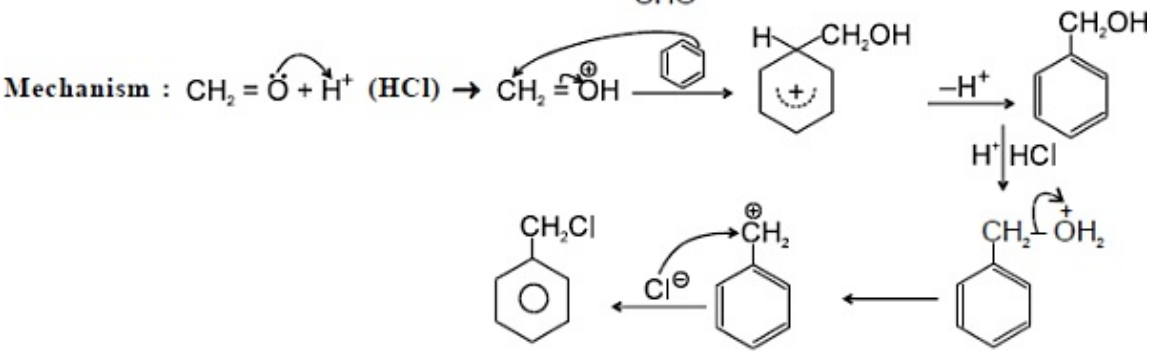




Chloromethylation :

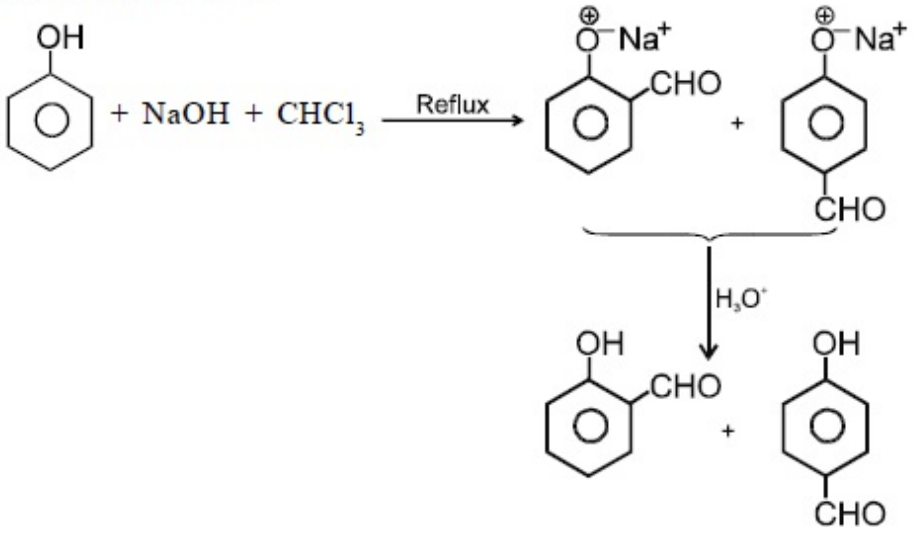
Substrate : Ar – R, ArOR, Ar – X etc.
Reagent : HCHO (Formalin) ;
Catalyst : Anhydrous $ZnCl_2$ or $AlCl_3$



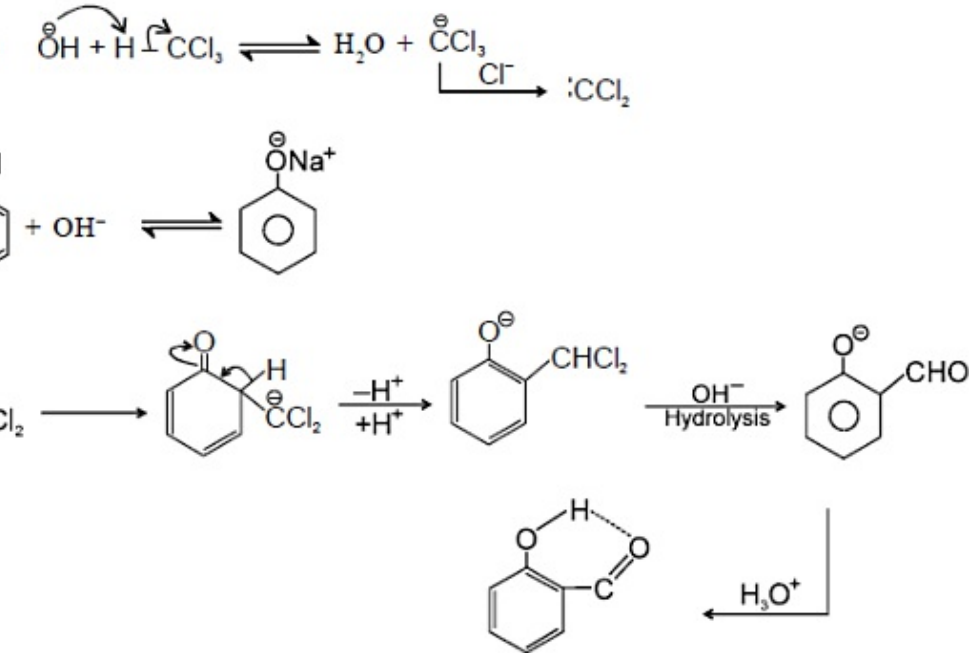


Reimer Tiemann's Reaction :
Substrate : Phenol
Reagent : $CHCl_3$, NaOH
Condition : Refluxing at 90°C

Reaction :

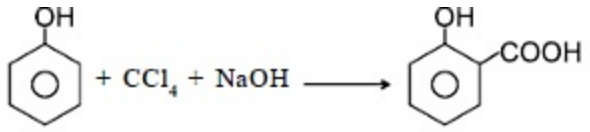


Mechanism :

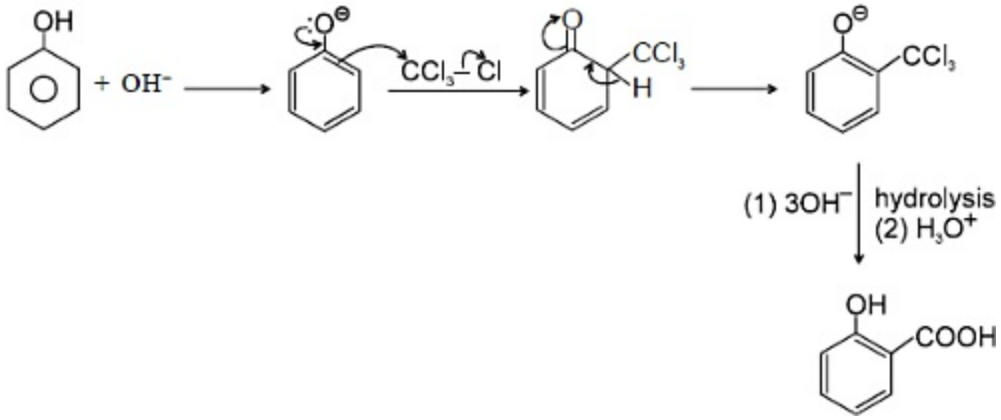


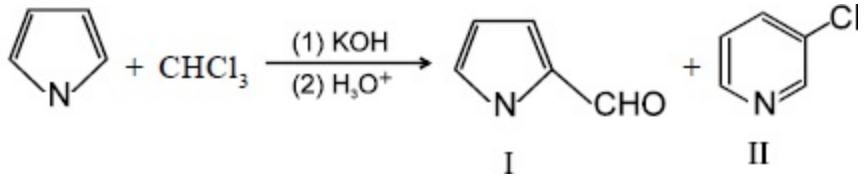
At low temperature salicaldehyde distills out due to intramolecular H-bonding. p-derivative is high boling because of intermoleduclar H – bonding.

Example.

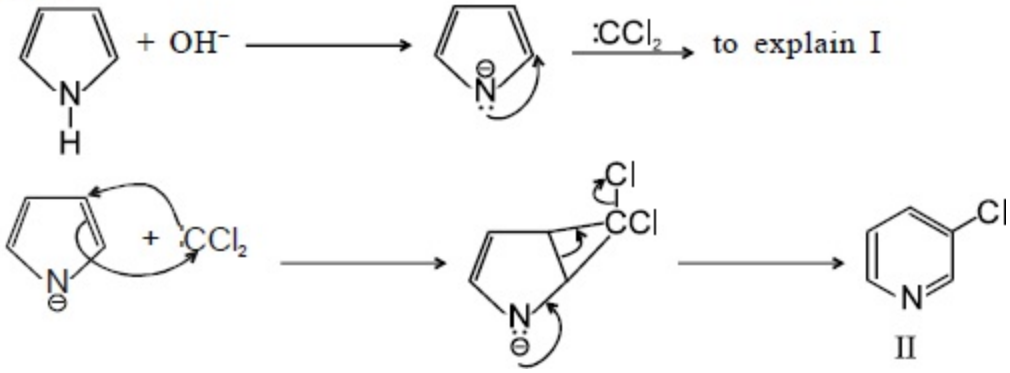
1. 

Mechanism :



2. 

Mechanism :



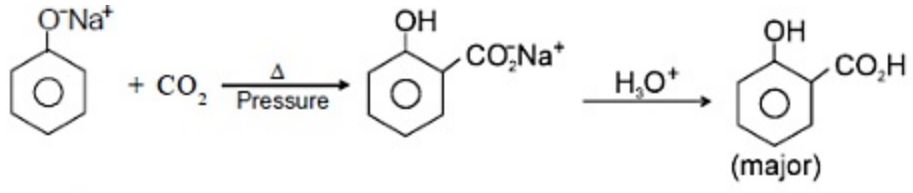
Kolbe Schmidt reaction :

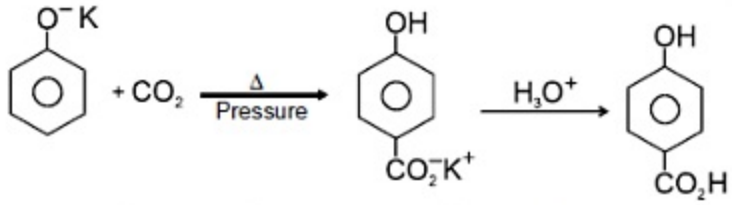
Substrate : Na or K – phenoxide

Reagent : CO_2

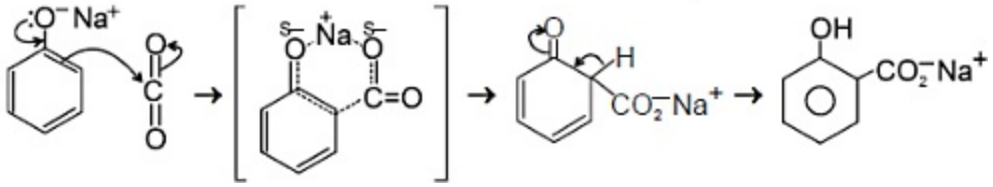
Condition : 250°C, 6-7 atm. pressure

Reaction :

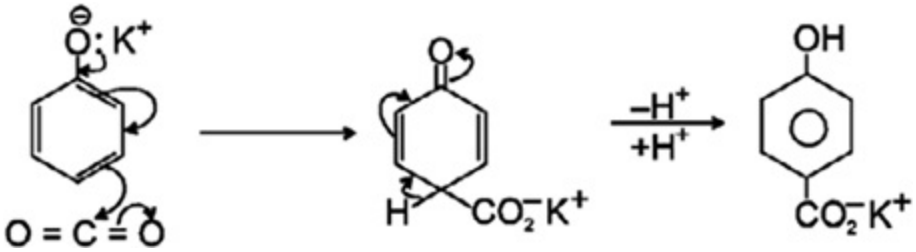




Mechanism :



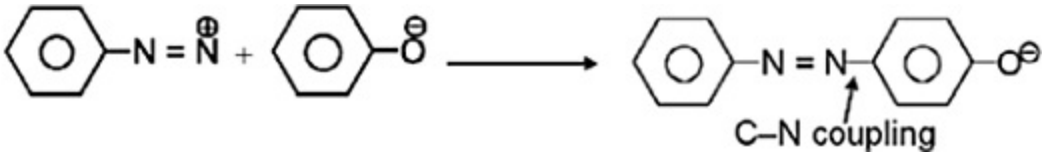
Chelate ring formation takes place due to smaller size of Na^+. This is not possible for K^+ due to larger size.Therefore ortho product is the major for sodium phenoxide. With K – salt the mechanism is ;



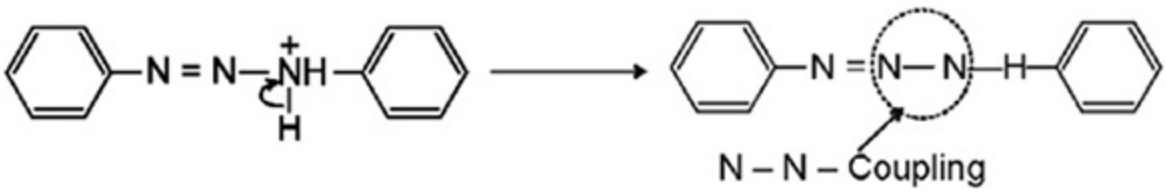
Diazonium coupling :

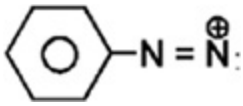
Substrate : Active aromatic compounds e.g. aniline , N – alkyl or N, N dialkyl aniline, Phenol (in alkaline medium) etc.

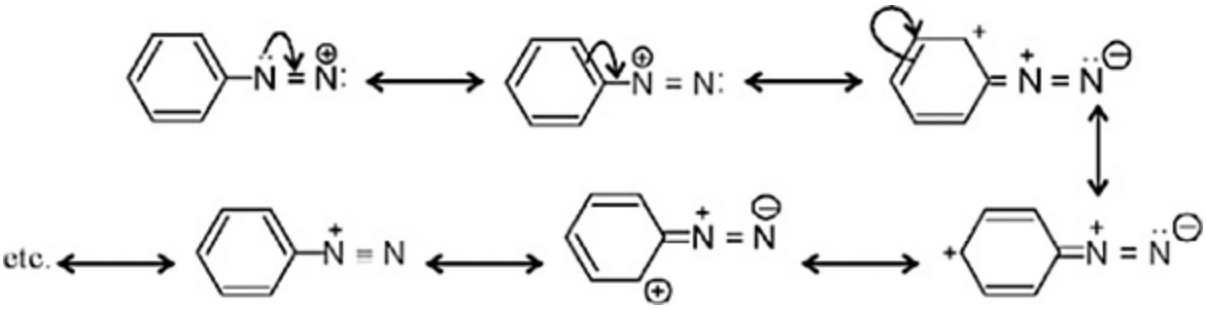
Reaction:



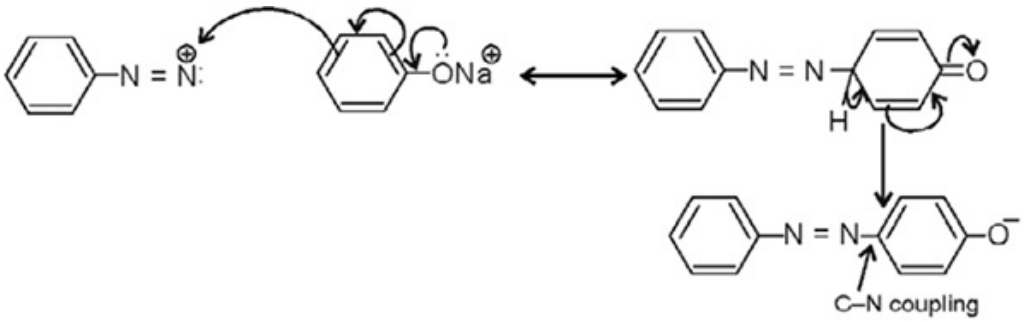
Theory : With Ph – NH_2, N – N coupling, with Ph NHR, N – N as well as N – C coupling and with Ph NR_2, PhO- only N – C coupling result. This is due to order of + R effect is $O^- > NR_2 > NHR > NH_2$.



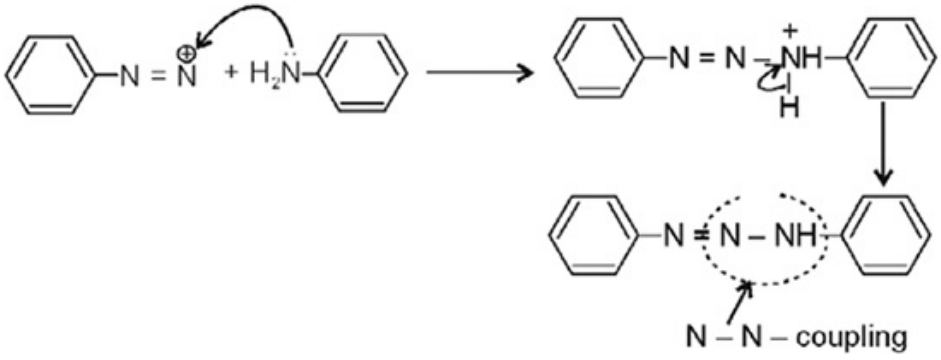
 is weak electrophile as it exists as resonating structure as shown below:



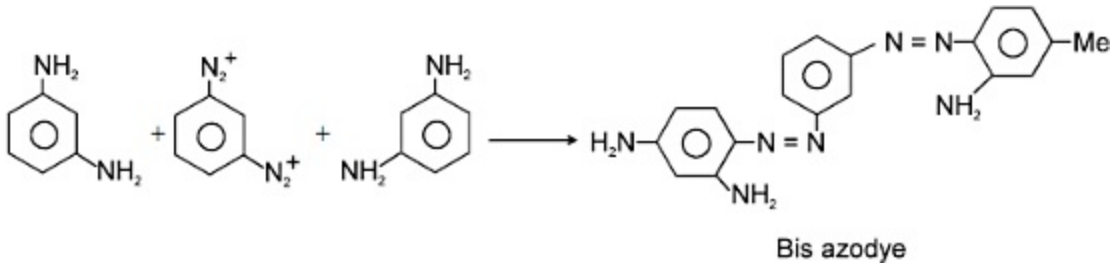
Therefore presence of vacant orbital on terminal nitrogen vanishes due to resonance and there by loses electrophilic character. At slightly alkaline medium (e.g. for phenol and for amines slightly acidic medium is required) coupling reaction is carried out. Strong basic condition is not allowed due to Ph – N = N – OH formation and strong acidic medium is not allowed as Ph–NH_3^+ formation for amines.



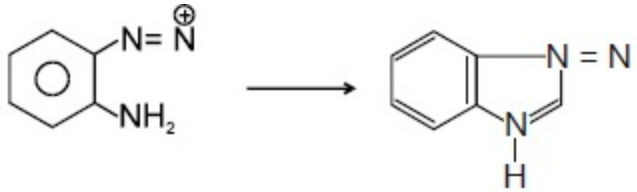
Mechanism :



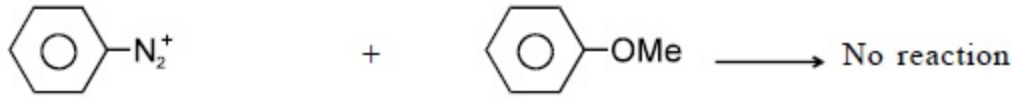
Some more examples :

1. 

Bis azodye

2. 

Benztriazole

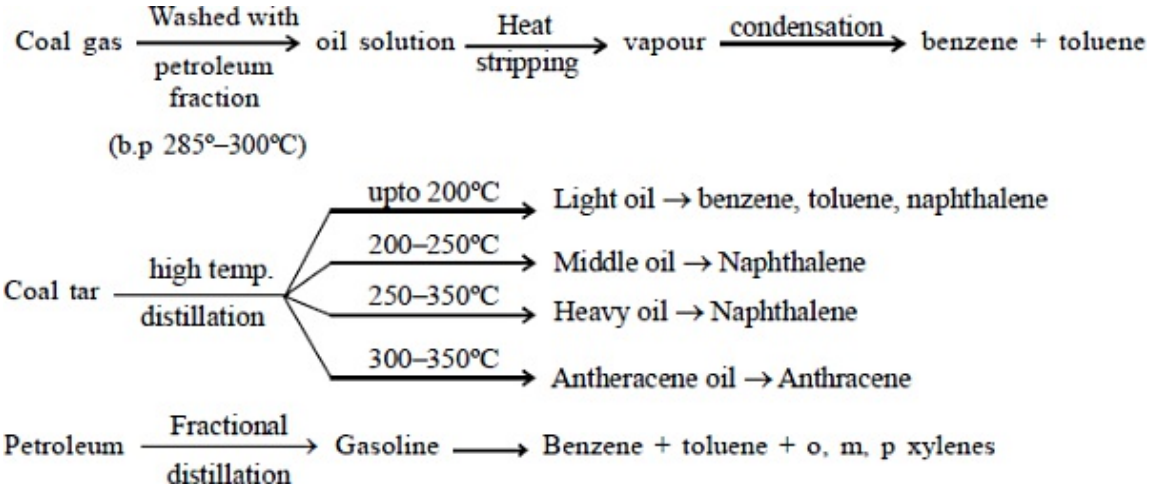
3. 

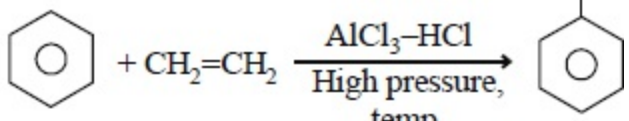
(weak electrophile) (weak nucleophile)

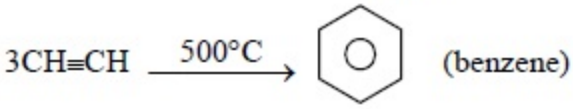
Aromatic hydrocarbon, Benzene, Toluene, Naphthalene

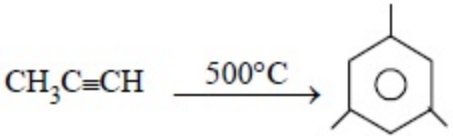
Preparation:

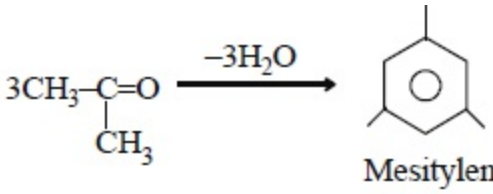
(1) Source:

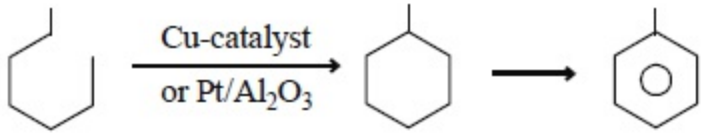


(2) 

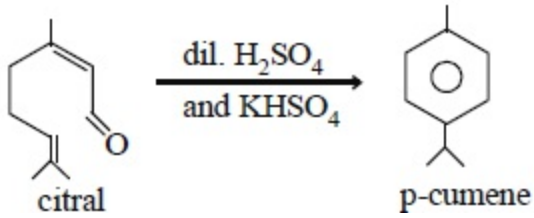
(3) 

(4) 

(5) 

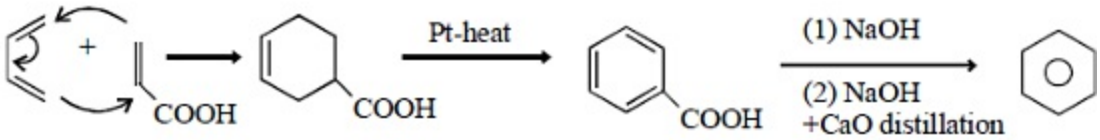
(6) 

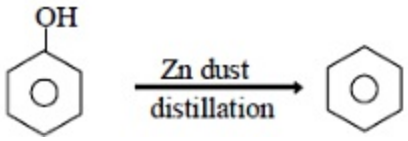
Toluene

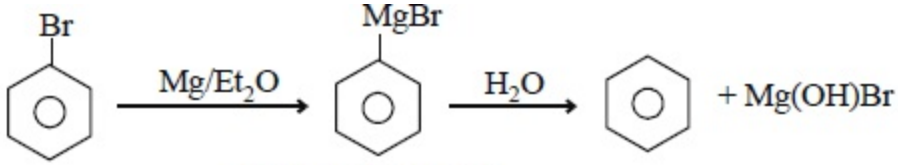
(7) 

citral p-cumene

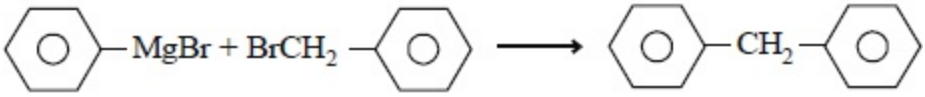
(8) **Diels Alder reaction:**



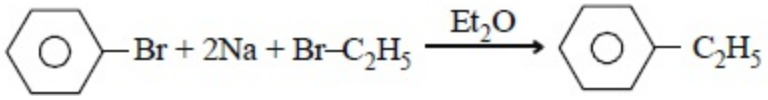
(9) 

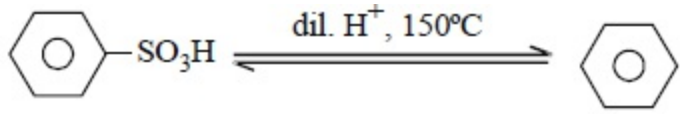
(10) (a) 

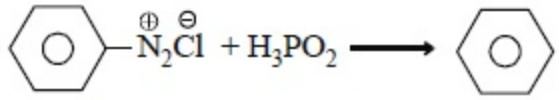
(Grignard reagent)

(b) 

(11) **Wurtz Fittig reaction:**

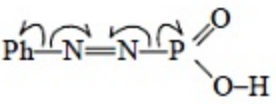
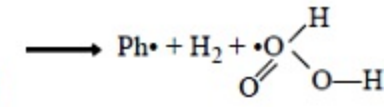


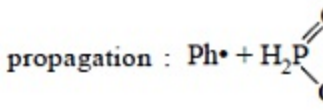
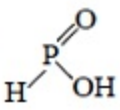
(12) 

(13) 

Benzene diazonium chloride

Mechanism:

Chain initiation: $PhN_2Cl + H_3PO_2 \rightarrow HCl +$  

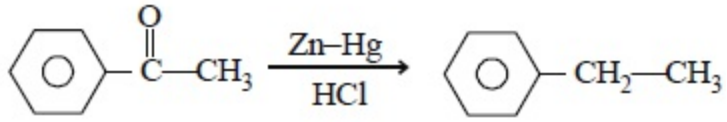
Chain propagation : Ph• +  PhH Benzene + 

$$PhN_2^+ + \bullet PH(O)OH \rightarrow PhN_2\bullet + PH(O)OH^+$$

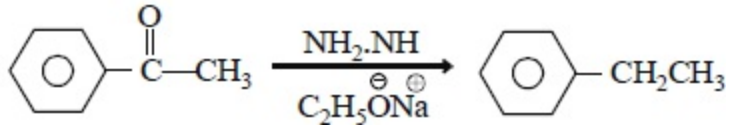
$PhN_2\bullet \rightarrow Ph\bullet + N_2$ etc.

$PH(O)OH^+ \xrightarrow{H_2O} H_3PO_3 + H^+$

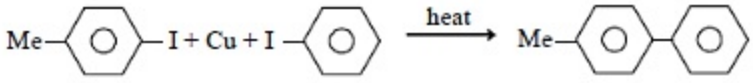
(14) **Clemensen's reduction:**



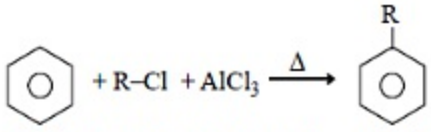
(15) **Wolff Kischner's reduction:**



(16) **Ullmann's reaction:**

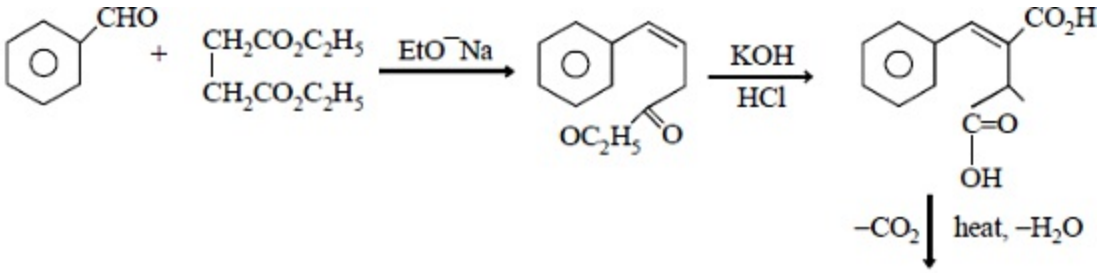


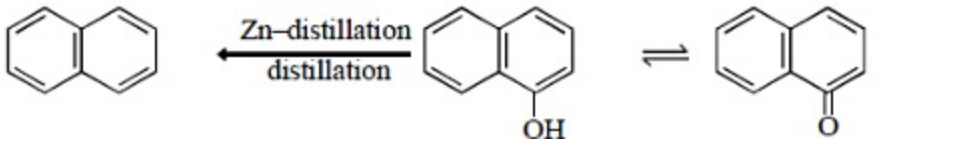
(17) **Friedel Craft's reaction:**



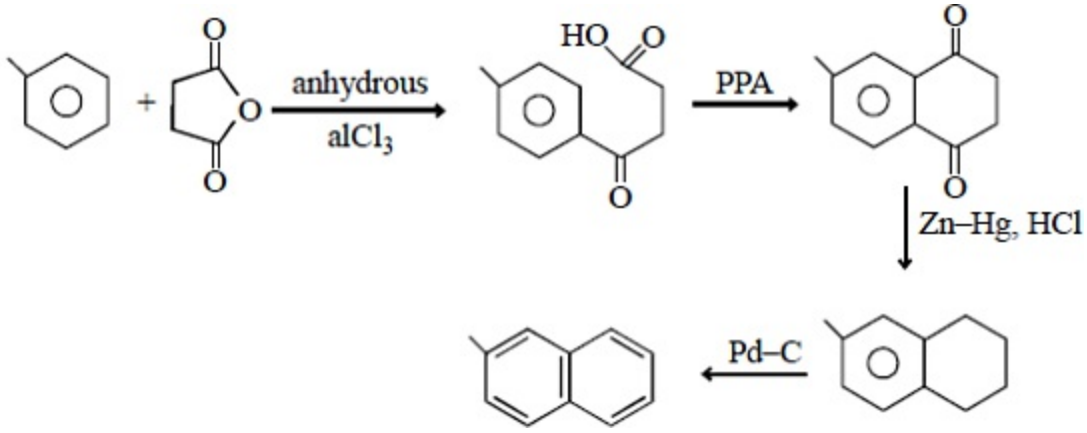
Reactivity order is t-R > s–R > p–R when X is same and RF > RCl > RBr > RI for a given type of alkyl group.

(18)



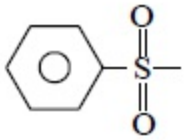


(19)



(20) $PhCH_2MgBr + 2TsO - nBu \rightarrow PhCH_2–nBu + Mg(OTs)_2 + nBu–Cl$

Where Ts =



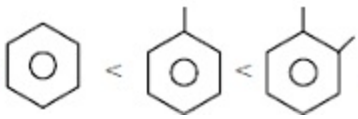
Tosyl group

Physical properties: Benzene has symmetrical charge density and toluene has more negative charge density within the ring due to +I effect of CH_3 group. Weak London's force exists between benzene molecules, so m.p. is low. But m.p. of toluene is lower as symmetrical molecule has higher m.p. due to good packing in the crystal. e.g.

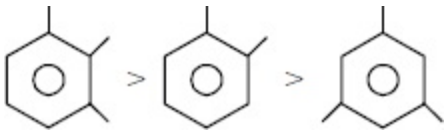
Melting point order



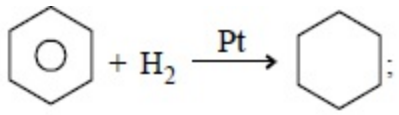
But the b.p order is

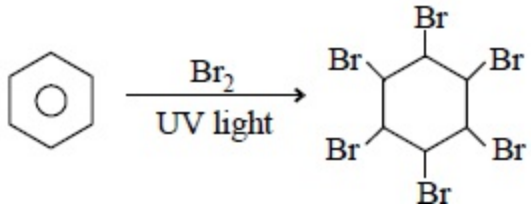


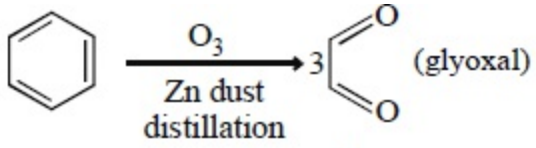
, as b.p. is a function of inter molecular forces.

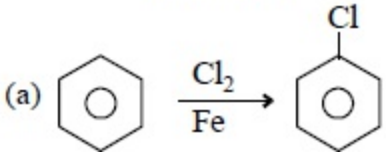
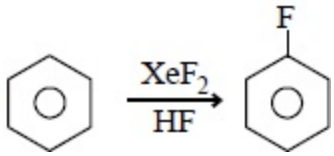
Also  is another b.p. order. The ArH are highly insoluble in water. Alkyl benzenes float on water and act as solvents. These donot have colour and have characteristic smell.

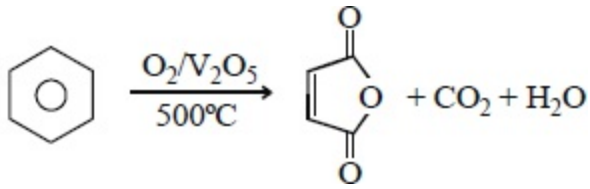
Chemical reactions:

(1)  ; $\Delta H = -51$ Kcal

(2) 

(3)  (glyoxal)

(4) (a)  (b) 

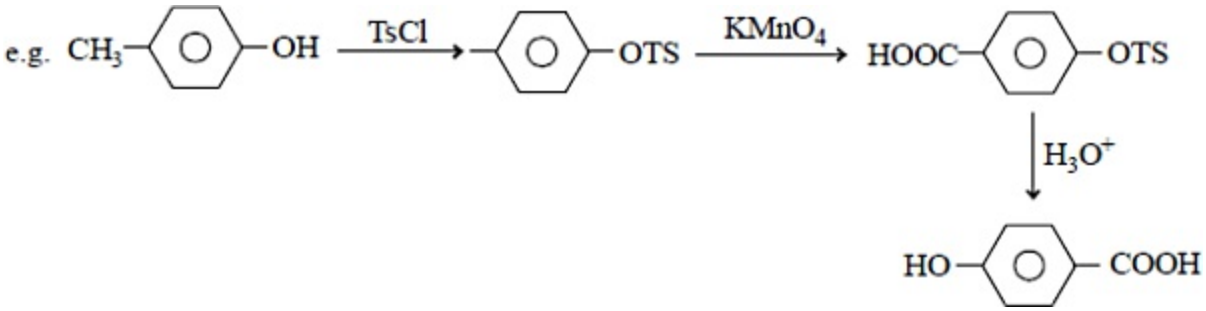
(5) 

Other sulphonation, nitration etc. reactions occur in benzene, toluene etc.which we have already seen.

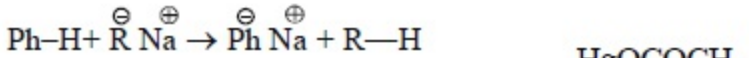
(6) Oxidation:

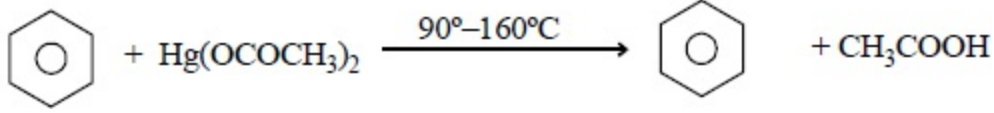
$$C_6H_5CH_2CH_3 \xrightarrow{KMnO_4} C_6H_5COCH_3 \longrightarrow C_6H_5COOH$$

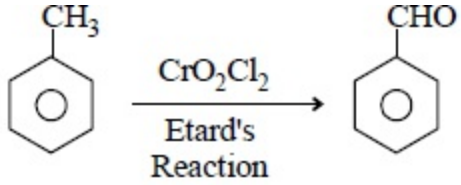
When the alkyl goup is t–R then oxidation is difficult, ring cleaves. Attack at α -C, occurs, by the attack of $KMNO_4$/H+ or OH^-. With deactiviting group side chain oxidise but in presence of –OH, $–NH_2$ because of their strong +R effect ring break down. Protection of –OH help oxidation as shown below:



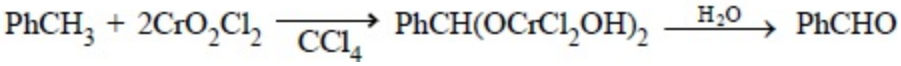
(7) Metallation of aromatic compounds:

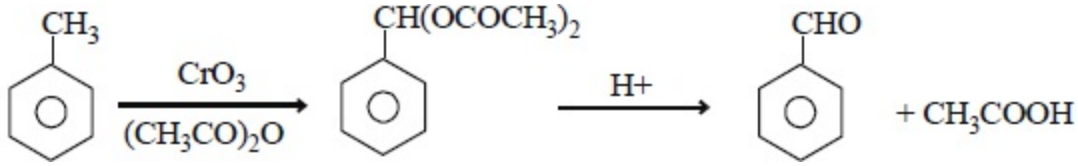


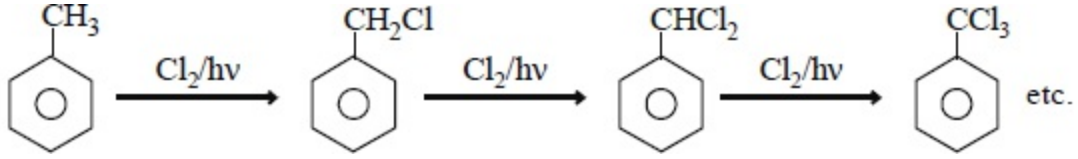
(8) 

(9) 

Mechanism:



(10) 

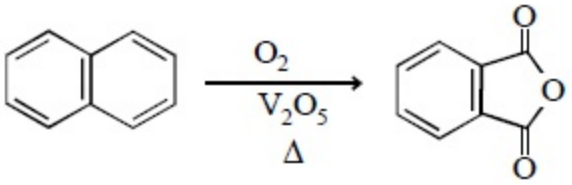
(11) 

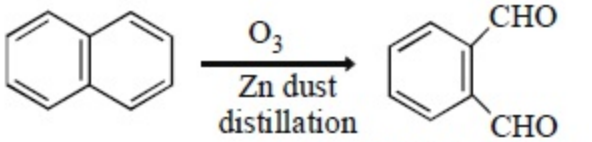
Mechanism:

$Cl_2 \longrightarrow 2Cl\bullet$

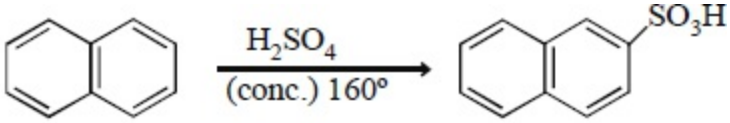
$Cl\bullet + Ph{-}CH_3 \longrightarrow PhCH_2\bullet + HCl$

$PhCH_2\bullet + Cl_2 \longrightarrow PhCH_2Cl + Cl\bullet$

(12) (a) 

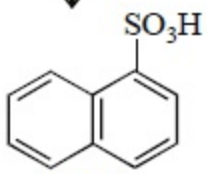
(b) 

Phthalaldehyde

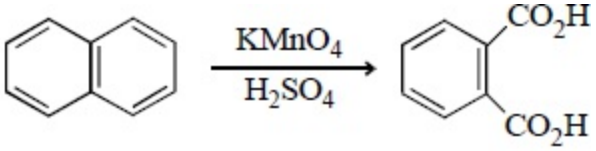
(13) 

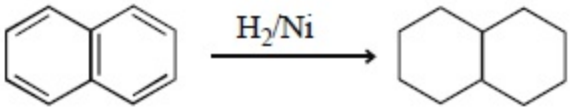
(TCP)





(KCP)

(14) 

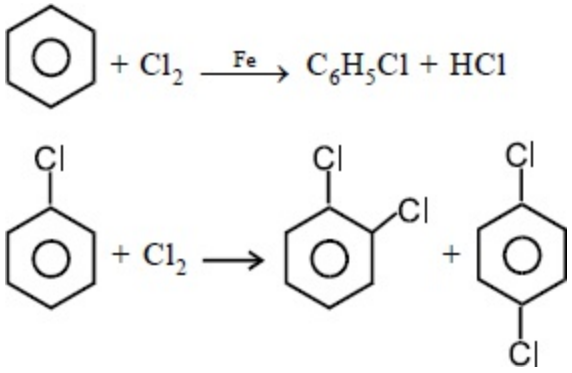
(15) 

decalin

Aromatic halide (Ar-X)

Preparation :

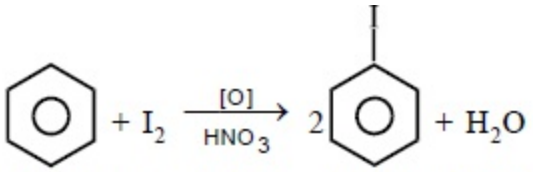
(1) Low temperature halogenation is carried out of benzene in presence of halogen carrier e.g.; $FeCl_3$, $A1C1_3$, $SbCl_3$ etc. Only Fe converts to $FeCl_3$ in presence of Cl_2 .



The rate law for catalytic halogenation is, rate = k[Ph H] [X_2] [Lewis acid]. Mechanism has been discussed already.

2. $ArOH + PCl_5 \longrightarrow ArCl + HCl$

3. $ArCO_2Ag + Br_2 \longrightarrow ArBr + CO_2 + AgBr$
With deactivating group like NO_2 yield is higher.

4. 

In presence of HNO_3 , HIO_3 , HgO the yield is good.

5. From the diazonium salts; $ArN_2^+Cl^- \xrightarrow[\text{Or Cu / HX}]{\text{CuX/H–X}} \text{Ar-X}$
[X = Cl, Br]

Mechanism:

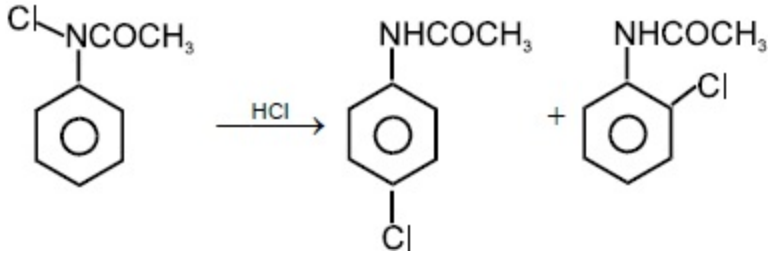
$$ArN_2^+Cl^- + CuCl \longrightarrow [ArN_2^+][CuCl_2]^- \longrightarrow Ar\cdot + N_2 + CuCl_2$$
$$Ar\cdot + CuCl_2 \rightarrow ArCl + CuCl$$

This is a free radical mechanism in which Cu change its oxidation state from +1 → +2 → +1

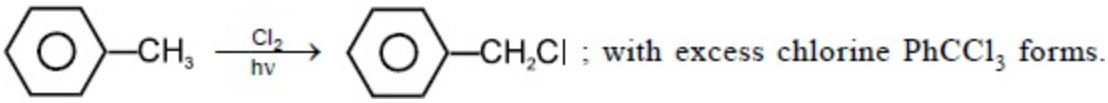
6. $ArN_2^+Cl^- \xrightarrow{KI} ArI$

$\xrightarrow[\text{or } HPF_6]{HBF_4, \text{ Heat}} Ar\text{-}F$

7. **Orton's Method:**



8. With Cl_2 , Br, and sunlight hexahalogenated ring rsults.



; with excess chlorine $PhCCl_3$ forms.

Physical Properties : These are colourless oils or crystalline solids and bp, density are higher than parent aromatic compound.

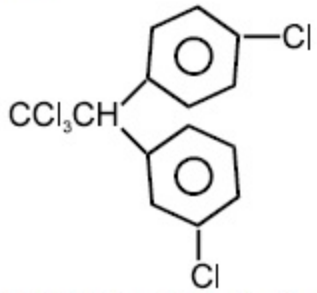
Structure and properties : Because of the less +R and strong–I effect of the halogen atom, benzene ring is deactivated . But X is o,p directing group due to its +R effect. F shows faster ArSE reaction and I shows ArSE reaction comparatively slowly .

Chemical Reactions :

1. $ArBr + Mg \longrightarrow ArMgBr \xrightarrow{HgCl_2} ArHgCl + MgClBr$

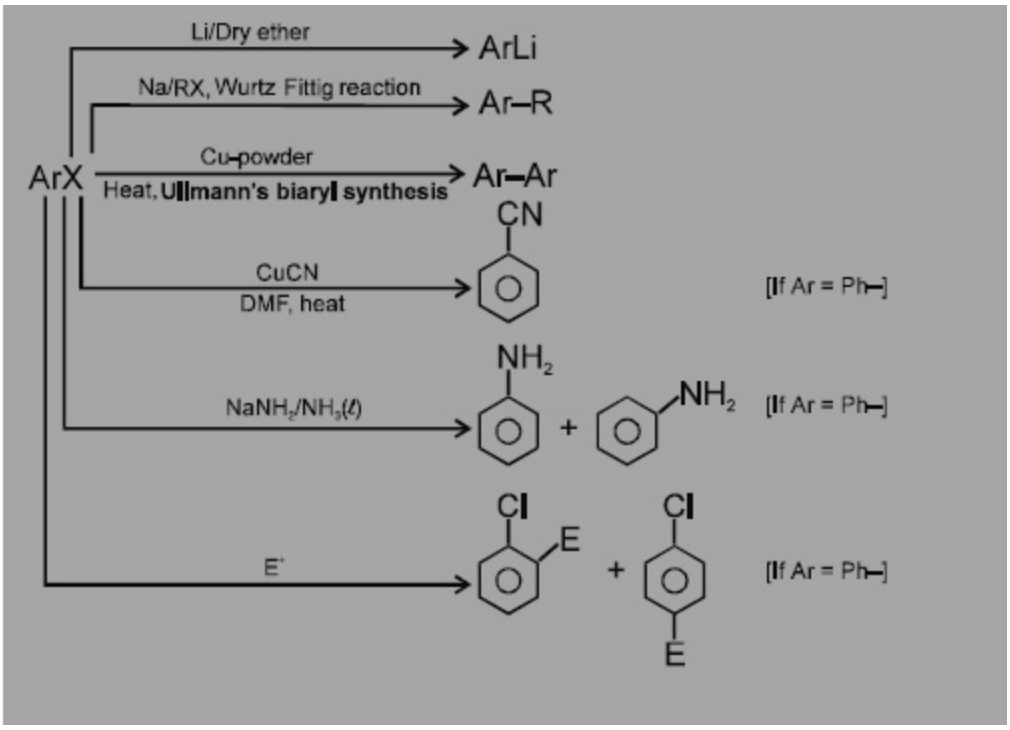
$\xrightarrow{H_2O} ArH$

2. $2C_6H_5Cl + CCl_3CHO \xrightarrow{Conc.H_2SO_4}$



[1,1,1 Trichloro-2,2 bis (p-chlorophenyl)ethane or DDT]

3.



Mechanism for Wurtz Fittig Reaction :

$$Ph{-}X + 2Na \longrightarrow Ph^{-}\,Na^{+} + NaX$$

$$\ddot{P}h + R{-}X \longrightarrow Ph - R + NaX$$

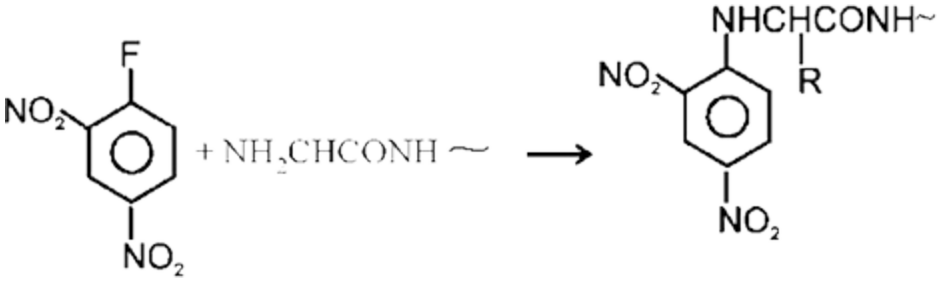
Also, $\ddot{P}hNa + Ph - X \longrightarrow Ph - Ph$

Mechanism for Ullmann's biaryl synthesis

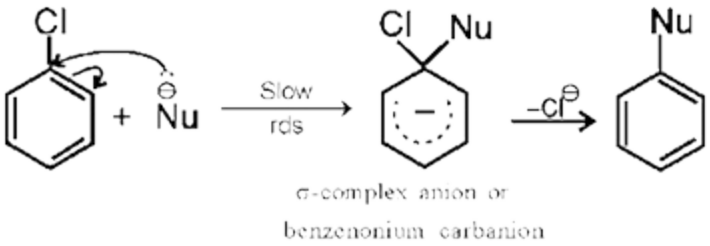
$$ArI + Cu \longrightarrow ArCuI \longrightarrow Ar^{-} \xrightarrow{Ar-I} \boxed{Ar - Ar} + I^{-}$$

$$+\overset{\oplus}{C}uI$$

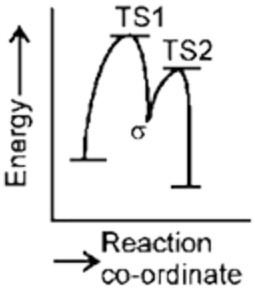
4. 2,4 D N F B is used to tag the amino end of a peptide or protein chain.

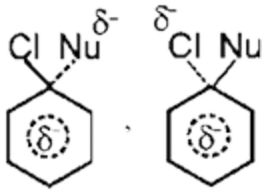


Aromatic halides undergo nucleophilic substitution (ArSN) and cine substitution product other than ArSE. ArSN is basically of the nature ArSN2 . Generally the reaction can be drawn as

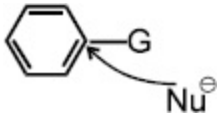


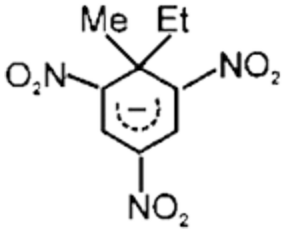
The energetics of the above reaction is as follows ;



Where TS1 and TS2 will look like  respectively. .-. Rate = R

[Ph-Cl] $[Nu^{\ominus}]$

The features of ArSN2 is (a) attack of $Nu^{\ominus}$ from the same side of the leaving group, i.e  as back side is hindered and (b) bond making of nucleophile along with bond breaking ot Nu leaving group donot take place simulatineously.

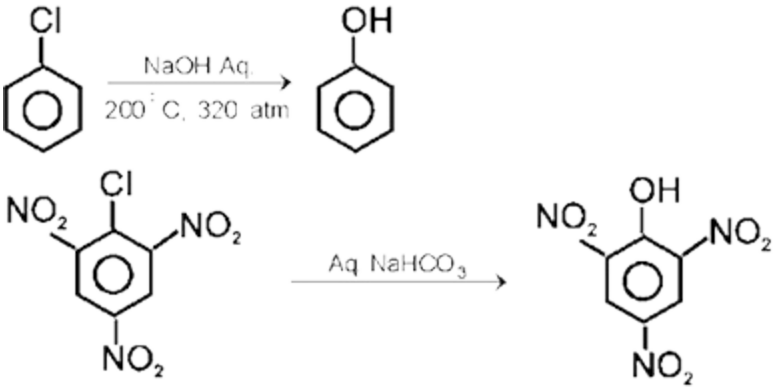
Detection of Meisenheimer complex which is  proves that σ

-complex anion appears during ArSN2 reactions.

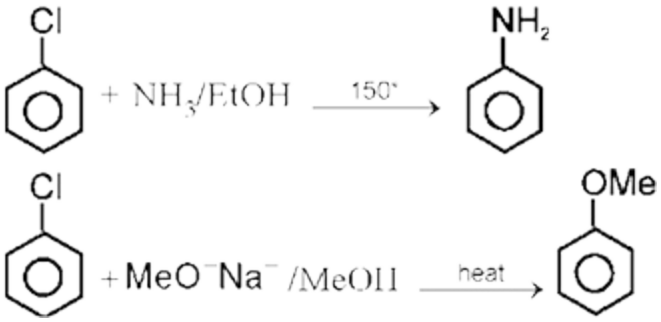
(c) Leaving group do not affect the rate of ArSN2 by experimental verification. If F is present as the substituent then ArSN2 rate is very fast compared to Cl, Br, I.

∴ Reactivity order is F>>Cl>>Br>I and this is due to strong-I effect which cause C of

C–F bond more partially positively charged and consequently $Nu^{\ominus}$ attacks easily. Electron donating groups towards benzene ring reduce the rate of ArSN2 but windrawing groups (-I,–R) activate from the 2,4 position by providing more stable σ -complex anion. Compare one case in which the vigourasity reduces from the former to the later ;



Such kinds of reactions are :

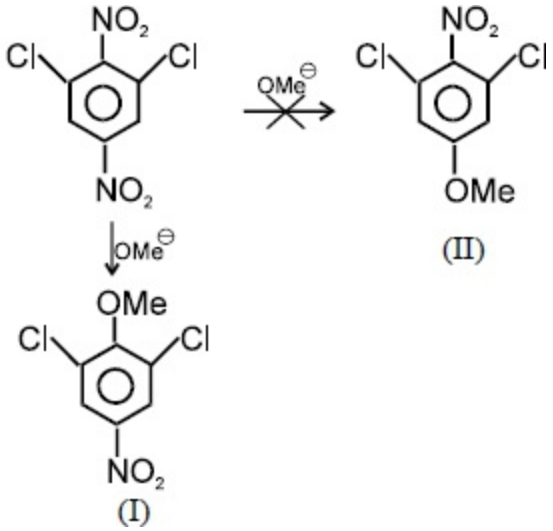


It is observed that –CN, –COMe, $–SO_2Me$ etc are the activators from the o,p positions and $[Zn(OH)Cl_2]$, $–HOPBr_2$, –OSOCl, $–OPCl_4$

$–NO_2$ are the most powerful activators.

Steric effect, polar effect of the solvent also interfere with the rate of reaction.

e.g.

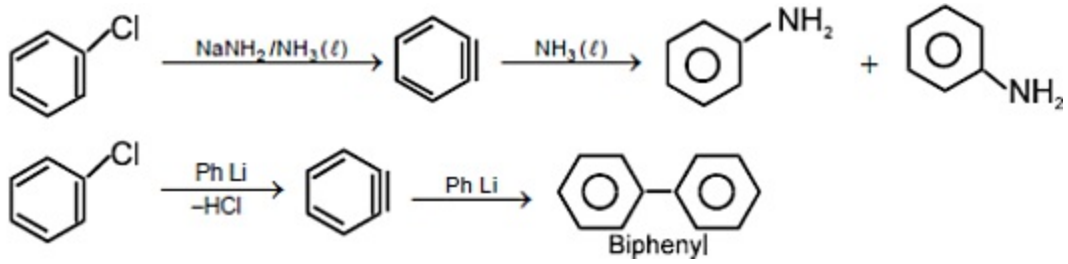


(I) forms due to σ -complex anion is stabilised but for (II) $-NO_2$ between 2-C1 atoms are under strong repulsion steric inhibition of resonance is observed, therefore σ -complex anion can not be stabilised.

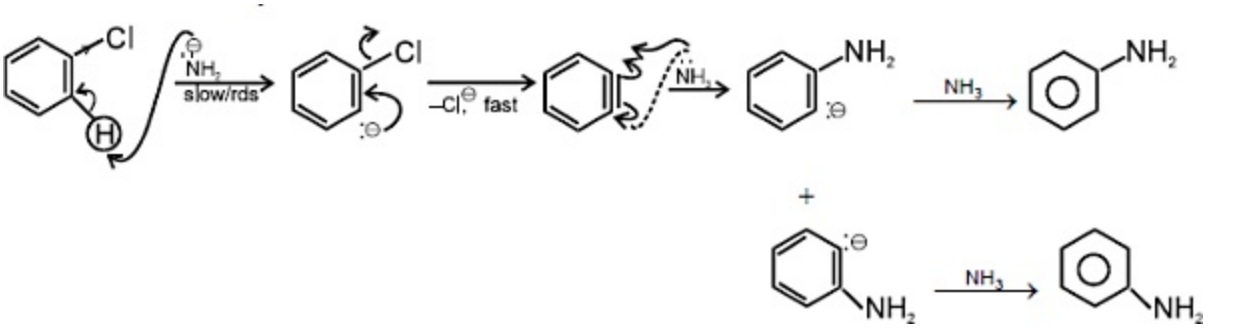
5. Benzyne Mechanism :

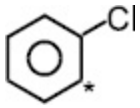
It occurs in halorane and in some other species. This is another way of incorporating nucleophile from outside.

e.g.



Mechanism of Benzyne Formation :

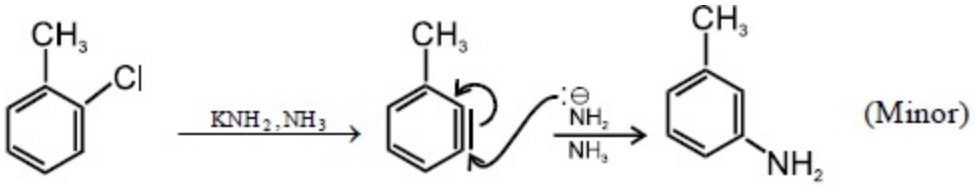


∴ Product I, II may look same now but with isotope labelled species 

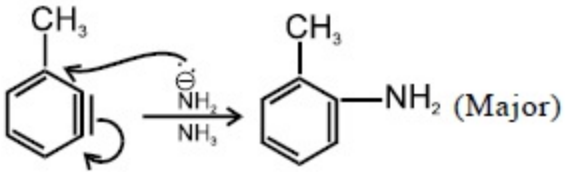
we get 50% each

C–N, $\overset{*}{C}$–N linkages. In the addition step only we consider the inductive effect of the substituent not the +R effect to stabilise carbanion.

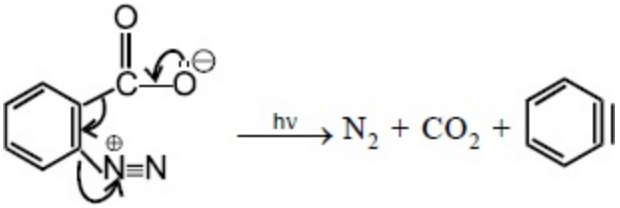
For example ;

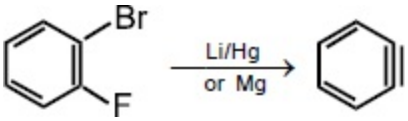


But



Also the other sources of benzyne formation are ;



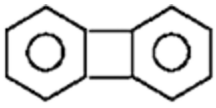


Structure of benzyne is supposed to be

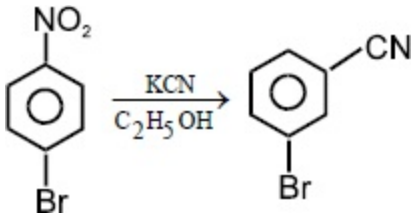


(Diradical) (Dipolar)

Benzyne can be called as 1,2 dehydrobenzene and the π -bond (extra) formed by overlap of two sp^2 hybrid orbitals of 'C and hence it is an aromatic intermediate. Benzyne is so unstable that imediately it dimerises to

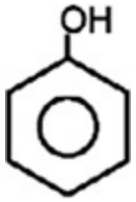


6. Another interesting reaction is Von Richter's reaction which is given as follows;



Here –CN enters the ring ortho to the position occupied by Br and NO_2 goes out as leaving group.

Phenol

Structure of phenol is 

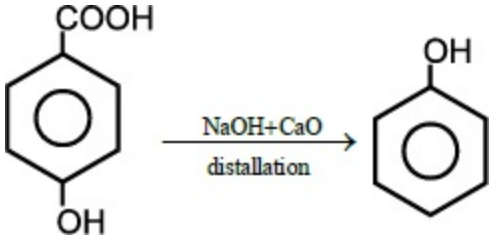
Preperation :

(1) $PhSO_3H \xrightarrow{NaOH} PhSO_3^-Na^+ \xrightarrow[Fusion]{NaOH(s)} PhO^-Na^+ \xrightarrow[SO_2]{H_2O} PhOH$

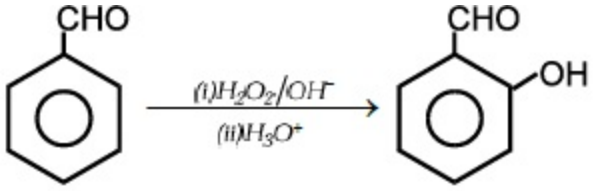
(2) $PhNH_2 \xrightarrow[dil.H_2SO_4(0^0-5^0C)]{NaNO_2} PhN_2^{\oplus}HSO_4^- \xrightarrow[Boil\ at\ 50^0-60^0C]{H_2O} PhOH$

(3) $PhMgBr \xrightarrow{O_2} PhO_2MgBr \xrightarrow{PhMgBr} PhOMgBr \xrightarrow{H_3O^+} PhOH$

(4) Soda lime distillation :

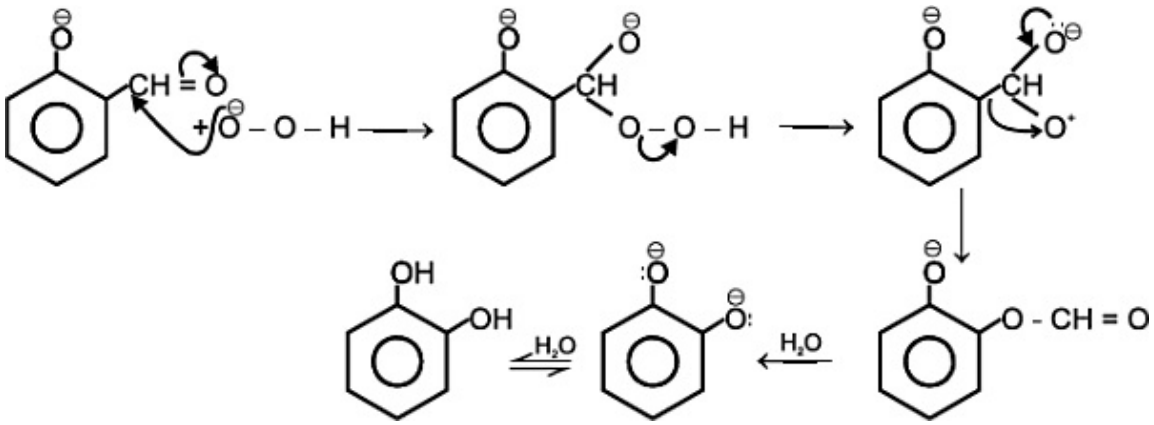


(5) Dakin's reaction :

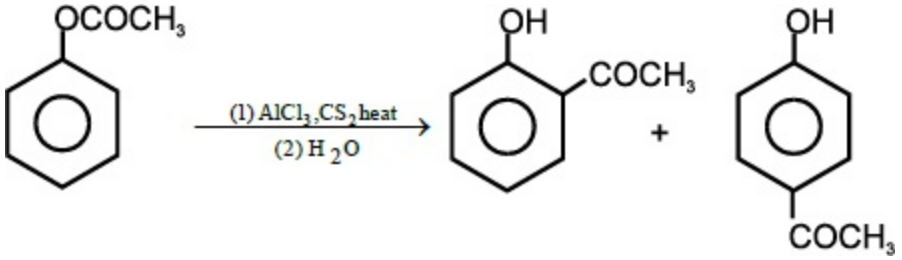


Mechanism :

$H-O-O-H + OH^- \rightleftharpoons H-O-O^- + H_2O$

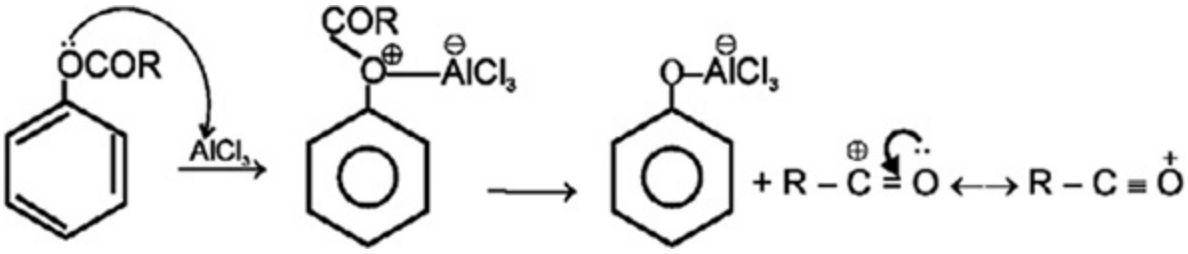


6. Frie's rearrangement :

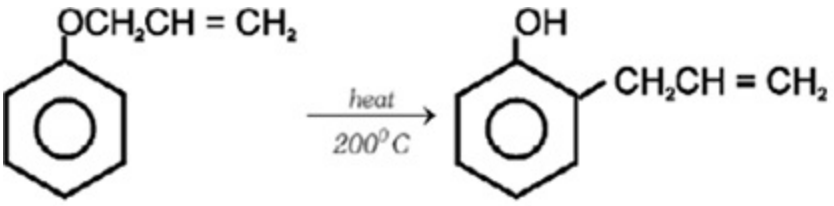


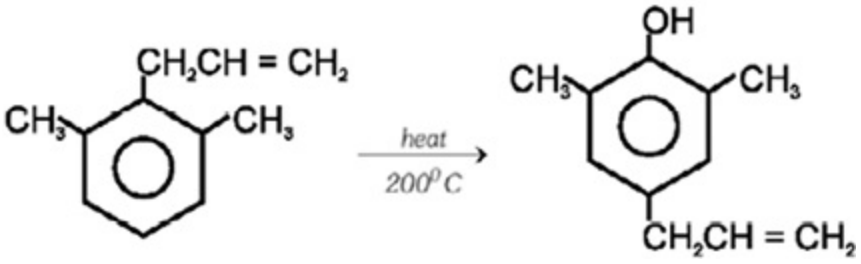
At low temperature (60°C) p-isomer forms and at high temperature (160°C) o-isomer forms in major amount. The mechanism is supposed to be intermolecular as well as intramolecular one . When a meta directing group is present then it interferes in the reaction.

Intermoleculer mechanism:

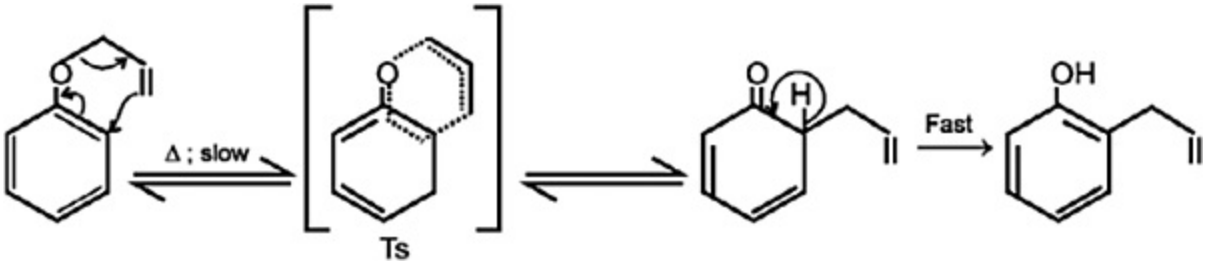


7. Claisen Rearrangement :



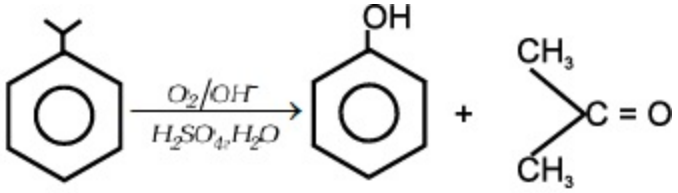


Mechanism :



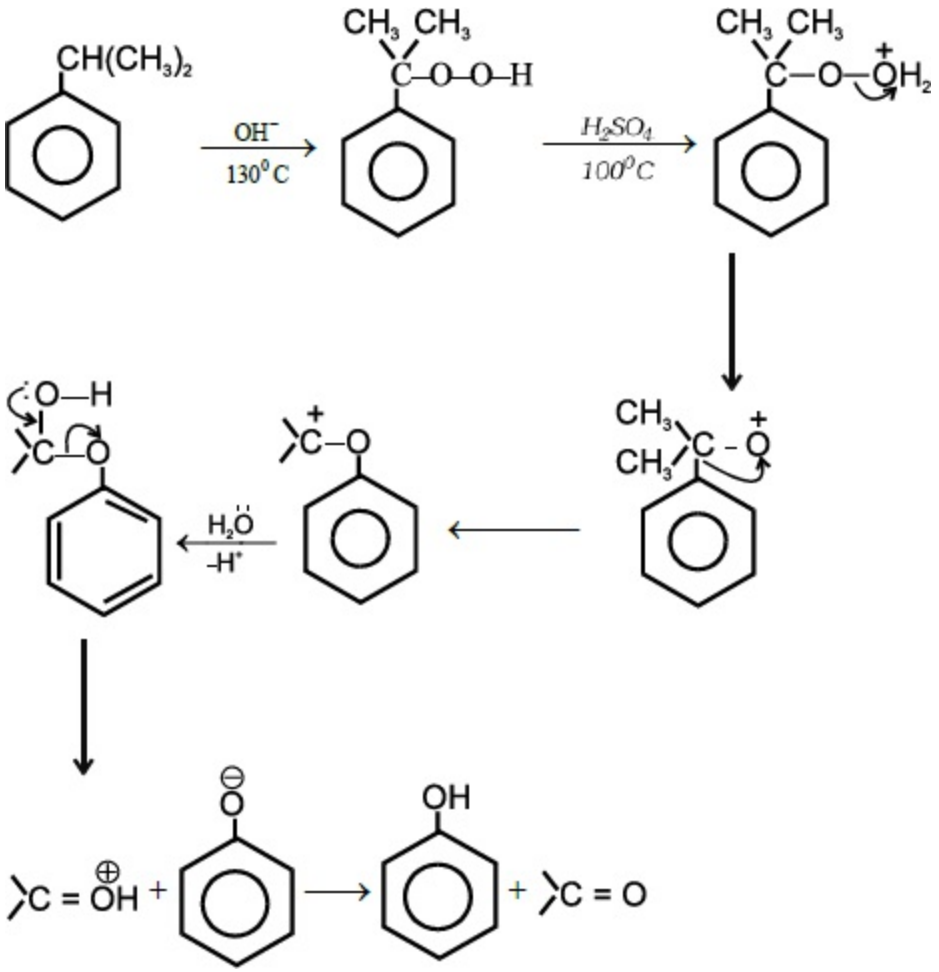
Here 'H' in the fast step migrate to the 'O' of dienone structure. Migration to para occur via ortho position and terminal-C of ortho get attached to the para C. This is called sigmatropic rearrangement.

8.



Cumene

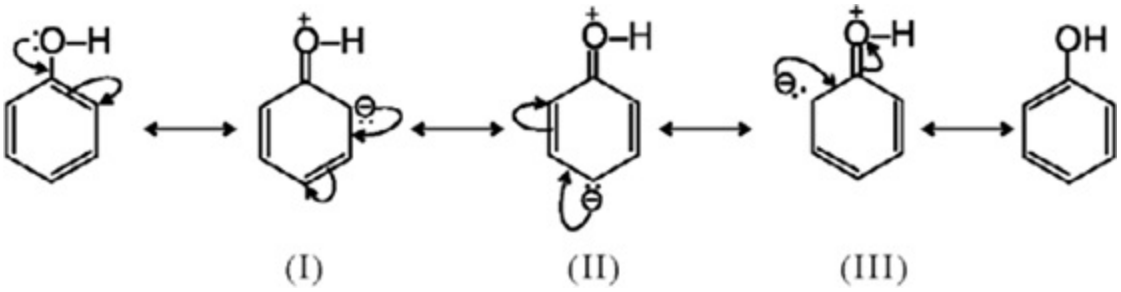
Mechanism :



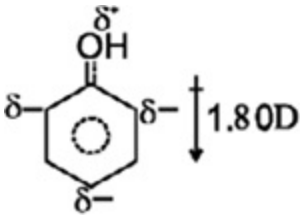
This is a sort of Bayer Villiger's oxidation and called as cummene phenol process, where Ph ring with bonded pair of electrons migrate to electron dificient species, O.

Structure and physical properties :

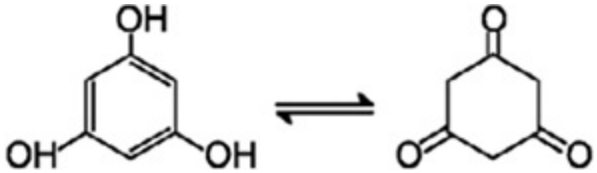
The lone pair on 'O' is in the $2p_z$ orbital and therefore 'O' is in sp^2 hybridized state. In phenol several resonating structures are possible.



(I) (II) (III)

Resonance hybrid of (I), (II), (III) is 

The above resonating structures show that H has partial positive charge to show acidic behavior. Phenol hardly shows keto-enol tautomerism. 1, 3, 5 trihydroxy benzene i.e. phloroglucinol shows large amount of triketo form which is energetically favourable structure also.

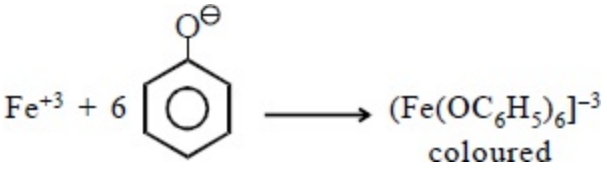


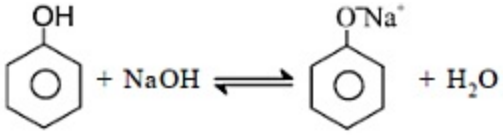
Phenol does not show the basic character as lp is highly involved into resonance with the benzene ring. PhOH shows intermolecular H-bonding therefore bp., mp. are much higher than the corresponding arenes. Phenol is moderately soluble in water but highly soluble in organic solvents. Phenol has carbolic smell. It has no colour and it is corrosive to skin.

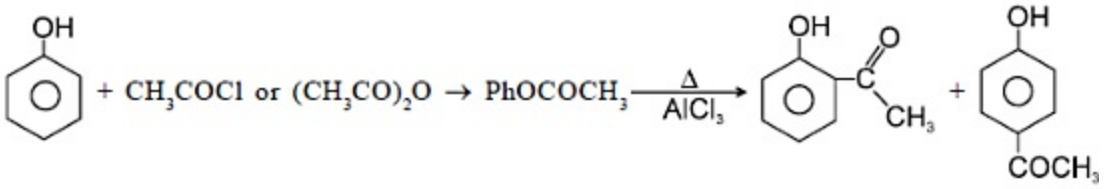
Chemical reactions :

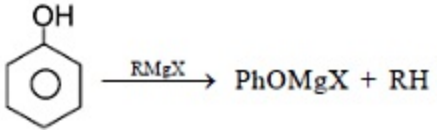
1. With $FeCl_3$

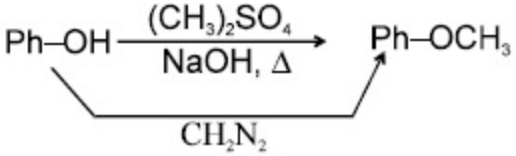
With few drops of freshly prepared $FeCl_3$ solution (just like enols) phenol form violet or green or blue colouration. The reaction may be



2. 

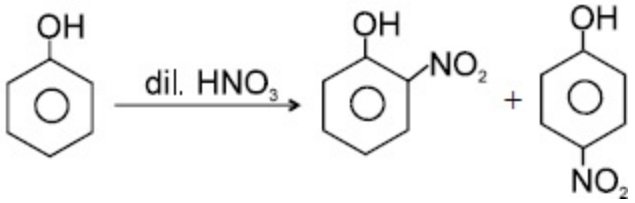
3. 

4. 

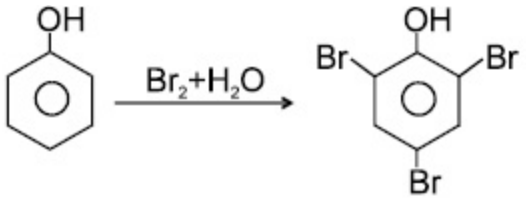
5. 

6. $PhO^{\ominus}\ Na^{+} + RI \xrightarrow{\text{Williamson's synthesis}} PhOR + NaI$

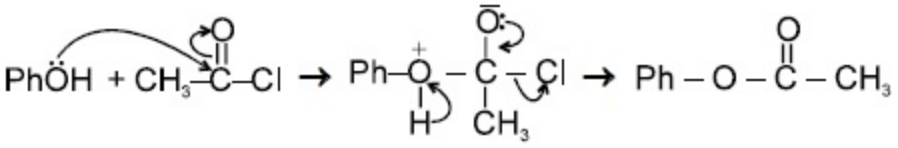
7. $Ph\text{–}OH \xrightarrow[\text{or } PCl_5]{POCl_3} (PhO)_3PO + HCl$

8. 

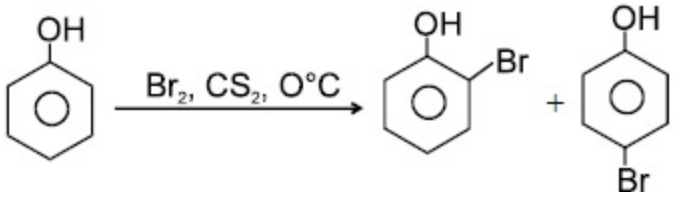
9. (a)



Mechanism:

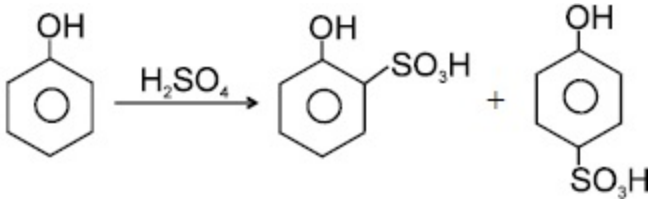


(b)



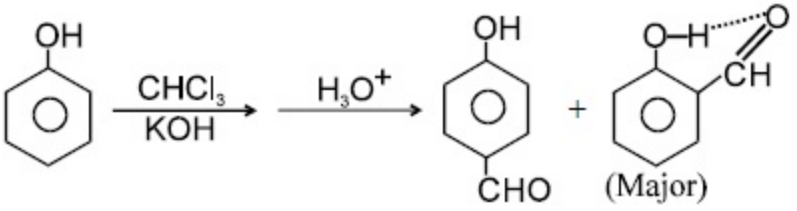
The difference between the products of the reactions (a) and (b) is due to the participation of phenoxide ion, which is the dissociated form of phenol in water and bromine in the reaction (a) but in (b) phenol takes part in the electrophilic substitution reaction with bromine. As $-O^{-}+R$) is stronger activating than OH (+R > –I), therefore we obtain the above result.

10.

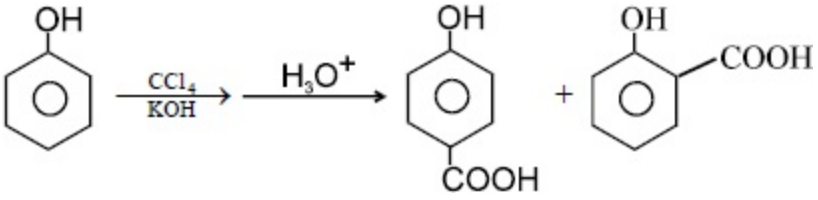


11. Reimer Tiemann's reaction :

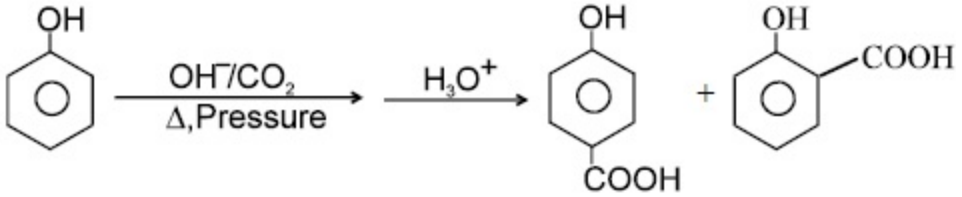
(a)



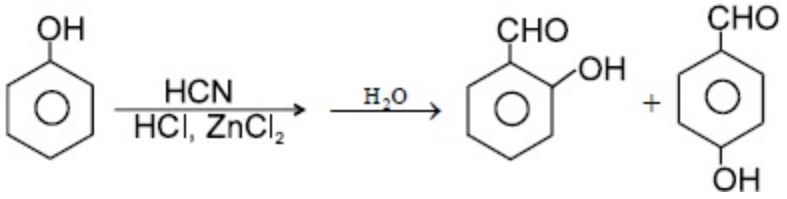
(b)



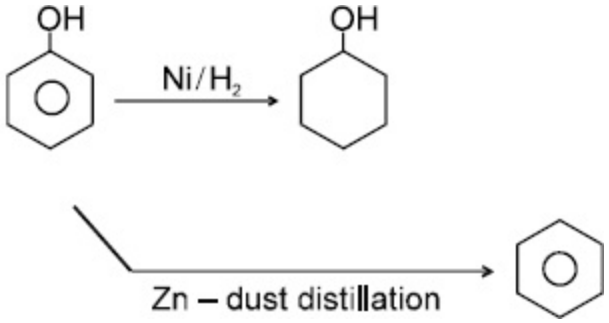
12. Kolbe Schmidt reaction :



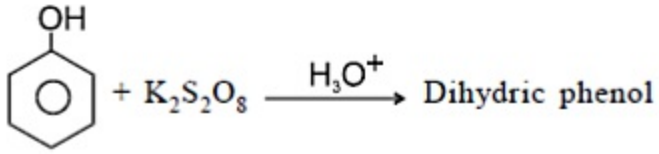
13.



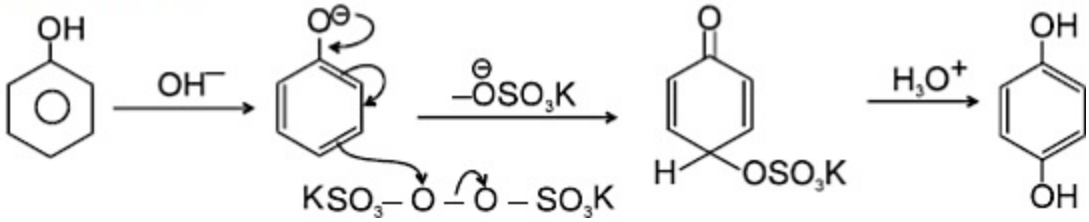
14.



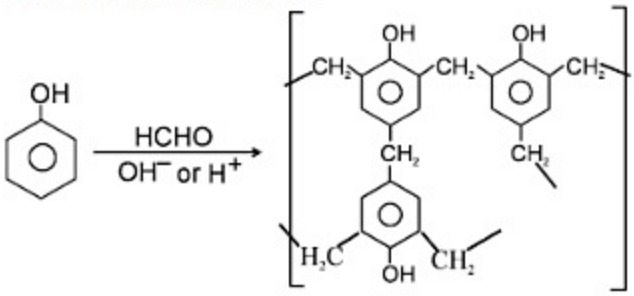
15. Elbs persulphate oxidation :



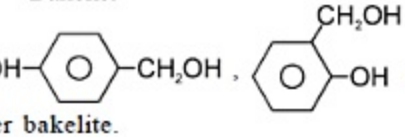
Mechanism :



16. Lederar Manasse reaction :



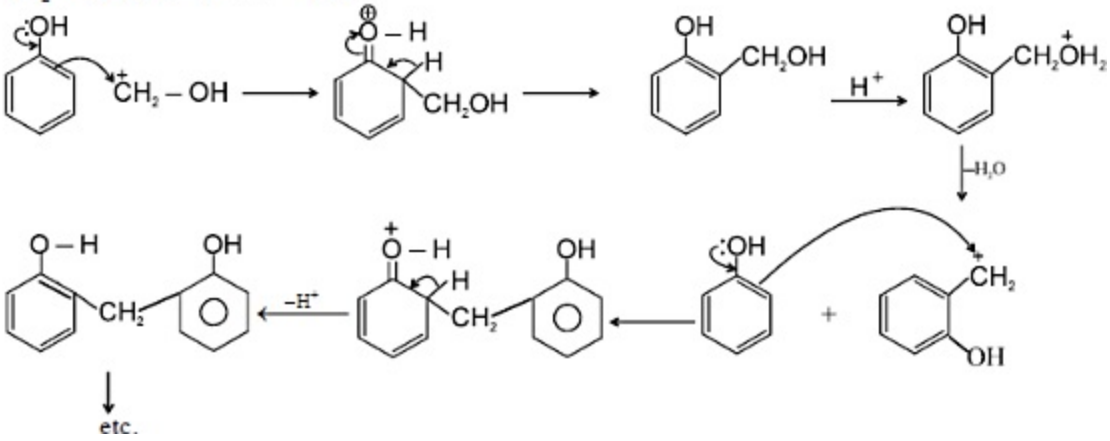
Bakelite

In the above reaction initially  form but with excess HCHO forms three dimensional polymer bakelite.

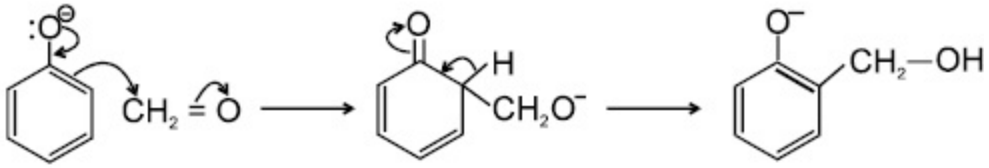
17. $CH_3CH = CH_2 \xrightarrow[PhOH]{H^+} CH_3 - \underset{\underset{CHOPh}{|}}{CH} - CH_3$

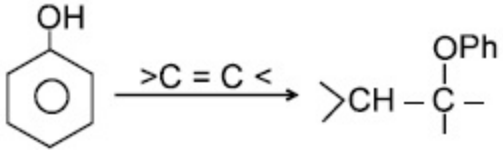
Mechanism :
Acid catalysis ;

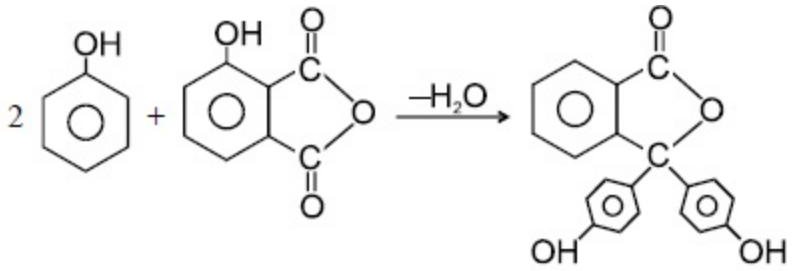
$CH_2 = O + H^+ \rightarrow \overset{+}{C}H_2 - OH$



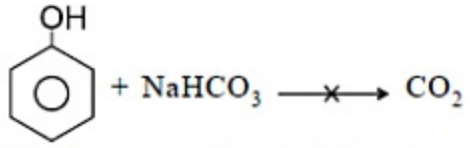
Base catalysis ;



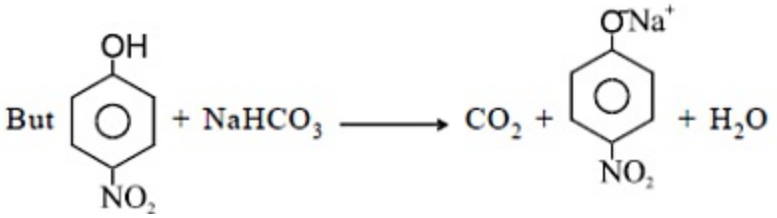
18. 

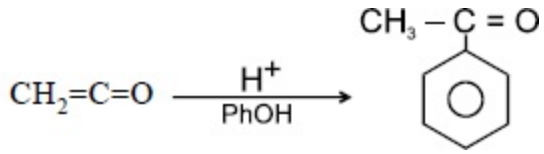
19. 

Phenolphthalein

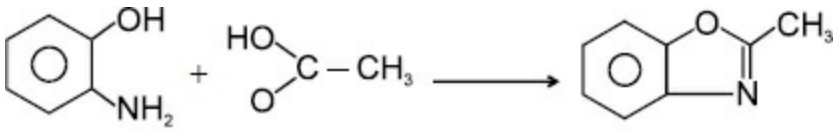
20. 

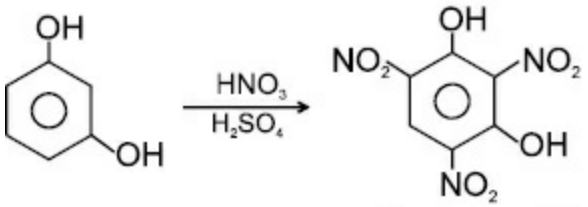
[Difference with – COOH, $-SO_3H$ functional groups as phenol is less acidic]



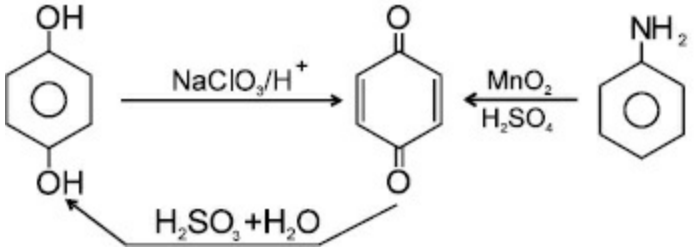
21. 

o, p-Aminophenols are weakly acidic therefore they donot form phenoxides with base. They easily form quinones but meta one does not. o-Amino phenol form cyclic compound easily by dehydration as shown in the following reaction.





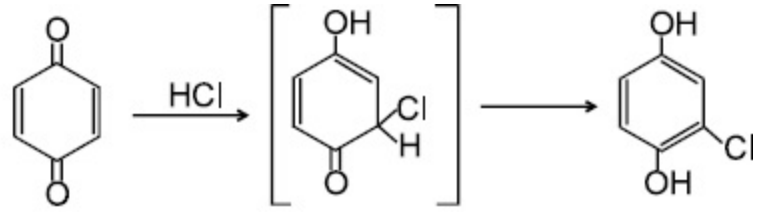
Styphnic acid



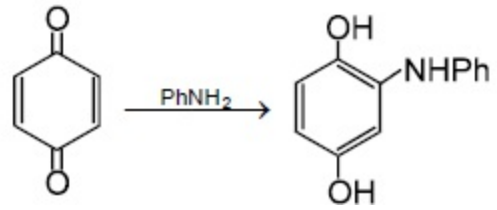
p Benzoquinone behaves as on α , β , unsaturated ketone and show 1, 4 addition reactions, followed by aromatization. In the above conversion, product gain stabilization energy due to high resonance energy of 125.5 kJ (mole) from 20.9 kJ/mol of quinone.

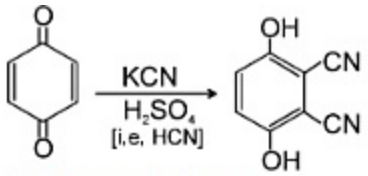
Examples of 1, 4, addition and subsequent aromatisation ;

(1)

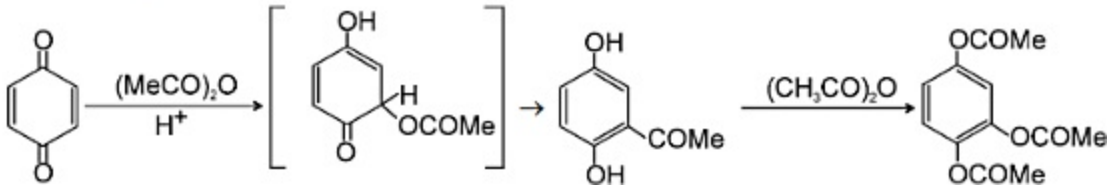


(2)

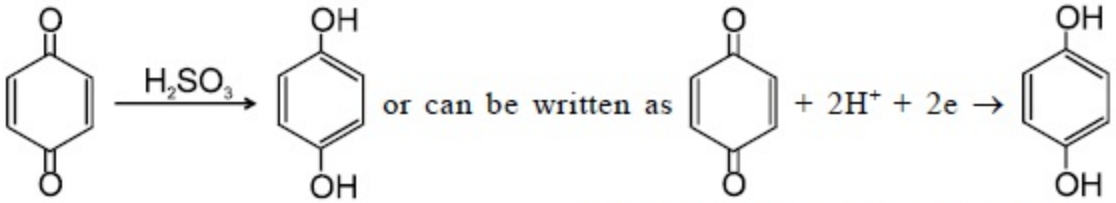


(3) 

(4) **Thiele acetylation :**

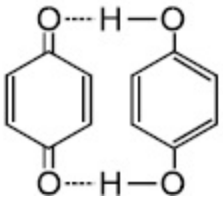


Reduction reaction :

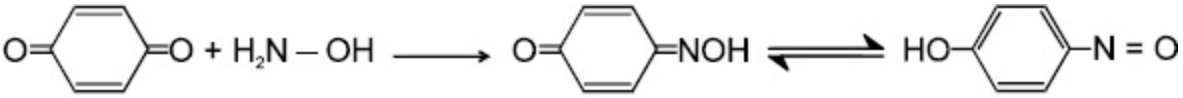


(1.6, addition), green coloured compound

Quinhydrone formed is stabilised by H-bonding with quinone as shown below ;



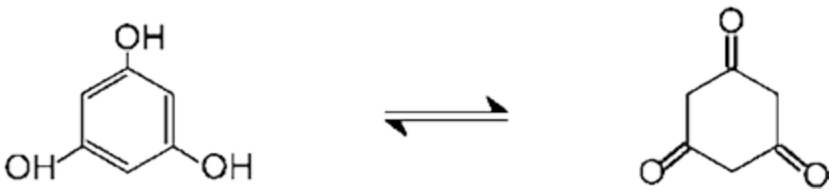
Other reactions of p-benzoquinone are,



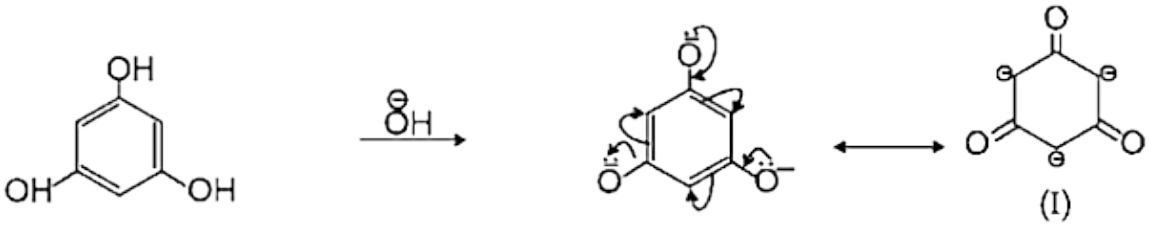
Tautomeries

Quinol when crystallized from saturated aq. solution with SO_2, a quinol sulphur dioxide complex forms. This inclusion compound is called clathrate compounds according to Powell. Formula is designated as n $C_6H_4(OH)_2$. X where X = SO_2 or CH_3OH or H_2S with which clathrate compounds form .

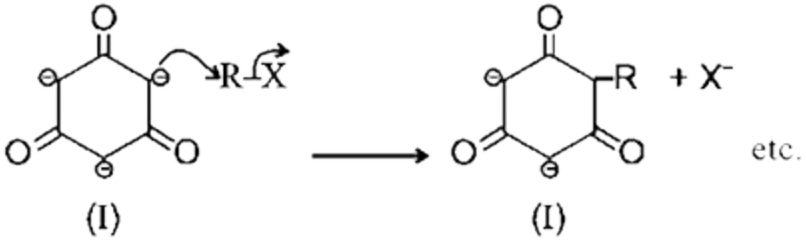
Among the trihydric phenols phloroglucinol is an important compound. This is a tautomeric compound.



In the solid state it is entirely enolic and also in solution. C – alkylation occur which proves that it take form(I) as shown below ;



Therefore in aqueous solution C– attack is possible as shown below ;

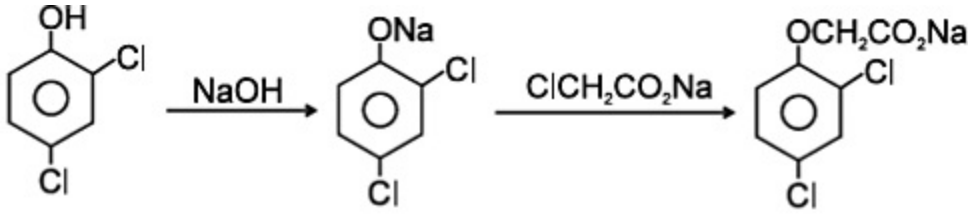


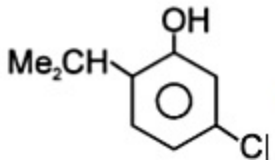
Use of phenol :

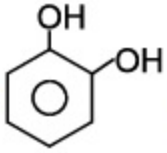
(1) In bakelite chiefly phenol is used.

(2) 2, 4, Dichlorophenoxyacetic acid is used as weed.

Preparation :

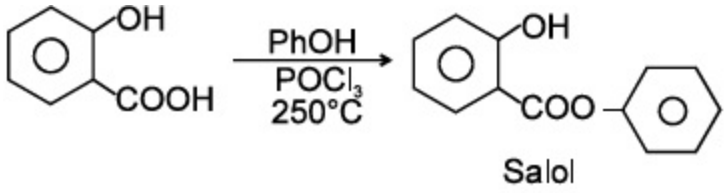


(3)  , **Thymol is used as antiseptic.**

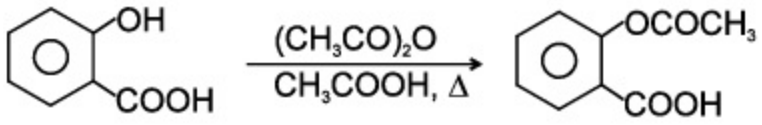
(4) **Catechol**  , **quinol**  **used as photographic developer.**

(5) Salol is used in medicinal coating and aspirin is used as analgesic. PASA (para amino salicylic acid) is used in tuberculosis.

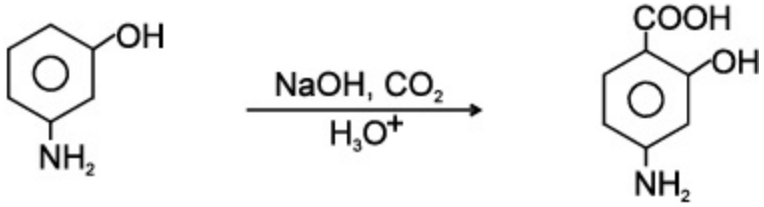
Preparation:



Salol



Aspirin



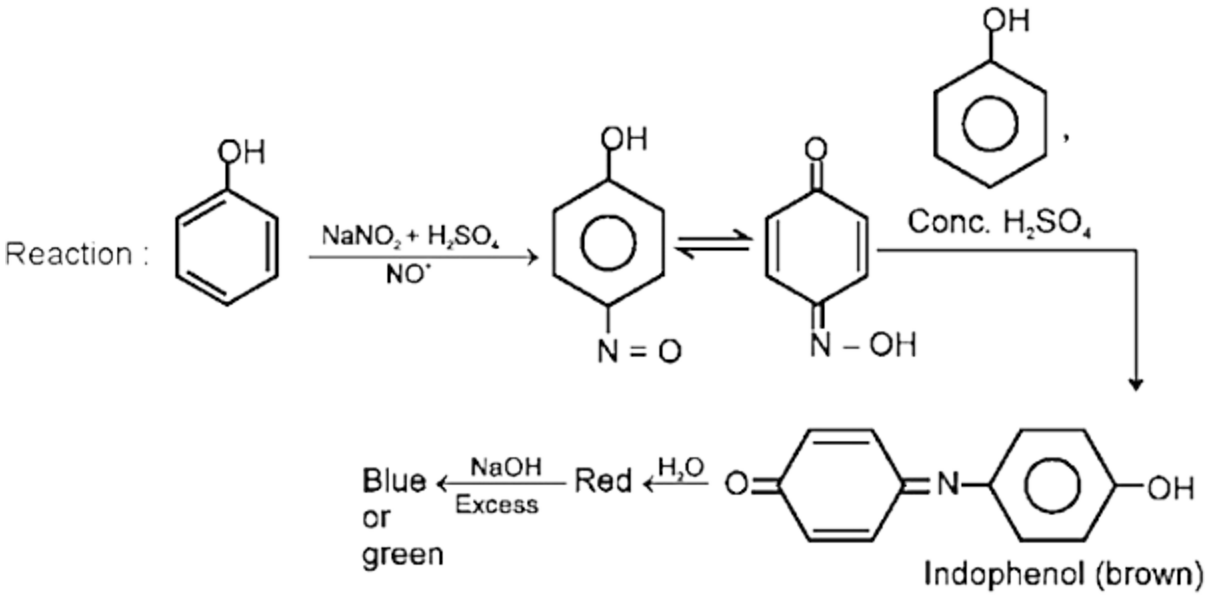
PASA (para amino salicylic acid)

Analysis :

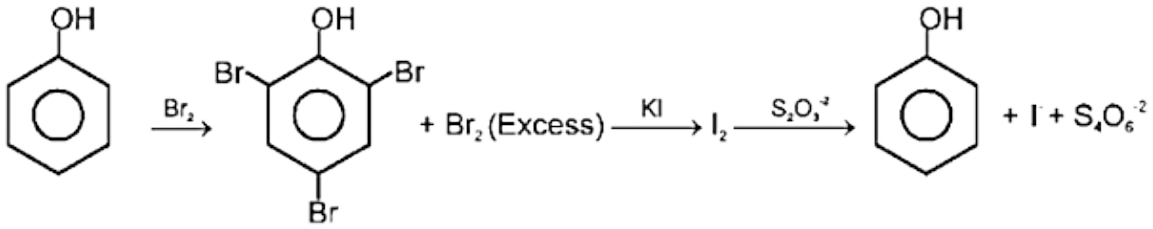
1. PhOH $\xrightarrow[Litmus]{Blue}$ red

2. PhOH $\xrightarrow{FeCl_3}$ Blue/violet/green/red (Depending on the reactant).

3. PhOH respond to Libermann's test.



Quantitative method :



By usual iodometry as shown above we estimate amount of phenol present quantitatively.

Thiols and Thiophenols

Preparation :

(1) $R\text{–}X \xrightarrow{NaSH} RSH$ [R=Alkyl or aryl]
(X=Cl, Br, I or any good leaving group)

(2) $ROH \xrightarrow{P_2S_5} RSH$ [R=Alkyl/phenyl) + P_2O_5

(3) $>C=C< \xrightarrow[NiS,\ 300^{\circ}C]{H_2S} -\overset{H}{\underset{}{C}}-\overset{}{\underset{SH}{C}}-$

(4) $RMgX \xrightarrow[(2)\ H_3O^+]{(1)\ S} RSH$

(5) $ArN_2^+ \xrightarrow{NaSH} ArSH$

(6) $ArSO_2Cl \xrightarrow{LiAlH_4} ArSH.$

Structure of properties:

–SH group has similar properties like that of –OH. 'H' of –SH is active hydrogen. H-bonding does not form among thiol molecules. Therefore b.p. and m.p. is less compared to alcohol. They are insoluble in water and have unpleasant odour.

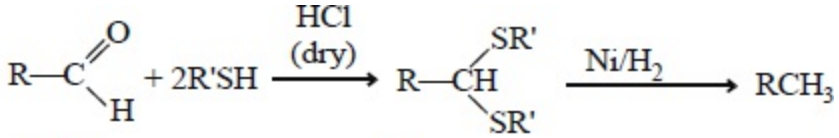
Chemical reactions:

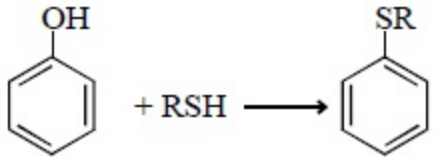
(1) RSH or ArS–H are more acidic than R-OH or ArOH due to longer bond length in S–H and also (–) ve charge can be held on $R\text{–}S^{\ominus}$ or $Ar\text{–}S^{\ominus}$

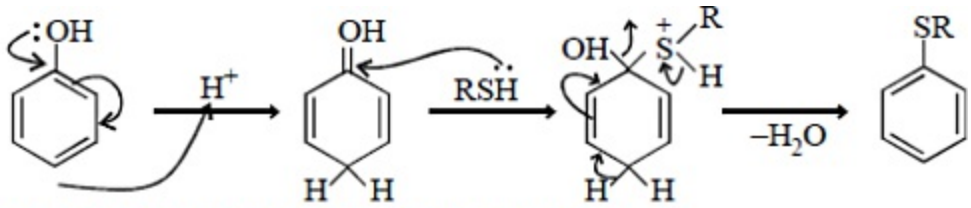
(1) $RSH \xrightarrow{Na/Li} RS^-\overset{+}{Na}/\overset{+}{Li} + \frac{1}{2}\ H_2$

(2) $RSH \xrightarrow{HNO_3} RSO_3H$

(3) $R\text{—}\overset{O}{\overset{\|}{C}}\text{—}Cl + R'SH \longrightarrow R\text{—}\overset{O}{\overset{\|}{C}}\text{—}SR'$

(4) 

(5) 

Mechanism: 

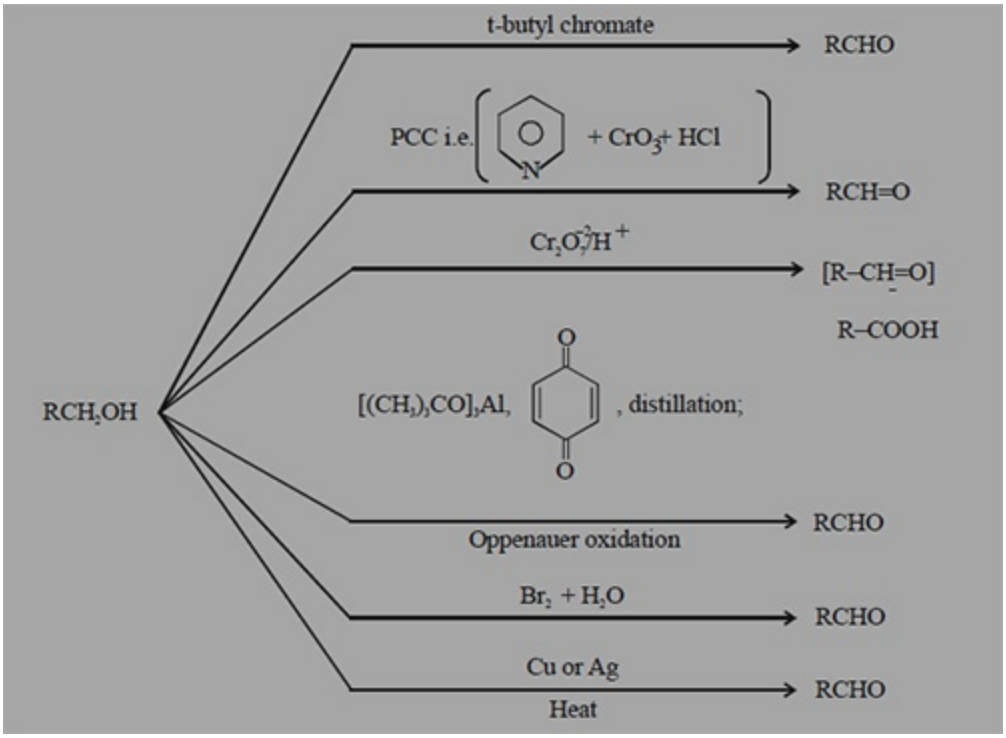
Interestingly RSH or ArSH donot turn blue litmus red.

Carbonyl Compound

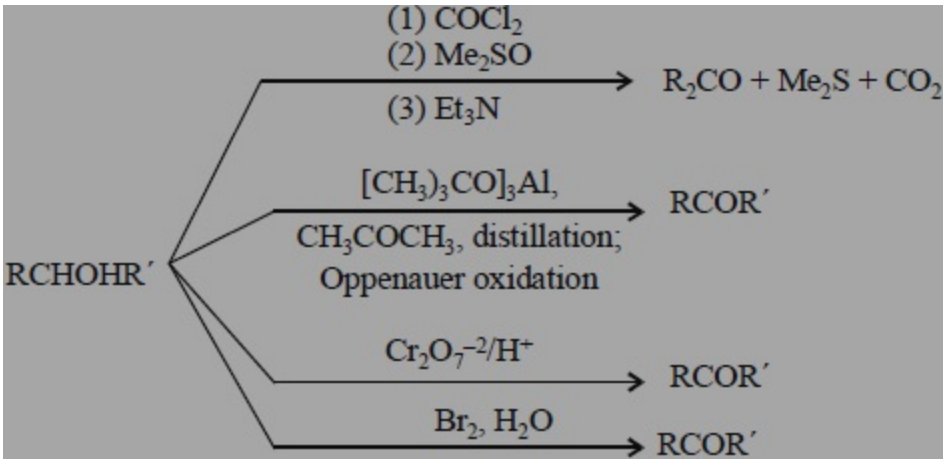
General formula is $C_nH_{2n}O$, which includes –CHO(aldehyde) >C = O (ketone) functinal groups. Other than these we will discuss other possibilities of functional groups present with –CHO, >CO groups.

Preparation:

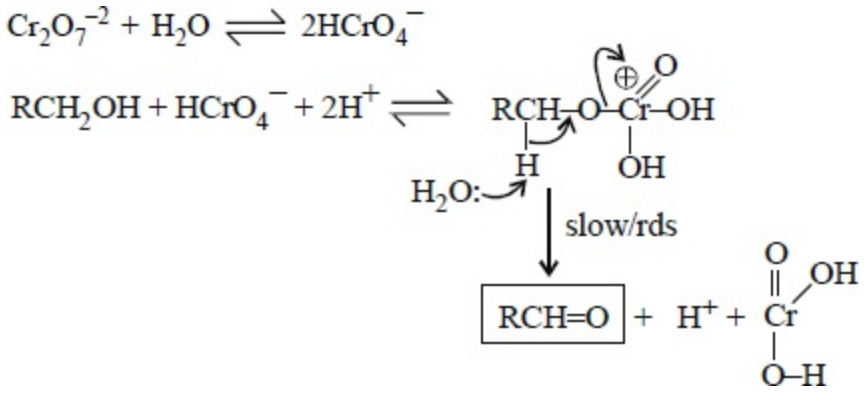
1. From 1° alcohol (1° alcohol always gives aldehyde on oxidation):



(2) From 2° alcohol (2° alcohol on oxidation gives ketone):



Mechanism:

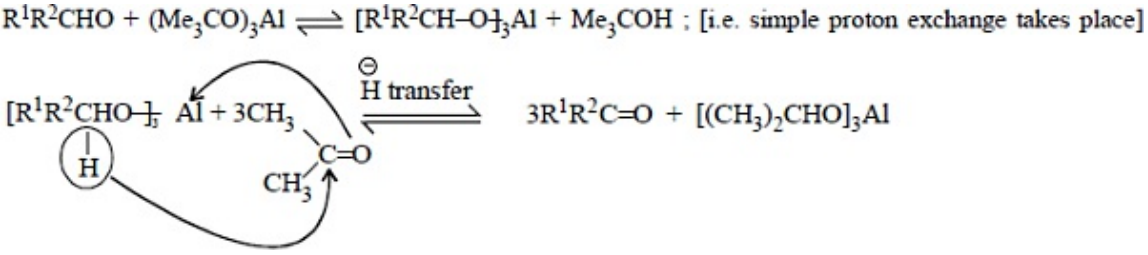


As we find in the rds deprotonation is taking place so primary kinetic isotope effect is observed. Therefore CH_3CD_2OH will oxidse solwer than CH_3CH_2OH. Secondary kinetic isotope effect is not observed. i.e. CD_3CH_2OH, CH_3CH_2OH will have same rate of oxidation.

Oppenauer oxidation:

It is mainly used for 2° alcohol → ketone conversion. Using p-benzo-quinone (the better $H^{\ominus}$ acceptor) we carryout the conversion from 1° alcohol → aldehyde.

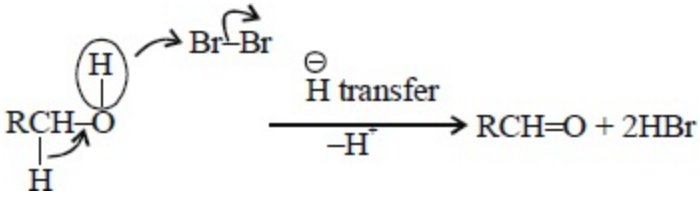
Mechanism:



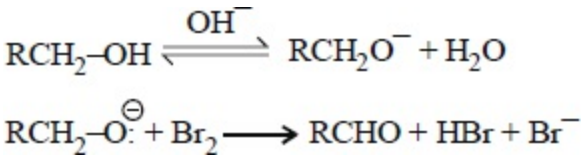
The condition is refluxing the mixture of alcohol and Al-salt and then addtion of acetone/p-benzo-quinone to complete the reaction.

Br_2 Oxidation:

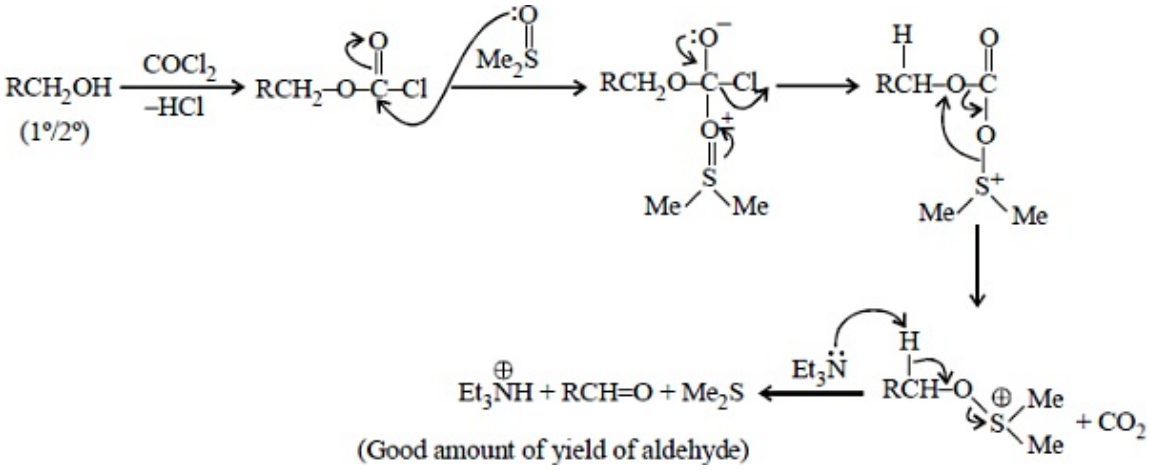
Mechanism: In water (H_2O) the mechanism takes place as follows;



Mechanism: In alkaline medium the mechanism is;

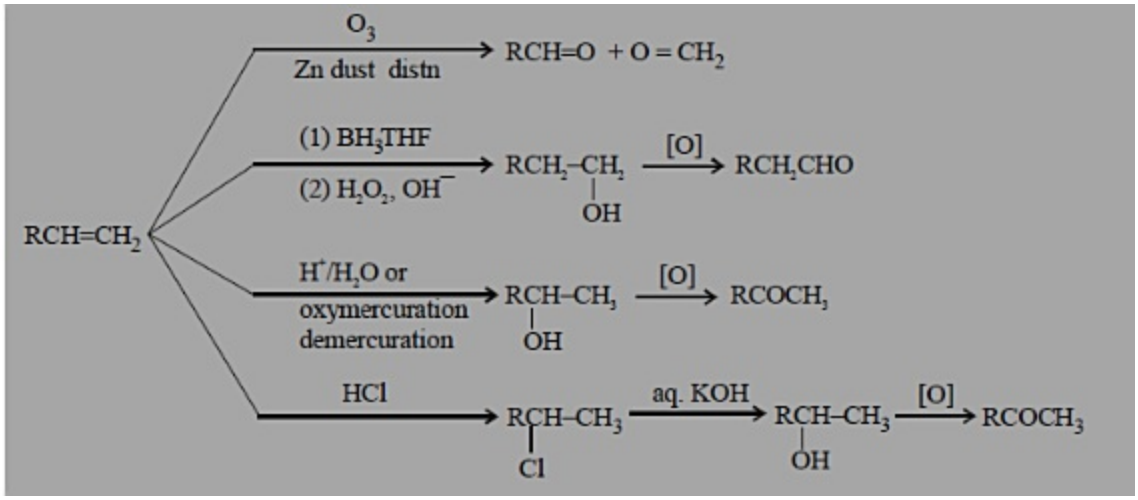


Mechanism with COCl2 ;



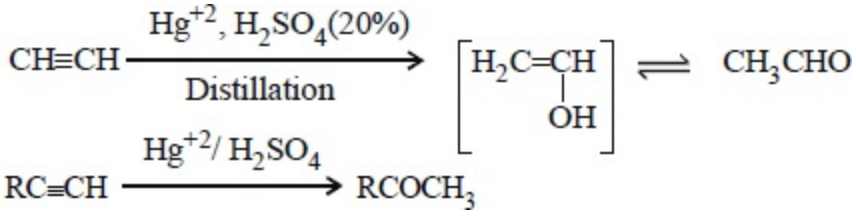
3. From alkene, alkyne and arene:

(A)



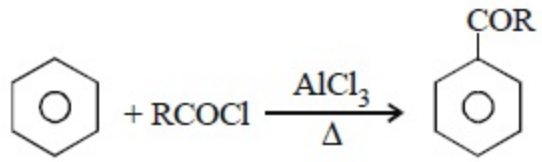
The mechanisms of the above reactions have already been discussed in the previous chapters.

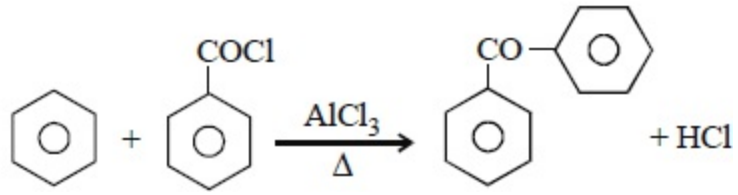
(B)



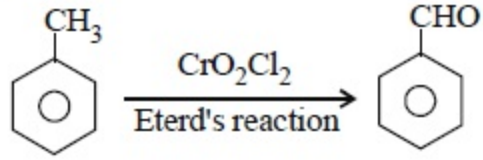
It should be rememberd that substituted alkyne always gives ketone.

$$CH_2{=}CH{-}C{\equiv}CH \xrightarrow[H^+]{Hg^{+2}} CH_2{=}CH{-}COCH_3$$

(C) 



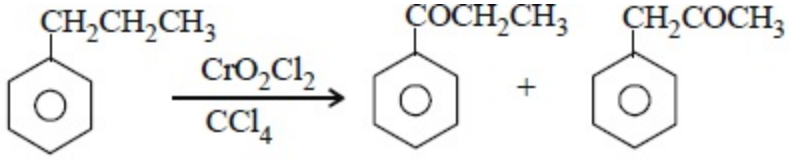
From alkyl benzene:

(1) 

Mechanism:

$$Ph{-}CH_3 \xrightarrow[CCl_4]{2CrO_2Cl_2} PhCH[OCrCl_2(OH)]_2 \xrightarrow{H_2O} PhCH{=}O$$

(ppt. forms)



If more than one CH_3 groups are present then only one is oxidised.

(2) $Ph{-}CH_3 \xrightarrow[(CH_3CO)_2O,H^+]{CrO_3} Ph{-}CH{=}O$

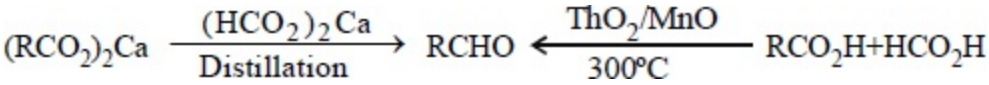
From alkyl or aryl halide:

(1) CH_3CH_2I ($1^\circ, 2^\circ$ or Aryl) $\xrightarrow{Me_2SO}$ CH_3CHO (Ar)

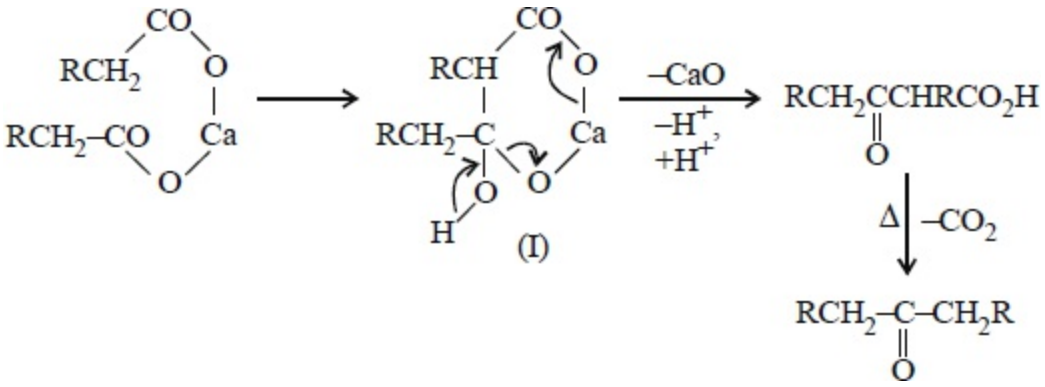
Experimentally iodo alkane has been found to give aldehyde.

(2) $PhCH_2Cl \xrightarrow[(2)H^+]{(1)(CH_2)_6N_4} PhCH{=}O + NH_3 + C_6H_5{-}CH_2NHCH_3$

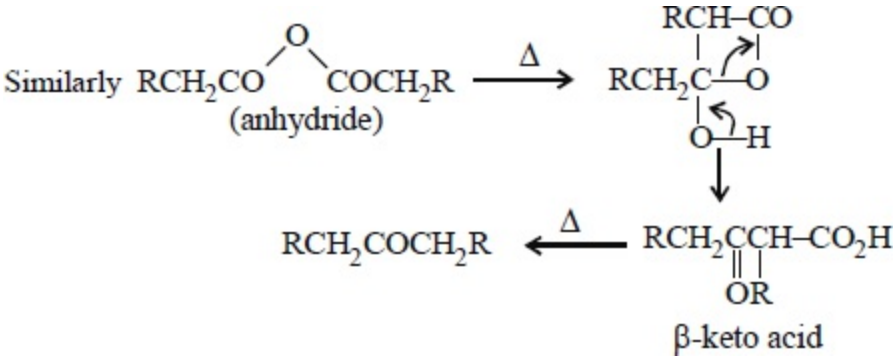
From carboxylic acid by reduction:



Mechanism:



Clearly there is an intramolecular aldol formation in (I)

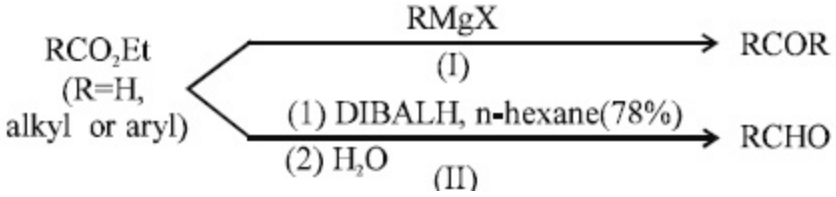


With mixture of Ca-salts mixed ketones are obtained which is given as follows;

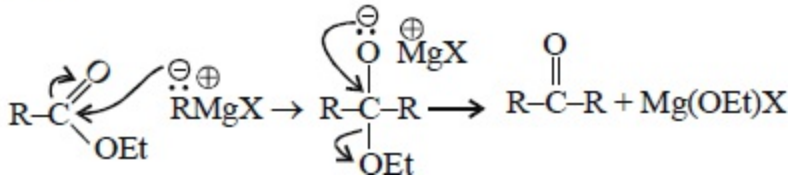
$(R^1CO_2)_2Ca+(R^2CO_2)_2Ca \xrightarrow{\Delta} R^1COR^2$ (only ketone not aldehyde form)

$(RCO_2)_2Ca \longrightarrow$ RCOOR (only ketone)

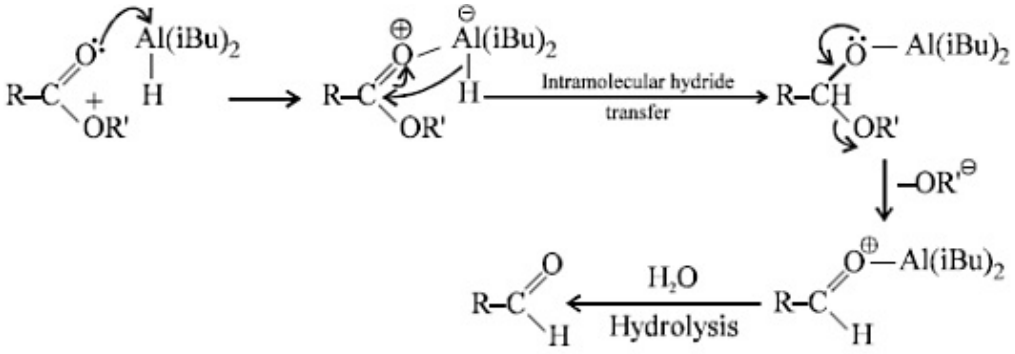
From ester, acid halide, nitrile etc.

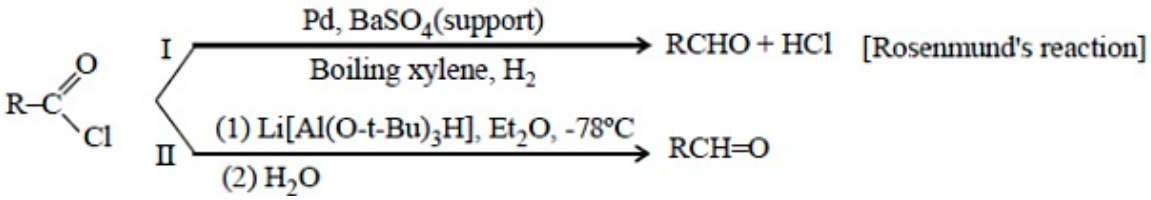


I. Mechanism:



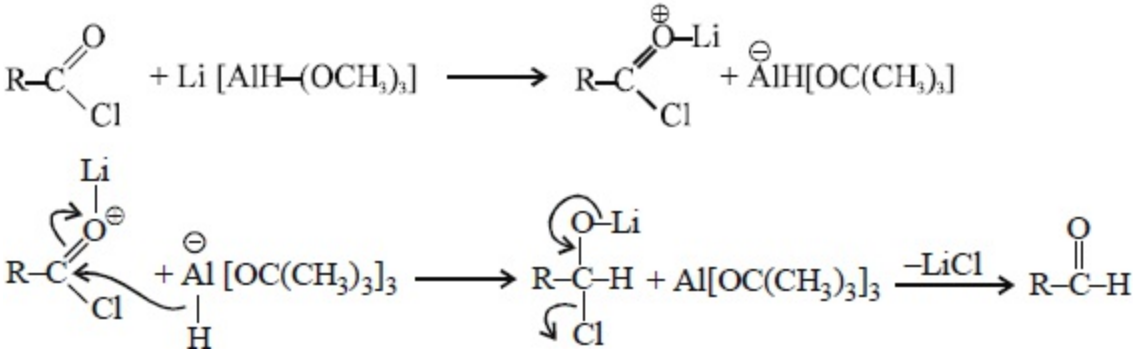
II. Mechanism:



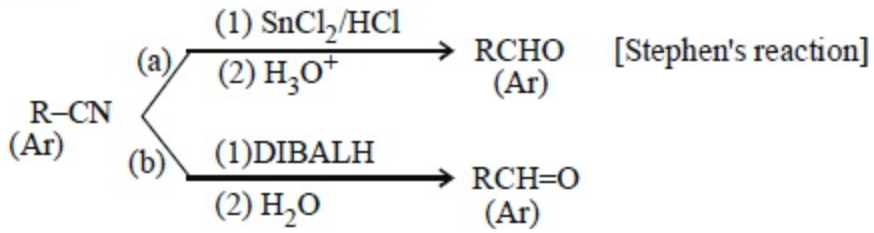


Mechanism of Rosenmund's reaction is uncertain and it is beyond the scope of this book.

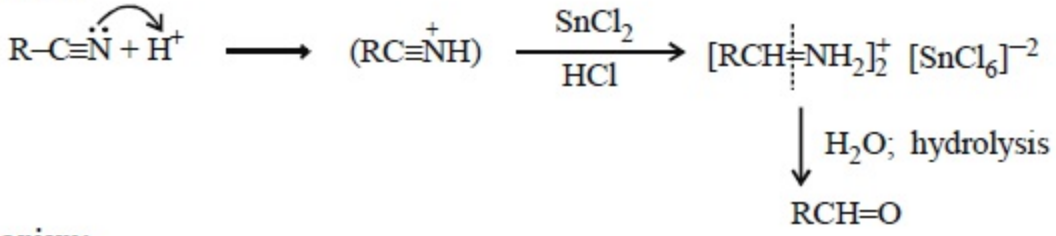
III. Mechanism with (TTBALH):



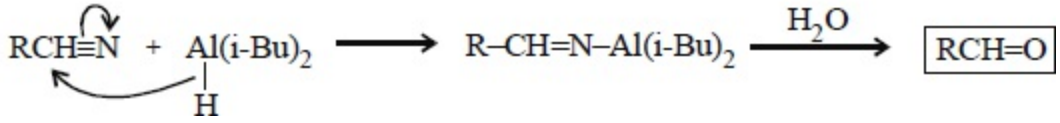
From nitrile:



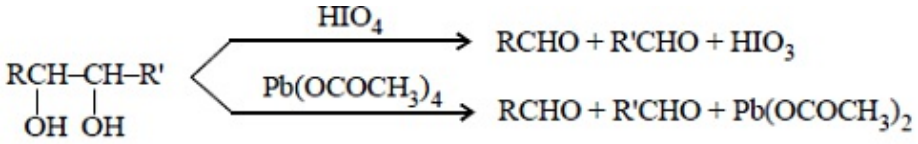
a. Mechanism:



b. Mechanism:



From diol compounds



Also RCH= CHR $\xrightarrow[\text{reagent}]{\text{Lemieux}}$ RCHO + R'CHO

Lemieux reagent is $OsO_4 + NaIO_4$ or $KMnO_4 + NaIO_4$, where $NaIO_4$ converts to $NaIO_3$.

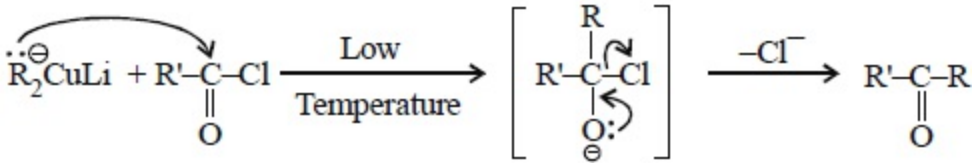
From lithium dialkyl cuprate and dialkyl cadmium:

$R_2CuLi + R'COCl \longrightarrow R'COR + RCu + LiCl$

$R_2Cd + R'COCl \longrightarrow R'COR + RCdCl$

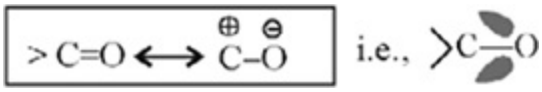
Mechanism:

It involves S_NTh bimolecular mechanism as shown below;



Structure, physical properties :

> C=O bond is highly polarised bond because of electronegativity difference between C, O and due to resonating structures as shown below;

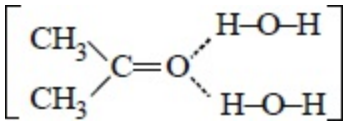


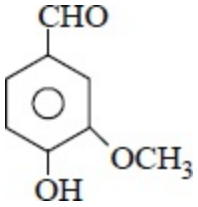
i.e., in which π MO is shifted much towards the oxygen atom.

Therefore C is electrophilic end and O is nucleophilic end. Also, Strong

pulling of >CO (-I) , α –H becomes acidic. H of  does not show acidic behaviour instead it show reducing behaviour (e.g, Cannizaro's reaction).

μ_{CH_3CHO} = 2.8D, $\mu_{CH_3COCH_3}$ = 2.9D as mentioned earlier due to hyperconjugation and +I effect. Therefore carbonyl compounds are having high m.p., b.p. due to dipole-dipole attraction (compared to ethers, alkanes). Solubility in water has been observed for lower members due to making of H-bond with water molecules.

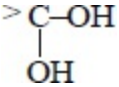
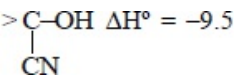


Some aromatic aldehydes are having fragrance. For example PhCHO(bitter almonds),  (vanilin), PhCH=CHCHO (trans) (cinnamaldehyde) etc.

Reactivity: Mainly it depends on the following factors :

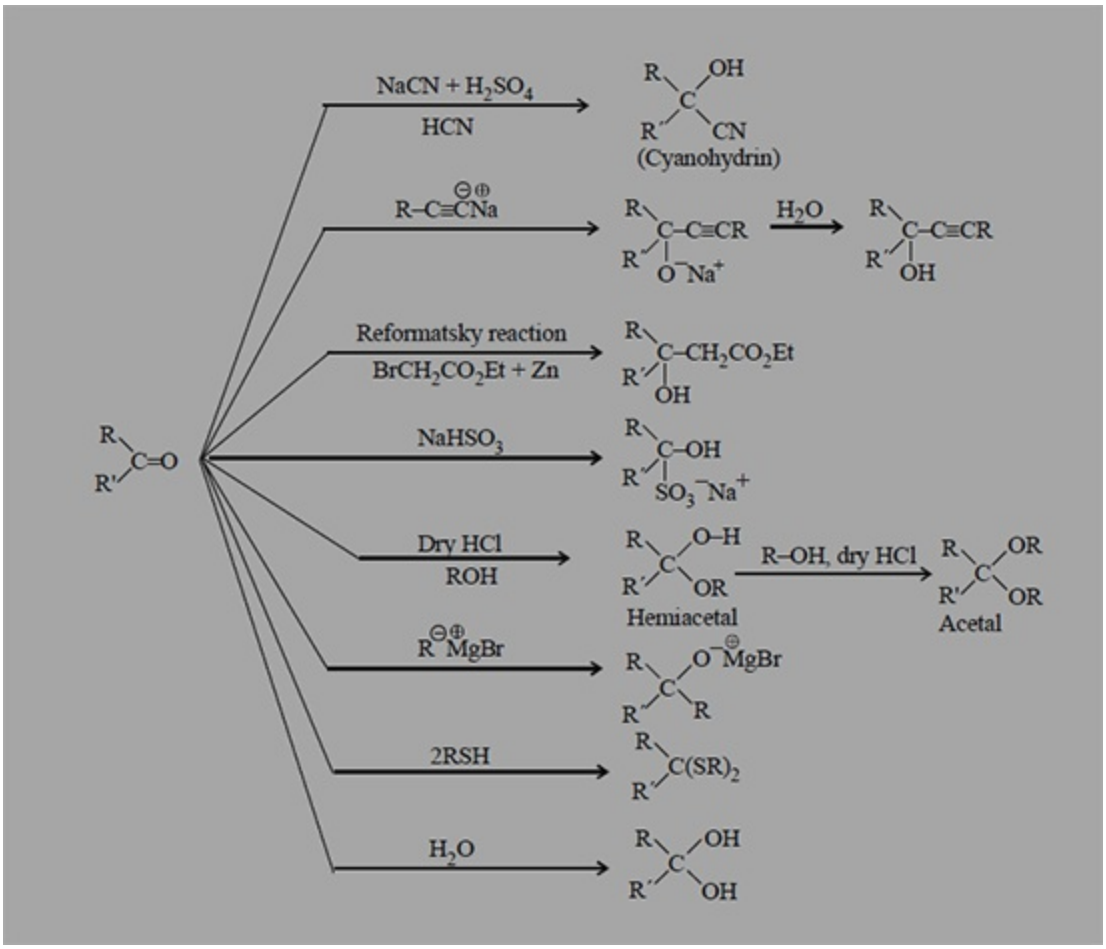
(1) δ + charge on C of (>C = O)

(2) steric crowding after the product form.

(3) energetically > C = O is very stable bond e.g., Addition of H_2O to form  register Δ H°= +6 kcal but in case of HCN addition  kcal by calculation of energy data.

Chemical reaction:

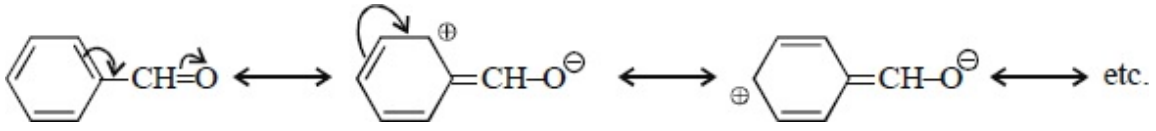
(1) Nucleophilic addition reactions ;



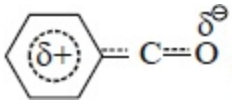
For the nucleophilic addition reaction to occur we must understand that more the δ + charge of C more will be reactivity. The reactivity order can be written as follows:

$\therefore$ $(CH_3)_3C-CHO$ << CH_3-CHO < $H-CHO$

Also, we must understand benzene ring bonded to > C=O group reduces δ + charge on carbonyl carbon because of resonance e.g.

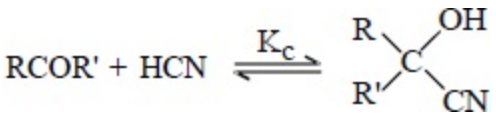


So, phenyl –C and carbonyl –C has n bond in most of the resonating structures alongwith C=O

$\therefore$ Resonance hybrid is  , where C of $-\overset{|}{C}=O$ loose $\delta^{\oplus}$ charge to a large extent.

∴ Reactivity of carbonyl carbon towards a $\ddot{\ominus}_{Nu}$ drop with lesser $\delta^{\oplus}$ on carbonyl carbon and as if it is π -electron clouded carbon. Look at the following results:

Reaction:



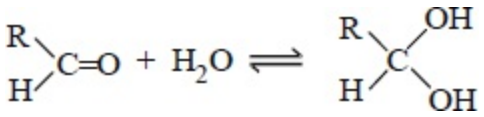
By the experimentally determined equilibrium constant values the following carbonyl compounds can be arranged in the decreasing order as follows ;

CH_3CHO (very large) > C_6H_5CHO > $C_6H_5COCH_3$ > $C_6H_5COC_6H_5$ (very small).

Another important factor is that the steric corwding appear in the product as reactant carbonyl compound changes from its planar triangular to tetrahedral form. Therefore if the size of R, R' is/are very large then the product becomes less stable and equilibrium lies far over to the left.

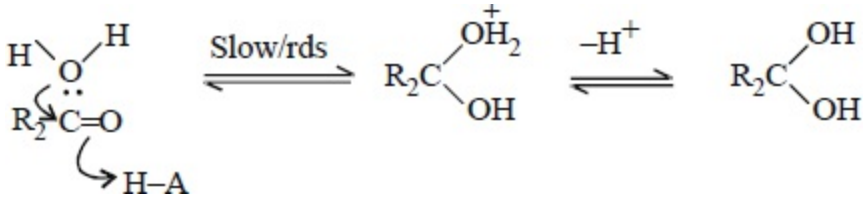
Addition of water (H_2O):

Reaction :



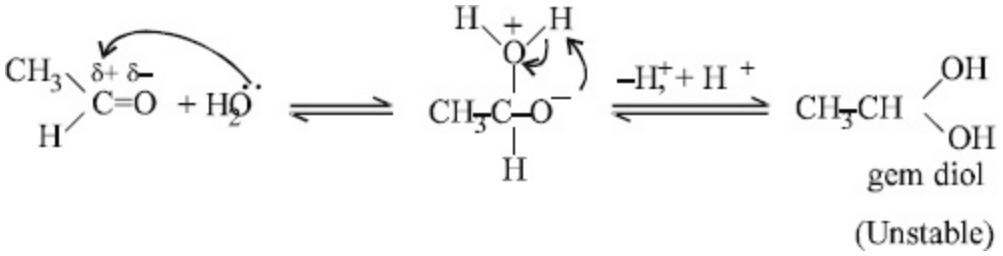
If R = H, then easy hydration takes place (K= 2 x 10^{-3}), for R = Me, K = 1.4 and for CH_3COCH_3, this is very less (2 x 10^{-3}). Reason has been mentioned in the above (i.e. gradual loss of δ + charge and increasing steric crowding in the product). Hydration of HCHO takes place at pH = 7 but for Me_2CO acid catalysis is required to increase $\delta^{\oplus}$ character of carbonyl carbon. However acid, base both simultaneously can catalyse $Me_2CO \rightarrow Me_2C(OH)_2$ conversion.

Mechanism:



Generally for aldehydes (aliphatic) not for ketones the following mchanism

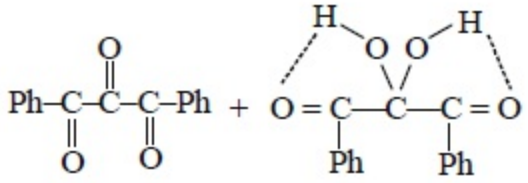
can be observed.



The following experimental results support the above mechanism:

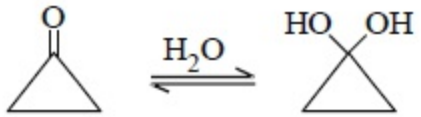
(1) $Me_2CO + H_2O^{18} \rightleftharpoons Me_2CO^{18} + H_2O$ [i.e. 'O' exchange occurs)

(2)



(Stable)

(3)



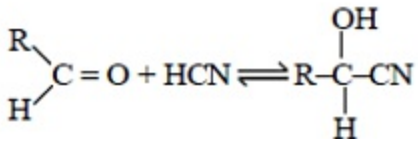
(unstable) (Relatively stable)

HCN addition :

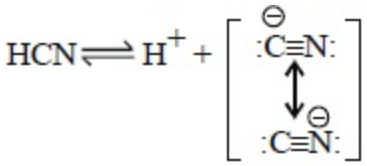
In Close to pH = 7 the addtion of HCN take place to the carbonyl compound. Reagent is $NaCN + H_2SO_4$ (dil.) At this conditon,

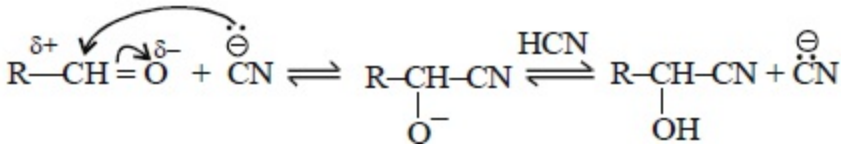
$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$ (Where $pK_a = 9.8$), which is close to pH = 7.

Reaction:



Mechanism:

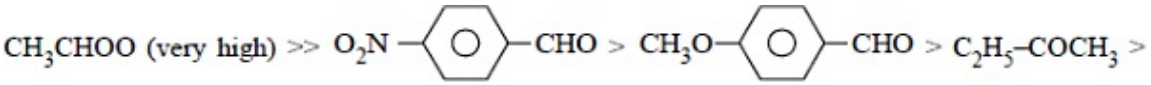


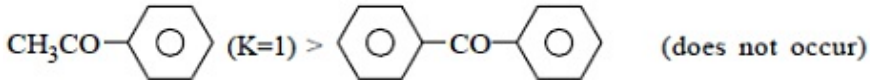


In basic condition, $HCN + OH^- \rightleftharpoons H_2O + \ddot{C}\overset{\ominus}{N}:$

It is observed that more the $[:\overset{\ominus}{C}N]$ faster is the reaction and experimental order in basic medium is rate = k[RCHO] [CN^-]. In acidic conditon the rate is retarded due to Le Chatellier's principle applied to weak acid HCN in presence of strong acid. The groups (–I, –R) attached to benzene ring enhance the rate of HCN addtion.

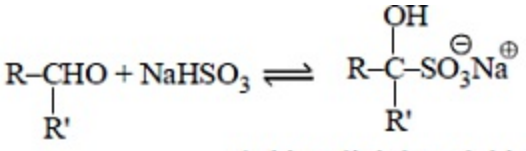
From equilibrium constant data the following aliphatic and aromatic carbonyl compounds can be arranged in the decreasing order, which is given as follows ;





$NaHSO_3$ addition:

Reaction:

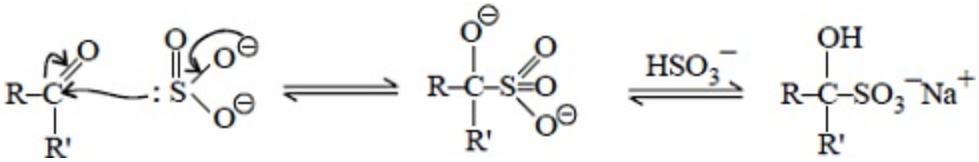


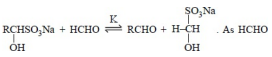
(white slightly soluble ppt.)

Mechanism:

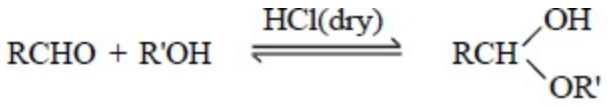
$NaHSO_3 \rightarrow Na^+ + HSO_3^-$

$H_2O + HSO_3^- \rightleftharpoons H_3O^+ + SO_3^{-2}$

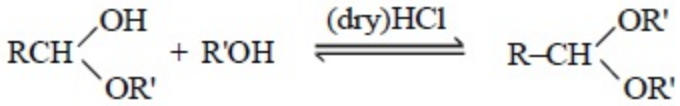


Here also the initial logic applies i.e. with increasing bulk and reducing $\delta\oplus$ character on carbonyl –C, rate of formation of cyanohydrin reduces. Many of the ketones or aldehydes are regenerated by using HCHO, as  . As HCHO forms adduct very fast and K lies far over to the right.

Addition of alcohol:

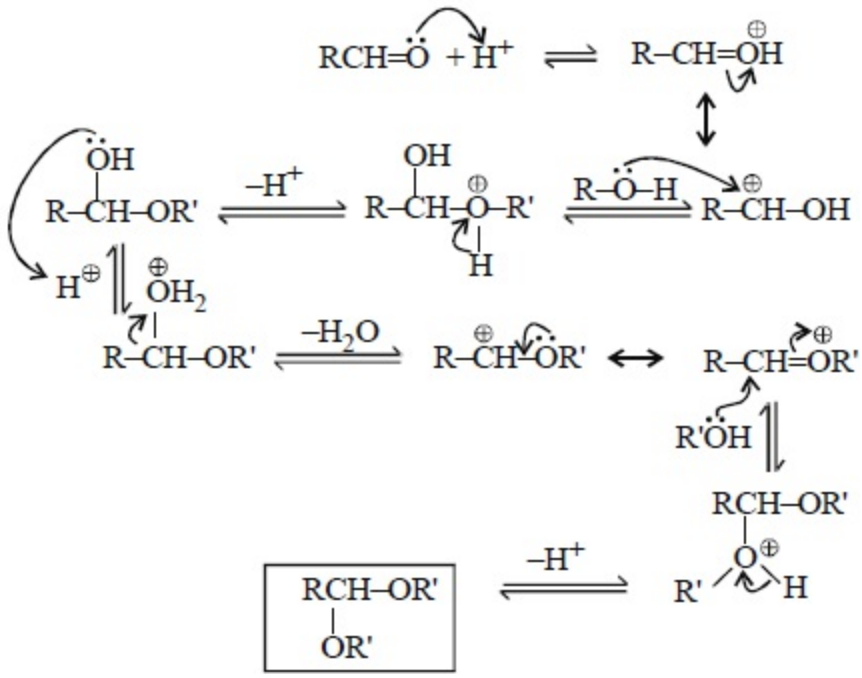
Reaction: 

Hemiacetal

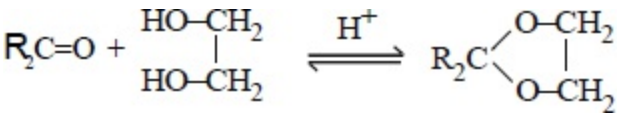


Acetal

Mechanism:



Forward process is formation and reverse is hydrolysis. During hydrolysis R'–O does not break. With ketone acetal formation is not at all favoured. However when ketone is treated with 1, 2-diol in presence of trace acid, cyclic acetal or ketal forms easily as shown below:



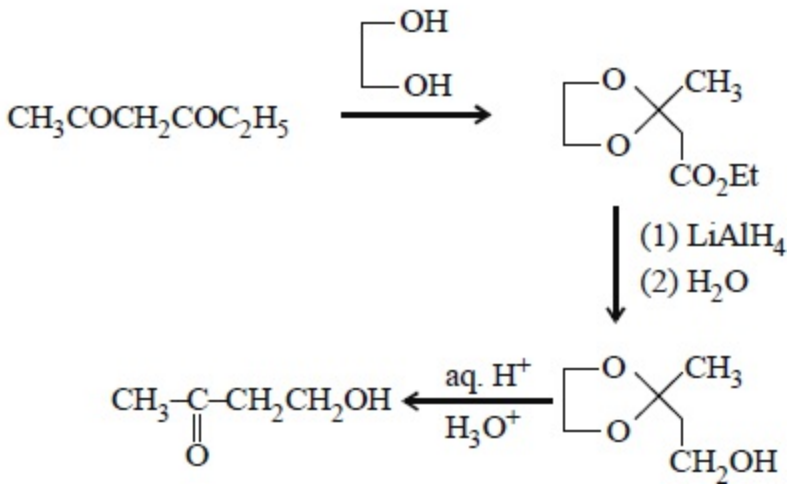
The mechanism is same. As in basic medium acetals are stable, therefore it acts as a **blocking reagent** to carbonyl group.

Let us consider the following reaction

Conversion:

$$CH_3COCH_2CO_2C_2H_5 \longrightarrow CH_3COCH_2CH_2OH$$

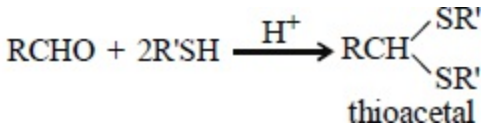
Solution:



Addition of thiol RSH :

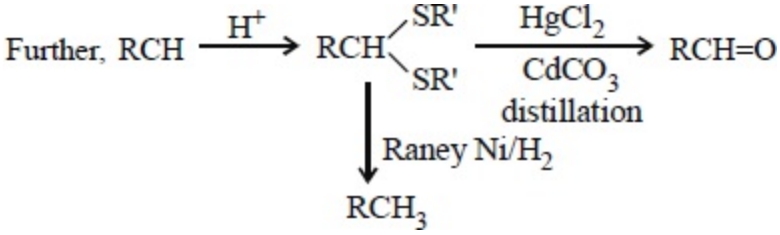
Thioacetal formation is carried out with RSH.

Reaction:

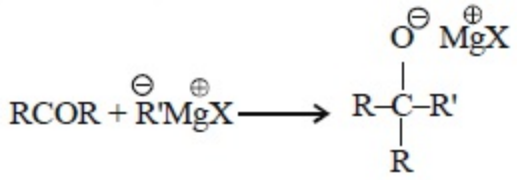


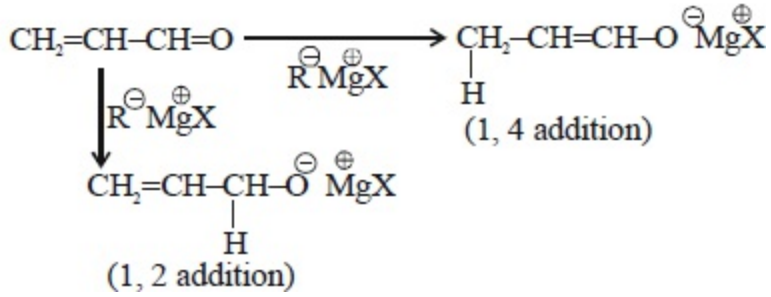
thioacetal

Stability of thioacetal is very high in acid as well as basic medium. Therefore R'SH is used for protection of >C=O in any medium, that is acidic as well as basic meidium.

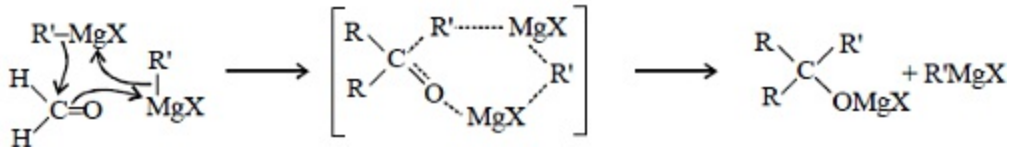


Addition of Grignard's reagent:

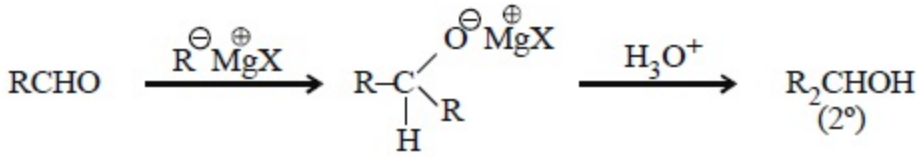
(1) 

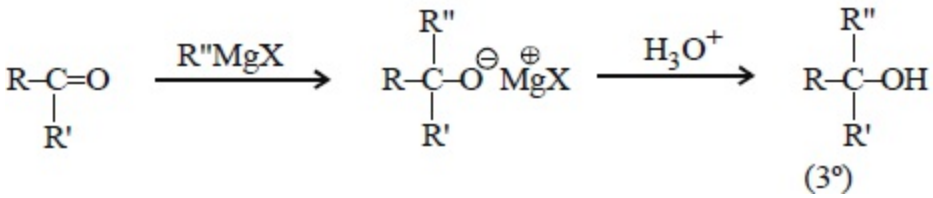
(2) 

Mechanism:

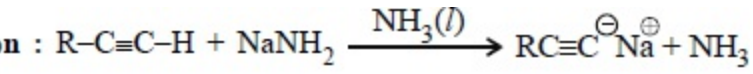


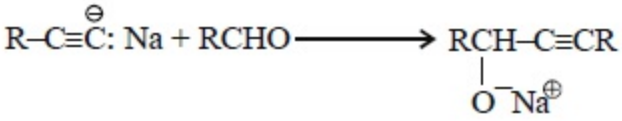
So, during addtion reaction two molecules of Grignard reagent are required. Finally after hydrolysis we can get alcohol.





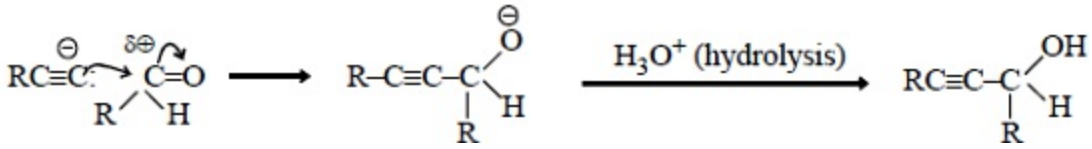
Addition of acetylides:

Reaction : 



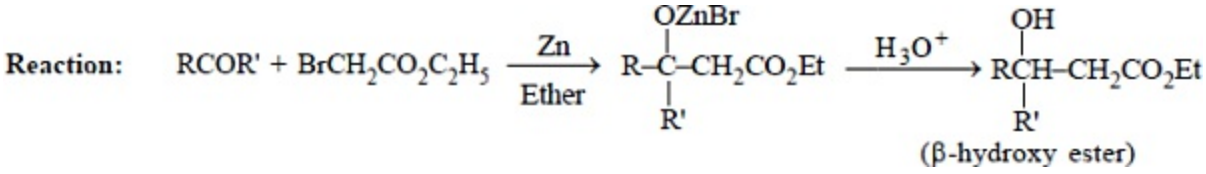
(Sodium ynolate)

Mechanism:

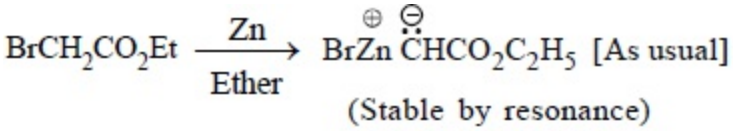


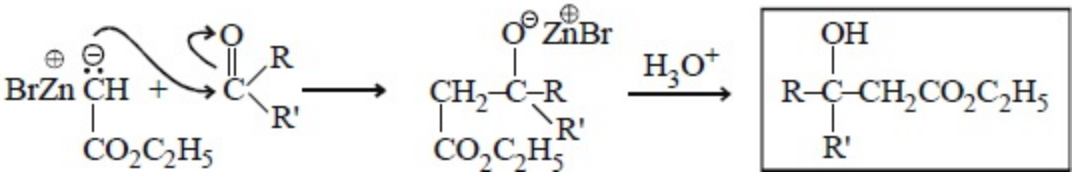
Reformatsky reaction:

It is same as Grignard's reagent addtion. Initially an organometalic i.e. organozinc compound forms and then nucleophilic addtion occurs at C δ^+ of >C=O as shown below;



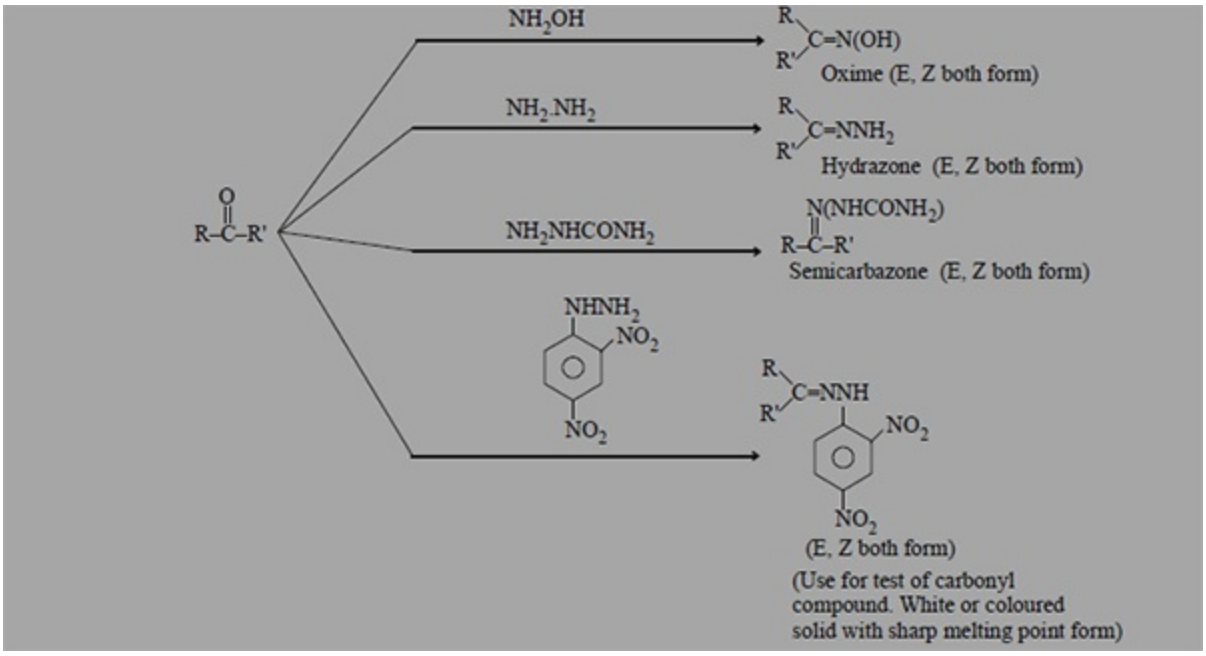
Mechanism:





Organo zinc compounds are less reactive than organo magnesium.

Addition elimination reactions:



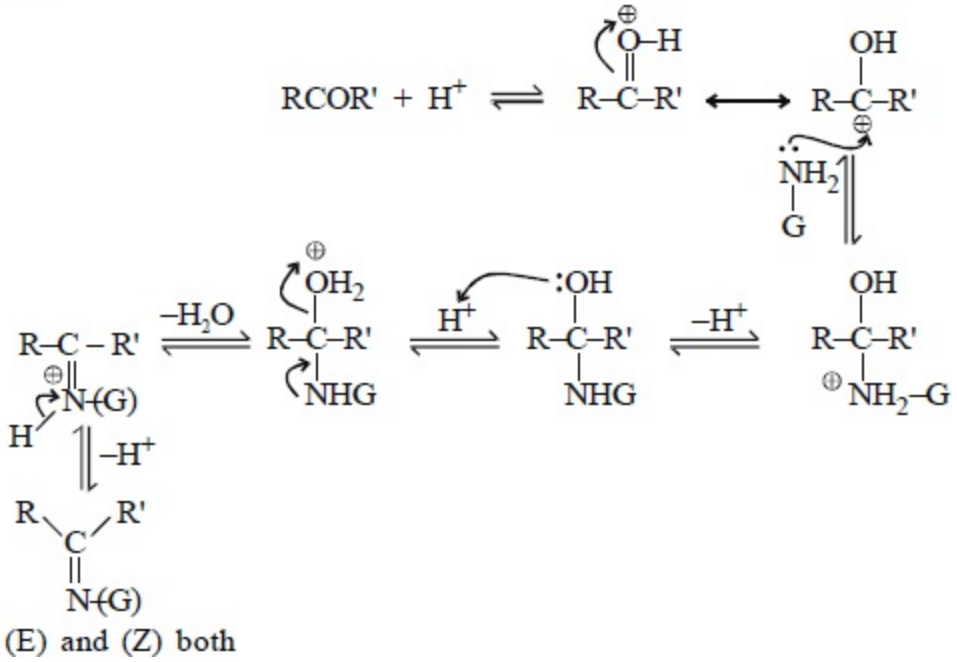
Addition elimination:

Reaction: $R-\underset{\underset{R'}{|}}{C}=O + NH_2-G \rightleftharpoons R-\overset{OH}{\overset{|}{\underset{\underset{R'}{|}}{C}}}-NHG \xrightleftharpoons{-H_2O} R-\underset{\underset{R'}{|}}{C}=NG$ (E/Z)

Here G = NH_2/OH/$NHCONH_2$/NHPh etc.

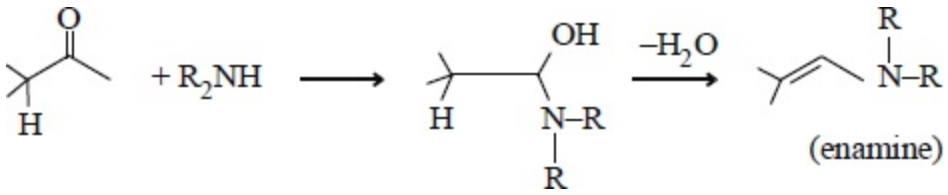
Neither at high pH (because of aldol condensation or other) nor at low pH(probable formation of $\overset{\oplus}{N}H_3-Z$ (salt) the reaction is carried out at optimum or slightly acidic pH i.e. 4-5 to enhance rate of elimination of water.

Mechanism:

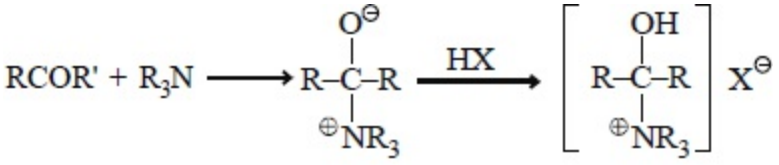


$RCH{=}NNH_2$ (hydrazone), $RCH{=}NNHCONH_2$ (semicarbazone), RCH=NOH (oxime), RCH=NNHOH (phenyl hydrazone) are obtained as products.

With 2° amine enamine results.With cyclic secondary amine stable enamine results.



With 3°amine salt forms.



Some more reactions:

(1) $RCH{=}O + NH_2{-}NH_2 \longrightarrow RCH{=}NNH_2$

(2) $PhCHO + NH_2NH_2 \longrightarrow PhCH{=}N{-}N{=}CHPh$

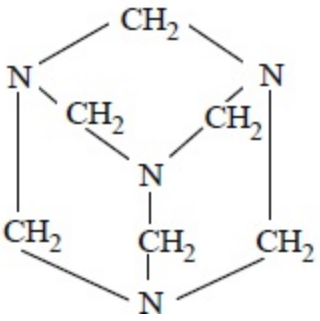
(3) $3PhCOCH_3 \xrightarrow{NH_3\ excess} Ph{-}\underset{Me}{C}{=}N{-}\underset{Me}{\overset{Ph}{C}}{-}N{=}\underset{Me}{C}{-}Ph + NH_3$

(4) $Ph{-}CH{=}O \xrightarrow{NH_3\ excess} \underset{OH}{PhCH{-}NH_2} \xrightarrow{-H_2O} PhCH{=}NH$

$3PhCH{=}NH \longrightarrow Ph{-}CH{=}N{-}\overset{Ph}{\underset{H}{C}}{-}N{=}CH{-}Ph + NH_3$

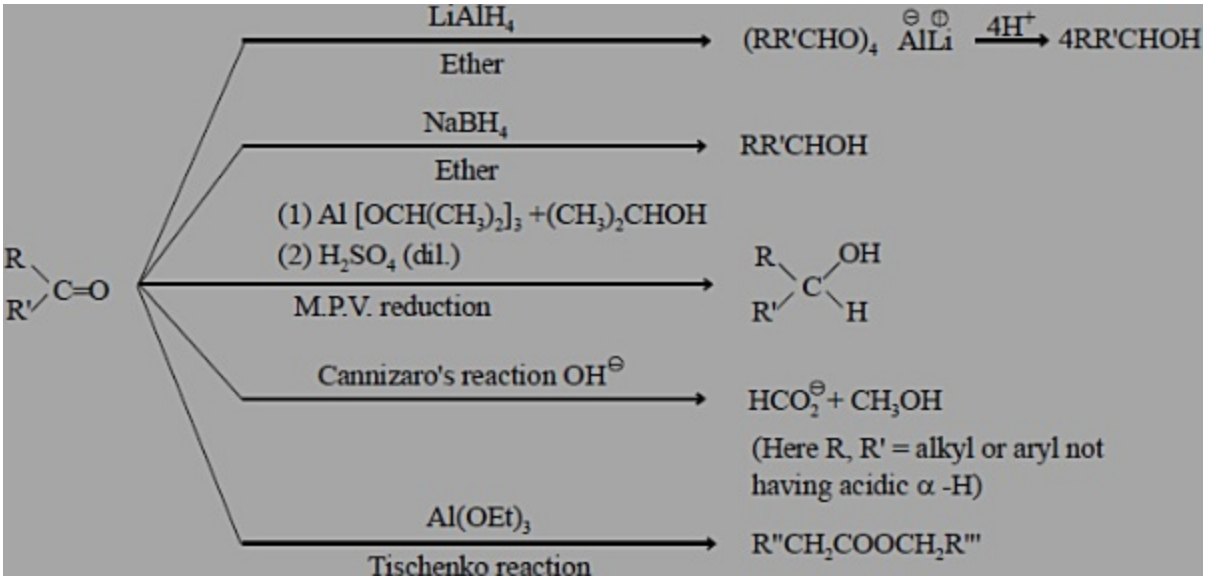
(5) $6HCHO + 4NH_3 \longrightarrow (CH_2)_6N_4$

Hexamethylene tetramine or Urotropin



is the structure of urotropin (trade name)

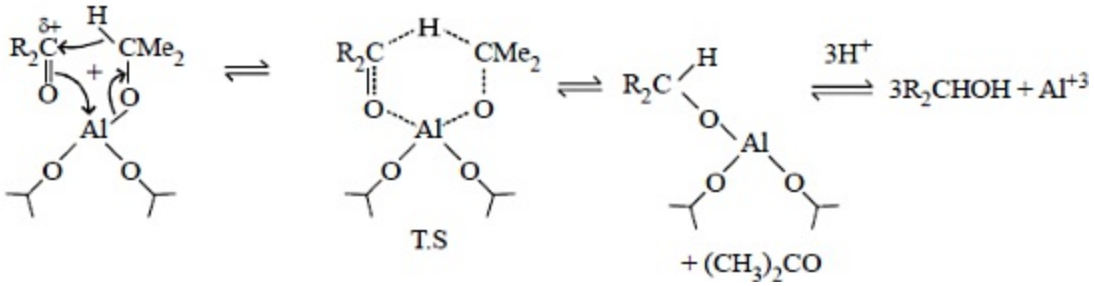
Hydride transfer reactions:



MPV reduction (Meerwein Pondorf Verley):

Reaction: $RCOR' + [Me_2CHO]_3Al \xrightleftharpoons[\text{dil. } H_2SO_4]{(CH_3)_2CHOH,\ \text{Distn.}} RR'CHOH + Me_2CO + Al^{+3}$

Mechanism:



It is clearly hydride transfer (intermolecular) reaction. This is highly specific for –CHO, > CO group and in presence of unsaturation, $–NO_2$, –OR etc. MPV reduction can be carried out. The ratio of $Al(OiPr)_3$: RCOR':

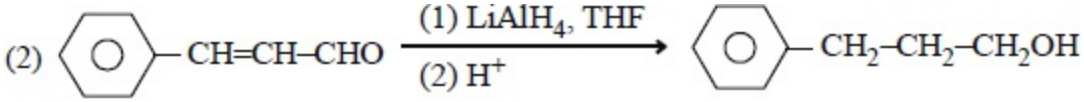
RR'CHOH(product) is 1 : 3 : 3.

Limitation: Carbonyl compounds like $CH_3COCH_2COCH_3$, $CH_3COCH_2CO_2C_2H_5$, which has high % enol content can not be reduced.

Reduction by $LiAlH_4$:

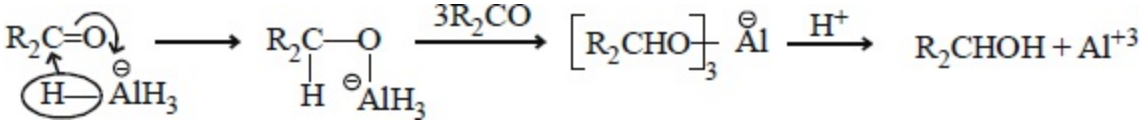
Reaction:

(1) $R–\underset{\underset{R'}{|}}{C}=O \xrightarrow{LiAlH_4} \underset{\underset{R'}{|}}{RCHOH}$

(2) 

(3) $CH_3CH=CH–CHO \xrightarrow[(2)\ H^+]{(1)\ LiAlH_4,\ THF} CH_3CH=CH–CH_2OH$

Mechanism:



Normally $LiAlH_4$ doesnot reduce =, ≡ but in conjugation with phenyl ring, = bond gets reduced. Similar mechanism has been observed for $NaBH_4$ (weak

reducing reagent) reduction. It does not reduce –CN , $–NO_2$, –COOH , –C ≡ C , >C=C< , unlike $LiAlH_4$.

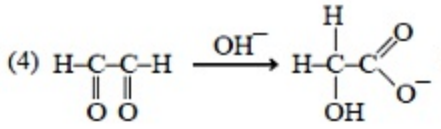
Cannizaro's reaction:

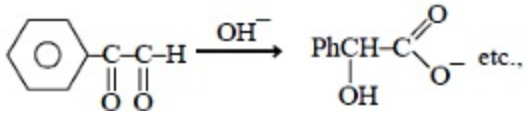
Carbonyl compounds **not having** α **–H** undergo disproportionation reaction (i.e. self redox) by intermolecular / intramolecular $H^{\ominus}$ transfer

Reaction: (1) $HCHO + HCHO \xrightarrow{OH^-} HCOO^- + CH_3OH$

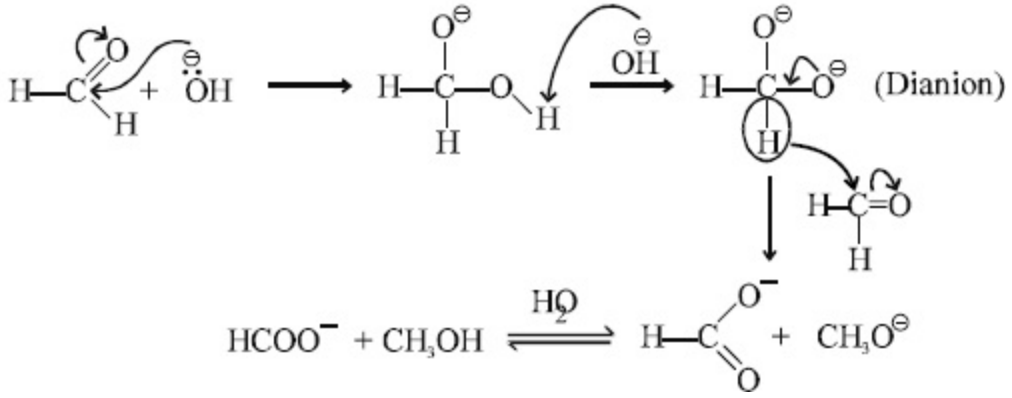
(2) $2PhCHO \xrightarrow{OH^-} PhCOO^- + PhCH_2OH$

Exception ⇒ (3) $2Me_2CHCHO \xrightarrow{OH^-} Me_2CHCH_2OH + Me_2CHCOO^-$

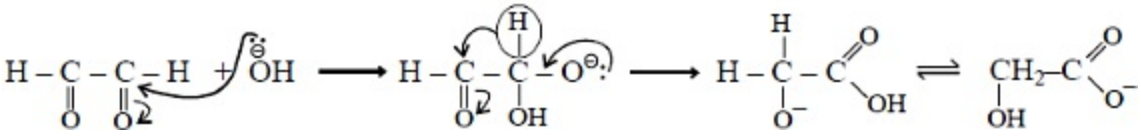
(4)  ; This is an example of intramolecular Cannizaro's reaction

(5)  etc.,

Mechanism: With HCHO;



Mechanism:



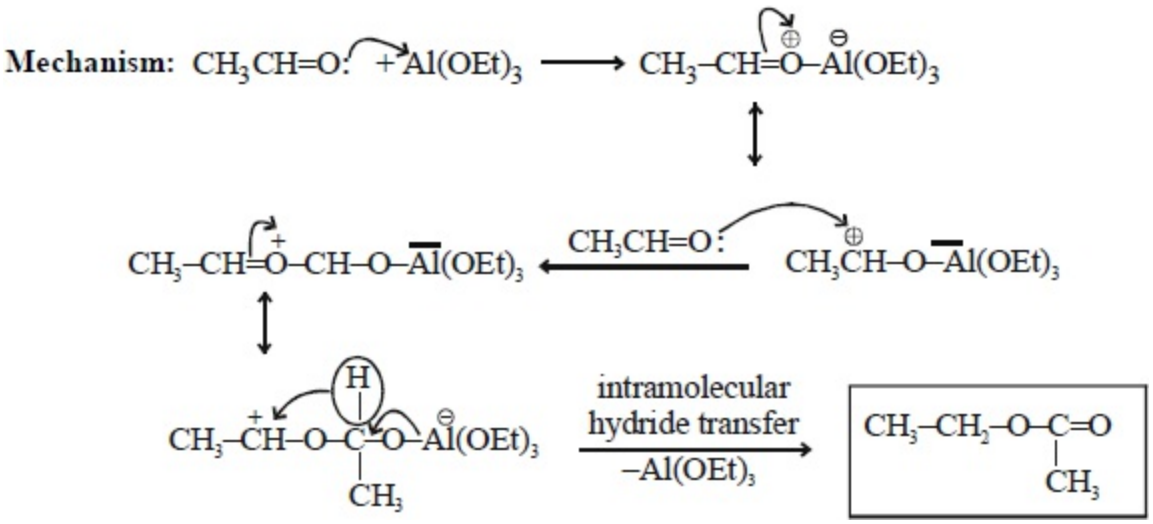
The mechanism is supported by the rate equation which is, rate = $k[HCHO]^2[OH^-]^2$; which is a fourth order kinetics. But for benzaldehyde, rate = $k[PhCHO]^2[OH^-]$; which is a third order rate equation.

Tischenko reaction:

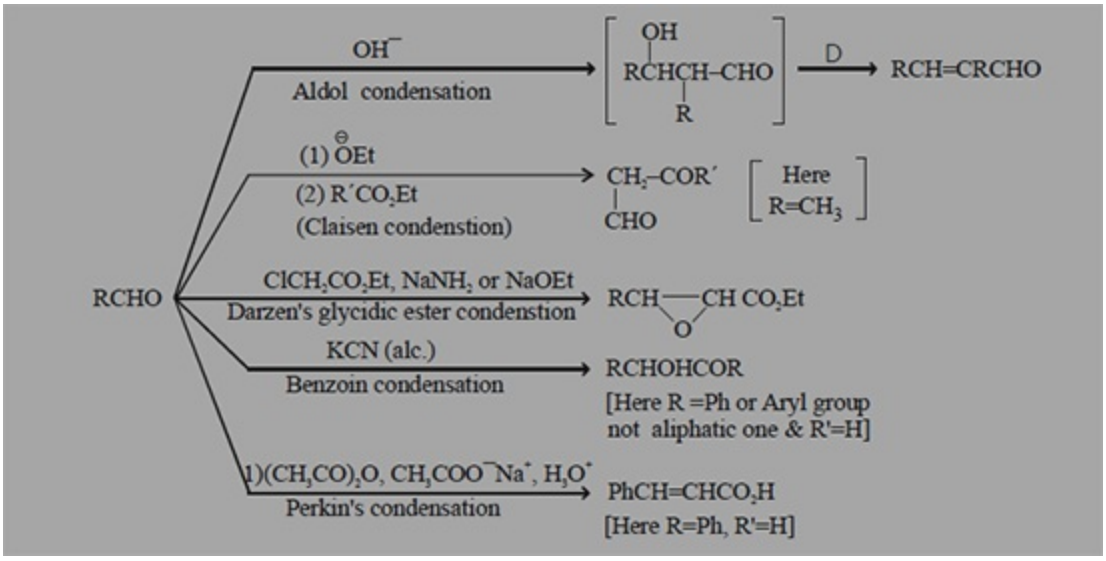
$$CH_3CHO \xrightarrow{Al(OEt)_3} CH_3COOCH_2CH_3$$

i.e. Aldehydes having α-H show forced Cannizaro's reaction and product is ester.

Mechanism:



Condenstion reactions :



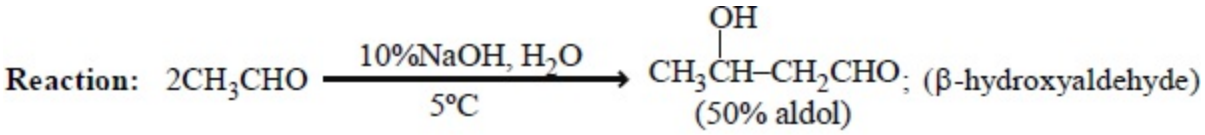
Aldol addition (or aldol formation reaction) and condensation reaction:

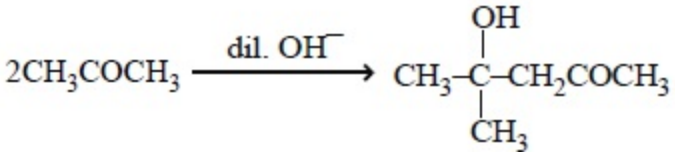
Carbonyl compounds having α –H undergoes addition to each other in presence of dil. base (10% NaOH) or dil. acid is called as aldol reaction and the product is aldol (alcohol + aldehyde).

Substrate: Carbonyl compound having α –H excepting $(CH_3)_2$ CHCHO.

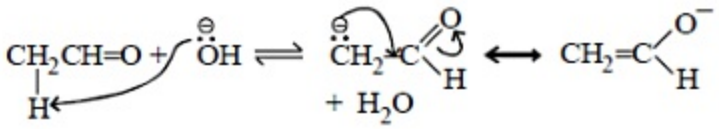
Reagent acts as catalyst: NaOH, KOH, $Ba(OH_2)$, K_2CO_3 HCl any one of these.

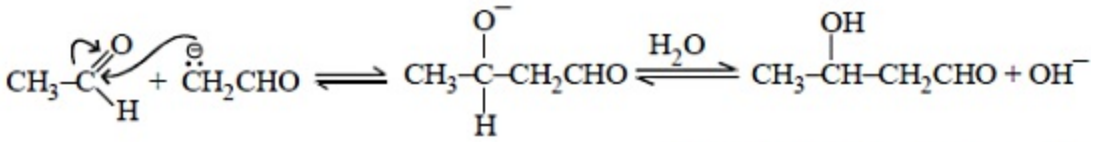
With acid catalyst the final product is always α , β unsaturated carbonyl compound by dehydration.In presence of base and heat the final product is also α , β unsaturated carbonyl compound.





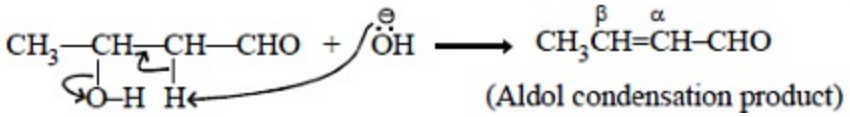
Mechanism:





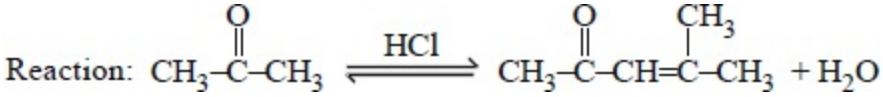
(β-hydroxy carbonyl compund)

Aldol

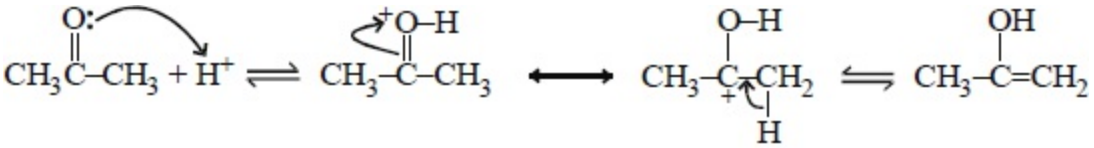


(Aldol condensation product)

Problem with ketone where equilibrium does not favour the formnation of aldol is carried out in Soxhlet apparatus and repeatative distillation is carried out.

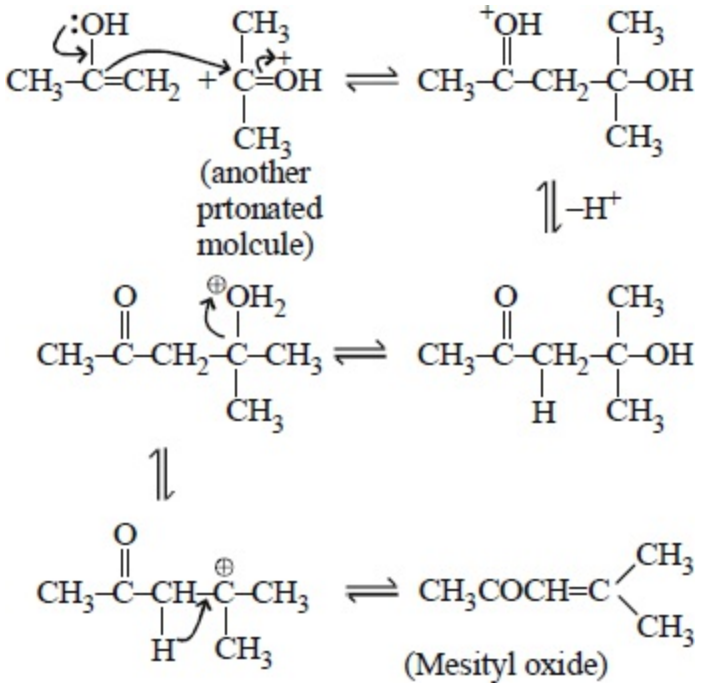


Mechanism of acid catalyzed aldol condensation:

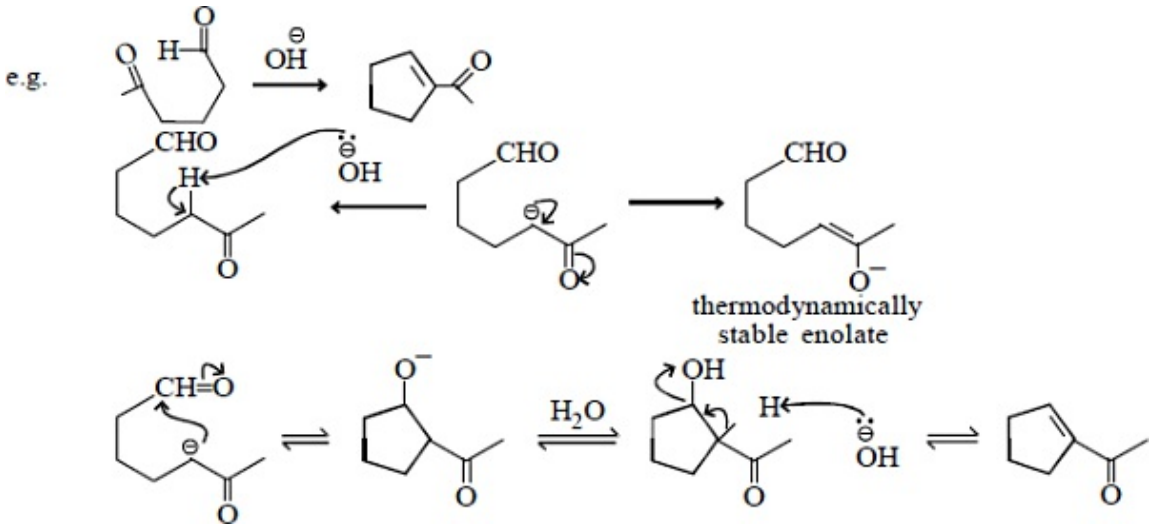


enol

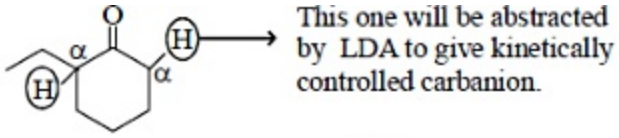
Therefore it should be remembered that enol must form for the aldol condensation reaction to proceed .

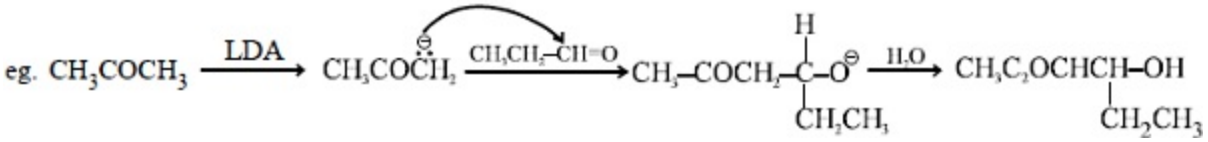


Always acid condition or even base condition leads to dehydraton when extended conjugation results in the product. Cyclisation by aldol reaction is also often found when 5/6 (sometimes even larger) membered ring form as the products and for that substrates taken are generally dialdehyde, ketoaldehyde, diketone etc.



Generally, 5 membered is preferred to 7 membered or 6 membered ring is preferred to 4/8 memberd ring. Also C of –CH=O has more δ + compared to C of > C=O. It has been observed that if we use base like LDA (lithium diispropyl amide) kinetically favoured enolate forms because of less steric crowding appear compared to the other end, e.g. ;



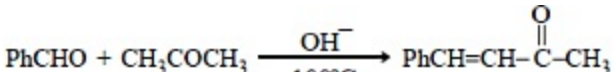


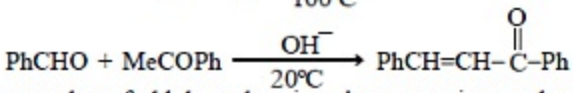
Therefore with base $\overset{\ominus}{O}H$ all sorts aldol reaction product result but with LDA the carbanion is always the kinetically stable one which attack the carbonyl carbon of other carbonyl compound.

Claisen Schmidt reaction:

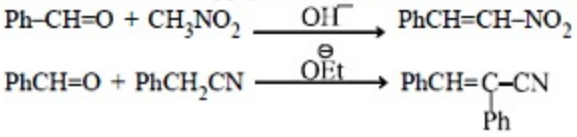
When ketone and aldehyde molecules are treated dil. base, then crossed aldol reactions, which happens, is called as Claisen Schimdt reaction.

Reaction:





Mechanism is same as that of aldol condenstion. As we are in search of acidic –H (i.e. α-H) then $CH_3CH_2NO_2$, $PhCH_2CN$ etc. can also supply carbanion in condensation type reactions as shown below;

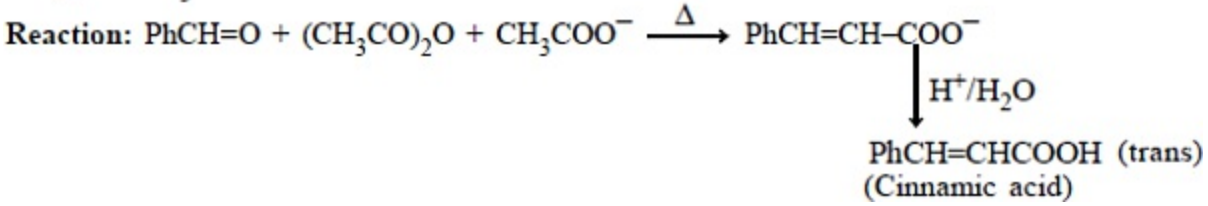


Perkin's reaction (condensation):

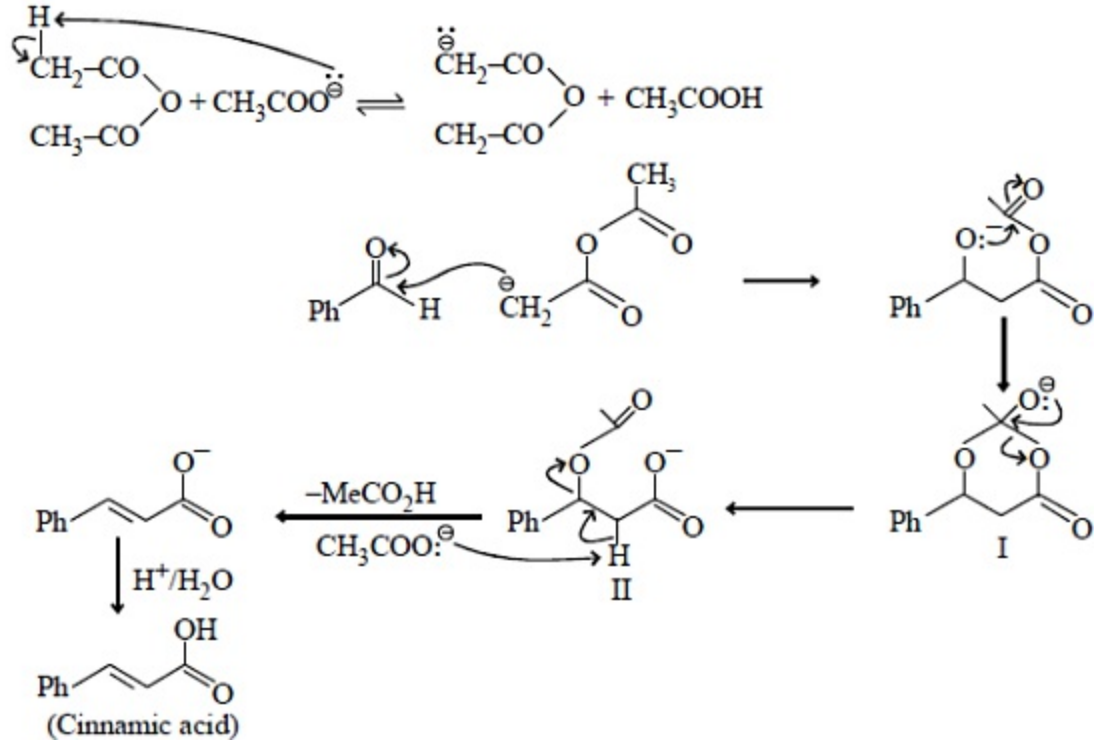
Substrate: Aromatic aldehyde and aliphatic acid anhydride.

Reagent: $CH_3COO^-\ Na^+$

Reaction:



Mechanism:



Comments:

(1) Enough evidence show that cyclic intermediate (I) form.

(2) If we use $(R_2CHCO)_2O$ then end product would be II.

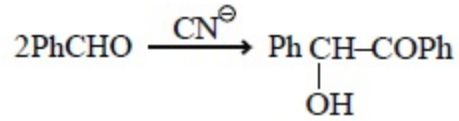
Benzoin condensation:

It is self condensation of aromatic aldehyde.

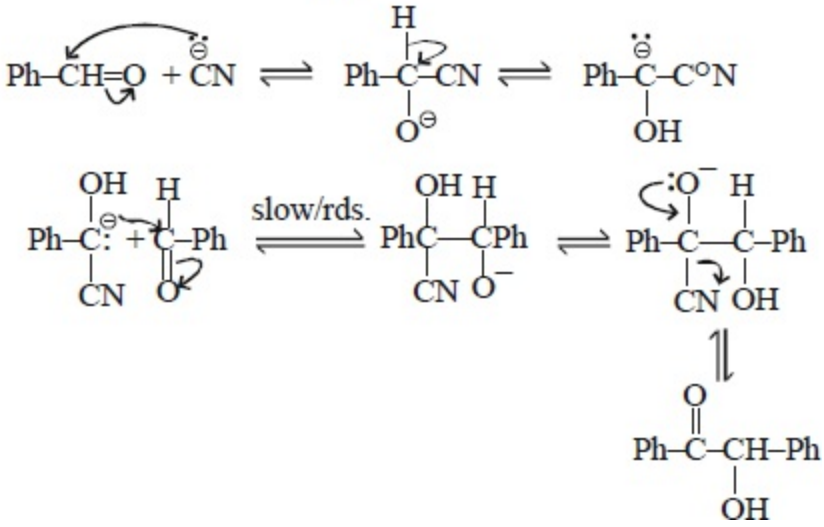
Substrate : Aromatic aldehydes

Reagent : KCN (alcoholic)

Reaction:



Mechanism:



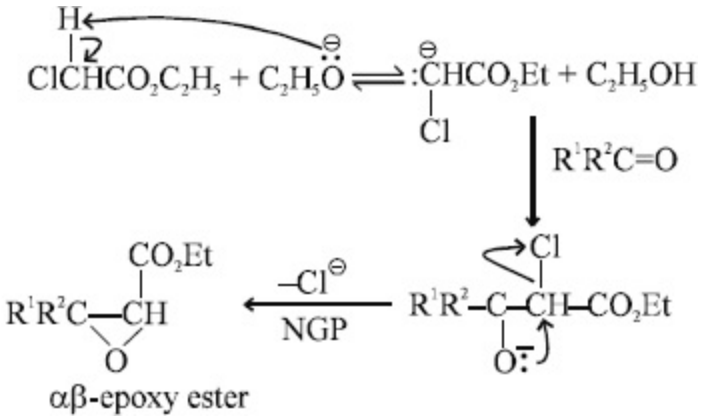
Comments: Here $\overset{\ominus}{CN}$ is a good nucleophile as well as a good leaving group. Reaction fails when strongly withdrawing groups are present at ortho, para to –CHO group.

Darzen's condensation :

Substrate: Aldehyde or ketone and α –Halogeno ester.

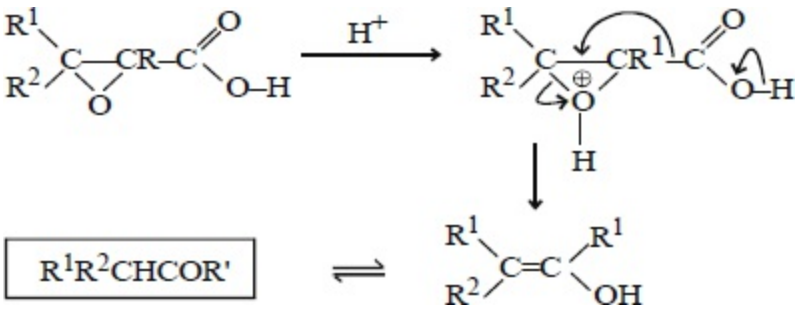
Reagent: $NaOC_2H_5$ or $NaNH_2$ like strong bases.

Reaction:



αβ-epoxy ester

When this α , β expoxy ester is hydrolysed by acid; then final product ketone result.



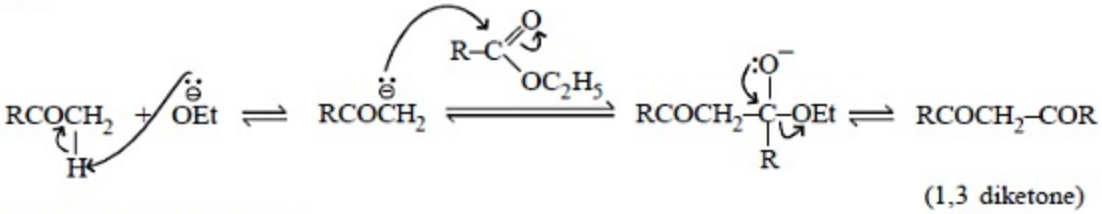
Claisen condensation:

Substrates: Ketones, ester by 1 mole or 2 moles of esters.

Reagent: $RO^{\ominus}Na^{\oplus}$ or $Ph^{\ominus}Na^{\oplus}$ as base.

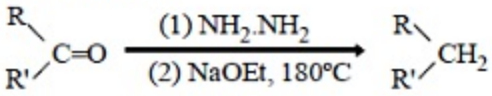
Reaction: $RCOCH_3 + RCOOEt \xrightleftharpoons{OEt^{\ominus}} RCOCH_2COR$

Mechanism:



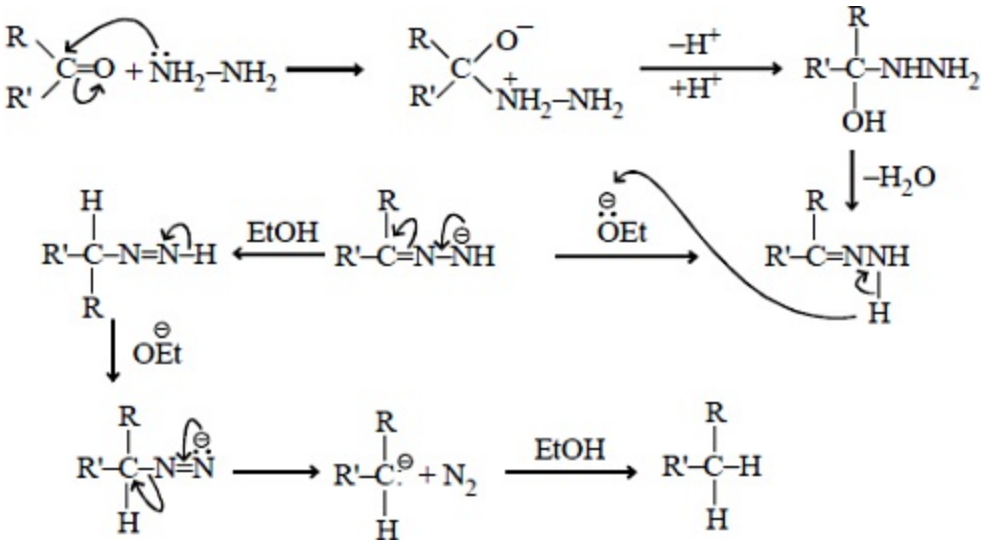
Other chemical reactions :

(1) Wolff Kischner's redcution:



(Aldeyde or ketone)

Mechanism:



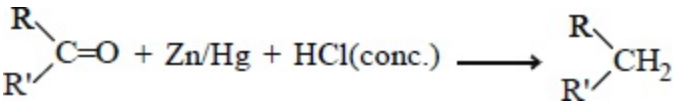
In the above reaction repalcement of O atoms by 2H atoms have taken place.

Comments:

(1) Sterically hindered ketones cannot be reduced.

(2) Double bond migrates in α , β unsaturated carbonyl compounds. By modification using KOH and refluxing ethylene glycol the above problems can be removed. NO_2 group, along with multiple bond will not be affected

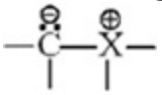
(2) Clemensen's reduction:



Comments: Best used for ketones and not very good for aldehydes. Mechanism is beyond the scope of this book.

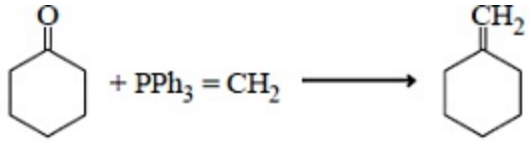
Wittig's reaction:

This reaction involves phosphorous ylides as the reagent. Ylides are species containing C with eive charge and bonded to hetero atoms like N, S, P etc.



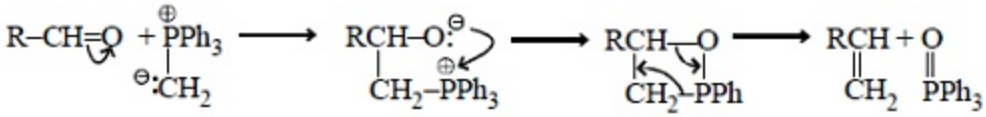
is general structure of an ylide.

Reaction:



(any ketone or aldehyde)

Mechanism:

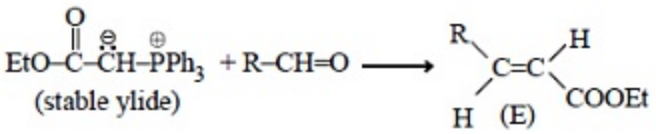


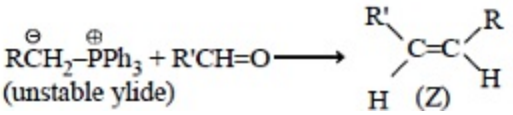
(Betaine) (oxaphosphetame intermediate)

Here the driving force is P=O bond formation which is highly exothermic.

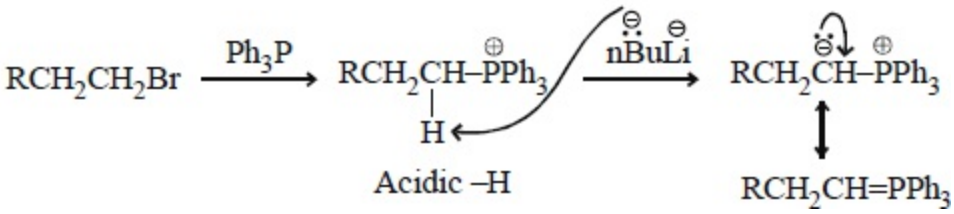
Comments: (1) With stabilised ylides the Wittig reaction is E –selective i.e. E forms in major.
(2) With unstabilised ylides the Wittig reaction is Z –selective i.e. E forms in minor.

For example;





Preparation of ylide:



(3) Electron withdrawing groups like: –COR, –CHO, –CN, –COOR etc. groups at α -position of the ylide gives excellent result with aldehyde not for ketones.

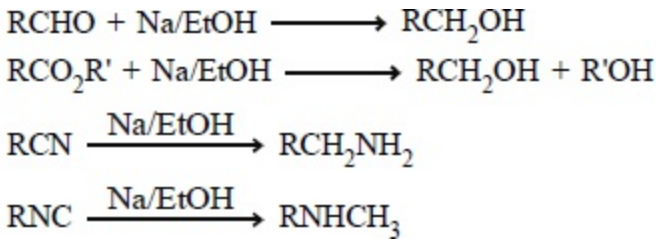
(4) Unsaturation already present does not get disturbed.

Bouvealt-Blanc reduction :

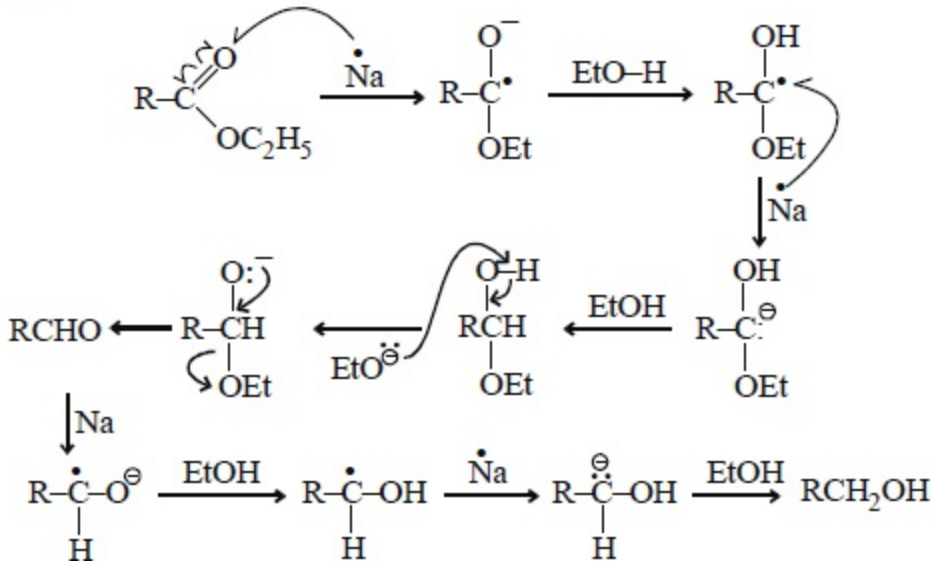
Substrate: Aldehydes, ketones, esters, nitriles, isonitriles.

Reagent: Na/EtOH

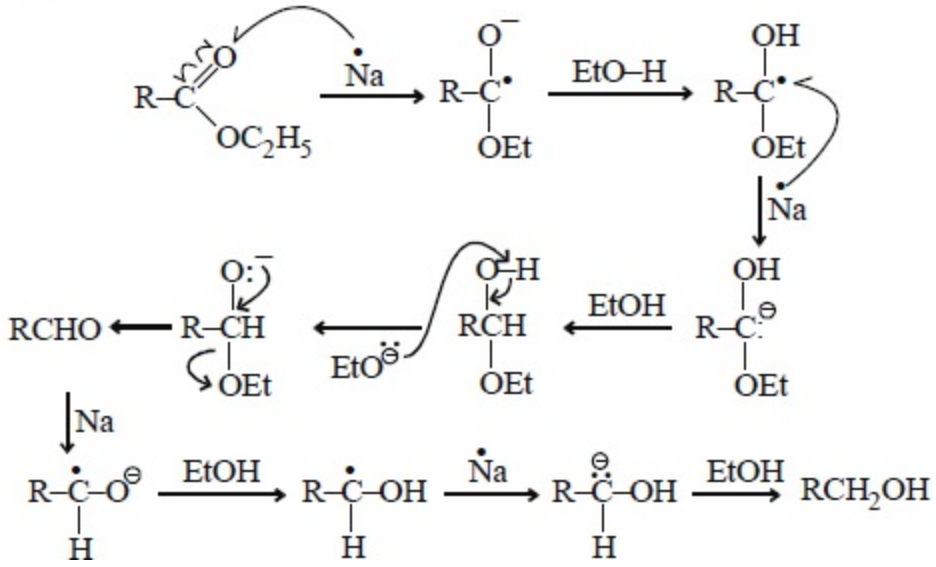
Reaction:



Mechanism:

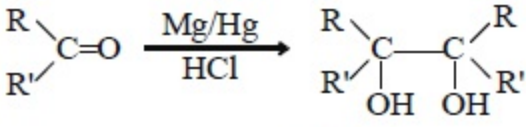


Mechanism:



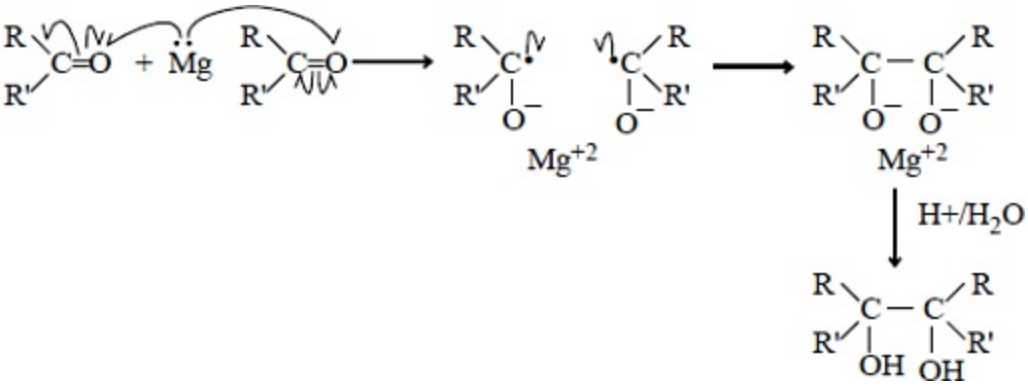
Formation of pinacol:

Reaction:



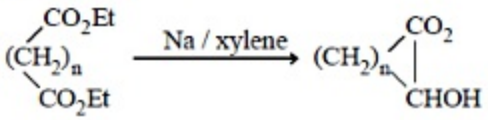
Pinacol

Mechanism:



Acyloin condensation:

Reaction;



Acyloin

[Here n = 8 – 18]

Mechanism happens through electron transfer from Na and it is beyond the scope of this book.

Haloform reaction:

Substrate: (1) Aldehyde or ketone having active H atoms eg. CH_3CHO, CH_3COCH_3 etc. (having CH_3CO group)

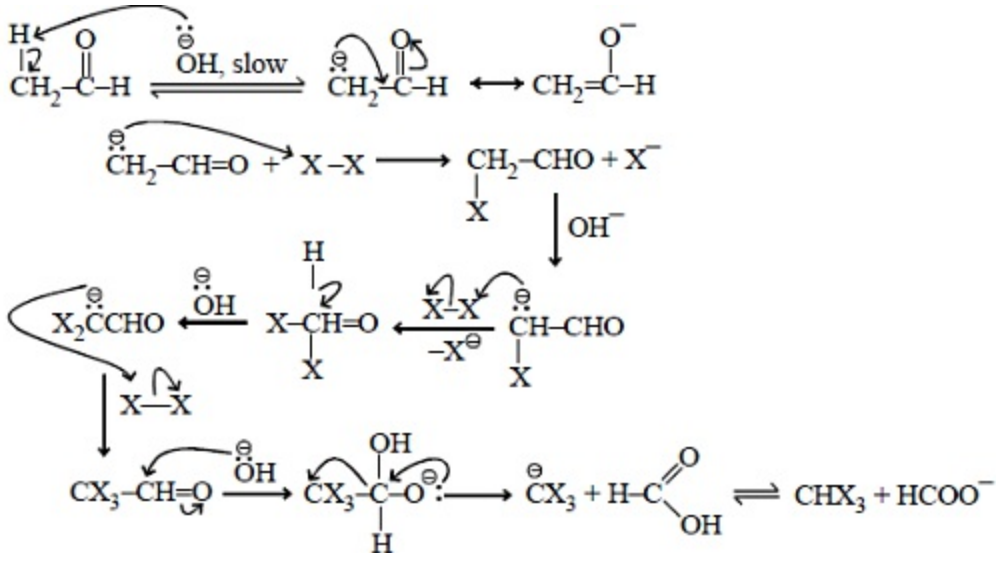
(2) Alcohols which can give ketomethyl group i.e. $CH_3-\overset{\overset{O}{\|}}{C}-$

Reagent: X_2 in alkaline medium (OH^-), or OX^-.

X=Cl, Br, I

Reaction: $CH_3CH{=}O + 3X_2 + OH^- \longrightarrow CHX_3 + HCOO^- + 3X^- + 3H_2O$

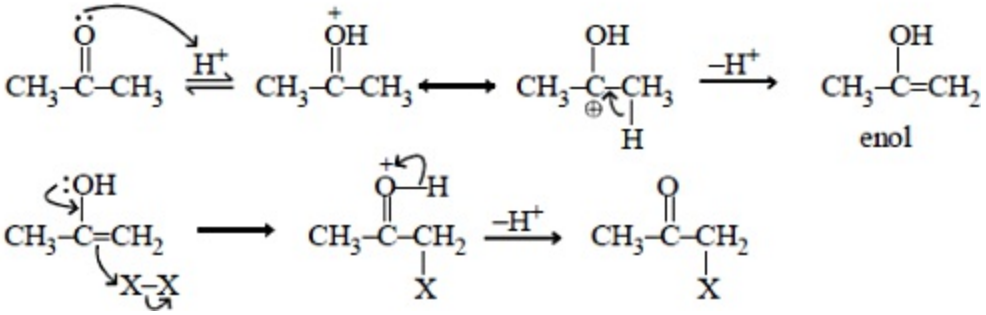
Mechanism:



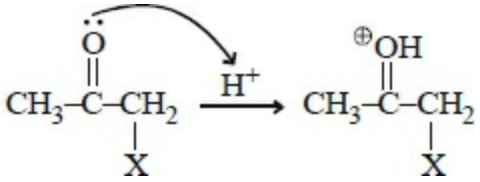
In case of acid catalysed condition monohalo derivative is the end product.

$$RCH_2COCH_3 \xrightarrow[X_2]{H^+} RCHXCOCH_3$$

Mechanism:



It has been observed that enol formation is slower than the α –Halogenation step. Thermodynamically favoured enol forms and which react successively. Further enolisation does not take place due to –I effect of X.

e.g. 

Comments:

(1) Presence of ketomethyl group is not the sufficient condtion. CH_3COOH, $CH_3COCH_2CO_2CH_3$ etc. donot respond to haloform test $CH_3COCH_2COCH_3$, $CH_3CHOHCH_2CHOHCH_3$, $CH_3CH(NHCOR)COCH_3$, give haloform test.

(2) Iodoform (yellow) is best prepared in the laboratory. $CH_3CH(NHCOR)COCH_3$

(3) Instead of X_2/NaOH, NaOX can also be supplied for haloform reaction.

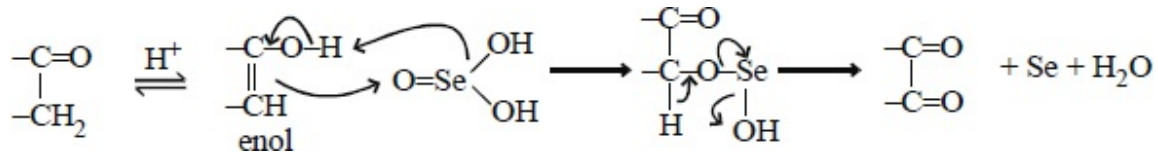
Oxidation by SeO_2

Aldehyde or ketones having methylene (>CH_2) group adjacent to carbonyl group can be oxidised by SeO_2 to dicarbonyl compound

(1) $CH_3CHO + SeO_2 \longrightarrow CHO–CHO$

(2) $CH_3CH_2COCH_3 \xrightarrow{SeO_2} \underset{\text{(minor)}}{CH_3COCOCH_3} + \underset{\text{(major)}}{CH_3CH_2COCHO}$

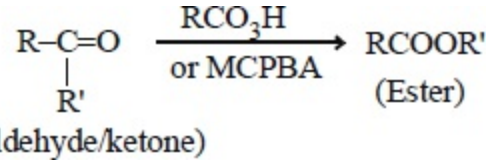
Mechanism:



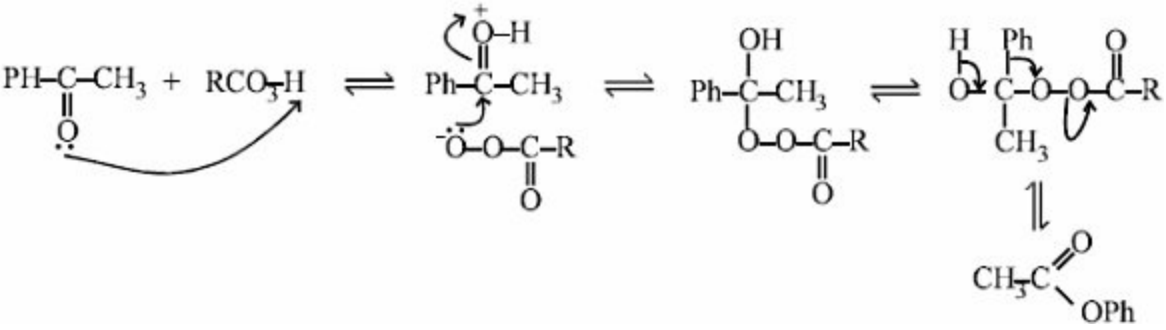
It shows that enol form first and then oxidation later (which may not completely support the thermodynamically stable enol in equation (2).

Bayer Villiger's oxidation:

Reaction:



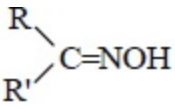
Mechanism:



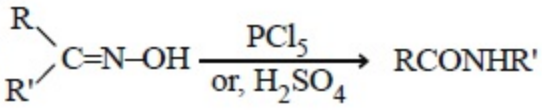
Migratory aptitude in this reaction is found to be $3^{o} > 2^{o} > 1^{o} > -CH_3$. Hydride shows more migratory aptitude than phenyl and phenyl also shows more migratory aptitude than 3°.

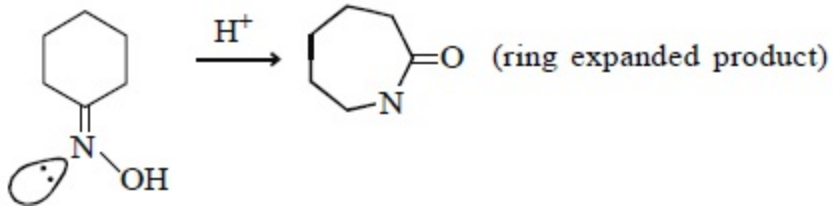
Beckmann's rearrangement:

Acid catalysed conversion of ketoximes to N substituted amide is called as Beckmann's rearrangement.

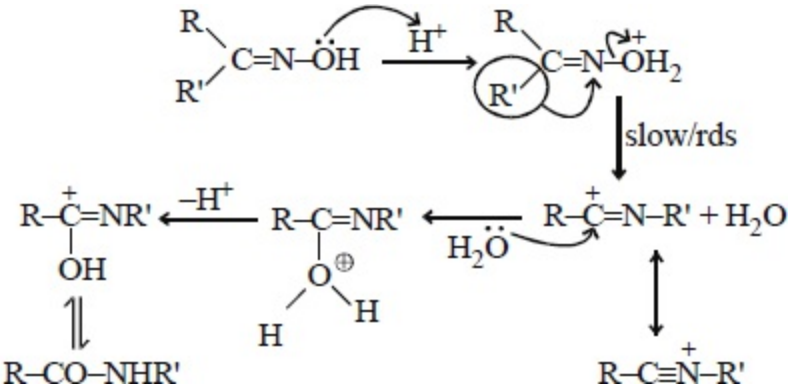
Substrate: 

Reagent as catalyst : H_2SO_4, HCl, PCl_5, $SOCl_2$, SO_3, BF_3, H_3PO_4 etc (any one)

Reaction: 



Mechanism:



Comments: (1) Anti group to the leaving group migrate

(2) No change in the configurtaion of migrating group

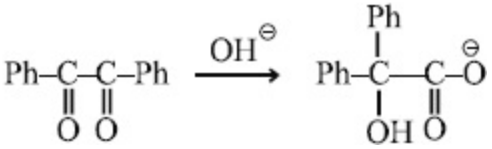
(3) More polar solvent make the reaction faster.

(4) Good leaving group make the reaction faster. e.g. CH_3COO^- < $PhSO_3^-$ etc.

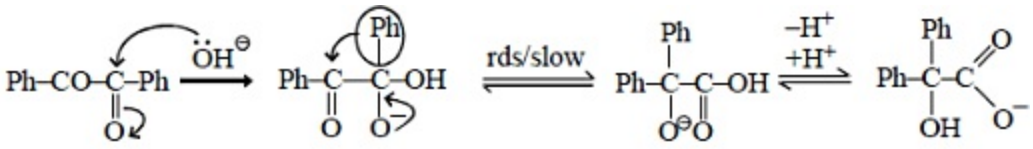
Benzil-benzilic acid rearrangement:

Substrate: Aromatic 1, 2 diketone.

Reagent: alcoholic $\overset{\ominus}{O}H$ or $\overset{\ominus}{O}Me$ as a base.

Reaction : 

Mechanism:



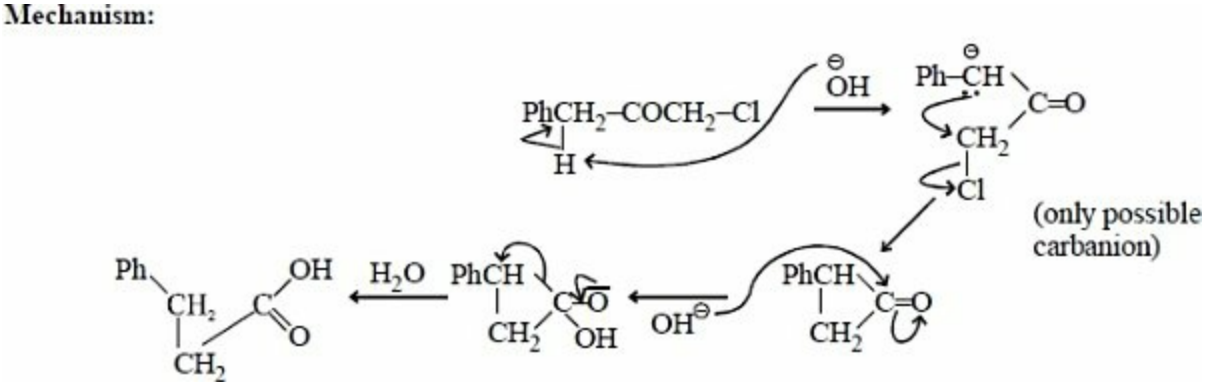
Favorski rearrangement:

Substrate: α-chlorobromoketones.

Reagents: RO^- or OH^- or amines as a base.

Reaction : $PhCH_2COCH_2Cl \xrightarrow{OH^\ominus} PhCH_2CH_2COOH$

Mechanism:



Carboxylic Acid

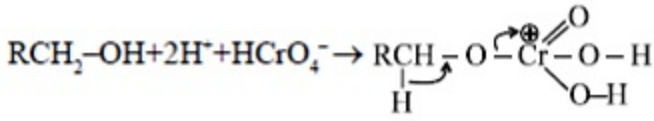
The functional group $-CO_2H$ is called as carboxylic acid group and it may be present with alkyl or, aryl radical.

Preparation :

1. $RCH_2 - OH$ or $ArCH_2OH \xrightarrow[\text{or } MnO_4^-, H^+]{Cr_2O_7^{2-}/H^+} RCOOH$ or $ArCOOH$
   (or RCHO or ArCHO)

   Mechanism :

   $Cr_2O_7^{-2} + H^+ \rightarrow HCrO_4^-$

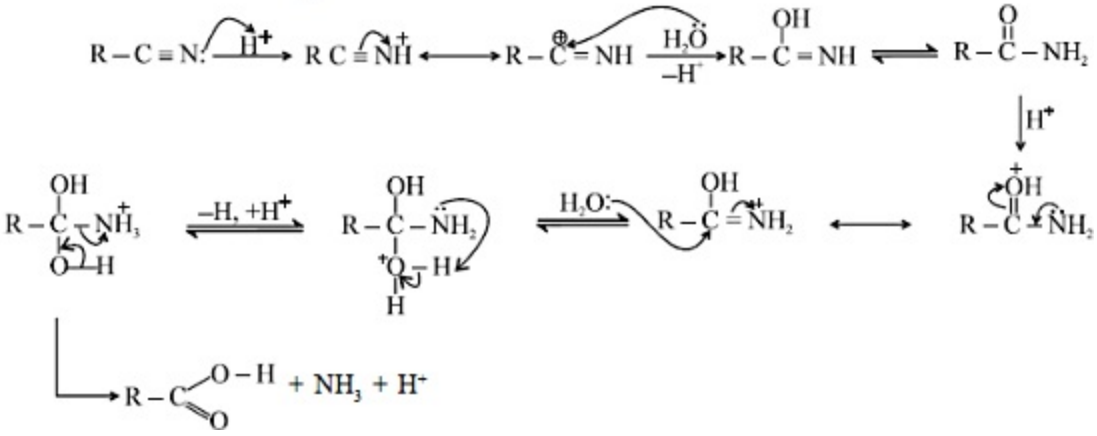
   $RCH_2{-}OH + 2H^+ + HCrO_4^- \rightarrow$  $\xrightarrow{\text{Slow}, -H^+} RCH=O + H_2CrO_3$

   $RCH=O \xrightarrow{[O]} RCOOH$

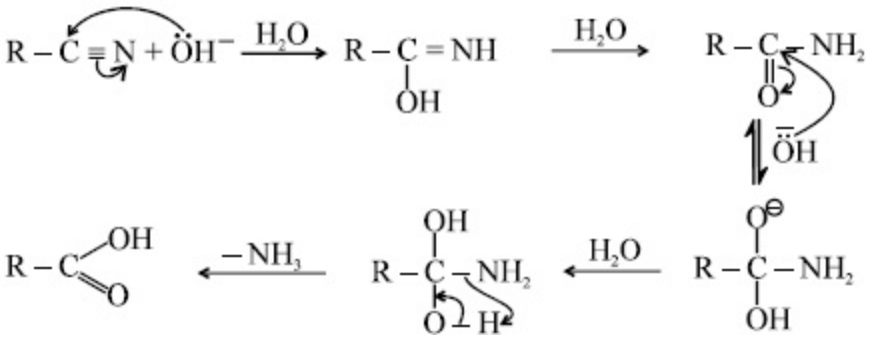
2. $RCOCH_3$ or $ArCOCH_3 \xrightarrow[(2)\ H_3O^+]{(1)\ I_2/NaOH} RCOOH + CHI_3$ [or $ArCOOH + CHI_3$]

3. R or ArCN $\xrightarrow{H_2SO_4}$ R or Ar − COOH

   Mechanism with acid catalyst :

With base catalyst :



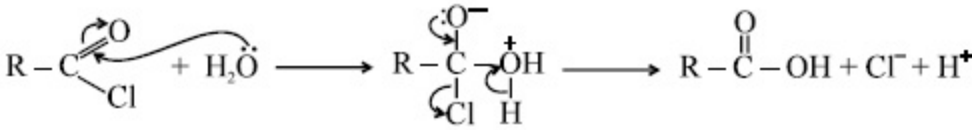
4. $R/Ar\,MgBr \xrightarrow{CO_2} R/Ar\,COOMgBr \xrightarrow{HCl} R/ArCOOH$

5. $RCH=CHR \xrightarrow[KMnO_4]{Acid} 2RCOOH$

6. $R/ArCONH_2 \longrightarrow RCOOH/ArCOOH$

7. $R/ArCOCl \xrightarrow{H_2O} R/ArCOOH$

Mechanism :



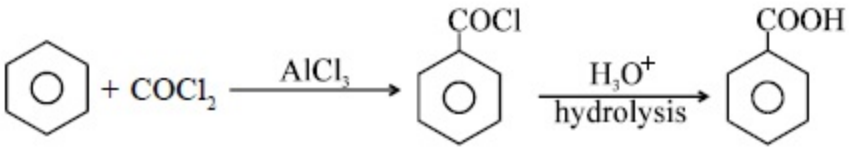
8. $R-COOR' \xrightarrow[OH^- \text{or } H^+]{H_2O} RCOOH + R'OH$

The mechanism is discussed later.

9. $RCH_2CCl_3 \xrightarrow[\Delta]{OH^-} RCH_2COOH$

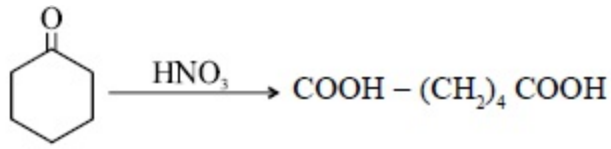
10. $ArH + COCl_2 \xrightarrow[H_3O^+]{\text{Anh. } AlCl_3} ArCOOH$

Mechanism

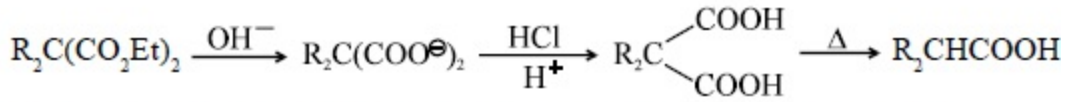


11. $PhCH=O + (CH_3CO)_2O + CH_3COONa \xrightarrow{H_3O^+} PhCH=CH-COOH$

(cinnamic acid)

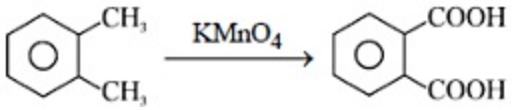
12. 

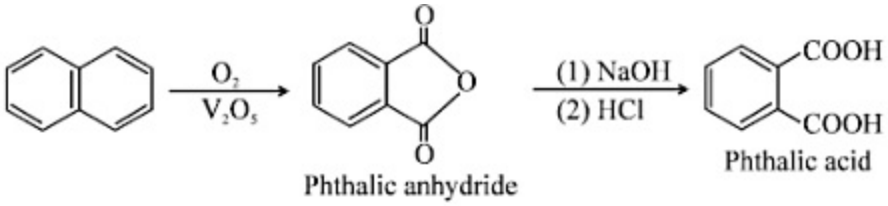
13. $R_2C(CO_2Et)_2 \xrightarrow[(2)\ HCl,\ \Delta]{(1)\ KOH} R_2CHCO_2H$



C containing two COOH groups always decarboxylates on heating.

14. $Ph - CH_3 \xrightarrow[h\nu]{1\ eq.\ Cl_2} Ph - CH_2 - Cl \xrightarrow{Na_2CO_3} PhCH_2 - OH \xrightarrow{MnO_4^-/H^+} PhCOOH$

15. 

16. 

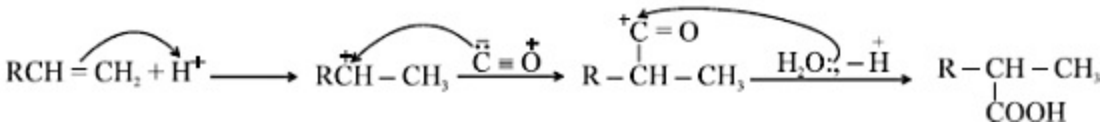
Phthalic anhydride

Phthalic acid

17. **Koch reaction :**

$RCH = CH_2 + CO + H_2O \xrightarrow{H^+} R - \underset{\displaystyle CH_3}{\underset{|}{CH}} - COOH$

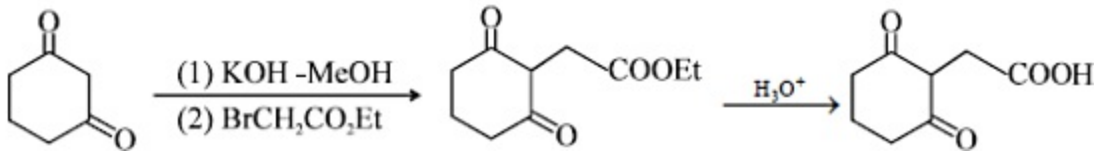
Mechanism :



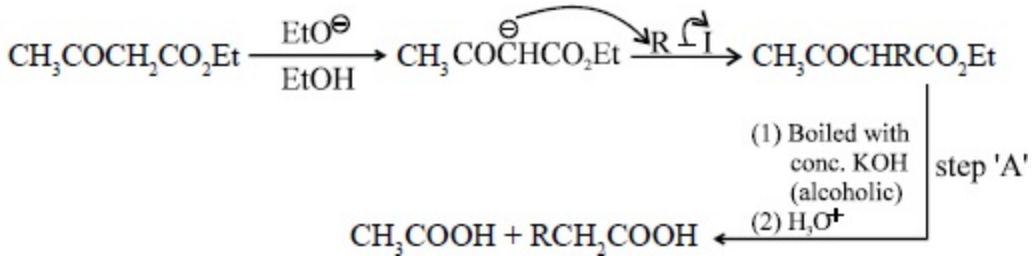
18. $R^{\ominus}Na^{\oplus} \xrightarrow{CO_2} RCOO^{\ominus}Na^{+}$ [where R = CH_3 or C_2H_5]

$RO^- Na^+ \xrightarrow{CO} RCOO^-Na^+$

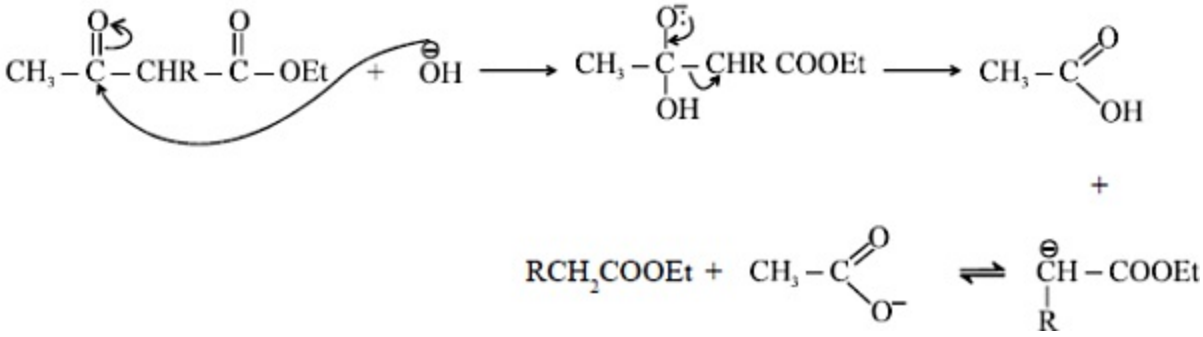
19. **Using α-hydrogen ;**



20. From acetoacetic ester ;



Mechanism of step 'A' :



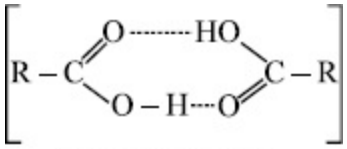
Physical properties :

C–atom of – COOH is sp^2 hybridised. C – O bond length is 0.143 nm and 0.124 nm and it indicates that none is pure single bond or double bond as shown below. So, resonance prevails.



Because of the δ + charge on O atom it shows the acidic behaviour and forms stable – $COO^{\ominus}$ ion (by resonance). C atoms has oxidation state + 3 in – COOH group. – CO_2H can be oxidised or reduced to + 4 or – 4 oxidation state.

Carboxylic acids can show H-bonding in all three states and even in solution with nonpolar solvent.



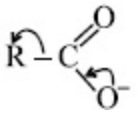
Dimer formed in the vapour phase of CH_3COOH and PhCOOH

B.P. increases from and RCHO or RCOR' to RCOOH and it increases due to

higher molecular mass. Carboxylic acids with even no. of carbon atoms are more symmetrical and therefore have higher mp. compared to carboxylic acids with odd number of C–atoms. RCOOH is more soluble than alcohol as the $RCOO^-$ hydrates rather than ROH. PhCOOH is soluble in hot water and other aromatic acids are slightly soluble in water.

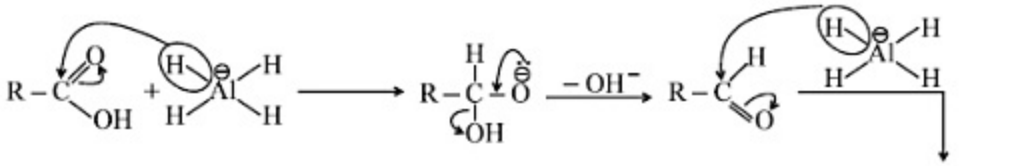
Chemical reactions :

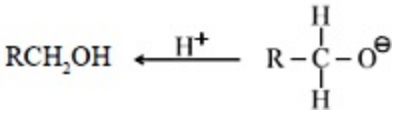
1. $RCOO^-Na^+ / ArCOO^- Na^+ \xrightarrow[\Delta]{NaOH+CaO} RH / Ar - H$

Mechanism :  $\xrightarrow{NaOH + CaO} RH + CO_2 + OH^-$

2. $Ar / RCOOH + LiAlH_4 \xrightarrow{Ether} Ar / RCH_2OH$

Mechansim :



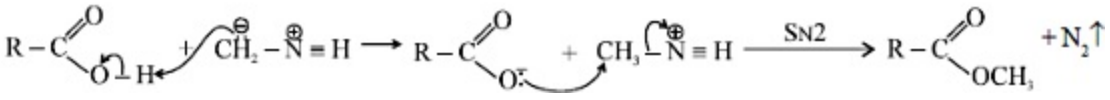


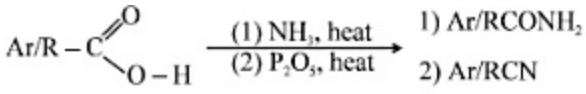
3. $R/ArCOOH \xrightarrow{Li/Na/K} R/Ar\ COO^- M^+ + \frac{1}{2}H_2$

4. $Ar/RCOOH \xrightarrow[R'OH]{Conc.H_2SO_4} R - COOR' \text{ or } (ArCOOR')$

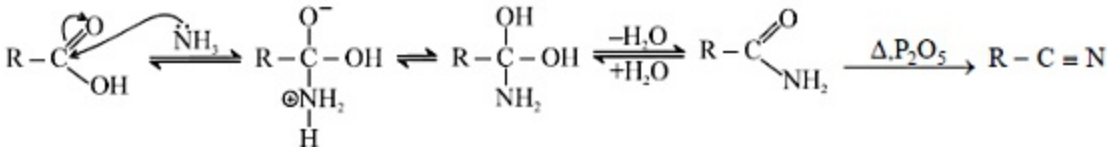
5. $R/ArCOOH \xrightarrow{CH_2N_2} RCOOCH_3 / ArCOOCH_3$

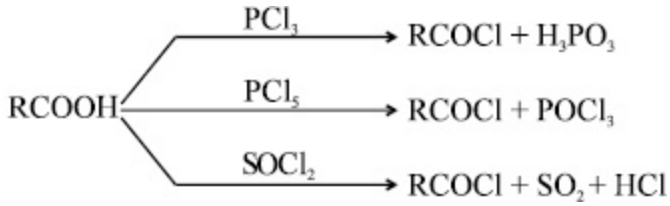
Mechanism :



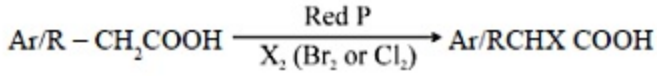
6. 

Mechanism :

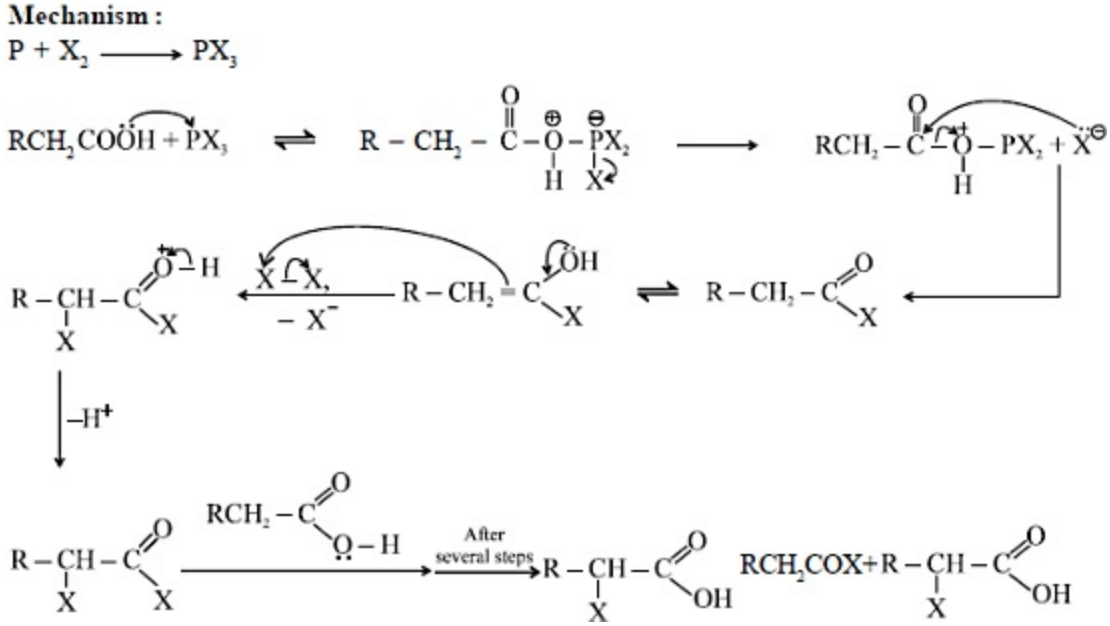


7. 

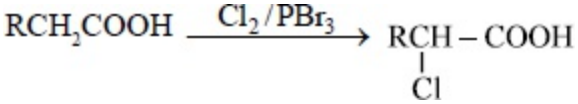
8. **HVZ (Hell Volhardt Zellinisky) reaction :**



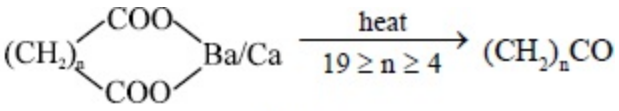
Mechanism :



By this reaction only α – H is substituted by Br_2 or Cl_2 not by F_2 or I_2. If two α – H atoms are there then both can be replaced and it is difficult to stop until both the halogenation is taking place. To support the above mechanism, we find that,



α –Halogenation of acyl halide & anhydride also takes place.

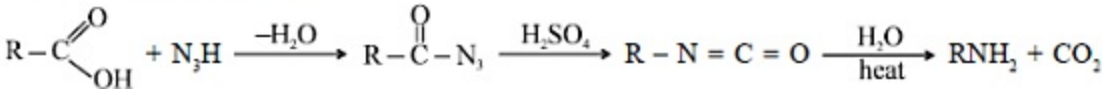
9. (a) 

(b) $(RCO_2)_2\,Ca/Ba \xrightarrow{heat} RCOR$

10. $R/ArCOOH \xrightarrow{(CH_3CO)_2O} (R/ArCO)_2O$ anhydride

11. $Ar/RCOOH \xrightarrow[distillation]{Conc.\,H_2O_2} Ar/RCO_3H$ (per acid)

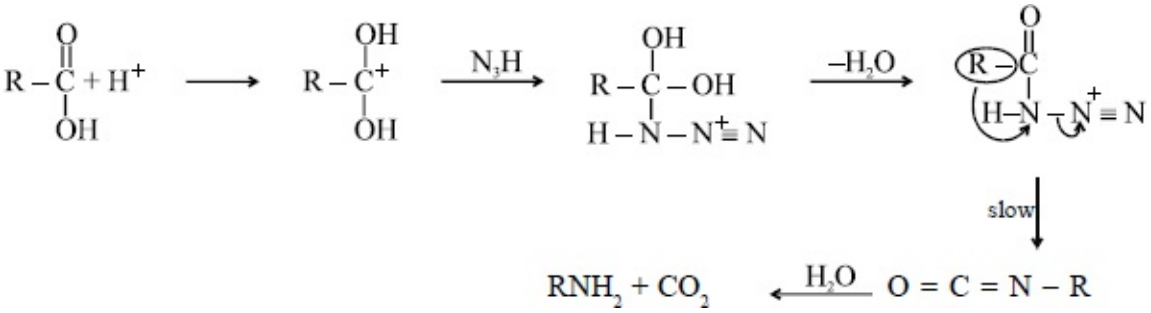
12. **Schmidt rearrangement :**



This rearrangement reaction is superior to Curtius or Hofmann's rearrangement as the acid can be directly converted to 1° amine without the formation of amide.

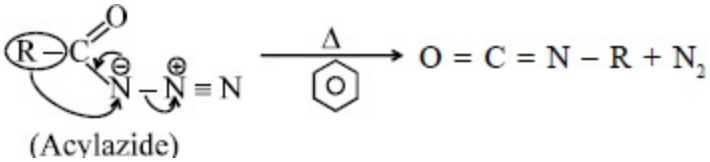
Mechanism :

The migration involves concerted step as shown below



13. $RCOOH + SOCl_2 \longrightarrow RCOCl$

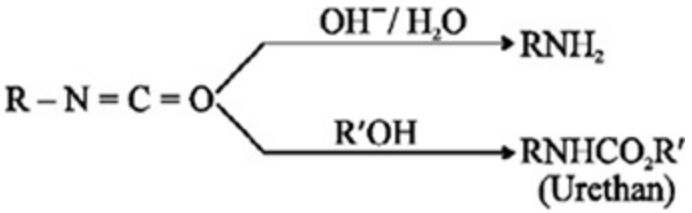
14. Curtius rearrangement :



(Acylazide)

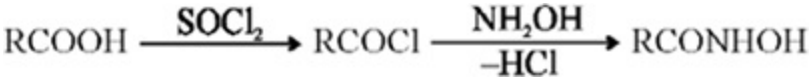
Therefore isocyanate is produced in Curtius rearrangement. The subsequent hydrolysis or alcoholysis gives amine or urethan respectively. This reaction involves intramolecular rearrangement and applied for all types of carboxylic acids, with unsaturation or other functional groups.

For example ;



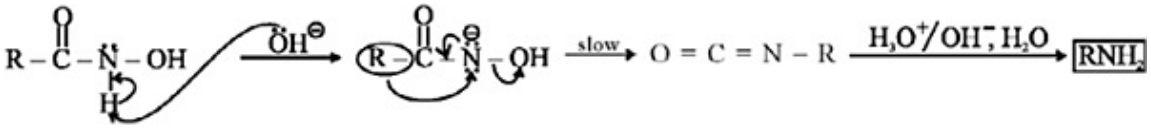
15. Lossen rearrangement :

RCONHOH (hydroxaminc acid) which can be obtained as follows;

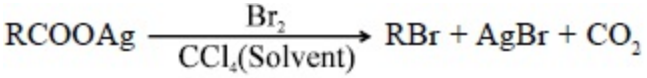


It undergoes rearrangement to give the isocyanate in presence of acid or base catalysis.

Mechanism :

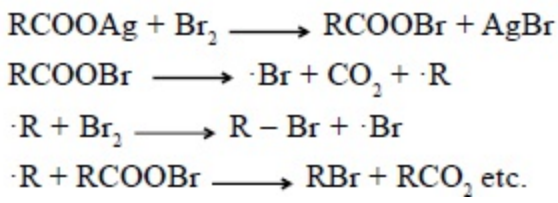


16. Hunsdiecker's reaction or Borodine Hunsdiecker's reaction :



The maximum yield is obtained for 1° and least for 3°. Chlorine gives poor yield.

Mechanism :



17. **Birnbaum Simmonini reaction :**

$$2RCO_2Ag + I_2 \longrightarrow RCO_2R + 2AgI + CO_2$$

18. $$RCHXCO_2H + H_2O \xrightarrow[(2)\ H^+]{(1)\ NaOH\ ;\ S_N2} RCH(OH)-CO_2H$$

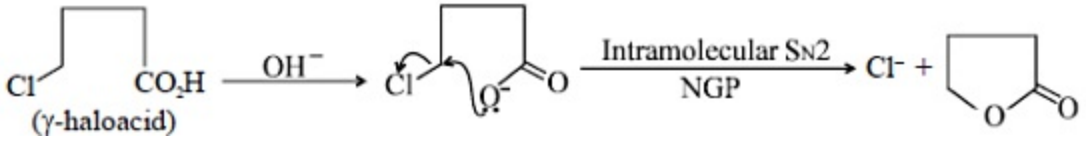
On the other hand, with base like 3° amine, elimination results.

$$RCH_2CHXCO_2H \xrightarrow[\Delta]{R_3'N\ ;\ E2} RCH=CHCO_2H$$

(α-haloacid)

19. $$RCH(X)-CH_2CO_2H \xrightarrow[S_N2]{NaOH} RCH(OH)-CH_2CO_2H \xrightarrow{\text{Reflux with NaOH}} RCH=CHCO_2^{\ominus}$$

(β-haloacid)

20. 

(γ-haloacid)

21. For δ - haloacid, ε - hydroxy acid lactone results in the simillar way.

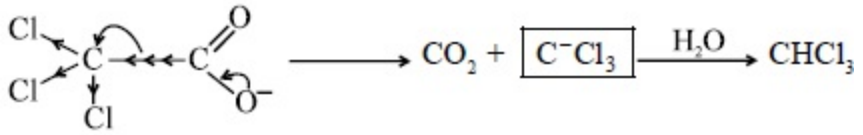
22. $$CHCl_2CO_2H + H_2O \xrightarrow[(2)\ H^+]{(1)\ NaOH} CH(=O)-CO_2H + 2HCl$$

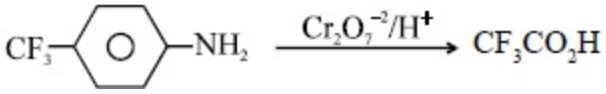
(α, α dichloro acid)

$$\xrightarrow{NaOH\ (intermolecular\ Cannizaro's\ reaction)} Na_2C_2O_4 + CH_2(OH)COONa + 2H_2O$$

23. $$CCl_3CO_2H \xrightarrow[NaOH]{\text{Boiled with}} CHCl_3 + CO_2$$

Mechanism :



24. 

25. $HCO_2H \xrightarrow{Cl_2} 2HCl + CO_2$

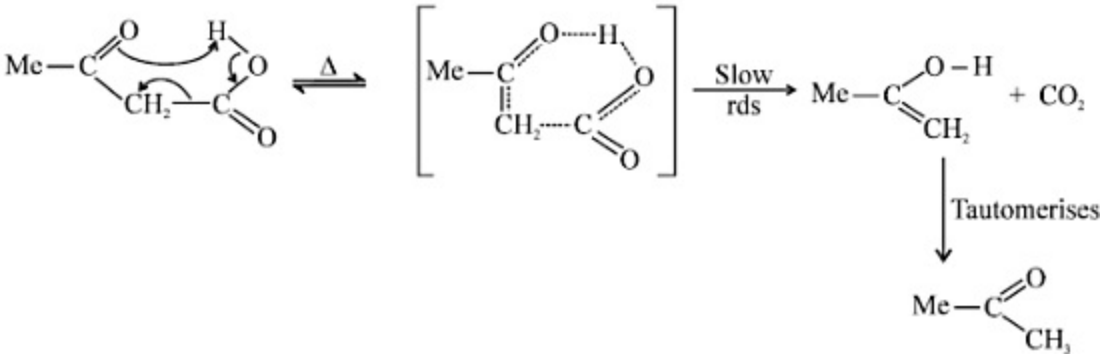
Formation of β-keto acid and corresponding decarboxylation while heated is very important. Synthesis of β-keto acid is done through β-keto ester. Keten in acetone solution dimerises and then while treated with alcohol produces β-keto ester and upon hydrolysis it gives β-keto acid. Ethyl acetoacetate (EAA) is neutral to litmus, gives Na – salt, does not given haloform reaction.

$$2CH_2=C=O \xrightarrow{C_2H_5OH} CH_3COCH_2CO_2C_2H_5 \xrightarrow{H_3O^+} CH_3COCH_2COOH$$

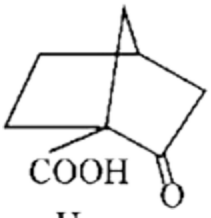
$$CH_3COCH_2CO_2H \xrightarrow{\Delta} CH_3COCH_3 + CO_2$$

$$CH_3COCH_2CO_2H \xrightarrow{HNO_2} CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{NOH}{\|}}{CH}-CO_2C_2H_5$$

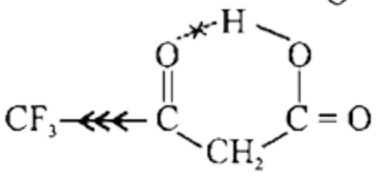
Mechanism of decarboxylation of β-keto acid :



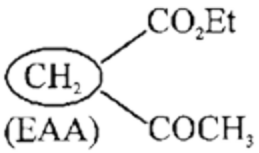
Decarboxylation does not take place when $CF_3COCH_2CO_2H$ or



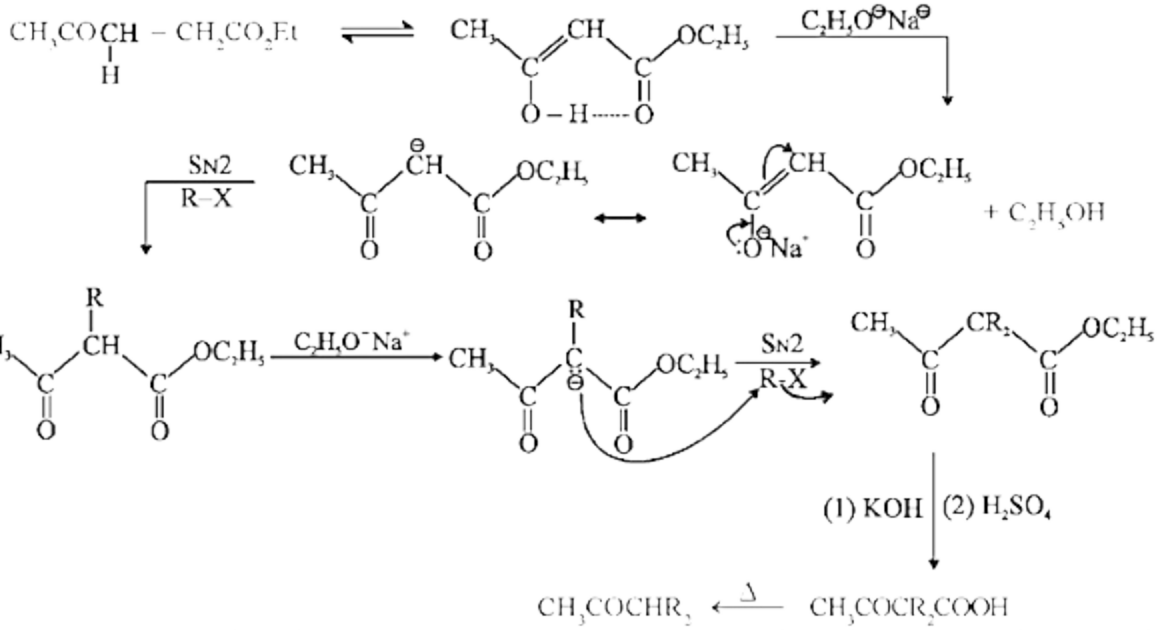
is heated. For the initial one, no transition state like



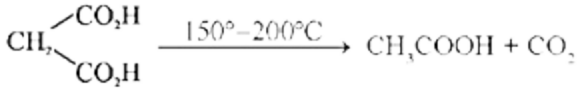
forms due to strong withdrawl of CF_3 group and for the second one by Bredt's rule double bond cannot form at bridgehead C which appears in the mechanism.



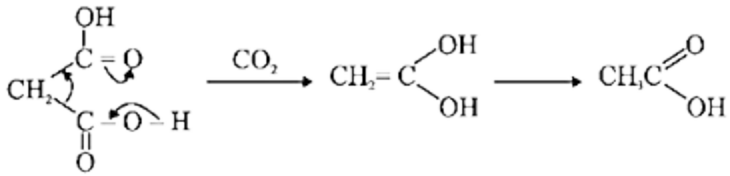
The rounded C – H bonds are highly acidic. This CH_2 is called as active methylene group. Some of the reactions involving this CH_2 are;



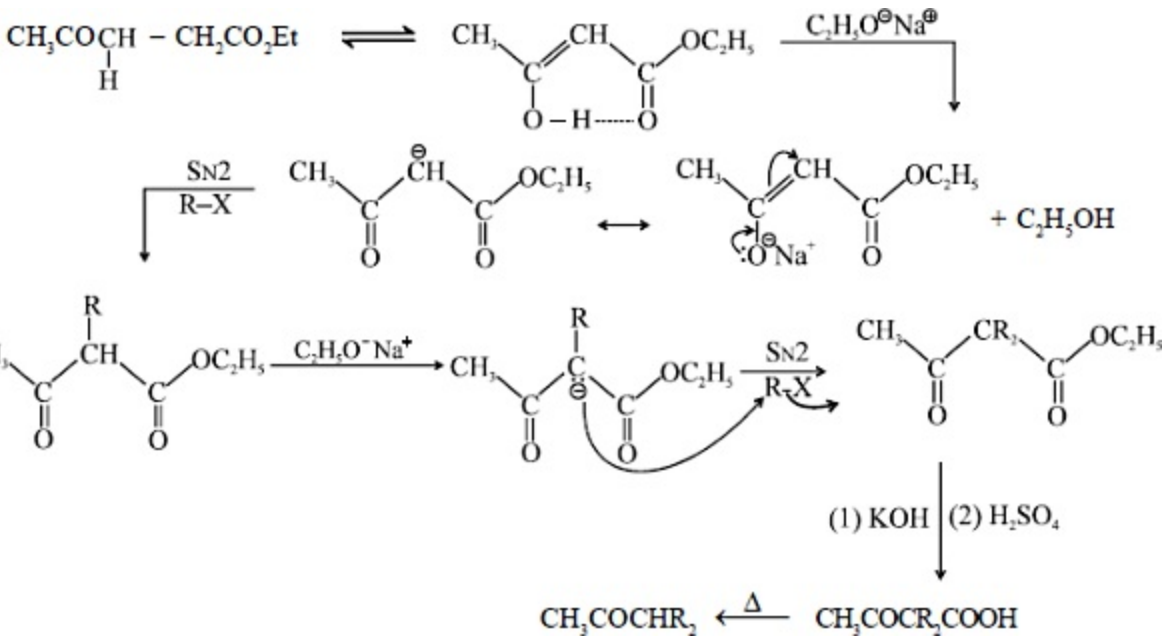
The above process in which $CH_3COCR_2CO_2C_2H_5 \rightarrow CH_3COCHR_2$ forms is called ketonic hydrolysis



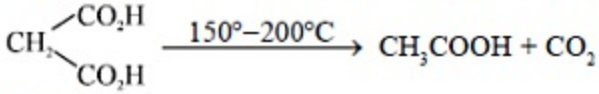
Mechanism :



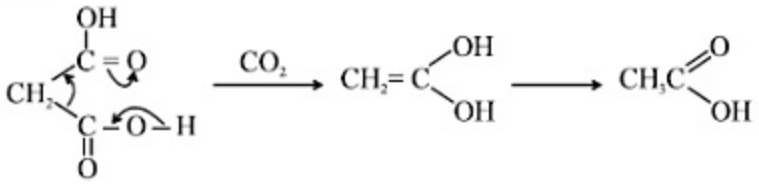
Unsaturated monocarboxylic acid :



The above process in which $CH_3COCR_2CO_2C_2H_5 \rightarrow CH_3COCHR_2$ forms is called ketonic hydrolysis



Mechanism :



Unsaturated monocarboxylic acid :

Preparation :

(1) $PhCHO + (CH_3CO)_2O + CH_3COO^-Na^+ \xrightarrow{H_2O} PhCH = CHCOOH$ (cinnamic acid)

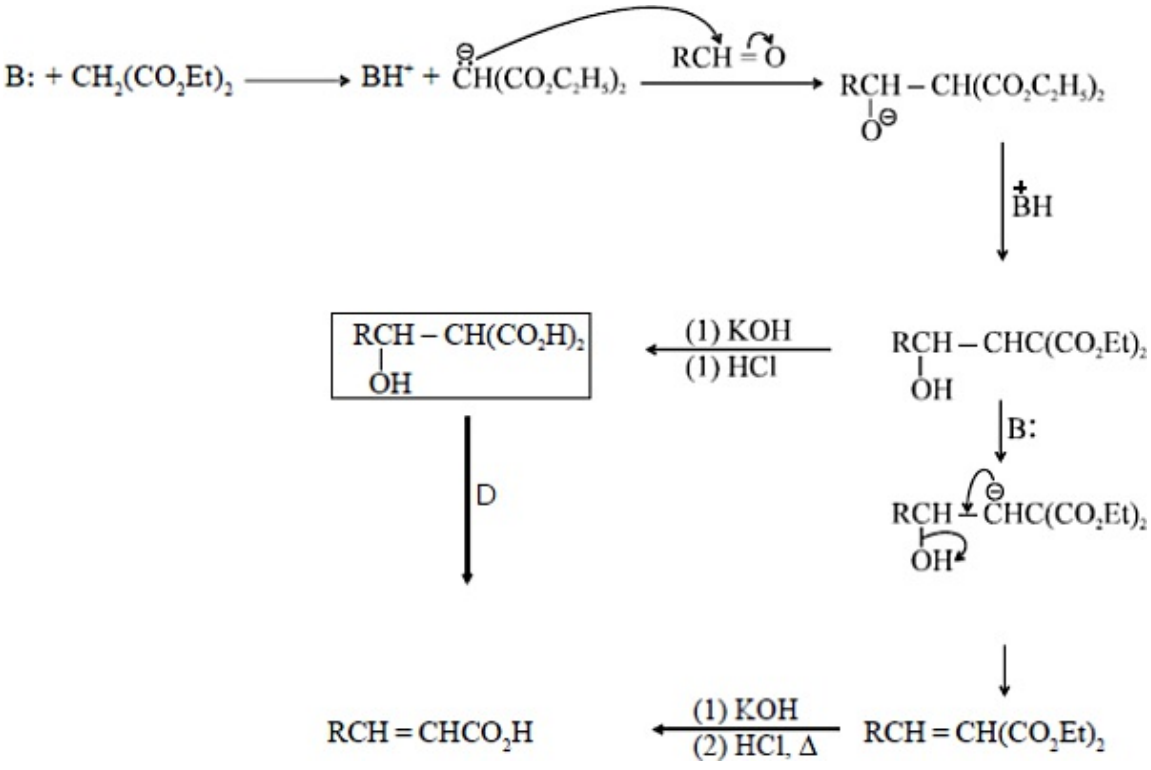
(2) $RCHO + CH_2(CO_2C_2H_5)_2 \xrightarrow[N]{} RCH = C(CO_2C_2H_5)_2 \xrightarrow[(2)\,HCl]{(1)\,KOH} RCH = C(CO_2H)_2$

$\downarrow 150° - 200°C$

$CO_2 + RCH = CHCO_2H$

The above reaction is just like aldol condensation.

Mechanism :



(3) $CH_2 = CH - CHO \xrightarrow{\text{Ammoniacal } AgNO_3} CH_2 = CHCO_2H$

Donot use $KMnO_4/H_2Cr_2O_7$, H^+ etc., otherwise double bond will be affected.

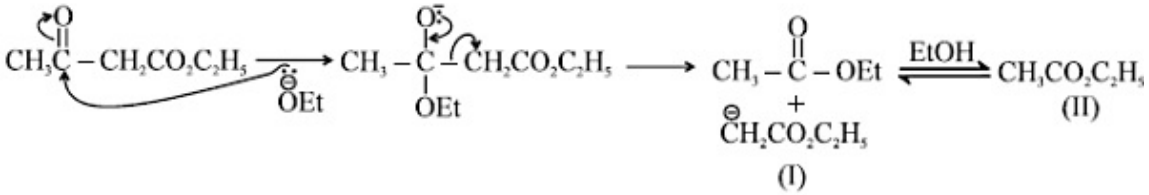
(4) $CH_2(OH)-CH_2CO_2H \xrightarrow[\Delta]{NaOH} CH_2=CHCO_2H \xleftarrow[\Delta]{\text{conc. } H_2SO_4} CH_2CH_2CO_2H(OH)$

$CH_2=CH-CN \xrightarrow{H^+} CH_2=CHCO_2H$

Also, $CH_3COCH_2CO_2C_2H_5 \xrightarrow[\text{boiling}]{[2KOH(conc) + C_2H_5OH]} CH_3COOK + CH_3CO_2K + C_2H_5OH$

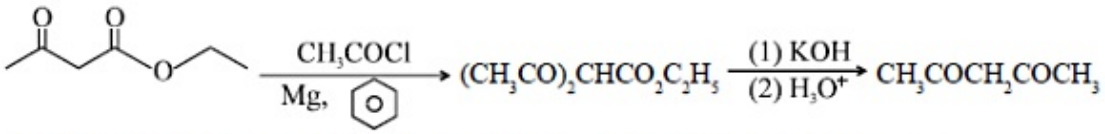
The above process is called acidic hydrolysis as acid is formed as the major product.

Mechanism:

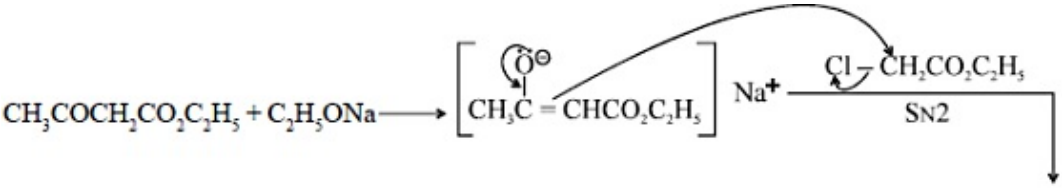


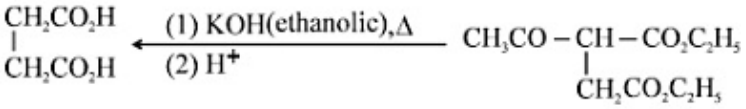
$\therefore$ I, II $\xrightarrow[\Delta]{KOH} CH_3COO^-K^+ + C_2H_5OH$

From the β-keto ester we can prepare 1, 3 diketone

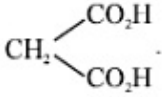


From the β-keto ester, we can prepare dicarboxylic acid as shown below;

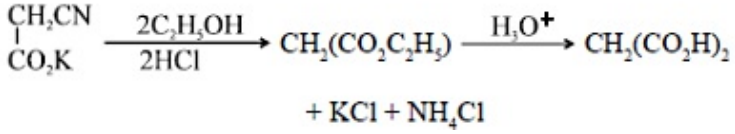




Malonic acid :

The structure of malonic acid is  .

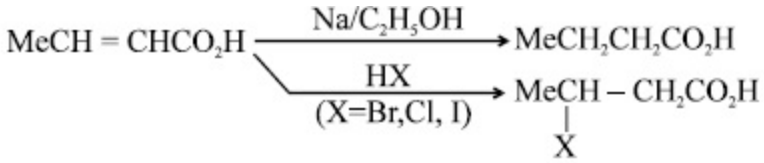
Preparation :



Chemical reactions:

This shows the reaction (usual) of double bond as well as CO_2H group.

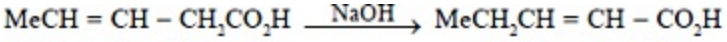
For example ;

1. 

Regioselectivity of the above reactions is anti Markownikoff's addition.

Mechanism :

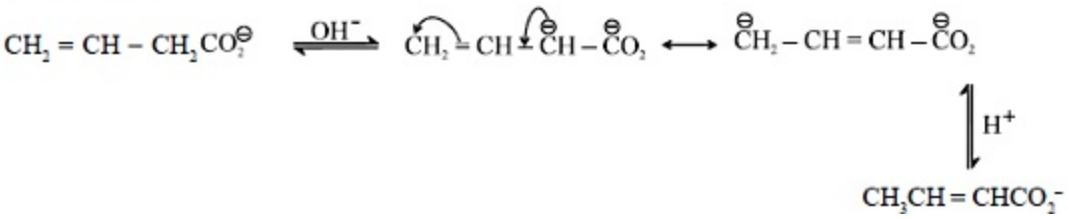


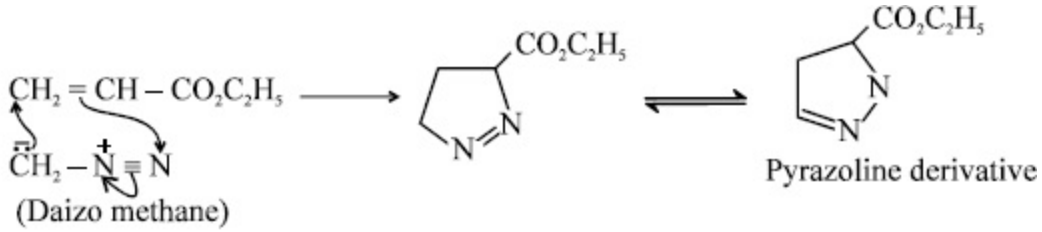
2. 

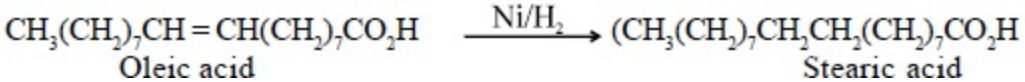
(β, γ unsaturated acid) (α, β unsaturated)

∴ Double bond migrates while warmed with NaOH to α, β position (important feature) from β, γ position, and it is a thermodynomically stable product.

Mechanism :



3. 

4. 

5. $CH \equiv C^{\ominus}Na^{\oplus} \xrightarrow{CO_2} CH \equiv CCO_2^{\ominus}Na^{\oplus} \xrightarrow{H^+(dil)} CH \equiv CCO_2H$ (Propiolic acid)

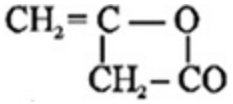
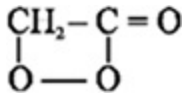
Ketens : Ketens are called as aldoketen (RCH = C = O) and ketoketen ($R_2C = C = O$).

Preperation :

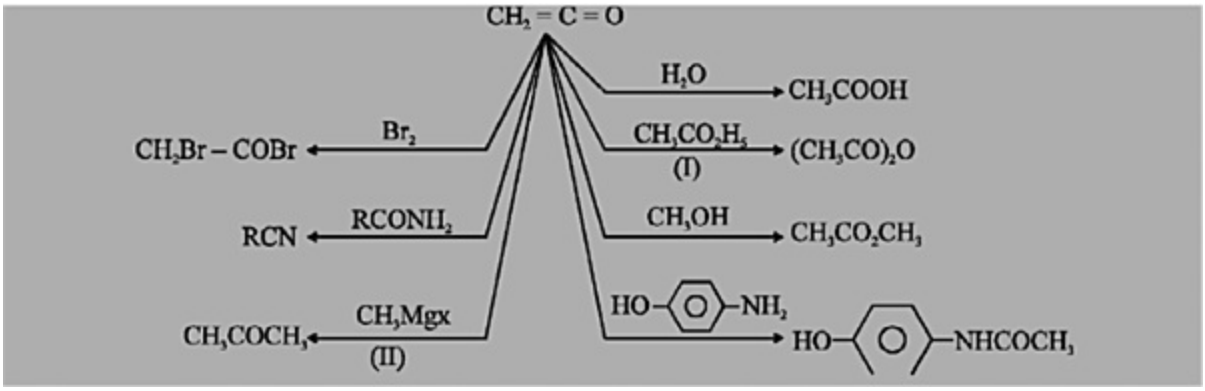
1. $CH_2(Br)-COBr \xrightarrow{Zn} CH_2 = C = O$

2. $CH_3COCH_3 \xrightarrow{\Delta} CH_2 = C = O$

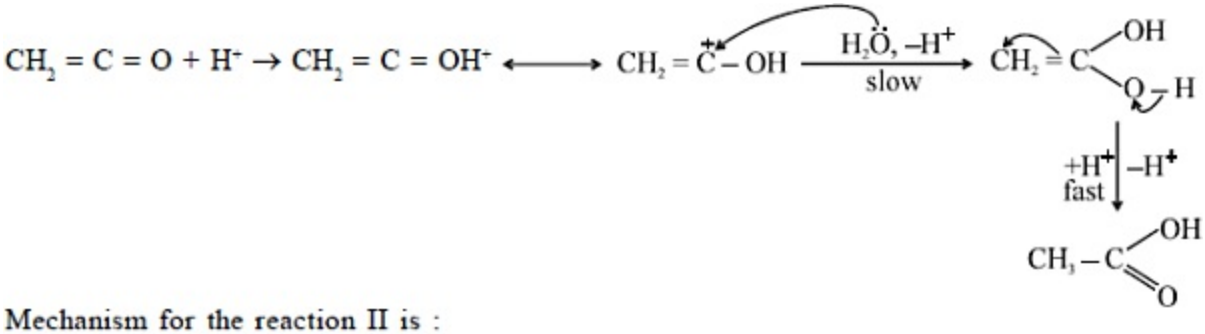
Physical properties :

It rapidly dimerises to diketen  and form peroxide  in air. Diketen can take part in Friedel Craft's reaction.

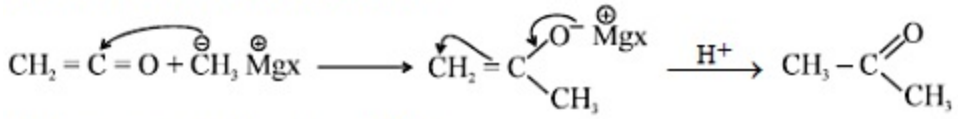
Chemical reactions :

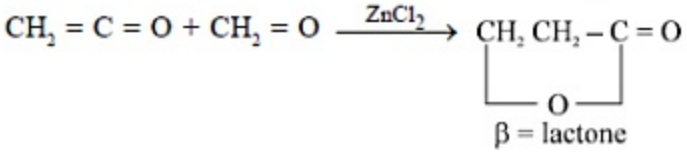


Mechanism is very simple. For the reaction I ;



Mechanism for the reaction II is :





Hydroxy acid :

1. $CH_2(Cl)-CO_2H \xrightarrow{NaOH} CH_2(OH)-CO_2H$

Similarly by hydrolysis β, γ etc. haloacids we get hydroxy acids.

Physical properties :

Two functional groups show their own properties and they are highly water soluble by extensive H-bonding with water.

Chemical reactions :

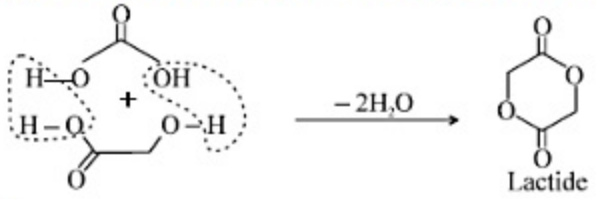
1. $CH_2(OH)-COOH \xrightarrow[\text{or } SOCl_2]{PCl_5} CH_2(Cl)-COCl \xrightarrow{H_2O} CH_2(Cl)-COOH$

2. $(CH_3)_2C(OH)CO_2H \xrightarrow{KMnO_4} (CH_3)_2CO + CO_2 + H_2O$ [Cleavage takes place]

$CH_3CH(OH)-CH_2CO_2H \xrightarrow{KMnO_4} [CH_3COCH_2CO_2H] \xrightarrow{-CO_2} CH_3COCH_3$

3. **Case - 1**

α-hydroxy acids by two moles gives lactide upon treatment with conc. H_2SO_4 or when heated.



Lactide

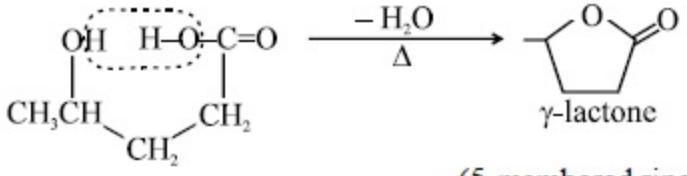
Case - 2

β-hydroxy acids when heated then α, β unsaturated carboxylic acid results.

$CH_3CH(OH)-CH_2COOH \xrightarrow{\Delta} CH_3CH=CH-CO_2H$

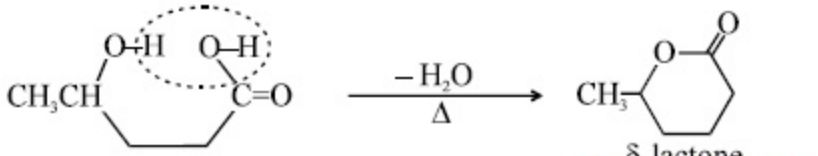
Case - 3

γ and δ hydroxy acids upon heating gives lactone.



γ-lactone

(5-membered ring, which is stable)

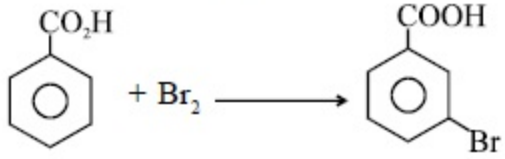


δ-lactone
(6-membered ring, highly stable)

Aromatic acids

1. **Schotten Baumann reaction :**

$PhCOCl + PhNH_2 + NaOH \rightarrow PhCONHPh$

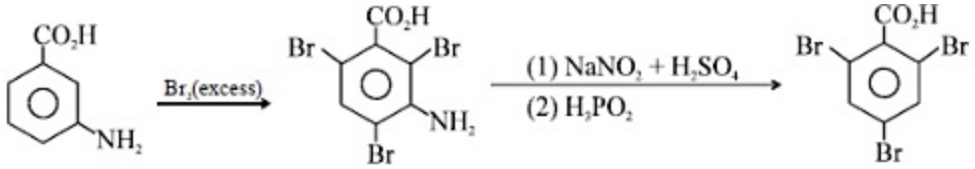
2. 

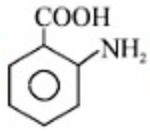
Benzoic acid also underoges normal ArSE reactions with other electrophiles.

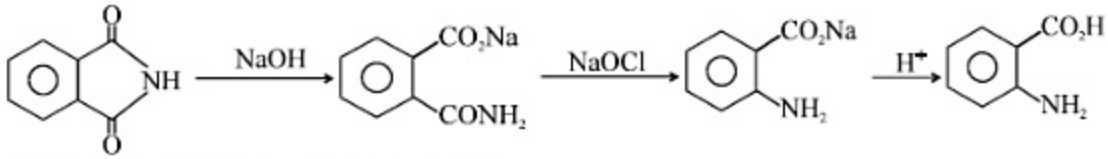
3. For iodination,

$$I_2 + AgSO_4 \xrightarrow[H_2O]{H^+} AgI + SO_4^{-2} + I^+.$$

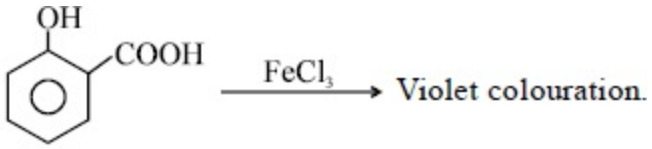


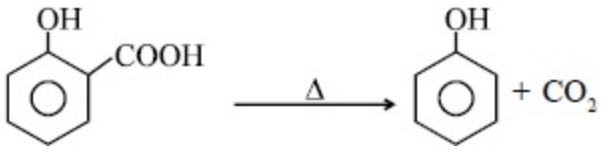
4. 

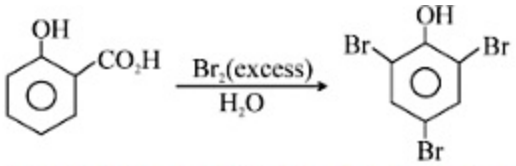
5. Anthralinic acid [] can be prepared in the following way;



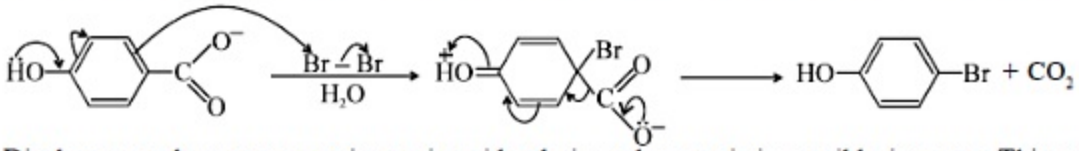
Anthralinic acid does not exist as zwitter ion.

6. 

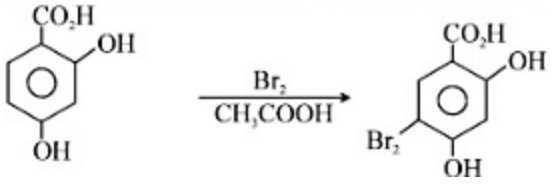


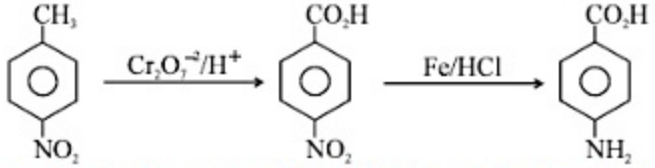
7. 

Decarboxylation is due to the assistance of –OH as shown by the following meachanism.



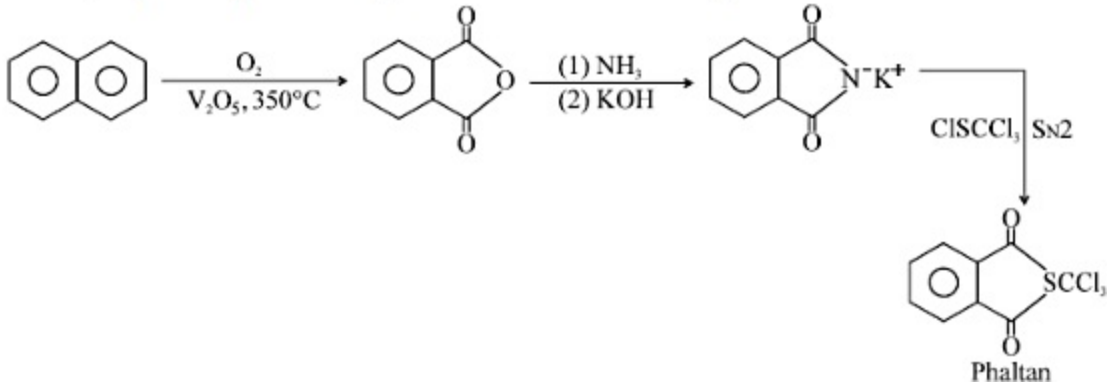
Displacement does not occur in acetic acid solution where as it is possible in water. This may be due to the common ion effect which may supress the $-COO^-$ formation.

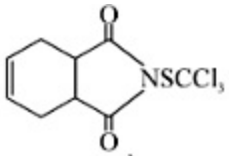


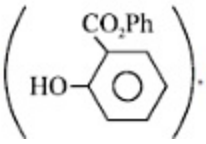
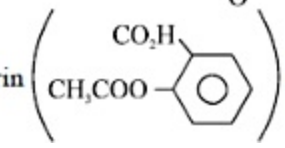
8. 

Para-aminno benzoic acid (PABA) is used in vitamin - B complex.

9. Phaltan, captan are poweful fungicides which are used in argriculture

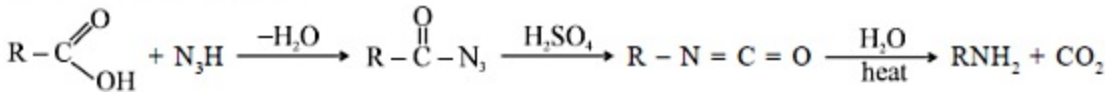


Also molecular structure of captan is 

10. Salol  , aspirin  are used as internal antiseptic and analgesic.

11. $Ar/RCOOH \xrightarrow[\text{distillation}]{\text{Conc. } H_2O_2} Ar/RCO_3H$ (per acid)

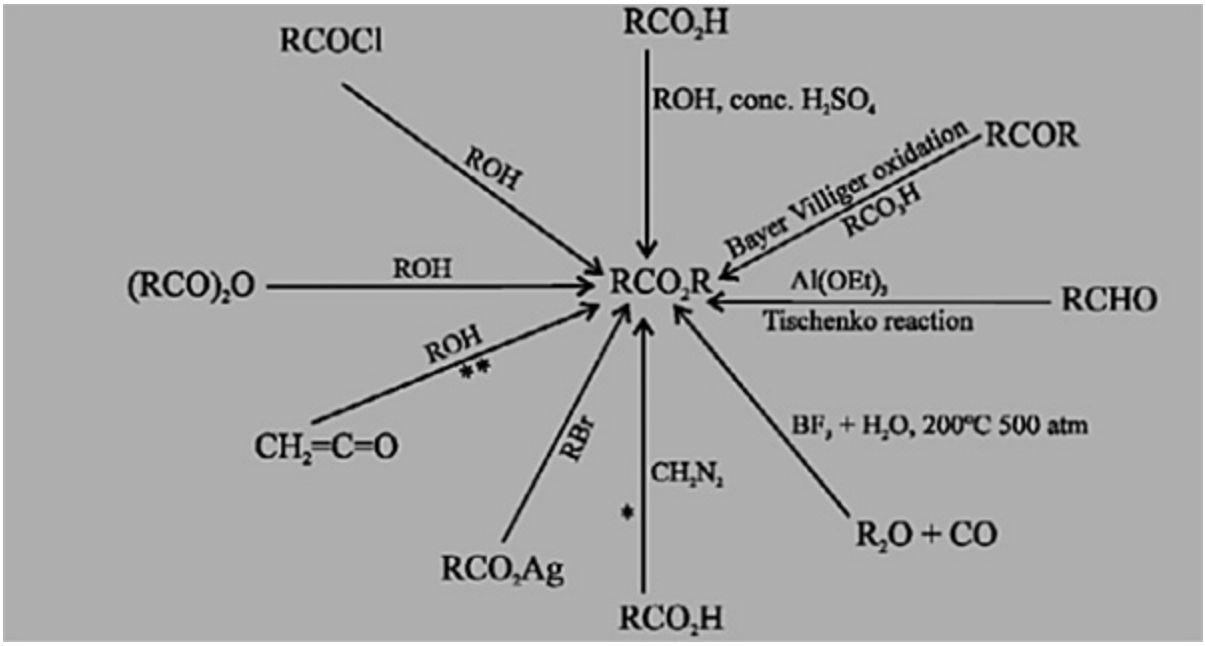
12. **Schmidt rearrangement :**



Carboxylic Acid Derivatives

Ester

Perparation :



*Product is RCO_2CH_3

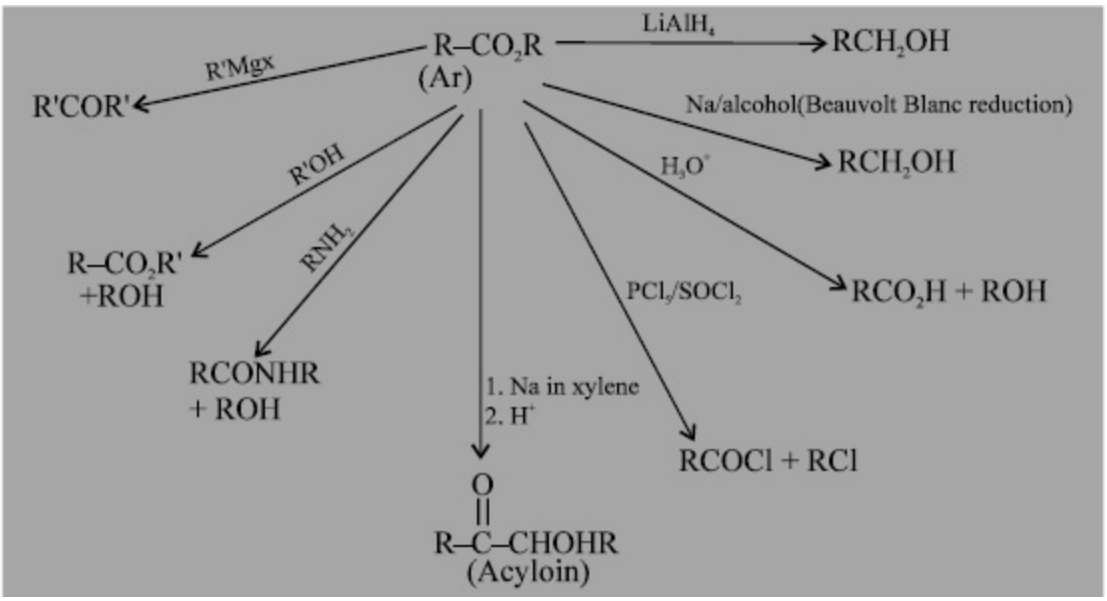
**CH_3CO_2R

The mechanisms for the above reactions already have been discussed.

Physical properties: Low boiling due to lack of H-bond and fair solubility in water is observed. They have pleasant odour.

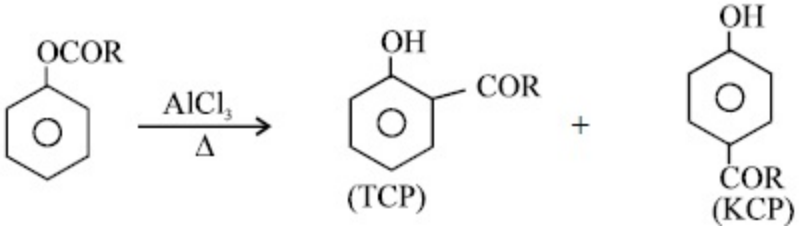
Chemical reactions :

1.



Other than the above reactions, some more important reactions are;

2. $R_2CO + CH_2CO_2Et \xrightarrow{R\bar{O}K^+} R_2C=C(CO_2Et)-CH_2CO_2Et$

3. 

4. **Ester Hydrolysis**

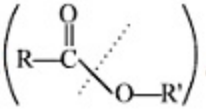
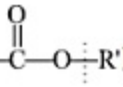
General reaction : $R-C(=O)-OR' + H_2O \overset{H^+}{\rightleftharpoons} RCOOH + R'OH$

The mechanism can be of eight types

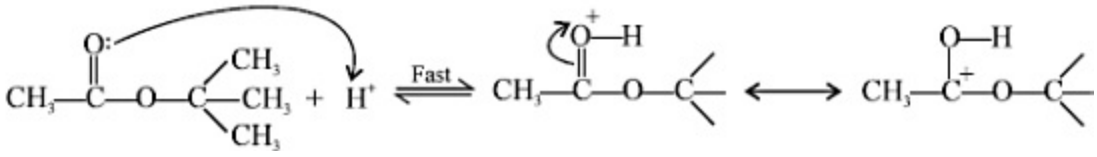
(1) AAL1 (very common for 3° alcohols)
(2) AAL2 (very very rare)
(3) AAC1 (special case)
(4) AAC2 (very common)

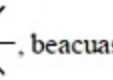
and similarly

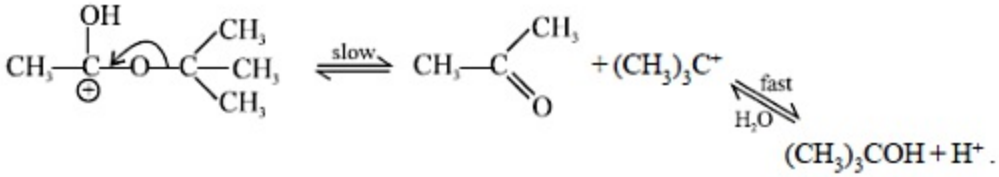
(5) BAL1 (special casses)
(6) BAL2 (rare)
(7) BAC1 (very very rare)
(8) BAC2 (very common)

Here A or B stands for acid or base catalysis, AC means acyl oxygen cleavage (i.e.  , AL means alkyl oxygen cleavage (i.e. ), 1, 2 means unimolecular, bimolecular respectively. We will discuss AAL1, AAC1, AAC2, BAC2 mainly which are actually of use.

Case - 1 : AAL1 :

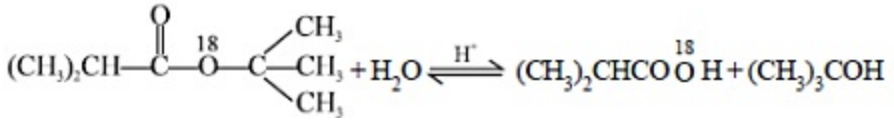


[Here we must understand sp^2 –O lp is a more donable basic site compared to  , beacuase of the stability of the conjugate acid]

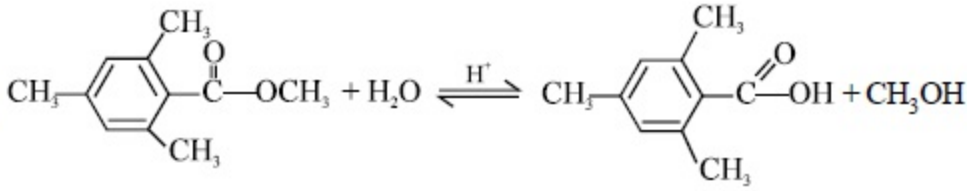


So, when it is a tert-methyl ester then only AAL1 is possible.

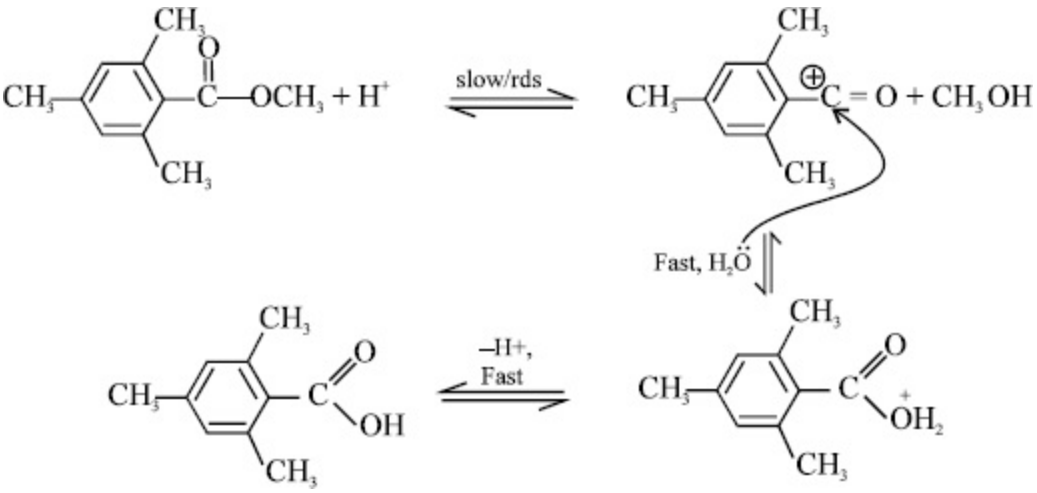
For example ;



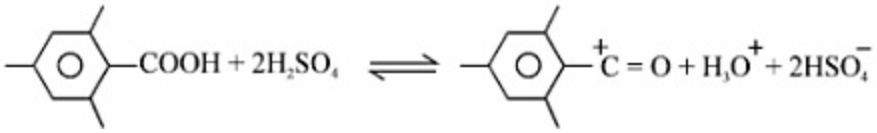
AAC1 : It is also a very rare mechanism and have been found with mesitoic ester.

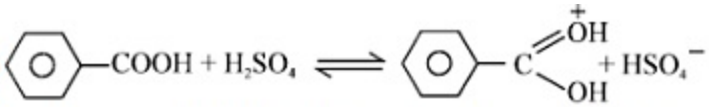
Reaction : 

Mechanism :



Actually this mechanism has been ascertained by the fact that when mesitoic acid is taken in conc. H_2SO_4, van't Hoff's factor '4' is observed and is due to,

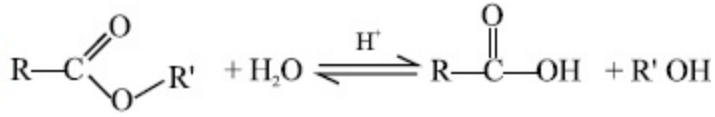


but for 

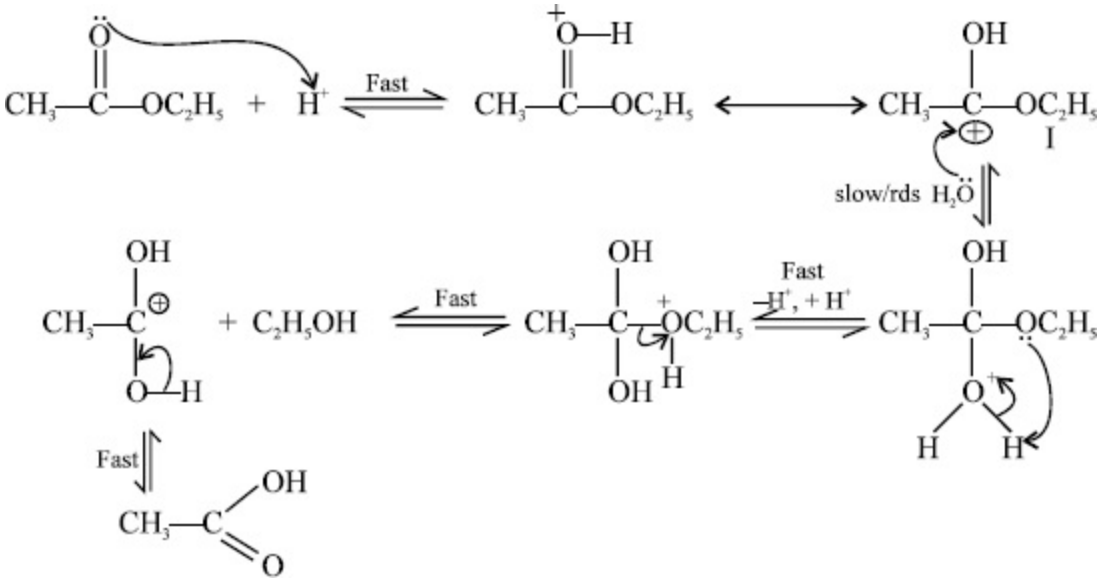
i = 2. Hence the reverse hydrolysis also must produce mesitoyl cation in the solution followed by attack by water. Therefore it is only applicable to mesitoic acid ester.

Case – 3: AAC2 :

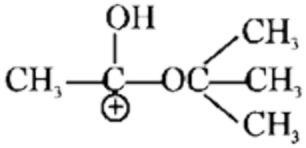
This is very common process and thus it is very important for us.

Reaction : 

Mechanism :



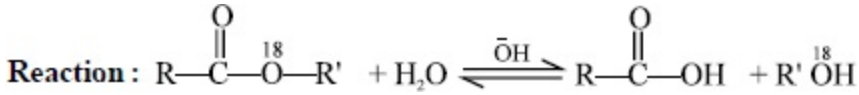
Look at the intermediate I, which is less sterically crowded compared to

 or no AACI,

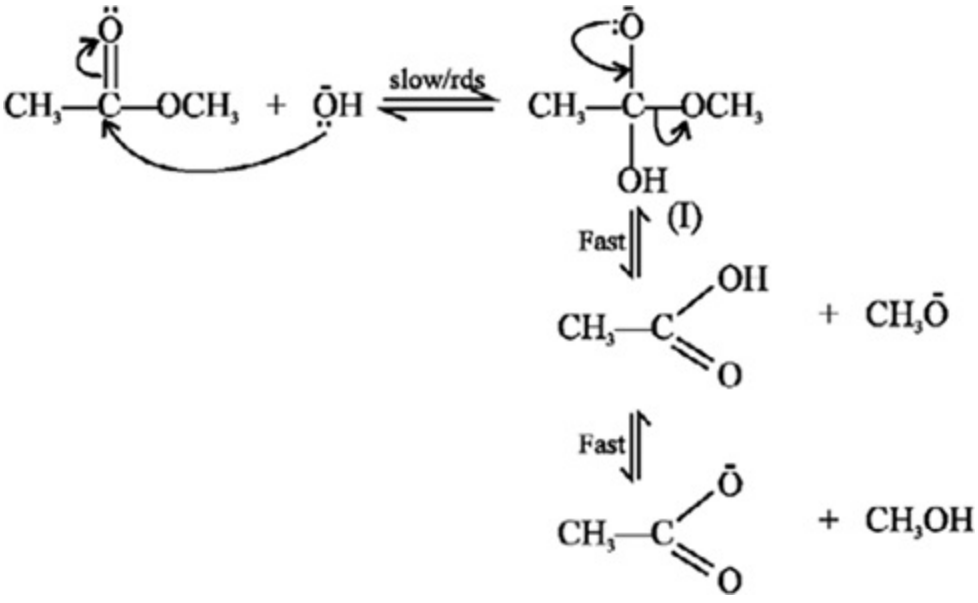
AAL1 is possible as $\overset{+}{C}H_3$ or $\overset{+}{C}_2H_5$ both are very unstable. Therefore the mechanism will follow AAC2.

Case-4 : BAC2

Only this mechanism is applicable in majority of the cases where base is a catalyst.



Mechanism :



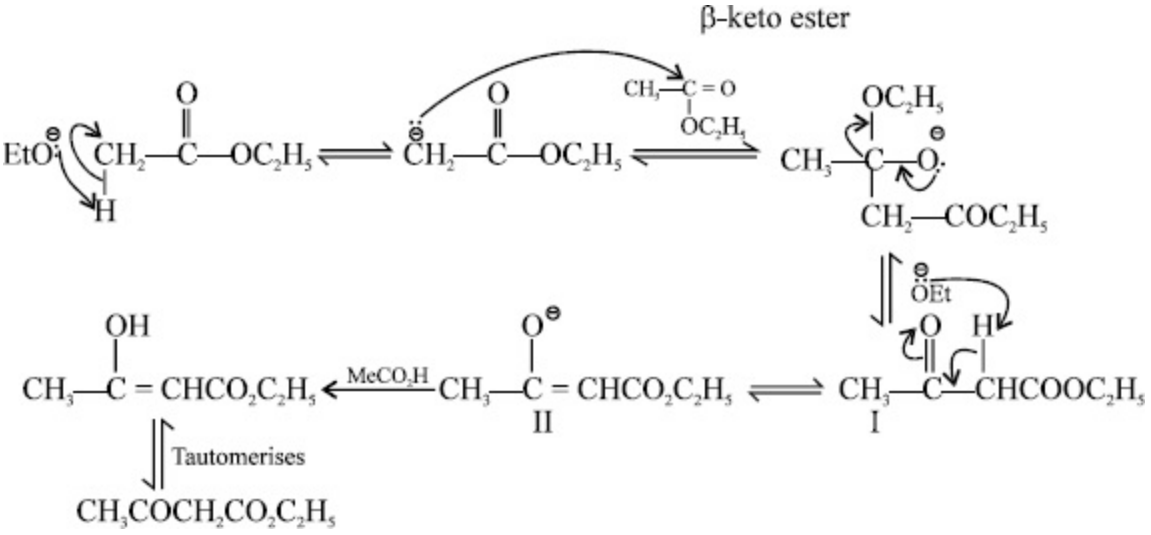
More and stronger withdrawing groups at R of $R-C(=O)-OR'$ and less the steric crowding at the tetrahedral intermediate I, faster will be the reaction.

For example ; $CH_2Cl-C(=O)-OC_2H_5$ hydrolyses faster than $CH_3-C(=O)-OC_2H_5$

Claisen ester condensation :

Reaction : $2CH_3CO_2C_2H_5 + \overset{\ominus}{O}Et \rightleftharpoons CH_3COCH_2CO_2C_2H_5 + EtOH$

Mechanism :



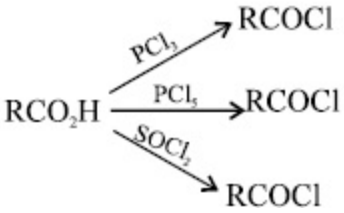
Upto I the yield is very very low and therefore further acidic −H is abstracted by the available base $\overset{\ominus}{O}Et$. I II formation is higly possible as I is stronger acid (pKa = 10.66) and removed in the anionic form from the solution and after that acidification leads to the present β−ketoester. I is very very less due to the fact that first equilibrium reaction lies mostly on the left due to low acidic strenger of $CH_3CO_2C_2H_5$ and also $CH_3COCH_2COOC_2H_5$ is stronger acid than C_2H_5OH (pKa = 15.9). Therefore if there is no acidic–H at I from the initial condition we use strong base like $\overset{\ominus}{Ph}\ Li^+$, $Ph_3\overset{\ominus}{C}Na^+$ etc. to make the first reversible reaction almost irreversible.

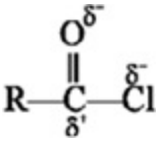
(2) Iodine value of fat or oil :

It means that number of gms of I_2 taken up by 100 gm of the fat or oil.

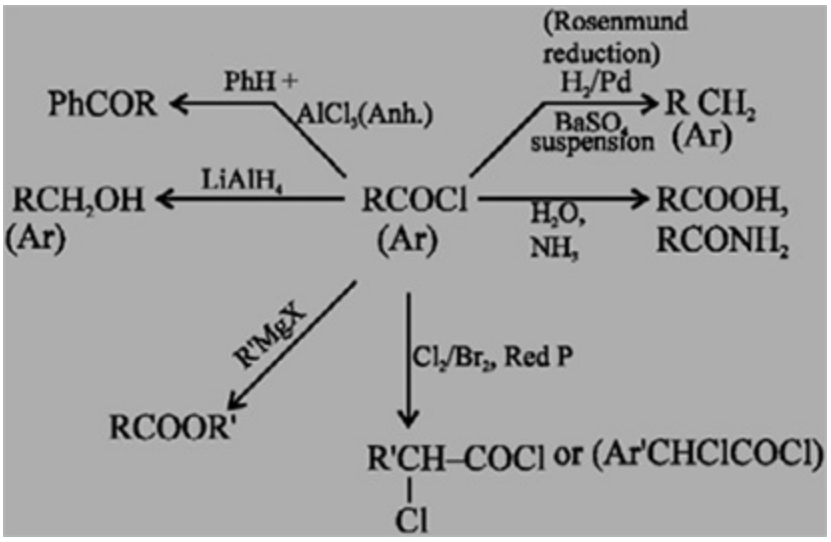
Acid Chloride (RCOCl)

Preperation:

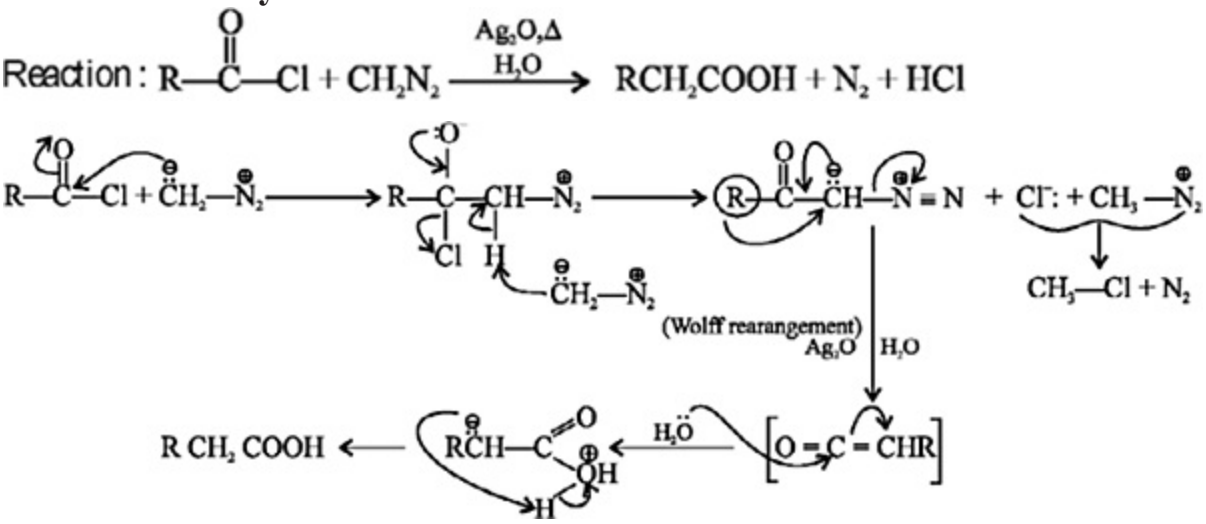


Structure and physical properties : As we know for chlorine –I > +R, therefore C of —COCl is more partially positively charged compared to that of ester.  has dipole moment μ = 2.9D. No inter-molecular hydrogen bond among the molecules and therefore it is low boiling and has irritating odour.

Chemical reaction :

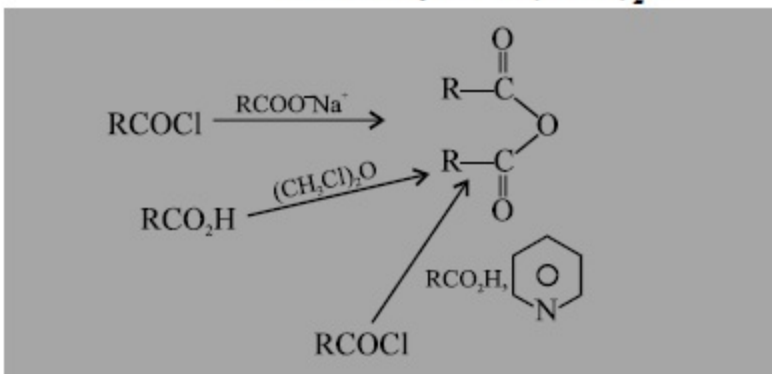


Arndt Eistert synthesis : Mecahanism :



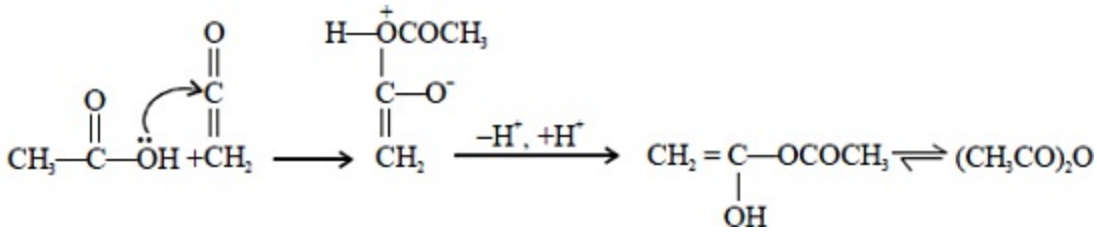
Acid anhydride $(RCO)_2O$

1.

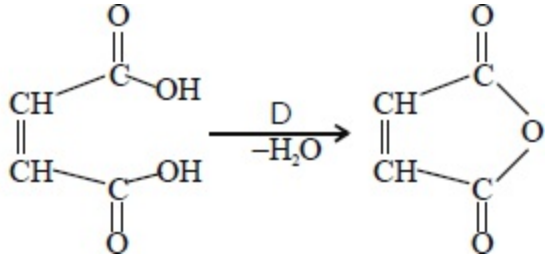


2. Also, $CH_2=C=O \xrightarrow{CH_3CO_2H} (CH_3CO)_2O$;

Mechanism :

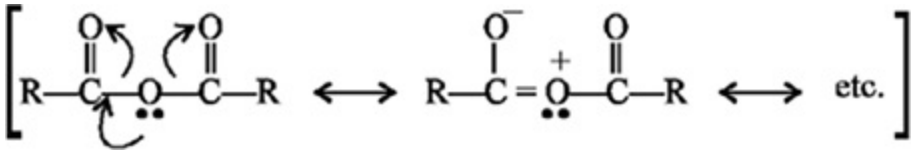


3.



Physical properties :

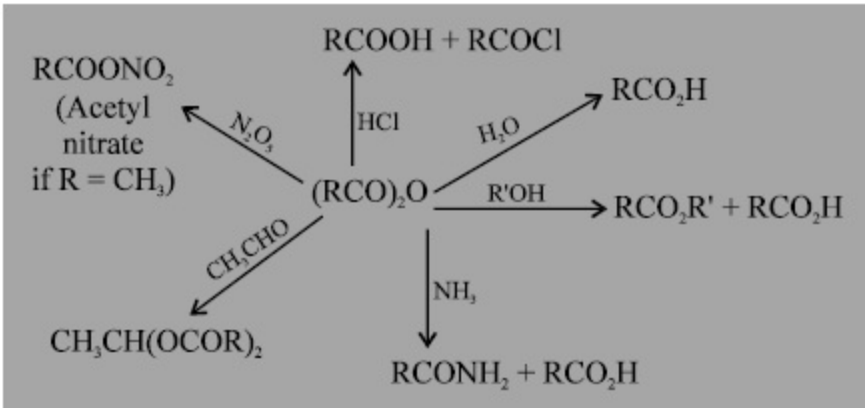
Because of high resonance energy (31 kcal/mole)



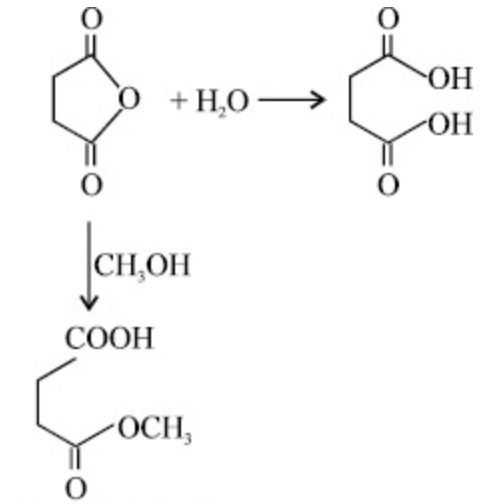
and negative charge delocalises on oxygen atoms therefore it cannot make H–bond with H_2O and therefore insoluble in water.

Chemical reactions :

1.

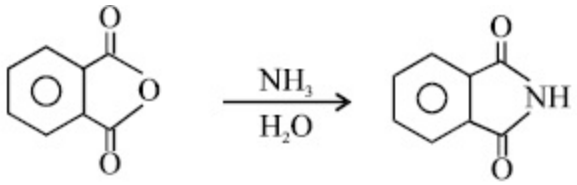


2.

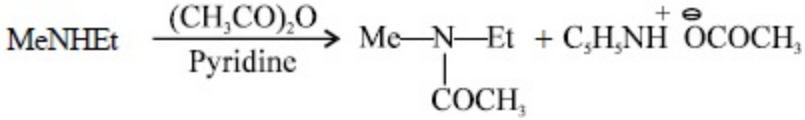


(Half acid ester)

3.



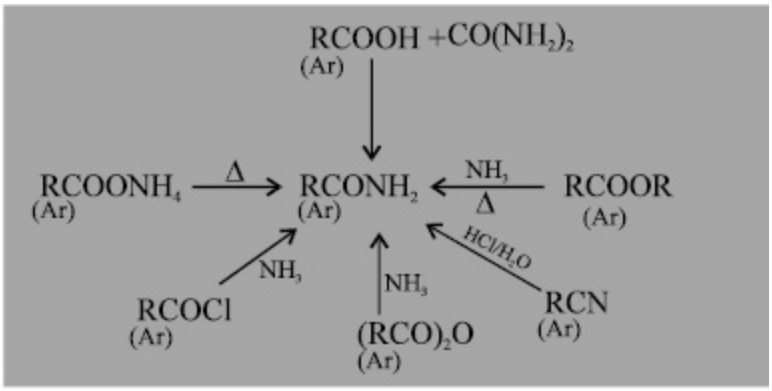
Phthalimide



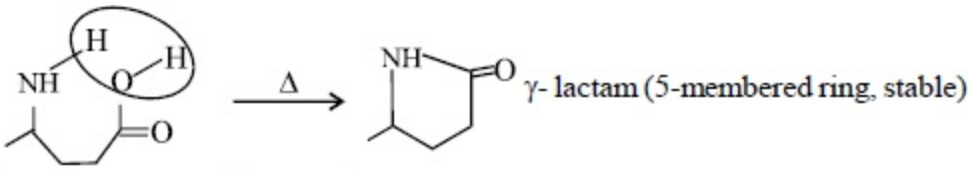
Amide ($-CONH_2$)

Preparation :

1.



Also,

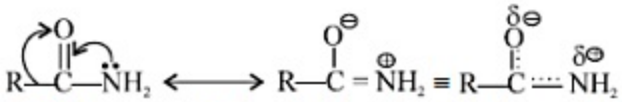
2. 

γ- lactam (5-membered ring, stable)

Also, in the above manner δ-lactam forms.

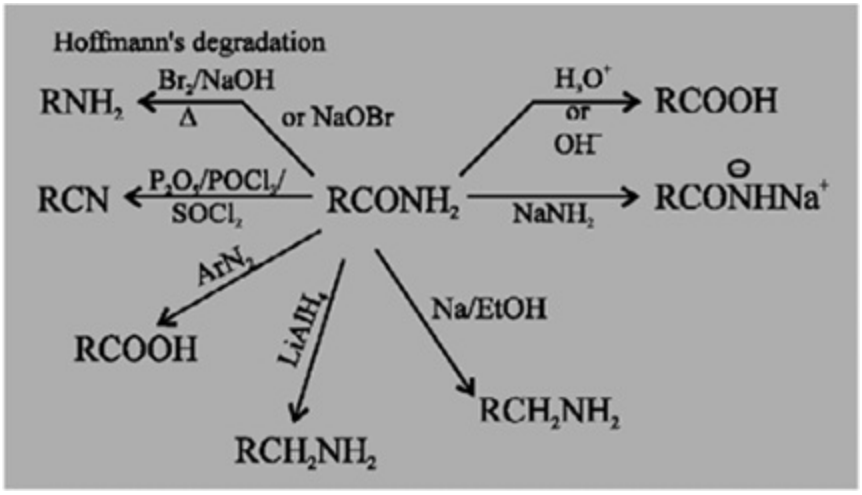
3. $RCH=CH_2 \xrightarrow[2)\ CO,\ R'NH_2]{1)\ H_2SO_4} RCH(CH_3)-C(=O)-NHR'$

Structure and physical propoerties:

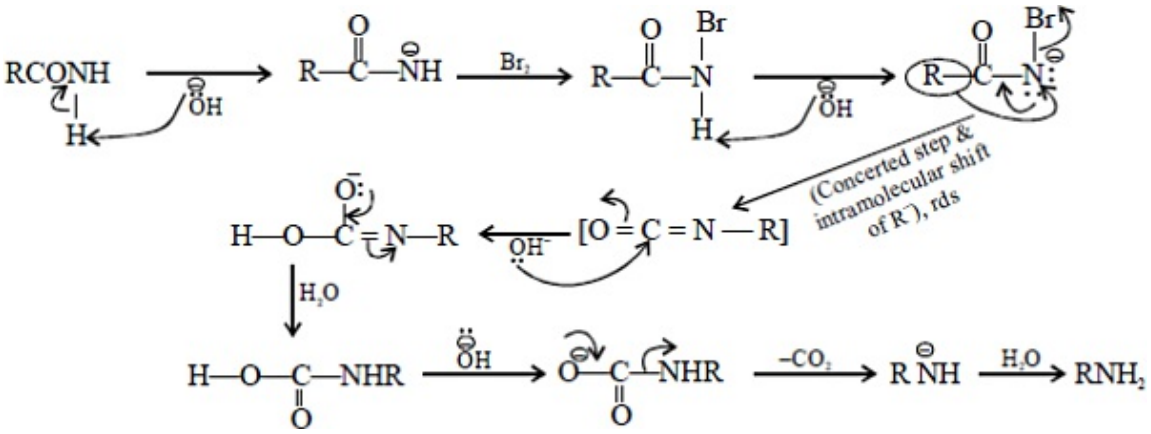


$\therefore NH_2$ has more +R than –I, therefore C is having less δ+ charge. Mp, bp are high because of H–bonding H of $-CONH_2$ is acidic.

Chemical reactions :

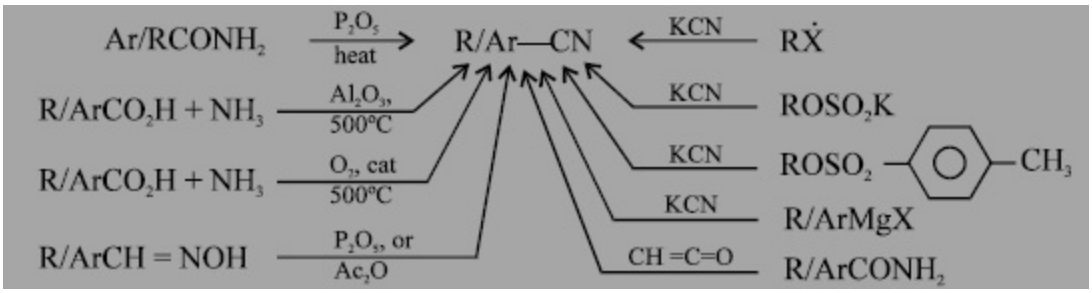


Mechanism for Hoffmann's bromamide synthesis or degradation :



Cyanide or Nitriles (-C ≡ N)

Preparation :



Physical properties :

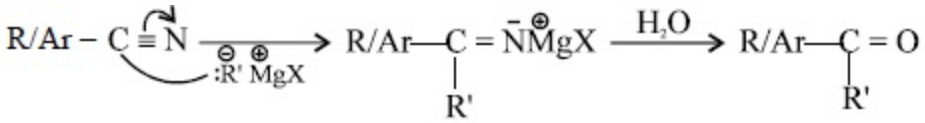
Alkane or arene nitriles $\left[\rightarrow C \equiv N\right]$ have large dipole moment values. Lower members of alkane nitriles are liquid, pleasant odour, but toxic. α –Hydroxy or α -amino nitriles are highly toxic. Due to high μ values they have high bps compared to alkane lower than R CO_2H. R – C ≡ N : are weak bases due to donable lps are on sp–N (of which electronegativity is vey high) $R—\overset{\delta+\ \delta-}{C}N$ work as an electrophiles

as well as nucleophiles and also can undergo addition reaction.

Chemical reactions :

(1) $Ar/RCN + LiAlH_4$ or Na/EtOH or $Pd/H_2 \rightarrow Ar/RCH_2NH_2$

(2) $R/ArCN \xrightarrow[\text{or}]{H_3O^+} R/Ar\,COOH + NH_3$
OH^-, H_2O

(3) 

(4) $R/Ar - C \equiv N \xrightarrow[\text{Distillation}]{SnCl_2, HCl / [H]} R/Ar\,CHO$ [Stephen's reduction reaction]

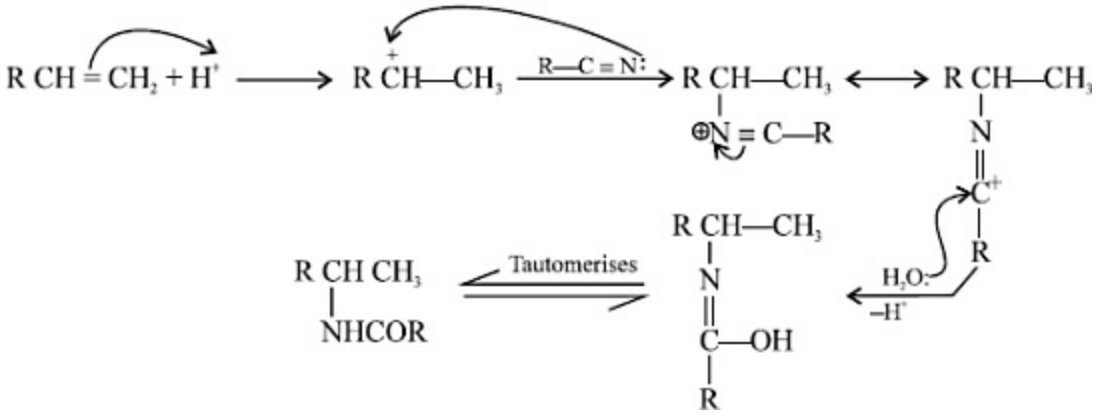
(5) $R/Ar{-}C \equiv N \xrightarrow[(\text{conc. } H_2SO_4)\ 2)\ H_2O]{1)\ R'OH,\ H^-} Ar/RCO_2R' + NH_4^+$

(6) $CH_2 = CH - C \equiv N \xrightarrow[(ii)\ H^+]{(i)\ HG,\ Base} G{-}CH_2CH_2CN$

[G = RO^-, RS^-, $RCOO^-$ R_2N^-, $R^-(Mg^+X)$] etc.

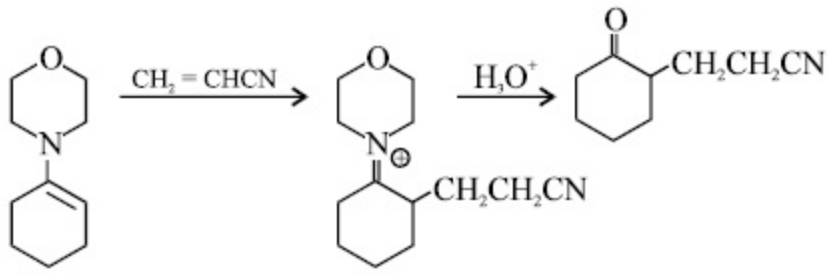
(7) $R - CH = CH_2 \xrightarrow[RCN]{H_2SO_4} R\,CH(CH_3){-}NHCOR$

Mechanism:



(8) $R/Ar - C \equiv N \xrightarrow{NH_3} R/Ar - \underset{\underset{NH}{\|}}{C}—NH_2$

(9)



(enamine)

Isocyanide or isonitriles (–N ≡ C)

Preparation :

(1) $R–X \xrightarrow{AgCN} RCN + RNC$ (as, $R–X + KCN \rightarrow RCN + RNC$]

(2) $RNH_2 + CHCl_3 + KOH$ (alcohol) $\xrightarrow{\Delta}$ RNC

Mechanism has been shown in the amine chapter.

(3) $Ar/RNHCHO \xrightarrow{POCl_3} R/ArNC$

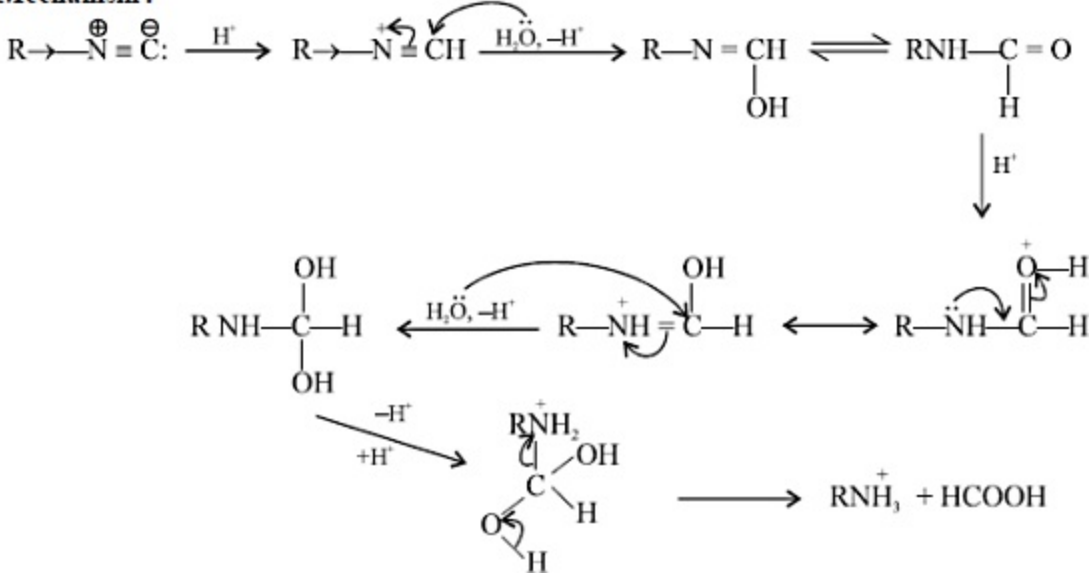
Physical Properties : $R\rightarrow\!\!—\overset{\oplus}{N} \equiv \overset{\ominus}{C} \longleftrightarrow R—N \overset{=}{=} C$

The above are the resonating structures of RNC. Similarly Ar–NC also has several resonating structures. In N—C, N is δ+, C is δ–, therefore they undergo addition reactions. RNC is basic through donable electron pair on carbon. RNC can not form H bond, therefore less soluble in water. Bp. of RCN > bp. of RNC, as they have less dipole moments compared to R–CN. These are very much poisonous.

Chemical Reactions :

(1) $RNC \xrightarrow{H_3O^+} \overset{+}{R}NH_3 + HCOOH$

Mechanism :



(2) $RNC \xrightarrow{Pt/H_2} RNHCH_3$

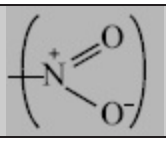
(3) $RNC + S \longrightarrow RNCS$

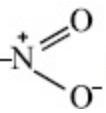
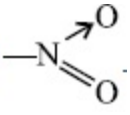
(4) $RNC + HgO \longrightarrow RNCO + Hg$

(5) $R-\overset{+}{N}\equiv\dot{C}: \xrightarrow{X-X} R-\overset{+}{N}\equiv C-X \xrightarrow{\ddot{X}^{\ominus}} R-N=CX_2$

(X = halogen ie, Cl_2, Br_2, I_2 etc.)

(6) $R-NC \xrightarrow[H_2O]{OH^-}$ No reaction.

Aliphatic and Aromatic nitro compounds 

The group nitro can be written as  or  . To understand the behaviour of $-NO_2$ group (-I. –R) it is better to represent nitro group in the initial fashion.

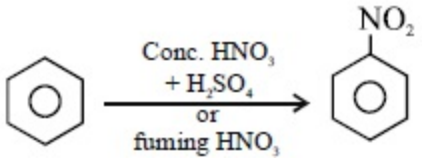
Preparation :

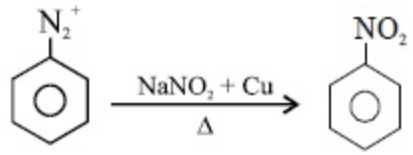
(1) $R-H \xrightarrow[\text{Liquid phase nitration}]{140^\circ C}$ Mixture of nitro alkanes (Already shown in alkane)

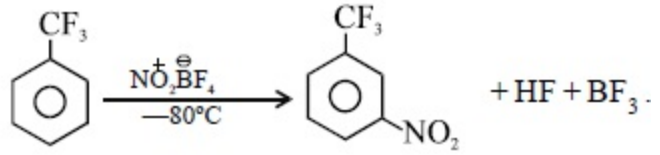
(2) $R-X \xrightarrow[\text{in } C_2H_5OH \text{ or DMF}]{AgNO_2} R-NO_2 + R-O-N=O$ (Nitrite)

(3) $R_3CNH_2 \xrightarrow{KMnO_4} R_3C-NO_2$

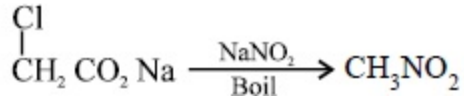
(4) $\begin{matrix} RCH=NOH \\ \text{or} \\ R_2C=NOH \end{matrix} \xrightarrow[\text{or } RCO_3H]{CF_3CO_3H} \begin{matrix} RCH_2NO_2 \\ \text{or} \\ R_2C=CHNO_2 \end{matrix}$

(5) 

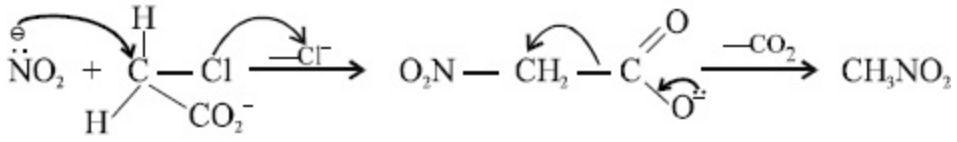
(6) 

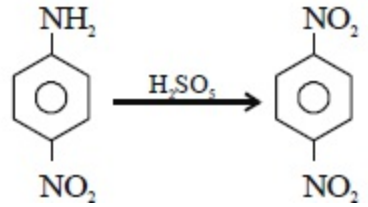
(7) 

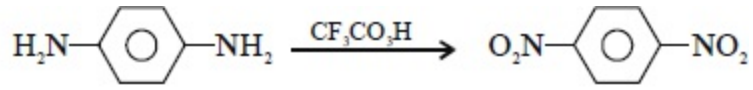
$+ HF + BF_3$.

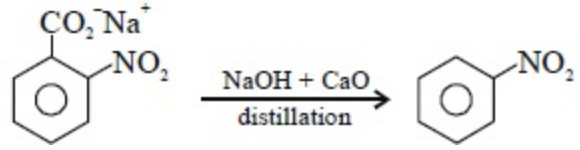
(8) 

Mechanism :



(a) 

(b) 

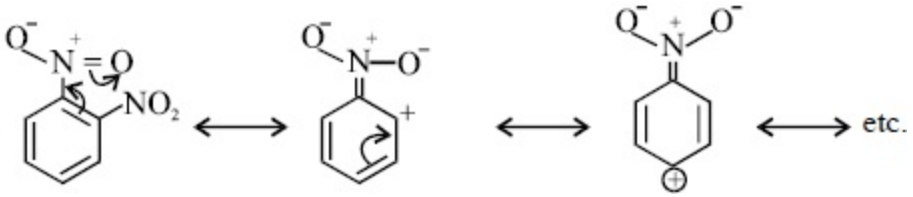
(c) 

Structure and Physical properties :

The following resonance occurs in nitro group for nitroalkanes.



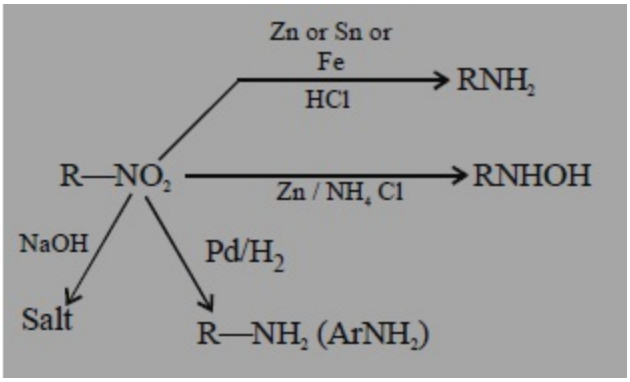
For nitro arenes,



Phenyl ring also takes part in resonance with $-NO_2$ group which has strong –I, –R effect. Nitroarenes have more dipole moment than nitroalkanes by usual reason of large charge separation. Nitroarenes are yellow in colour and soluble in organic solvents. Nitro alkanes show solubility in water due to H-bonding but not nitroaranes.

Chemical reactions :

(1)

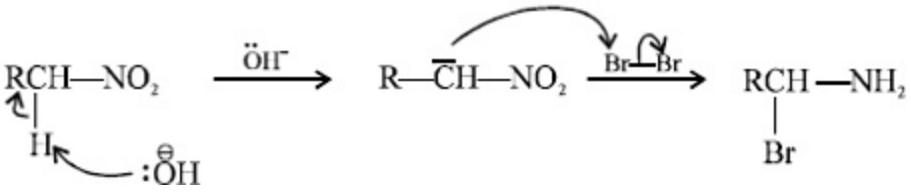


(2) $RCH=NO_2^-Na^+ \xrightarrow{SnCl_2/HCl} RCH=NOH$

(3) $RCH_2NO_2 \xrightarrow{\text{Boiling HCl}} RCO_2H + NH_2OH + HCl$

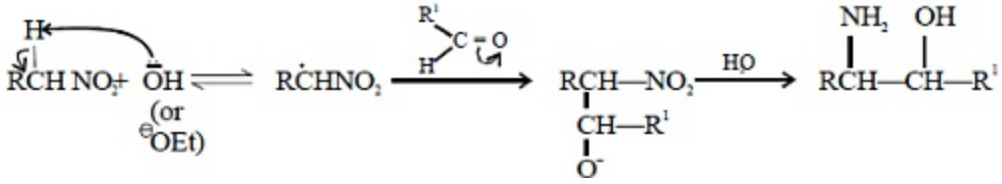
$RCH_2NO_2 \xrightarrow{NaOH + Br_2} RCH(Br)-NO_2$

Mechanism :



(4) $RCH_2NO_2 + R^1CHO \xrightarrow{OH^-} RCH(NO_2)-CH(OH)-R^1$

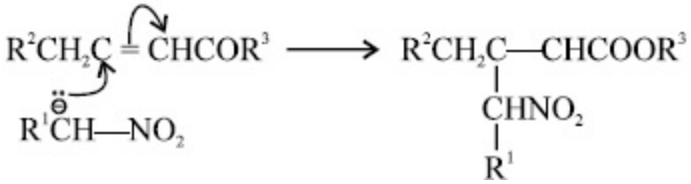
Mechanism :



(5) $R^1CH_2NO_2 \xrightarrow[2)\ HCl]{1)\ \overset{\ominus}{O}Et,\ R^2CH_2CH=CHCOOR^3} R^2CH_2C(CH_2CO_2R^3)(R^1)CHNO_2$

Mechanism :

$$R^1CH_2NO_2 + \overset{\ominus}{O}Et \rightleftharpoons R^1\overset{\ominus}{C}HNO_2 + EtOH$$

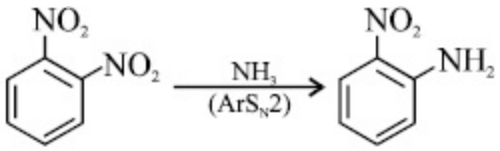


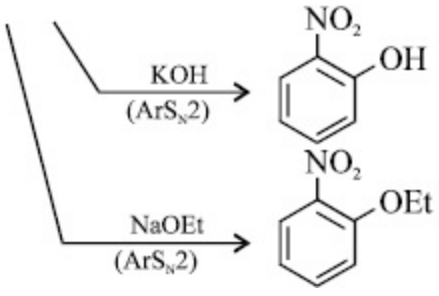
Initially 1, 4 addition and then 3, 4 addition. This above is an example of Michael addition.

(6) (a)

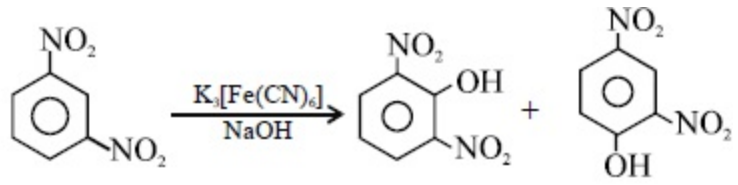


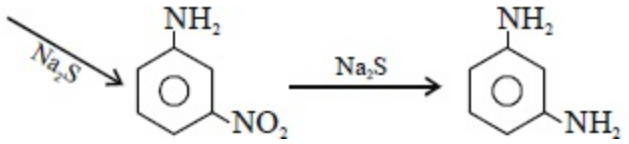
(b)



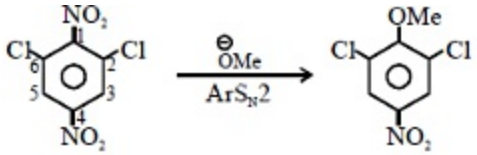


(7)



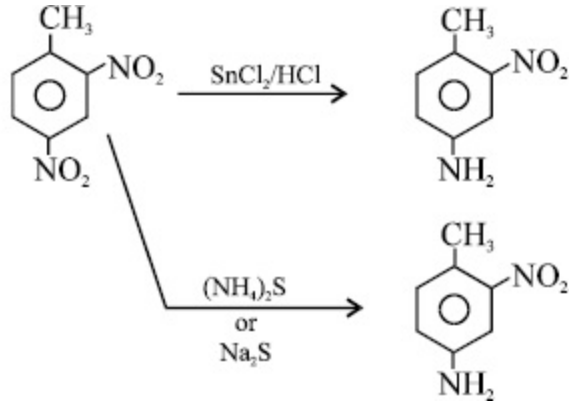


(8)

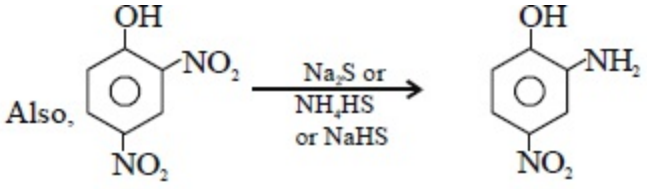


NO_2 at C_4 will not be displaced as σ-complex anion becomes stable when attacks at C1. It sholuld be remembered that NO_2 at C1 is out of plane due to steric inhibition of resonance.

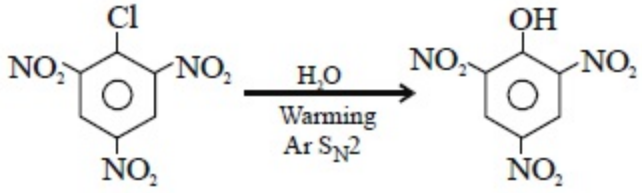
(9)



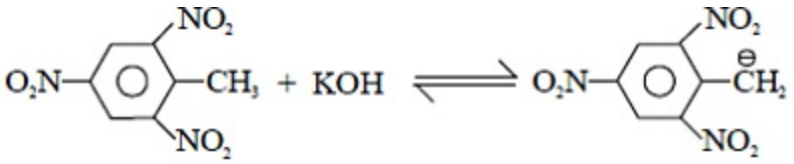
Here we should remember that selective reduction is taking place in the above reactions.



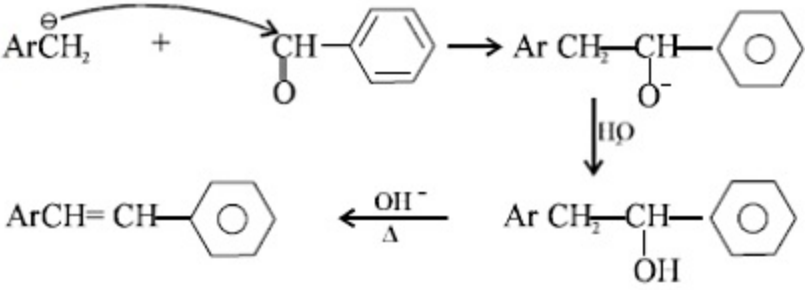
(10)

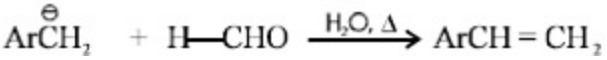


Activated ArS_N2 takes place due to high activation in S_N by NO_2 groups.

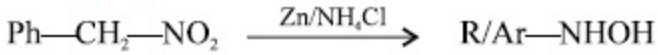
(11) 

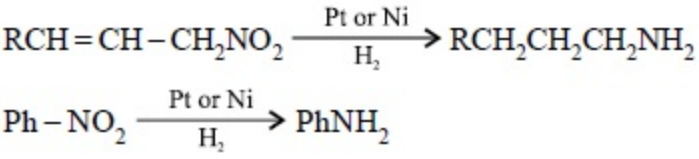
The above carbanion can easily undergo aldol condensation.

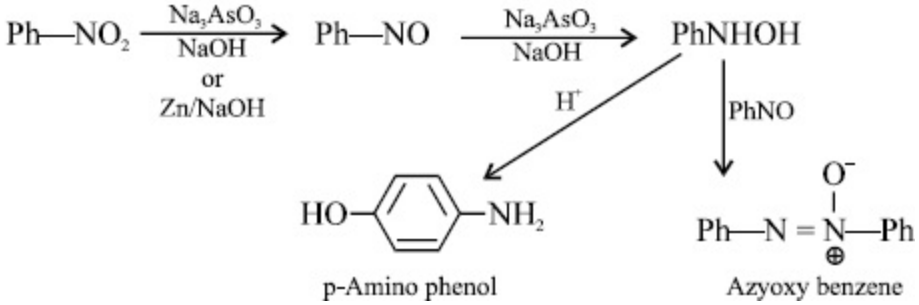
For example ; 

(b) 

(12) $PhCH_2NO_2$ shows tautomerism.

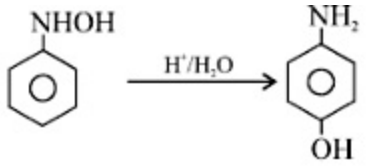


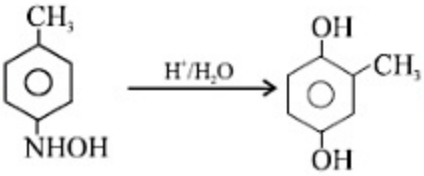
(13) 

(14) 

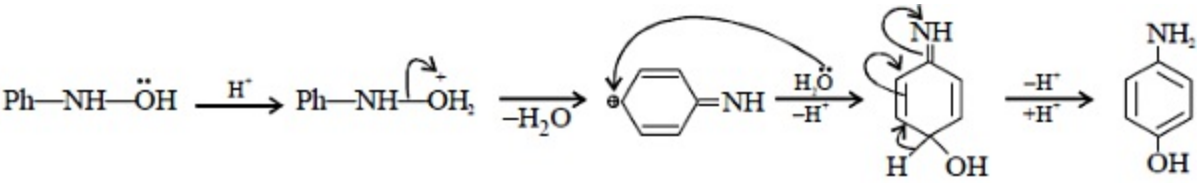
p-Amino phenol Azyoxy benzene

(15) Phenyl hydroxyl amine- p-amino phenol rearrangement:

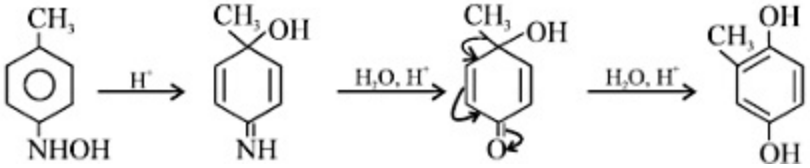


But ,

i.e., when p-position is blocked then, quinol derivative forms.

Mechanism :



For the second one,



(16) $RCH_2 - NO_2$ show acidic behaviour ($pKa \simeq 9$).

$$RCH_2NO_2 \xrightarrow{NaOH} RCH = N\begin{matrix} O^-Na^+ \\ O^- \end{matrix}$$

$$RCH_2NO_2 \xrightarrow[H_2O]{H^+,} RCOOH + \overset{+}{N}H_3OH.$$

(17) When 1°/2° nitroalkanes are treated with H_2SO_4, aldehydes and ketones are respectively formed and the process is called as Nef carbonyl synthesis.

$$RCH_2NO_2 \xrightarrow{H_2SO_4} RCH = O$$

$$R{-}\underset{R}{\underset{|}{CH}}{-}NO_2 \xrightarrow{H_2SO_4} R{-}\underset{R}{\underset{|}{C}} = O$$

3° nitroalkanes donot show Nef carbonyl synthesis reaction.

Aliphatic and Aromatic amines (– NH_2)

(i.e. aniline and its derivatives)

Amines are the derivatives of NH_3 in which alkyl or aryl group is present. It can be 1° (R– NH_2), 2° + (R_2NH), 3° (R_3N) and quarternary ammonium salt ($R_4N^+X^-$) as well as aminium salt ($RN^+H_3X^-$, $R_2\overset{+}{N}H_2X^-$, $R_3\overset{+}{N}HX^-$ etc.) . Amines can be mixed aliphatic and aromatic both.

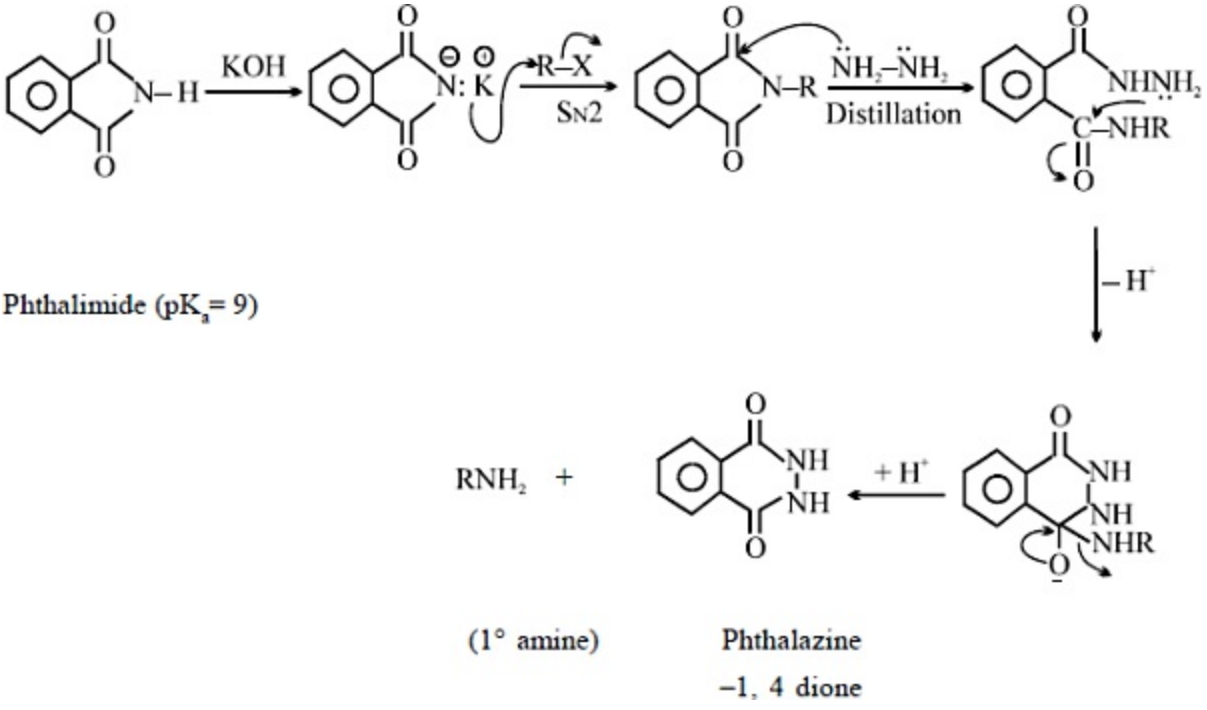
Preparation :

(1) $R\!-\!X + \ddot{N}H_3 \xrightarrow{S_N2} R\overset{+}{N}H_3\bar{X} \xrightarrow{OH^-} RNH_2\,(1°)$

(Alkyl halide)

By this method multiple alkylations occur and produce R_2NH, R_3N, $R_4N^+X^-$. Multiple alkylations can be reduced by using excess NH_3.

The best method is Gabriel's phtalimide synthesis using phthalimide as the starting material. The process is,



If we use 3°, R – X then we get elimination product.

(2) $R - X + \overset{-}{N}=\overset{+}{N}=\overset{-}{N} \xrightarrow{S_N2} R - N_3 + \overline{X}$

(Explosive)

$\downarrow$ Na / C_2H_5OH or $LiAlH_4$

RNH_2

(1°)

(3) $Ar- X \xrightarrow{NaNH_2 / NH_3(\ell)} Ar- NH_2$

(4) $RCHO \xrightarrow[Ni/H_2]{NH_3} RCH_2NH_2 + (RCH_2)_2 NH + (RCH_2)_3N$

(5) $Ar/RCN \xrightarrow[\text{or } Na / C_2H_5OH]{LiAlH_4} Ar/R–CH_2NH_2$

(6) $Ar/R.CONH_2 \xrightarrow{LiAlH_4} R/Ar - CH_2NH_2$

(7) $RCH{=}NOH$ (Oxime) $(ArCH = NOH) \xrightarrow[\text{or } LiAlH_4]{Na / C_2H_5OH} R/Ar\ CH_2NH_2$

(8) $R\ \overset{\ominus}{\underset{\oplus}{MgCl}} \xrightarrow[S_N2]{Cl–NH_2} R - NH_2 + MgCl_2$

(9) (a) $RCON_3 \xrightarrow[\text{Curtius rearrangement}]{\Delta} RN = C = O \xrightarrow{OH^-, H_2O} RNH_2 + HCO_3^-$

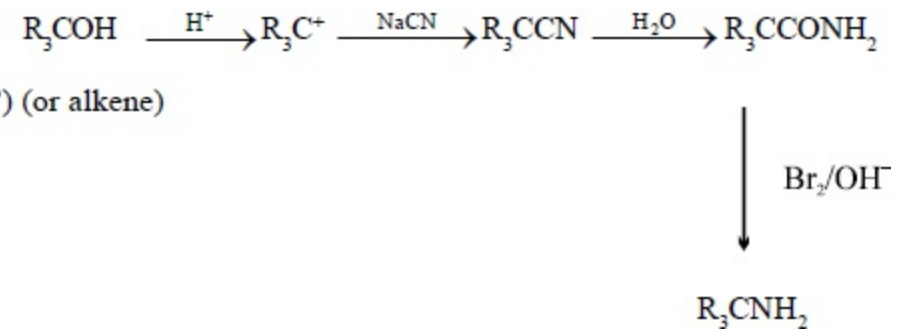
(b) $RCONHOH \xrightarrow[\text{Lossen rearrangement}]{H^+ \text{or } OH^-} R– N= C = O \xrightarrow{OH^-, H_2O} RNH_2 + HCO_3^-$

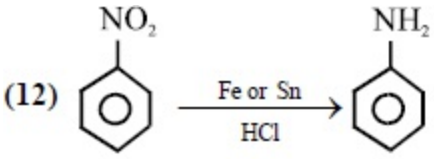
(c) $RCOOH \xrightarrow[\text{Schmidt rearrangement}]{N_3H, H^+} R - N = C = O \xrightarrow{OH^- / H_2O} RNH_2 + HCO_3^-$

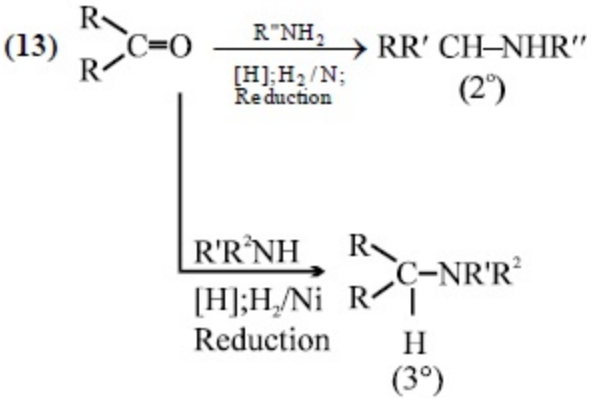
(10) $RCONH_2 \xrightarrow[\text{or } \overset{\ominus}{O}Br]{Br_2 / KOH} R –NH_2$

Hoffmann's degradation

(11) Ritter's reaction :

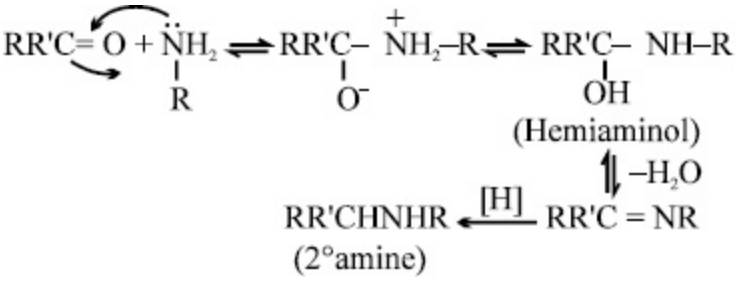




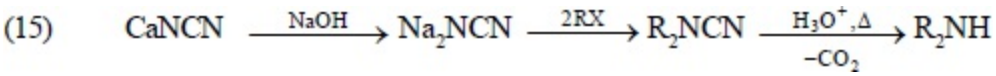


The above process in which 1°, 2°, 3° amines can be formed is called as reductive amination process.

Mechanism :

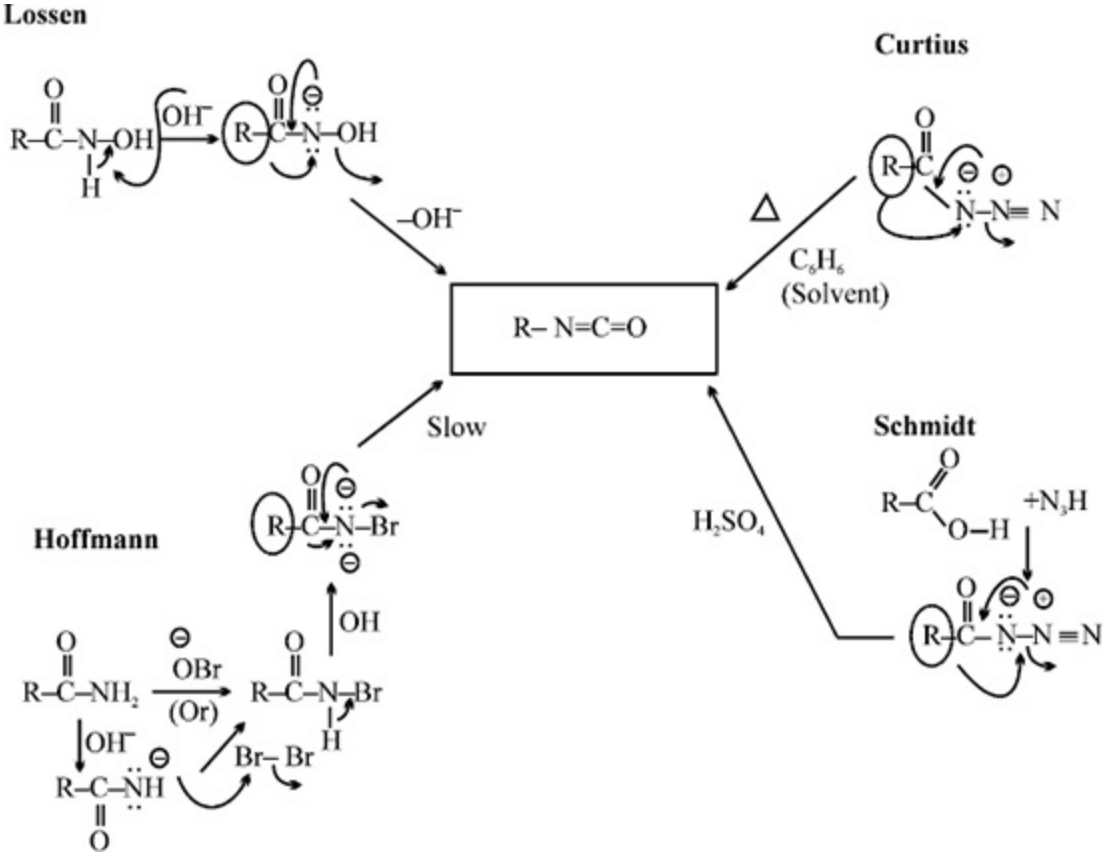


Reducing reagents also can be $NaBH_3CN$, $LiBH_3CN$ etc.



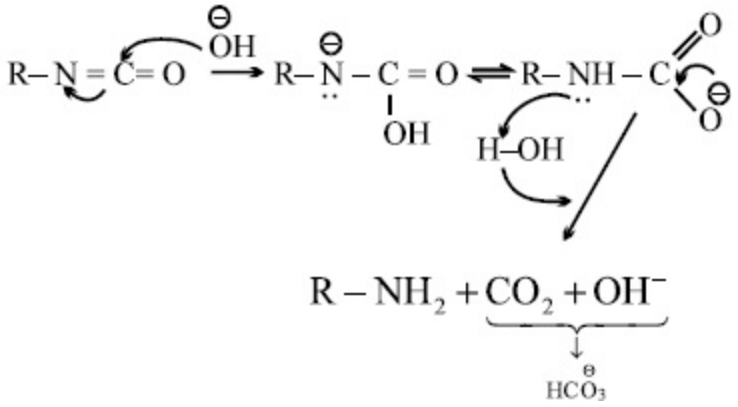
Lossen, Curtius, Schmidt and Hoffman's degradation all mentioned above in

which alkyl or aryl isocyanate compound is produced, on further hydrolysis (base catalysed) yield amine and bicarbonate ion (or CO_2) as shown below with mechanism.

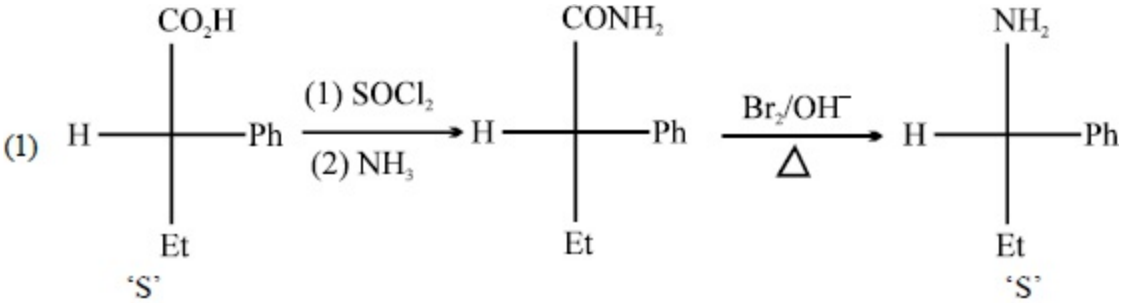


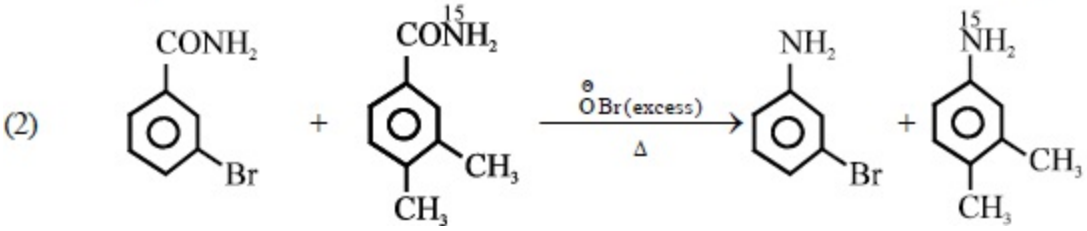
In every case loss of leaving groups $\bar{O}H$, N_2, Br– etc. and migrtion of the $\overset{\ominus}{R}$ is a concerted step i.e. both occur at the same time. If the migrating group is aryl with electron donating ability at the suitable position (eg. para) increases the rate of migration. Also in every cases the rearrangements are intramolecular in nature and no change in the configuration of the migrating group takes place. It is worth mentioning that the migration origin is C and migration terminus is N. Once R – N = C = O forms it can further be hydrolysed to $RNH_2 + HCO_3^-$ (or CO_2 etc.)

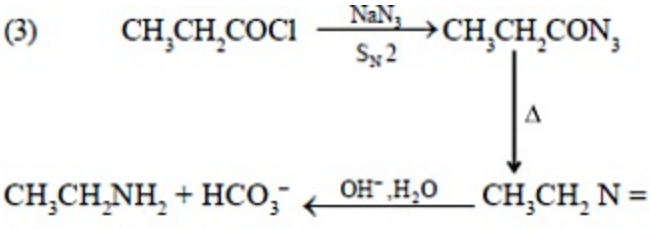
Mechanism :

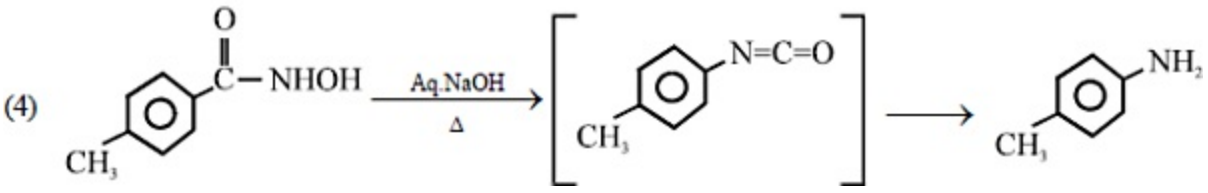


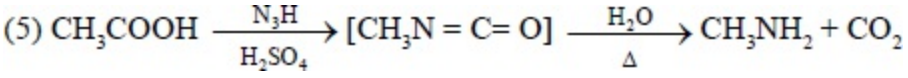
Examples of Hoffmann (1,2) , Curtius (3), Lossen (4) and Schmidt (5) rearrangement reactions ;





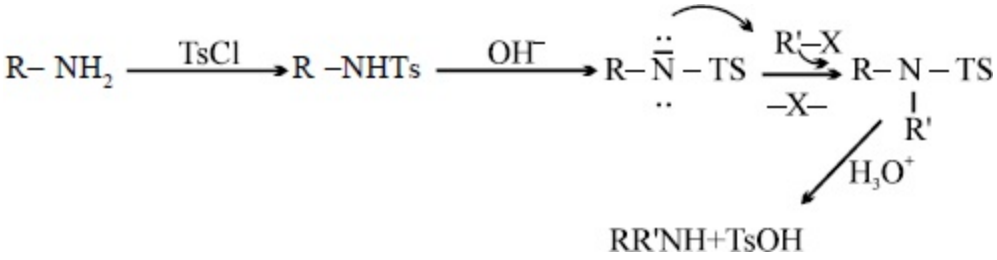






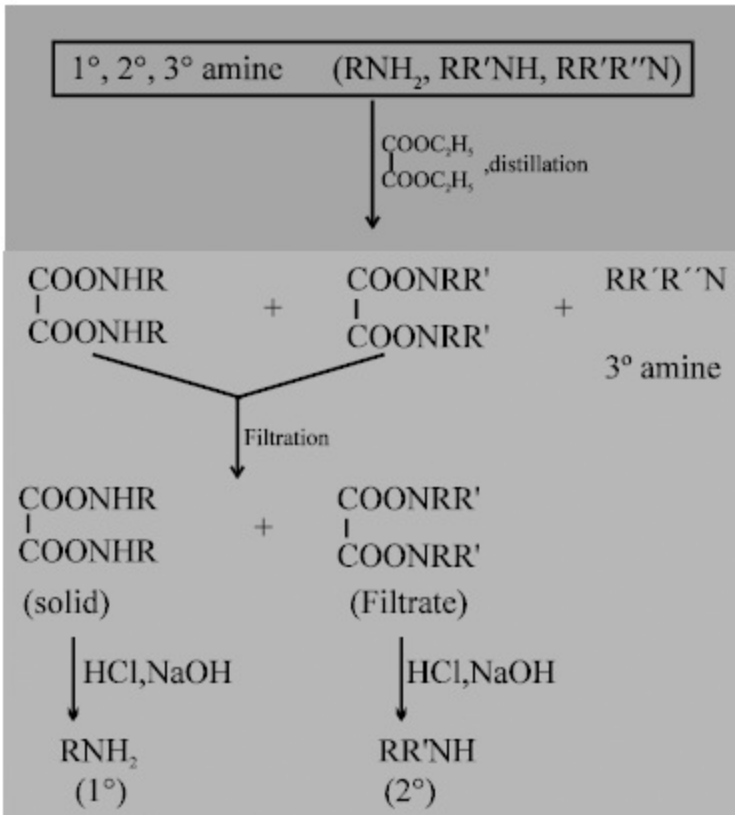
To prepare 2° amine, we convert R- NH_2 into RNH –Ts and then using base

NaOH, RX, H_3O^+, we get 2° amine as shown below.



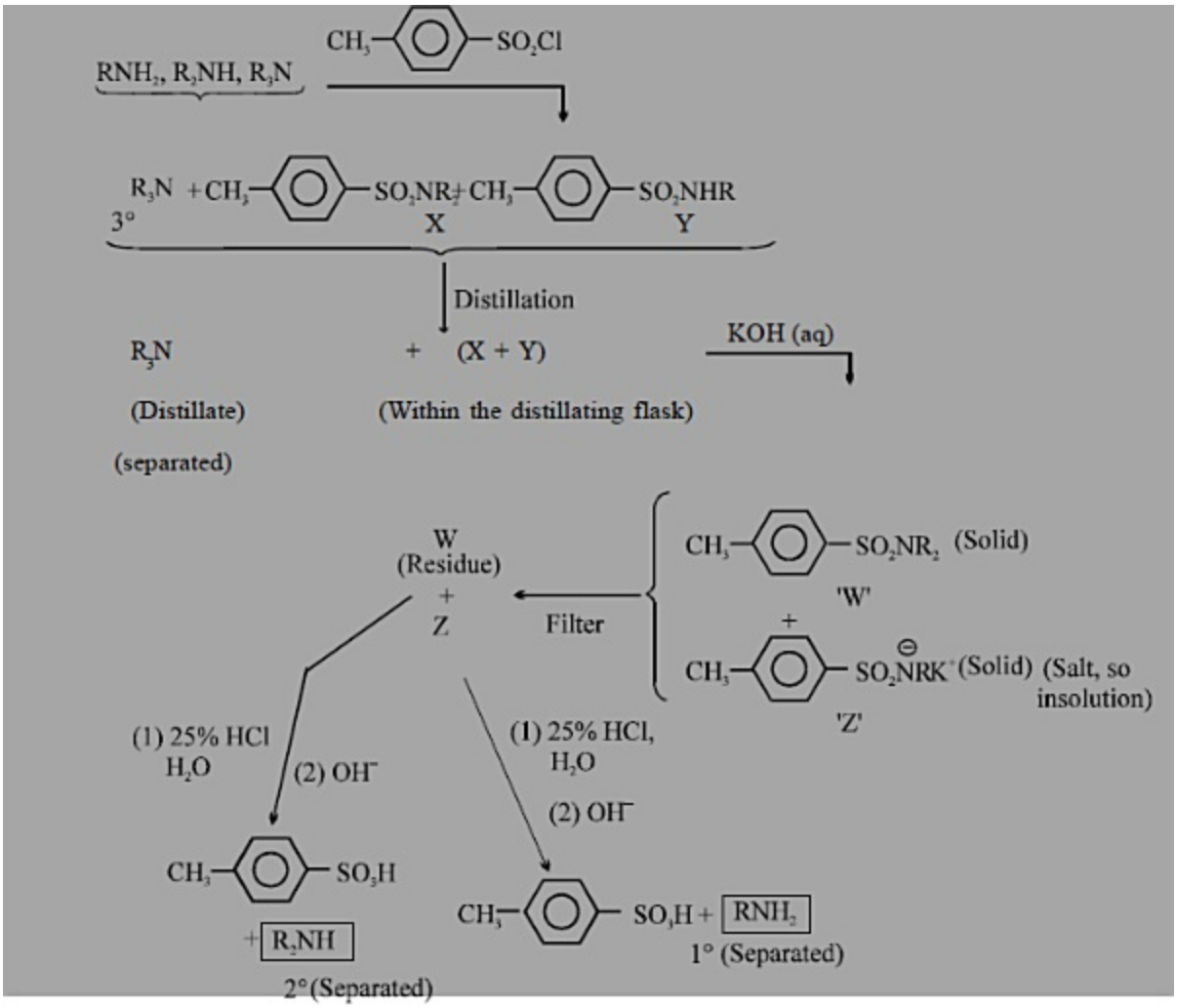
Separation of 1°, 2°, 3° amines from their mixtures :

(1) Hofmann's method ;



Always remember 1° forms solid salt with diethyloxalate, 2° liquid, 3° non reactive.

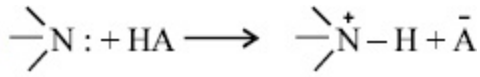
2. **Hinsberg's method :**

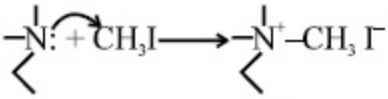


Physical properties:-

1°, 2° amines can form intermolecular H-bond due to which b.p. of 1° , 2° amines are higher compared to 3° amine. For example, dimethyl amine has b.p. + 7°C and trimethyl amine boils act +4°C. It is also observed that with higher molecular mass b.p. increases. All types of amines can form H-bond with water molecules therfore solublity of amine in water is observed. However with increasing molecular mass solubility decreases. For example aniline and another aromatic amines are almost insoluble.

Chemical Reactions :

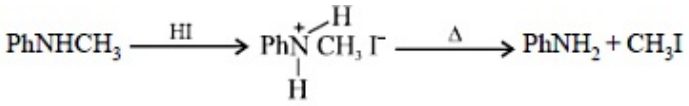
(1) **Acid-base reaction :** 

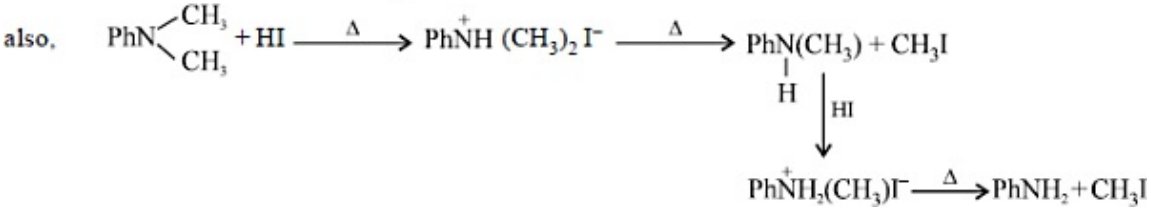
(2) **Alkylation : (a)** 

but, **(b)** $PhNHCH_3 + HI \xrightarrow{150^\circ C} PhNH_2 + CH_3I$

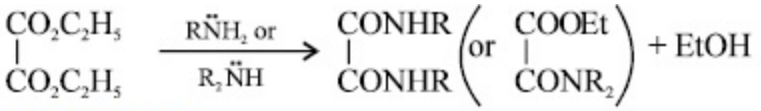
Pyrolysis of arylmethyl ammonium iodides at 150°C, gives CH_3 – I and derivatives of aniline. Estimation of CH_3I formed thereby helps to find out number of methyl groups in the amine and this method is called as Herzig-Meyer method.

For example ;

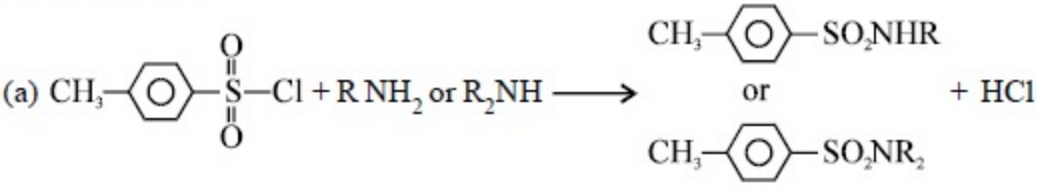


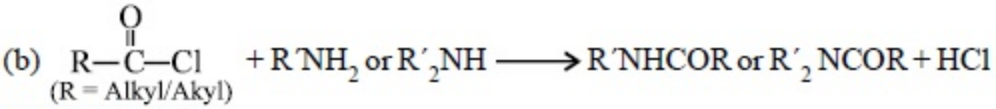
also, 

As we get two moles of CH_3I, therefore the original amine was $PhN(CH_3)_2$ (i.e., 3° aryl alkyl amine)

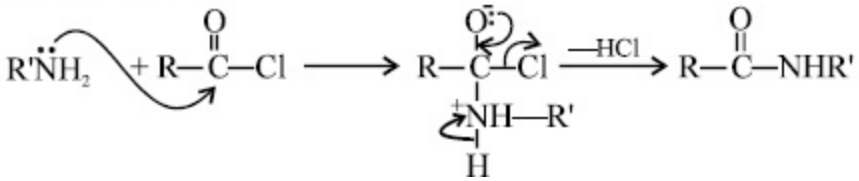
(3) 

Diethyl oxalate

(4) 

(b) 

Mechanism :



(5) Oxidation : (a) R_3N (3°) + H_2O_2 or RCO_3H or O_3 or H_2SO_5 $\longrightarrow$ $R_3\overset{+}{N}-O^-$ (Tertiary amine oxide)

(b) $R_3CNH_2 \xrightarrow{KMnO_4} R_3CNO_2$; $R_3CNH_2 \xrightarrow{H_2SO_5} R_3CNO$

(c) $RCH_2NH_2 \xrightarrow{KMnO_4} RCH=NH \xrightarrow{H^+, H_2O} RCHO + NH_4^+$

(d) $RCH_2NH_2 \xrightarrow{KMnO_4} R_2C=NH \xrightarrow{H^+, H_2O} R_2CO + \overset{+}{N}H_4$

(e) $R_2NH \xrightarrow{KMnO_4} R_2N-NR_2$

(f) $R_2NH \xrightarrow{H_2SO_5} R_2NOH$

(g) $R_2CHNH_2 \xrightarrow{H_2SO_5} R_2C{=}NOH$

Remember the final products of oxidation only .

(6) Reaction with HNO_2 (i.e. NO^+)

HNO_2 (Nitrous acid) is a weak unstable acid and always produced in situ (i.e. with in the reaction medium) by adding HCl or H_2SO_4 (aq) in $NaNO_2$.

$HCl + NaNO_2 \longrightarrow HNO_2 + NaCl$

$H_2SO_4 + NaNO_2 \longrightarrow HNO_2 + Na_2SO_4$

HNO_2 means NO^+ by the following mechanism.

$HNO_2 \rightleftharpoons H^+ + NO_2^-$; $H\ddot{O}-N=O + H^+ \longrightarrow H_2\overset{+}{O}-N=O \longrightarrow H_2O + :\overset{\oplus}{N}=\ddot{O}:$

$\overset{\oplus}{N}O$ is a weak electrophile due to resoanance,

$\overset{+}{N}\overset{\curvearrowleft}{=}\ddot{O} \longleftrightarrow :N\equiv\overset{+}{O}:$

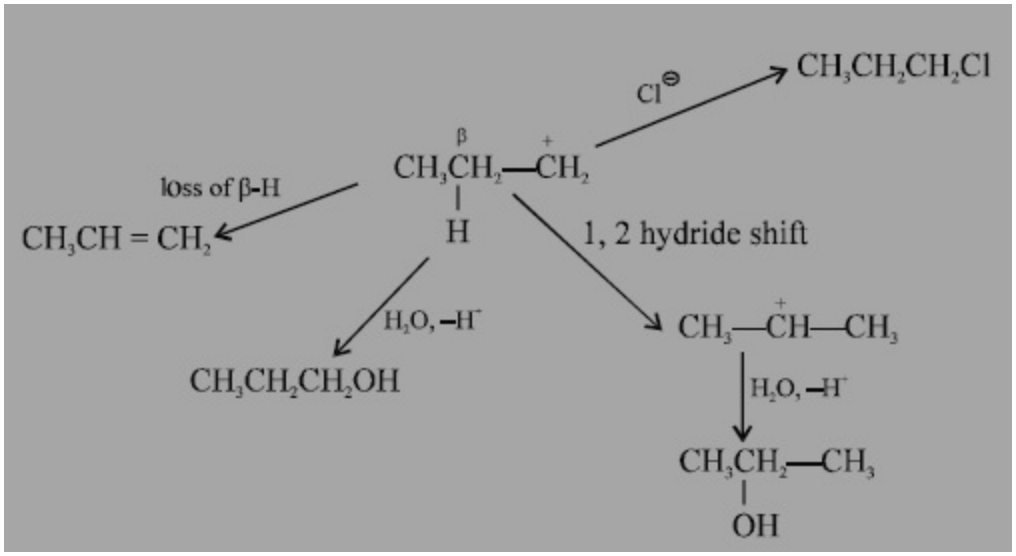
Case : 1. with 1° aliphatic amine :

$RNH_2 + NO^+ \longrightarrow R-\overset{H}{\underset{H}{\overset{|}{\underset{|}{\overset{+}{N}}}}}-N=O \longrightarrow R-NH-N=O \rightleftharpoons RN=N-\ddot{O}H$

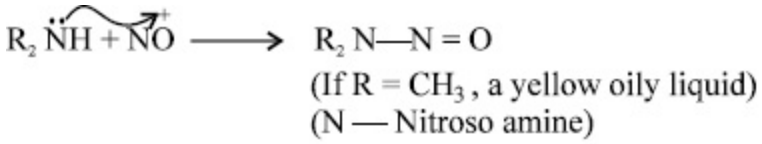
$RN=N-\ddot{O}H \xrightarrow{H^+} R-N=N-\overset{+}{O}H_2 \xrightarrow{-H_2O} R-N=\overset{+}{N} \longleftrightarrow R-\overset{\oplus}{N}\equiv N \longrightarrow \overset{\ominus}{R} + N_2$

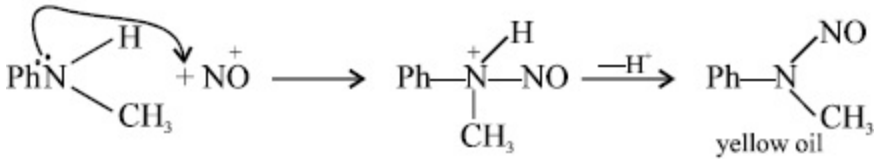
So, if R = $CH_3CH_2 - CH_2-$

Then, the possible products will be as follows :

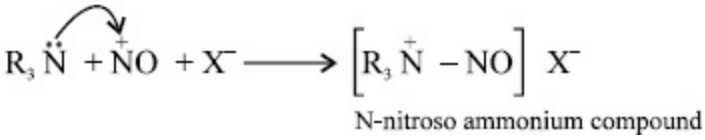


Case – 2 : With 2° amine (aliphatic and aromatic)

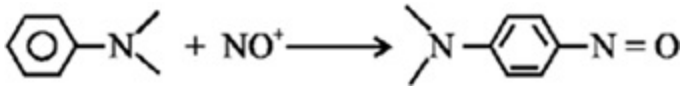




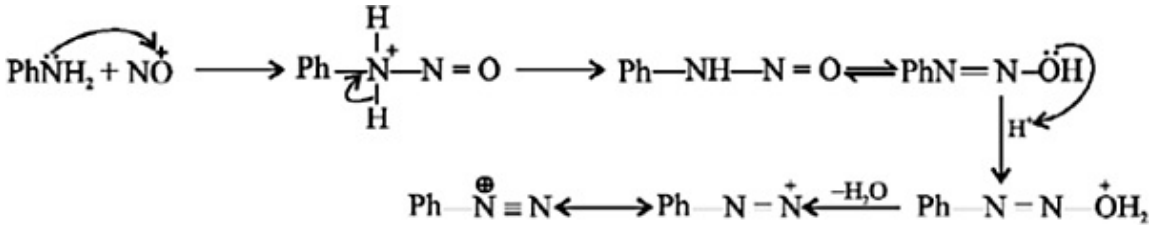
Case – 3 : With 3° amine (R_3N) :



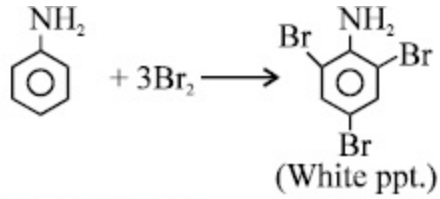
But with 3° aliphatic aromatic amine ArSE2 reaction takes place at para position almost exclusively.



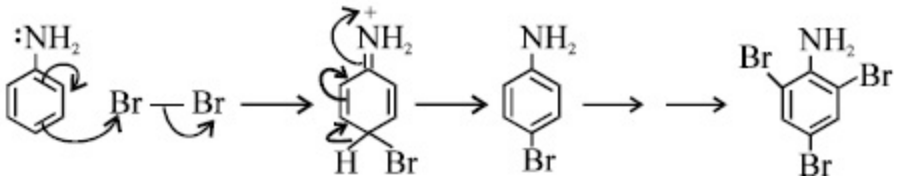
Case – 4 : With 1° aromatic amine i.e. aniline at low temperature produces aromatic diazonium cation following the mechanism given below ;



This aryl diazonium salt is very useful intermediate species in the synthesis of different substituted aromatic compounds, which will be discussed later along with stability factor.

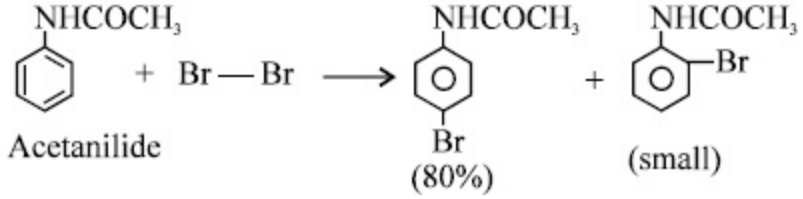
(9) 
(White ppt.)

Mechanism :

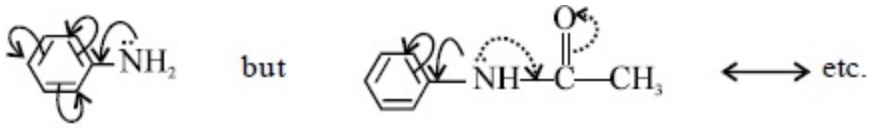


Rememeber each Br_2 molecule is supplying one $Br^{\oplus}$ and enters into the benzene ring by $ArSE_2$ reaction. To introduce one Br in benzene ring we reduce the effect of activating group $-NH_2$ by converting into $-NHCOCH_3$ and then add Br_2 – water.

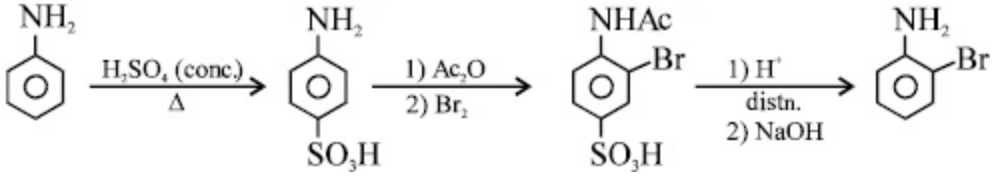
eg; $Ph-NH_2 + CH_3COCl \longrightarrow Ph-NHCOCH_3$


Acetanilide (80%) (small)

It is understood that initially N used to supply its lp into benzene ring but new $-COCH_3$ (–R group) can also share the lp electron of N as shown below etc.



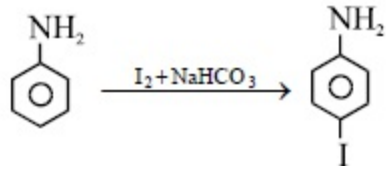
To get 100% ortho bromo product we follow the steps mention below ;



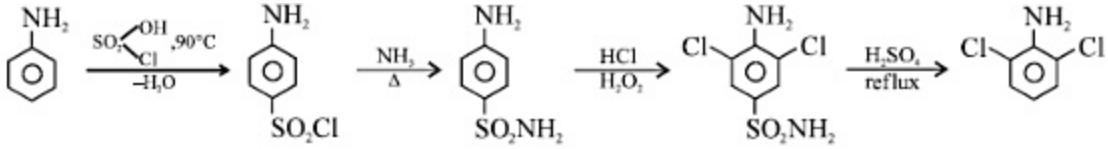
(10) $R^1NH_2 + RCHO \longrightarrow R-\underset{\oplus}{C}(O^-)(R^1-\overset{\oplus}{N}H_2)-H \longrightarrow RCH(OH)(NHR^1) \xrightarrow{\Delta} RCH=NR^1$ (imine)

(R1 = Alliphatic or aromatic)

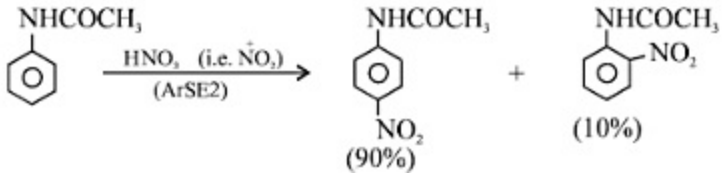
(11)



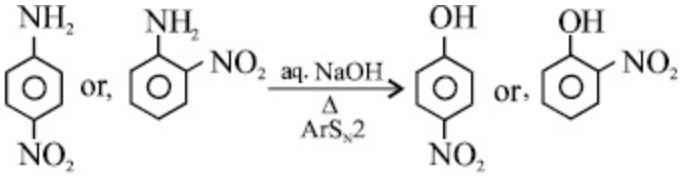
(12)



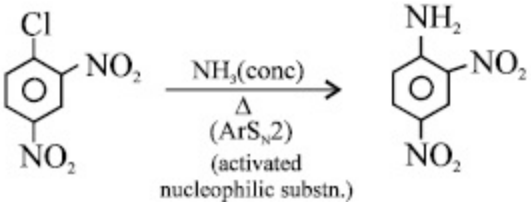
(13)



(14) (a)



(b)

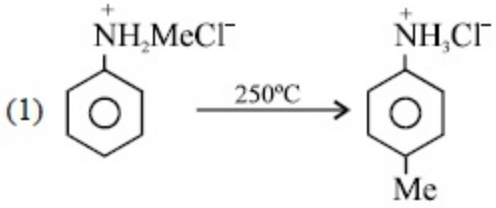


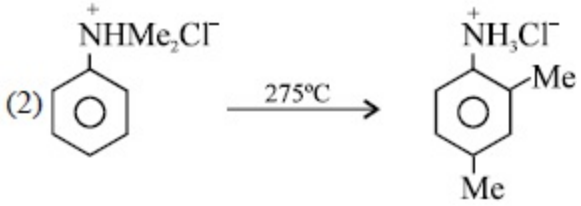
(15) Hofmann - Martius rearengment :

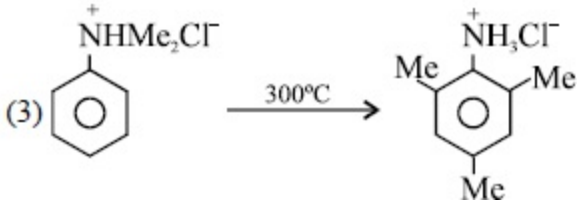
Subratrate : N – Alkyl aryl ammonium salt

Condition : only heating

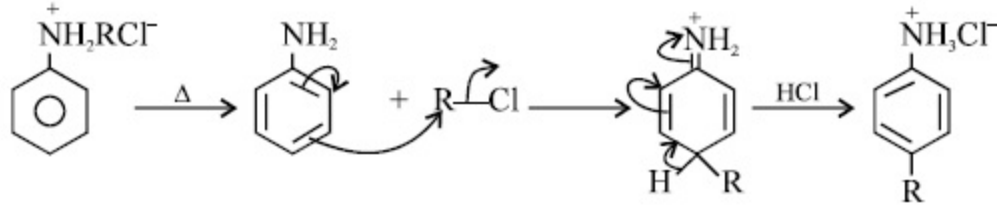
Reaction :







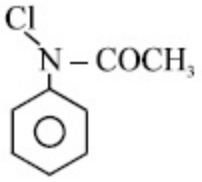
Mechanism :



The nature of mechanism is intermolecular and R – X has been isolated.

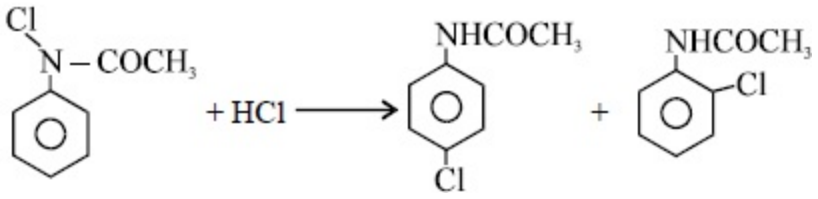
(16) Orton's (Chloramine) rearengment :

Substrate : N – Chloro acetanilide i..e.;

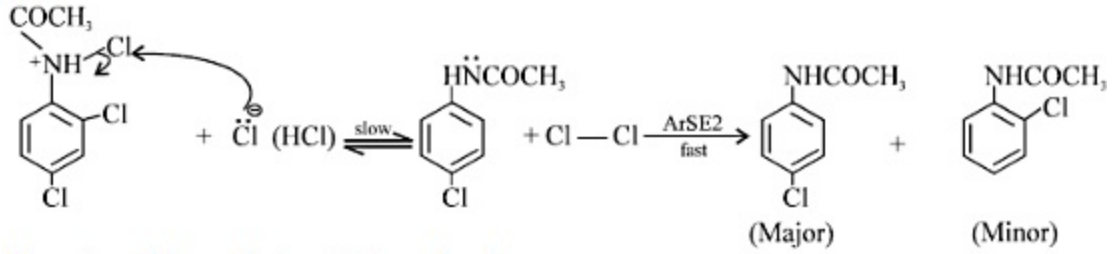


Reagent : HCl

Reaction :



Mechanism :



The nature of the mechanism is inter molecular.

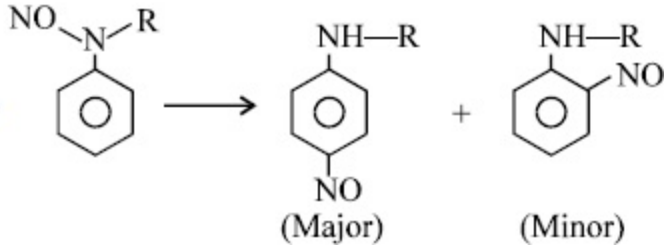
(18) **Fischer Hepp rearrangement :**

Substrate : N – Nitroso N–alkyl aryl amine

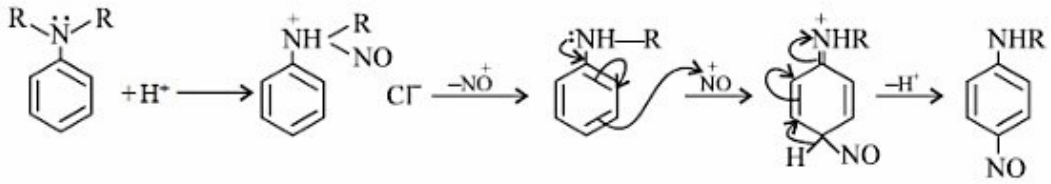
Reagent :- HCl

Condition :- Heating

Reaction :-



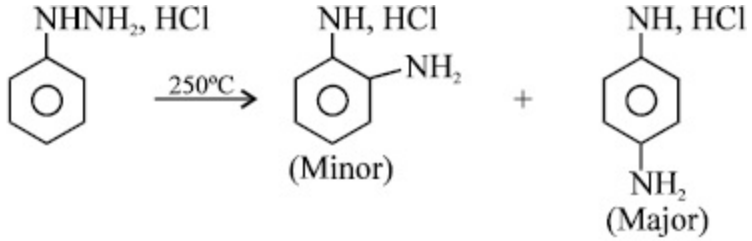
Mechanism :



The nature of mechanism is intermolecular as well as intramolecular (by evidence). The mechanism in detail for intramolecularity is beyond the scope of this book .

(18) Other than NO, it can be X, R, NH_2 , NO_2 etc. on N – atom and upon heating or with suitable regaent like HCl gives rearranged product para substituted compound (major).

eg;



(19) $Ph-OH + Ph-NH_2 \xrightarrow[260°C]{ZnCl_2} (Ph)_2NH + H_2O$

(20) $PhNH_2 + PhNH_2 \cdot HCl \longrightarrow (Ph)_2NH + NH_4Cl$

(21) $(Ph)_2NH \xrightarrow{Na} (Ph)_2 \ddot{N}^- Na^+$

Therefore N – H bond shows little acidic character.

(22) $Ph-C\equiv N \xrightarrow[\text{or } LiAlH_4]{Na/C_2H_5OH} PhCH_2NH_2 \xleftarrow{Na/C_2H_5OH} PhCH=NOH$

(23) Ph_3N dissolves in conc. H_2SO_4 and gives blue colouration. Ph_3N is a very very weak base due to delocalisation of lp of N.

Diamines

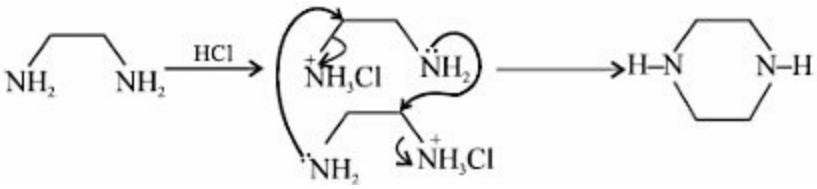
(1) $Ph-N=N-C_6H_4-NH_2 \xrightarrow{Na_2S_2O_4} PhNH_2 + NH_2-C_6H_4-NH_2 \xleftarrow[HCl]{Sn} NO_2-C_6H_4-NO_2$

Physical properties :

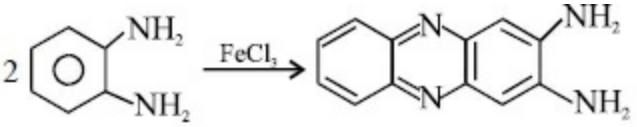
Diammines are colourless or white and turns brown in air and behaves like base.

Chemical reactions :

(1)



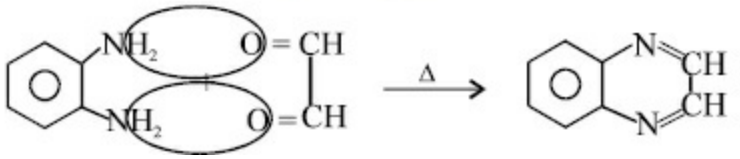
(2)



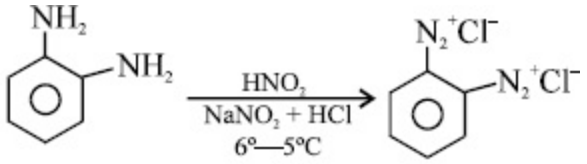
(2, 3 Diamino phenazine)

Dark Red

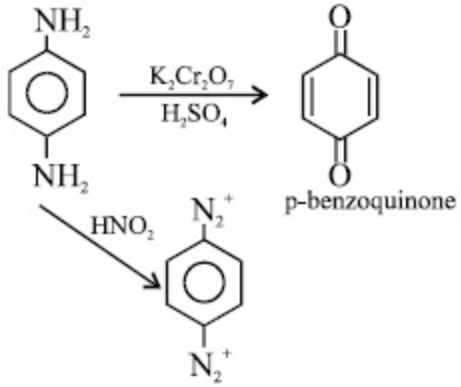
(3) O-phenylene diamine can easily undergo condensation reaction as shown below ;



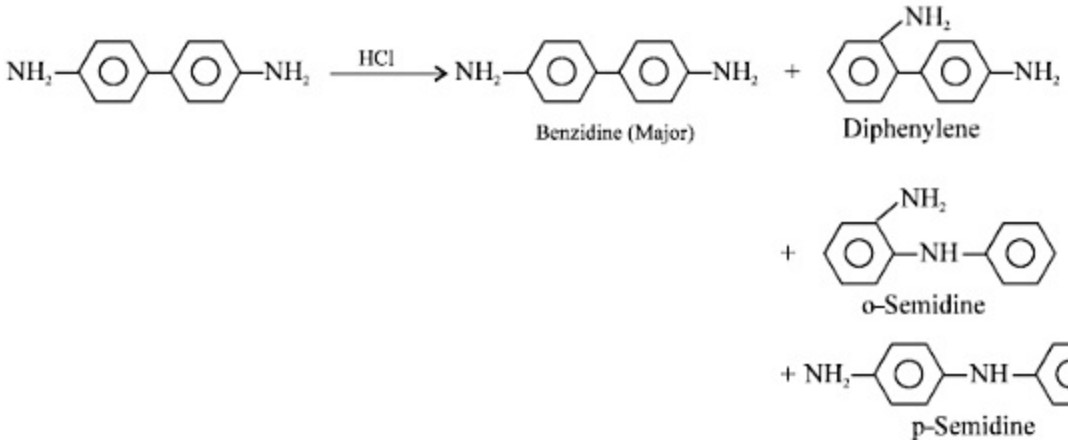
(4)



(5)

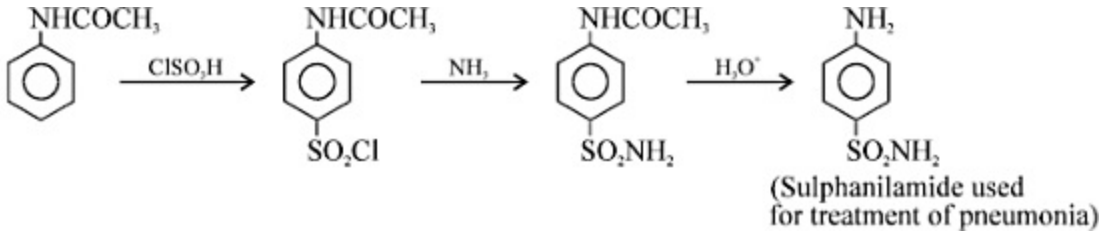


(6) **Benzidine and semidine rearrangement :**



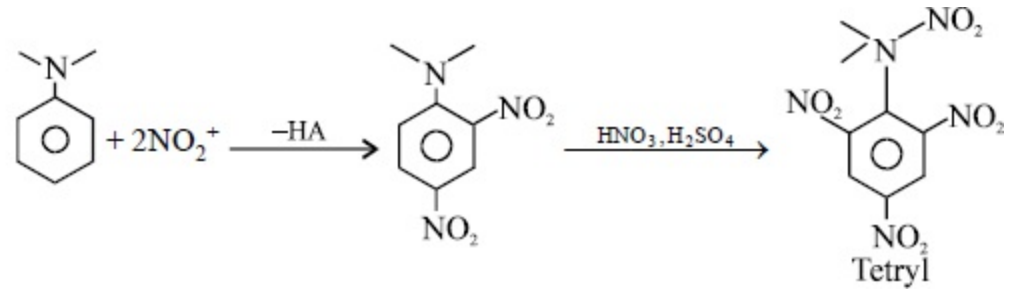
Some illustrative examples of conversion :

(1)

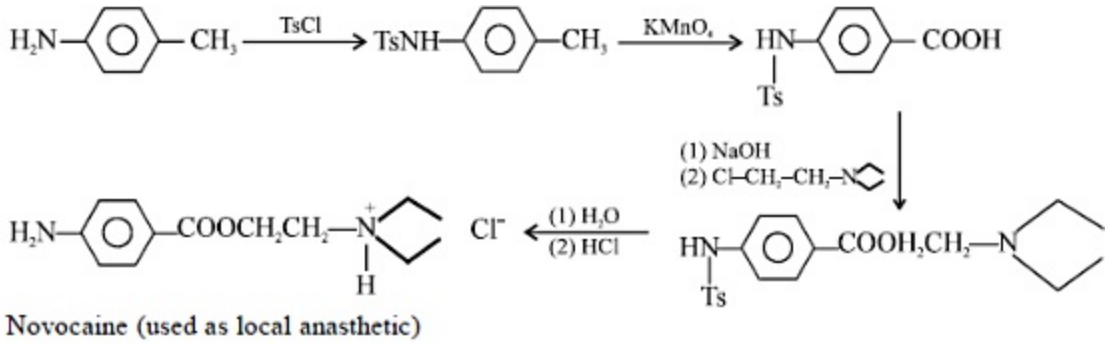


(Sulphanilamide used for treatment of pneumonia)

(2)

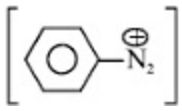


(3)

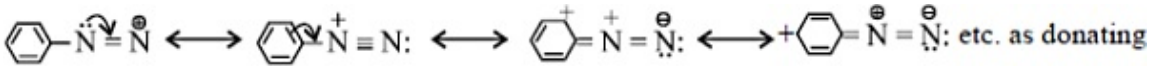


Novocaine (used as local anasthetic)

Benzene Diazonium cation ;

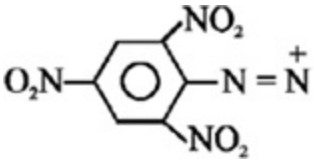


The preparation has already been disscussed that at 0° – 5° C (ice cold soln.) $PhNH_2$ reacts with HNO_2 to give PhN_2^+. Diazonium cations give large number of azodyes which are called as coupling reactions. Stability of aromatic diazonium cation at low temp. is due to ©ive charge delocalisation in the benzene ring.



It has also been observed that electron donating as well as electron withdrawing groups at para position increases the stability of aromatic diazonium cation due to C–N double bond character arises due to above shown resonating structures. It is a very weak electrophile as such. Electron withdrawing groups quite clearly increases electrophilicity by withdrawl of electron from benzene ring.

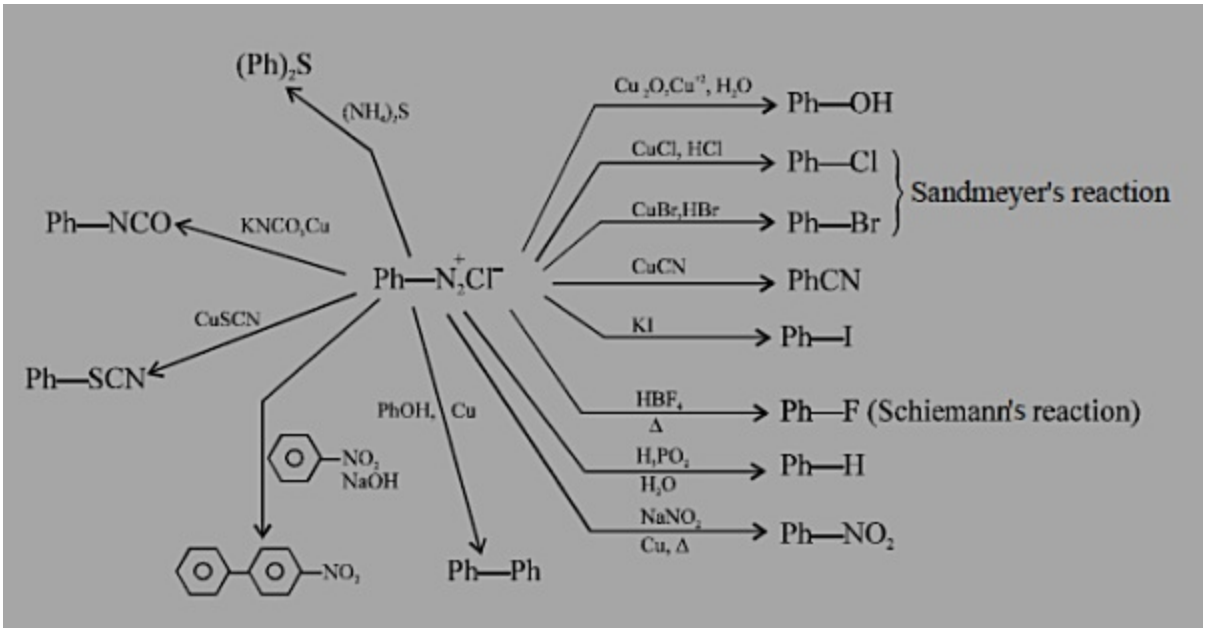
For example,

 is compartively stronger electrophile than benzene

diazonium cation.

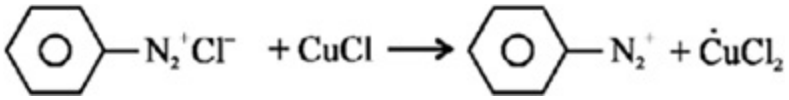
Chemical reactions :

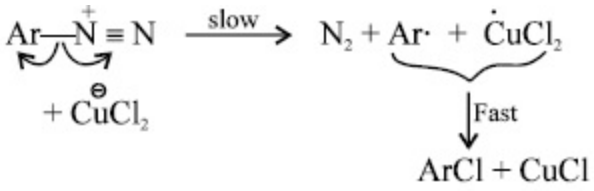
1. When – N_2 eliminates

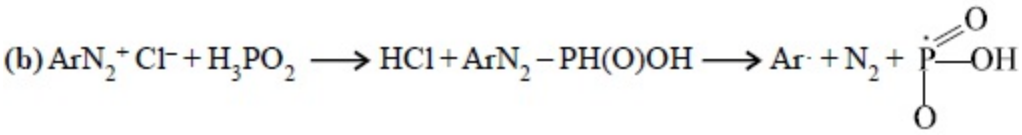


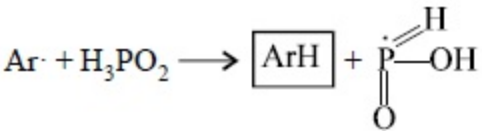
The above reactin in which loss of $–N_2^+$ group takes place and different substiutents come in benzene ring. We should not be intersted in the mechanism as it is beyond the scope of this book .
Two possible mecahnisms are :

(a) Mechanism for Sandmayer's reaction ;

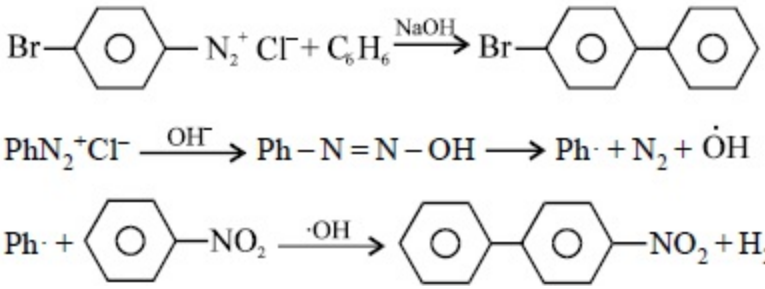








(c) Gomberg's reaction :

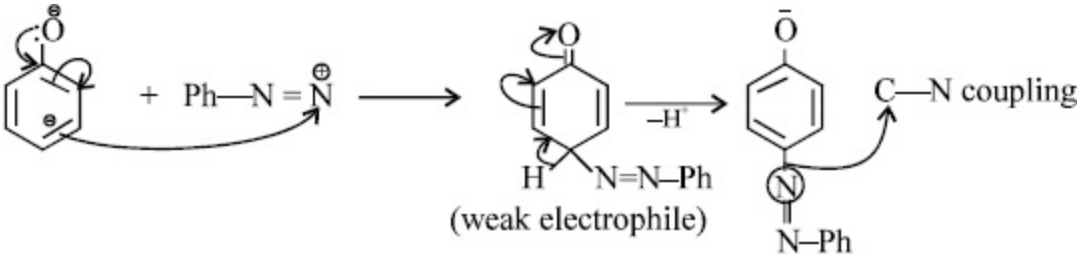


2. Coupling reaction :

This reaction can be of the type (a) C – N coupling and (b) N – N coupling. The following reactions take place where N_2 is retained.

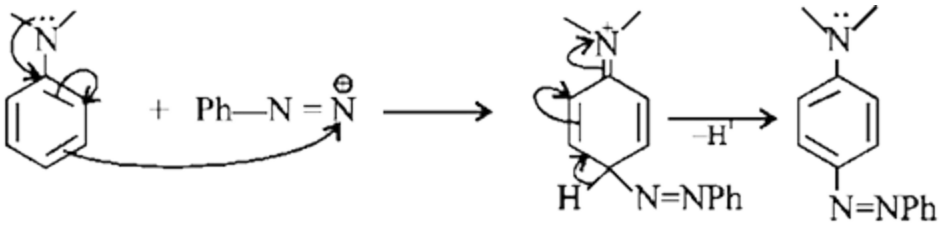
For example ;

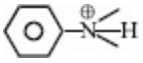
Case – 1: When $\ddot{\underset{\ominus}{O}}$ is present :



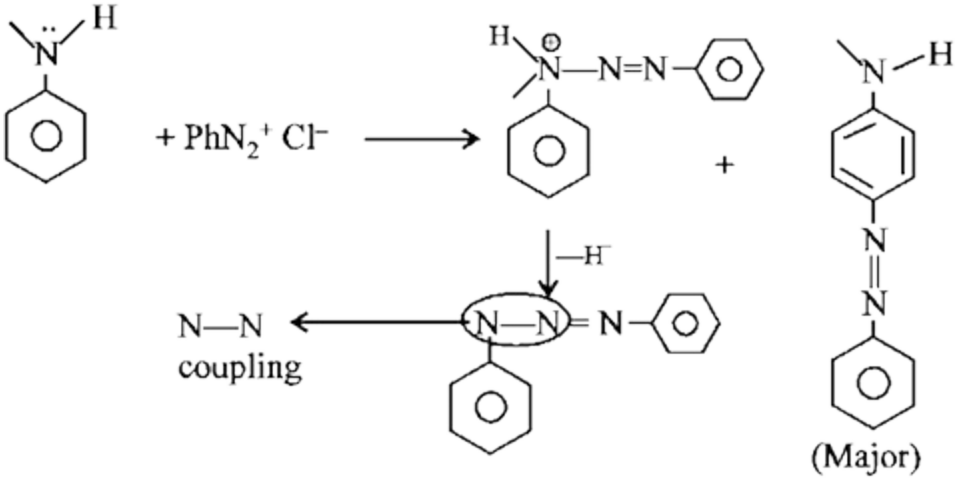
Since O^- – is a strong + R, +I group threfore always p-major or ortho coupling (when p-blocked) takes place in weakly alkaline solution.

Case –2 : When 3° amine ;



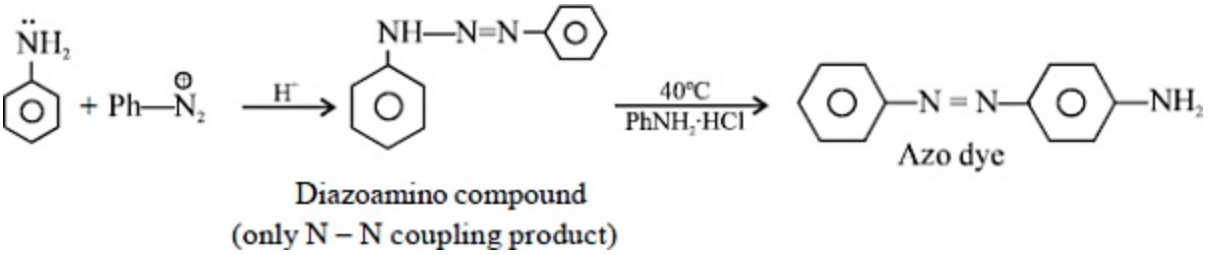
Thus with 3° alkyl aryl amine, C – N coupling takes place in weakly acidic sloution. We avoid alkaline solution, strongly acidic solution (due to possible protonation  formation).

Case – 3 : When 2° amine ;



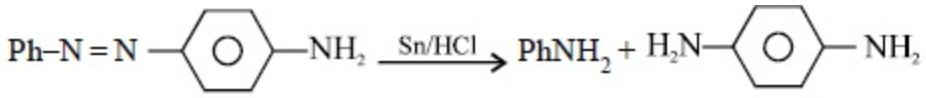
Therefore at mild acidic solution with 2° amine N–N, C–N coupling both take place.

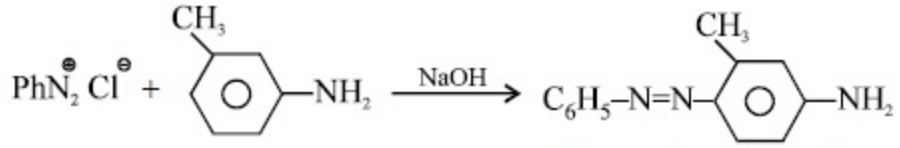
Case – 4 : When 1° amine ;



Here we must understand $-O^-$, $-\ddot{N}R_2$ are strongly + R groups therefore always C – N coupling takes place through ArSE2 mechanism where as –NHR, – NH_2 are not that strong +R therefore the above result appears.

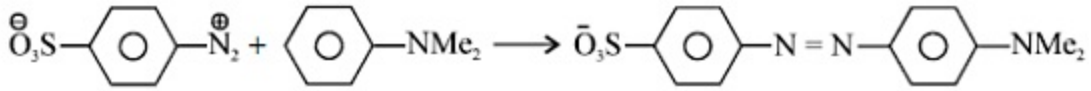
Some other reaction are ;

(1) 

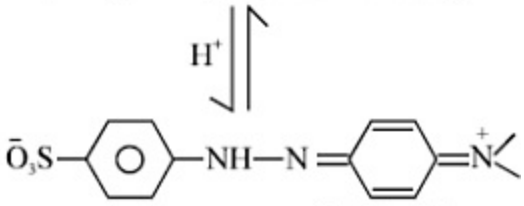
(2) 

4-amine 2-methyl azo benzene

Azodye formation ;

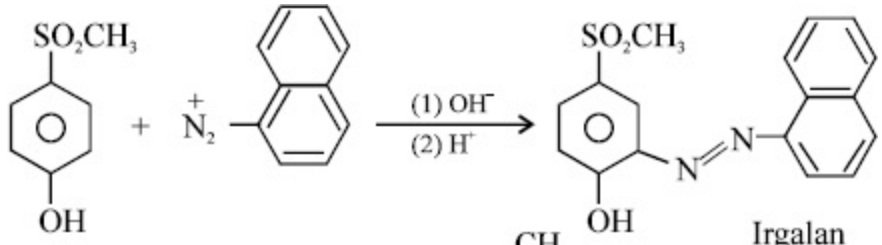
(3) 

(Methyl orange used as indicator)

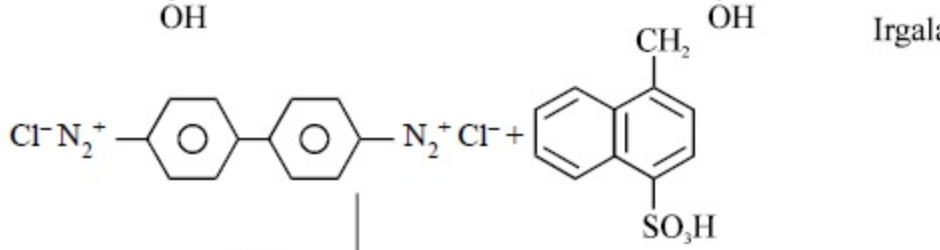


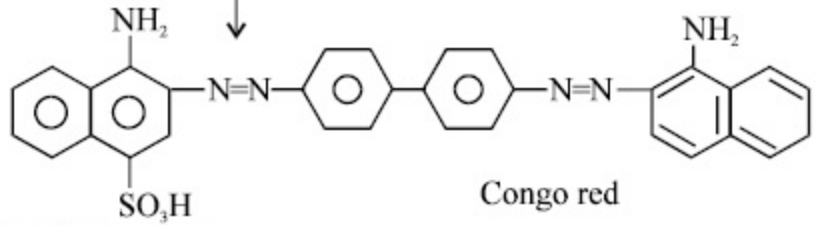
Red (in acid)

(4) Mordant dyes are those in which OH group is ortho to the azo group.



Irgalan

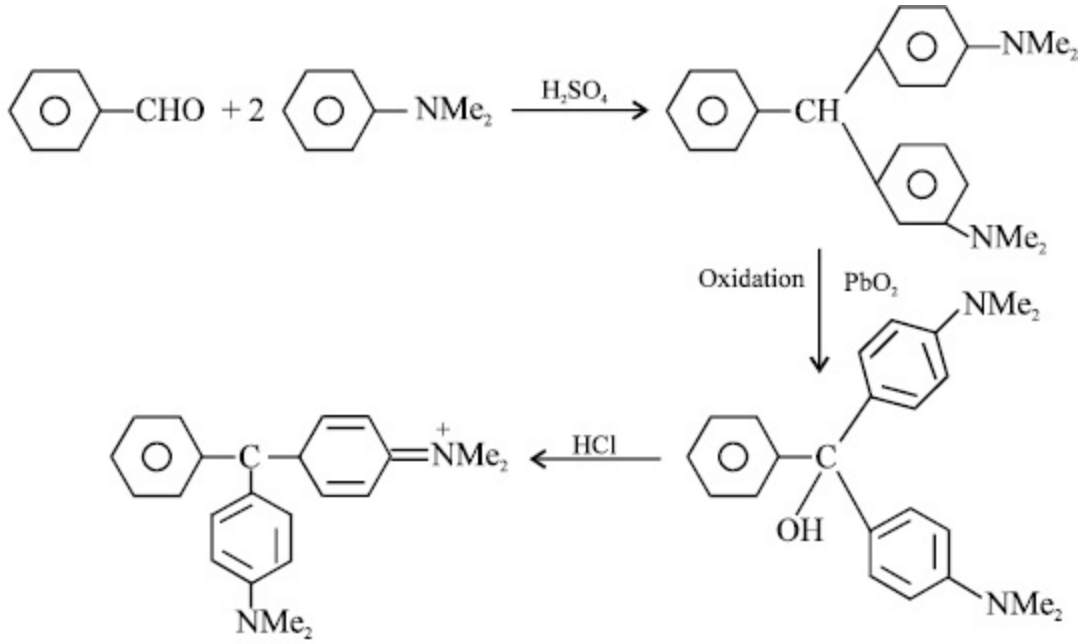
(5) 



Congo red

It is used to dye cotton.

(6)



Malachite green

It is used to dye wool and silk.

Carbohydrates

Carbohydrates include sugars and non-sugars. Example of sugars are glucose, fructose, sucrose and examples of non-sugars are cellulose, starch etc. Initially they were considered as hydrate of carbon and general formula assigned was $C_n(H_2O)_n$.

But it was found wrong e.g. $C_1(H_2O)_1$, which is formaldehyde (not a carbohydrate) or $\begin{matrix} CHO \\ | \\ CH_2OH \end{matrix}$ i.e. $C_2(H_2O)_2$, glyoxal as well as some sugars like rhamnose ($C_6H_{12}O_5$), fructose ($C_6H_{12}O_5$) etc. which do not conform to the molecular formula $C_n(H_2O)_n$.

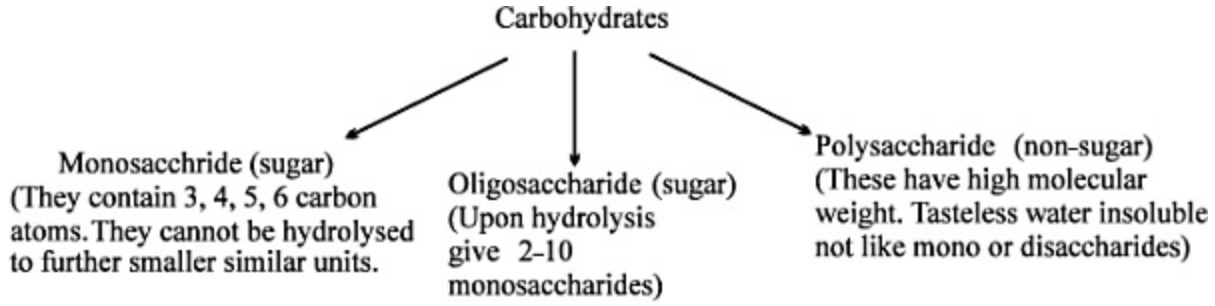
Definition : Carbohydrates are polyhydroxy aldehydes of carbohydrates or ketones or substances those can be hydrolysed to either of them (i.e.polyhydroxy carbonyl compounds). Carbohydrates are produced in green plants by photosynthesis by the reaction,

$$6CO_2 + 6H_2O \xrightarrow[\text{chlorophyll}]{h\nu} C_6H_{12}O_6 + 6O_2$$

In human body or in animal body carbohydrates burn by aerial O_2.

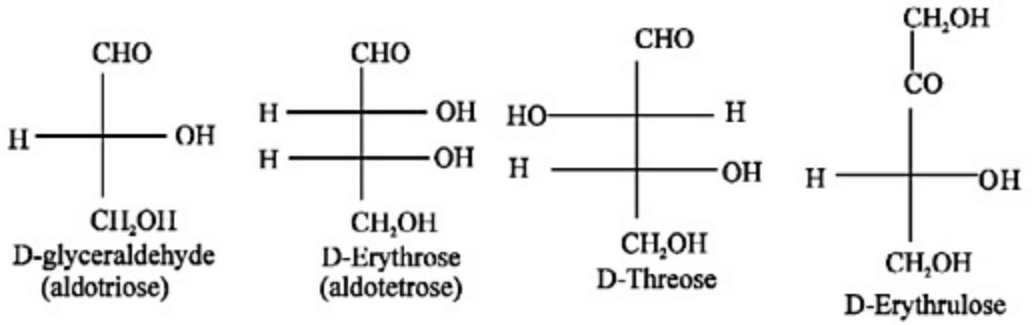
$$C_6H_{12}O_6 + 6O_2 \xrightarrow[\text{metabolism process}]{} 6CO_2 + 6H_2O + \text{energy}$$

CO_2 thus produced recycled in photosynthesis again.

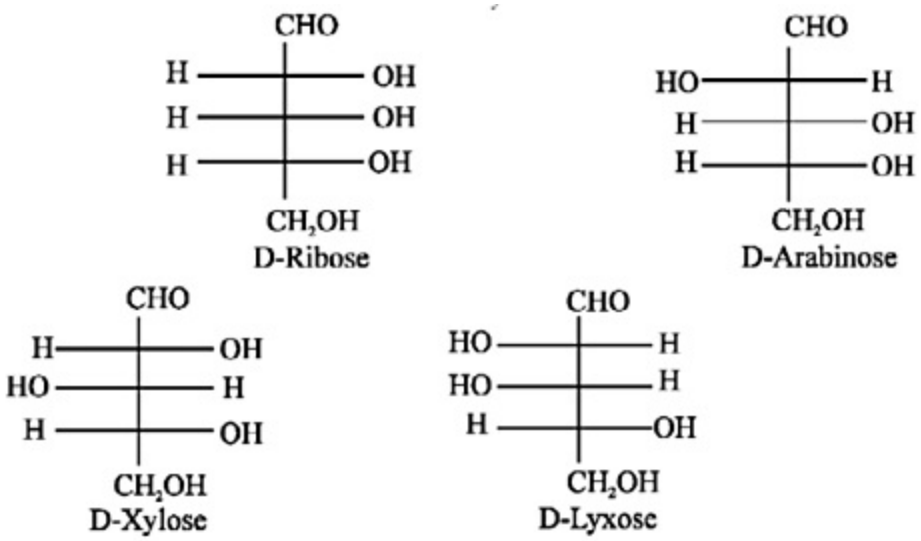


Monosaccharides :

There are colourless, sweet in taste and water soluble. They are optically active. Examples are;



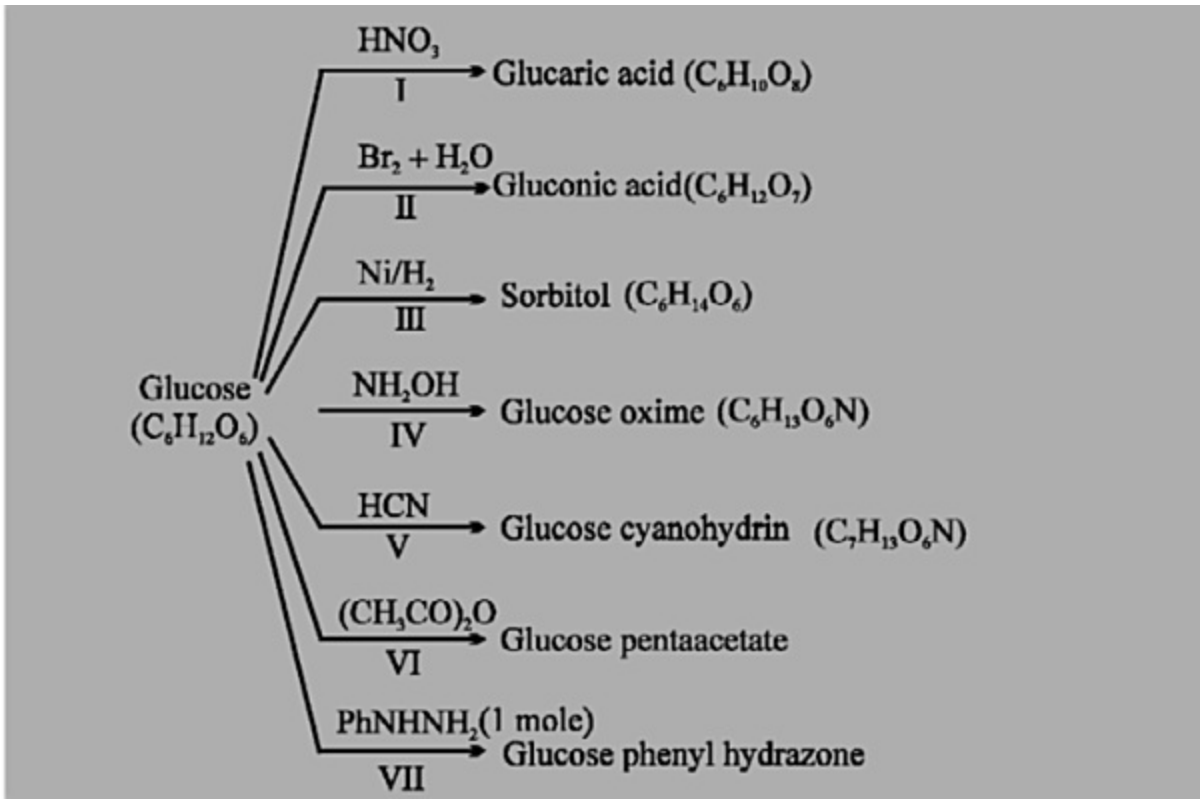
'D' is determined from the configuration of the second (chiral-C) C–atom from the bottom. If –OH in the right, it is called on 'D' and if OH is in the left called as 'L'



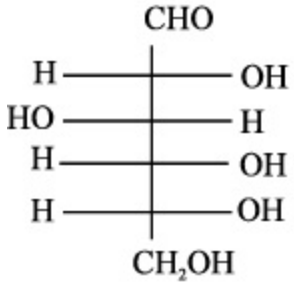
Similarly all mirror images of the above are in 'L' series (total optical isomers = $2^3 = 8$). For aldohexoses $2^4 = 16$ optical isomers are possible. Allose, altrose, glucose, gulose, mannose, idose, galactose, talose. Among these our interest is only on glucose.

Structure determination of glucose

Following are the tests of glucose

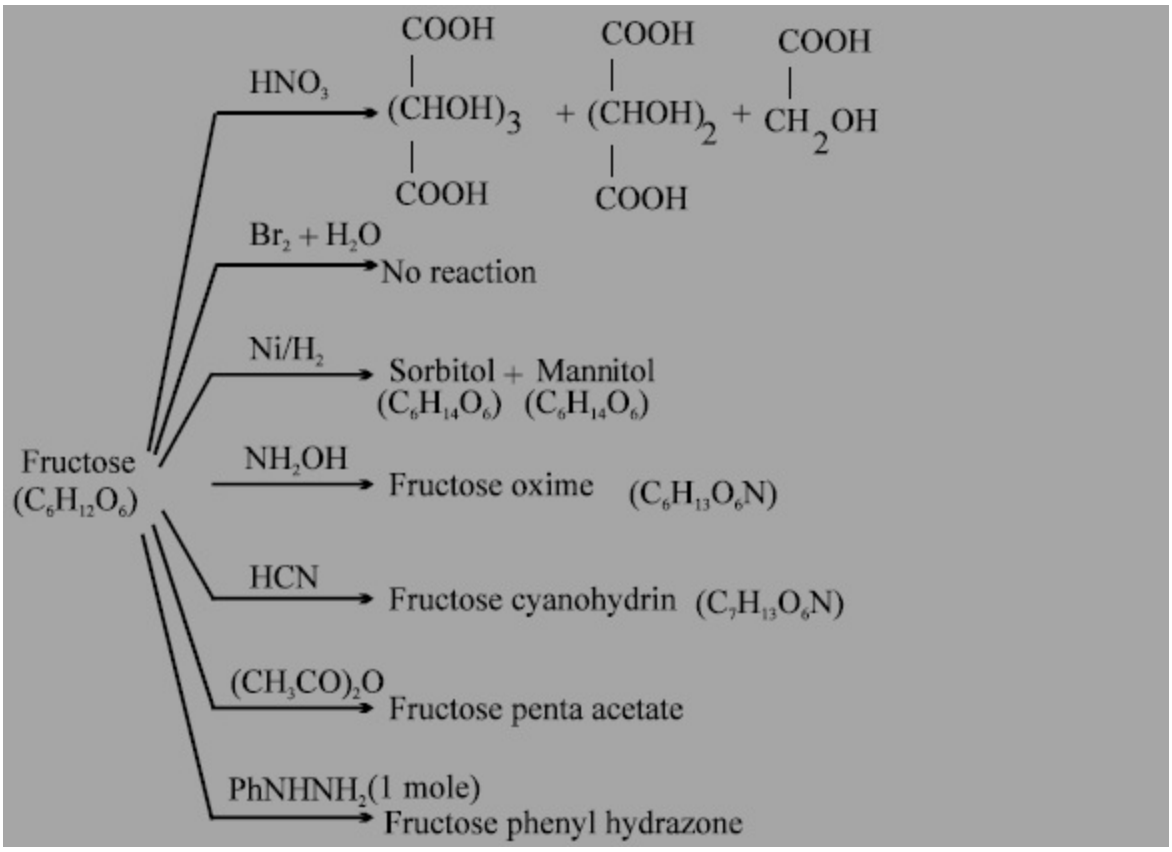


On the basis of above sequence of reactions, we can observe that – CHO (by step –II) at one end and CH_2OH at the other end (step – I also step III) may be present. IV, V, VII prove that definitely – CH= O is present alongwith 5 – OH groups (step VI). Therefore, a likely structure may be written as CHO $(CHOH)_4CH_2OH$. Actually the structure of D- glucose is;

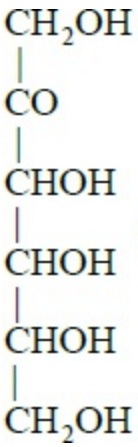


D(+) glucose [Remember the structure]

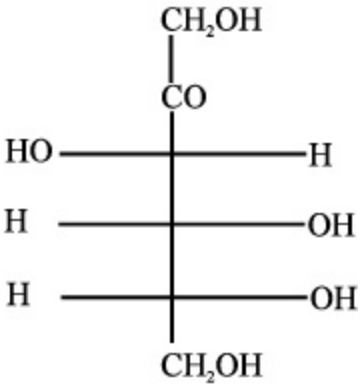
Structure determination of fructose :



On the basis of above reactions we can conclude that one $-\overset{|}{C}=O$ group and 5 – OH (alcoholic) groups are present. Therefore, the likely structure can be

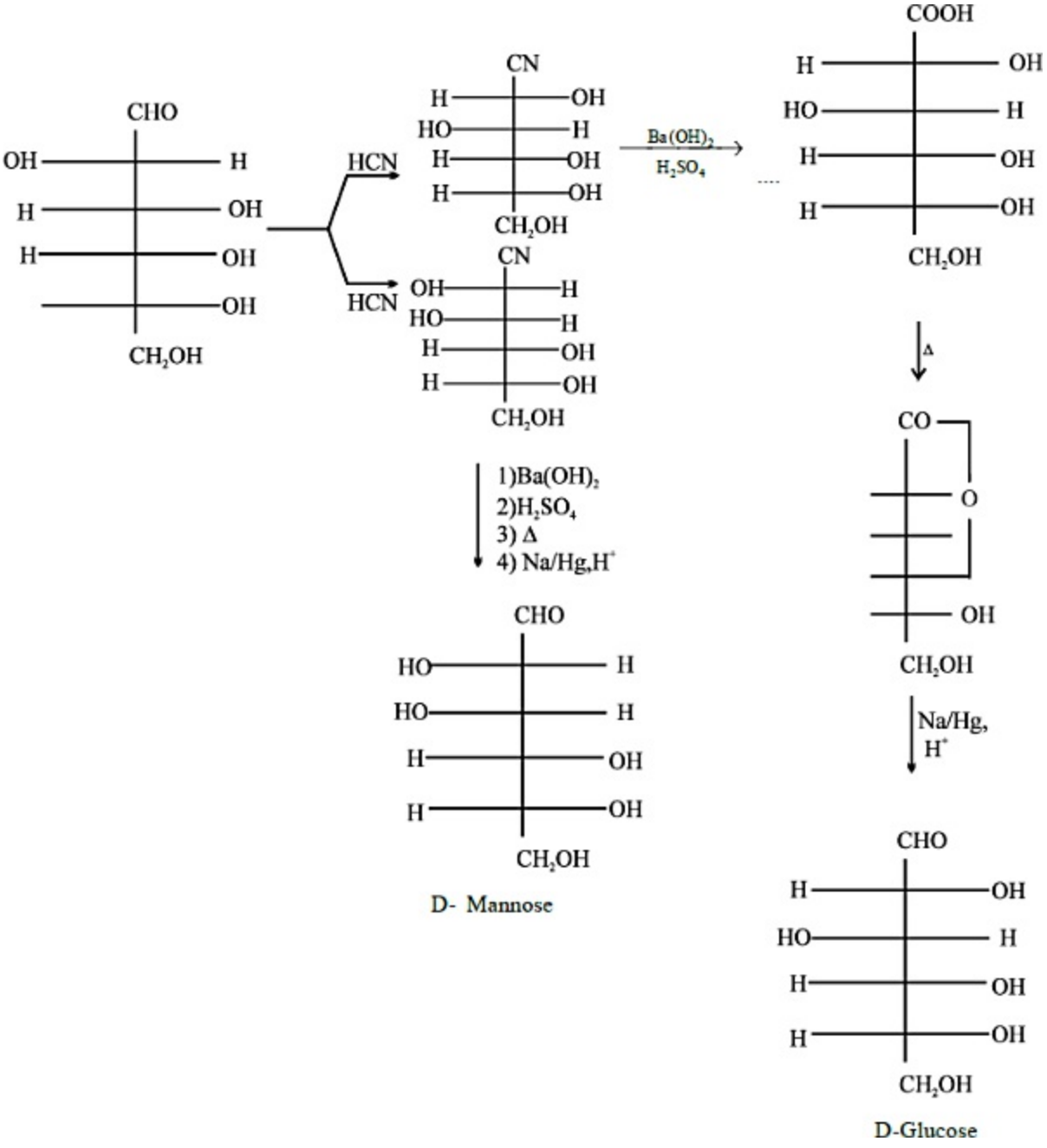


and actually, D(–) fructose is



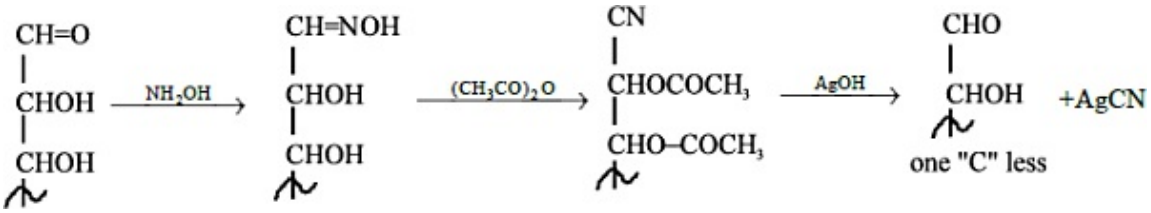
We must remember the orientation of OH groups in the Fischer's projection of fructose. **Preparation of sugar (Method of ascending sugar series) :**
i) Killani reaction : In this reaction HCN is treated with carbonyl functional group to produce cyanohydrin, then hydrolysis and successive reduction of lactone by Na- Hg/HCl yield higher aldose.

For example :

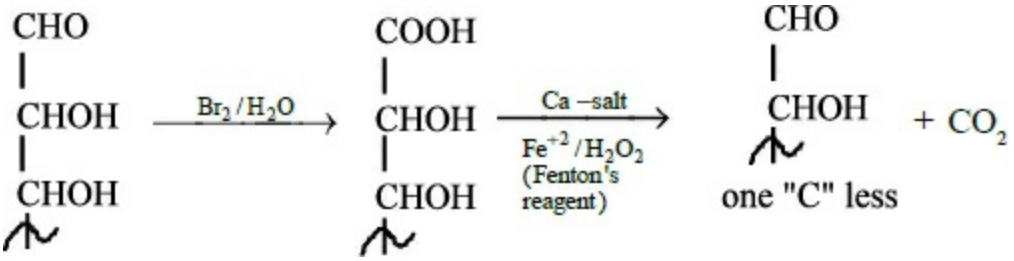


Method of descending sugar series :

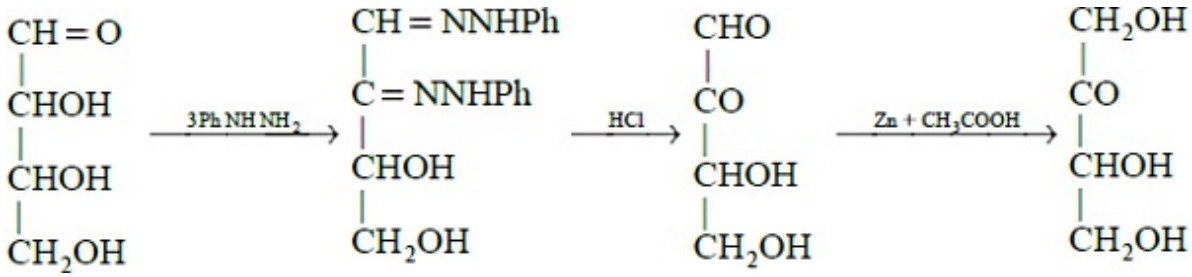
i) Wohl's method :



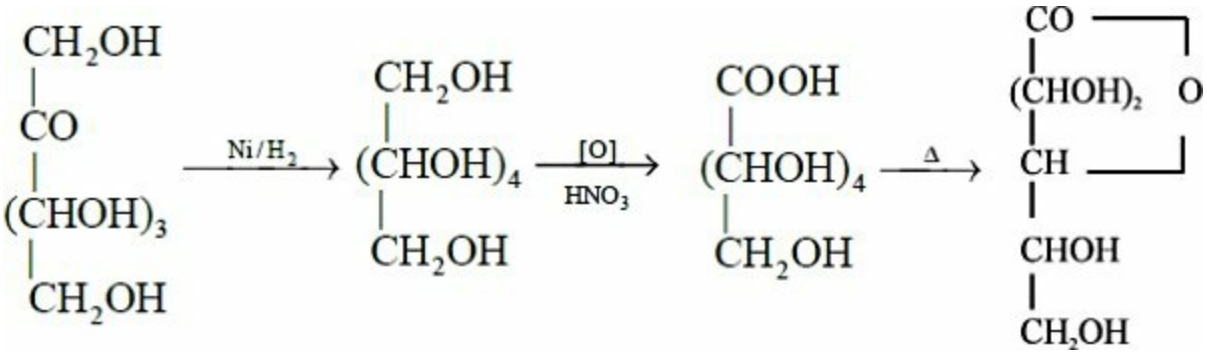
ii) Ruff's method :



Conversion of aldose into ketose:



Conversion of ketose into aldose:

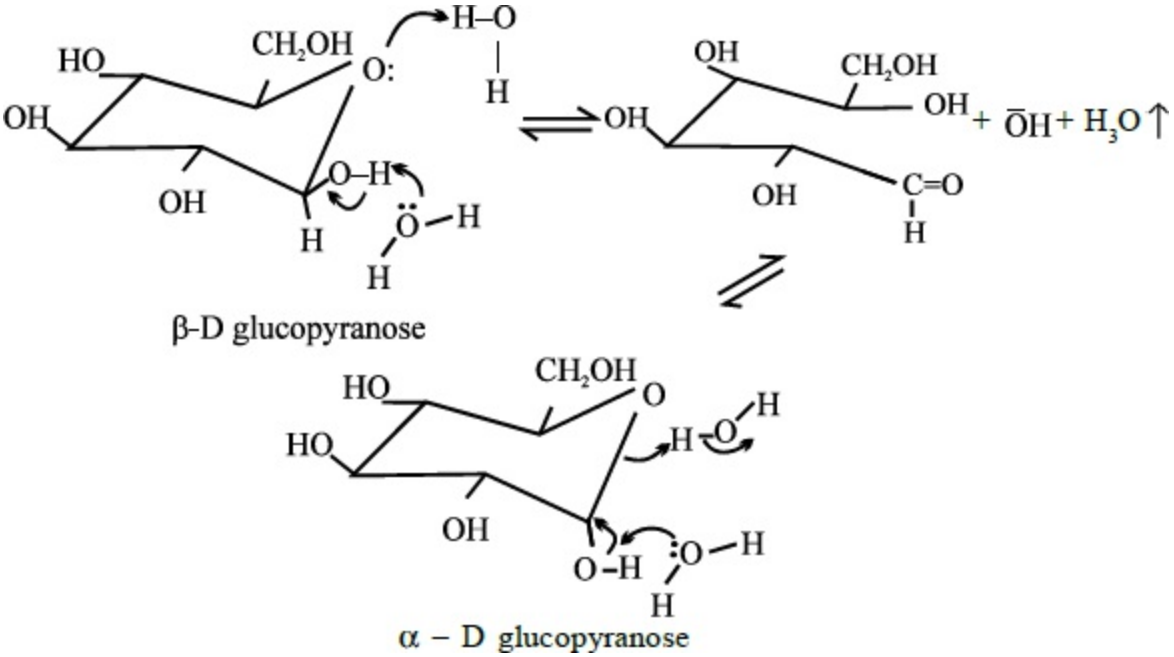


Chemical properties of aldoses and ketoses :

1) Action of water on aldoses & ketoses : Mutarotation

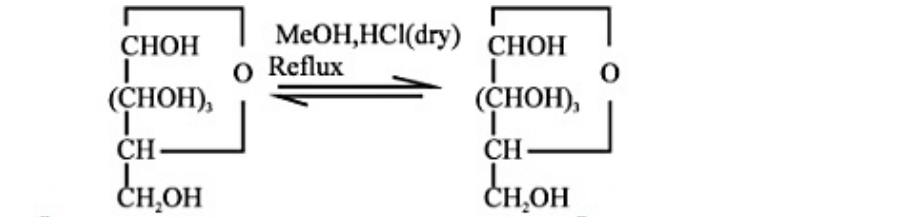
Mutarotation : When a – D glucopyranose $\left([\alpha]_D^{20} = +113^\circ\right)$ is dissolved in water then optical rotation change to $[\alpha]_D^{20} = +52.5^\circ$ This spontaneous change in optical rotation monosaccharides termed as mutarotation. All the monosaccharides mutoratate in water (and in other solvents also).

Mutarotation is general acid base catalysed reaction



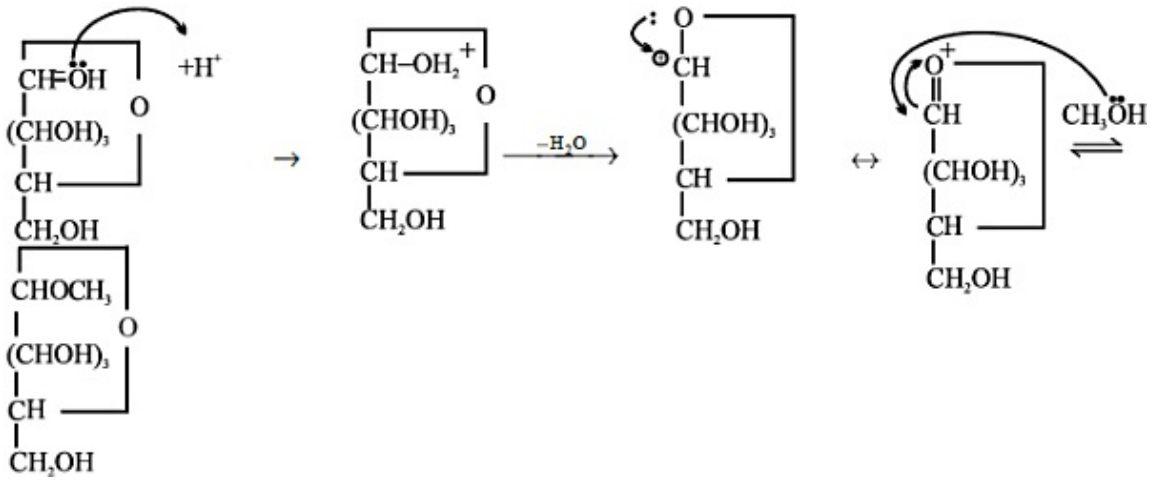
The above general acid base catalysed mechanism is proven by the fact that mutarotation does not take place only in presence of pyridine (base) or only in presence of phenol (acid). Presence of both is required.
In other system also mutoration is observed.

2) Action of alcohol (in presence of dry HCl)



α/β - D glucopyranoside α or β Methyl-D-glocopyranoside

Mechanism :

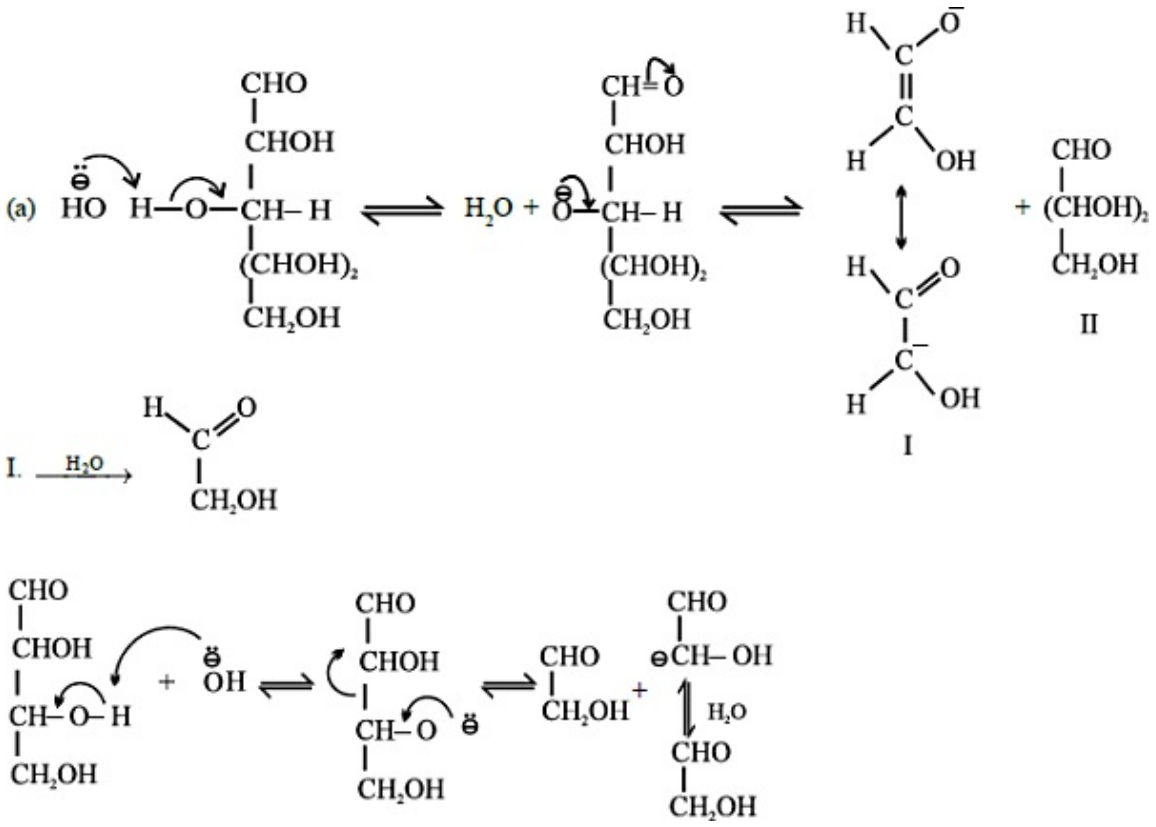


As the $\overset{\oplus}{C}$ is stable therefore only anomeric – OH (i.e. OH at C_1) gets methylated not the other alcoholic – OH groups.

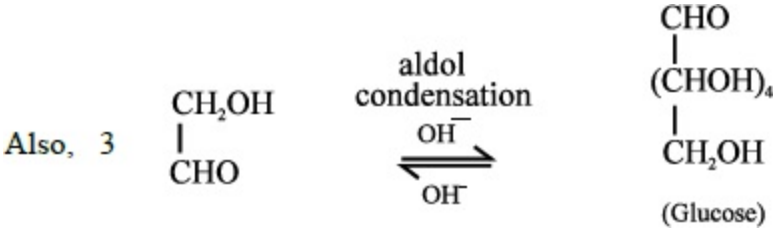
3) Action of alkalis :

Aldoses and ketoses are not stable in presence of base. In presence of base a) reverse aldol condensation., b) Lobry de Bruyn Ekenstein rearrangment takes place.

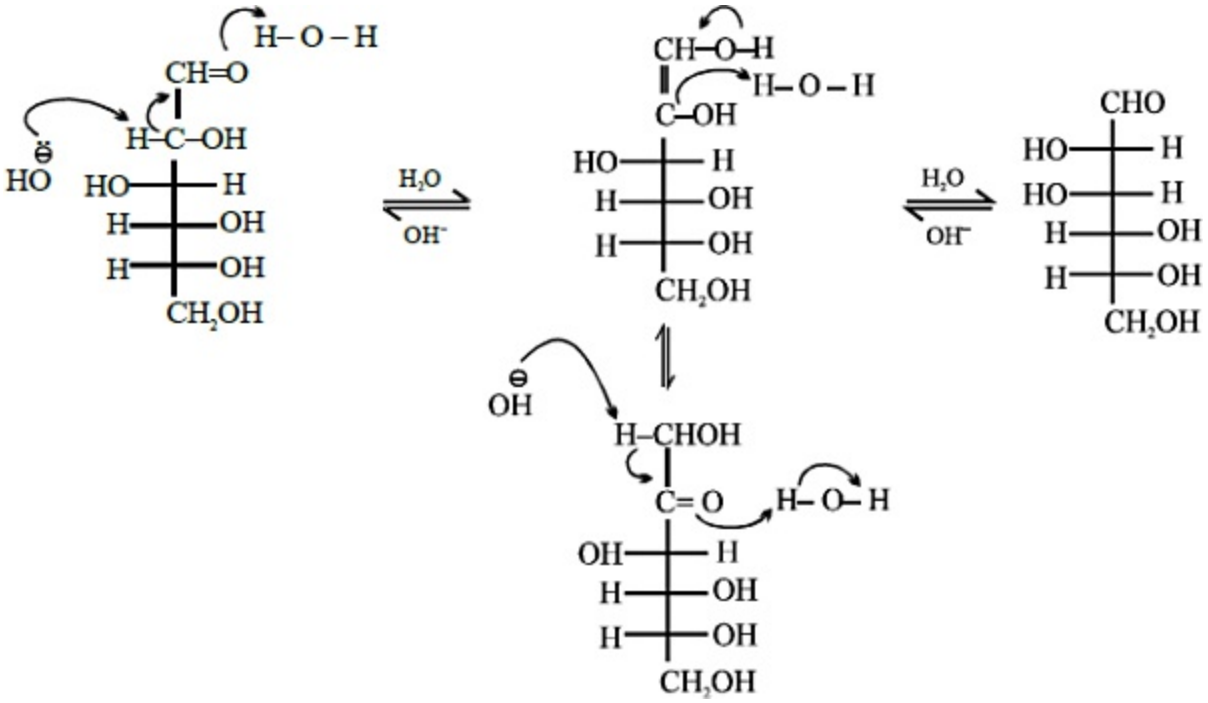
Mechanism :



The above breakdown in presence of dilute base takes place through E1CB mechanism. The reaction takes place in the open chain form

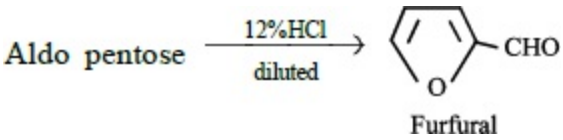


(b) Epimerisation : Conversion of D- glucose to D- mamose through enediol tautomer formation In the alkline medium and also D- glucose → D- fructose in equilibrium



When two optical isomers having more than one asymmetric atom (carbon) differ from each other in configuration about one such atom, the two optical isomers are called epimers. Therefore this is basically inter conversion of diastereoisomers.

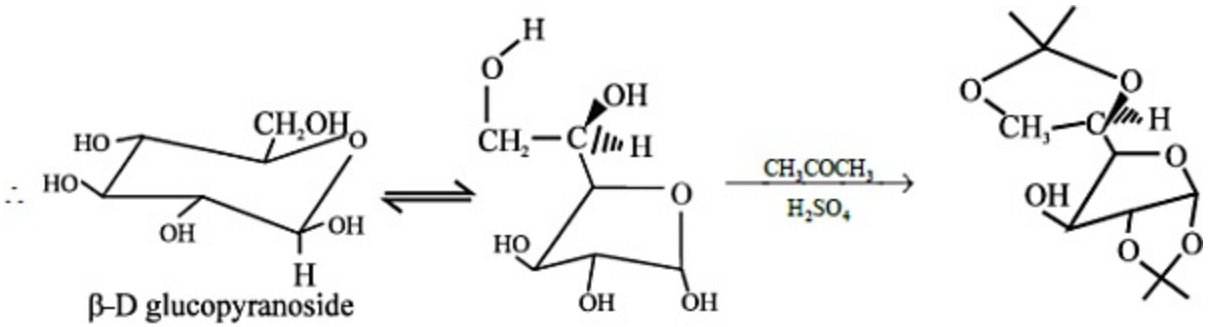
Action of mineral acid : Only interchange of α into β glucose. No other effect is observed at room temperature. But with hot mineral acid, dehydration takes place as shown below; For example;



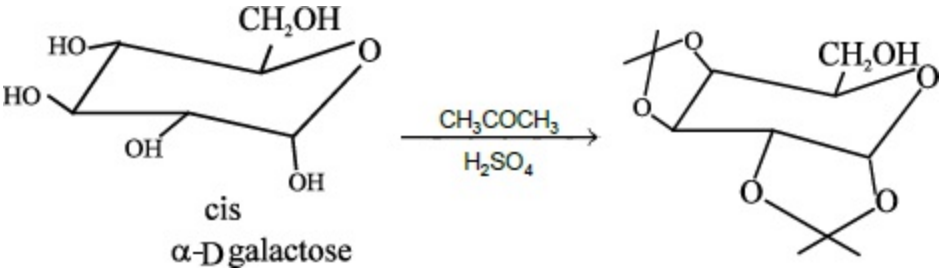
Furfural

Action of carbonyl compounds :

Polyhydroxy carbonyl compounds react with $-\underset{|}{C}=O$ in presence of acids. PhCHO, CH_3COCH_3 are generally used and basically to block – OH groups. cis 1, 2 Diols or out of two OH if one is primary then the acetal or ketal forms. This is the nature of sugars.

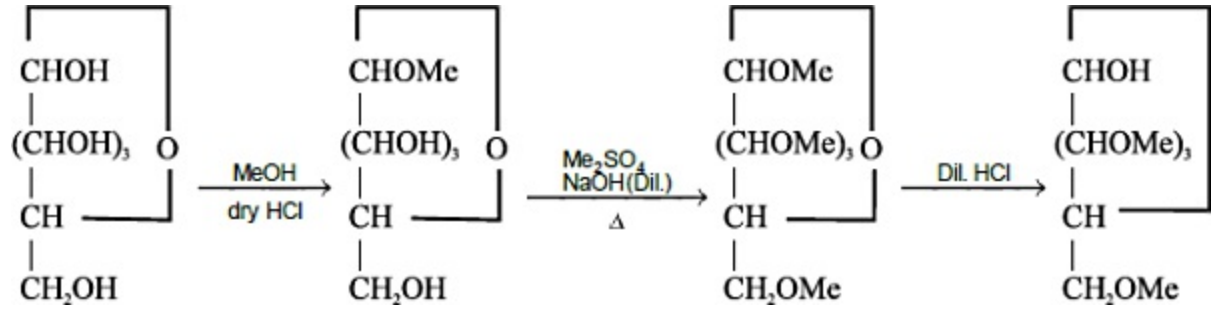


I
1, 2 : 3, 6
di-o-isoprypylidlue
-α-oglucofur
-anoside

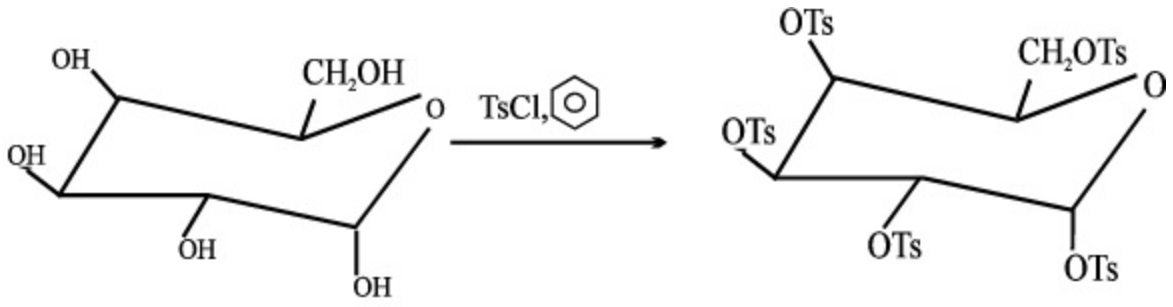


Mild hydrolysis of I with CH_3COOH and further with HCl/ H_2O give D-glucose

Methylation of – OH groups other than C$_3$– OH :



Esterification :



Reduction : D- glucopyranose $\xrightarrow{\text{Red P+HI}}$ $\left\{\begin{array}{l} CH_3(CH_2)_4CH_3 \\ + CH_3CH(CH_2)_3CH_3 \\ \quad\quad\quad | \\ \quad\quad\quad I \end{array}\right\}$

Oxidation of aldoses and ketoses :

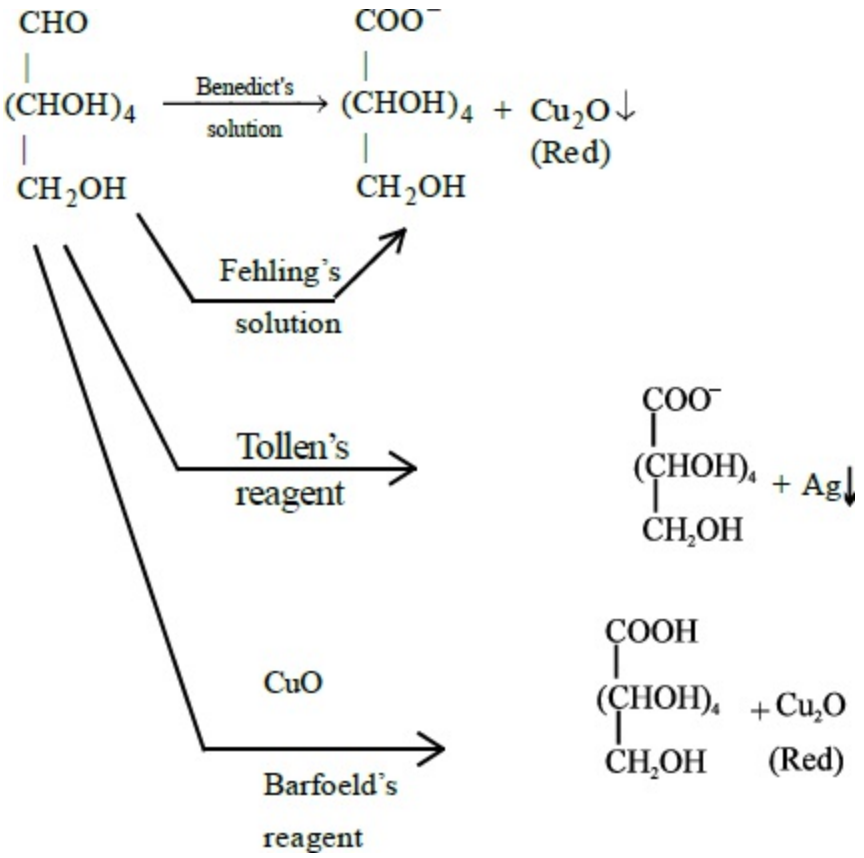
Oxidation reactions have been studied with

a– Benedict's solution [Alkaline solution of copper citrate complex]

b– Fehling's solution [Alkaline solution of copper tartrate]

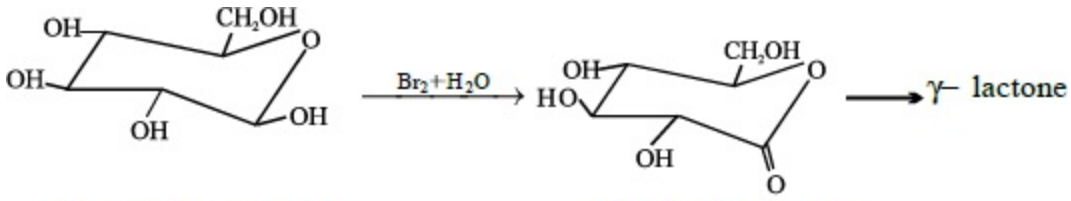
C– Tollen's reagent [Ammoniacal $AgNO_3$]

d– Barfoed's reagent [Cu $(CH_3COO)_2$ + 1% CH_3COOH]



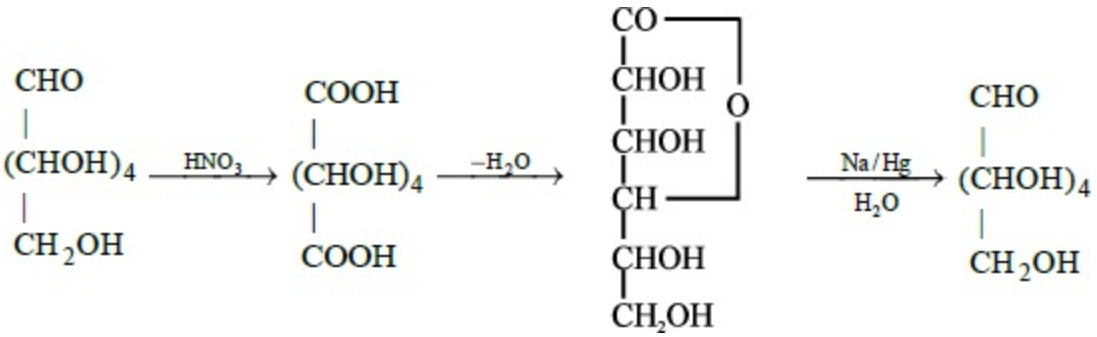
Ketoses cannot convert into aldoses in acidic medium (which happens in basic medium), therefore no reaction with Barfoed's reagent is observed.

Br_2 - water also can oxidise aldoses but fails to oxidise ketoses. It cannot oxidise – CH_2OH group also For example –

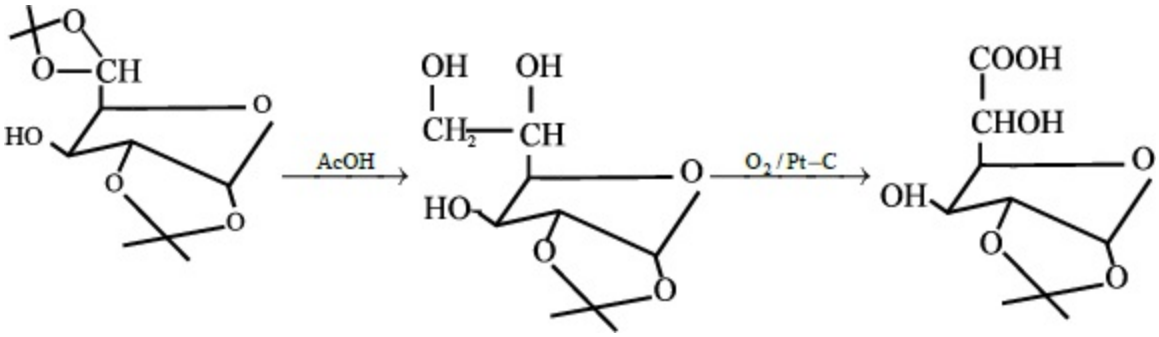


β - D glucopyranone δ- gluconolactone

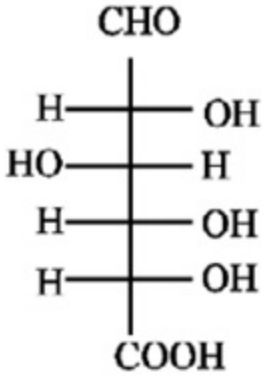
Hot HNO_3 can oxidise aldoses to hydroxy carboxylic acids, called aldaric acids.



Oxidation of CH_2OH group by blocking other hydroxyl groups by $(CH_3)_2CO$ is shown as follows;

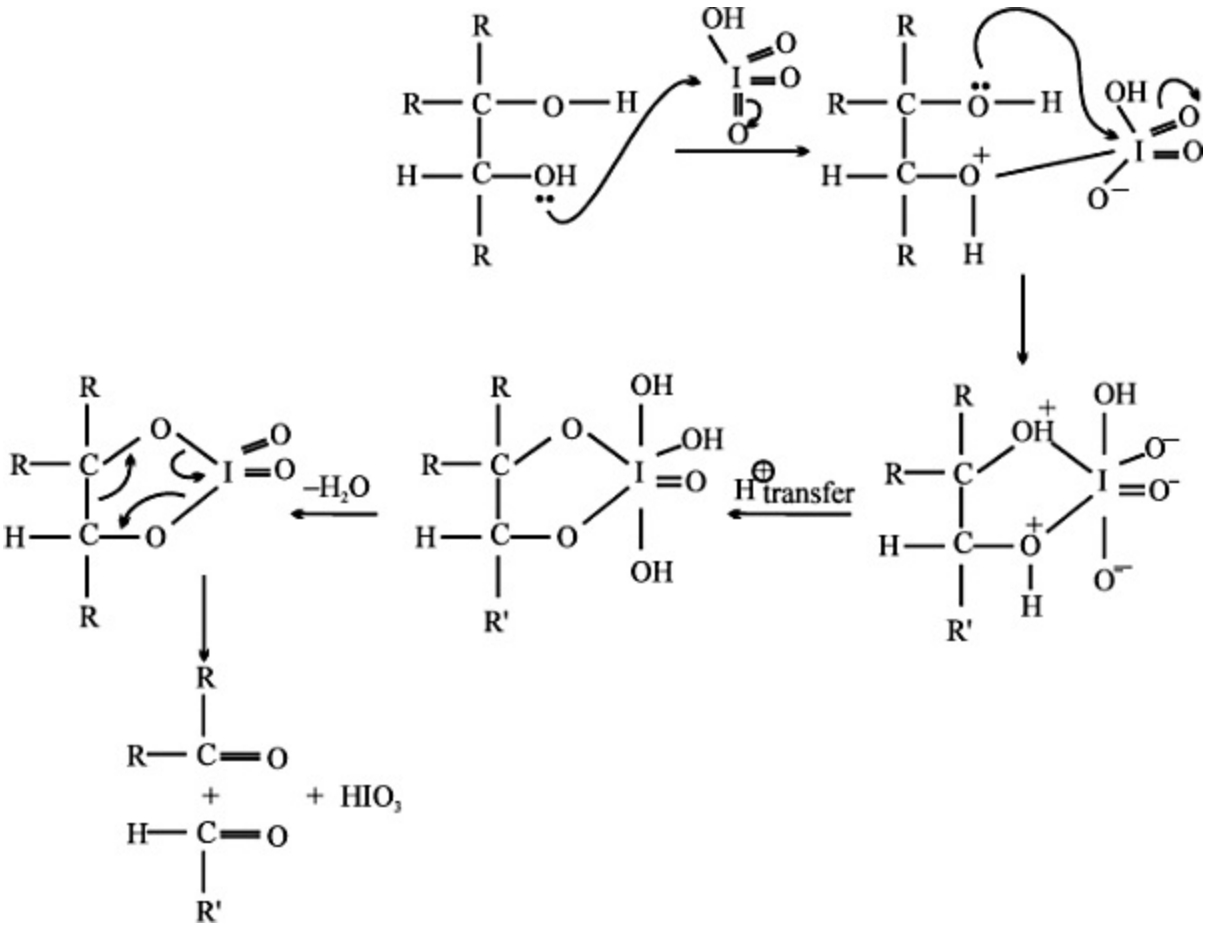


The open chain form of glucouronic acid is



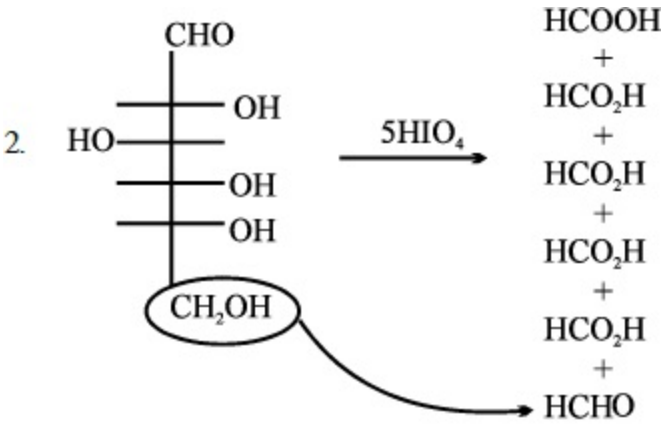
Oxidation by HIO_4 :

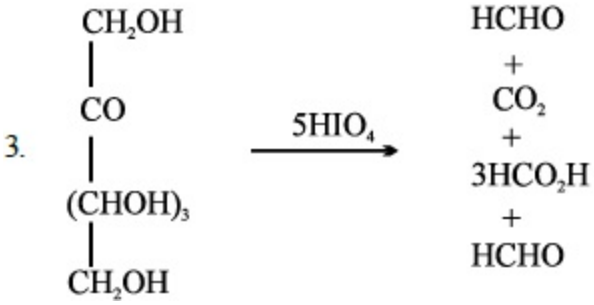
The oxidation by HIO_4 follows the mechanism given below,



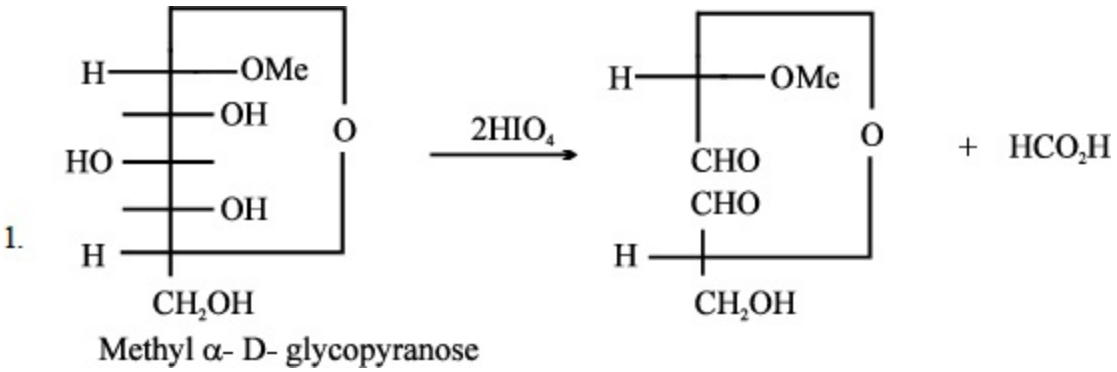
Few examples are,

1. $CH_3COCHO \xrightarrow{HIO_4} CH_3-\overset{\overset{O}{\|}}{C}-OH + HCOOH$





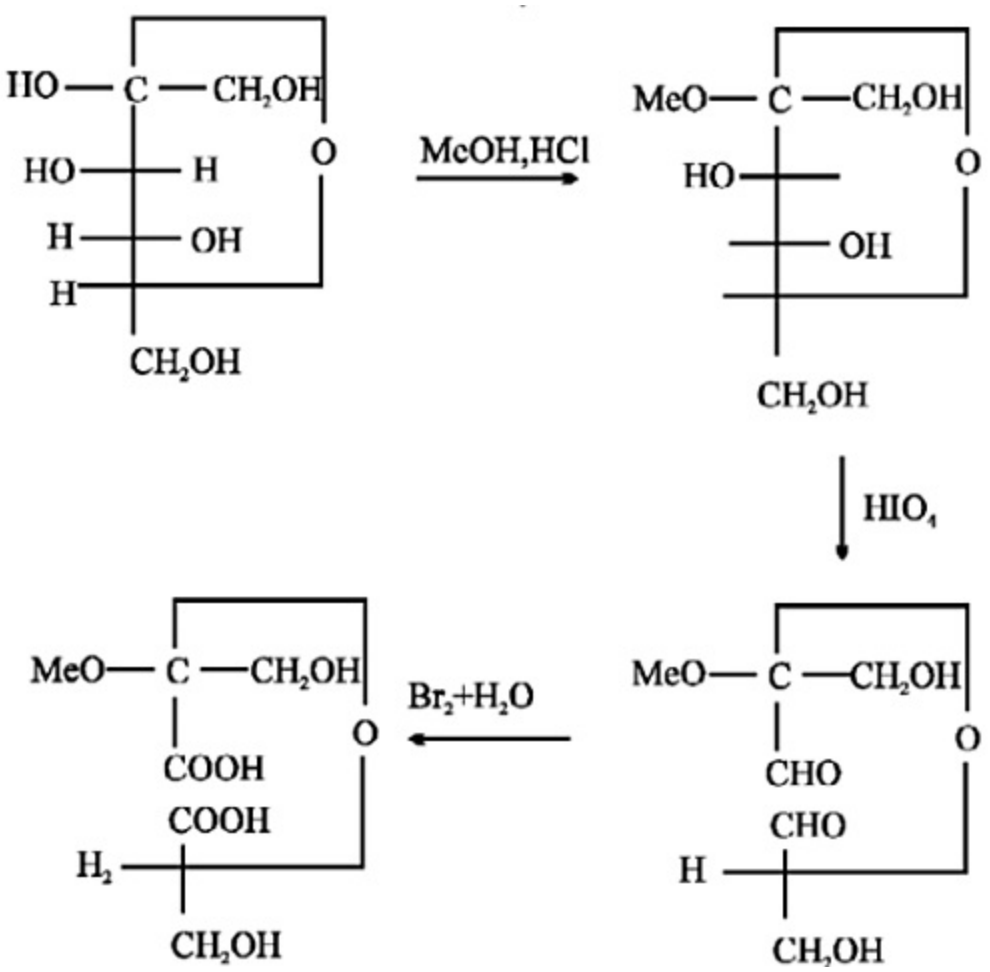
Ring size of sugars are determined by HIO_4 oxidation as shown below ;



Methyl α- D- glycopyranose

Therefore α - D glucose exists in 6 membered pyranose ring structure, since methyl α -D glucofuranoside does not give HCOOH. Therefore 6-membered pyronose ring exists.

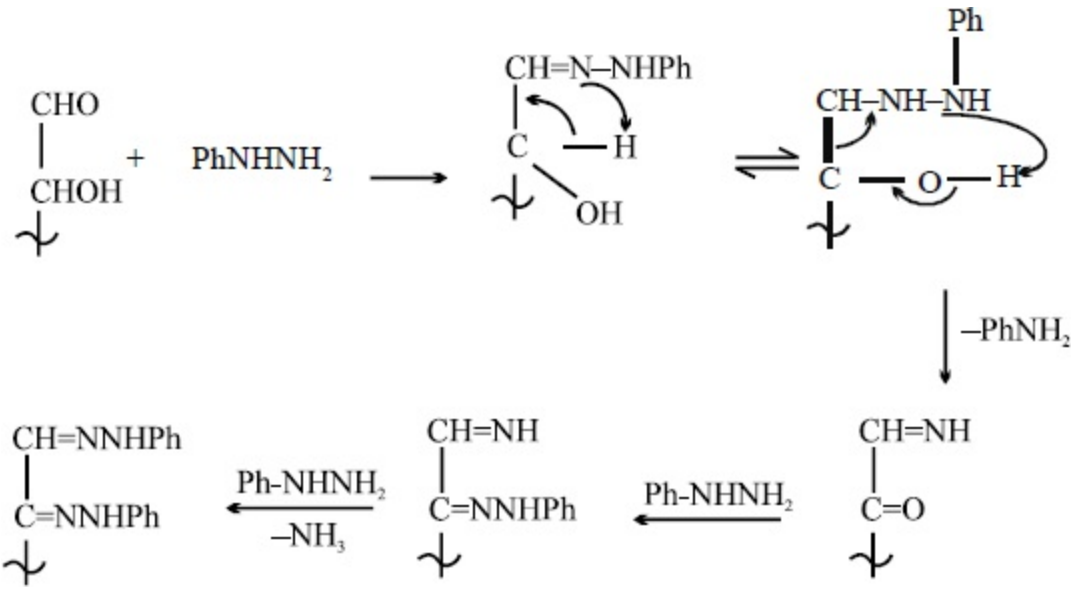
2. For the fructose, the ring structure is determined by the following sequence.



As there is no formic acid (HCOOH) formation therefore it has furan ring structure.

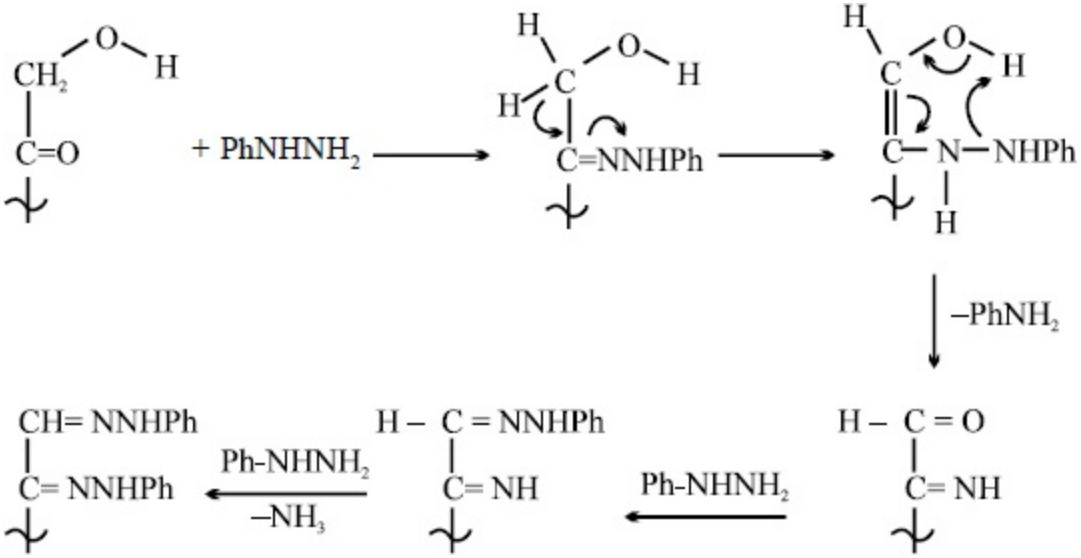
Action of Ph $NHNH_2$:

Reaction of glucose, mannose, fructose give same osazone by Amadori rearrangement. For Glucose

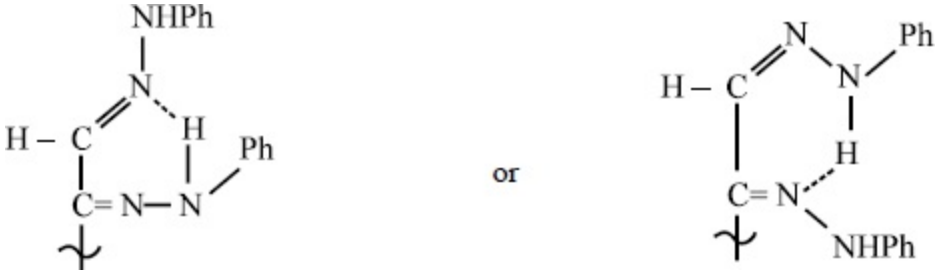


'Osazone' (Bright yellow in colour)

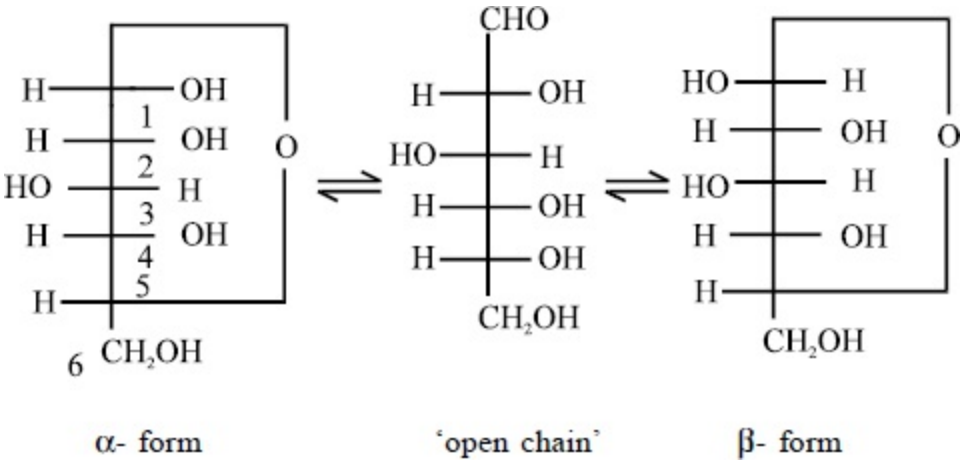
With fructose :



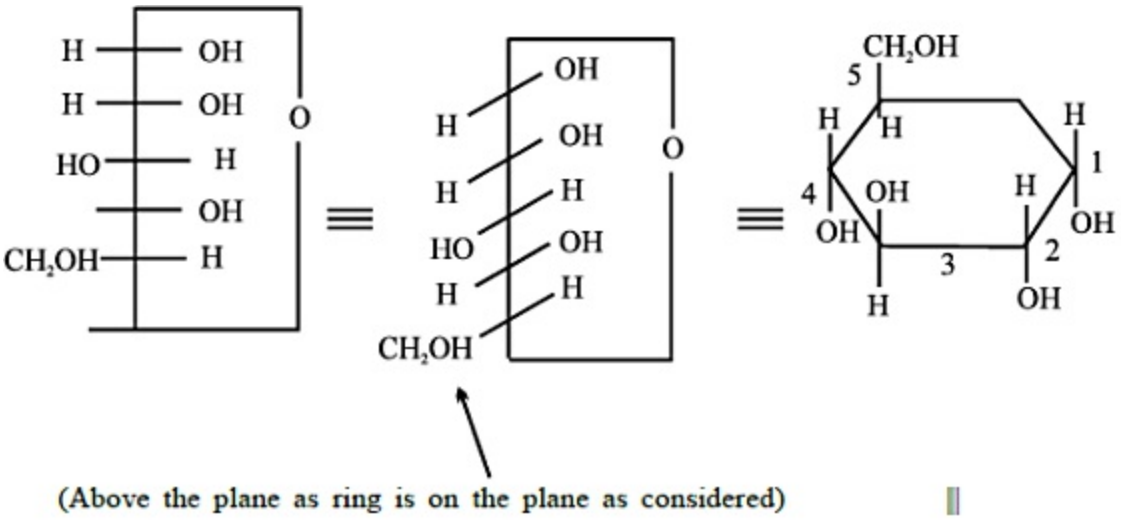
After osazone formation the reaction stops due to high stability of osazone by chelation by H- bond.



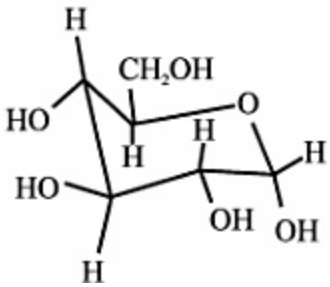
If α -D-glucopyranose is taken in aqueous solution then the observed rotation changes from +111° to + 53° and this phenomenon is called as mutarotation. This occurs due to the equilibrium which sets up among α - form, β - form and the open chain form of glucose as shown below. α and β forms are called as the anomers to each other.



To draw α - form in planar cyclic form, we give two Walden inversions at C_5,



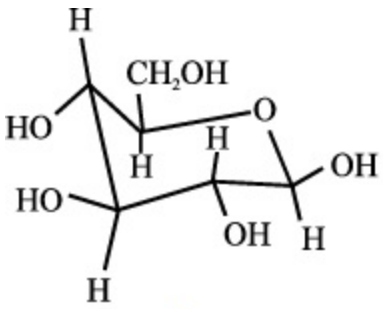
(I)



That is we just put the groups in the chair conformation as below and above

the plane in the previous diagram I.

Smilarly, β will be



(II)

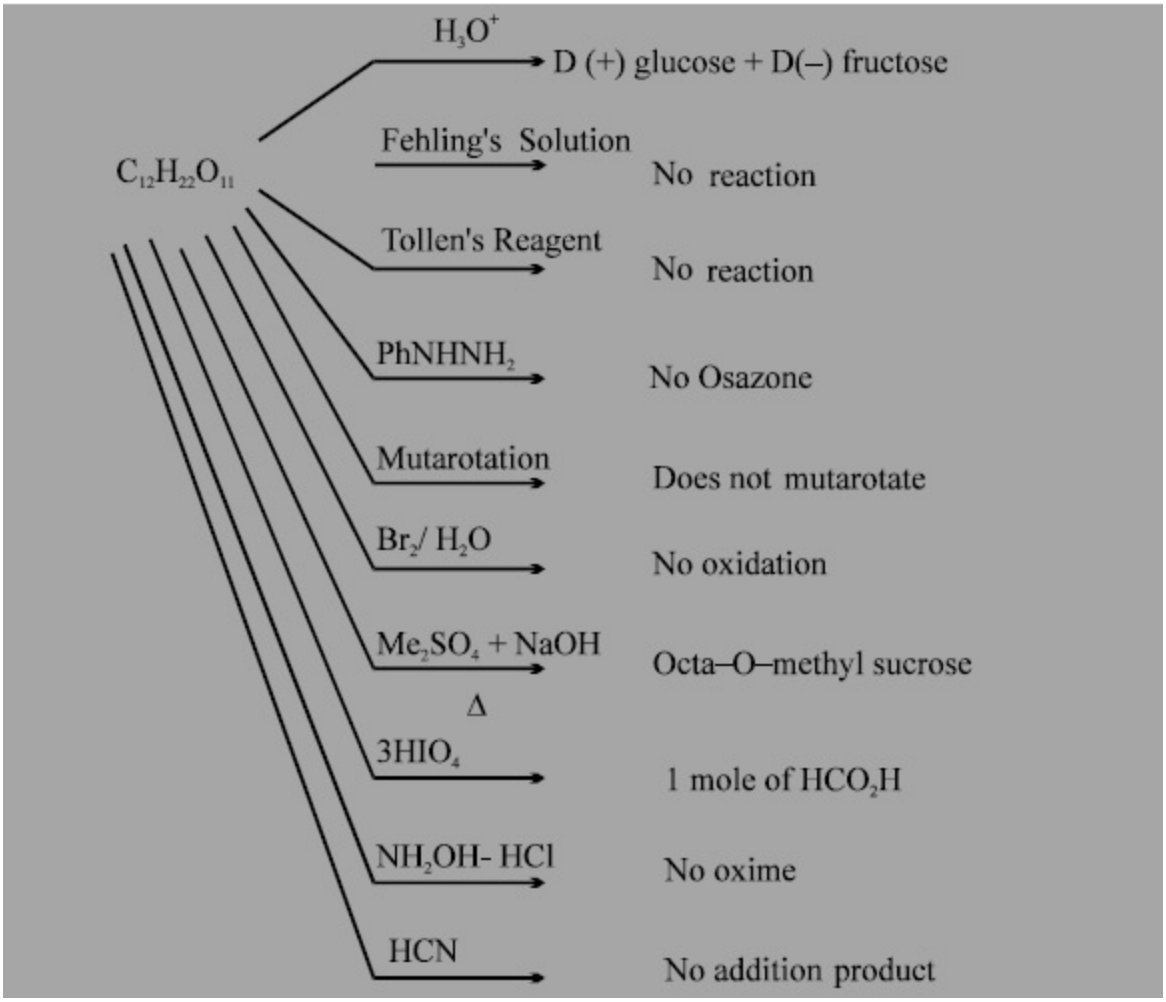
β

As all groups in β - conformation are situated equatorially, therefore it is stabler than α - form as one – OH is axial in α , which causes 1,3 trans annular strain.

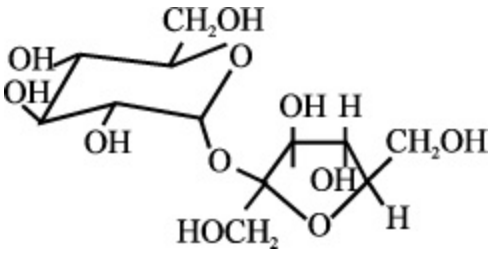
Disaccharide:

Sucrose ;

Sucrose ; ($C_{12}H_{22}O_{11}$) , which is a disaccharide $\left\{\begin{matrix}[\alpha]_D^{25^\circ} = +66.5^\circ \\ \text{Soluble in water}\end{matrix}\right\}$ as on hydrolysis by HC1 gives glucose, fructose the following are the reactions shown by sucrose.

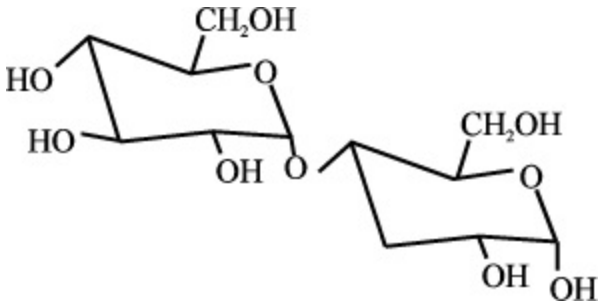


Therefore sucrose is,

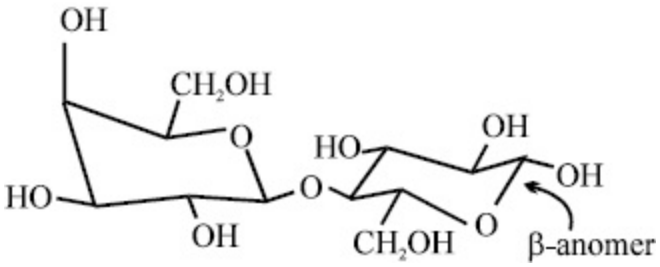


Maltose (α - D glucopyranosyl – α -D glucopyranose) ;

Maltose $\xrightarrow[\text{solution}]{\text{Fehling's}}$ reduction is possible of the reagent. Maltose also reduces Tollen's reagent, Benedict's solution etc. Therefore maltose is a reducing sugar.The structure of maltose is shown below and it has α - glycosidic linkage.



Lactose is a reducing sugar and reduces all Fehling's solution, Tollen's reagent etc. The structure of lactose is;



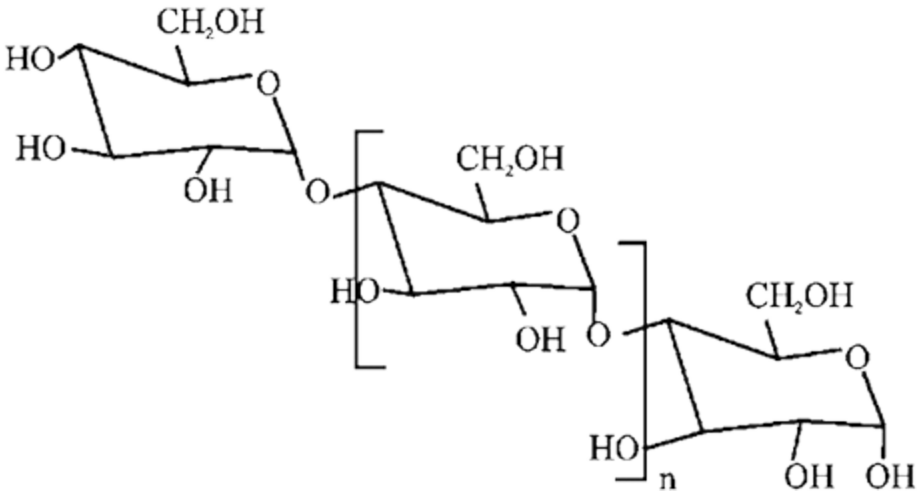
Lactose is composed of D + glucose, D(+) galactose. It has β -glucoside link.

Polysaccharides :

Starch ;

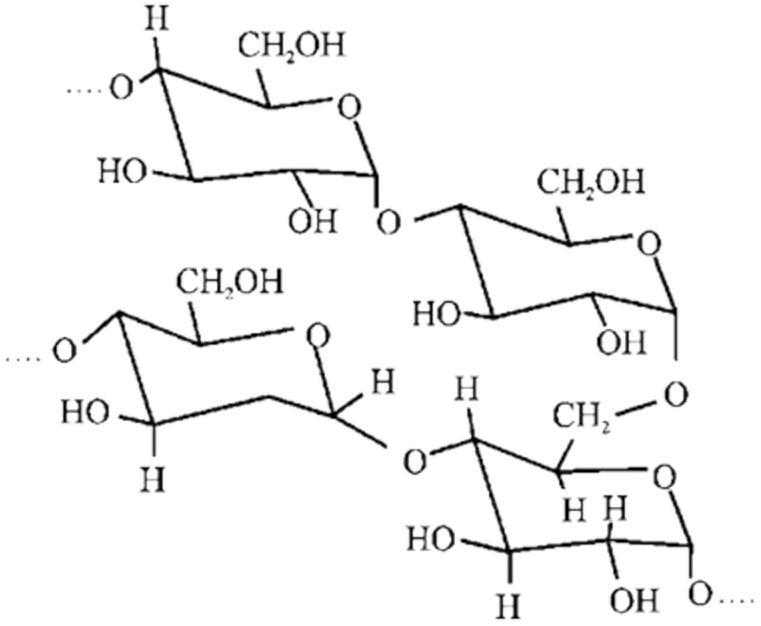
This is non sugar. Wheat, rice, potatoes etc. are the examples of starch. Amylose and amylopectin are the two fractions which make starch of the molecular formula $(C_6H_{10}O_5)_n$. Both hydrolyse to give maltose, finally D(+) glucose.

Amylose : It is a condensation polymer made up of (+) maltose, joined by α -linkage to C– 4 of the next one. The structure is,



This has molecular weight of 40,000 (approx.). Amylose is a linear polymer containing about, 200 D(+) glucose units, each joined by α - linkage.

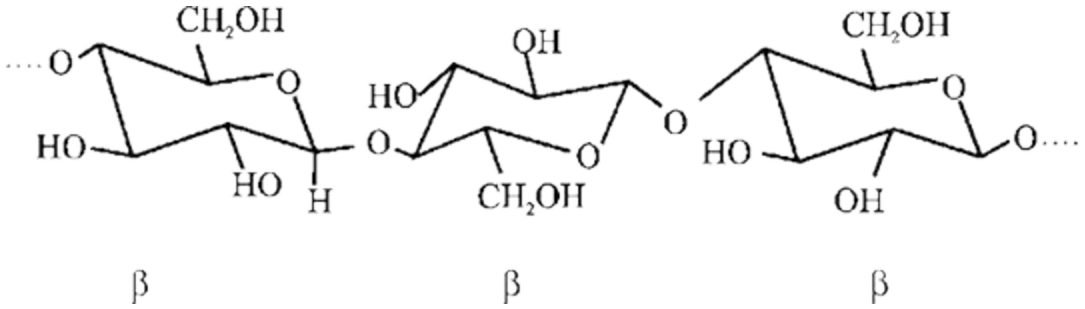
Amylopectin : This is highly branched structure which consists of hundreds of chains of 20-25 glucose units. Each of them is joined to the other by C–l, C– 6 linkage. Starch is completely hydrolysed to give glucose. 1000 glucose units consist of one molecule of amylopectin. Glucose thus formed can be used for sweets and candy. Starch is used as stiffening agent in the laundry work and in adhesives.



Cellulose :

It is the major component of plant. It doesn't have any taste and highly

insoluble in water. Molecular formula of cellulose is $(C_6H_{10}O_5)_n$ and upon hydrolysis produces glucose molecules. In cellulose D(+) glucose units each joined by glycosidic linkage to C–4 of the other one. The structure is shown as follows



In maltose α - linkage is observed but in cellulose β - linkage is present in individual cellobiose units from which forms cellulose . Multiplication of cellobiose leads to cellulose. Approximately 1500 glucose units/ molecules are observed. H- bond holds the long chains. Cellulose on treatment with HNO_3 produces cellulose nitrate, which is used as detonating agent. Pyroxylin is mono or dinitrated glucose molecules in the cellulose, and used in the manufacture of celluloid, and photographic film. Cellulose acetate is used as textile fibre and clothing. Cellulose xanthate (solution of which in NaOH + CS_2 is called as viscose), used as threads of rayon and cellophane.Cellulose gum (sodium carboxy methyl cellulose) is used as adhesive gel and has use in detergent.

Amino acids and peptides

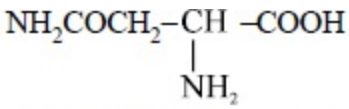
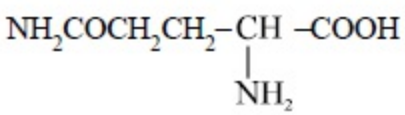
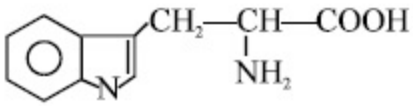
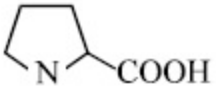
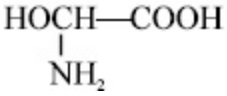
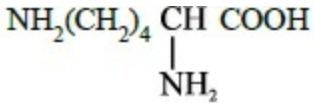
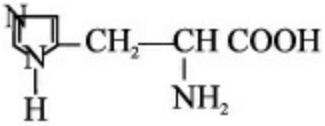
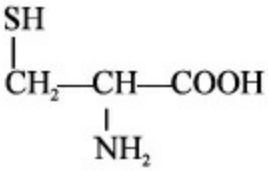
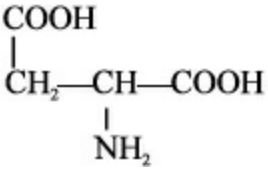
Amino acids, from the name itself we understand the compound has two functional groups present $–NH_2$, –COOH. $–NH_2$ can be present at α, β, γ, δ etc with respect to –COOH group. You will be astonished to know that all proteins are made up of these amino acids. 10 amino acids out of 20 naturally occuring amino acids are essenteial for life and these are called as essential amino acids, which can not be synthesised in human body. Amino acis are divided into three main classes;

1. Neutral amino acids (having same number of NH_2 and –COOH group/s eg; glycine NH_2CH_2COOH)
2. Basic amino acids (where the number of $–NH_2$ groups are more than –COOH group/s).
3. Acidic amino acids (where the number of –COOH group/s are more than – NH_2 group/s).

Excepting glycine all α -amino acids are chiral and all naturally occuring α -amino acids are L at α -C, or S (absolute configuration).

By protein hysdrolysis the following amino acids are obtained

		Symbol
glycine (Gly)	NH_2CH_2COOH	G
Alanine (Ala)	$CH_3CH(NH_2)COOH$	A
Valine (Val)	$(CH_3)_2CH—CH(NH_2)COOH$	V
Leucine (Leu)	$(CH_3)_2CH—CH_2—CH(NH_2)—COOH$	L
Isoleucine (Ile)	$CH_3CH_2CH(CH_3)—CH(NH_2)—COOH$	I
Phenylalanine (Phe)	$Ph–CH_2–CH(NH_2)–CH\,COOH$	F

Aspargine (Asp)		N
Glutamine (Glu)		Q
Tryptophan (Try)		W
Proline (Pro)		P
Serine (Ser)		S
Lysine (Lys)		K
Histidine (His)		H
Cysteine (Cys)		C
Aspartic acid		A

Isoelectric point and dipolar ion :

In dry solid state amino acids exist as dipolar ion or zwitter ion (ampholytes). However in aq. solution, equilibrium exists having dipolar ion, anionic, cationic forms.

$$\underset{\text{I}}{\overset{+}{NH_3CH_2COOH}} \overset{Ka_1}{\rightleftharpoons} \underset{\text{II}}{\overset{+}{NH_3CH_2COO^-}} + H^+ \quad \ldots\ldots (1)$$

$$\underset{\text{II}}{\overset{+}{NH_3CH_2COO^-}} \overset{Ka_2}{\rightleftharpoons} \underset{\text{III}}{NH_2CH_2COO^-} + H^+ \quad \ldots\ldots (2)$$

In acidic medium I exist in large extent but in basic medium III exist in large extent. There is a pH called as pi at which $[NH_3^+ CH_2COOH] = [NH_2CH_2COO^-]$

Derivation of pI :

By equation (1), (2) we get,

$$Ka_1 = \frac{[\overset{+}{N}H_3 CH_2COO^-][H^+]}{[\overset{+}{N}H_3 CH_2COOH]} \quad \ldots(3)$$

$$Ka_2 = \frac{[NH_2CH_2COO^-][H^+]}{[\overset{+}{N}H_3 CH_2COO^-]} \quad \ldots(4)$$

Multiplying equation (3), (4) we get,

$$Ka_1 Ka_2 = [H^+]^2$$

$$\therefore \quad [H^+] = \sqrt{Ka_1 Ka_2}$$

$$\therefore \quad pH = 1/2\ (pKa_1 + pKa_2)$$

$$= pI.$$

At pI amino acid, does not move towards electrodes. Actually at pI, $[NH_3^+ CH_2 COO^-]$ is maximum.

For example ;

$$\text{For glycine, } pI = \frac{1}{2}(2.4 + 9.6)$$

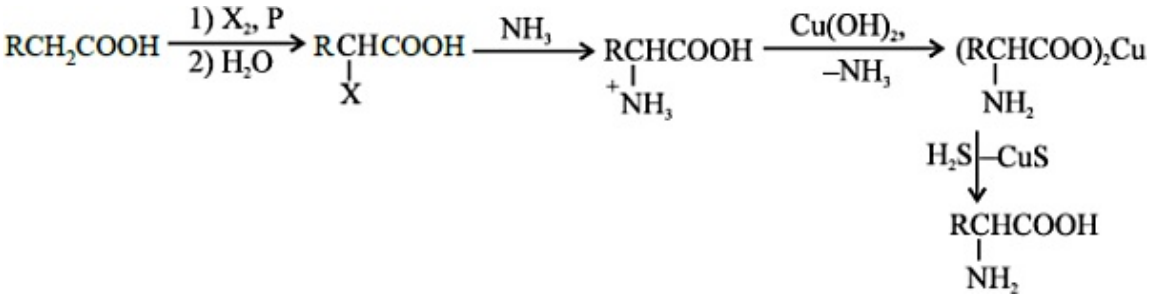
$$= 6.0$$

Optical rotatory power is found to be different for I, II, III. So, their sp. rotation also change depending on pH of the solution. Because of dipolar nature solid AA conduct electricity and has high bp, mp. At pI any amino acid is least soluble therefore it can be separated by the process of filtration.

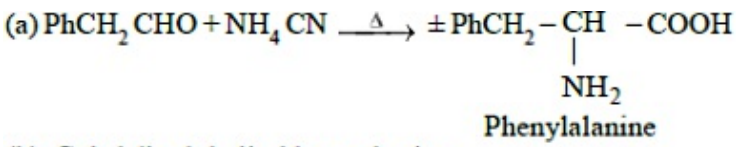
For basic amino acids, for example histidine, pI = 1/2 (pKa_2 + pKa_3). For acidic amino acid, for example aspartic acid, pI = 1/2 (pKa_1 + pKa_2) by calculation as shown above.

Synthesis of amino acids

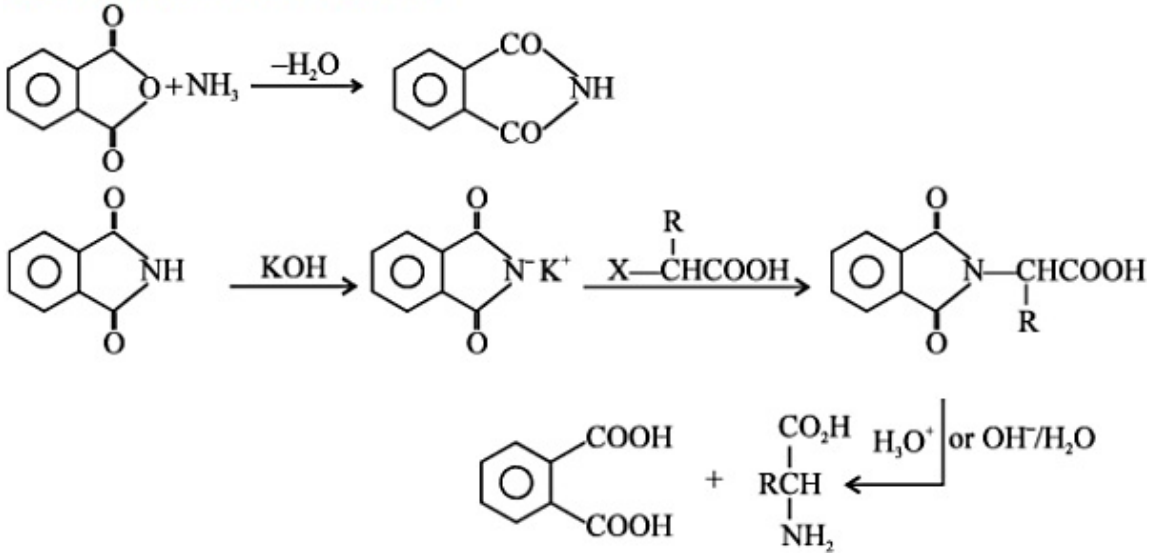
(1) For glycine, alanine, valine etc the following method is very good method.



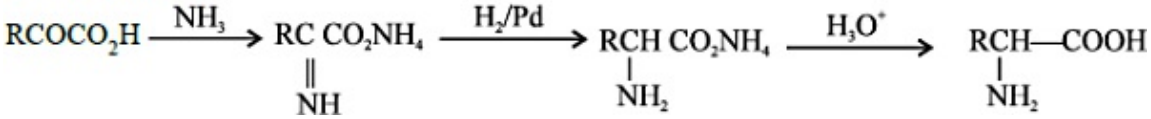
(2) Strecker's synthesis :



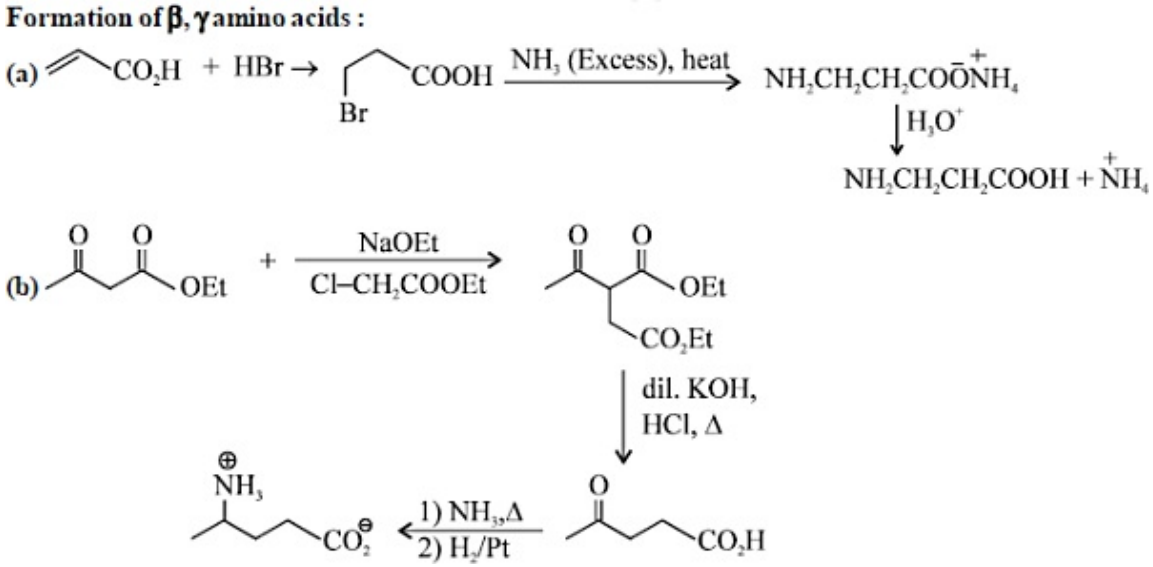
(b) Gabriel's phthalimide synthesis :



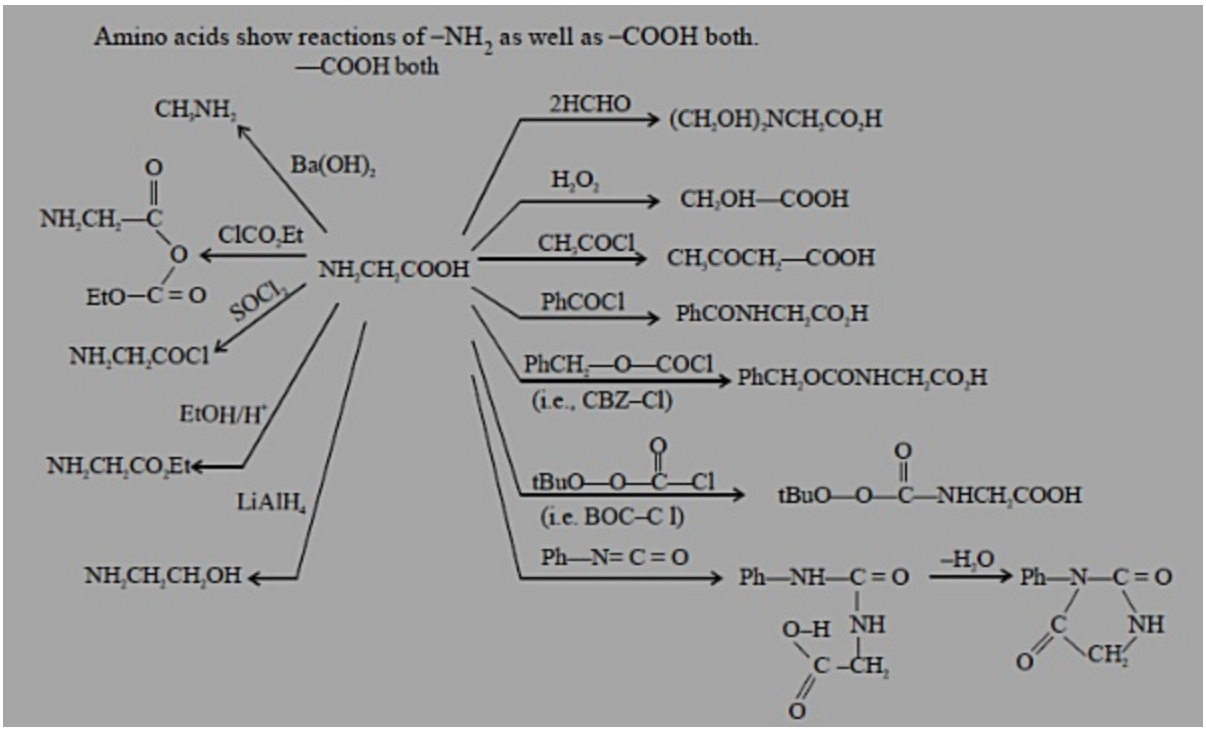
Form Keto Acid :



Formation of β, γ amino acids :



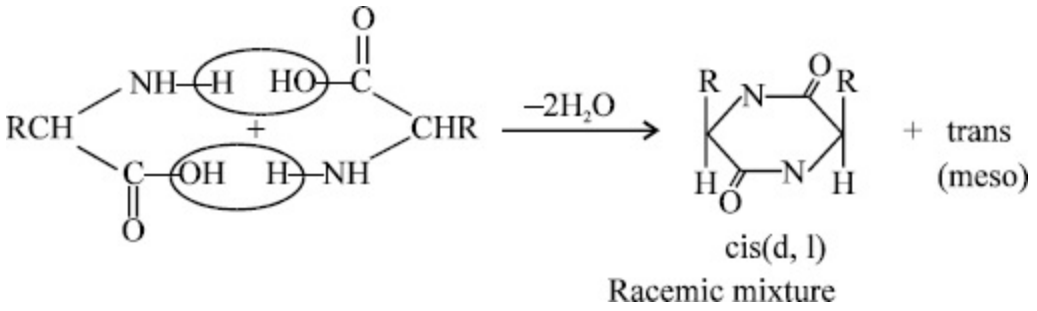
Chemical reactions :



By using HCHO, estimation of amino acid is done (by acid base titration method given by Sorensen) . Van Slykes method is used to determine amino acid quantitatively by producing N_2 using HNO_2. Proline, hydroxy proline containing –NH- do not respond to this test.

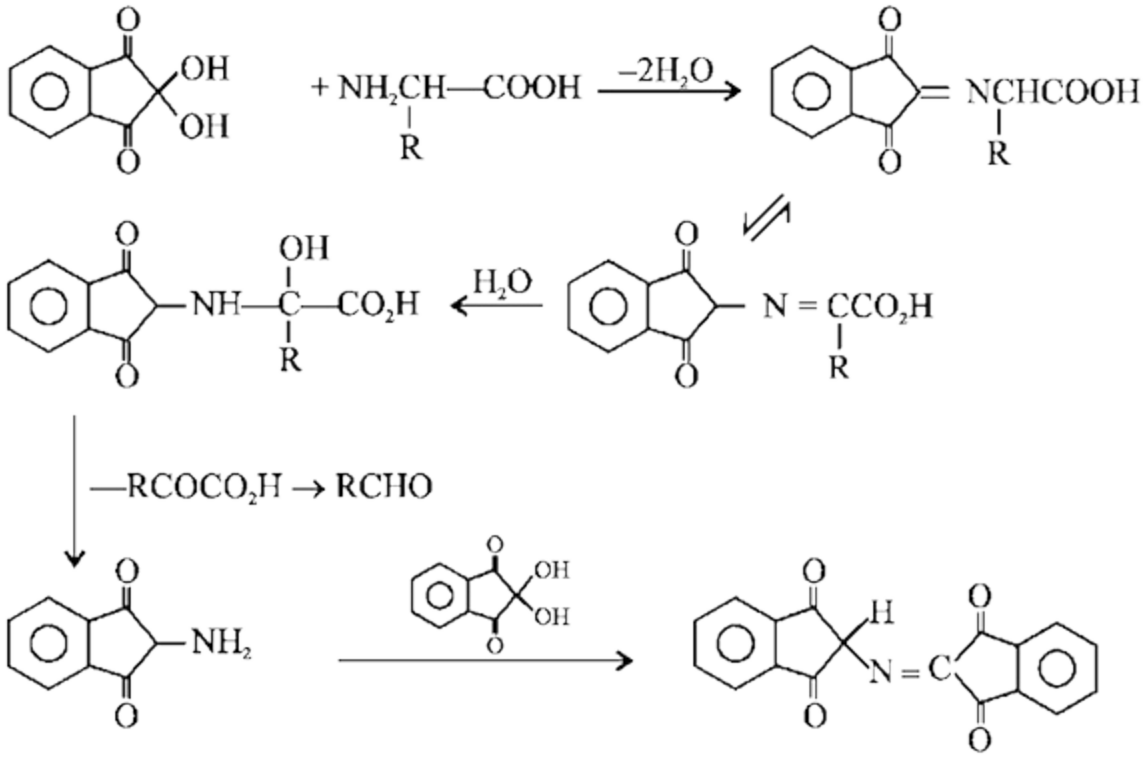
-COCl, $–COOCO_2Et$, $–COOC_6N_4–NO_2$ (p) are required to activate –COOH group. When neutral α -amino acid is heated diketopiperazine

results as shown below.



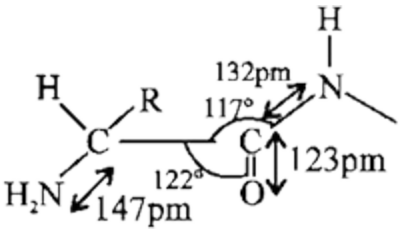
Test for amino acid :

Ninhydrin test is carreid out where an α -amino acid (excepting proline, hydroxy proline) develops blue violet coloured product.



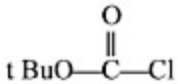
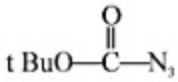
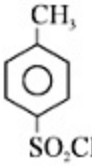
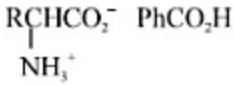
Peptide and pohypeptide :

Several amide linkages in protein (made up of α -amino acids) are catted peptide linkages.

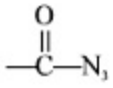
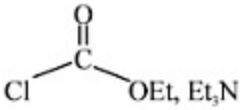
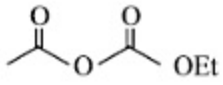
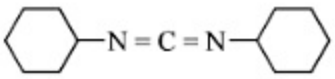
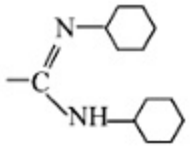


A large number of α -amino acid molecule when join gives polypeptides. Dipeptide has two amino acid units, tripeptide has three amino acids etc. linked to each other.

Therefore blocking and deblocking agent for NH_2 which is required to synthesize the polypetides can be tabulated as follows;

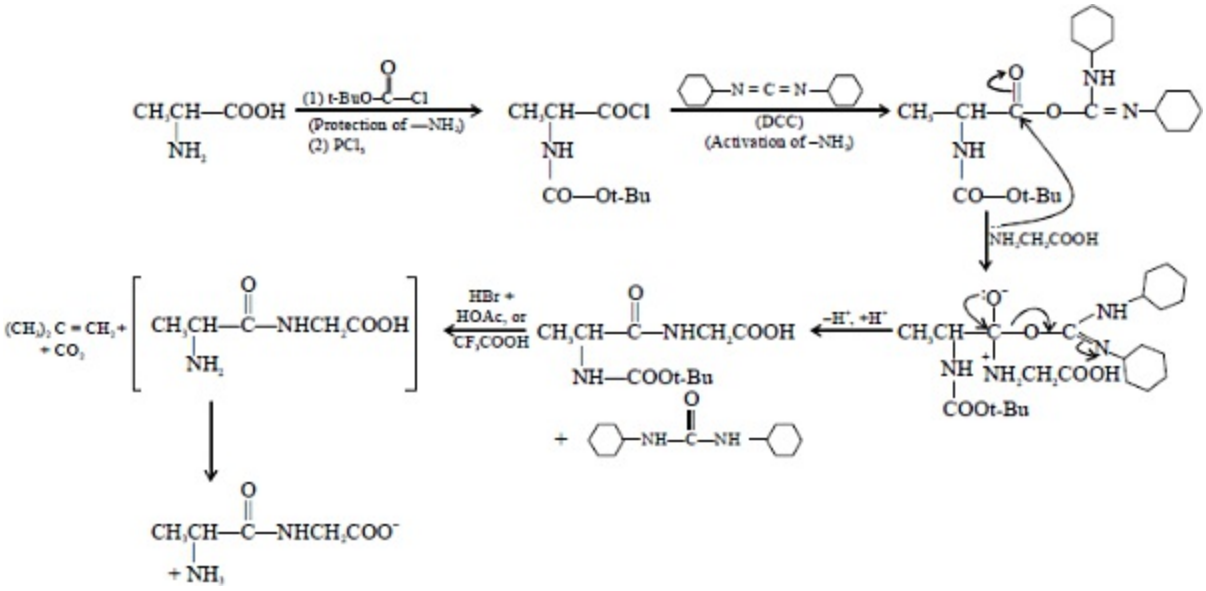
	Reagent	Doblocking reagent	Products
1.	$PhCH_2OCOCl$, OH^- (Benzyloxy carbonyl chloride)	H_2/Pd or H_2/Pt or HBr/HOAC (cold)	$PhCH_3 + CO_2$ + Peptide or $PhCH_2Br + CO_2$ + Peptide
2.		CF_3CO_2H in HOAC or HCl	$(CH_3)_2C=CH_2 + CO_2$ + Peptide
3.		CF_3CO_2H in HOAC or HCl	$(CH_3)_2C=CH_2 + CO_2$ + Peptide
4.		Na/NH_3	 + Peptide
5.	PhCOCl, Base, Ac_2O	HCl/H_2O	

Activation of carboxylic acid group :

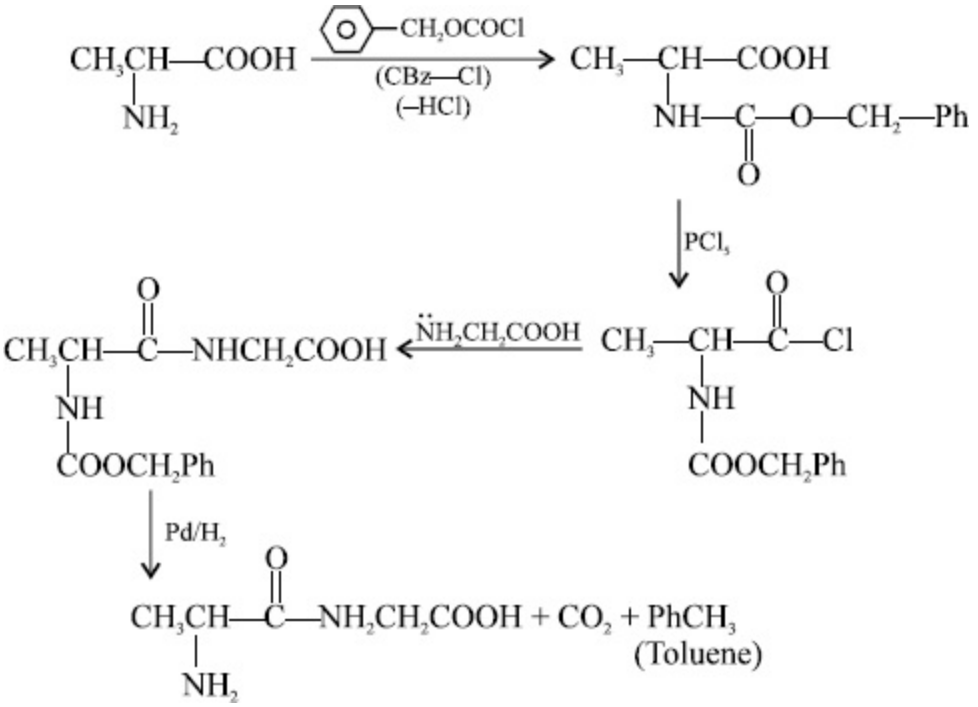
	Activating reagent	Activated group
(1)	1) $EtOH/H^+$ 2) NH_2NH_2, 3) HNO_2	
(2)		
(3)		

Synthesis of dipeptide :

For example ala.gly;



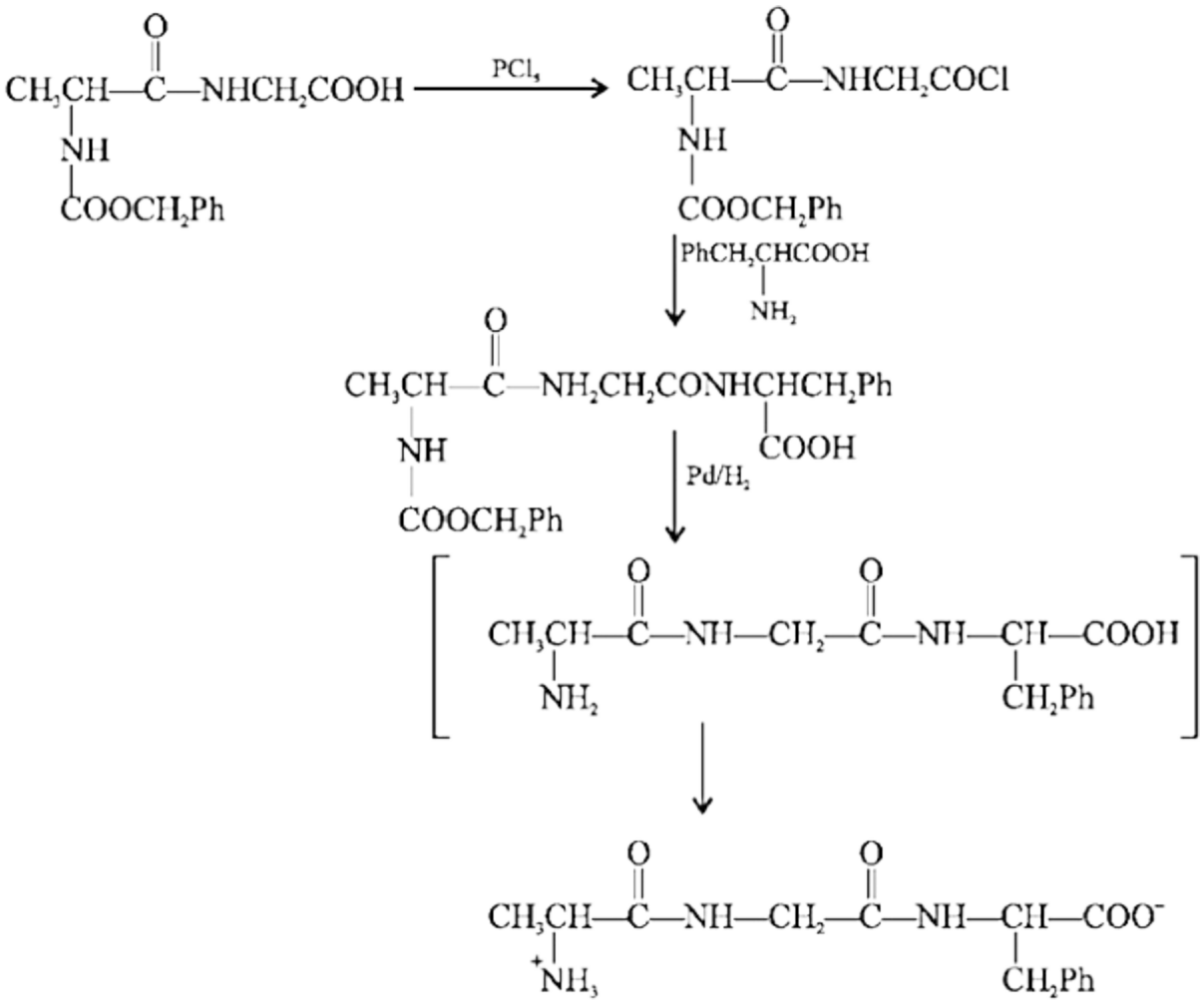
Alternatively :



Here with with/without activating the $–CO_2H$ group we have syntherized a dipeptide ala.gly.

Similarly look at how a tripeptide gly.ala.phe can be synthesised below.

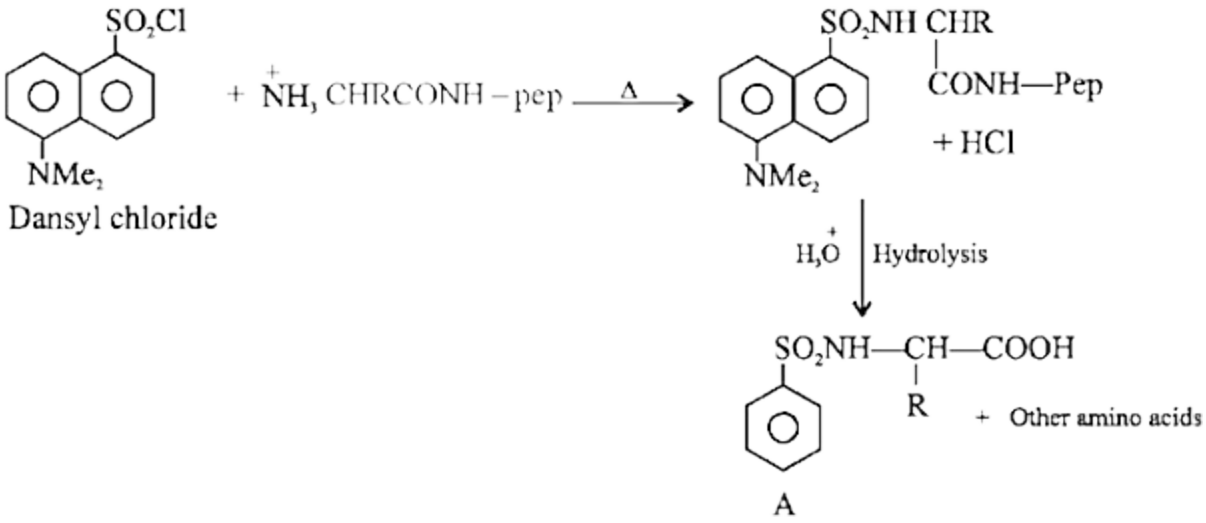
After preparing gly-ala and getting NH_2-blocked we can proceed as follows;



Determination of Structure :

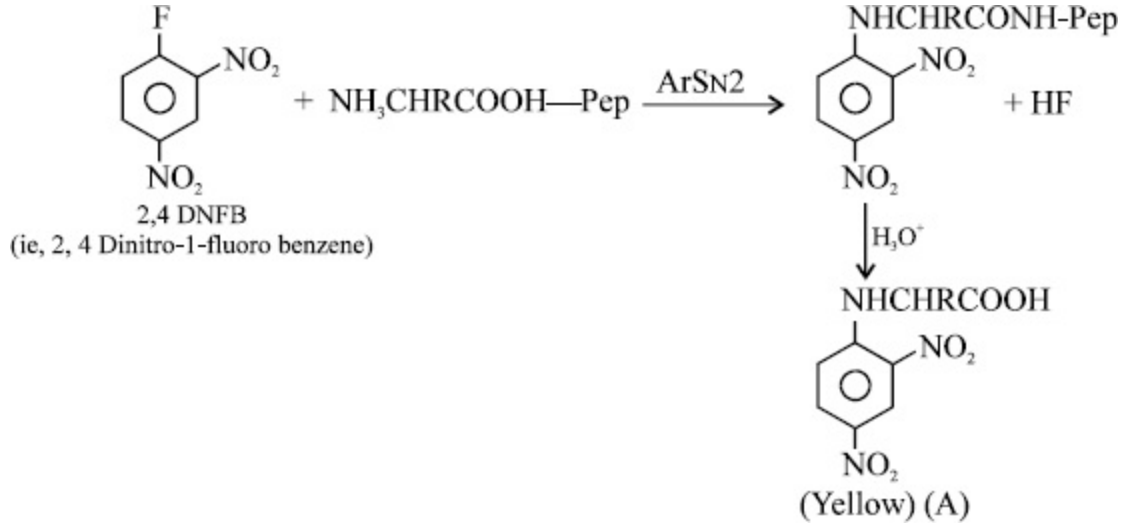
(1) Using dansyl chloride : By using dansyl chloride N-terminal amino acid can be identified.

For example .



Thus produced 'A' can be identified by using fluorescence property of 'A' by standard data.

(2) Using Sanger's reagent :



Comparing the colour of N-DNP, amino acid (A) and standard N-DNP-amino acid chromatographically we find out N-terminus amino acid.

(3) C–Terminal amino acid identification :

Peptide is incubated with the enzyme carboxypeptidase. Upon hydrosis by the enzyme with prolonged incubation, each new amino acid is hydrolysed and appear one by one. A study of the rate of appearance of each newhy released amino acid can give information about the sequence of amino acids.

Polymers

Polymers are very large molecules consisting of several monomers joined together in a regular fashion. Synthetic fabrics for clothing, synthetic rubber for automobile tyres, plastic for toys, utencils etc. all come under polymers. The classification of synthetic polymers are made on physical properties.

Elastomers: Ability to return to its original shape after the removal of force (eg. natural rubber).

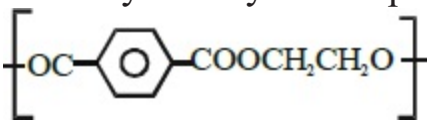
Fibre : In molten condition when it is passed through hole thin thread form (eg. dacron, polythene).

Thermoplastic : These are hard at room temperature, soft when heated (PVC, polystyrene).

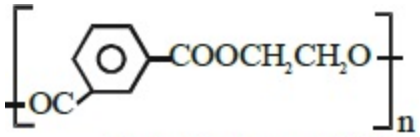
Thermosetting : They undergo chemical changes on heating and on cooling set to hard masses. The change is irreversible and so the polymer cannot be melted again.

Fibre has high tensile strengh and it is necessary that the polymer must be linear to have good strength.

Axial symmetry in the polymer greatly favour the fibre forming ability eg.



i.e. fibre polyethlene as tetraphthalate compared to nonfibre forming ability of



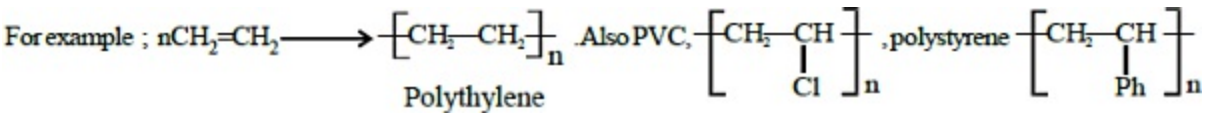
Polyethylene phthalate

Based on the method of preparation polymer is divided into two parts.

(1) Addition or chain growth polymerisation.

(2) Condensation step growth polymesisation :

Addition or chain growth polymerisation : These are prepared by simple addition of C atoms which are bonded by double bond in the momners.

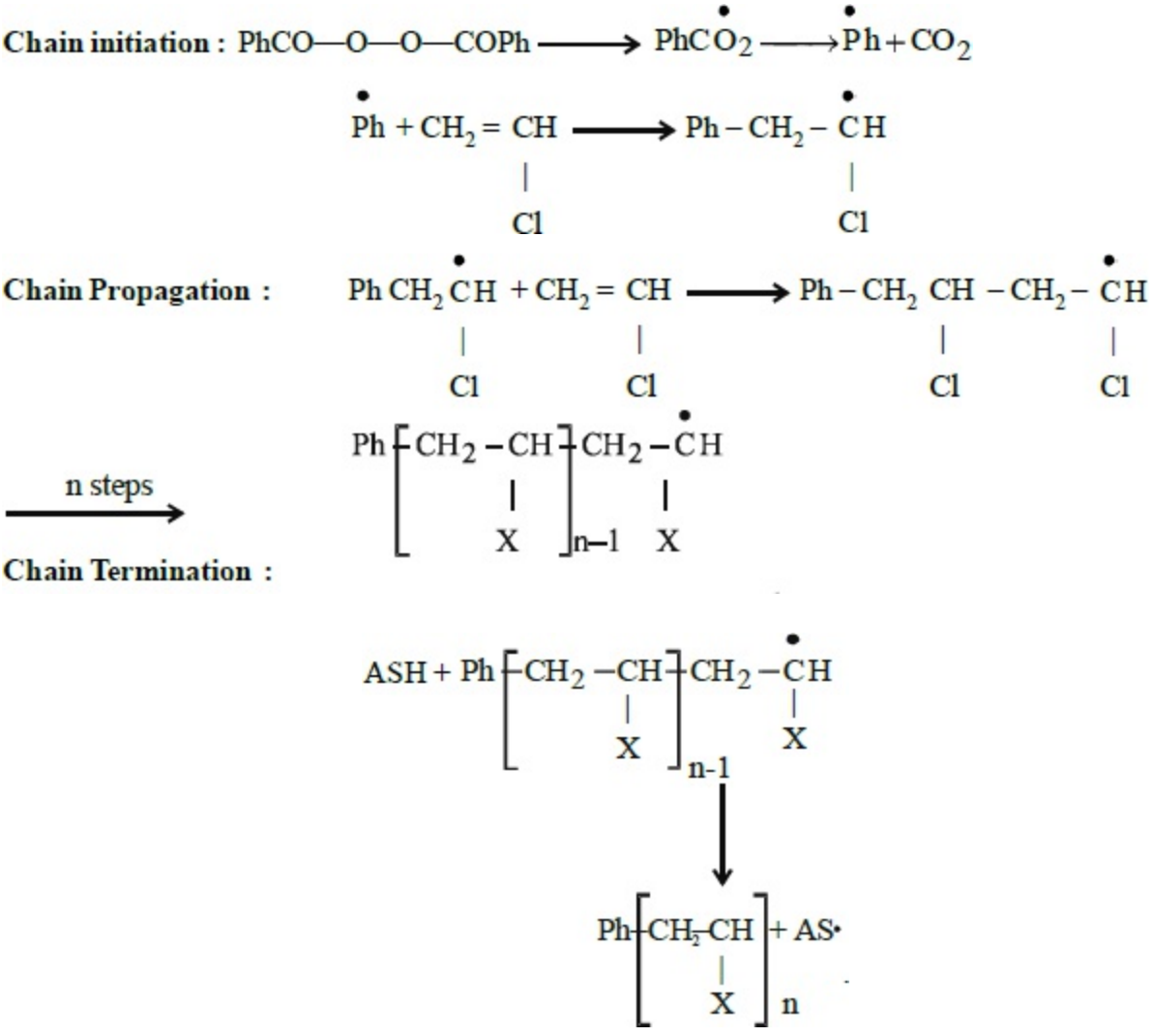


etc.

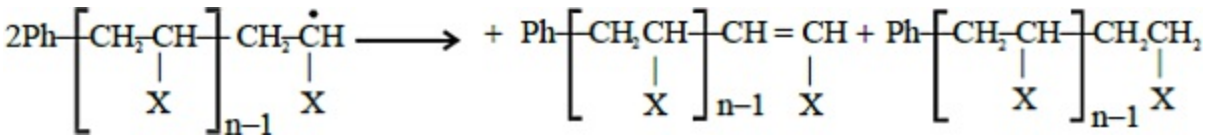
Mechanism of polymerisation can be

(a) Free radical (vinyl polymerisation) :

Mechanism;



ASH is chain transfer reagent. CCl_4 , CBr_4 can act as chain transfer reagent. Disproportion reaction can also take place with the above radicals reaction as shown below.

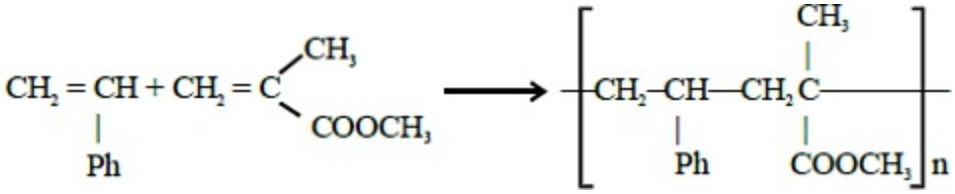


Ph or other group which inserts at the begining do not have any effect on the polymer.

Coplymerisation :

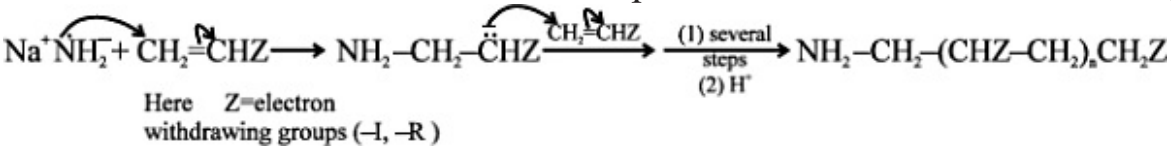
Two different monomers give co-polymer upon polymerisation.

For example ;



(b) Anionic polymerisation : It takes place through anion formation.

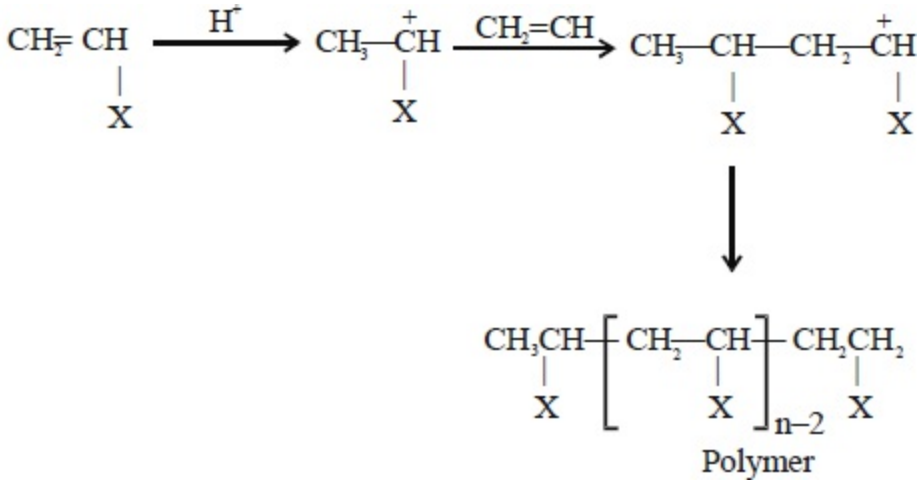
For example ;



(c) Cationic polymerisation : It takes place through cation formation.

For example ;

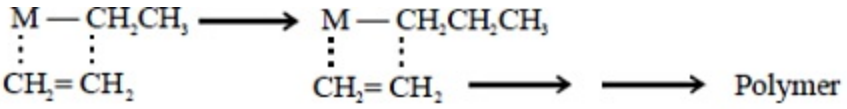
For example ;

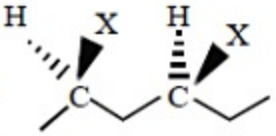


Zieglar Natta polymerization (i.e. coordination polymerisation)

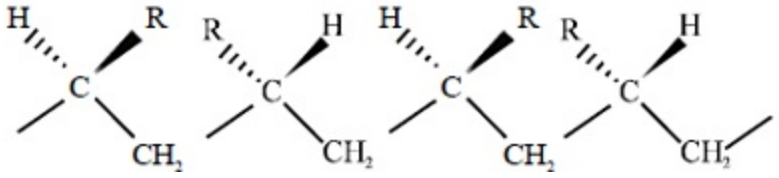
Catalyst : Al Et_3 + $TiCl_4$,

Solvent : Heptane



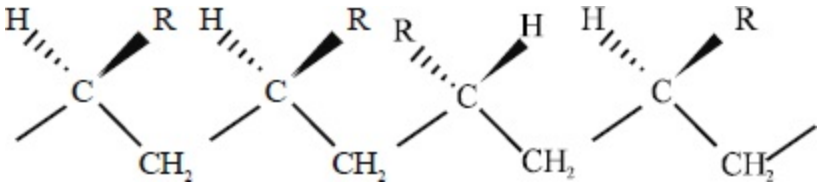
Product may be isotactic, in which identical groups in the same side  etc.

Syndiotactic, R – substituents can be in alternate fashion as shown below;



Zieglar Natta catalyst thus gives the polymers in stereoregular fashion.

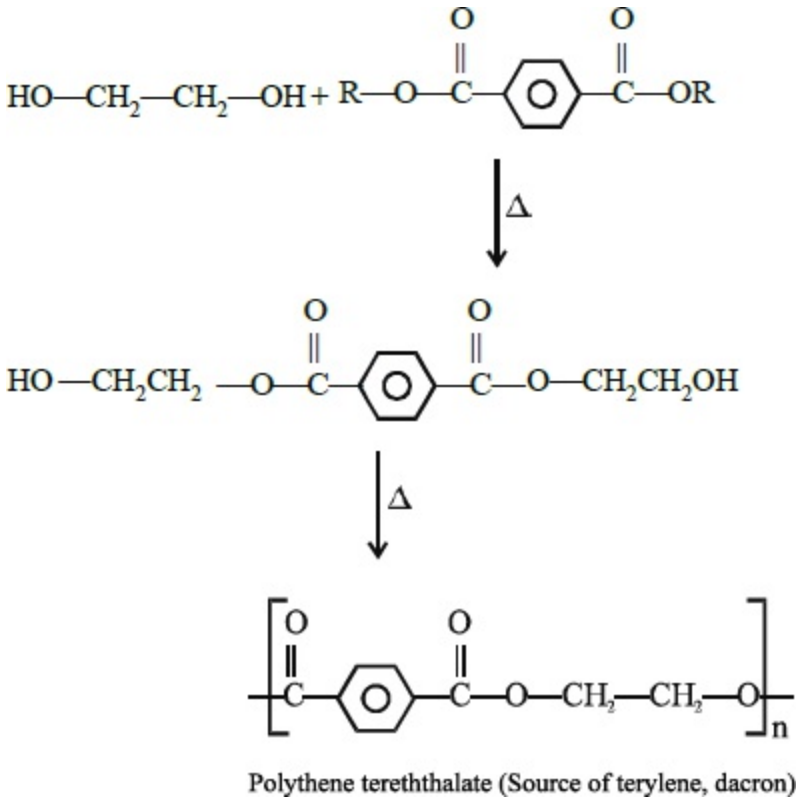
There is another type of polymer which is called as atactic polymer in which the groups arrange randomly as shown below.



Condensation or step growth polymerisation :

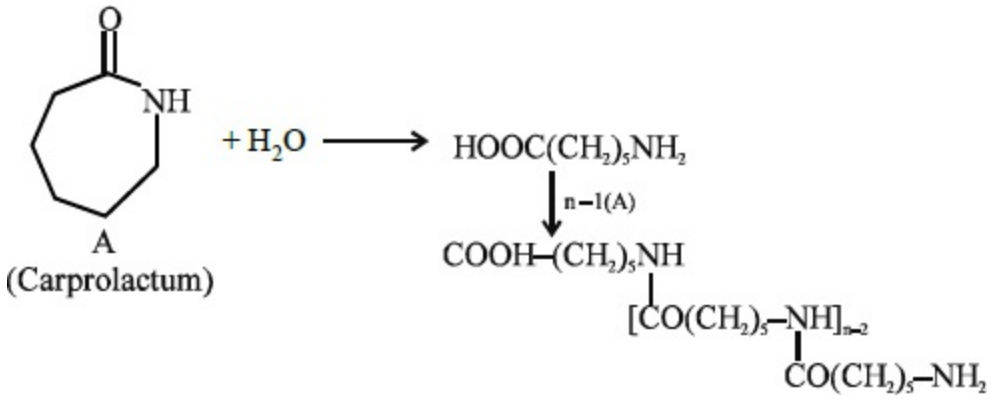
Two molecules when add up and small molecule goes out then the reaction is called as condensation or step growth polymirsation . Followings are the examples of condensation polymers.

1. Polyesters :

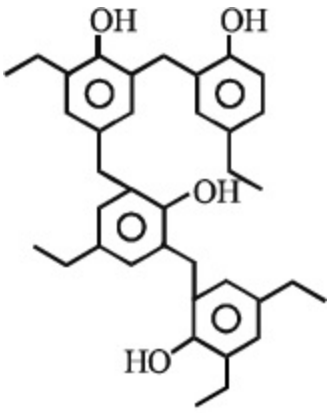


Polythene tereththalate (Source of terylene, dacron)

2. Nylon-6 :



3. Bakelite : This is made up of phenol and formaldehyde in presence of aqueous NaOH.

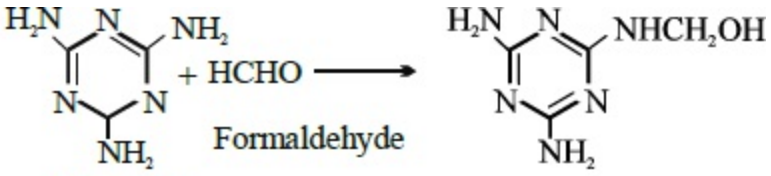


Bakelite

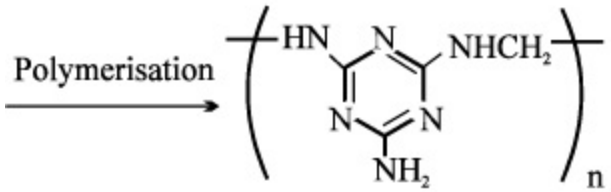
4. Nylon 66 :

$$(HOOC(CH_2)_4COOH + NH_2(CH_2)_6NH_2 \rightarrow \text{Salt} \xrightarrow[-H_2O]{\text{Heat}} -(NH(CH_2)_6NHCO(CH_2)_4CO)_n-$$

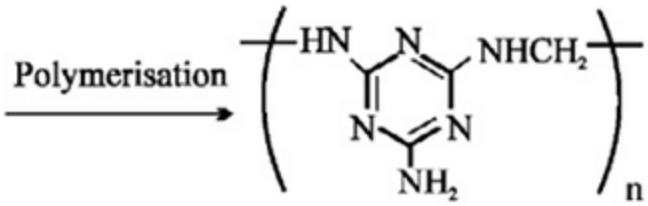
5. Melamine- formaldehyde resins :



Melamine resin intermediate

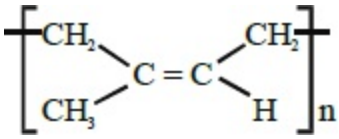


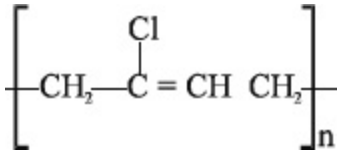
Melamine polymer



Melamine polymer

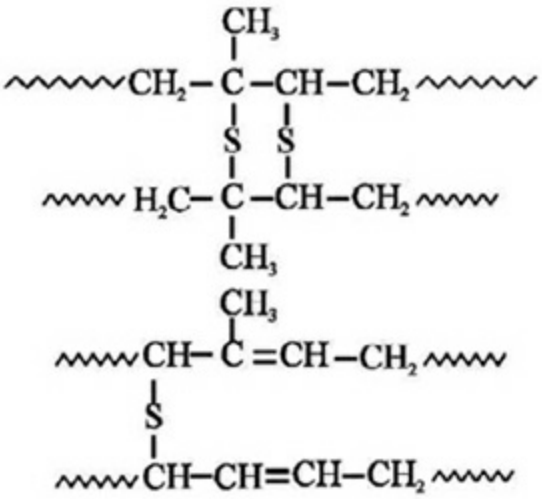
Rubbers : Natural rubber is obtained from rubber tree, consisting of isoprene units $\left[CH_2 = \underset{\displaystyle CH_3}{\overset{|}{C}} - CH = CH_2 \right]$

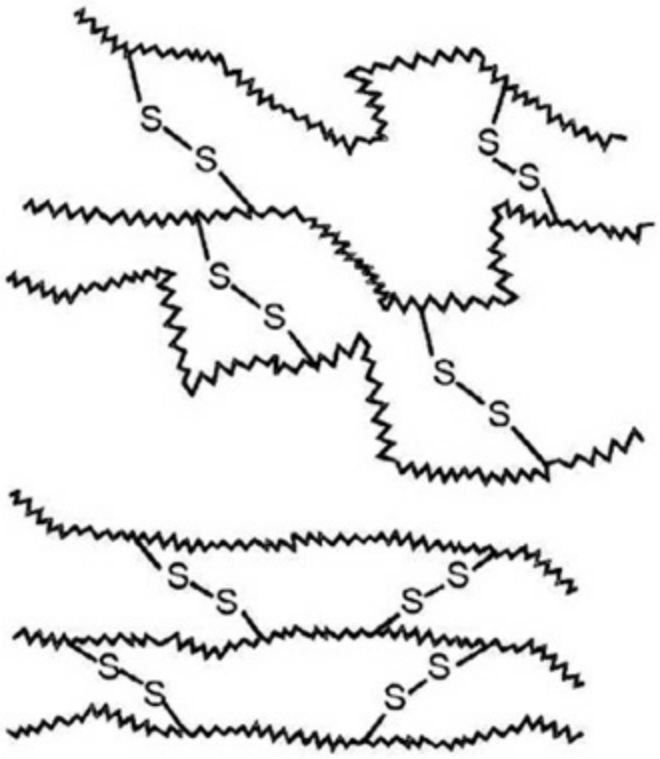
joined together to give  in cis 1, 4 fashion. Similarly neoprene



is obtained from the monomer chloroprene .

Vulcanization of Rubber : Rubber in the temprature range 280 to 350 K becomes soft and acquires brittle–Ness at low temprature. If sulphur is added to hot rubber excellent physical properties are found to appear in it. This process is called as vulcanization and the work was done by Charles Goodyear. Additives like zinc oxide are used to accelerate the vulcanization process. Sulphur establishes the cross linkage between the reactive sites of the allylic carbon atoms. The possible structure of the vulcanized rubber is shown below. Vulcanized rubber is used in tyre rubber, rubber case etc.





Note : Average molecular mass (Mn) = $\frac{\sum_{i=1}^{n} NiMi}{\sum_{i=1}^{n} Ni}$

Mass average molecular mass(Mw)= $\frac{\sum_{i=1}^{n} N_i M_i^2}{\sum_{i=1}^{n} N_i M_i}$

Poly dispersity index = Mw/Mn

Practical Organic Chemistry

This chapter includes

(1) analysis of elements,

(2) qualitative analysis of elements,

(3) finding out molecular formula,

(4) qualitative detection of functional groups.

(1) To detect the elements (C, H) we carry out the following tests

1. Detection of C,H

$$\text{Sample (C,H)} + CuO \xrightarrow{\Delta} CO_2\uparrow + H_2O + Cu$$

$$CO_2 + Ca(OH)_2 \longrightarrow \underset{\text{Milky}}{CaCO_3} + H_2O$$

(lime water)

$$CO_2 + CaCO_3 + H_2O \longrightarrow \underset{\text{Transparent clear}}{Ca(HCO_3)_2}$$

(excess)

If SO_2 is present then it is responds to the lime water test. But CO_2 does not change the colour of $K_2Cr_2O_7$ (orrange) to green or decolourise purple colour of $KMnO_4$. So, If SO_2 is present then it is eliminated by passing (CO_2 + SO_2) mixture through $K_2Cr_2O_7$ solution. CO_2 comes out as such

$$H_2O\ (l) + \underset{\text{(White)}}{CuSO_4(\text{anhydrous})} \rightarrow \underset{\text{(Blue)}}{CuSO_4.5H_2O}$$

By observation of white $CuSO_4$ changing its clour to blue gives indication of H present.

2. Detection of N, S, X(Cl, Br, I)

Lassigne's test:

$$\boxed{\text{Sample}} + \text{Na (s)} \xrightarrow{\text{Fuse}} \boxed{\text{Residue}} \xrightarrow{\text{Water}} \boxed{\text{Solution}} \quad (CN^-, S^{-2}, X^-, CNS^-)$$

Individual ions are the detected by inorganic reactions.

(1) $6NaCN + FeS_4$ (Freshly prepared) $\rightarrow Na_4[Fe(CN)_6) + Na_2SO_4$

$2\,NaOH + FeSO_4$ (excess) $\rightarrow Fe(OH)_2 \downarrow + Na_2SO_4$; [Excess FeSO4 is alway required]

Now $FeCl_3$(yellow) is added to the solution

$$3Na_4(Fe(CN)_6] + 4FeCl_3 \rightarrow Fe_4\,[Fe(CN)_6]_3 \downarrow + 12\,NaCl$$

blue

(prussian blue ppt)

Formation of blue ppt. or solution indictes CN^-, therefore C, N are present

While 'S' is present, then FeS(Black) forms therefore S^{-2} is removed by $FeSO_4$ and H_2SO_4 successively

$$FeSO_4 + Na_2S \rightarrow FeS \downarrow + Na_2SO_4$$

$$FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S \uparrow \text{ (It goes out)}$$

Then, the $FeCl_3$ test is done with $Na_4(Fe(CN)_6]$. It is to be worth mentioned that the solution sould be kept acidic (little) as $Fe_4(Fe(CN)_6]_3$ decomposes in alkaline medium.

$$Fe_4(Fe(CN)_6]_3 + 12NaOH \rightarrow 4Fe\,(OH)_3 + 3Na_4\,[Fe(CN)_6]$$

In, complete fusion due to the Na, may give NaCNS. But excess Na breaks down NaCNS as

$$NaCNS + 2Na \rightarrow Na_2S + NaCN.$$

If we donot remove CNS^- then Fe^{+3} produces blood red colouration $[Fe(CNS)_6]^{-3}$ To detect S^{-2} we use $Na_2[(Fe(CN)_5NO]$ i.e., sodium nitroprusside, to get purple colour of $Na_4[Fe(CN)_5$–NOS]

$$Na_2[Fe(CN)_5NO] + Na_2S \rightarrow Na_4[Fe(CN)_5NOS]$$

$$\text{Also, } H^+ + S^{-2} \rightarrow H_2S \uparrow \xrightarrow{Pb(OCOCH_3)_2} PbS\text{; It is used to detect } S^{-2}.$$

(Black)

Detection of Cl^-, Br^-, I^-

Is done after removal of S^{-2}, CN^-, are carried out otherwise upon addtion of $AgNO_3$

Ag_2S(Black) or AgCN(white) interferes. Therefore HNO_3 is added

$$\therefore \quad NaCN + HNO_3 \rightarrow HCN\uparrow + NaNO_3$$
$$Na_2S + 2HNO_3 \rightarrow H_2S\uparrow + NaNO_3$$

Now, if we add $AgNO_3$, AgCl (white), AgBr(yellowish) AgI(yellow) ppt forms.

$$AgCl + NH_3 + 2H_2O \rightarrow [Ag(NH_3)_2]\,OH + NH_4Cl$$ [$\therefore$ AgCl easily dissolves in NH_3]

Dissolution

$$AgBr + NH_3 \rightarrow [Ag(NH_3)_2]OH + NH_4Br$$ [AgBr dissolves in NH_3 with difficulty]

AgI does not dissolve in NH_3.

If Cl^- , Br^- , I all are present, then we use Cl_2 water in one part taking then in a solution of CCl_4/ $CHCl_3$ and red colour layer due to Br_2, voilet layer due to I_2 forms indicate Br^- , I^- ,. If no colour appears then it must be Cl_2

Dection of halogen is done by Beilstein test other than Lassigne's test.

$Cu + X_2 \rightarrow CuX_2$

For halogen copper halide shows green flame colouration. Amide interferes

Detection of 'S'; We carryout the following tests

$$\text{Sample (C,H,S)} \xrightarrow[\text{fuse}]{KNO_3+Na_2CO_3} SO_4^{-2} \xrightarrow[\text{or } Ba(NO_3)_2 \text{ in } HNO_3]{BaCl_2} BaSO_4 \text{ ppt. (white)}$$

White ppt. of BaSO4 indicates 'S' in the sample

For the P, PO_4^{-3} forms above, treate with $(NH_4)_2\,MoO_4$.

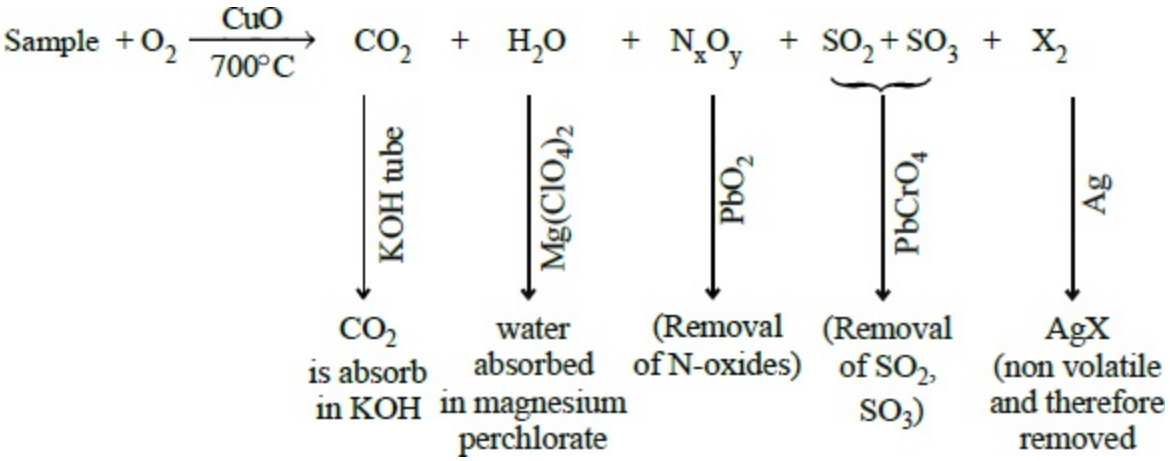
$$(NH_4)_2MoO_4 + PO_4^{-3} + \rightarrow (NH_4)_2\,PMo_{12}O_{40}\downarrow +$$

(canary yellow ppt)

Thus 'P' is identified

Quantitative estimation

%Carbon:



Weight of sample = W gm

Weight of KOH tube = Wj gm; weight of KOH tube after absorption of CO_2 = W_1'

Weight of $MgClO_4$ tube = W_2 gm; weight of $Mg(ClO_4)_2$ tube after absorption of H_2O = W_2'

%C calculation

44 gm CO_2 contains 12 gm C

$$(W_1' - W_1) \text{ gm } CO_2 \text{ contains } \left(\frac{12}{44} \times W_1' - W_1\right);$$

$$\therefore \text{ \% C in the sample} = \left[\frac{12}{44} \times \frac{(W_1' - W_1)}{W} \times 100\right]$$

To find out %N two process are there.

(1) Duma's method involves again oxidation of the sample with CuO but in presence of Cu at high temperature

$$\text{Sample (C, H, S, X , N)} \xrightarrow{CuO} CO_2 + SO_2 + N_2O + N_2 + N_xO_y + X_2$$

$$N_xO_y + Cu \rightarrow CuO + N_2 \text{ [By using Cu we reduce all N-oxides to } N_2\text{]}$$

X_2, CO_2, SO_2 are removed by KOH. N_2 obtained is collected in nitrometer and collected over KOH solution. Let us say,

Volumes of $N_2 = V_1 l$ Volume of N_2 at STP = V*l*

Presure of $N_2 = P_1$ atm

aq. tension = p atm

Temperatuer = T_1K

$\therefore$ At STP $\dfrac{P_1 \times V}{273} = \dfrac{(P_1 - p)V_1}{T_1}$

$\therefore$ $V = \dfrac{(P_1 - P)V_1}{T_1}$ x 273 lit

$\therefore$ W gm sample contains $\left[\dfrac{28}{22.4} \times V\right]$ gm nitrogen

$\therefore$ 100 g sample contains $\left[\dfrac{28}{22.4} \times \dfrac{V}{W} \times 100\right]$ gm nitrogen

$= \%N$

Kjeldahl's method:

$$\underset{(C, H, N\ W\ gm)}{\text{Sample} + H_2SO_4} + K_2SO_4 \xrightarrow[\Delta]{\substack{HgSO_4 \\ CuSO_4}} CO_2 + H_2O + (NH_4)_2SO_4$$

$$\downarrow \text{NaOH}, \Delta$$

$$2NH_3$$

$$\downarrow H_2SO_4$$

$$\underset{\text{point}}{\text{Titration end}} \xleftarrow[\text{NaOH}]{V_2 \text{ml } N_2(N)} H_2SO_4 \quad V_1 \text{ ml } N_1(N) \text{ (excess)}$$

Calculation

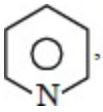
Number of equivalants $H_2SO_4 = \frac{(V_1N_1 - V_2N_2)}{1000}$

$\therefore$ Number moles of H_2SO_4 $\left(\frac{V_1N_1 - V_2N_2}{1000}\right) \times \frac{1}{2}$ = number of moles of $NH_3 = x$

$\therefore$ 17 gm NH_3 contains 14 gm N

17 x gm NH_3 conntains $\frac{14}{17}$ x 17x = 14 x gm N]

$\therefore$ $\%N = \left[\frac{14x}{W} \times 100\right]$

Note:  , $-NO_2$, $-N=N-$ cannot respond to Kjeldahl's test therefoer they can be detected by Duma's method quantatively.

%X (halogen):

Sample (C, H, X) $\xrightarrow[AgNO_3]{HNO_3}$ $AgX + H_2O + CO_2$

W gm

Let's say, weight of Ag X = W gm

$\therefore$ (108 + x) gm AgX contains x gm X [x = atomic weight of X]

$\therefore$ W gm $AgX = \left(\frac{x \times \omega}{108 + x}\right)$

$\therefore$ $\%X = \left(\frac{x\omega}{108 + x}\right) \times \frac{100}{W}$

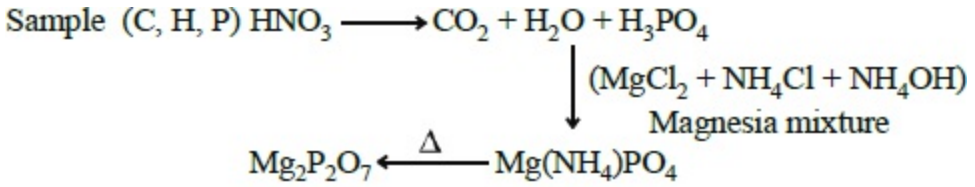
% S (sulphur)

Sample + $HNO_3 \rightarrow CO_2 + H_2O + H_2SO_4 \xrightarrow{BaCl_2} BaSO_4$

(C, H, S) x gm (say)

So, $\%S = \left(\frac{32}{233.34} \times x \times \frac{100}{W}\right)$

%P (phosphorus)



$$\therefore \quad \%\,P = \left(\frac{2 \times 31 \times W_1 \times 100}{222 \times W}\right)$$

Where at mass of P = 31, molecular mass of $Mg_2P_2O_7 = 222$.

$\therefore$ % O = 100 – [% C + % N + % H + %S + %X + %P]

Empirical formula:- which expresses the relative number of atoms of each elements present in the compound but molecular formula expresses the actual number of atoms present in the molecular. For example in C_2H_2 (acetylene) C : H is 1 : 1 ($\therefore$ empirical formula is CH) and molecular formula is C_2H_2. To find out, empirical formula let's say
C, N has % x , %y in a compound by mass.
So, the way of finding out empirical formula is

Elements	%	%/at. wt.	
C	x	x/12 = x'	1
N	y	y/14 = y' y'/x'=z'	

$\therefore$ (C_1N_z,) is empirical fomrmul .. If the result comes in the last column comes as fraction then simplest common multiple to get whole number.

To find out molecular formula

We carryout certain measuremens

(1) determination of vapour density (Victor Meyer's method) which is applicable to gasses and volatile liquids,

(2) depression of freezing point,

(3) elevation of boiling point.

Also we can measure molecular mass of acid by

(4) Simple tirtration or

(5) Ag-Salt method and for bases

(6) bychloropplatinate method

(1) Victor Meyer's method

Weight of organic compound = W gm (which is volatile or gaseous) Volume of dispersed air = V ml (by the sample)

Room temperature (during experiment° TK

Pressure of the sample = P atm, aq. tenstion = p atm at TK

$$\therefore \quad V_{STP} = \left[\frac{V(P-p)273}{T\times 760}\right] \text{ ml}$$

$$\therefore \quad \text{Density of sample} = \frac{W}{V_{STP}}$$

$$\therefore \quad \text{Vapour density} = \frac{W\times T\times 760}{V\times(P-p)\times 273\times 0.00009}$$

$\therefore$ Molecular weight = [2 x vap. density]

(4) $\text{Org. acid} + NH_3 \rightarrow NH_4\text{–Salt} \xrightarrow{AgNO_3} \text{Ag-salt} \xrightarrow{\Delta} Ag\downarrow$

$[\text{eq.; } CH_3COOH + NH_3 \rightarrow CH_3COONH_4 \xrightarrow{AgNO_3} CH_3COOAg]$ $(w_2 gm)$

$\therefore$ w_2 gm Ag comes from w_1 gm salt

$$108 \text{ gm Ag comes from } \left[\frac{w_1}{w_2}\times 108\right] \text{ gm}$$

$$\therefore \text{ molecular mass} = \frac{w_1}{w_2}\times 108 - 108 + 1$$

when basicity = 1

$$\text{when basicity} = 2,\ 2\left(\frac{w_1}{w_2}\times 108 - 108 + 1\right)$$

$$\therefore \text{ for basicity 'n' molecular mass} = n\left(\frac{w_1}{w_2}\times 108 - 108 + 1\right)$$

(5) $$\text{Molecular mass of acid} = \frac{\text{basicity}\times w_{acid}\times 1000}{\text{volume of base}\times\text{normality strength}}$$ [by acid-base titration method]

(6) Let us consider a base $\begin{matrix}(CH_2)_2{-}NH_2\\ |\\ NH_2\end{matrix}$ (diacidic)

$$\therefore \quad \begin{matrix}NH_2\\ |\\ (CH_2)_2\\ |\\ NH_2\end{matrix} + H_2PtCl_6 \rightarrow \underset{w\ gm}{\left[\begin{matrix}\overset{+}{N}H_3\\ |\\ (CH_2)_2\\ |\\ \overset{+}{N}H_3\end{matrix}\right] PtCl_6^{-2}} \xrightarrow[\Delta]{\text{Several Process}} \underset{x\ gm}{Pt\downarrow}$$

$\therefore$ x gm Pt comes from w gm salt

$\therefore$ 195.2 gm Pt comes from $\left(\frac{w}{x}\times 195.2\right)$ gm salt

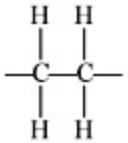
$\therefore$ $M = \left[\left(\frac{w}{x}\times 195.2\right) - \text{Molecular wt. of } H_2PtCl_6\right]$

$\therefore$ for acidity = 10 for a base,

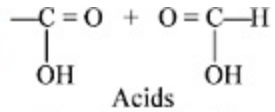
$$M = \text{molecular wt.} = \frac{1}{2}\left[\left(\frac{w}{x}\times 195.2\right) - \left(MW_{H_2PtCl_6}\right)\right]$$

Qualitative detection of functional groups

After finding out the molecular formula we carry out the tests for the detection of functional groups

Group	Reagent	Observation / Comments
(1) $>C=C<$	a) Br_2, H_2O b) Cold (room temp.) alk. $KMnO_4$ (Baeyer's test) c) O_3, Zn – dust distillation.	a) Red Br_2 solution decolourises b) purple colour becomes colourless. c) ($>C=O + O=C<$) formation. Tests of carbonyl groups confirm the position of double bond.
(2) $-C\equiv C-H$	a) Na/Liq. NH_3 b) $AgNO_3$ c) Ammoniacal Cu_2Cl_2 d) Ni/H_2	a) H_2 gas evolves b) white ppt of $-C\equiv C-Ag$ c) $-C\equiv C-Cu$ red ppt. d)  (alkane formation)

e) O_3, H_2O

e) 

Acids

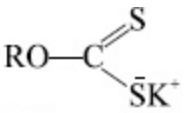
Detection of acids identifies the position of C = C along with nature of unsaturation.

Note : Unsaturation test can be shown by cycloalkenes, cycloalkynes. C = C – C = C. Cyclopropane reacts with Br_2 to give  .

---

(3) C – X (Halide Cl, Br, I)	$AgNO_3$(Alcoholic), boiling	White ppt. of AgX. Therefore it is aliphatic halide. If no ppt appears then aryl halide and if no heating to get ppt then ionic halide.
(4) R – OH	a) Na b) $(NH_4)_2[Ce(NO_3)_6]$ (Cerric ammonium nitrate)	a) $H_2\uparrow$ b)$(NH_4)[Ce(NO_3)_5(OR)]$. Red colour solution in ether forms.

c) Xanthate test, in which RO^-K^+ salt is added in CS_2



Yellow ppt. forms

d) Iodoform test by I_2 + NaOH, heating — d) CHI_3 froms for CH_3CH_2OH, $CH_3CH(OH)CH_3$

e) Solubility in hot conc. H_2SO_4 — e) Due to $ROH_2^+ HSO_4^-$ formation

f) $RCOOH + R^1OH\ (+H^+) \rightleftharpoons RCOOR^1 + H_2O$ — f) Pleasant small of ester.

Note : * Phenol, some aromatic amines which readily oxidise to coloured compounds also give green to brown ppt.

g) Lucas test : [$R-OH + ZnCl_2$ (Anhydrous) + HCl (Conc.)

at room temp.

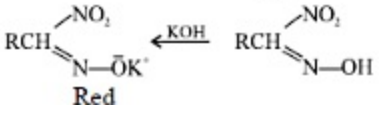
Case-1 : R – Cl (White ppt forms immediately. So, 3° alcohol, allyl, benzyl alcohol. Allyl halide is soluble in Lucas reagent.

Case-2 : R – Cl forms after 4 – 5 units.
∴ 2° alcohol is present.

Case-3 : No ppt. forms
∴ 1° ROH is present.

h) Victor Meyer's test :

(i) $RCH_2OH \xrightarrow{HI(conc.)} RCH_2I \xrightarrow{AgNO_2} RCH_2NO_2$



Red

Red colour means 1° alcohol

(ii) $R_2CHOH \xrightarrow[HNO_2]{HI, AgNO_2} R_2C(NO_2)(NO) \xrightarrow{KOH}$ Blue

Blue colour means 2° alcohol

(iii) $R_2CHOH \xrightarrow[AgNO_2]{HI} R_2CNO_2 \xrightarrow{HNO_2}$ No reaction

No colour means 3° alcohol

(i) Oxidation test :

$RCH_2OH \xrightarrow{Cr_2O_7^{-2}/H^+} RCOOH + Cr^{+3}$ (green) — 1°

$R_2CHOH \xrightarrow{Cr_2O_7^{-2}/H^+} R_2CO + Cr^{+3}$ (green) — 2°

$R_3COH \longrightarrow$ No oxidation — 3°

Catalytic oxidation

(i) $RCH_2OH \xrightarrow[Heat]{Cu} RCHO$ — 1°

(ii) $R_2CHOH \xrightarrow[H]{Cu} R_2C=O$ — 2°

(iii) $R_2\overset{CH_3}{\overset{|}{C}}OH \longrightarrow R_2C=CH_2$ — 3°

Phenolic –OH

1) $Ph—OH + NaHCO_3 \longrightarrow x$ (or Na_2CO_3)

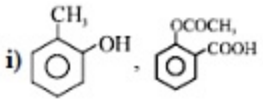
No effervescence i.e. no CO_2 forms
Therefore insoluble in aq $NaHCO_3$ and Na_2CO_3 as ($H_2CO_3 > C_6H_5OH > H_2O$) acidic strength order.

2) but $PhOH + NaOH \longrightarrow PhO^-Na^+ + H_2O$

So, soluble in NaOH Solution.

3) $FeCl_3 + PhOH \longrightarrow [(PhO)_6Fe]^{-3}$ (blue)

Phenolic OH is present but some compounds also respond which are;

i) 

(aspirin)

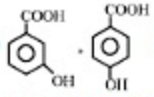
The above compounds give violet colour.

ii)  , pyrogallol gives blue to red solution.

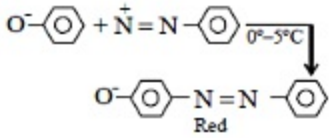
iii) Catechol gives green colour

iv) m, p nitrophenols give violet red solution.

v) Resorcinol gives green solution.

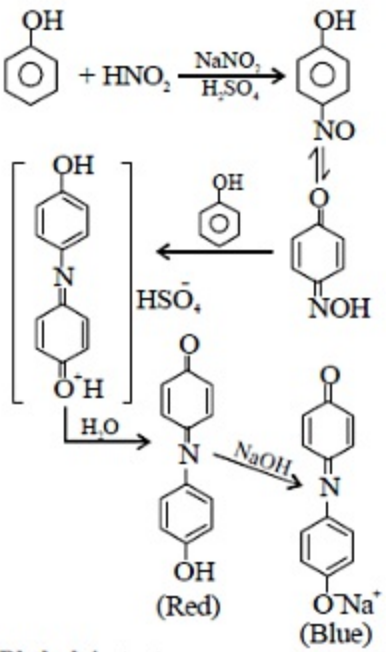
vi)  and dinitro phenol donot give coloured solution.

4) Azo dye formation :



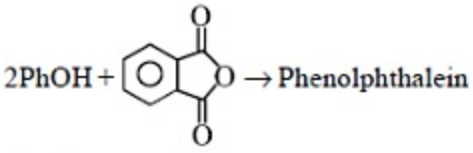
Red coloured azo dye ie. phenolic –OH present
[The azo dye formation wtih β-naphthol is characteristic test of $ArNH_2$ (1°)]

5) Libermann's test :



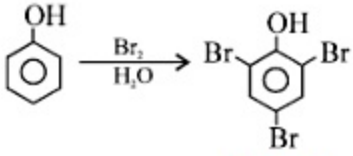
Initially formed deep green to blue solution with H_2SO_4 (conc.) turns red when water is added. If again base is added then blue solution reappears.

6) Phthalein test :



In pH < 7 colourlss, > 7 pink

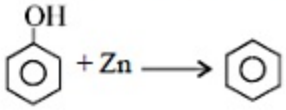
7) Br_2 water test :



White ppt

It indicates phonolic –OH present.

8) Zn - dust distillation :



Ether

R–O–R

1) $R–\ddot{O}–R' + H_2SO_4$ (conc., cold) $\longrightarrow [RR'O^+H]HSO_4^-$ — Ether dissolves.

2) $Na + ROR' \not\longrightarrow H_2$ — No hydrogen evolution.

3) Insoluble in H_2O

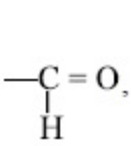
4) $R{-}OR + HI \xrightarrow{cold} RI + ROH$

$RI + AgNO_3 \longrightarrow AgI$

(Zeisel method)

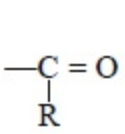
5) $ROR + PCl_5 \not\longrightarrow$ No reactions

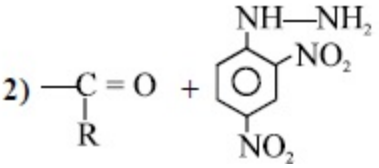
Carbonyl compounds



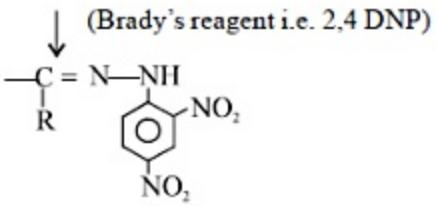
1) 

White ppt of addition product



2) 

Yellow to red crystelline ppt.



3) Reaction for aldehyde :

a) –CHO restores pink colour of fuschine when heated with Schiff's reagent	–CHO present
b) Fehling's Soln + RCHO (Not for ArCHO) $\rightarrow Cu_2O$	Red ppt. of Cu_2O forms. Therefore –CHO is present.
b) Tollen's reagent + RCHO $\rightarrow$ Ag	Silver mirror forms. Therefore –CHO is present.

4) Test for ketone :

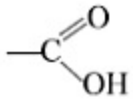
$Na_2Fe(CN)_5NO + RCOR'$	Ketone is present.

Sodium nitroprusside

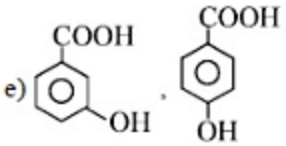
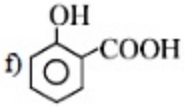
$\downarrow$ NaOH

Red or purple colour

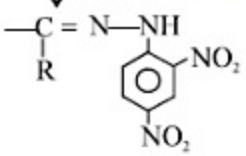
Test for



group

1) R/Ar – COOH + Blue Litums	Red colour, $-CO_2H$ present
2) R/Ar COOH + Na	H_2 evolves
3) R.ArCOOH + KI + KIO_3	I_2 evolves
4) (R/ArCOOH + R′OH + few drops of H_2SO_4) and poured into water wtih little $NaHCO_3$	Oil with fruity smell evolves
5) R/ArCOOH + $NaHCO_3$ or Na_2CO_3	CO_2 evolves (SO_3H intereres)
6) $FeCl_3$ test	
a) Cinnamic acid, anisic acid	a) yellow ppt.
b) RCOOH	b) reddish brown ppt.
c) ArCOOH	c) buff ppt.
d) CH_2(OH)—COOH (α-hydroxy acid)	d) yellow colouration
e) 	e) red brown colour.
f) 	f) violet colour.

↓ (Brady's reagent i.e. 2,4 DNP)



3) Reaction for aldehyde :

a) –CHO restores pink colour of fuschine when heated with Schiff's reagent	–CHO present
b) Fehling's Soln + RCHO (Not for ArCHO) → Cu_2O	Red ppt. of Cu_2O forms. Therefore –CHO is present.
b) Tollen's reagent + RCHO → Ag	Silver mirror forms. Therefore –CHO is present.

4) Test for ketone :

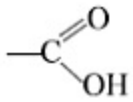
$Na_2Fe(CN)_5NO$ + RCOR′	Ketone is present.

Sodium nitroprusside

↓ NaOH

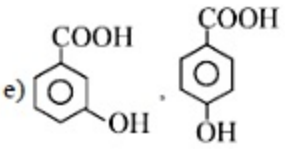
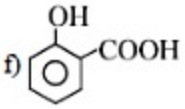
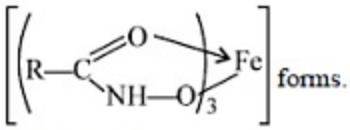
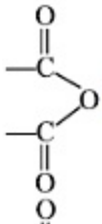
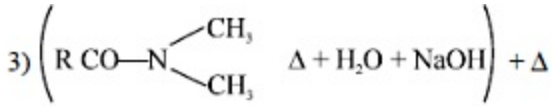
Red or purple colour

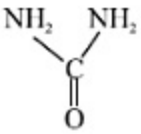
Test for

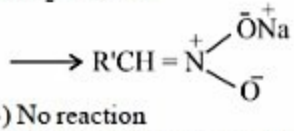
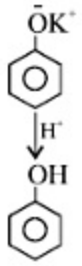


group

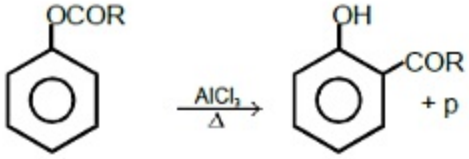
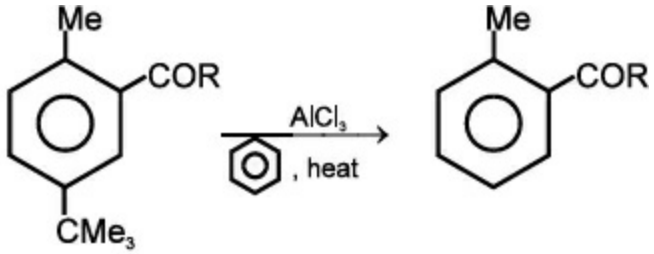
1) R/Ar – COOH + Blue Litums	Red colour, $–CO_2H$ present
2) R/Ar COOH + Na	H_2 evolves
3) R.ArCOOH + KI + KIO_3	I_2 evolves
4) (R/ArCOOH + R′OH + few drops of H_2SO_4) and poured into water wtih little $NaHCO_3$	Oil with fruity smell evolves

	5) $R/ArCOOH + NaHCO_3$ or Na_2CO_3	CO_2 evolves (SO_3H intereres)
	6) $FeCl_3$ test	
	a) Cinnamic acid, anisic acid	a) yellow ppt.
	b) RCOOH	b) reddish brown ppt.
	c) ArCOOH	c) buff ppt.
	d) $CH_2(OH)$—COOH (α-hydroxy acid)	d) yellow colouration
	e) 	e) red brown colour.
	f) 	f) violet colour.
–COOR (Ester)	1) $RCOOR' + H_2O \xrightarrow[OH^-]{\Delta} RCOOH + R'OH$ + Phenolphlhthalein	Pink colour becomes colourles due to R CO_2H formation.
	2) $RCOOR' + NH_2OH \longrightarrow R{-}C(=O){-}NHOH$	
	R CONH OH + $FeCl_3$	Red colour complex  forms.
 **(Anhydride)**	$[(CH_3CO)_2O + PhNH_2]$ + heat in C_6H_6 solution	White solid $C_6H_5NHCOCH_3$ forms.
 **(Amide)**	1) $(RCONH_2 + NaOH + H_2O) + \Delta$	NH_3 evolves
	2) Similarly, $(RCONHCH_3 + NaOH + H_2O) + \Delta$	CH_3NH_2 forms.
	3) 	$(CH_3)_2NH$ forms.
RCOCl Acid (Chloride)	1) $RCOCl + AgNO_3$ (solution)	AgCl white ppt. forms immediately.
	2) $RCOCl + H_2O + \Delta \longrightarrow RCOOH + HCl\uparrow$	White fumes of NH_4Cl forms
	$HCl + NH_3 \longrightarrow NH_4Cl$	
Carbohydrates	1) Action of conc. $H_2SO_4 + \Delta$	The solution chars & blackens.
	2) Anthrone reagent + carbohydrate	Green or bluish green colour develops

	3) Molisch test :	
	Carbohydrate + Molisch reagent (alcoholic α-napthol) + conc. H_2SO_4	violet ring develops
	4) $C_6H_{12}O_6 + 3PhNHNH_2$	Osazone forms.
NH_2 (Amine)	1) For 1° amine $RNH_2 + CHCl_3 + KOH + Heat$	RNC (Poisonous gas) evolves.
	2) **Hoffmann**'s mustand oil reaction	(already told in amine chapter)
	3) Action of **Hinsberg**'s reagent	
	i.e. 	$PhSO_2\overset{\ominus}{N}Na^{\oplus}$ forms (1°) 
	4) $\left[PhSO_2Cl + R_2NH + NaOH\right]$ (2°)	$PhSO_2NR_2$ is insoluble in NaOH
	5) $PhSO_2Cl + R_3N$	No reaction.
	6) Test with Hoffmann's reagent (already taught)	
$-NHCOCH_3$ (Anilide group)	1) $(PhNHCOCH_3 + H_2O + H^+ + heat)$	 forms and can show characteristic test of NH_2 (diazo test)
	2) Taffle's test :	
	$ArNHCOCH_3 + K_2Cr_2O_7 + H_2SO_4 + heat$	Red colour changes to green shows the presence of anilide group.
Diamide group	**Biuret test :**	
	$NH_2CONH_2 + \Delta \longrightarrow NH_3 +$ Residue 	Violet solution indicates urea.
	violet solution $\xleftarrow{CuSO_4}$ solution $\xleftarrow[\Delta,\ Cool]{NaOH}$ Biuret	
$-NO_2$ (Nitro)	$R-NH_2 + TiCl_2 +$ dil. $HCl + CH_3COCH_3$	Mauve colour of $TiCl_2$ discharges within few minutes.
	Mulliken test :	
	$R/ArNO_2$ (s) + Alcohol (solvent) + Zn + NH_4Cl (or Zn + $CaCl_2$) + Boil (5 minutes)	[We can use this test when NH_2 present with NO_2 in aromatic ring as it does not affect $-NH_2$
	 filter after cooling	
	Filtrate (R/ArNHOH)	otherwise to detect $-NO_2$ if we

	$\downarrow$ $[Ag(NH_3)_2]^+$ Tollen's reagent Ag-mirror	reduce it to $-NH_2$ and then carry out diazo test then $-NH_2$ already present also responds and also even if not $-NO_2$ is present and do the above tests we will never be sure]
	(3) $R/ArNO_2 + NaOH$	Yellow solution
	(4) $R/ArNO_2 + Fe$ or Zn/HCl $\longrightarrow -NH_2 \longrightarrow$ Diazo test $\longrightarrow$ carbyl amine test	Also done for $-NO_2$ group. NH_2 present. NH_2 present.
–ONO (Nitrito)		
	1) $R-ONO + LiAlH_4 \longrightarrow ROH + NH_3 + H_2O$	1) Test for NH_3 confirms ONO. Whereas RNO_2 gives RNH_2
	2) $R-ONO + NaOH \longrightarrow R-OH + NaNO_2$	2) –ONO group present whereas $RNO_2 + NaOH$ 
	3) $RONO + HNO_2$	3) No reaction (but we know 1°, 2°, 3° $-NH_2$ reacts).
	4) $R-ONO + HCl$	$R-OH + HNO_2$
–CN	1) $R/ArCN + H_2O + H^+$ $\longrightarrow RCOOH + NH_4^+$	RCOOH is identified by usual process and –CN is detected
–NC	(1) Smell	Detected by characteristic disagreeable odour.
	(2) $RNC + HgO \xrightarrow{\Delta} RNCO + Hg$	Metallic mercury detects the –NC group.
$-SO_3H$	(1) $R/Ar-SO_3H + Na_2CO_3$	CO_2 effervescence confirms $-SO_3H$
	(2) $Ph-SO_3H + KOH \xrightarrow{Fuse}$ 	Formation of phenol confirms the presence of $-SO_3H$ group.

Reagent List

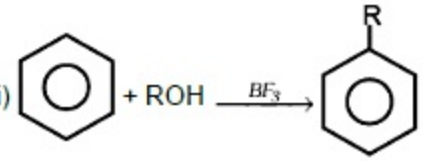
	Reagents	Reactron	Comments
1.	**Anhydrous $AlCl_3$**	(i) $RX + C_6H_6 \xrightarrow[\Delta]{AlCl_3} C_6H_5R$	Reacts as a Lewis acid
(a)	Friedal Craft's reaction ;	(ii) $RCOX + C_6H_6 \xrightarrow[\Delta]{AlCl_3} C_6H_5 - COR$	
		(iii) $(RCO)_2O + C_6H_6 \xrightarrow[\Delta]{AlCl_3} C_6H_5 - COR$	
(b)	Frie's rearrangement ;		Reacts as a Lewis acid
(c)	Gatthermann Koch reaction ;	$[Ph - H + CO + HCl \xrightarrow{AlCl_3} PhCHO]$	Reacts as a Lewis acid
		$Ph - H + COCl_2 \xrightarrow{AlCl_3} PhCOCl$	
(d)	Isomerisation	$CH_3CH_2CH_2 - CH_3 \xrightarrow[\Delta]{AlCl_3} (CH_3)_3CH$	Reacts as a Lewis acid
(e)	Dealkylation		
(f)	Addition of alkene	$CH_2 = CH_2 \xrightarrow[CH_3COCl]{AlCl_3} CH_2 - CH_2Cl$ (with $COCH_3$)	
2.	$Al-[OCH(CH_3)_2]_3$ i.e. Al-isopropoxide	$R_2CO \underset{(CH_3)_2CHOH\ (distn.)}{\overset{Al(OiPr)_3,}{\rightleftharpoons}} R_2CHOH$ (MPV reduction)	(i) Ketone gives 2° alcohol, aldehyde gives 1° alcohol in presence of other reducible groups like =, ≡ etc. (ii) MPV reduction does not occur with the compounds having high enol content.

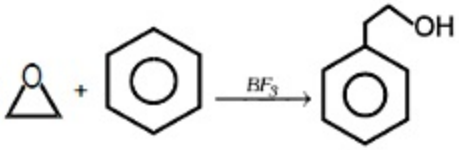
3. $Al(Ot\text{-}Bu)_3$, Acetone or p-benzoquinone

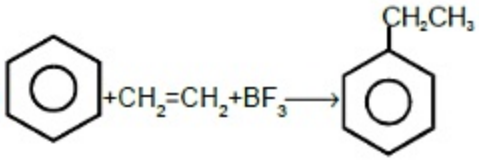
$$RCHOHR' \underset{(CH_3)_2CO}{\overset{Al(OtBu)_3}{\rightleftharpoons}} RCOR'$$

1° alcohol gives aldehyde and 2° alcohol gives ketone

4. BF_3 (Boron tri fluoride)

(i)  Lewis acid and can be used in place of $AlCl_3$

(ii) 

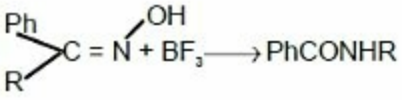
(iii)  Alkylation of benzene

(iv) $CH_3COCH_3 + (CH_3CO)_2O + BF_3 \longrightarrow CH_3COCH_2COCH_3$ Acylation of ketones

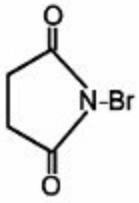
(v) $ROR + CO + BF_3 \xrightarrow[pressure]{\Delta} RCOOR$ Ester formation

(vi) $ROH + CO + BF_3 \xrightarrow[pressure]{\Delta} RCOOH$ Acid formation

(vii) $Ph - H + H_2SO_4 \xrightarrow{BF_3} PhSO_3H$

(viii)  Beckmann's rearrangement

(ix) Frie's rearrangement also can be take place if BF_3 is used instead of $AlCl_3$

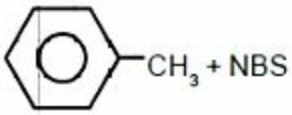
5. 

N-bromosuccnimide

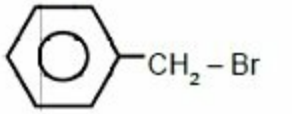
(i) $CH_3 - CH = CH_2 + NBS$ Allylic or benzylic bromination

$CH_2 - CH = CH_2$

|
Br

(ii)  + NBS

↓



6. RCO_3H — (i) Bayer Villiger's oxidation — Ester formation

Peroxy acid

$RCOR'R \xrightarrow{CF_3CO_3H} RCOOR'$

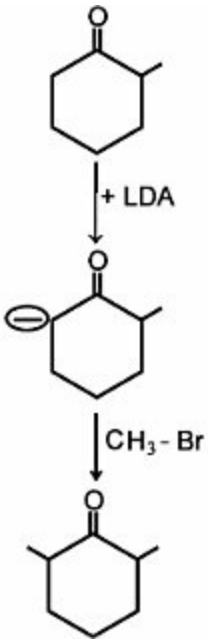
eg. CF_3CO_3H, — (ii) Epoxide formation — Epoxide formation

CH_3CO_3H, MCPBA etc.

$RCH = CH_2 \xrightarrow{MCPBA} RCH\text{—}CH_2$ (O)

7. $Li^{\oplus} N^{\ominus} [CH(CH_3)_2]_2$

Lithium di isopropyl amide



Kinetically controlled carbanion forms and leads to the product.

8. Di isobutyl aluminium hydride in short DIBALH

(i) $CH_3CN \xrightarrow{DIBALH} CH_3CHO$ — Good reducing reagent

(ii) $RCO_2R' \longrightarrow RCHO$

(iii) $RCHO \longrightarrow RCH_2OH$

(iv) $R_2CO \longrightarrow R_2CHOH$

(v) $RCO_2R' \longrightarrow RCH_2OH + R'OH$

9. $\overset{\ominus}{C}H_2 - \overset{\oplus}{N} \equiv N$ — (i) $ROH + \overset{\ominus}{C}H_2\text{–}\overset{\oplus}{N}_2 \xrightarrow{BF_3} ROCH_3$ — Ether formation

Diazomethane

(ii) $RCOCl + \overset{\ominus}{C}H_2\text{–}\overset{\oplus}{N}_2 \xrightarrow[H_2O]{(i)Ag_2O(moist),heat} RCH_2COOH$ — RCH_2COOH is produced (higher acid homologue)

(iii) $RCOOH + \overset{\ominus}{C}H_2\text{–}\overset{\oplus}{N}_2 \longrightarrow RCOOCH_3$ — Ester formation

(iv) $RCHO + \overset{\ominus}{C}H_2\text{–}\overset{\oplus}{N}_2 \longrightarrow R - CH(O) - CH_2$ (Epoxide) — Insertion of CH_2 between C = O atom

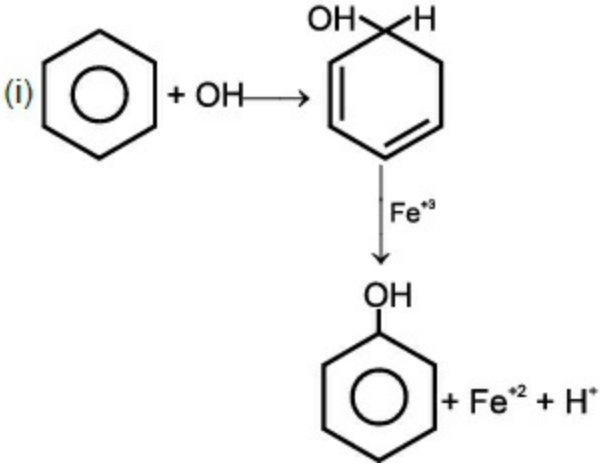
(v) $CH_2 \| CH_2 + \overset{\ominus}{C}H_2 - N \| \overset{\oplus}{N} \longrightarrow$ Pyrazoline

(vi) $\overset{\ominus}{C}H_2\text{–}\overset{\oplus}{N}_2 \xrightarrow{\Delta} CH_2 \xrightarrow{CH_3\text{–}CH_3} CH_3 - CH_2 - CH_3$ — Insertion of carbene with in C – H bond.

10. Fenton's reagent ($Fe^{+2} + H_2O_2$)

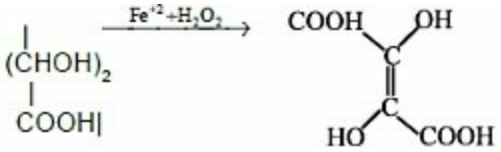
Actually $Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + \dot{O}H + OH^-$

i.e. Fe^{+3}, $\dot{O}H$, OH^- exists and acts as an oxidising agent oxidised by OH.

(i) 

(iii) $(COO)_2Ca \xrightarrow[-CO_2]{Fe^{+2}+H_2O_2} CHO - (CHOH)_3 - CH_2OH$ — Higher aldose to lower aldose formation

(iv) COOH

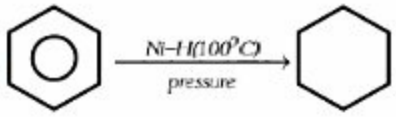


Oxidation of tartaric acid

11. Raney Ni
This is black sopngy metal powder with a weak Ni – H bond

(i) $CH_2 = CH_2 \xrightarrow[Room\ temp]{Ni-H} CH_3 - CH_3$
Alkene

Normal pressure & room temperature



Stable C = O requires high temp., pressure

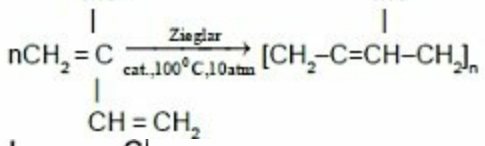
(iii) $R - NO_2 \xrightarrow[60^0C]{Ni-H} R - NH_2$

(iv) $RCN \xrightarrow[pressure]{Ni-H} RCH_2NH_2$

(v) $Ph - X \xrightarrow[NaOH]{Ni-H} PhH$ X=halogen

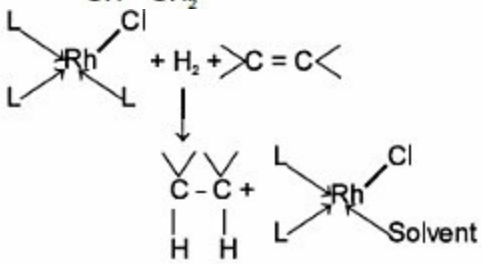
(vi)  Desulphurisation

12. Zieglar Natta catalyst ($Et_3Al + TiCl_4$)

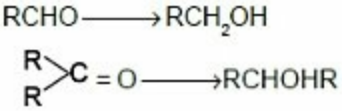


Isotactic, syndiotactic polymers are obtained which are mechanically strong, crystralline high melting.

13. Wilkinson's catalyst

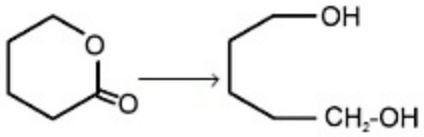


14. $LiAlH_4$ in ether and after that H_2O or H_3O^+ is to be



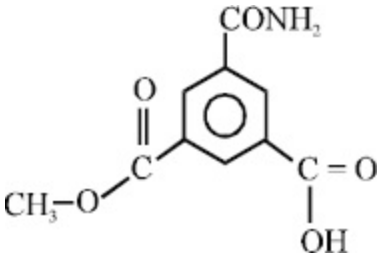
$LiAlH_4$ reduces by H^- transfer reaction order

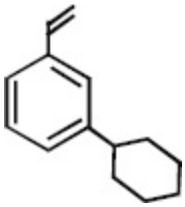
$-CHO > -\underset{|}{C} = O > -COCl$

	added	$RCH=NOH \longrightarrow R CH_2NH_2$ $R-NO_2 \longrightarrow RNH_2$	$> -CO_2R > -CO_2H >$ $-CONH_2 > -CONAR$ $> -C\equiv N > -CH=NOH$
			$> NO_2 > -CH_2Br$
		$RCONH_2 \longrightarrow RCHO \longrightarrow RCH_2OH$ $RCN \longrightarrow RCH_2NH_2$	Does not reduce $C=C$, $C\equiv C$, $ArNO_2$, ArX Exception : $PhCH=CHCHO \longrightarrow$ $PhCH_2CH_2CH_2OH$
15.	$Li[Al(Ot\ Bu)_3H]$ [LTBAL-H] in THF and then addition of H_2O	$RCHO \longrightarrow RCH_2OH$ $R_2CO \longrightarrow R_2CHOH$ $RCOOPh \longrightarrow RCHO$ $R-NO_2 \longrightarrow RNH_2$ $R-X \longrightarrow RH$ $R-C\equiv N \longrightarrow RCH_2NH_2$ etc.	Weaker reducing com– pared to $LiAlH_4$
16.	$NaBH_4$ + Diglyme or ether and then water is added	(i) $RCHO \longrightarrow RCH_2OH$ (ii) $RCOR' \longrightarrow RCHOHR'$ (iii) $RCOCl \longrightarrow RCH_2OH$	These reactions take place in presence of $C=C$, $C\equiv C$, $-CO_2H$, $-CONR_2$, $-NO$, $-CN$, $R-X$, $ROSO_2R'$
17.	$Ph_3\ Sn\ H$	(i) $Ph-X \longrightarrow Ph-H$ (ii) $1° > 2° > 3°\ R-X \longrightarrow RH$	
18.	H_2/Pd, H_2/Pt	All the groups which is reduced by $LiAlH_4$ & also =, ≡ gets reduced	Reactivity order $-COCl > NO_2 > C\equiv C >$ $> -CHO > C=C > C=O$ $> CN > COOR > Ph-H$
19.	H_3PO_2	From benzene diazonium cation benzene is formed	
21.	KCN + CuCN	Used in cyano benzene formation from benzene diazonium chloride	
22.	H_3PO_4	For dehydration of alcohols and cyclisation	
23.	$NaOAc + Ac_2O$	Reagent used in Parkin's reaction	

25.	P_4O_{10}	Used in dehydration of alcohols
26.	Alc.KCN	Used in benzoin condensation
27.	$NaHSO_3$	Used to hydrolyse osmic ester to produce diol
28.	$NaHCO_3$	Used to detect active -H, except phenol
29.	SO_2Cl_2/ ROCl	Used to produce chloro alkane or side chain chlorination of arenes
30.	Li or Na/NH_3 (l)	Usedas Birch reducing agent and as removes active -H from terminal alkyne
31.	$NH_2–NH_2/H_2O_2$, OH^-	Diimide forms, which reduces C,Cdouble bond, triple bond
32.	$NH_2–NH_2$ + NaOEt	Wolff-Kischner reducing reagent
33.	$NH_2–NH_2$	Hydrazone forms with carbonyl compounds
34.	$CHCl_3$ + KOH + heat	Reagent used for Reimer Tiemann's reaction
35.	CO_2	Used to prepare benzoic acid by Kolbe Schmidt reaction
36.	Zn dust	For reductive ozonolysis, dehalogenation etc.
37.	Cu + heat	Alkyne trimerisation, oxidation of alcohols
38.	OsO_4 + $NaHSO_3$	For trans diol formation from alkene
39.	$KMnO_4$ (alk.,cold)	For trans diol formation from alkene and oxidation
40.	HIO_4 or Pb-acetate	For the cleavage of C-C bond in the diol compounds
41.	Li + CuI	Corey house synthesis

IUPAC Nomenclature

1. Name of the compound,  is,.....

2.  is

(a) 3- cyclohexyl-1- vinylbenzene

(b) 3- cyclohexyl-1- ethenylbenzene

(c) (a) and (b) both are correct

(d) None of these

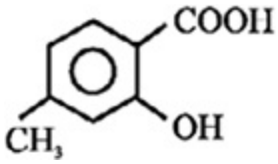
3. $CH_2 = CH - Cl$ is named as

(a) 1–Chloroethene

(b) ethenylcloride

(c) Chloroethene

(d) (a, c) both

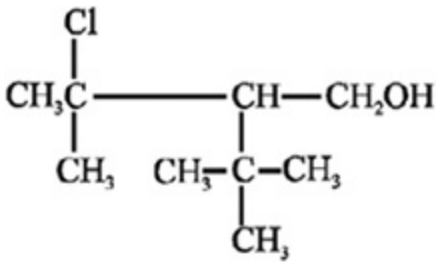
4.  is

(a) 4 – methyl-2- hydroxybenzoic acid

(b) 4 – ethyl-2- hydroxybenzoic acid

(c) 2 – carboxy – 5 – methylphenol

(d) none of these

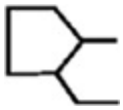
5.  is

(a) 2- tert- butyl-3-chloro-3-methyl-1- butanol

(b) 2- tert- butyl-3-chlorobutan-3-methylbutanol

(c) (a, b) both are correct

(d) None of these

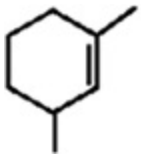
6.  is

(a) 1- methyl- 2- ethylcyclopentane

(b) 2- methyl-1- ethylcyclopentane

(c) 1- ethyl-2- methylcyclopentane

(d) None of these

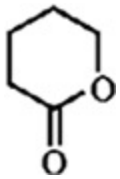
7.  is,

(a) 1, 3- dimethylcyclohexane

(b) 1, 3- dimethylcyclohex-2-ene

(c) both (a), (b) are correct

(d) None of these

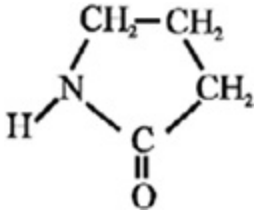
8.  is named as,

(a) 5- pentanolactone

(c) both (a), (b) are correct

(b) 4- pentanolactone

(d) None of these

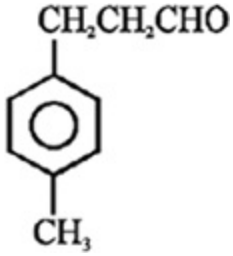
9.  is named as-

(a) 4- butanolactum

(b) 5- butanolactum

(c) both (a), (b) are correct

(d) None of these

10.  is named as,

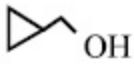
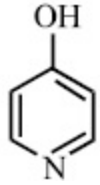
(a) 3- (4- methylphenyl)propanal

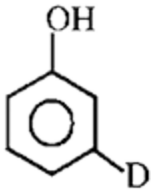
(b) 3- (p-tolyl)propanal

(c) both (a), (b) are correct

(d) None of these

11. Match the following

A. $CH_3COO^-NH_4^+$	1. 4- hydroxypyridine
B. $CH_3-CH(CH_3)-COO^-Na^+$	2. Ammonium ethaonate
C. 	3. Sodium-2- methylpropanoate
D. 	4. Cyclopropyl methanol

12.  is named as,

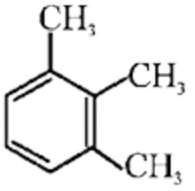
(a) Phen-m-d-ol

(b) Benzene -m-d-ol

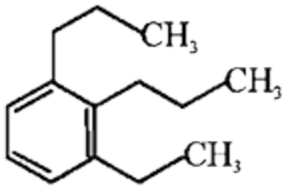
(c) benzene d_3 -1- ol

(d) None of these

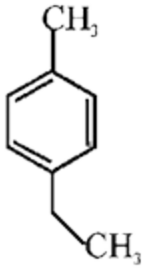
13. Which one is not the correct IUPAC name among the followings –

(a) 

1,2,3–Trimethylbenzene

(b) 

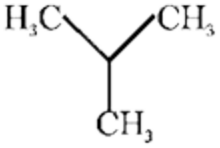
1-Butyl-3-ethyl-2-propylbenzene

(c) 

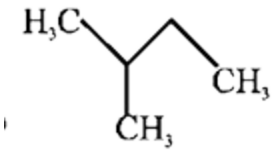
1,4-Divinylbenzene or
p-Divinylbenzene

(d) None of these

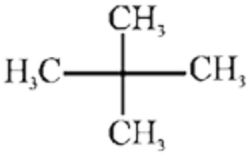
14. Which is not the correct name/s (IUPAC) written under the compounds ?

(a) 

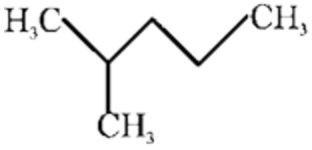
Isobutane

(b) 

Isopentane

(c) 

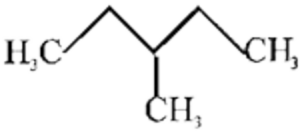
Isohexane

(d) 

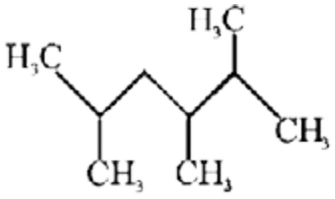
Neopentane

15. Read the following passage and answer the question :

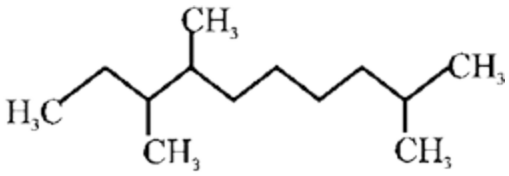
The longest chain is numbered from one end to the other by Arabic number, the direction being so chosen as to give the lowest numbers possible to the side chains. When series of locants containing the same number of terms are compared term by term, that series is "lowest" which contains the lowest number on the occasion of the first difference. This principle is applied irrespective of the nature of the substituents. Which name is not written correctly under the compounds given –

(a) 

3-Methylpentane

(b) 

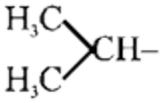
2,3,5-Trimethylhexane
(not 2,4,5-Trimethylhexane)

(c) 

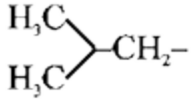
2,7,8-Trimethyldecane
(not 3,7,9-Trimethyldecane)

(d) None of these

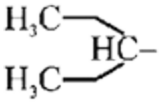
16. Which IUPAC name/s is/are not written correctly for the radicals given below –

(a) 

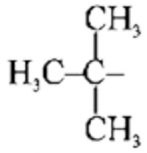
Isopropyl

(b) 

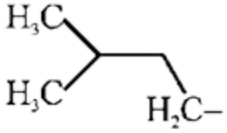
Isobutyl

(c) 

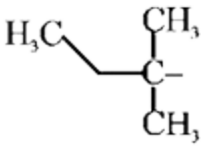
sec-butyl

(d) 

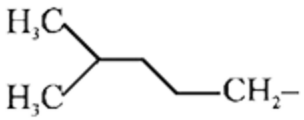
Isopentyl

(e) 

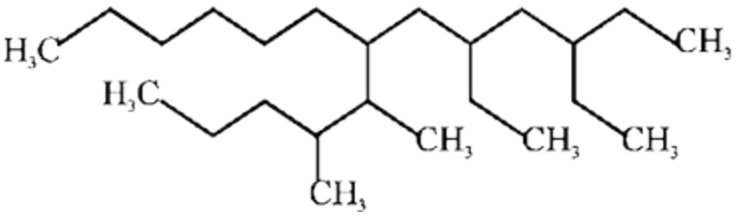
Neopentyl

(f) 

tert-pentyl

(g) 

Isohexyl

17. 

Which one is the correct name of the above compound –

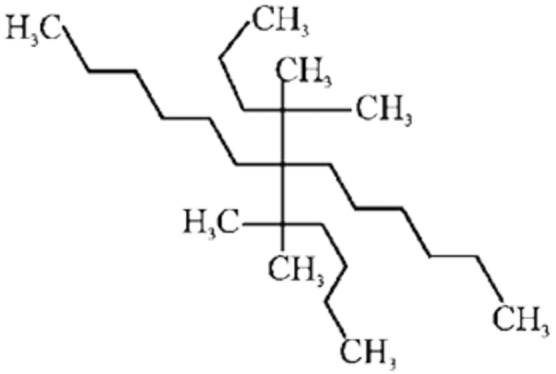
(a) 7-(1,2-Dimethylpentyl)-5-ethyltridecane

(b) 5-(1,2-Dimethylpentyl)-5-ethyltridecane

(c) 7-(1,2-Dimethylpentyl)-3-ethyltridecane

(b) None of these

18. The correct name of the following compound is



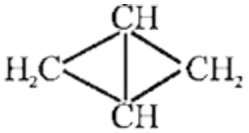
(a) 7-(1,1-Dimethylbutyl)-7-(1,1-demethypentyl)tridecane

(b) 7-1',1 '-Dimethybutyl)-7-1",1' '-demethypentyltridecane

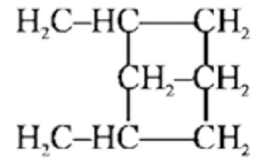
(c) 7-1 ',1'-Dimethybutyl-7-1 ",1"-trimethylpentyltridecane

(d) None of these

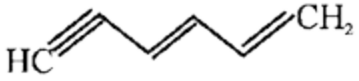
19. Which is not the correct name written for the following compounds –

(a) 

Bicyclo[1.1.0] butane

(b) 

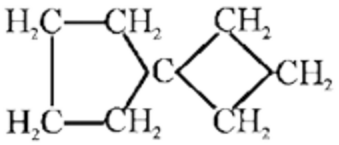
Bicyclo[3.2.1] octane

(c) 

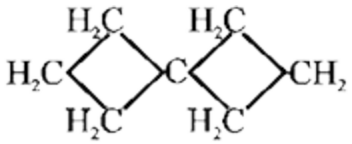
1,3–Hexadien–5–yne

(d) None of these

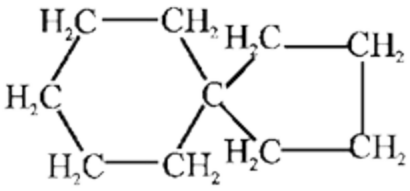
20. Which is not the correct name for the followings –

(a) 

Spiro [3.4] octane

(b) 

Spiro [3.3] octane

(c) 

Spiro [4,3] decane

(d) None of these

Answer & Hints

1. 3- Carbamoyl-5- methoxycarbonyl benzoic acid

2. (c)

3. (d)

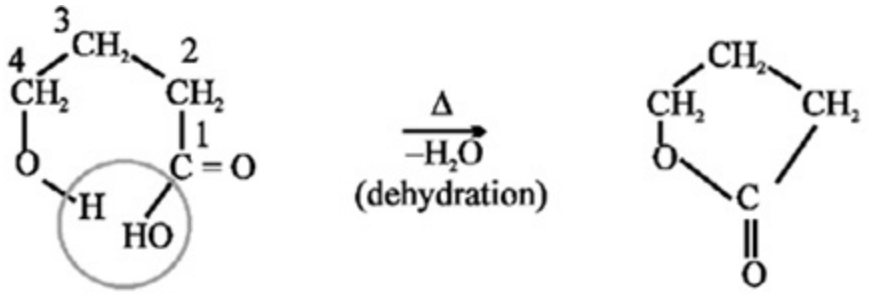
4. 4-Methyl - 2 - hydroxybenzoic acid

5. (c)

6. (c)

7. (b)

8. (b) **[Hint :** Loot at the origin of lactose]



[4 - hydroxybutanoic acid] [Butano-4- lactone]

Actually number indicates the position of –OH

9. (a)

10. (c)

11. A-2, B-3, C–4, D-1

12. (a) **[Hint :** Deuterium is indicated as 'd']

13. (d) [Hint : not methylxylene, not Dimethyltoluene for (a) or not paravinylstrene for (c)]

14. (c), (d)

15. (d)

16. Each of them is correct

17. (a)

18. (a), (b) **[Hint :** If we use prime number then we do not have to consider the brcket as taken in (a)]

19. (d) [**Hint :** Actually for the bridge head compounds, the number of carbon atoms with respect to the bridge head carbon atoms are written in decreasing numbers and with in the square bracket].

20. (d) **[Hint :** Actually for the spiro compounds, the number of carbon atoms with respect to th common carbon atom are written in increasing numbers and within the square bracket.]

General Organic Chemistry

1. Which group at para will cause zero dipole moment?

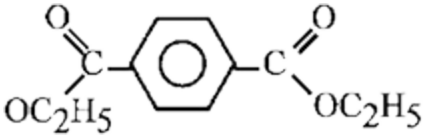
(a) – OH, – OR, NHR

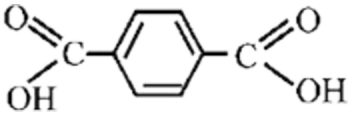
(b) – NH_2 , – NHR, – NR_2

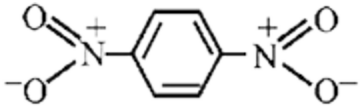
(c) – NR_2, –CHO, – COCl

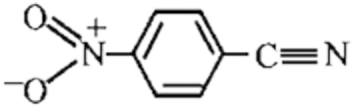
(d) –CN, –Cl, – NO_2

2. Which compound/s should have zero dipole moment.

(a) 

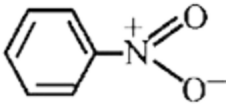
(b) 

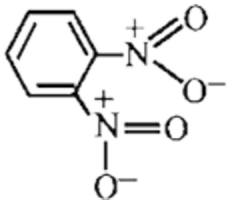
(c) 

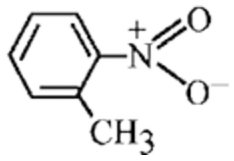
(d) 

3. Which one should have maximum dipole moment?

(a) 

(b) 

(c) 

(d) 

4. Which one should have maximum dipole moment?

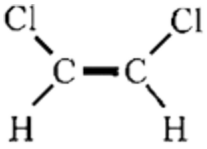
(a) $CH_2 = CH - Cl$

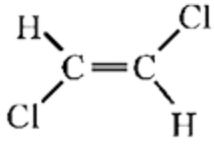
(b) $CH^{\circ} C - Cl$

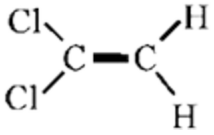
(c) $CH_2 = CH - CH_3$

(d) CCl_4

5. Which one should have maximum dipole moment?

(a) 

(b) 

(c) 

(d) All of them are equal

6. Find the maximum dipole moment among the following compounds-

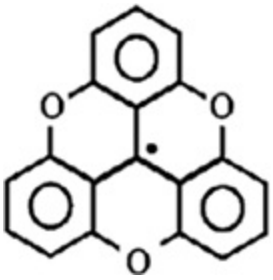
(a) HCHO

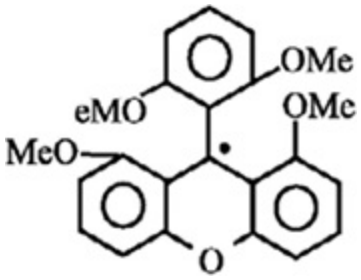
(b) CH_3CHO

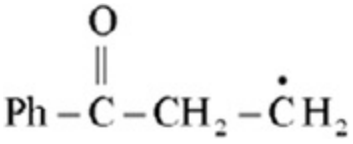
(c) $CH_3CH = CHCHO(cis)$

(d) CH_3CH_2CHO

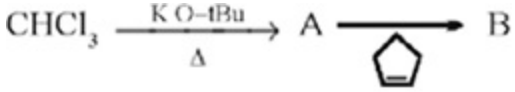
7. Which is maximum stable,

(a) 

(b) 

(c) 

(d) CH_2= CH •

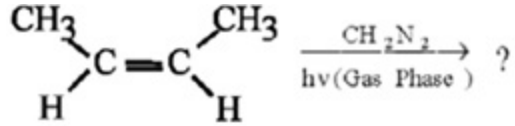
8. 

Select 'B' from the followings -

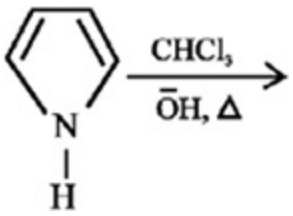
(a) 

(b)  (c) 

(d) 

9. 

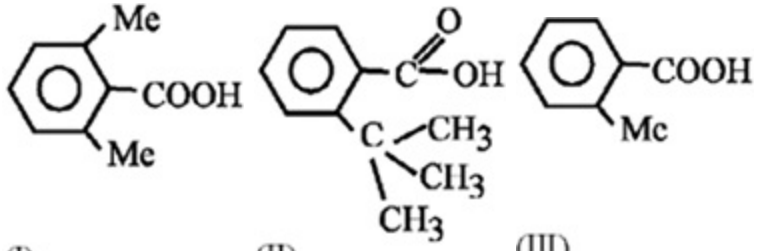
Products are....., ...

10. 

A (Ring expanded product)

What is A?

11. Which one is most acidic ?



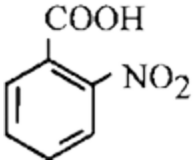
(I) (II) (III)

(a) I

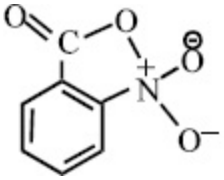
(b) II

(c) III

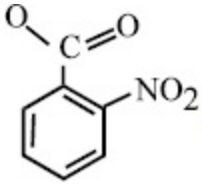
(d) II, III

12. 

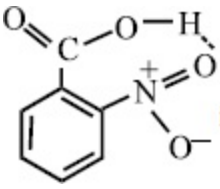
is very strongly acidic due to

(a) 

formation

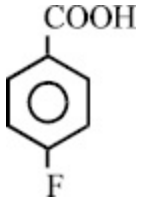
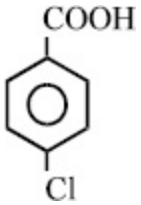
(b) 

formation

(c) 

formation

(d) None of these

13.  is less acidic than  may be due to

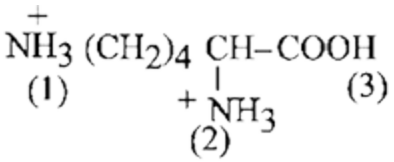
(a) +R of F cause $\delta\ominus$ on C (of the nucleus) which is joined with C of COOH, thereby reduce 8+ of C of CO_2H and hence it has less acidic strength.

(b) - I of F

(c) (a, b) both

(d) None of these

14. In the dicationic form of lycine arrange the proton donating sites which will release proton one after another serially.



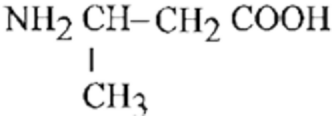
(a) (1, 2, 3)

(b) (3, 2, 1)

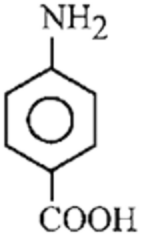
(c) (3, 1, 2)

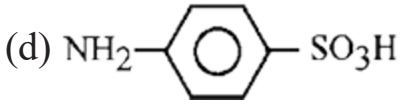
(d) (2, 1, 3)

15. Which one will not show Zwitter ion or dipolar ion structure ?

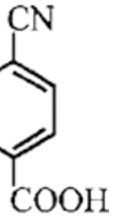
(a) 

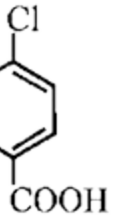
(b) NH_2CH_2COOH

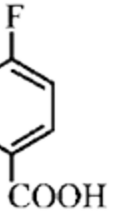
(c) 

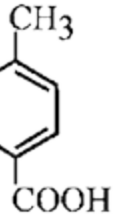
(d) 

16. Which one is the strongest acid ?

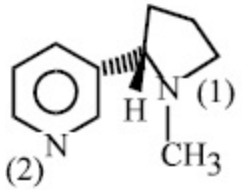
(a) 

(b) 

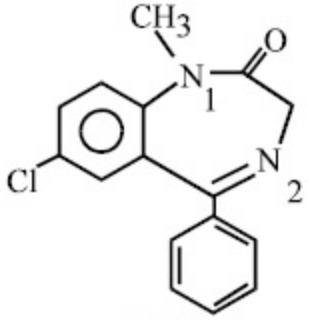
(c) 

(d) 

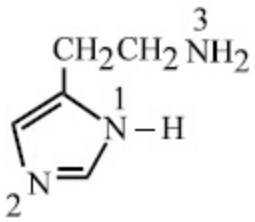
17. Which ones are the most basic sites of the following compounds?



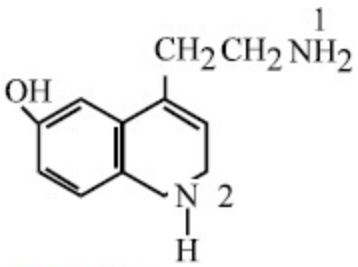
Nicotin



Valium



Histamine



Serotonin

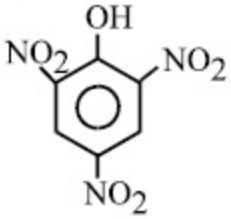
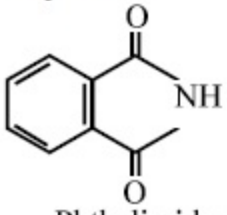
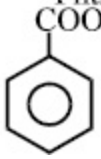
(a) (1, 2, 3, 1)

(b) (1, 2, 2, 1)

(c) (1, 2, 3, 2)

(d) (1, 2, 2, 2)

18. Match the pK_a values with the given compounds

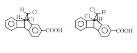
	Acid	pK_a
A.		1.4
B.	CH_3COOH	2.9
C.	 Phthalimide	3.5
D.		4.0.74

(a) (A – 3, B- 4, C – 2, D – 1)

(b) (A- 3, B – 2, C – 4, D- 1)

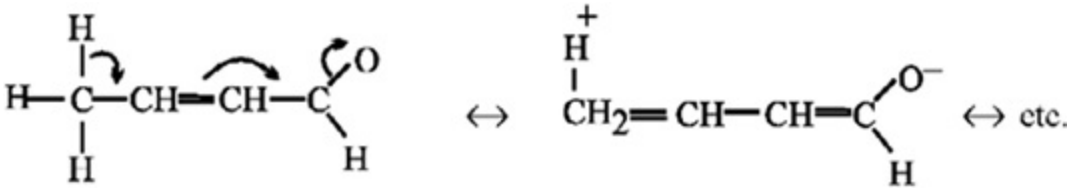
(c) (A- 4, B – 3, C– 2, D-1)

(d) None of these

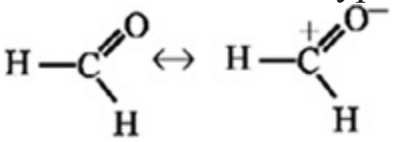
19. Which one is stronger acidic between the two acids given below ; 

Answer

(1) (d)
(2) (c)
(3) (c)
(4) (c) [Hint : order will be $CH_3CH = CH_2 > CH_2 = CHCl$ (1.44D) > CH° C–Cl $(0.44D)_n > CCl_4$]
(5) (c)
(6) (c) [Hint. CH_3CH= CHCHO (3.67D) > CH_3CHO > CH_3CH_2CHO (2.73D) > HCHO (2.27D) Answer lies in the fact that, in

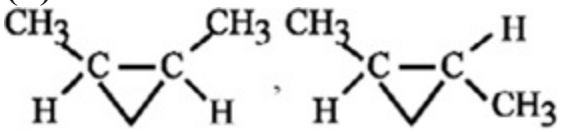


Where hyperconjugation and resonance play the role by which large charge separation takes place. In HCHO no hyperconjugation only resonance plays the role as shown,

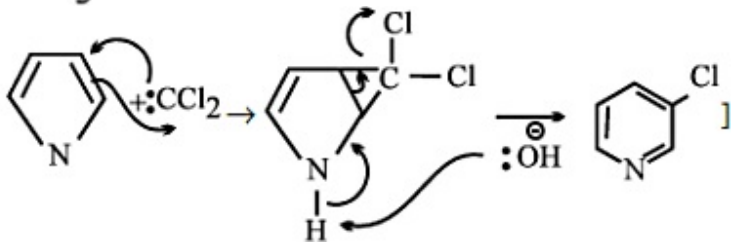


.

Effects will be discussed later]
(7) (a)
(8) (d)
(9)



(10) [Hint : $CHCl_3 + \overset{\ominus}{O}H \rightarrow \ddot{C}Cl_2$;



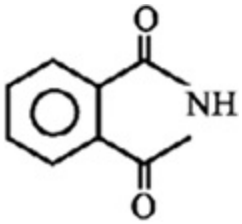
]
(11) (a) **[Hint :** I > II > III, as steric repulsion reduces gradually]
(12) (a)
(13) (a)
(14) (b)
(15) (c)

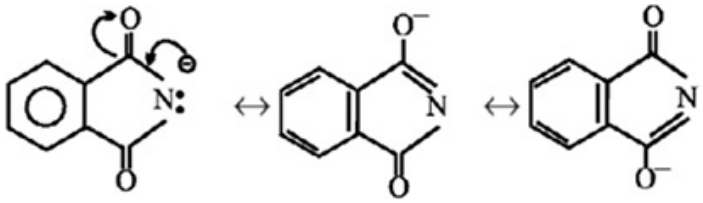
(16) (a)

[Hint : Due to – R of – CN will be more effective than – R of Cl and Cl also can to some extent show +R (which causes reduction of acidity)]

(17) (b)

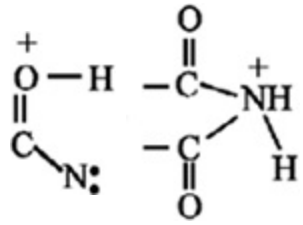
(18) (c)

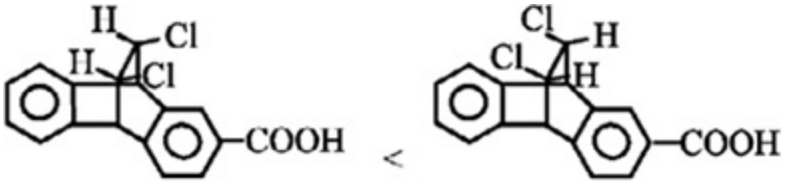
Hint : [Remember  is acidic instead of basic due to three resonating structures of conjugate base.

as shown in the adjacent diagram,  ; it

shows that conjugate base is very stable. The basic site in phthalimide is ⁚O⁚ not the ⁚N⁚ atom. Again

it is due to resonance stabilisation ofmore than etc.]

19. Let us look at the famous example, 



$pK_a = 6.0$ $pK_a = 5.5$

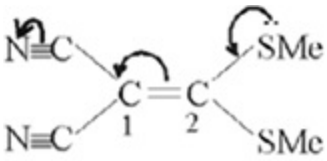
according to their acidic strength.

By inductive effect of Cl atoms acid strength should be same but if we see the stability of the conjugate base – COO^-, then it may be that lps of Cl repels the negative charge on – COO^- and destabilise the conjugate

base.

Isomerism

1. >C≡C< Energy = 62.65 K cal/mole (260 – 270 kJ/mole)

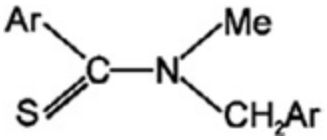


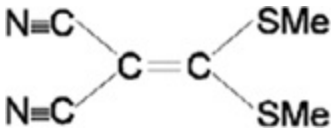
Push pull molecule
(I)

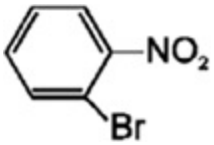
; Energy = 55 kJ/mole for the rotation w.r.t. C–C bond.

In the molecule (I) do you expect the geometrical isomerism ?

2. cis/trans Isomerism is observed in double bond. Contrary to this fact which molecule can show the geometrical isomerism even w.r.t. single bond between two atoms.

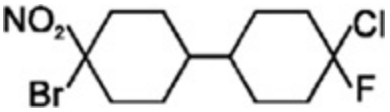
(a) 

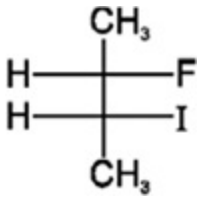
(b) 

(c) 

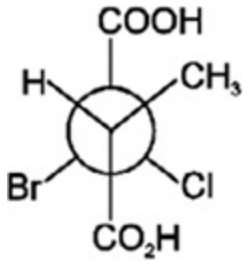
(d) None of these

3. Find out the plane of symmetry present or absent in the following molecules and state whether they are optically active or not.

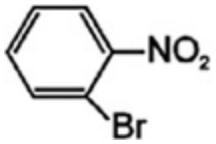
(a) 

(b) 

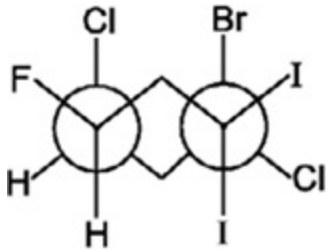
(c)



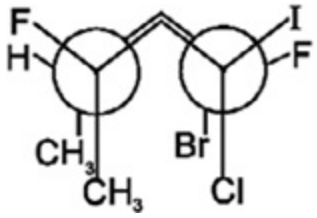
(d)



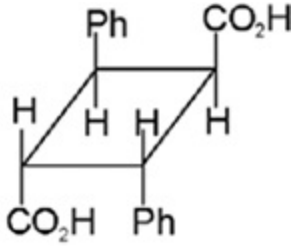
(e)



(f)

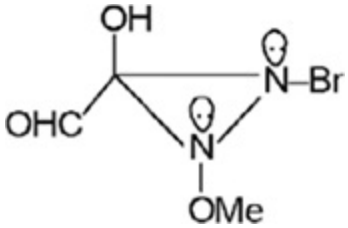


(g)

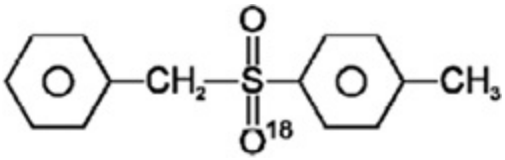


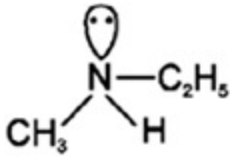
α-Truxillic acid

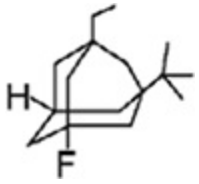
(h)

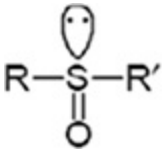


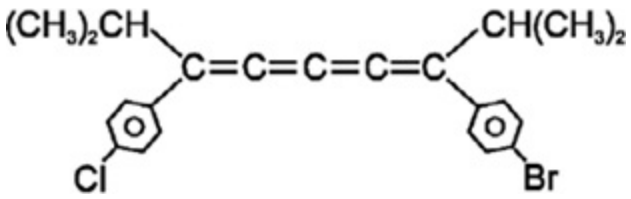
(i)

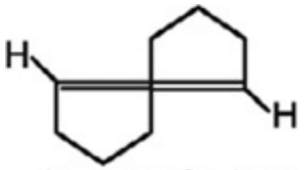


(j) 

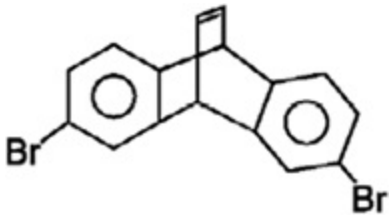
(k) 

(l) 

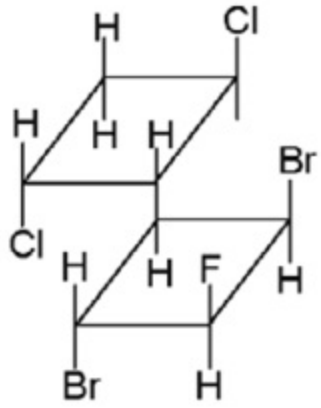
(m) 

(n) 

trans cycloctene

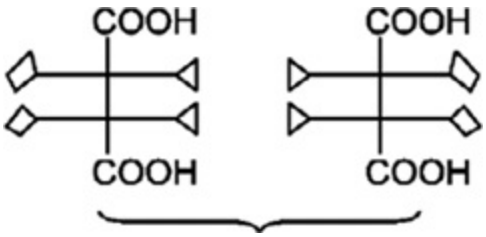
(o) 

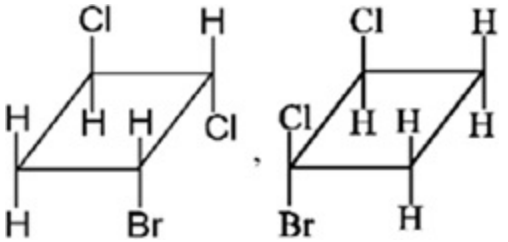
4. Find out centre of symmetry in the following if present.

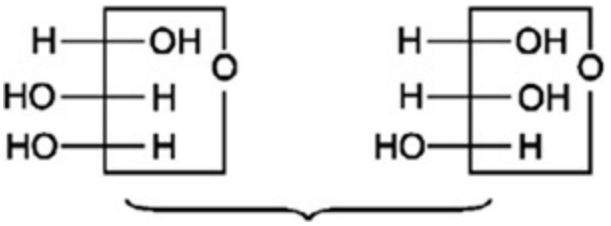
(a) 

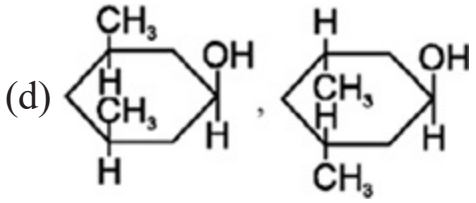
(a) 

5. Which are enantiomers, diastereomers, epimers, identical or non identical among the following pairs ?

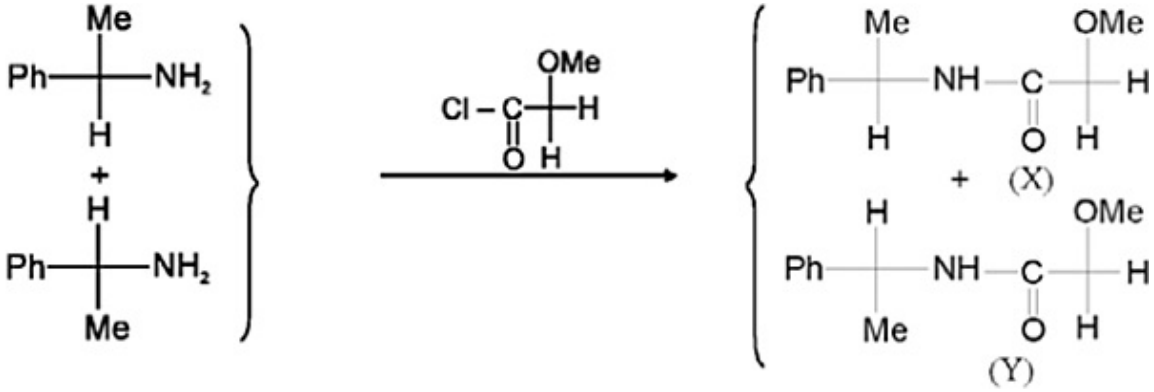
(a) 

(b) 

(c) 

(d) 

6. Find out the % optical purity for the following observation :



(X) has specific rotation + 60° and the observed rotation of the mixture found to be – 20°. Find out the % optical purity and composition of the mixture.

Answer & Hints

1. No, because free rotation take place w.r.t. C=C bond as it assume mainly C–C single bond character.

2. Rotation w.r.t C – N σ-bond is very slow in amides & thioamides, therefore C–N bond assume almost double bond character and show geometrical isomerism.

3. (a) Inactive

(b) Active

(c) Acitve

(d) Inactive

(e) Active

(f) Active

(g) Inactive

(h) Active

(i) Inactive

(j) Active

(k) Active

(l) Active

(m) Active

(n) Active

(o) Inactive

4. (a) Not present

(b) Mid of the bond at which two benzene rings are fused.

5. (a) Enantiomers

(b) Nonidentical

(c) Diastereomeres

(d) Diastereomers

6. $\frac{-20}{-60} \times 100 = 30\%$ (Y) in excess

Nucleophilic substitution

Write the product in the following reactions : 1.

1. $nPr-Br + \overset{\ominus}{N}O_2 \longrightarrow ?$
2. $iPr-Br + S_2O_3^{-2} \longrightarrow ?$
3. $ClCH_2CH_2-I + CN^- \longrightarrow ?$
4. $nPrONO_2 + N_3^- \longrightarrow ?$
5. $nBu\text{–}OSO_2Cl \xrightarrow{I^{\ominus}} ?$

6. The order of rates of reactions carried out by the following nucleophiles in actone is

(a) LiI > LiBr > LiCl > LiF

(b) LiI > LiCl > LiBr > LiF

(c) LiBr > LiF > LiCl > LiI

(d) none of these

7. The order of rates of reactions carried out by the following nucleophiles in actone is

(a) CsF > RbF > LiF > NaF

(b) CsF > LiF > RbF > KF

(c) CsF < RbF < LiF < NaF

(d) CsF > RbF > NaF > LiF

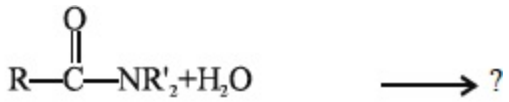
8. The order of rates of reactions carried out by the following nucleophiles in actone is

(a) $Bu_4N^+ Cl^- > Bu_4N{+}Br^- > Bu_4N^+ I^-$

(b) $Bu_4N^+ Br^- > Bu_4N{+}Cl^- > Bu_4N^+ I^-$

(c) $Bu_4N^+ Cl^- > Bu_4N{+}I^- > Bu_4N^+ Br^-$

(d) $Bu_4N^+ Cl^- > Bu_4N{+}I^- > Bu_4N^+ Br^-$

9.  ?

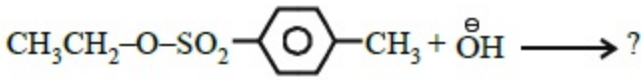
10. $RCOX + Li[AlH(Ot-Bu)_3] \longrightarrow$?

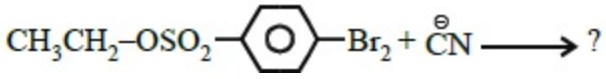
11. $R\text{–}COX + (CH_3)_2CuLi \longrightarrow$?

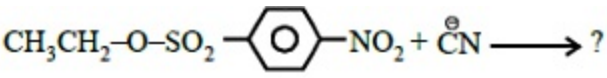
12.  ?

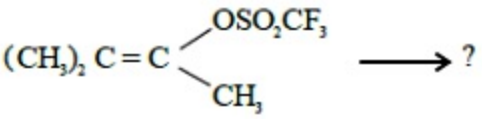
13. $CH_3X + CH_3 - C \equiv C^{\ominus}: \longrightarrow$?

14. $CH_3CH_2\text{–}OSO_2\text{–}OPh + Br^{\ominus} \longrightarrow$?

15.  ?

16.  ?

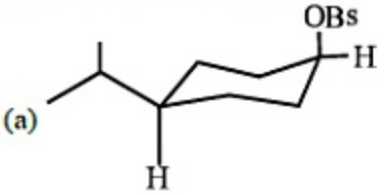
17.  ?

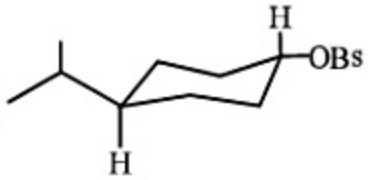
18.  ?

19. Where the S_N1 is more for tBu–Cl ?

(a) C_2H_5OH (100%)
(b) H_2O (80%) + C_2H_5–OH (20%)
(c) H_2O (80%) + C_2H_5OH (70%)
(d) none of these

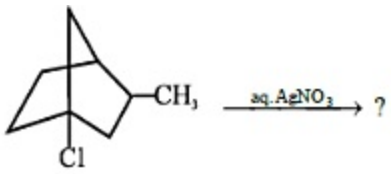
20. S_N1 reaction will be faster in

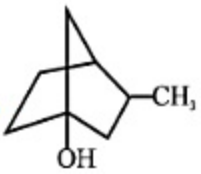
(a) 

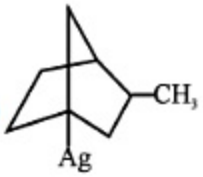
(b) 

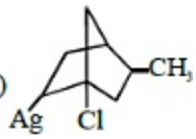
(c) same

(d) none of these

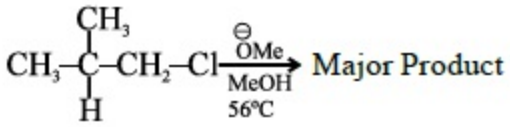
21. 

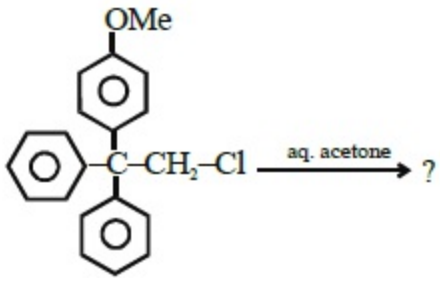
(a) No reaction (b) 

(c) 

(d) 

22. $(CH_3)_3CCl \xrightarrow[+20\%H_2O]{80\%\ C_2H_5OH} \underbrace{\text{?} + \text{?}}_{\text{Major}}$

23. 

24. 

Answer & Hints

1. $nPr - NO_2$

2. $i - Pr - S_2O_3$

3. $ClCH_2\ CH_2\ CH_2CN$

4. $nPrN_3$

5. nBuI

6. (a) ; **Hint :** [due to less solvation of I^- by weakly polar solvent CH_3COCH_3 and Li^+ , I^- are very bad ion pairs due to difference in size but F^- forms strong bond with Li^+ ion due to simillar size].

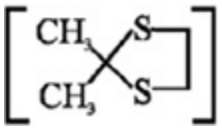
7. (d)

8. (a)

9. $RCOOH+R'_2NH$

10. RCHO

11. $RCOCH_3$; Hint : Here CH_3^- is the nucliophile

12. 

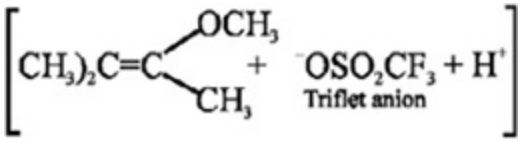
13. $CH_3\text{-}C{=}C{-}CH_3$

14. $CH_3CH_2 - Br$

15. $CH_3CH_2{-}OH + \overset{\ominus}{O}Ts$ (Tosylate anion)

16. $CH_3CH_2{-}CN + \overset{\ominus}{O}Bs$ (Brosylate ion)

17. $CH_3CH_2\text{-}CN$ + oNs (Nosylate)

18. 

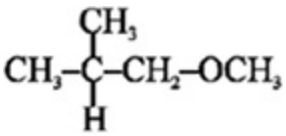
19. (b)

20. (a) ; **Hint:** [As there is steric repulsion between iPr, OBs as they are falling in the same side, so easy C^+ formation to get relief and faster S_N1 reaction results.]

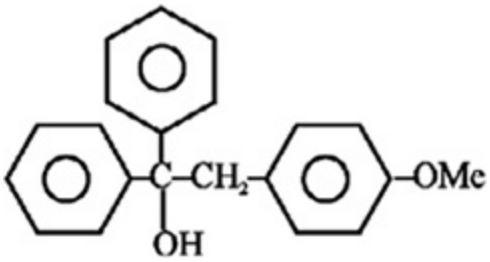
21. (a) ; **[Hint :** Bridge head $\overset{\oplus}{C}$ is very less stable because of strain, so no reaction occurs].

22. [80% $\{(CH_3)_3\ COH + (CH_3)_3\ COC_2H_5\}$]

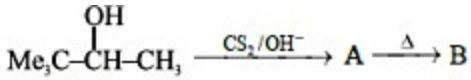
23.

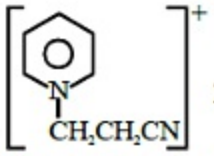


24.

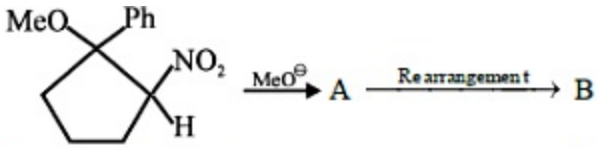


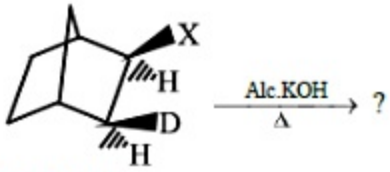
Elimination

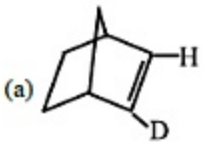
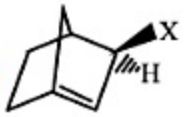
1. 
A and B are _____ and _____ (Only elimination product)

2. 
The mechanism is
(a) E_1 (b) E_2 (c) E_1CB (d) None of these

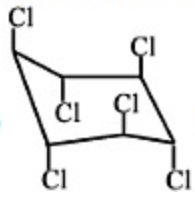
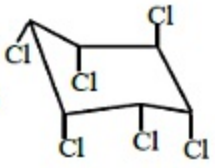
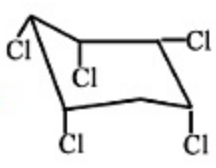
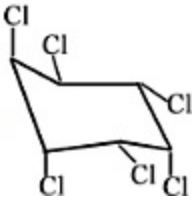
3. $MeCH_2CH_2CH_2CH_2Cl \xrightarrow[LDA]{} ?$
The product is
(a) $MeCH_2CH_2CH{=}CH_2$ (b) $MeCH{=}CH_2CH_3$
(c) $MeCH{=}CHCH_2CH_3$ (d) All of these

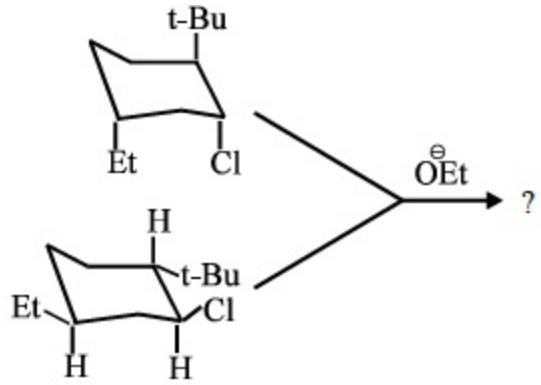
4. 
B on ozonolysis give $PhCOCHCH_2CH_2CHO$ (NO$_2$ on CH). A and B are _____ , _____

5. 
Product is

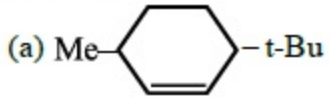
(a)  (b)  (c)  (d) 

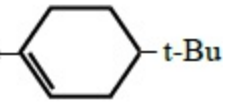
6. Which one will show fastest elimination with $\overset{\ominus}{O}Et$?

(a)  (b)  (c)  (d) 

7. 

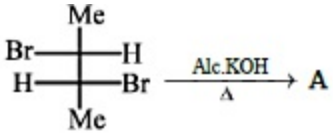
The Product is

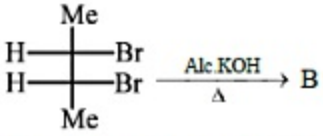
(a) 

(b) 

(c) 

(d) None of these

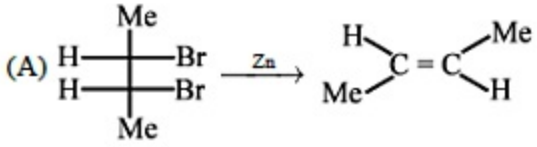
8. 

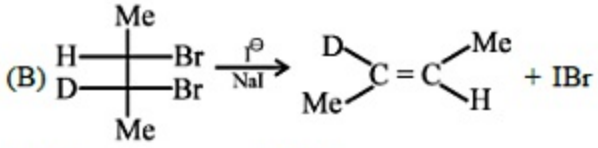


The relation between A, B is

(a) Enantiomer (b) Diastereomer (c) Configurational isomer (d) None of these

9. Can you predict the following mechanism from the results ?

(A) 

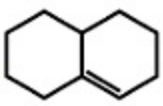
(B) 

(a) E1 (b) E2 (c) E1CB (d) Ei

10. Which one can be possible products by the dehydrohalogenation reaction ?

(a) 

(b) 

(c) 

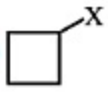
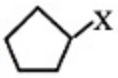
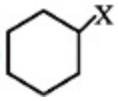
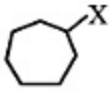
(d) 

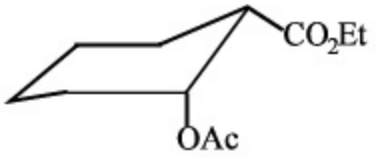
11. For the substrate $(CH_3)_2\underset{\underset{Br}{|}}{CH}-CH_2C(CH_3)_3$, with which have you expect high % yield of Hofmann's product ?

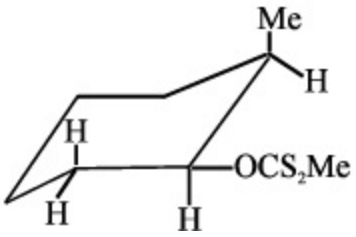
(a) $EtO^{\ominus}$ (b) Me_3CO^- (c) Et_3CO^- (d) $Me_2EtCO^{\ominus}$

12. $RR'CH-CRR'\overset{\oplus}{N}Me_3 \xrightarrow{OH^{\ominus}}$?

13. Maximum % yield by syn elimination process should be observed in

(a)  (b)  (c)  (d) 

14.  $\xrightarrow{\Delta}$? + ?

15.  $\xrightarrow{\Delta}$?

16. According to increasing % yield of olefine as the product with $\overset{\ominus}{O}Et$, the compounds

CH_3CH_2Br, (I) $(CH_3)_3CBr$ (II) $(CH_3)_2CHBr$, (III) $CH_3CH_2CH_2Br$ (IV) $(CH_3)_2CHCH_2Br$ (V)

can be arranged as _____

17. Which one is not a dehydrating agent among the followings

H_2SO_4, H_3PO_4, Al_2O_3, P_2O_5, $ZnCl_2$, DMSO, $KHSO_4$, anhydrous $CuSO_4$,  , HMPA, NaCl ?

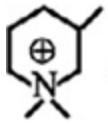
18. Hofmann's product is obtained when $(CH_3)_2\underset{\underset{OH}{|}}{CHCH_2}-CH_3$ is heated with –

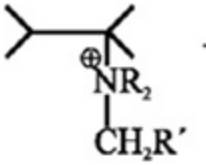
(a) Al_2O_3

(b) conc. H_2SO_4

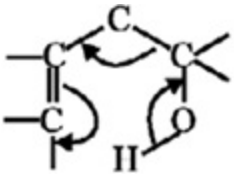
(c) ThO_2

(d) $KHSO_4$

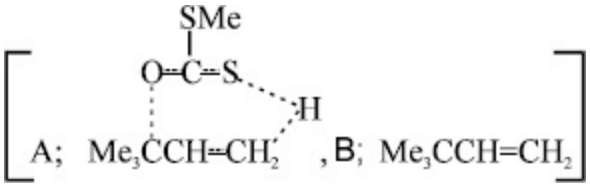
19.  $OH^- \xrightarrow{\Delta}$?

20.  $\xrightarrow{PhLi}$? + ?

21. $R_2CX-COX \xrightarrow{Zn}$?

22.  $\xrightarrow{\Delta}$ ..... + ...

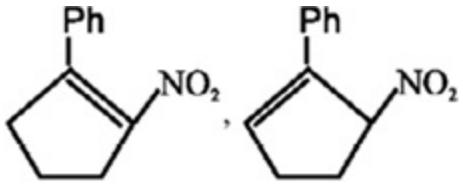
Answer and Hints

1. 

(See mechanism also)

2. (c)

3. (a) ; **[Hints :** 1,1 Elimination]

4. 

; **Hint :** Actually unstable A rearranges to B under this condition.]

5. (b) ; [**Hint :** No free rotation with respect to α (C) β (C) bond, therefore E2 takes place from syn coplanar arrangement]

6. (d) ; [**Hint :** Maximum no. of anti coplanar H, Cl atoms are present in (d)].

7. (a), (c)

8. (b), (c)

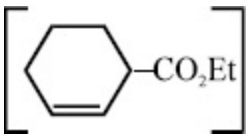
9. (b)

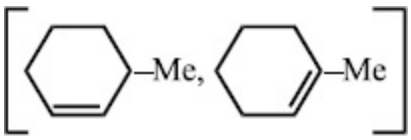
10. (d) ; **[Hint :** Maximum no. of anti coplanar H, Cl atoms are present in (d)].

11. (b), (c)

12. (b), (c), (d) ; **[Hint :** By the Bredt's rule double bond at bridgehead C is not acceptable in (a) due to strain]

13. [PP'C=CPP']

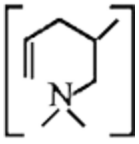
14. 

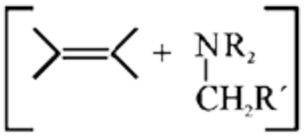
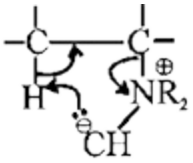
15. 

16. [I < IV< V<III<II] and the mechanism of elimination is E2

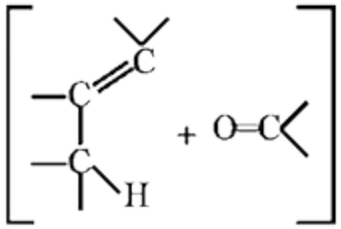
17. NaCl

18. (c)

19. 

20.  ; [Hint :  i.e. mechanism is Ei]

21. [$P_2C = C{=}O$]

22.  ;[Hint : β hydroxyallyl compounds undergo elimination with rearrangement.]

Alkane

1. How many chiral centres will be formed after the reaction

$CH_3(CH_2)_3CH_3 \xrightarrow{Cl_2} ?$

(a) 1

(b) 2

(c) 3

(d) 4

2. If relative reactivity of chlorination of 1° : 2° : 3° H is 1 : 3.25 : 4.4, the % 3° monochloro product for, $(CH_3)_2$ CH CH_2CH_3 is,

(a) 40

(b) 50

(c) 20

(d) 16

3. Which one is more reactive during chlorination

(a) SO_2Cl_2

(b) Cl_2

(c) SOCl

(d) None of these

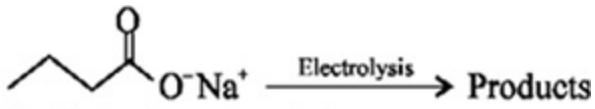
4. How does $Me_2C(CN) - N = N - C(CN)\ Me_2$ helps in chloriation while carried out by SO_2Cl_2 .

(a) by supplying N_2

(b) by supplying $\dot{S}O_2Cl$

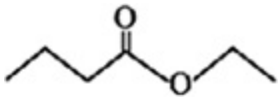
(c) by supplying $Me_2C(CN)$

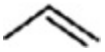
(d) None of these

5. 

Products do not contains

(a) 

(b) 

(c) 

(d) None of these

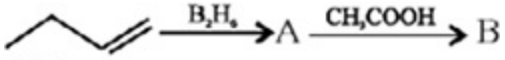
6. Wurtz reaction does not apply to

(a) 1° R – X

(b) 2° R – X

(c) 3° R – X

(d) allylic R – X

7. 

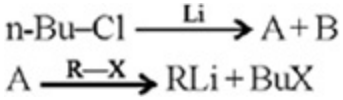
'B' is

(a) 

(b) 

(c) 

(d) None of these.

8. 

'A' is

(a) n BuLi

(b) LiCl

(c) n-Bu-Bu–N

(d) None of these.

9.

A. $3^{\circ}\,R-X \xrightarrow{Zn/C_2H_5OH} R-H$

B. $2^{\circ}\,R-X \xrightarrow{Zn/C_2H_5OH} R-H$

C. $1^{\circ}\,R-X \xrightarrow{Zn/C_2H_5OH} R-H$

D. $CH_3-X \xrightarrow{Zn/C_2H_5OH} CH_4$

Among the abovereactions, which reaction is fastest ?

(a) A

(b) B

(c) C

(d) D

10. Which shows the highest reactivity with Zn + C_2H_5OH

(a) R – I

(b) R – Br

(c) R – Cl

(d) R – F

11. Which cannot produce alkane from R – X

(a) Pd – H_2

(b) Ni – H_2

(c) Ph_3 SnH

(d) NH_2– NH_2^+ C_2H_5– Na^+

12. RCHO $\xrightarrow{2R'SH}$ A $\xrightarrow{Ni/H_2}$ B ? Product 'B' is

(a) RCH_2CH_3

(b) R-CH_3

(c) RCH_2SR'

(d) $RCH(SR')_2$

13. The maximum reactivity in thermal or photohalogenation is due to

(a) 3^{o} –H

(b) 2^{o} – H

(c) 1^{o} – H

(d) Methyl –H

14. Rate of fluorination is highest among other halogenation is due to

(a) highly exothermic chain propagation step

(b) low activation energy

(c) (a), (b) both

(d) None of these

15. $CoF_3 + R - H \xrightarrow{N_2} CoF_2 + HF + A$?

'A' is

(a) RF (b) CoRF

(c) RHF_2

(d) None of these

16. $RH + I_2 \rightleftharpoons RI + HI$

Therefore which is true?

(a) $RH + HI \longrightarrow RI + H_2$

(b) $RI + HI \longrightarrow RH + I_2$

(c) $RH + I_2 \longrightarrow RI_2 + H_2$

(d) None of these

17. Pyrolysis of C_2H_6 at 500º–800ºC, can produce

(a) C_2H_4

(b) CH_4

(c) $CH_3 - CH_3$

(d) None of these

18. Pyrolysis reaction starts through

(a) C – H bond breaking

(b) C – H bond breaking homolytically

(c) C – C bond breaking heterolytically

(d) None of these

19. If triplet carbene $(\overset{\uparrow}{\underset{\uparrow}{CH_2}})$ insertion is more with 3º H then 2ºH and then 1ºH, then which insertion product (%) will be more for $\overset{1}{CH_3}\overset{2}{CH_2}\overset{3}{CH_2}\overset{4}{CH_2}\overset{5}{CH_3}$?

(a) $C_1 - H$

(b) $C_2 - H$

(c) $C_3 - H$

(d) equal at all C–H bonds.

20. The nitration process of R – H has found to be free radical at 400°C. Which step is not feasible in your opinion?

(a) $HO - NO_2 \longrightarrow \dot{O}H + \dot{N}O_2$

(b) $RH + HO\cdot \longrightarrow R\cdot + H_2O$

(c) $R\cdot + HO - NO_2 \longrightarrow RNO_2 + \dot{O}H$

(d) $R\cdot + \underset{\underset{OH}{|}}{NO_2} \longrightarrow ROH + \dot{N}O_2$

(a) a

(b) d

(c) b

(d) None of these

21. $\left[CH_2 = CH \right]_2 CuLi \xrightarrow[I]{} A \xrightarrow[CH_3COOH]{BH_3\cdot THF} B$

The product 'B' is,

(a) $CH_2 = CH - CH_2CH_2\ CH_3$

(b) $CH_3CH_2CH_2CH_2CH_3$

(c) $CH_2 = CH - CH = CH_2$

(d) None of these

22. $RH + SO_2 + Cl_2 \longrightarrow A + HCl$

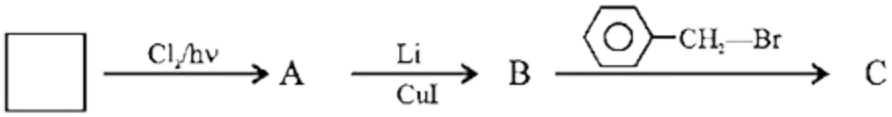
'A' is

(a) RCl

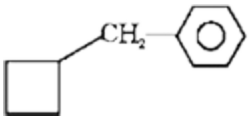
(b) RSO_2Cl_2

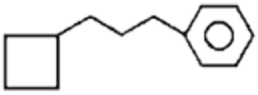
(c) RSO_2Cl

(d) $RSO_2(OH)Cl$.

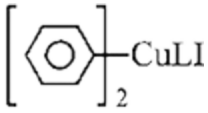
23. 

'C' is

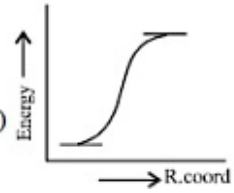
(a) 

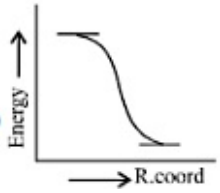
(b) 

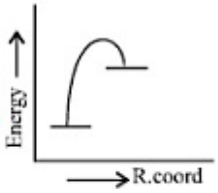
(c) 

(d) 

24. Which one is the correct energy profile for $Cl^{\cdot} + Cl^{\cdot} \longrightarrow Cl_2$ reaction ?

(a) 

(b) 

(c) 

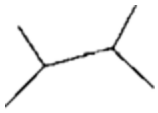
(d) All of these.

25. Which one should have maximum stability ?

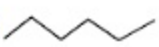
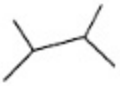
(a) 

(b) 

(c) 

(d) 

25. Which one should have maximum stability ?

(a)  (b)  (c)  (d) 

26. If 20 molecules of reactant R in excited state converts to product by the absorption of light of $\lambda = 4000$ Å, by 100 quanta, than the quantum yield (ϕ) is,

(a) $\frac{20}{4000}$ (b) $\frac{20}{100}$ (c) 20 (d) all of these

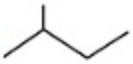
27. $RCH=CH_2 \xrightarrow[2)\ AgNO_3 + NaOH]{1)\ BH_3\text{-}THF} ?$

Product is

(a) $RCH_2CH_2CH_2CH_2R$ (b) RCH_2CH_3 (c) RCH_2CH_2OH (d) None of these

28.  $\xrightarrow[\Delta]{RCl,\ AlCl_3} ?$

Product may contain

(a)  (b)  (c)  (d) 

Answer & Hints

1. (a) **Hint :** $\left[\mathrm{CH_3—(CH_2)_2\underset{\displaystyle Cl}{\underset{|}{CH}}—CH_3}\right]$

2. (c) **Hint:** [Actually it is 22% by $\left[\frac{1 \times 4.43}{9\times1 + 2 \times 3.25 + 2 \times 4.43} \times 100\right]$

3. (b)

4. (b),(c)

5. (d)

6. (c)

7. (a)

8. (a)

9. (a)

10. (b), (c) **Hint :** [Due to good leaving group nature of I^-]

11. (d)

12. (b)

13. (a)

14. (c)

15. (a)

16. (b)

17. (a),(b),(c)

18. (b)

19. (b), (c) **Hint :** [Product is $\mathrm{\underset{\displaystyle CH_3}{\underset{|}{CH_3CH}—CH_2CH_2CH_3}}$ insertion of singlet carbene is not selective.]

20. (d) **Hint :** [Actually by the above mechanism, nitration takes place]

21. (b)

22. (c) ; **Hint :** [The above process is called chlorosulphonation]

23. (a)

24. (b)

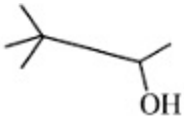
25. (c)

26. (b)

27. (b)

28. (a), (b) ; **Hint :** [Isomerisation can take place in presence of RCl, $AlCl_3$]

Alkenes

1.  $\xrightarrow[80°C]{H_3PO_4(85\%)}$ $\underset{80\%}{?}$ + $\underset{20\%}{?}$

2. Which one is chiral ?


I
Cis


II
cyclooctene


III
trans


IV
cyclooctene

3. $CH_2=CHCH_2Cl \xrightarrow{HI} X$

$X \xrightarrow{HOCl} Y$

Write the products X and Y.

4. $CCl_3CH=CH_2 \xrightarrow{HOBr} ?$ Write the product.

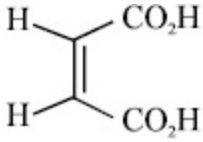
5. Fill in the blanks ; $Ph—CH=CH_2 \xrightarrow{Br_2} \underset{}{?} + \underset{(Major)}{?}$

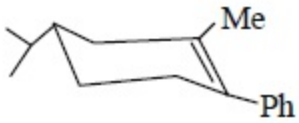
6. $CH_2=CH—\underset{\displaystyle OH}{\underset{|}{CH}}—CH=CH\ Et \xrightarrow[H_2SO_4]{MeOH} [?]$

7. Stability order of the following compounds

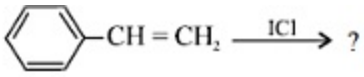
$\underset{I}{MeCH=CH_2}$, $\underset{II}{Me_2C=CHMe}$, $\underset{III}{Me_2C=CMe_2}$ is _____.

8. $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C=\overset{14}{C}H_2 \xrightarrow{Cl_2} \underset{(Major)}{?} + \underset{Minor}{?}$

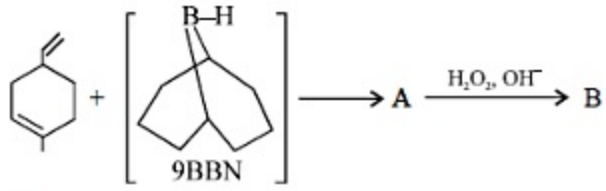
9.  $\xrightarrow{Br_2}$?

10.  $\xrightarrow{HBr} \underset{only}{?}$

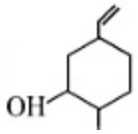
11. $CH_3CH_2CH=CH_2 \xrightarrow[ROH]{H^+} ?$

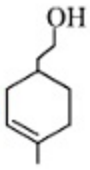
12. 

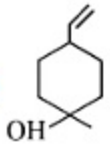
13. $CH_3CH=CH_2 \xrightarrow[RCOOH]{H^+} ?$

14. 

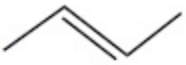
'B' is

(a) 

(b) 

(c) 

(d) None of these.

15. 3  $\xrightarrow{BD_3}$ A $\xrightarrow{CH_3COOH}$ B.

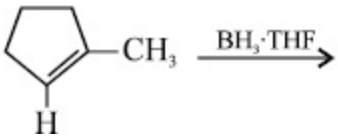
Product 'B' is

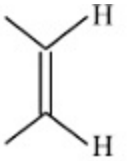
(a) $CH_3CH(D)-CH_2OH$

(b) $CH_3CH(D)-CH(OH)-CH_3$

(c) $CH_3CH(D)-CH(D)-CH_3$

(d) (±) $CH_3CHDCHDCH_3$

16. 

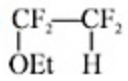
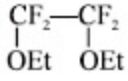
17.  $\xrightarrow[CCl_4]{Br_2}$? + ? [Mention the R/S configurations also]

18. $R_2C=CH_2 \xrightarrow[2)\ NaBH_4,OH^-]{1)\ Hg(OCOCH_3)_2/THF,\ H_2O}$ (X) ?

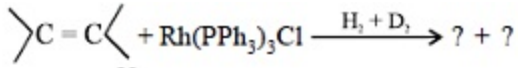
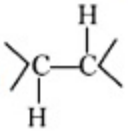
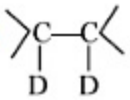
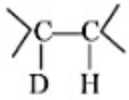
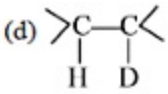
$\downarrow$ 1) $Hg(OCOCF_3)_2$/THF, ROH | 2) $NaBH_4,OH^-$

(Y)?

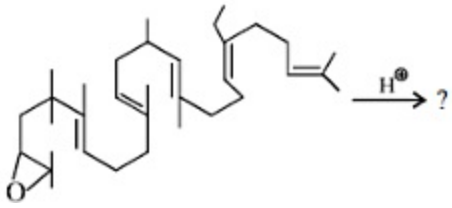
19.  ?

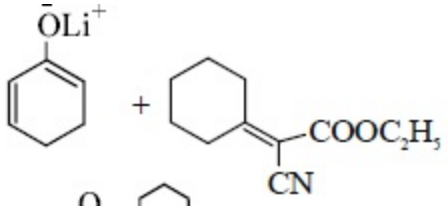
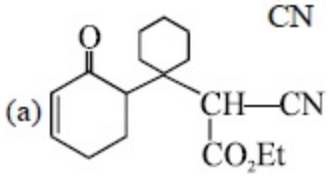
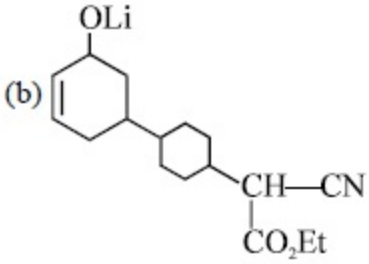
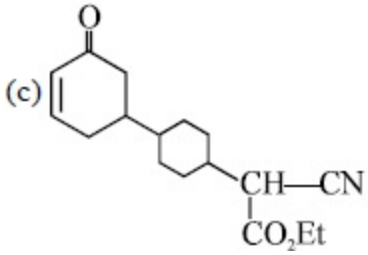
20. $CF_2=CF_2 \xrightarrow{EtO^{\ominus}} A \xrightarrow{EtOH} B$
B is
(a) no product (b)  (c)  (d) none of these.

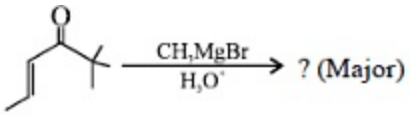
21. $CH_3=CHCH_3 \xrightarrow[\text{reagent}]{\text{Lemiux}}$? [with OsO_4]
Which one is/are not the product.
(a) HCOOH (b) CH_3COOH (c) $NaIO_3$ (d) $CH_2=O$

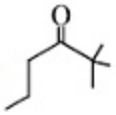
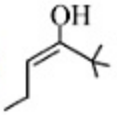
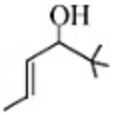
22.  Product(s) is/are :
(a)  (b)  (c)  (d) 

23. Birch reduction rate can be increased by the group present in benzene ring is/are.
(a) –COOH (b) $-CONH_2$ (c) –OMe (d) Me

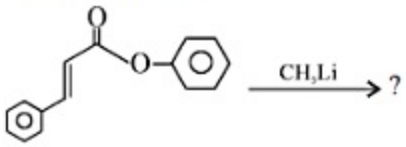
24. Write the product 

25.  A Product 'A' is
(a) 
(b) 
(c) 
(d) None of these

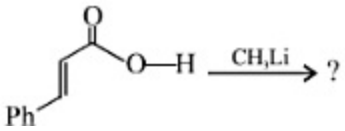
26. 

(a)  (b)  (c)  (d) All of these.

27. Write the product



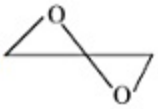
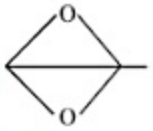
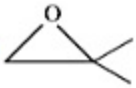
28. Write the product



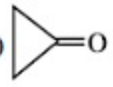
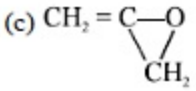
29. $CH_2=CH_2 + PhCOCl \xrightarrow{HRh(CO)(PPh_3)_2} ?$

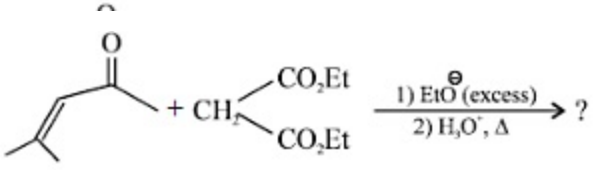
30. $CH_3CH=CH_2 \xrightarrow{IN_3} ?$

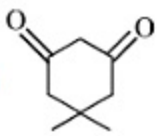
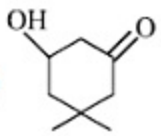
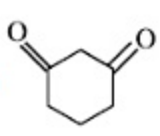
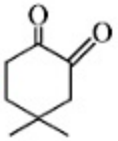
31. $CH_2=C=CH_2 \xrightarrow{2CF_3CO_3H} ?$

(a)  (b)  (c)  (d) None of these

32. $CH_2=C=O + CH_2N_2 \xrightarrow{CH_2Cl_2} ?$

(a)  (b)  (c)  (d) None of these.

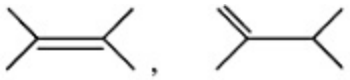
33. 

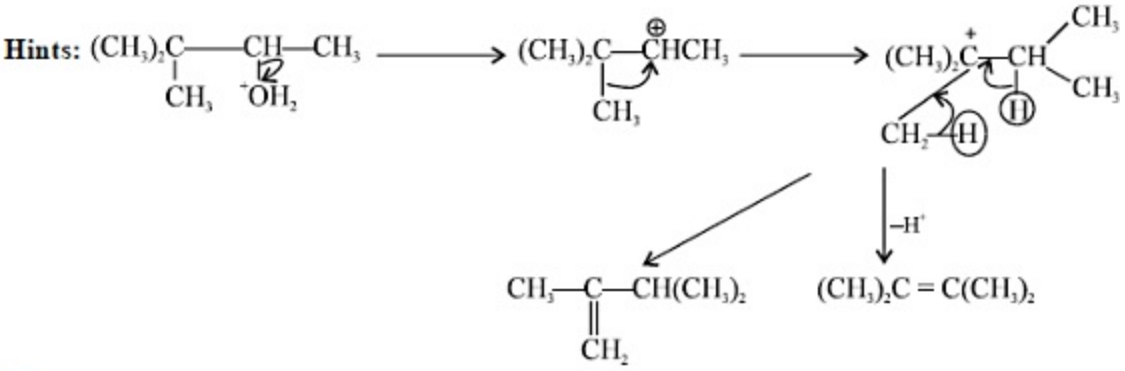
(a)  (b)  (c)  (d) 

34. Among α, β conjugated aldehyde (a), ketone (b), ester (c), which gives 1, 2 addition easily?

(a) a (b) b (c) c (d) All of these

Answer & Hints

1. 

Hints: 

2. II

3. X; CH_3CHICH_2Cl, Y; $CH_2(OH)CHClCH_2Cl$]

4. $CCl_3CH(Br)CH_2OH$]

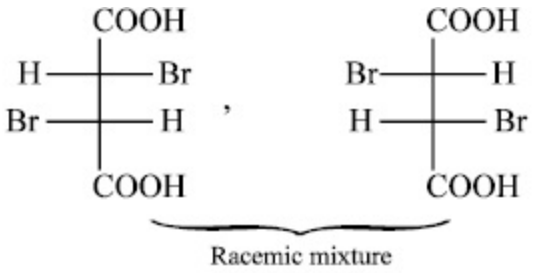
5. $PhCH(Br)CH_2Br$ + $PhCH(Br)CH_2Br$

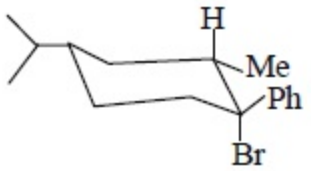
Hint : If $Ph\overset{\oplus}{C}HCH_2Br$ or $(CH_3)_2\overset{+}{C}CH_2Br$ form which are stable, then cis, trans both additions are possible.

6. $CH_2=CH-CH=CH-CH(OMe)-Et$

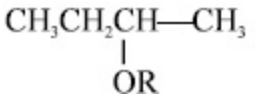
7. [III > II > I]

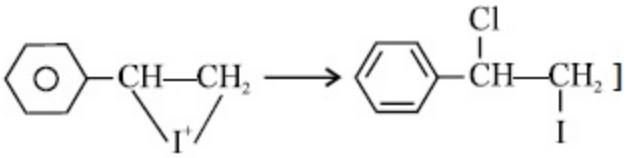
8. $CH_3-C(=CH_2)-{}^{14}CH_2-Cl$, $CH_3CH(Cl)-{}^{14}CH_2Cl$

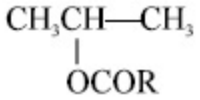
9. 

10. 

, 100% trans addition product

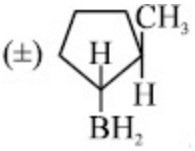
11. 

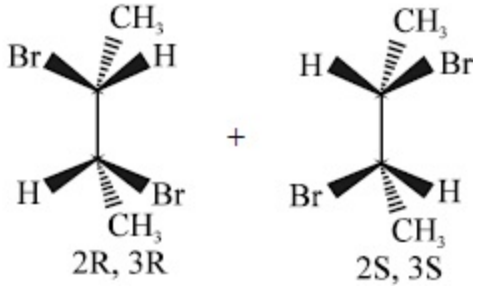
12. 

13. 

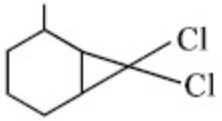
14. (b)

15. (d)

16. 

17. 

18. $X = R_2C(OH)—CH_3$, $Y = R_2C(OR)—CH_3$

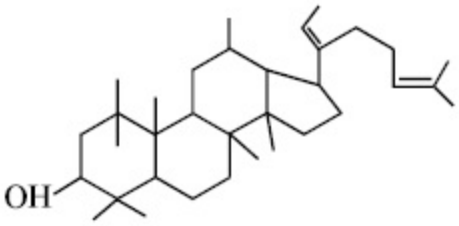
19. 

20. (b)

21. (d) **Hints :** [MnO_4^- further oxidises the aldehydes to acids]

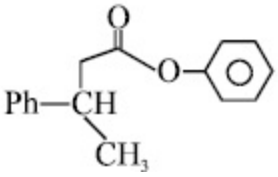
22. (b)

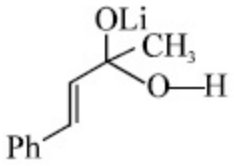
23. (a), (b) **[Hint :** With drawing pronps enhance the rate].

24. 

25. (a)

26. (a)

27. 

28. 

29. CH_3CH_2COPh

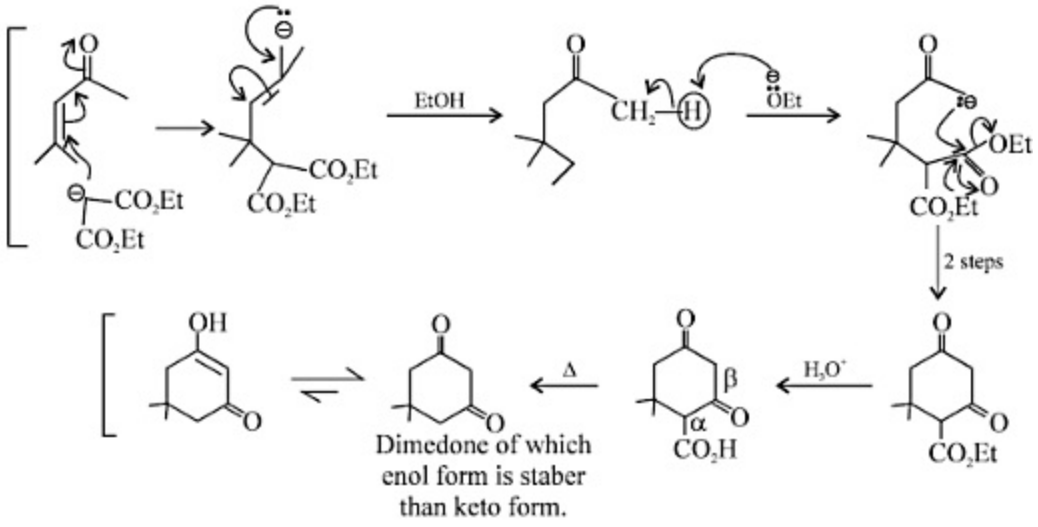
30. $CH_3\underset{\underset{N_3}{|}}{CH}—CH_2I$ **Hint :** Addition takes place through cyclic iodinium ion.

31. (a) **Hint :** {spiro dioxide is produced}

32. (a)

33. (a)

Hint :



34. (a)

Alkyne

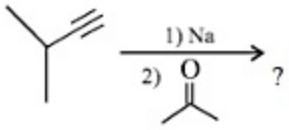
1. $CH_3CH_2\underset{\underset{Br}{|}}{CH}-\underset{\underset{Br}{|}}{CH}CH_2CH_3 \xrightarrow[\Delta]{\text{Excess alc, KOH}} ?$

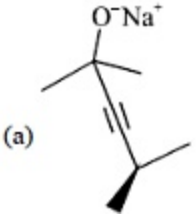
(a) $CH_3CH_2C=CCH_2CH_3$

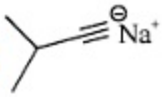
(b) $CH_3CH=CH-CH=CH-CH_3$

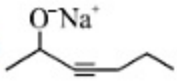
(c) $CH_3CHCH=\underset{\underset{Br}{|}}{C}HCH_2CH_3$

(d) None of these

2. 

(a) 

(b) 

(c) 

(d) None of these.

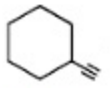
3. $Cl-CH_2-CH(OC_2H_5)_2 \xrightarrow[\Delta]{NaNH_2\text{(Excess)}} A \xrightarrow{Na} B \xrightarrow[2)\ H_3O^+]{1)\ CH_3CHO} C$

(a) $ClCH_2\underset{\underset{OC_2H_5}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-CH_3$

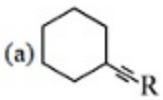
(b) $CH_3-\underset{\underset{OH}{|}}{CH}-CH=C(OC_2H_5)_2$

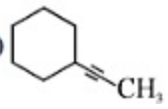
(c) $CH_3\underset{\underset{OH}{|}}{CH}-C\equiv C(OC_2H_5)$

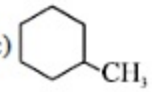
(d) None of these

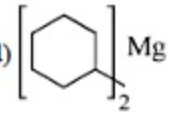
4.  $\xrightarrow{RMgBr} A \xrightarrow{CH_3Br} B$

'B' is

(a) 

(b) 

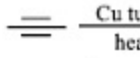
(c) 

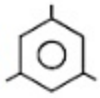
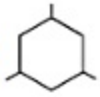
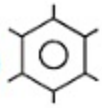
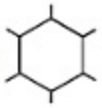
(d) 

5. $CH_3C\equiv C-(CH_2)_4CH=CH_2 \xrightarrow[2)\ H_2O]{1)\ 1\ mole\ O_3} ?$

(a) $CH_3COOH + (CH_2)_4(OH)-CH=CH_2$ (b) $CH_3C\equiv C-(CH_2)_4COOH + HCOOH$

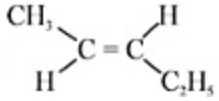
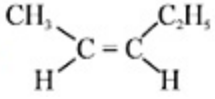
(c) $CH_3COOH + HCOOH$ (d) All of these.

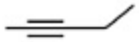
6.  ?

(a)  (b)  (c)  (d) 

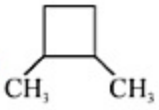
7. $CH_3-C\equiv C\,C_2H_5 \xrightarrow[2)\ NH_4Cl]{1)\ Na,\ EtNH_2} A \xrightarrow[2)\ H_3O^+]{1)\ KMnO_4,OH^-} B + C$

A and B is

(a) A:  (b) A:  (c) B : CH_3CHO (d) B: CH_3COOH

8.  $\xrightarrow[2)\ NaNH_2\ (2\ eq.),\ \Delta]{1)\ X_2} A \xrightarrow[2)\ NH_4Cl]{1)\ Li,\ EtNH_2} B \xrightarrow[Zn\text{-}Cu\ couple]{CH_2I_2} C$

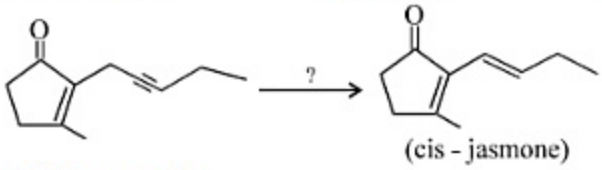
'C' is

(a)  (b)  (c)  (d) None of these

9. $CH_3C\equiv C-H \xrightarrow{O_3} A \xrightarrow{Zn,\ HOAC} B + C.$

'B' or 'C' may be

(a) CH_3COOH (b) HCOOH (c) CH_3CHO (d) HCHO

10. 

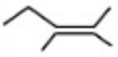
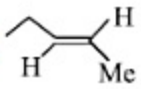
(cis - jasmone)

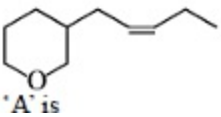
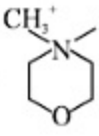
Suitable reagent is

(a) Na/NH_3 (b) $NH_2-NH_2 + C_2H_5ONa$ (c) $Pd-CaCO_3$ (d) $Zn-Hg/HCl$.

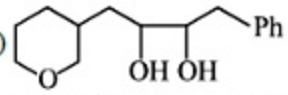
11.  $\xrightarrow[R_2O_2]{HBr} A \xrightarrow[\Delta]{Li,\ CuI} B \xrightarrow{Me-Br} C$

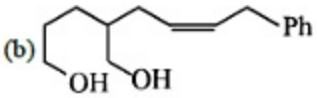
Product 'C' is

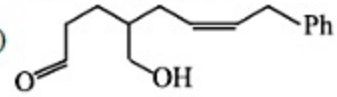
(a)  (b)  (c)  (d) None of these.

12.  $\xrightarrow[NMO,\ 25°C]{OsO_4} A$; [NMO is ]

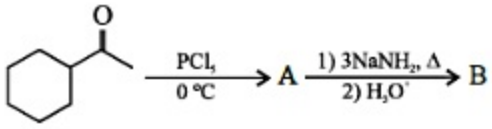
'A' is

(a) 

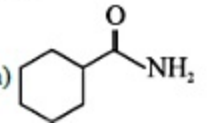
(b) 

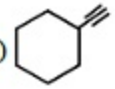
(c) 

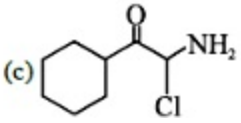
(d) None of these

13. 

'B' is

(a) 

(b) 

(c) 

(d) None of these

14. Which one is the most appropriate basicity order ?

(a) $\overline{O}H > \overline{O}R > \overline{C} \equiv CR$

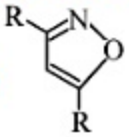
(b) $RC \equiv \overline{C} > \overline{O}R > \overline{O}H$

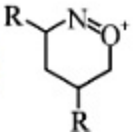
(c) $RCH_2\overline{C}H_2 > RCH = \overline{C}H > \overline{N}H_2 > R-C \equiv \overline{C}$

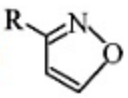
(d) $RCH_2\overline{C}H_2 > ROH = \overline{O}H > \overline{N}H_2 > R-C \equiv \overline{C} < \overline{O}R > \overline{O}H$

15. $R-C \equiv \overset{\oplus}{N}-O^- + RC \equiv C-H \longrightarrow ?$

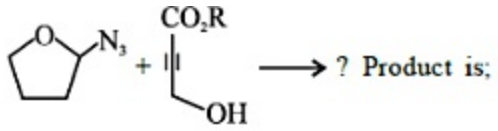
The product may be

(a) 

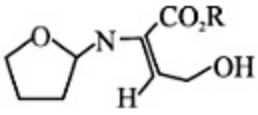
(b) 

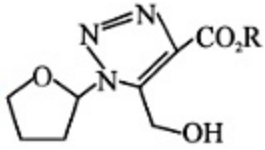
(c) 

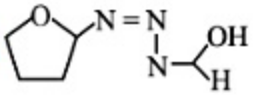
(d) all of these.

16. 

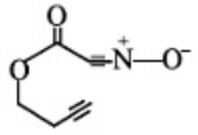
? Product is;

(a) 

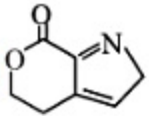
(b) 

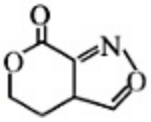
(c) 

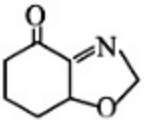
(d) None of these

17. 

? Product is';

(a) 

(b) 

(c) 

(d) All of these

Answer & Hints

1. (a)

2. (a)

3. (c) **[Hint :** $CH \equiv C(OC_2H_5)$ is (a)]

4. (b)

5. (b) **[Hint :** $\equiv$ is less reactive than =]

6. (c)

7. (a), (d)

8. (a)

9. (c), (d)

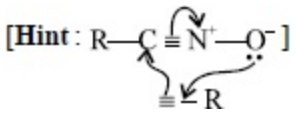
10. (c)

11. (c)

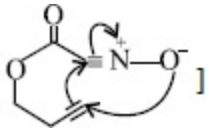
12. (a)

13.

14. (d)

15. (a) **[Hint :**  **]**

16. (b)

17. (b) **[Mech :**  **]**

Alkyl halide

1. Which one has strongest C – F bond strenth

(a) CH_3F

(b) CH_2F_2

(c) CHF_3

(d) CF_4

2. $CCl_4 + H_2O \xrightarrow[\text{Hydrolysis}]{500^\circ C} \xrightarrow{?} + \xrightarrow{?}$

$[COCl_2, HCl]$

3. Pyrene is the name of what among the followings as it is used in fire exting nisher ?

(a) CF4

(b) C2F4

(c) CCl4

(d) CBr3 Cl.

4. $CHCl_3 + O_2 \longrightarrow \xrightarrow{?} + \xrightarrow{?}$

(a) $COCl_2$ + HCl

(b) CO + HCl

(c) CO_2 + HCl

(d) none of these

5. Which one is used as antiseptic?

(a) $CHCl_3$

(b) $CHBr_3$

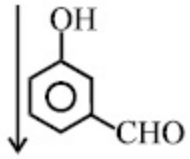
(c) CHI_3

(d) Cl + F_3.

6. $(CH_3)_3C\,CH_2-Cl \xrightarrow[\Delta]{AlCl_3} \xrightarrow{?}$

$CH_3MgCl \xrightarrow{BrCH_2CH_2OH} ?\,(A) + ?\,(A')$

7.



$?\,(B) + ?\,(B')$

8. Match the following consider the reaction of CH_3MgBr with the compounds in column A and product are written in column B.

Column A	C olumn B
(i) $ClNH_2$	(p) CH_3CN
(ii) ClCN	(q) CH_3NH_2
(iii) CH_3COCl	(r) $C_2H_5COCH_3$
(iv) $C_2H_5COC_2H_5$	(s) CH_3COCH_3

9. $(CH_3)_2C{=}CH{-}CH{=}O \xrightarrow{CH_3MgBr} ? + ?$

Which one is the major product ?

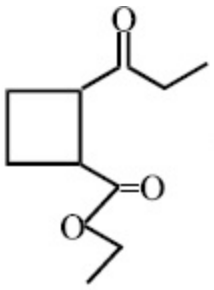
(a) 1, 2 addition

(b) (1,4) addition

(c) 3,4 addition

(d) None of these

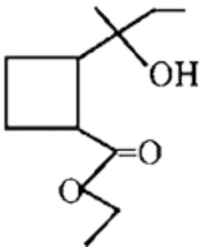
10.

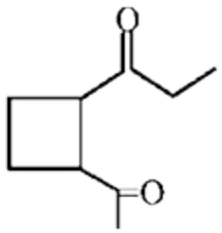


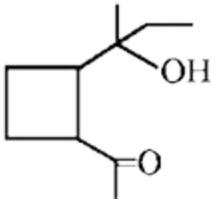
1 Mole
(i) CH_3MgBr
(ii) H_3O^+
?

The product is –

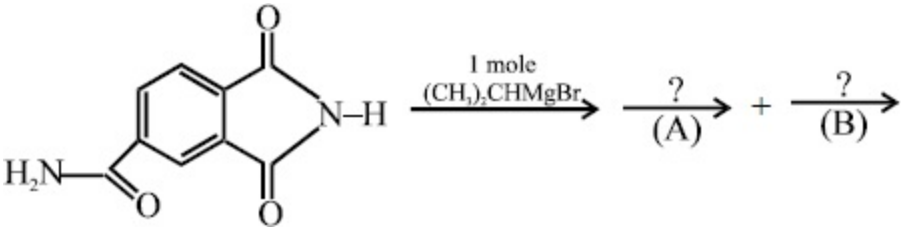
(a)



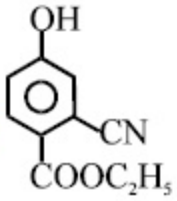
(b) 

(c) 

(d) All of these

11. 

12. We want to produce alcohol from the given substrates in column 'A'. Match the number of CH3MgX required under column 'B

Column A	**C olumn B**
(i) $CH_3COOC_2H_5$	(p) 1
(ii) CH_3COCl	(q) 2
(iii) 	(r) 3
(iv) $HOCH_2COOC_2H_5$	(s) 4

Answer & Hints

1. (d)

2. [$COCl_2$, HCl]

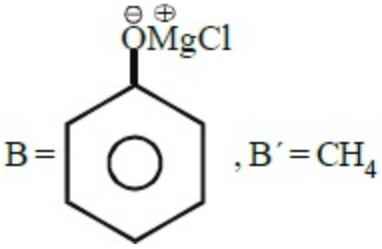
3. (a)

4. (a)

5. (d)

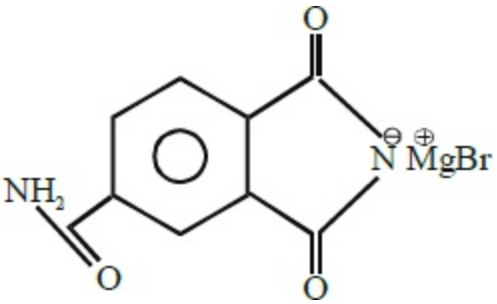
6. $(CH_3)_2\underset{\displaystyle Cl}{\underset{|}{C}}-CH_2CH_3$

$A = CH_4$, $A' = CH_2CH_2MgCl$

7. 

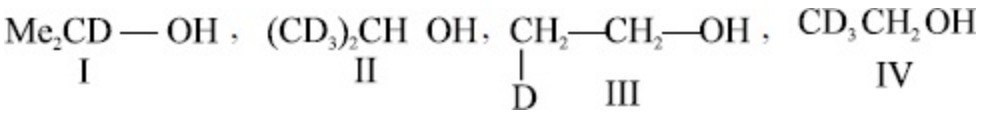
$B =$, $B' = CH_4$

8. (a)

11. $(CH_3)_2CH_2 + NH_2$ 

12. (i)–(q); (ii–q); (iii)–(r); (iv)–(s)

Alcohol

1. 

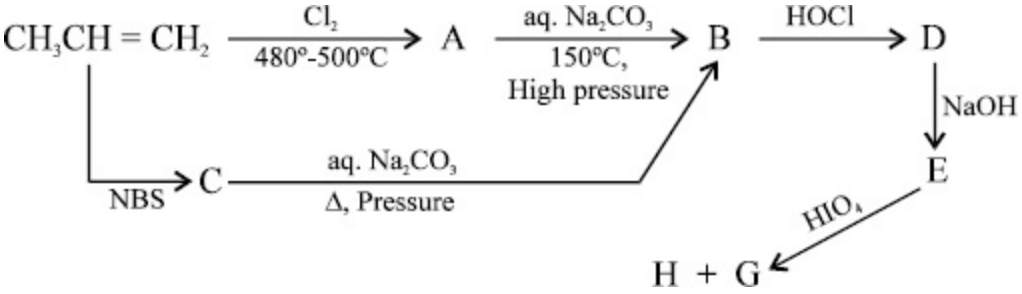
Among the above four compoundswhich one undergoes slowest oxidation by $Cr_2O_7^{-2}$ / H+ ?

(a) I

(b) II

(c) III, IV

(d) IV only

2. 

Find out G, H

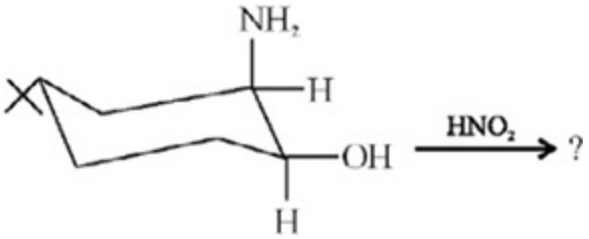
(a) G ; HCOOH H ; HCHO

(b) only HCOOH

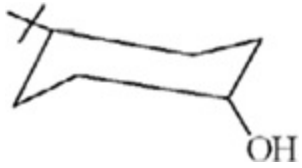
(c) only HCHO

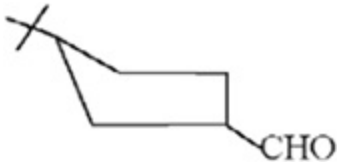
(d) None of these

3. Write the product

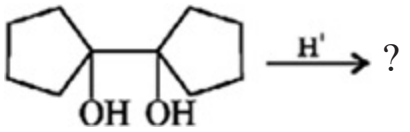


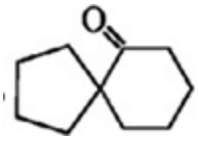
(a) 

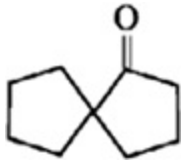
(b) 

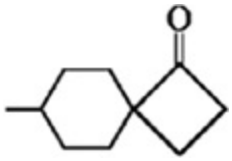
(c) 

(d) None of these

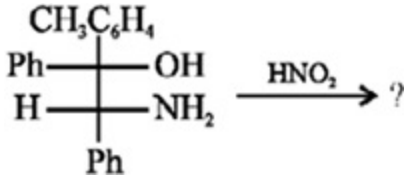
4. 

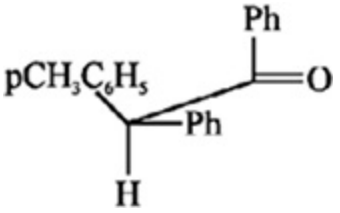
(a) 

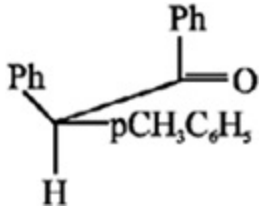
(b) 

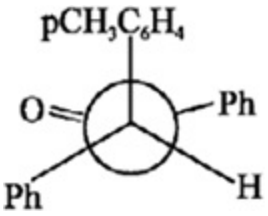
(c) 

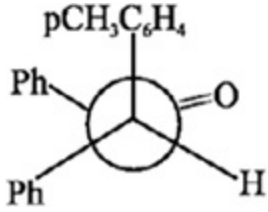
(d) All of these.

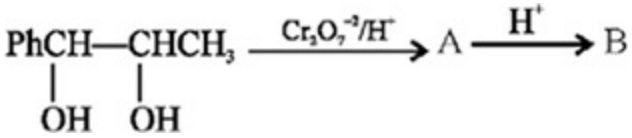
5. 

(a) 

(b) 

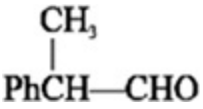
(c) 

(d) 

6. 

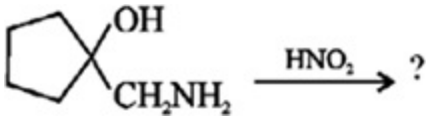
'B' is

(a) $PhCH_2\ COCH_3$

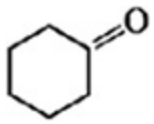
(b) 

(c) CH_3CH_2COPh

(d) All of these

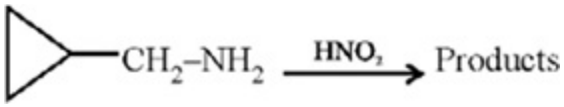
7. 

(a) 

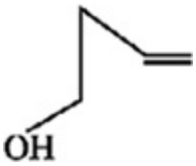
(b) 

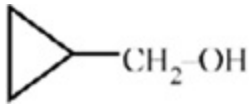
(c) 

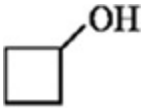
(d) 

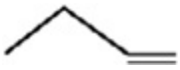
8. 

Products do not contain

(a) 

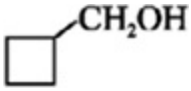
(b) 

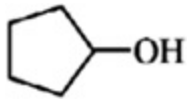
(c) 

(d) 

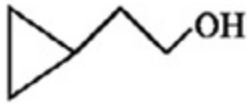
9. 

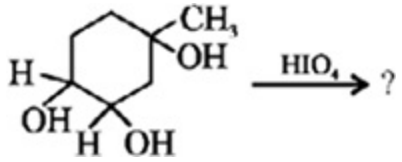
Which one should be the major product?

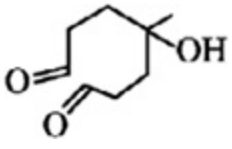
(a) 

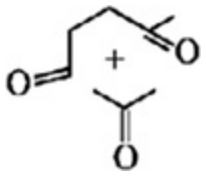
(b) 

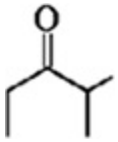
(c) 

(d) 

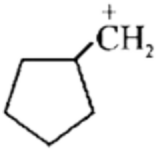
10. 

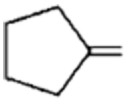
(a) 

(b) 

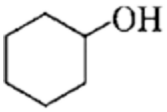
(c) 

(d)  only

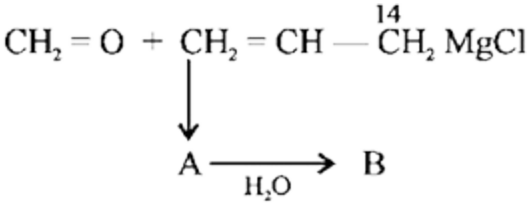
11. What are the products  can lead to

(a) 

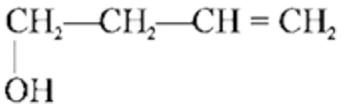
(b) 

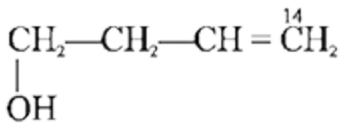
(c) 

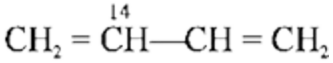
(d) All of these.

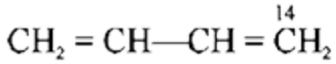
12. 

'B'can be,

(a) 

(b) 

(c) 

(d) 

Answer & Hints

1. (a)

2. (a)

3. (a)

4. (a)

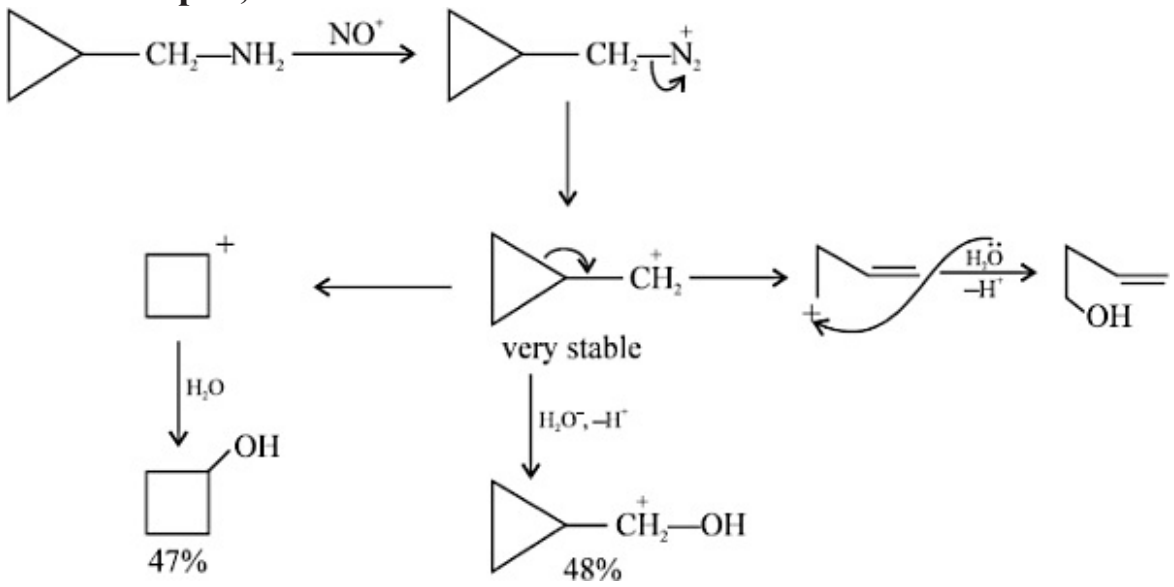
5. (a), (c)

6.

7. (b)

8. (d) **[Hint :** This is Demyanov rearrangement in which ring expansion, ring opening all takes place.]

For Example ,



9. (b)

10. (a)

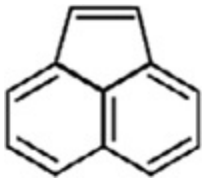
11. (d)

12. (a), (b)

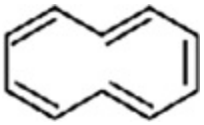
Aromaticity and aromatic electrophilic substitution

1. Find out one which is aromatic among the followings ;

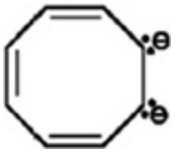
(a) 

(b) 

(c) 

(d) 

2.  + 2K ⟶ A + B (gas), Identify A, B

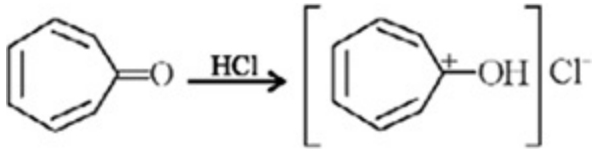
(a) 

(b) H_2

(c) 

(d) All of these

3. Why does the reaction produce stable salt ?



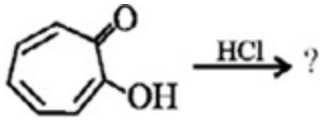
Because

(a) In 'A' the ring is aromatic

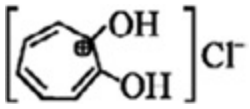
(b) 6π electrons are present

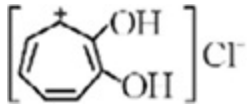
(c) Ring in A is stabilised by closed loop conjuation

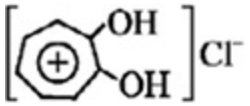
(d) All of these

4. 

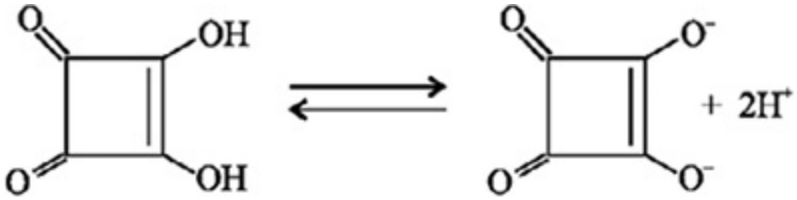
The product has aromatic part. What is the exact representation of the product ?

(a) 

(b) 

(c) 

(d) None of these

5. 

Squaric acid

It shows stronger acidity even greater than CH_3COOH. It is due to

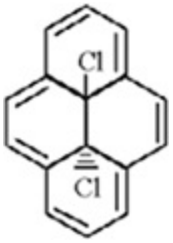
(a) stabilisation of the cojugate base by resonance

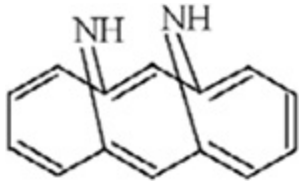
(b) stabilisation due to aromaticity of the dianion

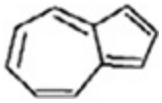
(c) stable due to 4p electrons

(d) all of these.

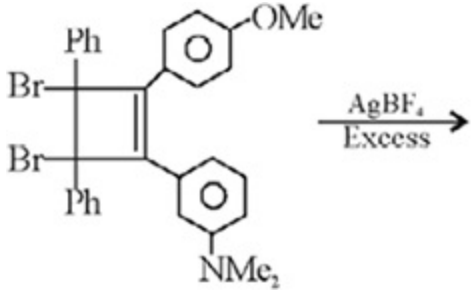
6. Which one is not aromatic among the followings ?

(a) 

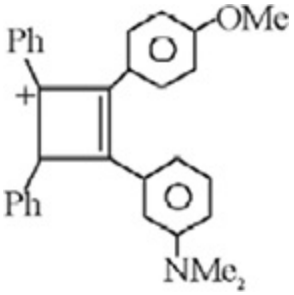
(b) 

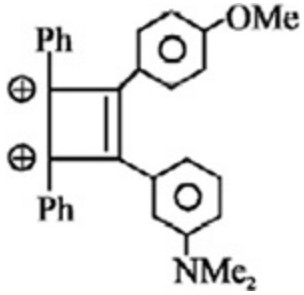
(c) 

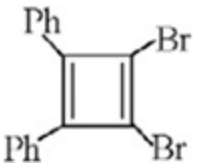
(d) 

7. 

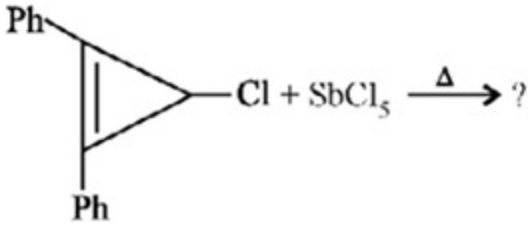
? The product mixture will contain

(a) 

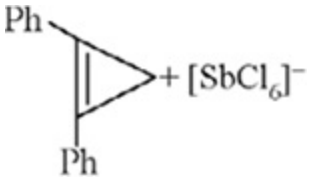
(b) 

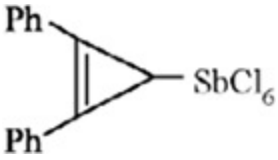
(c) 

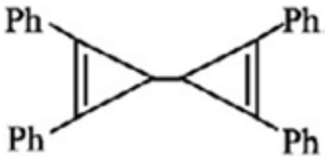
(d) None of these

8. 

The product contain

(a) 

(b) 

(c) 

(d) None of these

9. Which one M.O. picture shows the aromatic character?

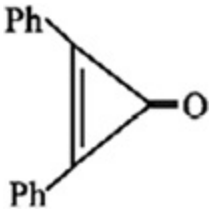
(a) Non bonding line 

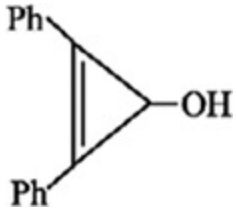
(b) Non bonding line 

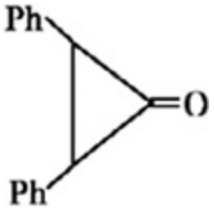
(c) Non bonding line 

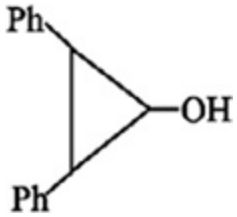
(d) Non bonding line 

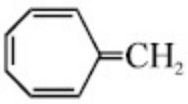
10. Which has maximum dipole moment ?

(a) 

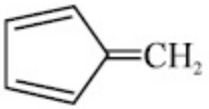
(b) 

(c) 

(d) 

11. 

Heptafulvene
(A)



Pentafulvene
(B)



(C)

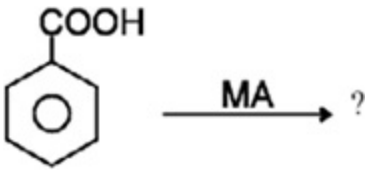
Dipole moment is maximum is

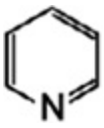
(a)

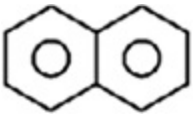
(b) B

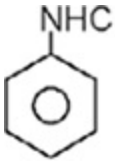
(c) A, B equal

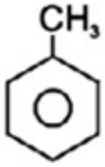
(d) C

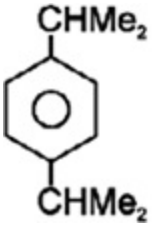
12. 

13.  $\xrightarrow{MA}$?

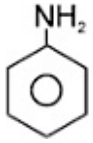
14.  $\xrightarrow[50°-60°C]{MA}$?

15.  $\xrightarrow[25°-40°C]{MA}$?

16.  $\xrightarrow[Heat]{MA}$?

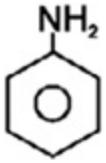
17.  $\xrightarrow{[NO_2^+][BF_4^-]}$? + ?

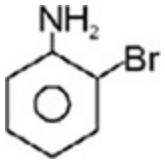
18. Freezing point depression for MA mixture should be _____

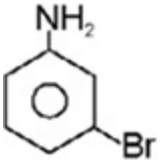
19.  $\xrightarrow[\Delta]{H_2SO_4(conc.)}$ A $\xrightarrow{(CH_3CO)_2O}$ B $\xrightarrow{Br_2}$ C $\xrightarrow[(2)\ NaOH]{(1)\ H_3O^+,\ \Delta}$ D.

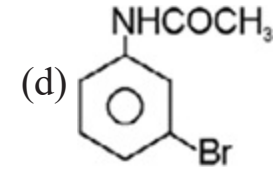
’.

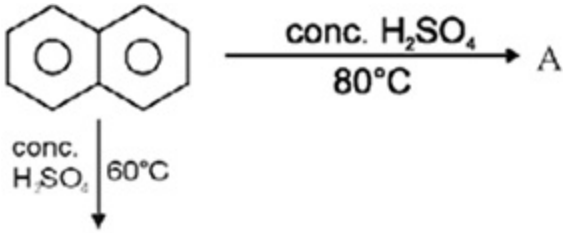
Find out D.

(a) 

(b) 

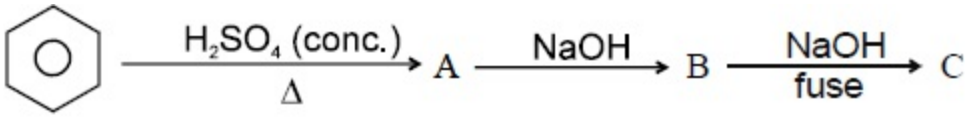
(c) 

(d) 

20. 

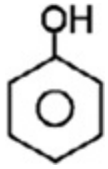
A + B

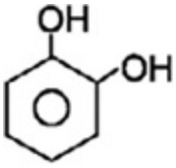
Find out A and B.

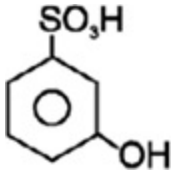
21. 

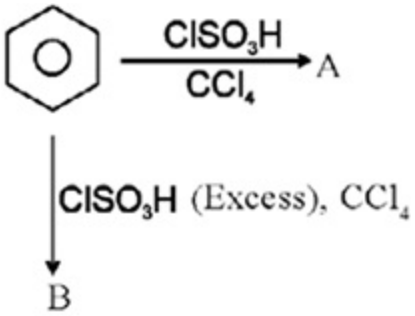
'C' is

(a) 

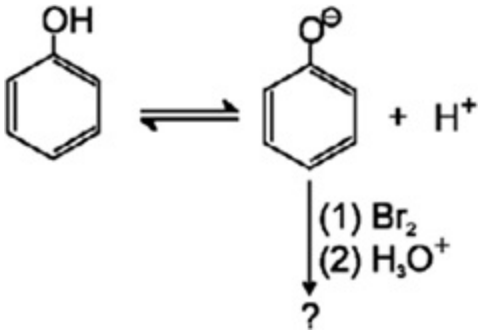
(b) 

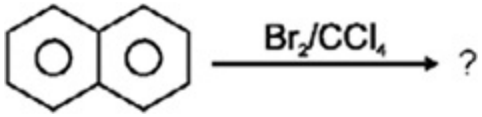
(c) 

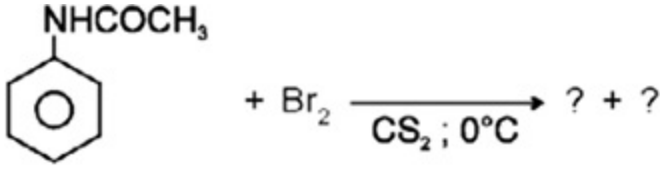
(d) 

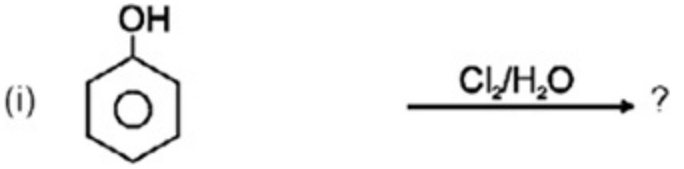
22. 

Find out A, B.

23. 

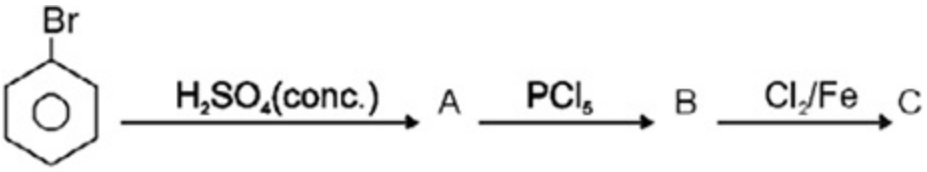
24. 

25. 

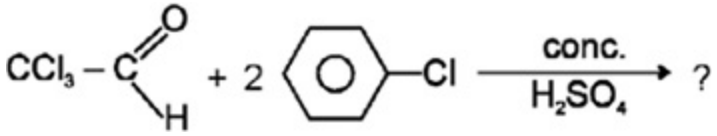
26. (i) 

(ii) 

(iii) 

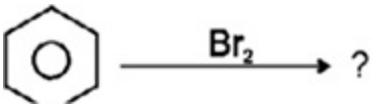
27. 

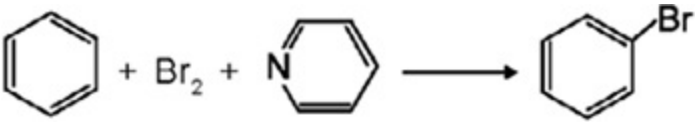
Find out A, B, C .

28. 

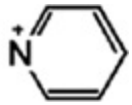
29. 

30. 



31. 

; Which one is correct?

(a) Due to $Br^{\ominus}$  formation

(b) Due to easy $Br^{\ominus}$ formation

(c) Due to π c-complex formation

(d) none of these

32. During sulphonation the electrophile is found to be

(a) SO_3

(b) $SO_3^{\oplus}H$

(c) both

(d) $SO_3H^{\ominus}$

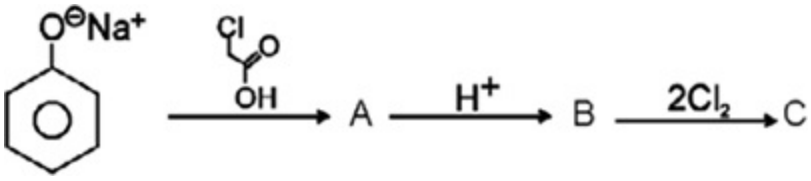
33. $PhSO_3H + NaCl \rightarrow$ A (Crystalline solid) A can be

(a) $PhSO_3$- Na+

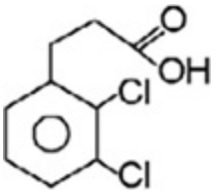
(b) $PhSO_2Cl$

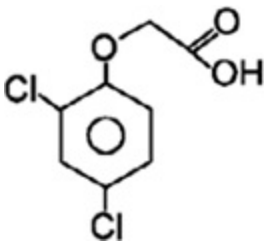
(c) $PhSO_3H$

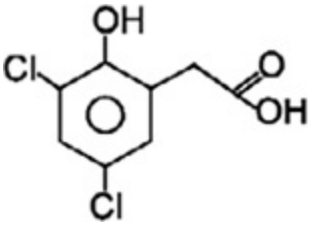
(d) $PhSO_2H$

34. 

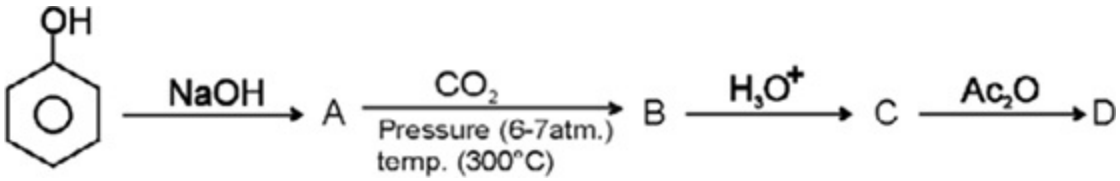
'C' is called as "2, 4, D" which is herbicide. 'C' is

(a) 

(b) 

(c) 

(d) none of these

35. 

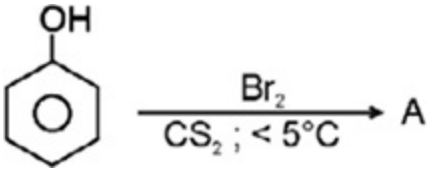
'D' is

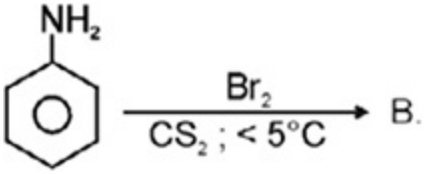
(a) Aspirin

(b) vanilin

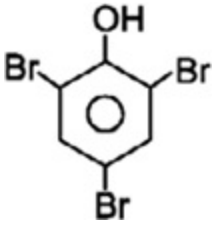
(c) cumene

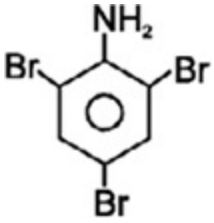
(d) salicylic acid

36. 



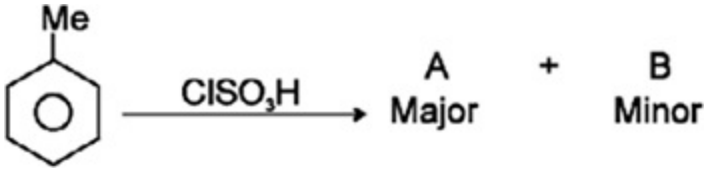
A, B are :

(a) A is 

(b) B is 

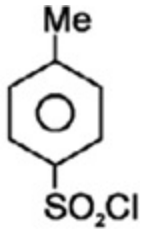
(c) A is 

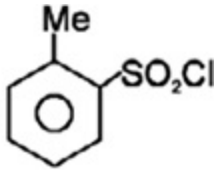
(d) B is 

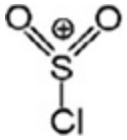
37. 

; A can be seperated by fractional distillation.

Which one(s) is / are correct?

(a) B is 

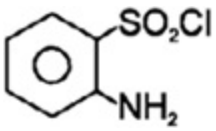
(b) A is 

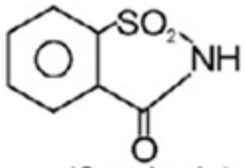
(c) electrophilic is 

(d) electrophile is SO_2

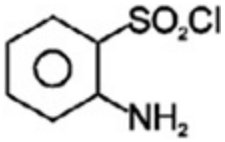
38. (a) $\xrightarrow{(NH_4)_2CO_3}$ (A′) $\xrightarrow{KMnO_4}$ A″ $\xrightarrow{HCl}$ A‴

A‴ is

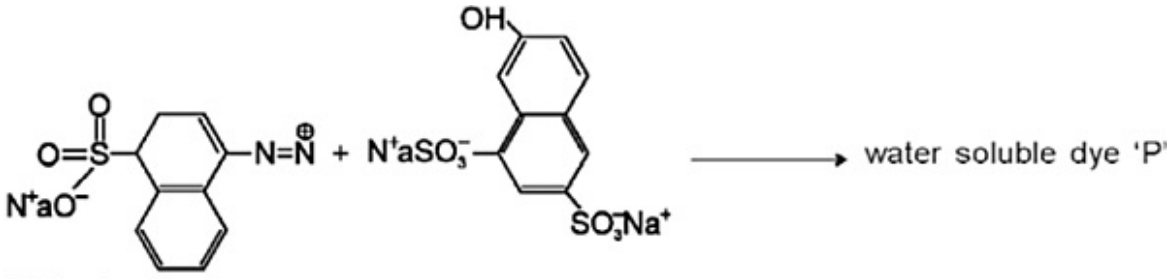
(a) 

(b) 

(Saccharin)

(c) 

(d) none of these

39. 

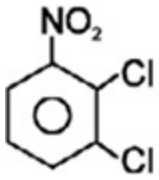
'P' is due to

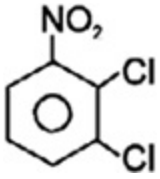
(a) C – N coupling

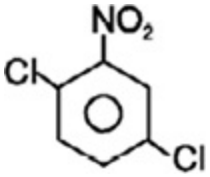
(b) N – N coupling

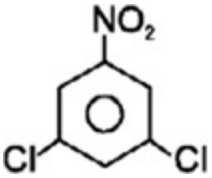
(c) C – C coupling

(d) N – O coupling

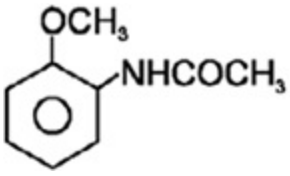
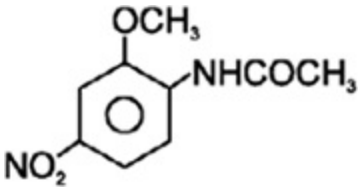
40. The major product of  + Cl_2/Fe is ,

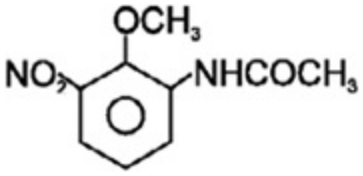
(a) 

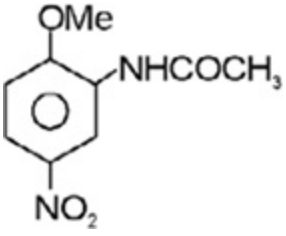
(b) 

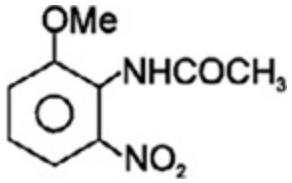
(c) 

(d) none of these

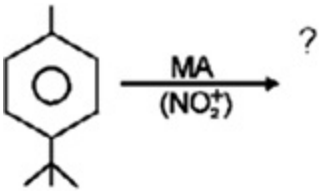
41.  ? Least quantity (a) 

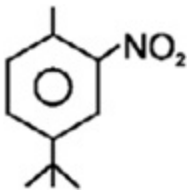
(b) 

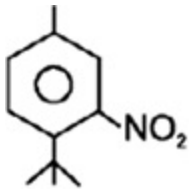
(c) 

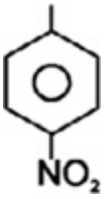
(d) 

42. The major product ?

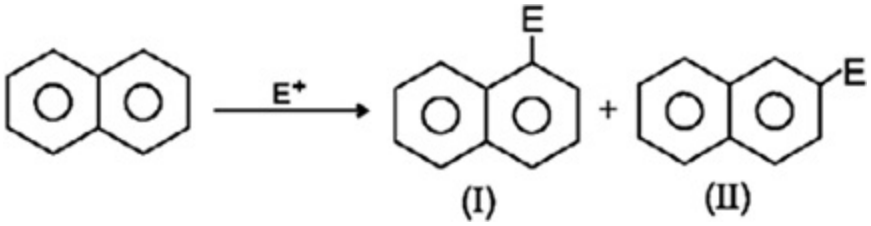


(a) 

(b) 

(c) 

(d) 

43. 

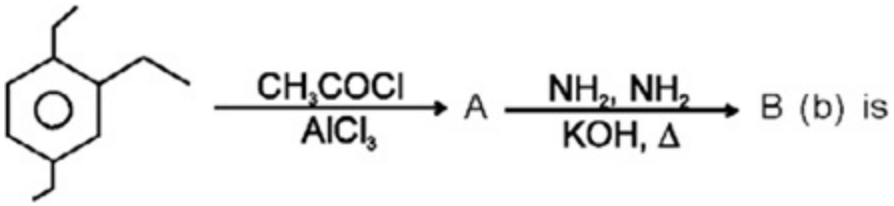
which statement is correct?

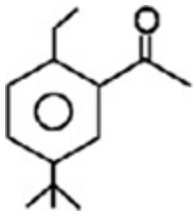
(a) (I) form in large quantity

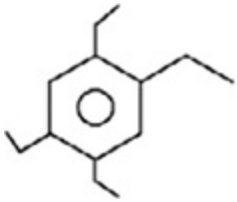
(b) (II) form in large quantity

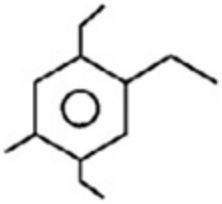
(c) (I), (II) form in equal quantity

(d) none of these

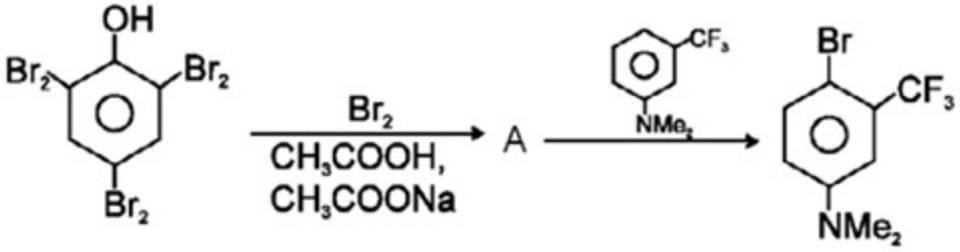
44. 

(a) 

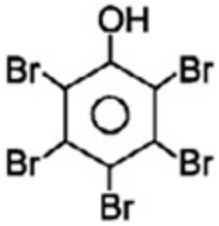
(b) 

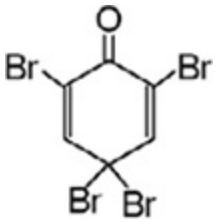
(c) 

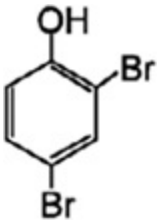
(d) none of these

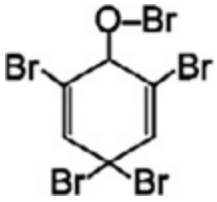
45. 

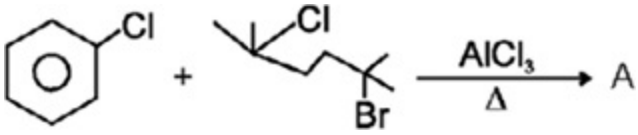
So. 'A' can be

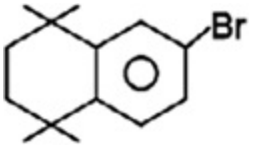
(a) 

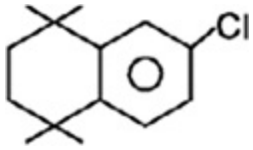
(b) 

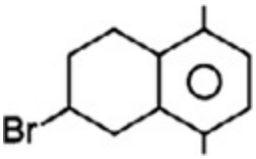
(c) 

(d) 

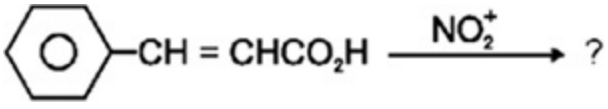
46.  Product 'A' is

(a) 

(b) 

(c) 

(d) none of these

47. 

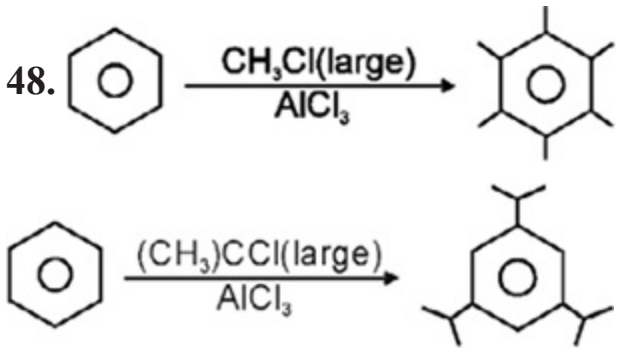
The product is

(a) o

(b) p

(c) m

(d) o, p

48. 

The reason for trisubstituted product in the second case is –

(a) + I effect

(b) steric effect

(c) hyperconjugation

(d) none of these

49. Given Compounds are

$Ph - CH_3$,	$PhCH_2Cl$	$Ph\ CH - Cl_2$	$PhCCl_3$
I	II	III	IV
Meta product percentage			
5%	15%	35%	65%
(a)	(b)	(c)	(d)

Which are is correct regarding electrophilic substition.

(a) a, IV

(b) b, II

(c) c, III

(d) d, I

50. Predict the reactivity order of following electrophiles

NO_2^+,	$CH_3\overset{+}{C}H_2$,	$\overset{+}{Cl}$
I	II	III

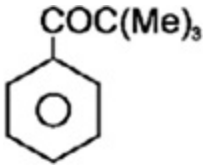
(a) I > II

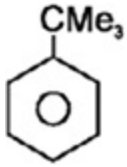
(b) II > III

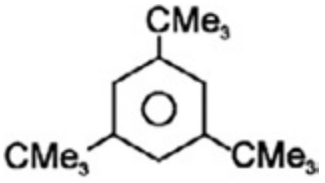
(c) I < II < III

(d) II > I > III

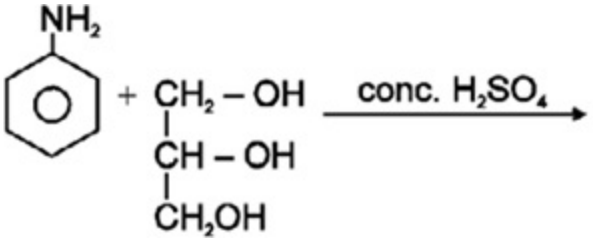
51. $Me_3COCl + AlCl_3 +$  $\xrightarrow[\text{(strong heating)}]{\Delta}$?

(a) 

(b) 

(c) 

(d) none of these

52. 

?

Answer & Hints

1. (b)

2. (a), (b)

3. (a) , (b) , (c)

4. (c)

5. (a)

6. (d)

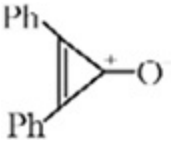
7. (b)

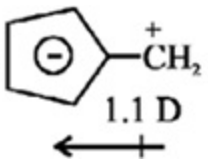
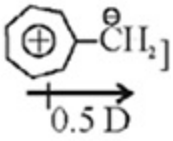
8. (a) **[Hint :** Here in all cases 7, 8 the aromatic cation evolves, therefore makes stable salt.]

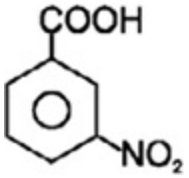
9. (d) **[Hint :** The centre lines with in the circle are Bericenre line and electrons are shown to fill up the π BMOs, π BMOs and π ABMOs.

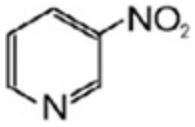
NB = non bonding, B = Bonding, AB = Antibonding

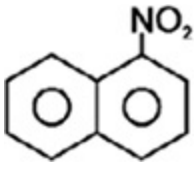
All BMOs and are filled up for 6π electrons eg benzyne, therefore benzyne is aromatic]

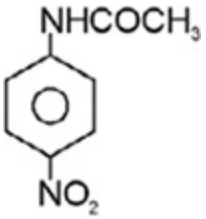
10. (a) **Hint :** [Its is due to  resonating structure.]

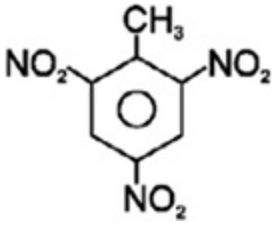
11. (b) **Hint:**  compaged to ]

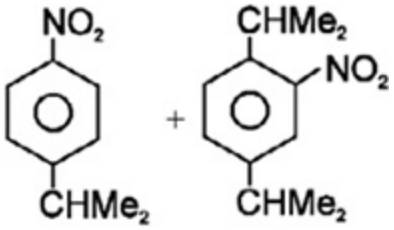
12. 

13. 

14. 

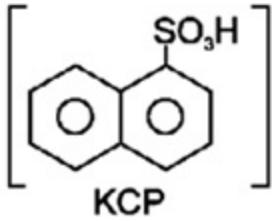
15. 

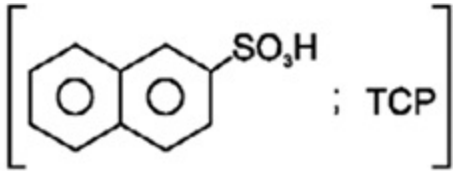
16. 

17. 

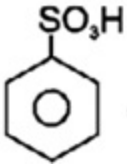
18. 4.

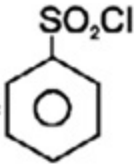
19. (b)

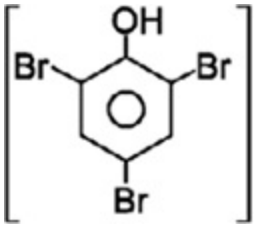
20. **A =** 

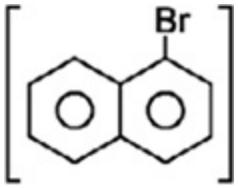
B = 

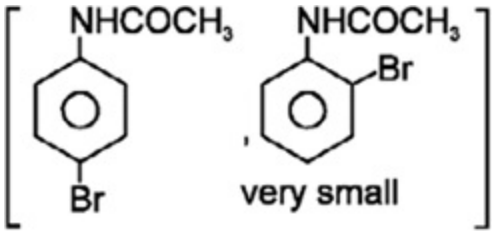
21. (b)

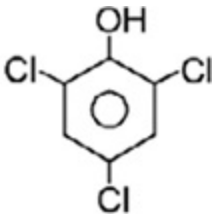
22. A = 

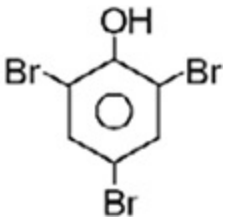
, B = 

23. 

24. 

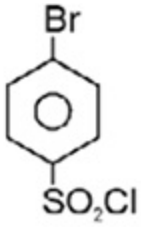
25. 

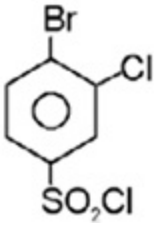
26. (i) 

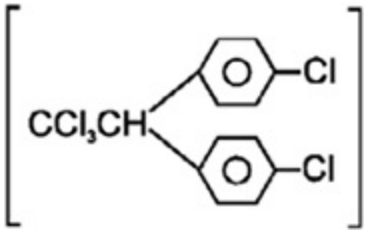
(ii) 

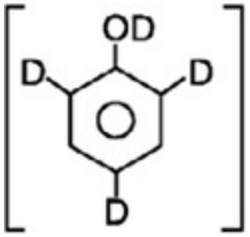
(iii) 

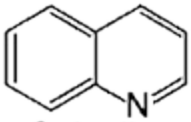
27. A = 

(major), B = 

, C = 

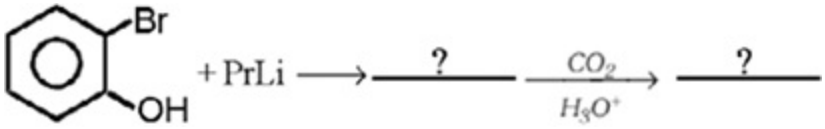
28. 

29. 

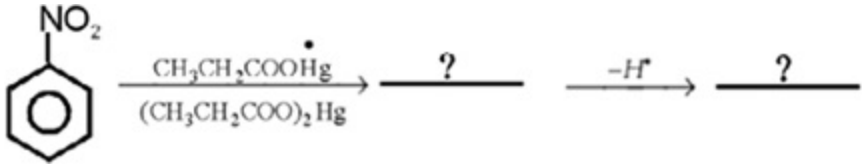
30. [No reaction]
31. (a)
32. (c)
33. (a)
34. (b)
35. (a)
36. (b), (c)
37. (a),(b),(c)
38. (b)
39. (a)
40. (b)
41. (c)
42. (a)
43. (c)
44. (b)
45. (b)
46. (b)
47. (d)
48. (b)
49. (b), (c)
50. (b), (d)
51. (b)
52. 

Quinoline **Hint :** [It is called Skraup's quinoline synthesis]

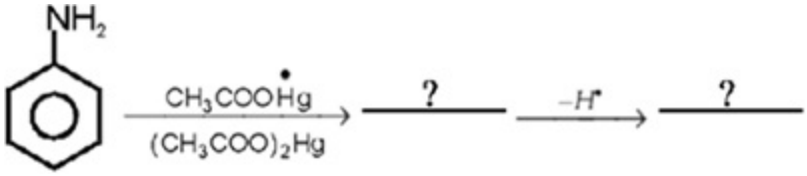
Aromatic halide

1. 

Find the products ?

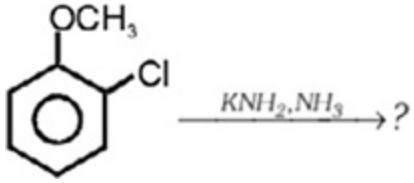
2. 

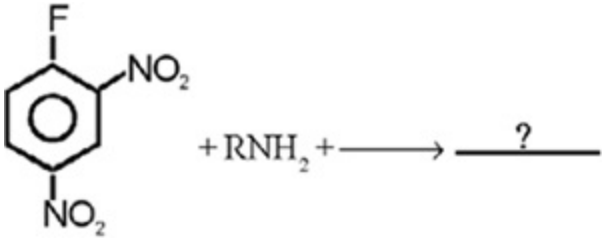
Fill in the blanks with the appropriate substances.

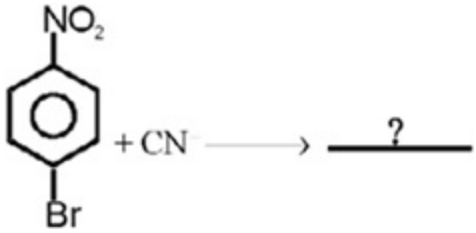
3. 

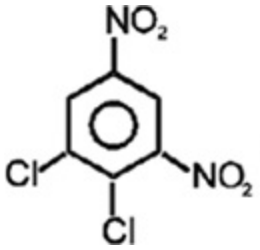
Fill in the blanks.

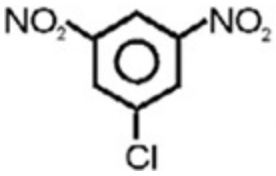
4. Write the product of the following reaction.

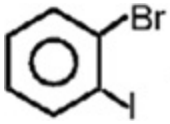


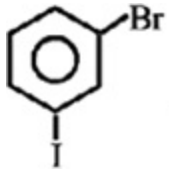
5. 

6. 

7.  $+ {}^{\ominus}OMe \longrightarrow$?

8.  $\xrightarrow{Ph\overset{\ominus}{S}}$?

9.  $\xrightarrow{Mg}$? Intermediate

10.  $\xrightarrow{1\ mole\ Mg}$?

11.  $\xrightarrow{1\ mole\ Mg}$?

$tBuOCl \xrightarrow{50^{0}} tBuO\cdot + Cl\cdot$

(tert butyl hypochlorite)

Which products do you expect below ;

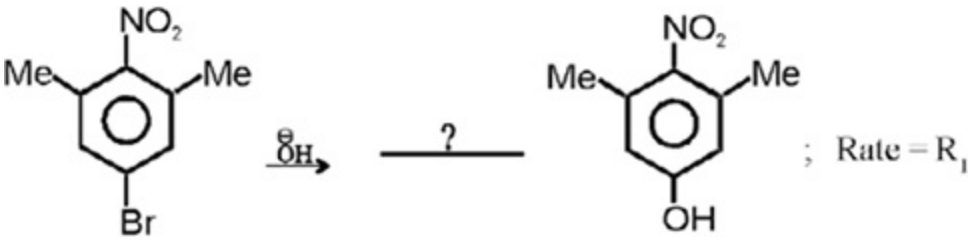
12. $PhCH_3 + BuO\bullet \longrightarrow$? (A) + ? (B)

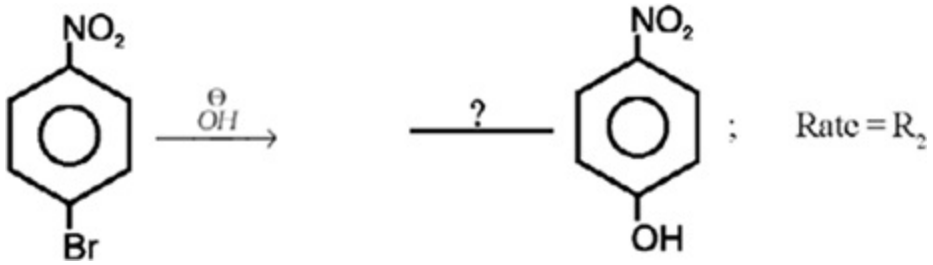
$PhCH_2\bullet + BuOCl \longrightarrow$? (C) + ? (D)

13.  $\xrightarrow{Br_2}$?

14.  $\xrightarrow{[O]}$?

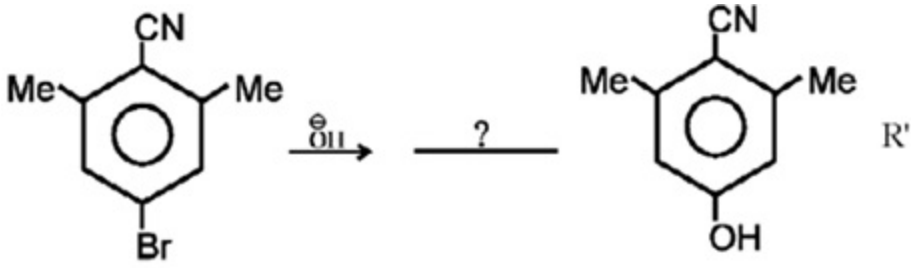
15.

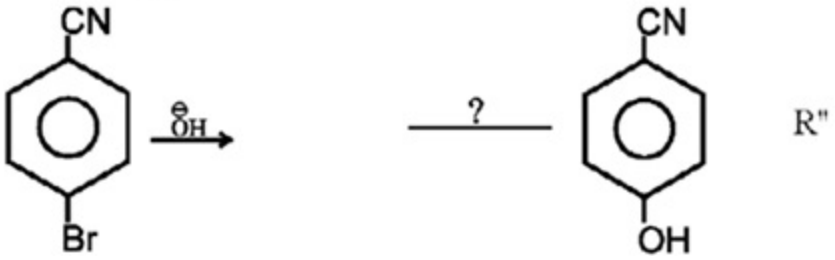




Which one is greater and why ?

16.

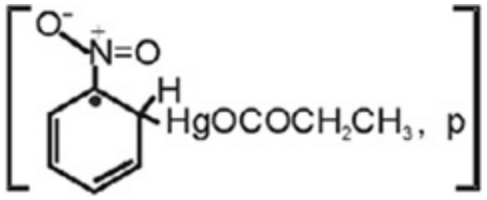


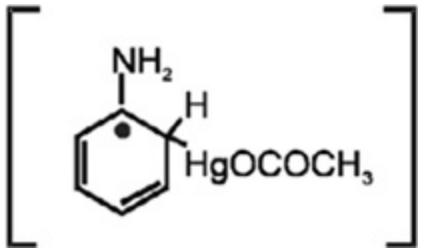


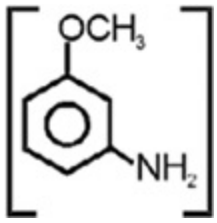
Why R' ≃ R" ?

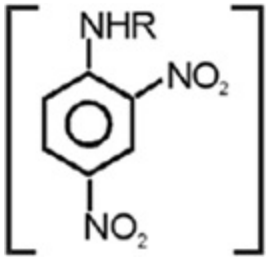
Answer & Hints

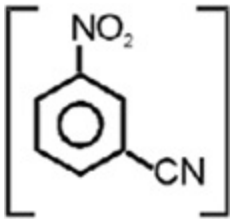
1. 

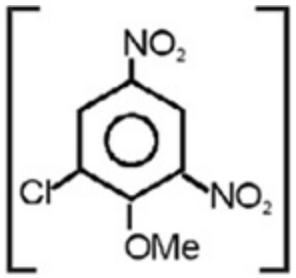
2.  , [o,p oxymurcurated products]

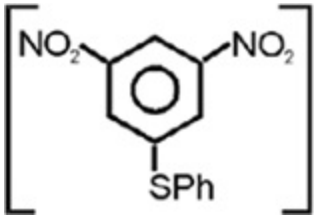
3.  , [o,p oxymurcurated products]

4. 

5. 

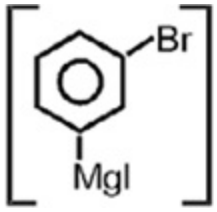
6. 

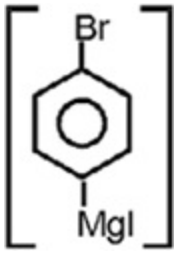
7. 

8. 

9. 

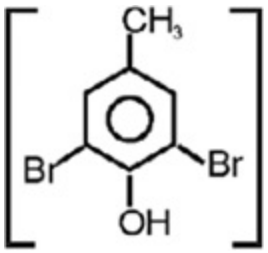
Benzyne

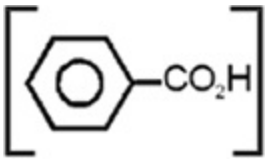
10. 

11. 

12. [A; $PhC\dot{H}_2$, B; tBuOH]

[C ; $PhCH_2Cl$, D; $tBuO\cdot$]

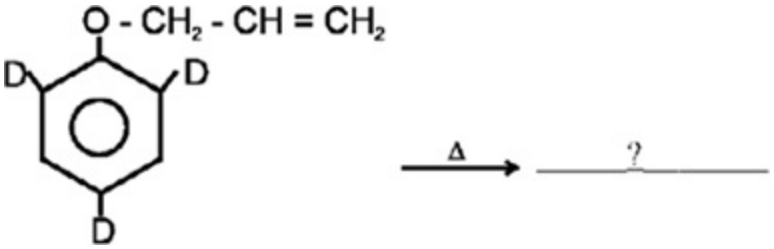
13. 

14. 

15. [$R_2 > R_1$ due to steric inhibition of resonance NO_2 cannot take part in stabilasation of σ -complex anion for the initial one. Hence the rate.]

16. [$C\overline{N}$ is a linear group so less steric repulsion with Me groups occur . Therefore stabilisation of σ -omplex in both the cases (ArSN2) arises and hence the rate.]

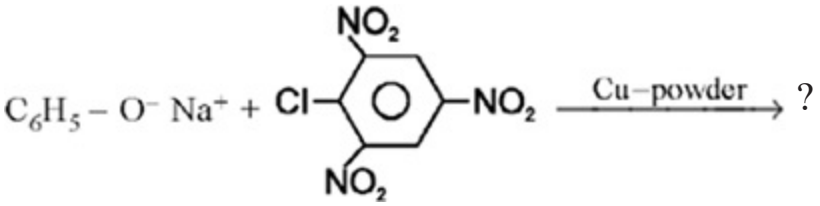
Phenol

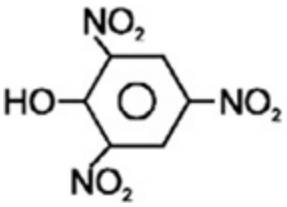
1. 

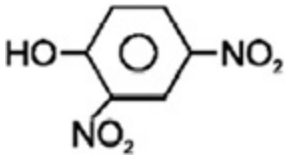
2. Predict which one is slow reaction ?

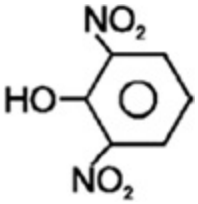
(a) $Ph - OH + CH_3COCl \rightarrow PhOCOCH_3$

(b) $R - OH + CH_3 - COCl \rightarrow ROCOCH_3$

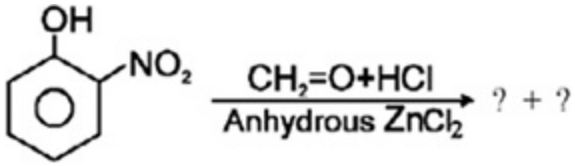
3. 

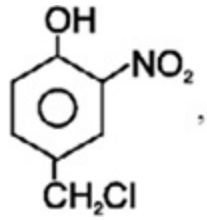
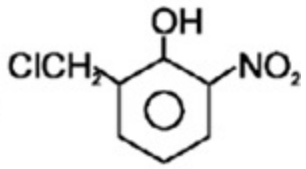
(a) 

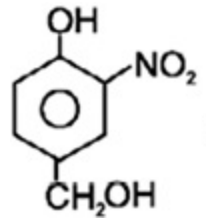
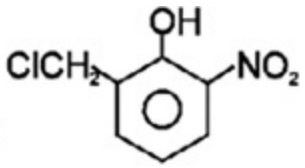
(b) 

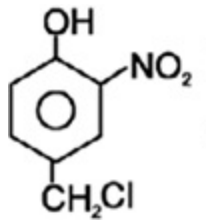
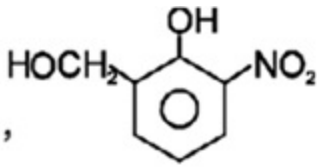
(c) 

(d) No reaction

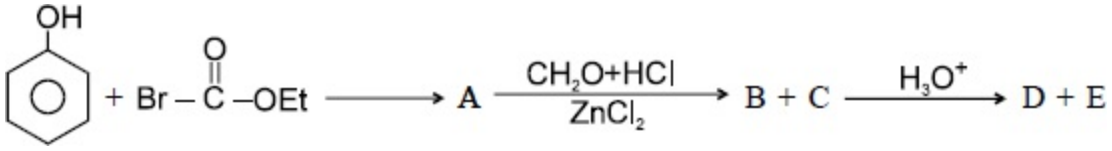
4. 

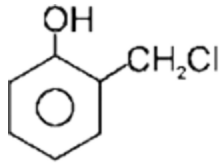
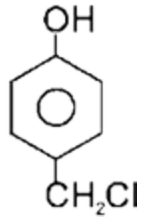
(a)  , 

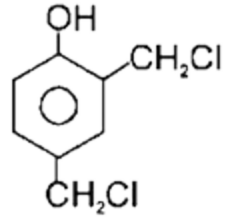
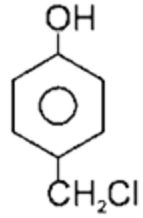
(b)  , 

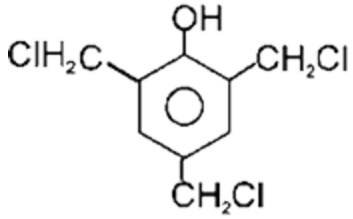
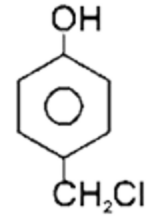
(c)  , 

(d) No reaction

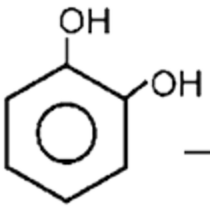
5.  D, E are ?

(a)  , 

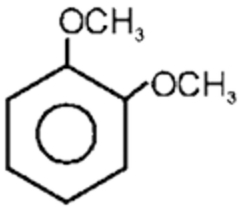
(b)  , 

(c)  , 

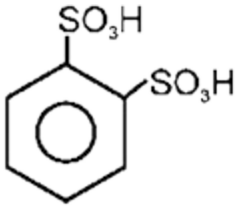
(d) No reaction

6. 

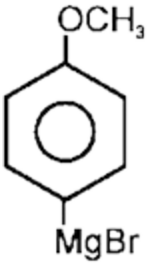
$\xrightarrow[NaOH,\ \Delta]{(CH_3)_2SO_4}$ A 'A' is

(a) 

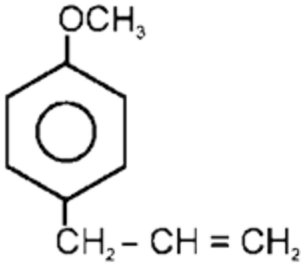
(b) 

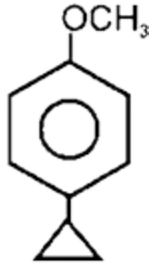
(c) 

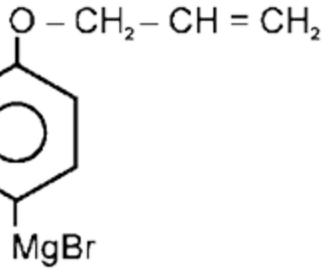
(d) None of these

7. 

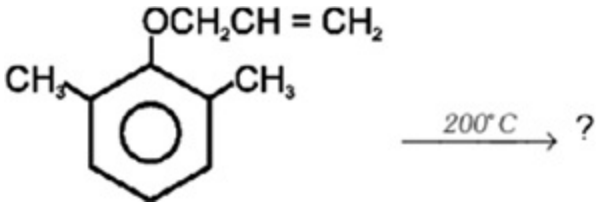
$\xrightarrow{CH_2 = CH - CH_2 - Br}$ A 'A' is

(a) 

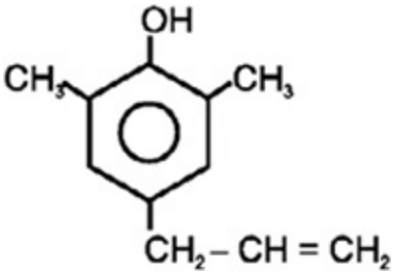
(b) 

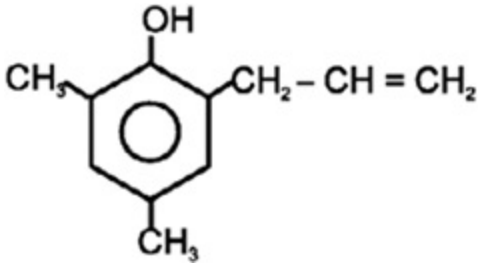
(c) 

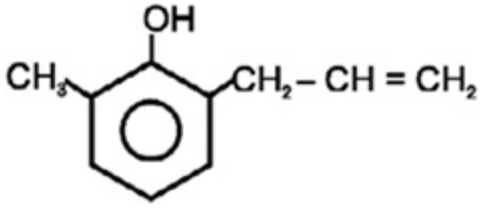
(d) none of these

8. 

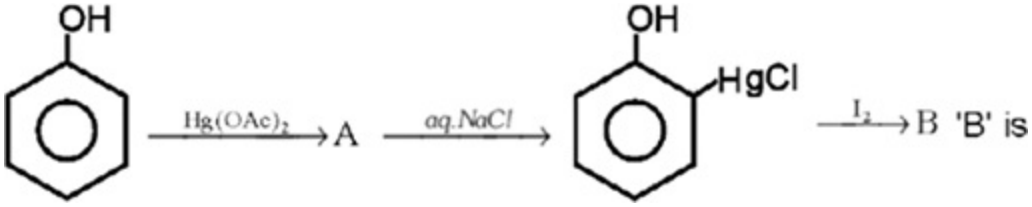
$\xrightarrow{200^\circ C}$?

(a) 

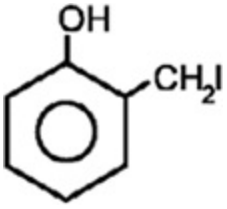
(b) 

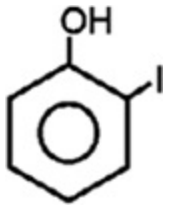
(c) 

(d) none of these

9. 

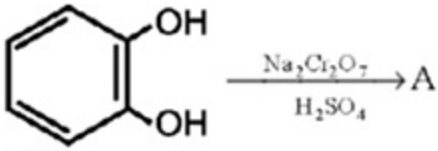
'B' is

(a) 

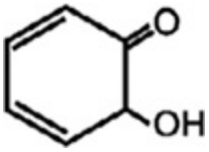
(b) 

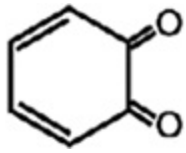
(c) 

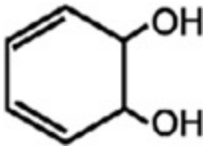
(d) None of these

10. 

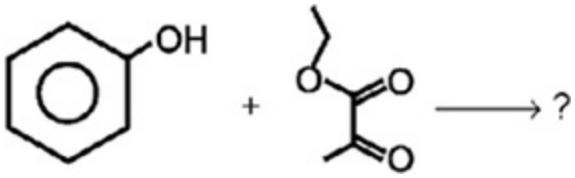
'A' is

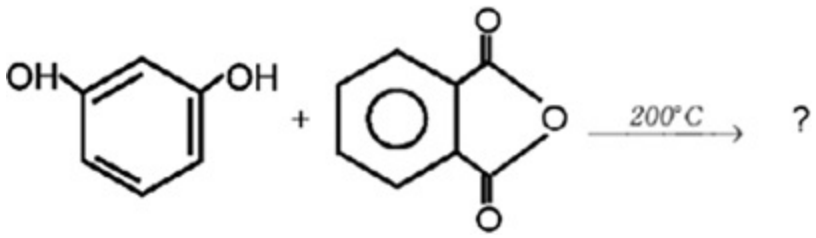
(a) 

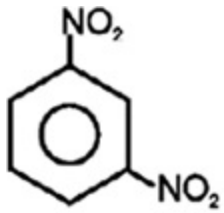
(b) 

(c) 

(d) None of these

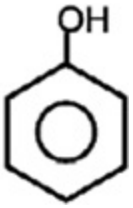
11. 

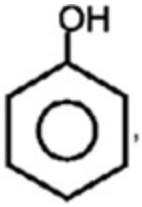
12. 

13. 

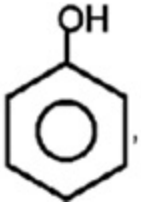
$\xrightarrow{NH_4HS}$ A $\xrightarrow[H_2SO_4]{NaNO_2}$ B $\xrightarrow{H_2O}$ C $\xrightarrow{H_3PO_2}$ D

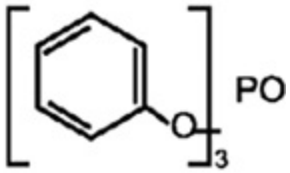
Identify C, D.

(a) C =  , D = 

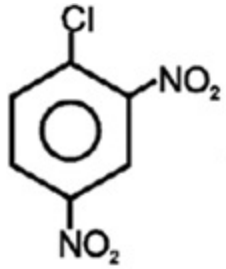
(b) C = 

, D = 

(c) C = 

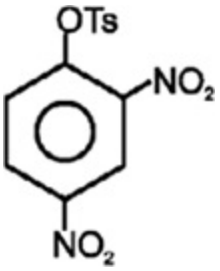
, D = 

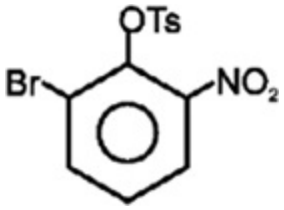
(d) All of these

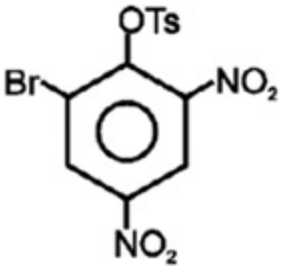
14. 

$\xrightarrow[Na_2CO_3]{aq.}$ A $\xrightarrow{TsCl}$ B $\xrightarrow{Br_2/FeBr_3}$ C

'C' is

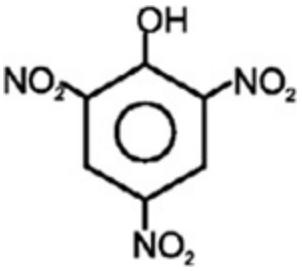
(a) 

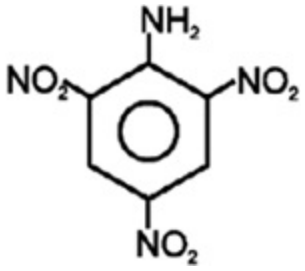
(b) 

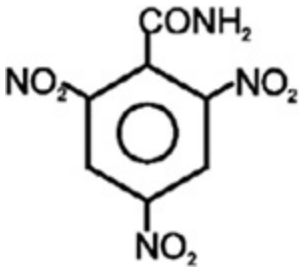
(c) 

(d) none of these

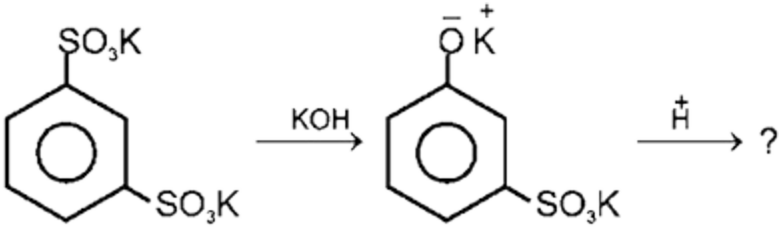
15. Identify picramide

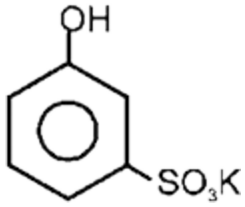
(a) 

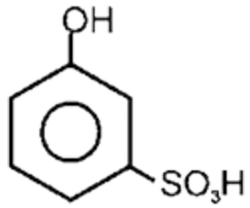
(b) 

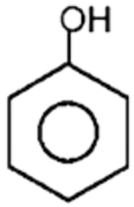
(c) 

(d) none of these

16. 

(a) 

(b) 

(c) 

(d) 

17. Creosote (used for preservative purpose) is,

(a) o-xylene

(b) m-xylene

(c) p-xylene

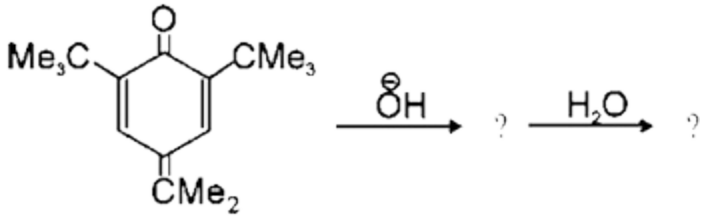
(d) mixture of a, b, c with little phenol

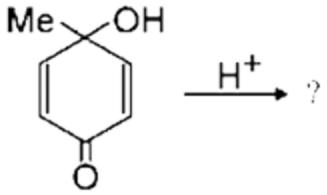
18. Match the columns while $FeCl_3$ test is carried out below :

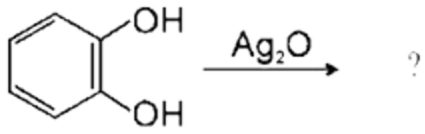
(a) Catechol (1) green (which turns red on addition of Na_2CO_3)

(b) Resorcinol (2) react with Fehling's solution and Tollen's reagent

(c) Styphnic acid (3) used as photographic developer

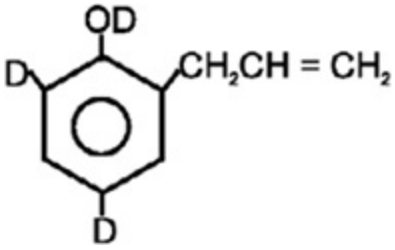
19. 

20. 

21. 

Answer & Hints

1.



2. (a)

3. (a)

4. (a)

5. (a)

6. (a)

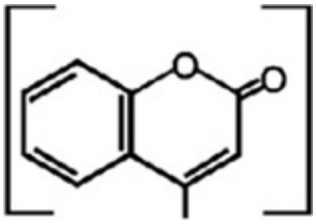
7. (a)

8. (a)

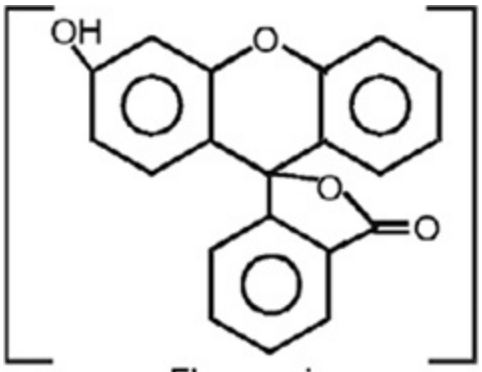
9. (b)

10. (b)

11.



12.



Fluorescin

13. (b)

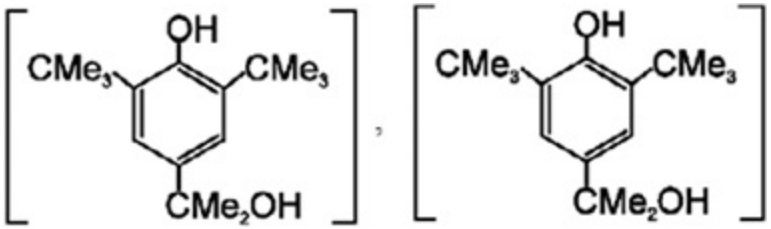
14. (c)

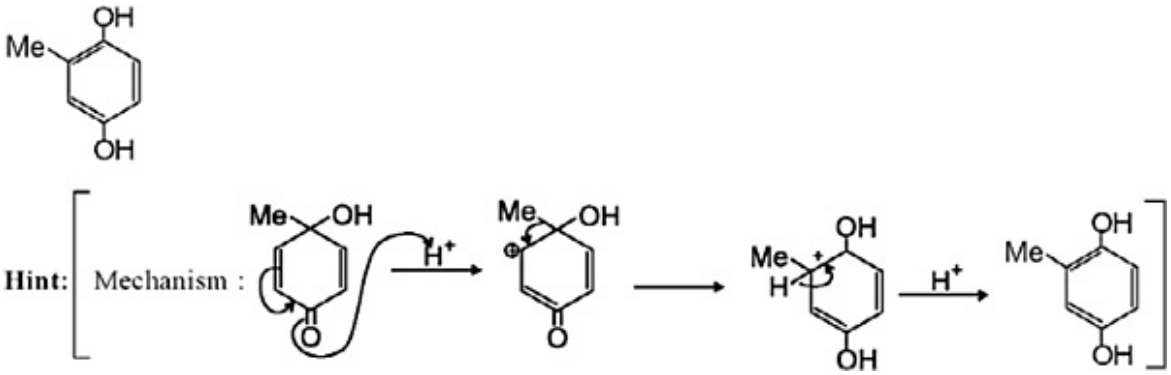
15. (b)

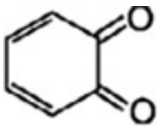
16. (b)

17. (d)

18. (a)

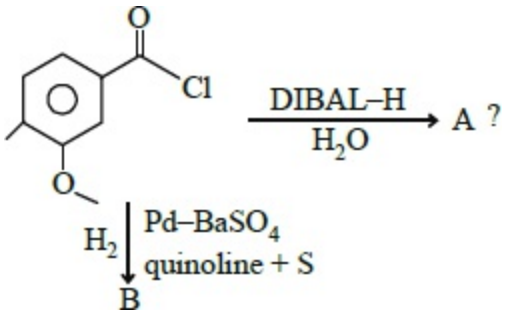
19. 

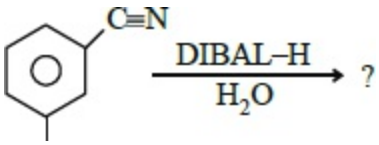
20. 

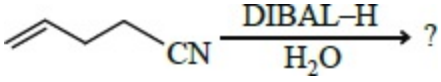
21. 

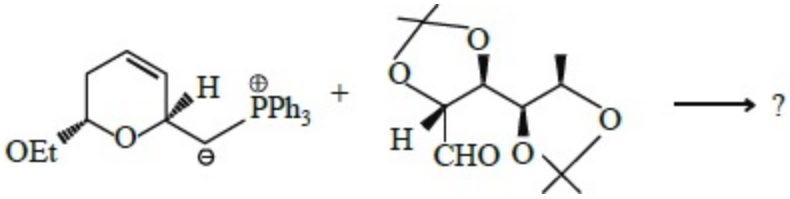
Carbonyl compound

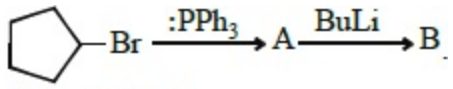
Write the products of the following reaction.

1. 

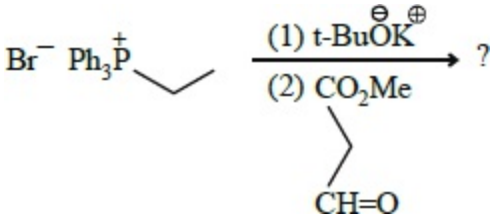
2. 

3. 

4. 

5. 

Write A, B ?

6. 

7. $CH_2=C=O + (CH_3)_2C=PPh_3 \longrightarrow ?$

8. Which ylide/s is/are stable?

(a) Phosphorous

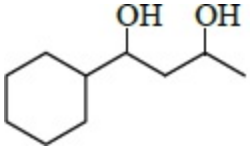
(b) Sulphur

(c) Nitrogen

(d) None of these

9. $CH_3\overset{*}{C}H_2CHOHCH_3 \xrightarrow[\text{excess}]{Br_2/OH^-} ?$

10. $CH_3\overset{*}{C}H_2CHOHCH_3 \xrightarrow{Br_2/H^+} ?$

11.  $\xrightarrow{NaOI(excess)}$?

12. Which one can be the product of the following reaction?

$CH_3COCH_2CO_2Et \xrightarrow{OH^-/I_2} ?$

(a) $CI_3COCH_2CO_2Et$

(b) $CH_3COCI_2CO_2Et$

(c) $CH_3COCHCO_2Et$ (H below CHCO$_2$Et)

(d) None of these

13. Base can be used for haloform reaction. Choose the base which can take part in haloform reaction?

(a) NH_4OH

(b) NaOH

(c) KOH

(d) NH_3

14. $CH_3CO\overset{14}{C}H_2COCH_3 \xrightarrow{I_2/OH^-}$ Haloform

Haloform contains

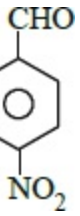
(a) C^{12}

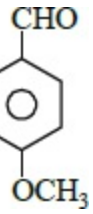
(b) C^{14}

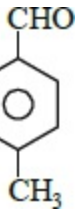
(c) Both

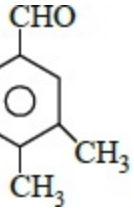
(d) None of these

15. Which one can easily hydrate?

(a) 

(b) 

(c) 

(d) 

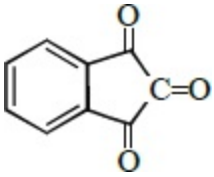
16. Which one can easily hydrate?

(a) CCl_3CHO

(b) CH_2ClCHO

(c) $CHCl_2CHO$

(d) none of these

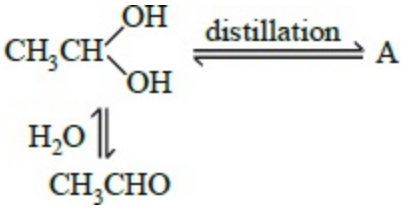
17.  can undergo (ninhydrin)

(a) addition of H_2O easily

(b) haloform

(c) elimination

(d) none of these

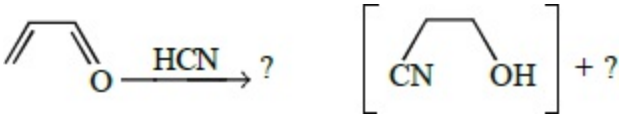
18.  find out A.

(a) CH_3CHO

(b) HCHO

(c) Same

(d) None of these

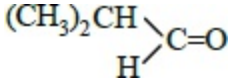
19. 

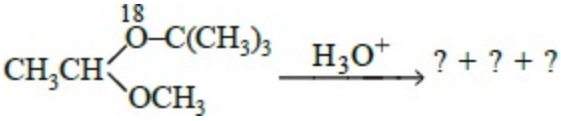
20. Rate of $NaHSO_3$ addition will be maximum for

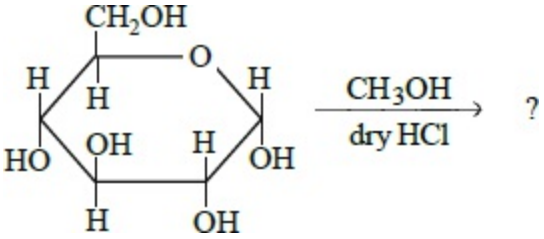
(a) PhCHO

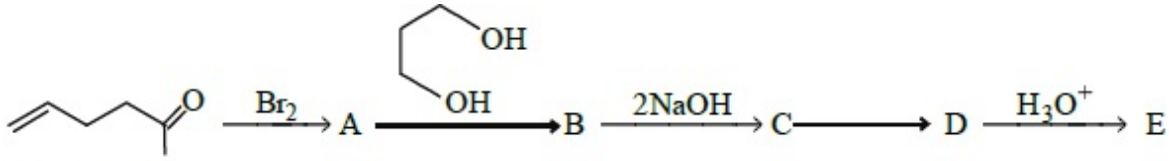
(b) CH_3CHO

(c) HCHO

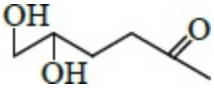
(d) 

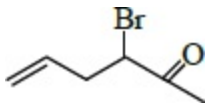
21. 

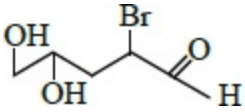
22. 

23. 

What is E?

(a) 

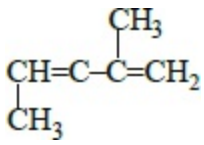
(b) 

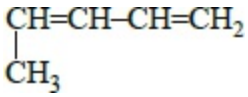
(c) 

(d) none of these

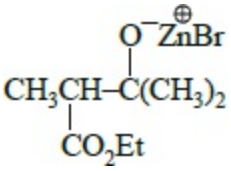
24. $CH_3COCH_3 \xrightarrow{CH_3C\equiv\overset{\ominus}{C}\overset{\oplus}{N}a} A \xrightarrow{H_2O} B \xrightarrow{Pd\text{–}CaCO_3,\ H_2} C \xrightarrow{Al_2O_3} D$. D is:

(a) $CH_2=CH\text{-}CH=CH_2$

(b) 

(c) 

(d) None of these

25.  $\xrightarrow{H_3O^+}$ A $\xrightarrow[(2)\ KOH,\ (3)HCl]{(1)\ \Delta}$ B. Find out B.

26. In the reactivity order among the followings, max. and minimum are:

(a) Orgainozinc

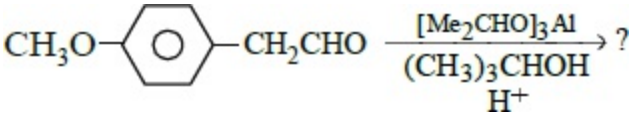
(b) Grignard's reagent

(c) Organolithium

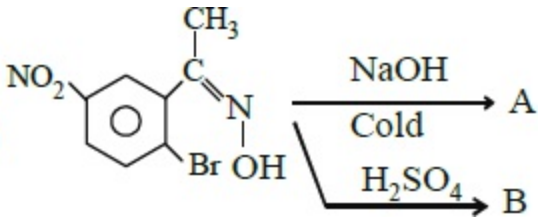
(d) all of these

27.  $= NNHPh + HCHO \longrightarrow ? + ?$

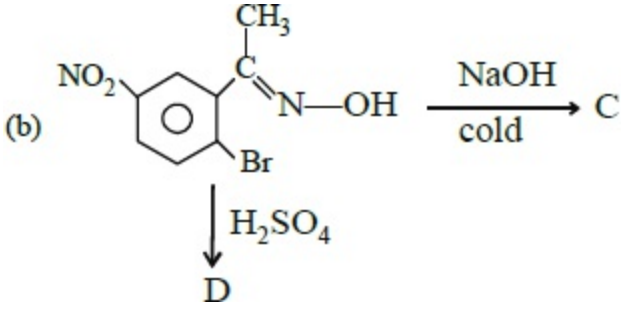
28. Write the product of the following reaction.



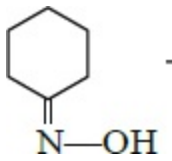
29. (a)



(b)

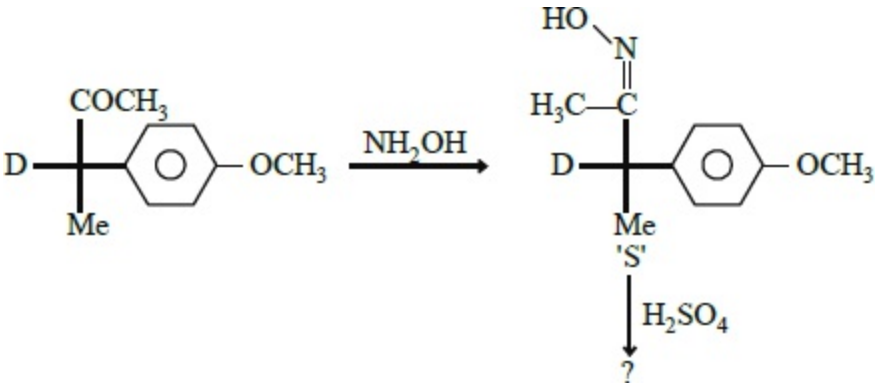


30.

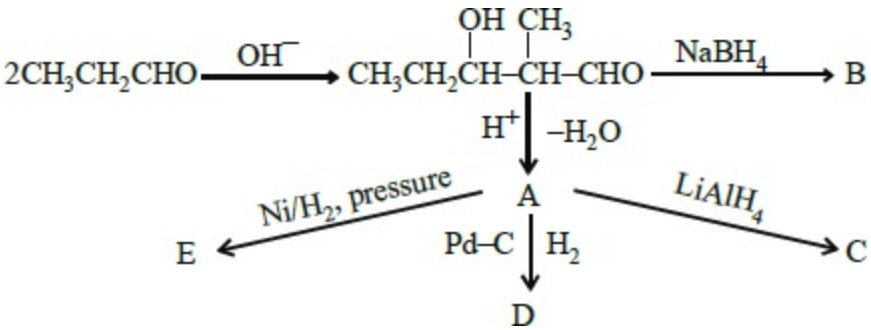


$\xrightarrow{PCl_5}$ A $\xrightarrow{OH^-/H_2O}$ B. What is B?

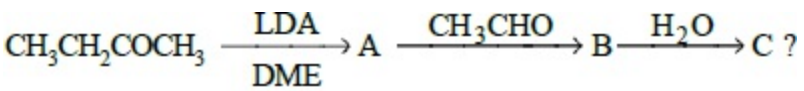
31.



32.



33.



(solvent 1,2-dimethoxy ethane)

What do you expect with base $\overset{\ominus}{O}H$ in place of LDA?

34. $CH_3CHO + CH_3CH{=}CH{-}CHO \xrightarrow[\Delta]{OH^-}$?

35. $HCHO + (CH_3)_2CHCHO \xrightarrow[40^\circ]{\text{dil. } Na_2CO_3} ?$

36. $4HCHO + CH_3CHO \xrightarrow[40^\circ]{\text{dil. } Na_2CO_3} ? + ?$

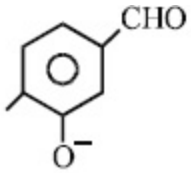
37. $CH_3CHO + CH_3CH_2CHO \xrightarrow{NaOH} ?$ (Major)

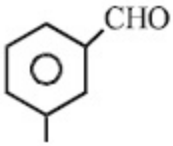
38. $CH_3CHO + CH_3CH_2CHO \xrightarrow{HCl} ?$ (Major)

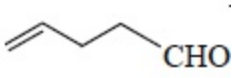
39. $CH_3COCH_3 + CH_3CHO \xrightarrow{OH^-} ?$ (Major)

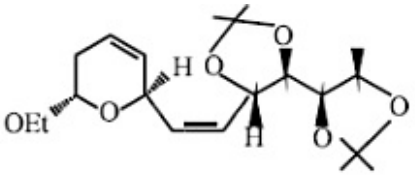
40. $3CH_3COCH_3 \xrightarrow{HCl} ?$

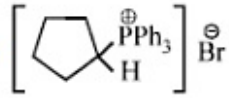
Answer & Hints

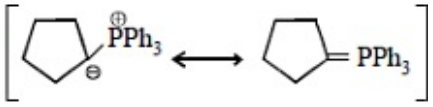
1. 

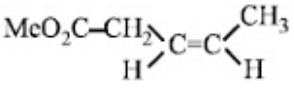
2. 

3. 

4. 

5. A: 

   B: 

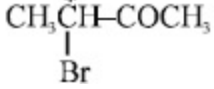
6. 

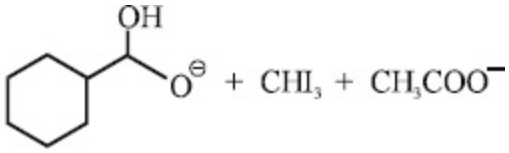
   'Z'

7. $CH_2=C=C(CH_3)_2$

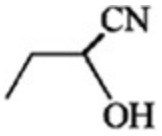
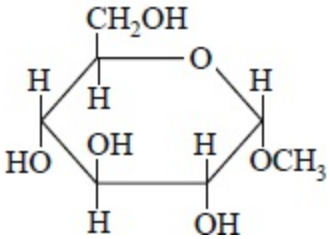
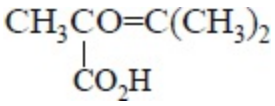
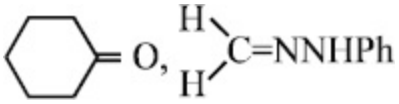
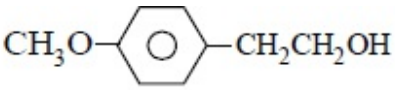
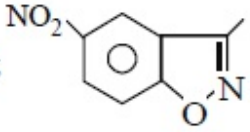
8. (a), (b)

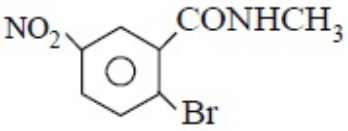
9. $CH_3\overset{*}{C}H_2COO^- + CHBr_3$

10. 

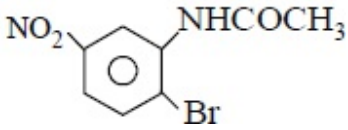
11. 

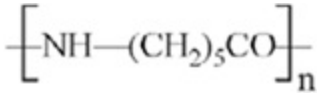
12. (b)

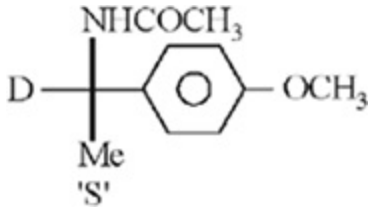
13. (b), (c)
14. (b)
15. (a)
16. (a)
17. (a)
18. (a)
19. 
20. (c)
21. $[CH_3CHO,\ (CH_3)_3C^{18}OH,\ CH_3OH]$
22. 
23. (a)
24. (b)
25. 
26. (c), (a)
27. 
28. 
29. A; 

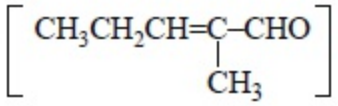
B; 

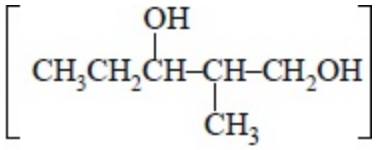
C: No reaction product

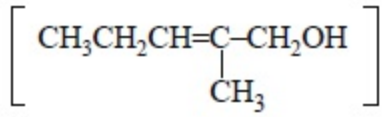
D; 

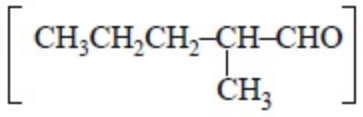
30.  , nylon 6

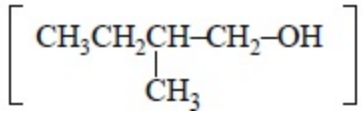
31. 

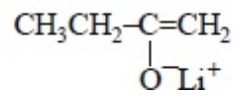
A; 

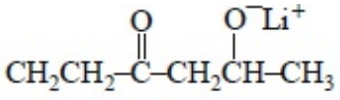
B; 

32. C; 

D; 

E; 

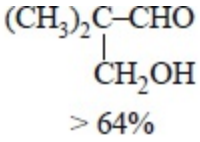
33. A; 

B; 

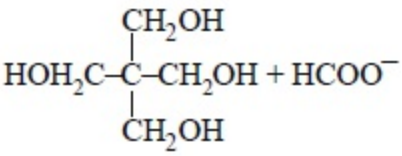
C: $CH_3CH_2COCH_2CH(OH)CH_3$

Hint : [Both the kinetically and thermodynamically stable enolats may react]

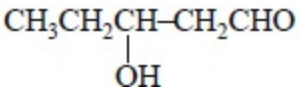
34. [CH_3CH=CH-CH=CHO]

35. 

> 64%

36. 

Penta erythritol

37. 

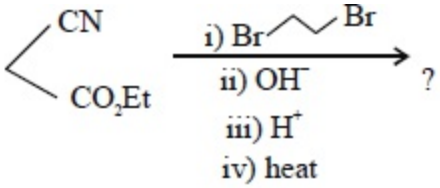
38. $CH_3CH(OH)-CH(CH_3)CHO$

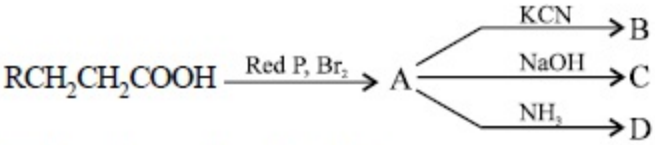
39. $CH_3CH(OH)CH_2COCH_3$

40. $CH_3-C(CH_3)=CH-C(=O)-CH=C(CH_3)-CH_3$

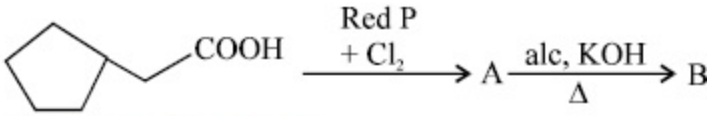
Phorone

Carboxylic acid derivative

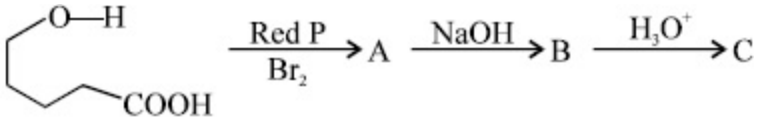
1. 

2. 

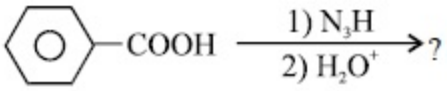
Find out the products B, C, D .

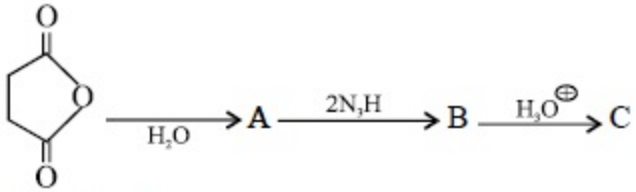
3. 

Write the products A, B.

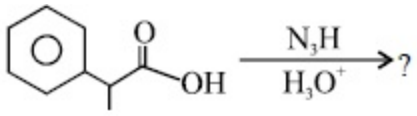
4. 

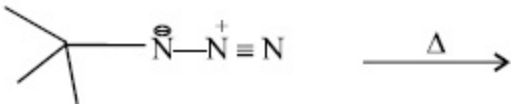
What is 'C' ?

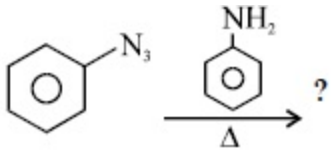
5. 

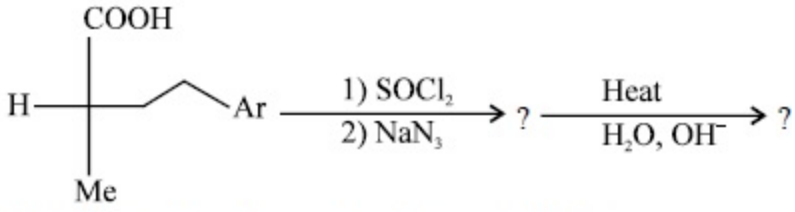
6. 

Write B and C.

7. 

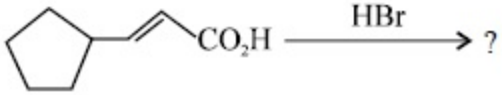
8. 

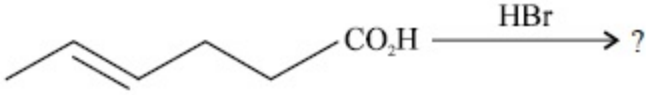
9. 

10. 

Write the final products and configuration R/S.

11. $RCH(CO_2H)_2 \xrightarrow[\text{Red P}]{Br_2} ? \xrightarrow{\Delta} ?$

12. 

13. 

14. $R_1R_2CClCOOH \xrightarrow{LiAlH_4} ?$

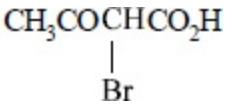
Predict the products.

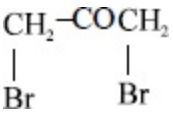
15. $2CH_2=C=O + C_2H_5OH \longrightarrow ? \xrightarrow{H_3O^+} ?$

16. Green colouration of the compound is due to the formation of while EAA (ethyl aceto acetate) reacts with Cu^{+2} salt?

17. Which one can also be the product during decarboxylation of $CH_3COCH_2CO_2H$ in presence of bromine

(a) CH_3COCH_2Br

(b) 

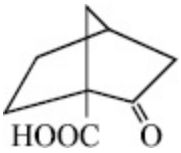
(c) 

(d) None of these.

18. Which one will not decarboxylate upon heating among the followings;

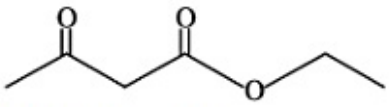
(a) $CF_3COCH_2CO_2H$

(b) $CH_3CH_2OCOCH_3$

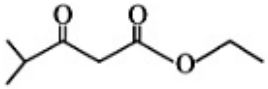
(c) 

(d) All of these

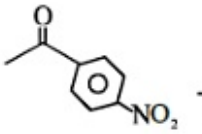
19. $CH_3COCH_2CO_2C_2H_5 \rightleftharpoons CH_3-\overset{OH}{\overset{|}{C}}=CHCO_2C_2H_5 \xrightarrow{C_2H_5-ONa} ?$

20.  $+ BrCH_2CO_2Et \xrightarrow{LiH} ? \xrightarrow[2)\ H_3O^+]{1)\ KOH} ? \xrightarrow{\Delta} ?$

Identify the products.

21.  $\xrightarrow{C_2H_5O^-Na^+} A \xrightarrow{CH_3I} B \xrightarrow{dil.\ KOH,\ H^+} C.$

What is C?

22.  $\xrightarrow[2)\ \text{—I}]{1)\ NaNH_2} A \xrightarrow[2)\ \text{—I}]{1)\ NaNH_2} B \xrightarrow[2)\ CH_3I]{1)\ NaNH_2} C \xrightarrow[2)\ S_N2(Th)]{1)\ NaNH_2} D \xrightarrow{HNO_2} E$

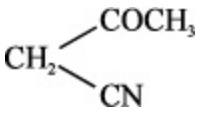
Write the products D and E.

23. From the following compounds which will show active –H ?

(a) $CH_3COCH_2CO_2C_2H_5$

(b) $CH_3COCR^2CO_2C_2H_5$

(c) $CH_2(CO_2C_2H_5)_2$

(d) 

24. $CH_2(CO_2C_2H_5)_2 \xrightarrow{C_2H_5O^-Na^+} A \xrightarrow{CH_3I} B \xrightarrow{C_2H_5O^-Na^+} C \xrightarrow{CH_3I} D \xrightarrow{KOH} E \xrightarrow{HCl} F \xrightarrow{150°\text{-}200°\,C} G$

Find out G ?

25. $ArCH_2CO_2Et + (CO_2Et)_2 \xrightarrow{\overset{\ominus}{O}EtONa^+} A + B$

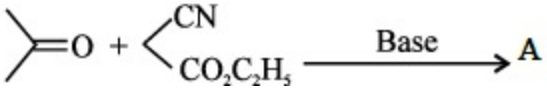
$\downarrow$ Heat

$C + D$

Find out C, D ?

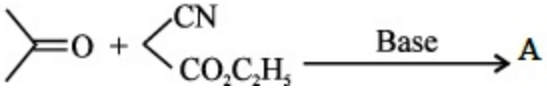
26. $R'CH(CO_2R^2)_2 \xrightarrow[2)\ R'COCl]{1)\ NaH} A \xrightarrow[CH_3CO_2H]{TsOH} B$

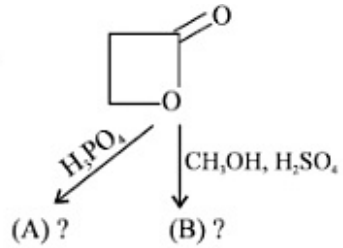
Find out B ?

27.  Find out A ?

26. $R'CH(CO_2R^2)_2 \xrightarrow[2)\ R'COCl]{1)\ NaH} A \xrightarrow[CH_3CO_2H]{TsOH} B$

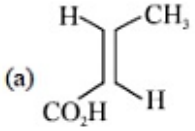
Find out B ?

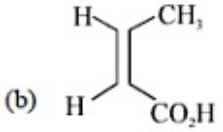
27.  Find out A ?

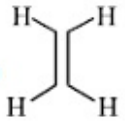
28. $CH_3COOH \xrightarrow{Pyrolysis} CH_2=C=O \xrightarrow{CH_2O}$ 

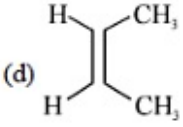
Find out A, B ?

29. Which one is having the highest melting point among the followings?

(a) 

(b) 
Isocrotonic acid

(c) 

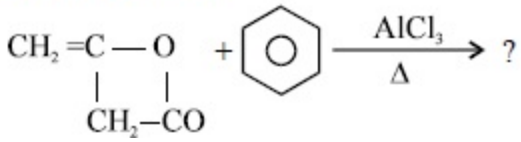
(d) 

30. $CH_3CHO + CH_2(CO_2H)_2 \xrightarrow[20^\circ C]{\text{Pyridine}} ?$

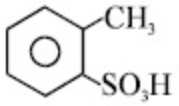
31. $CH_3COOH \xrightarrow{As_2O_3} ?$

32. $CH \equiv C(CN) \xrightarrow{H_3O^+} A \xrightarrow{\text{Sunlight}} B$

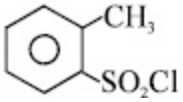
Find out A and B.

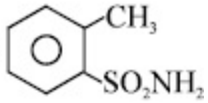
33.  $\xrightarrow[\Delta]{AlCl_3} ?$

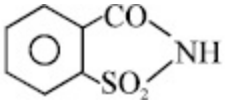
34. $ArCHO + PhCOCl + NH_2CH_2CO_2H \longrightarrow ?$

35.  $\xrightarrow{PCl_5} A \xrightarrow{NH_3} B \xrightarrow{KMnO_4/OH^-} C \xrightarrow[2)\ Heat]{1)\ H_3O^+} D$

Find out the correct option :

(a) A = 

(b) B = 

(c) D =  (Saccharin)

(d) All of these

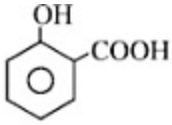
36. Saccharin is insoluble in water, but is sold as ;

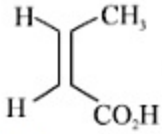
(a) Na–salt

(b) Mg–salt

(c) Cd– salt

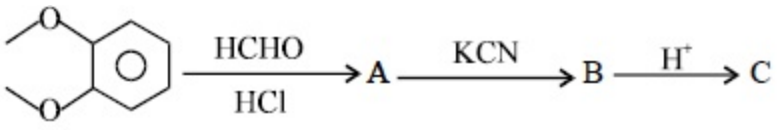
(d) none of these

37.  $\xrightarrow[CH_3COOH]{(CH_3CO)_2O} ?$

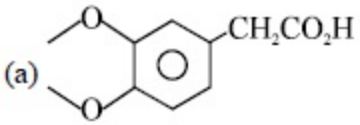
38.  $\xrightarrow{Ni/H_2} A \xrightarrow{\text{heat}} B \xrightarrow{NH_3, \Delta} C \xrightarrow[\substack{NaOH \\ 0^\circ C}]{Br_2} D$

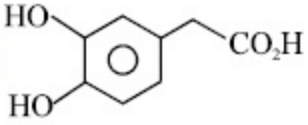
'D' is

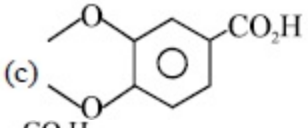
(a) NBS (b) Succinimide (c) Succinic anhydride (d) None of these

39. 

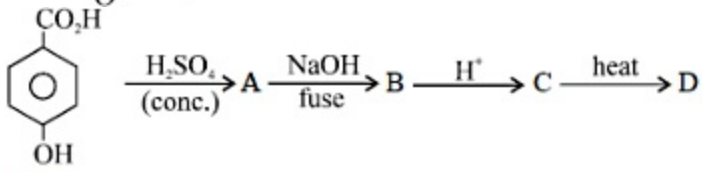
'C' is

(a) 

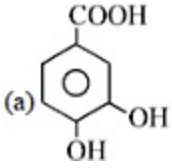
(b) 

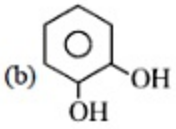
(c) 

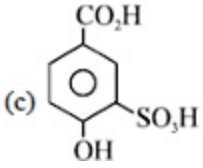
(d) None of these

40. 

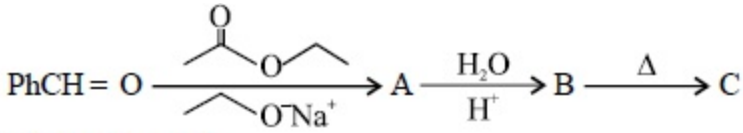
'D' is

(a) 

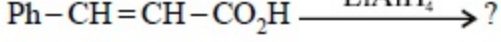
(b) 

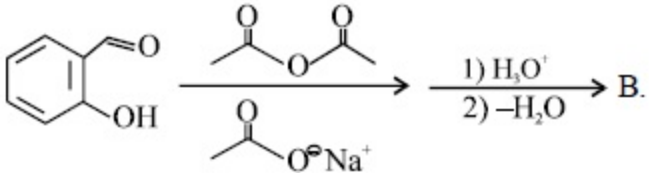
(c) 

(d) None of these

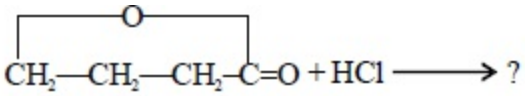
41. 

Find out B and C.

42. 

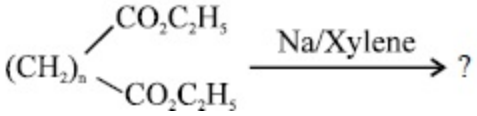
43. 

Find out 'B'.

44. 

45. $HCHO + CO + H_2O \longrightarrow A \xrightarrow{PCl_5} B.$
Find out A, B.

46. $CH_3CHOH—CO_2H$ (Lactic acid) $\xrightarrow[\text{(Fenton's reagent)}]{H_2O_2/Fe^{+2}}$?

47. 

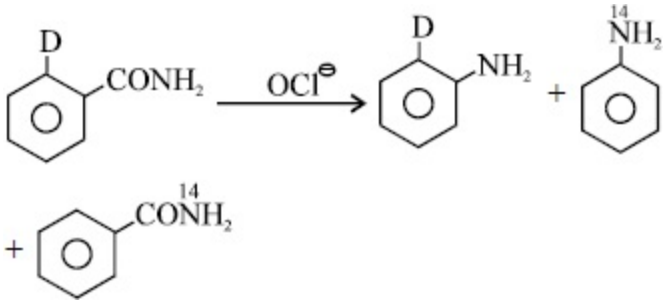
48. Which is having the highest bp ?

(a) $HCONH_2$

(b) **HCOHMe** (H)

(c) $HCONMe_2$

(d) C_2H_6

49. 

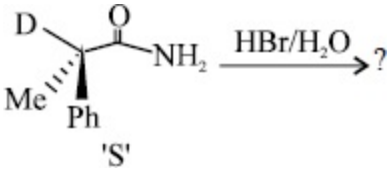
Are the products according to Hofmann's mechanism ?

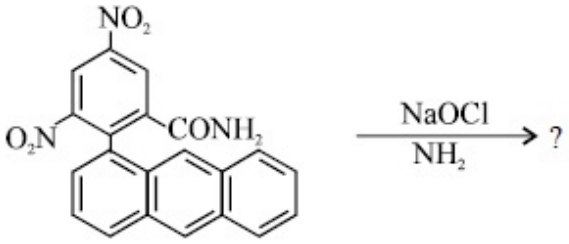
(a) yes

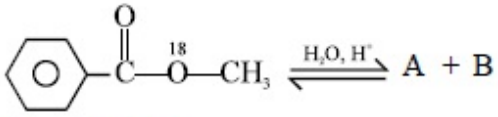
(b) no

(c) cannot be said

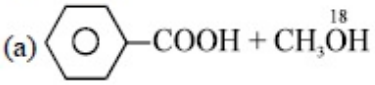
(d) None of these

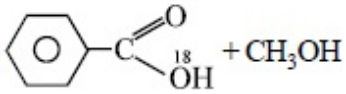
50. 

51. 

52. 

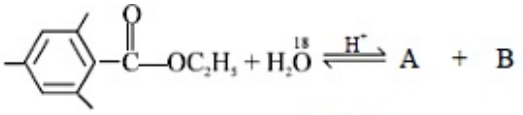
(a) and (b) are

(a) 

(b) 

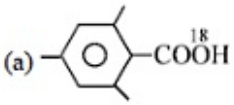
(c) (a), (b) are both

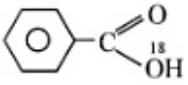
(d) None of these

53. 

(Acid)

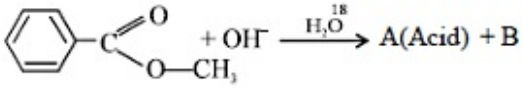
(A) is

(a) 

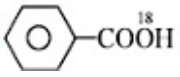
(b) 

(c) CH_3COOH

(d) C_2H_5COOH

54. 

(A) is

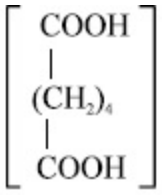
(a) 

(b) CH_3COOH

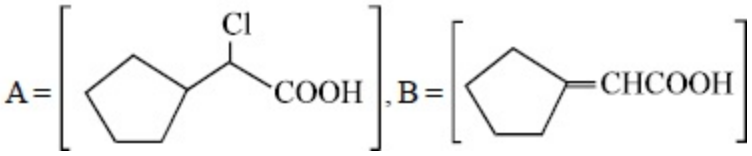
(c) CH_3OH

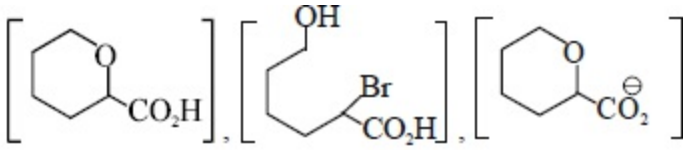
(d) None of these

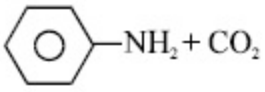
Answer & Hints

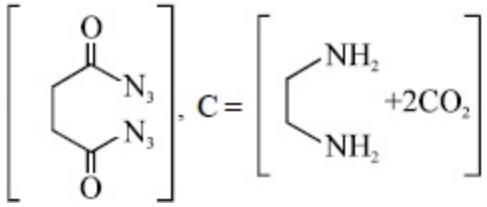
1. 

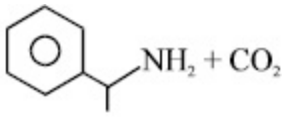
2. $B = RCH_2CH(CN)CO_2H$
   $C = RCH_2CH(OH)CO_2H$
   $D = RCH_2CH(NH_2)CO_2H$

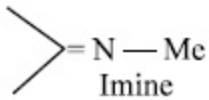
3. 

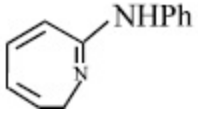
4. 
   (c) (a) (b)

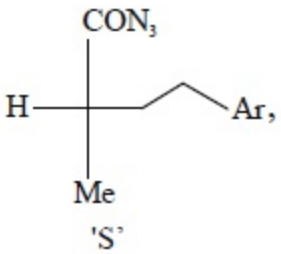
5. 

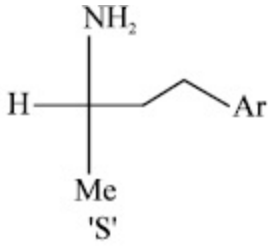
6. 

7. 

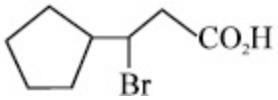
8. 
   Imine

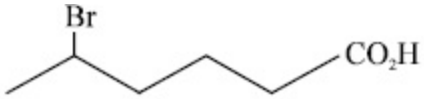
9. 

10. 



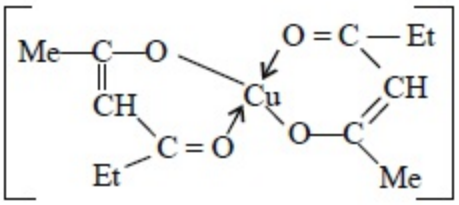
11. [RCBr$(CO_2H)_2$], [RCHBrCOOH]

12. 

13. 

14. [$R^1R^2CClCH_2OH$, $R^1R^2CHCH_2OH$, R^1R^2CHCHO, $R^1R^2C(OH)CH_2OH$]

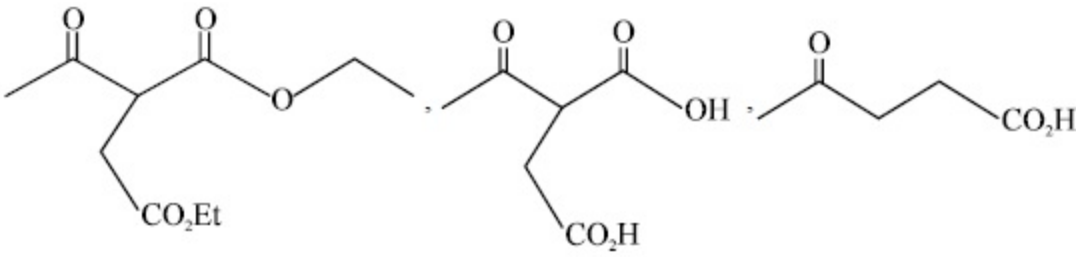
15. $CH_2COCH_2CO_2C_2H_5$, CH_3COCH_2COOH

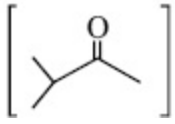
16. 

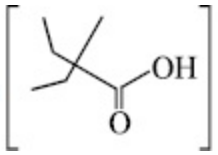
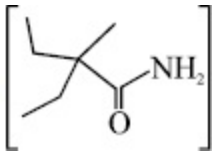
17. (a)

18. (d)

19. 

20. 

21. 

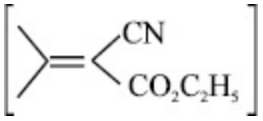
22. E=  D= 

23. (a), (c), (d)

24. G = $(CH_3)_2$ $CHCO_2H$

25. $ArCH(CO_2Et)_2$, CO.

26. [R'COCHXR']

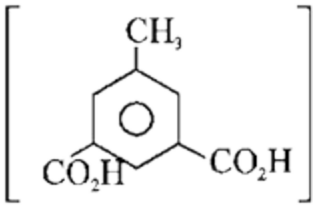
27. 

28. [A: CH_2 = $CHCO_2H$, B: CH_2 = $CHCO_2CH_3$]

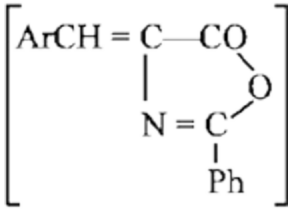
29. (a)

30. [CH_3CH = $CHCO_2H$ + CO_2 + H_2O] The above reaction is called as Knovenged reaction.

31. [Me_2As – O – $AsMe_2$]; Cacodyl oxide, which is a poisonous gas and is used to identify acetic acid.

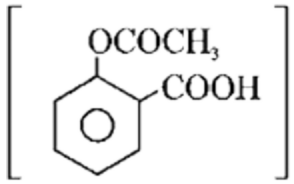
32. A ; CH° C (CO_2H); B ; 

33. 

34.  [The above reactgion is called Erlenmayer azlactone synthesis]

35. (d)

36. (a)

37. 

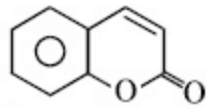
Aspirin

38. (a)

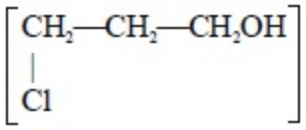
39. (a)

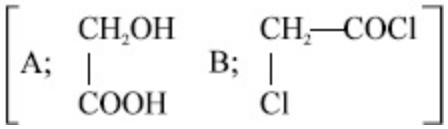
40. (b)

41. [Ph – CH_2 CH_2 – CH_2OH]. $LiAlH_4$ reduces double bond in conjugation with phenyl ring]

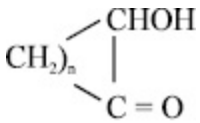
43. B= 

Coumarin, used in perfumary

44. 

45. 

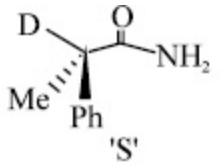
46. [CH_3COCO_2H Pyruvic acid]

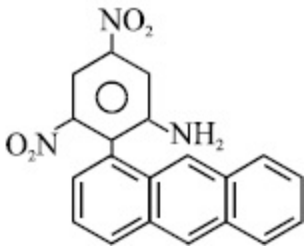
47. 

Acyloin

48. (a)

49. (a)

50. 

51. 

52. (a)

53. (a), (b)

54. (a)

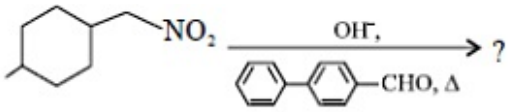
Nitro compound

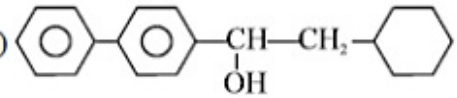
1. Which will show the red colouration at the end of the treatement with HNO_2, NaOH in the Victor Mayer's test?
(a) 1° (b) 2° (c) 3° (d) All of these.

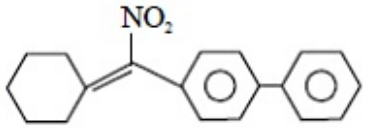
2. Which nitro compound will show blue colouration after Victor Mayer's test?
(a) 1° (b) 2° (c) 3° (d) None of these

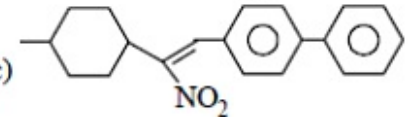
3. $RC(=NOH)(NO_2)$ (Nitrolic acid) forms for
(a) 1° (b) 2° (c) 3° (d) All of these

4. $R_3CNO_2 \xrightarrow{HNO_2} ?$
(a) $R_2C(NO_2)(NO)$ (b) RNO (c) no reaction (d) none of these

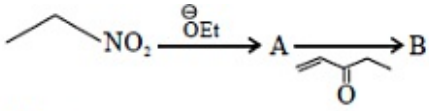
5. 

(a) 

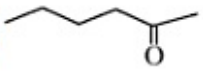
(b) 

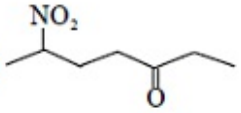
(c) 

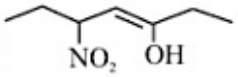
(d) All of these.

6. 

'B' is

(a) 

(b) 

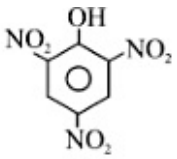
(c) 

(d) All of these

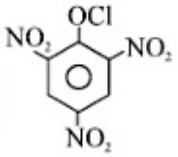
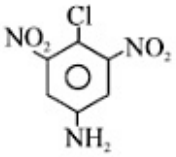
7. $(CH_3CO)_2O + 4HNO_3 \longrightarrow A \xrightarrow[HO^-]{H_2O_2} B$

$CH_2 = C = O + 4HNO_3$

(a) $C(NO_2)_4$, $CH(NO_2)_3$ (b) $CH(NO_2)_3$, $C(NH_2)_4$ (c) $CH_2(NO_2)_2$ (d) all of these.

8.  $\xrightarrow{NaOCl}$ A (used as tear gas) . What is 'A'?

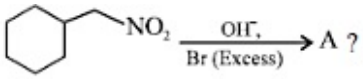
Picric acid

(a) CCl_3NO_2 (b)  (c)  (d) None of these

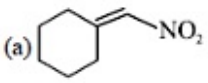
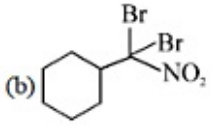
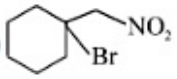
[$CCl_3 - NO_2$ is chloropicrin]

9. TNT, TNB (Trinitrobenzene) are used as

(a) explosive (b) refrigerant (c) insecticide (d) fabric

10. 

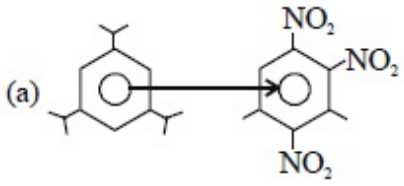
'A' is

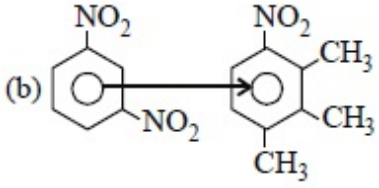
(a)  (b)  (c)  (d) None of these.

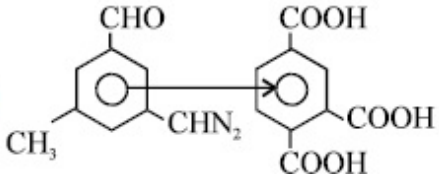
11. $Ph - NO_2 \longrightarrow$ PhNO transfer can take places by metal and acid. The reduction take place through successive ----------and protonation ?

(a) electron transfer (b) H atom transfer (c) $H^{\oplus}$ transfer (d) none of these

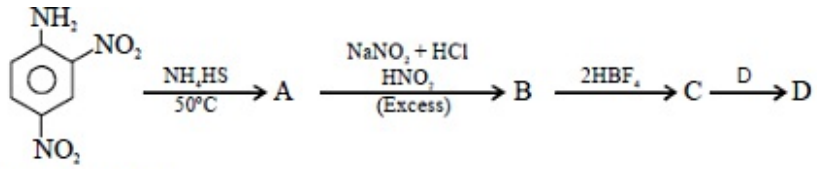
12. Which one is charge transfer complex and show colour?

(a) 

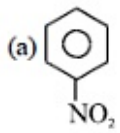
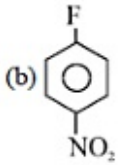
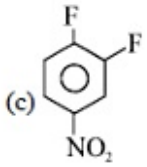
(b) 

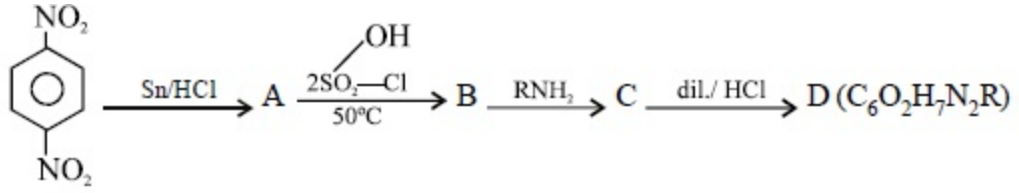
(c) 

(d) None of these

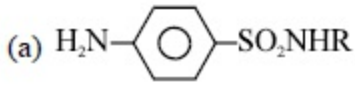
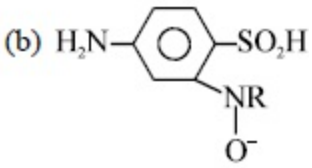
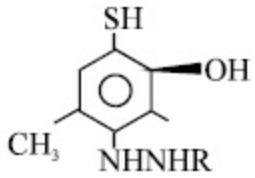
13. 

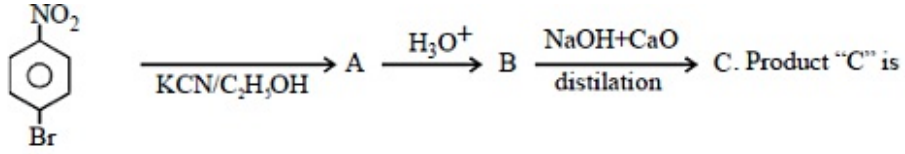
Therefore 'D' is

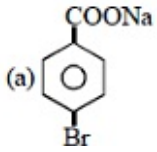
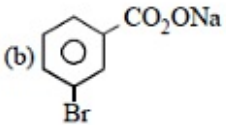
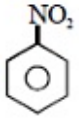
(a) 
(b) 
(c) 
(d) None of these

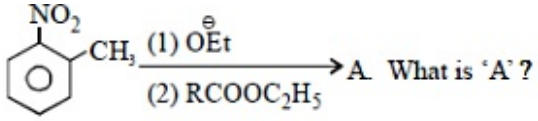
14. 

'D' is :

(a) 
(b) 
(c) 
(d) None of these.

15. 

(a) 
(b) 
(c) 
(d) None of these

16. 

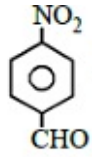
17. $RCH_2NO_2 + (CH_3COO)_2Mg \longrightarrow A \xrightarrow{H^+} B$. Product 'B' is:

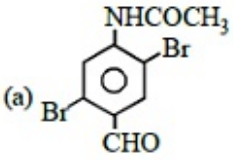
(a) $RCH(NO_2)COOH$ (b) RCH_2COOH (c) $RCH(NH_2)COOH$ (d) All of these

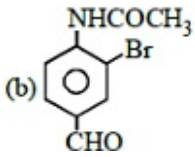
18. $PhNO_2 \xrightarrow[\text{reduction}]{\text{Electrolytic}} A$ (Weakely acidic medium)

$PhNO_2 \downarrow$ (Strongly acidic medium) $\rightarrow B$

Write the products A, B

19.  $\xrightarrow{SnCl_2/HCl,\ \Delta} A \xrightarrow[CH_3COCl]{} B \xrightarrow{Br_2/H_2O} C$. Product C is

(a) 

(b) 

(c) (a) and (b) both

(d) none of these

Answer & Hints

1. (a)

2. (b)

3. (a)

4. (c) [**Hint:** Since there is no acidic –H]

5. (c)

6. (b)

7.

8. [Hint: $CCl_3 - NO_2$ is chloropicrin]

9. (a)

10. (b)

11. (b)

12. (a)

[Hint : In charge thransfer complex the electron donor should have low ionisation potential and high electron density and acceptor should have very low electron density.]

13. (c)

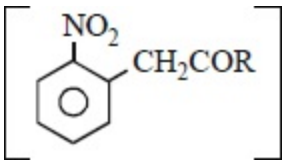
14. (a)

15. (c)

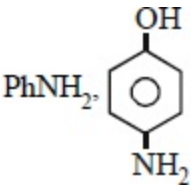
15. (c)

[Hint: This involves von Richter's rearrangement to produce A and the mechanism is beyond the scope of this book. Actually $\overset{\ominus}{CN}$ takes position wrt NO_2 at ortho which is also close Br]

16.

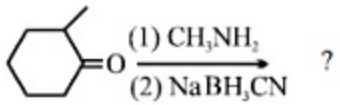


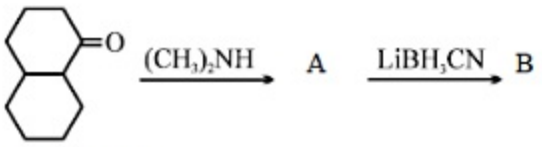
17. (a)

18. 

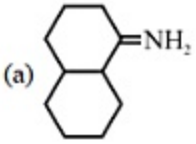
19. (b)

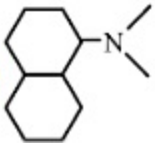
Amine

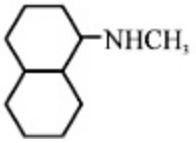
1. 

2. 

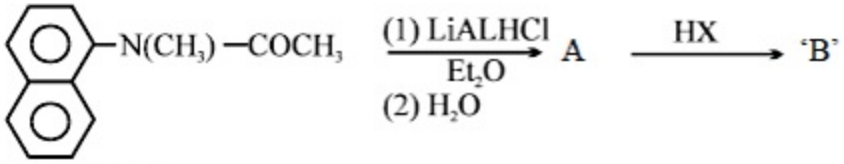
What is 'B'?

(a) 

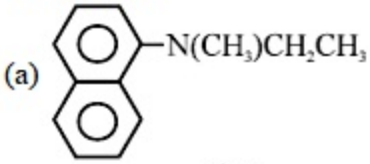
(b) 

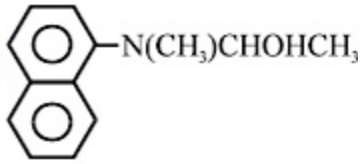
(c) 

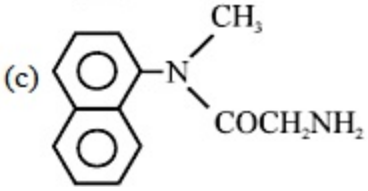
(d) None of these

3. 

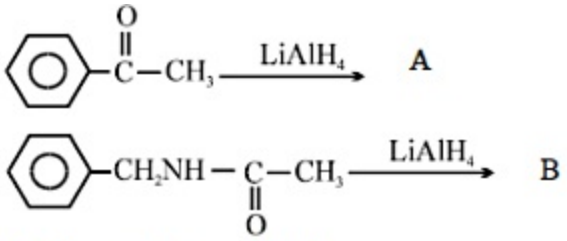
What is 'B'.

(a) 

(b) 

(c) 

(d) None of these

4. 

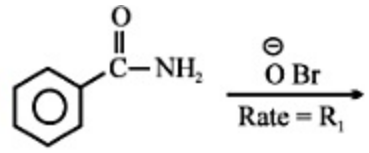
Difference between A & B is

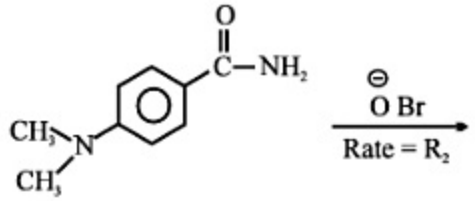
(a) – C= O reduces in B not in A.

(b) $-\underset{|}{C}=O$ reduces in B not in A

(c) in both cases $-\underset{|}{C}=O$ will be reduced.

(d) All of these

5. (i)  Products

(ii)  Products

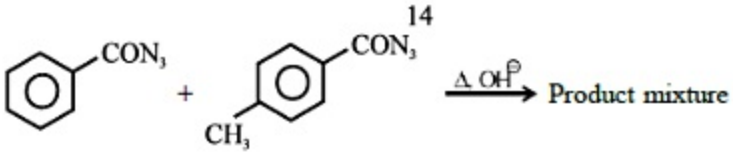
What is the exact relation between R_1, R_2

(a) $R_1 = R_2$ (b) $R_1 < R_2$ (c) $R_1 > R_2$ (d) can't be said

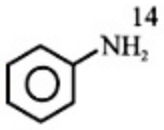
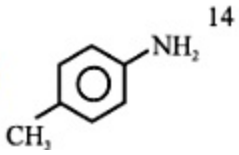
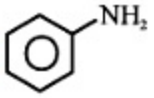
6. $NH_2CONH_2 \xrightarrow{\ominus O Br} A$

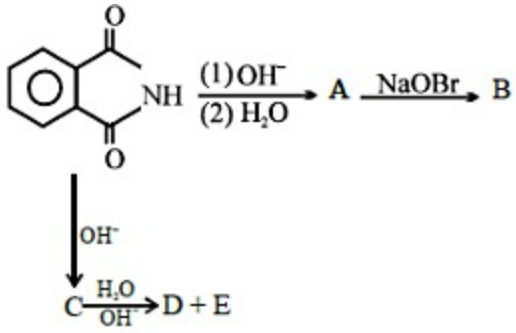
Product 'A' is

(a) $NH_2 - NH_2$ (b) NH_3 (c) NH_2OH (d) None of these

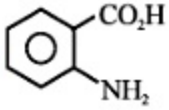
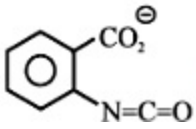
7.  Product mixture

Product does not contain

(a)  (b)  (c)  (d) All of these

8. 

Which one among the following is/ are correct?

(a) D =  (b) $E = HCO_3^-$ (c) C =  (d) All of these

9. $CH_3(CH_2)_7 CONH_2 \xrightarrow[Br_2]{NaOH} A \xrightarrow{Ni/H_2} B$

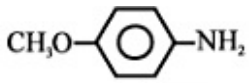
'A' is-

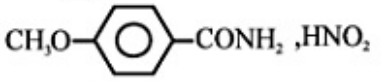
(a) $CH_3(CH_2)_6$ CN

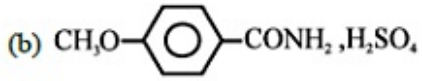
(b) CH_3 $(CH_2)_6CH_2NH_2$

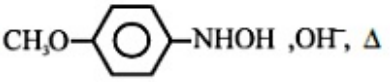
(c) $CH_3(CH_2)_6$ CONHBr

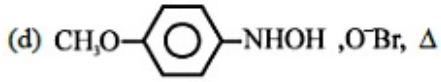
(d) None of these

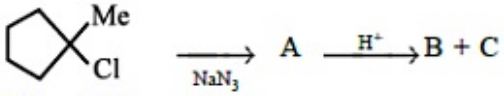
10.  can best be prepared using

(a) 

(b) 

(c) 

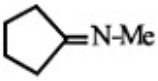
(d) 

11. 

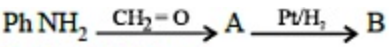
'B' and 'C: can't be

(a) 

(b) 

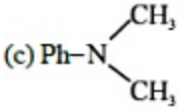
(c) 

(d) 

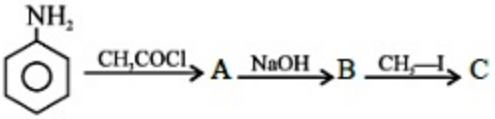
12. 

Products A, B are

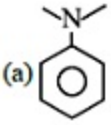
(a) $PhN=CH_2$, $PhNHCH_3$ (b) $PhNH_2$

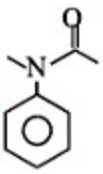
(c) 

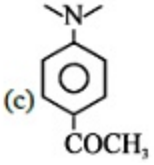
(d) None of these

13. 

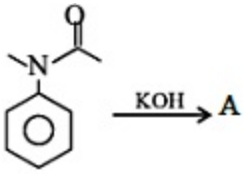
Product 'C' is

(a) 

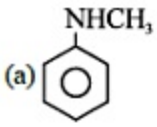
(b) 

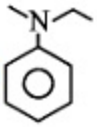
(c) 

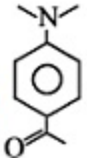
(d) all of these

14. 

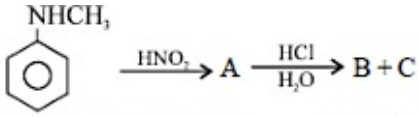
'A' is

(a) 

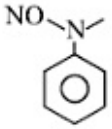
(b) 

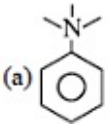
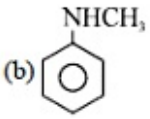
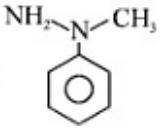
(c) 

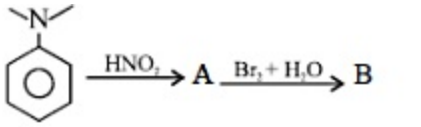
(d) All of these

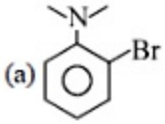
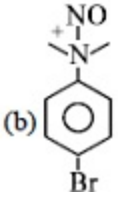
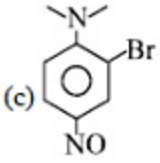
15.  B and C are,

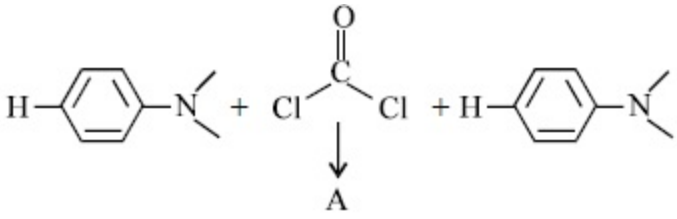
(a) $PhNHCOCH_3, HNO_3$ (b) $PhNHCH_3, HNO_2$ (c) $PhNH_2, HNO_2$ (d) All of these

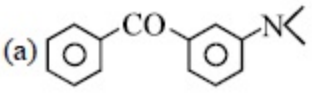
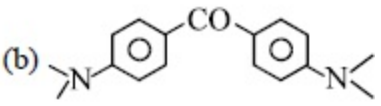
16.  Product 'A' is

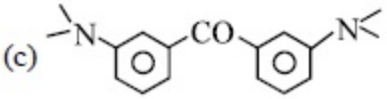
(a)  (b)  (c)  (d) None of these.

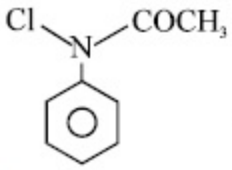
17.  'B' is is

(a)  (b)  (c)  (d) All of these

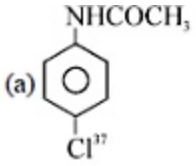
18.  Product 'A' is

(a)  (b) 

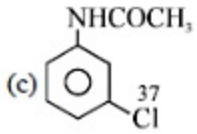
(c)  (d) None of these

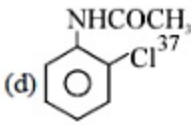
19.  

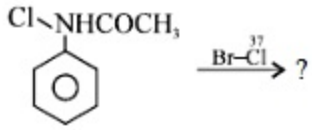
Product never contains

(a) 

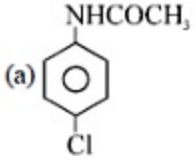
(b) 

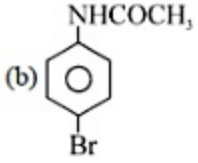
(c) 

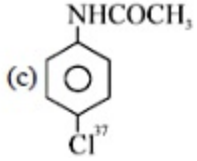
(d) 

20. 

Major product is ?

(a) 

(b) 

(c) 

(d) All of these.

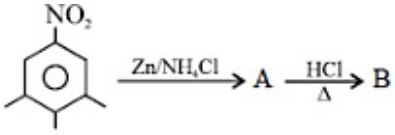
21. Which one can show colour upon decomposition in C_6H_6

(a) $(Ph)_2N - N(Ph)_2$

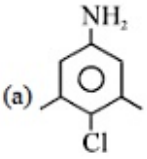
(b) $Ph - NH_2$

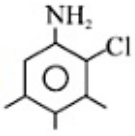
(c) $Ph,N - NH_2$

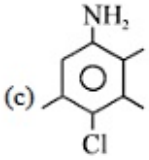
(d) None of these

22. 

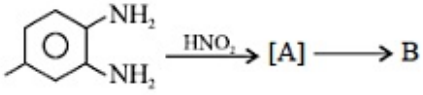
'B' is,

(a) 

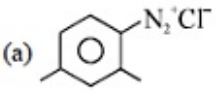
(b) 

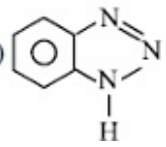
(c) 

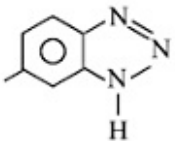
(d) None of these

23. 

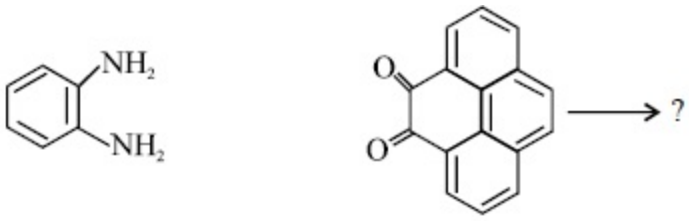
Product 'B' is

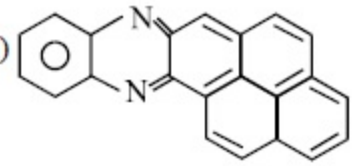
(a) 

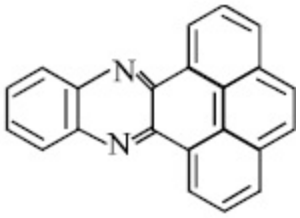
(b) 

(c) 

(d) All of these

24. 

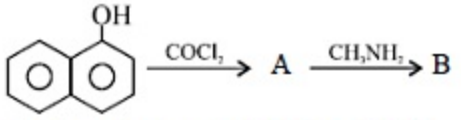
(a) 

(b) 

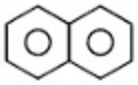
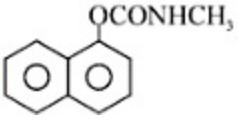
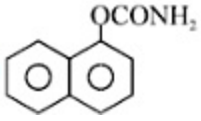
(c) (a), (b) both (d) None of these.

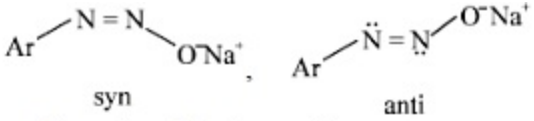
27. Which one will respond to Liebermann's test ?

(a) 1° amine (b) 2° amine (c) 3° amine (d) none of these.

28. 

'B' is used as insecticide. What is 'B' ?

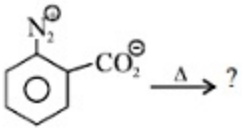
(a)  (b)  (c)  (d) All of these.

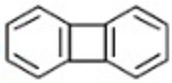
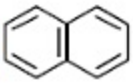
29. 

syn anti

can be produced by the reaction

(a) $ArN_2^+Cl^- + H_2O$ (b) $ArN_2^+ + OH^-$ (c) $ArN_2^+ + CH_3COO^-$ (d) None of these

30. 

(a)  (b)  (c)  (d) All of these

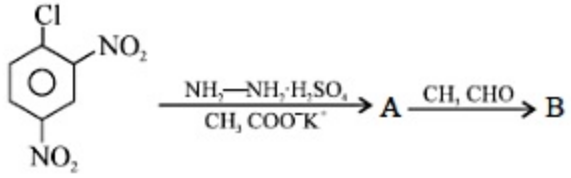
31. $Ph-N_2^+Cl^- \xrightarrow{SnCl_2/HCl} A \xrightarrow{RCH=O} B$

'B' is

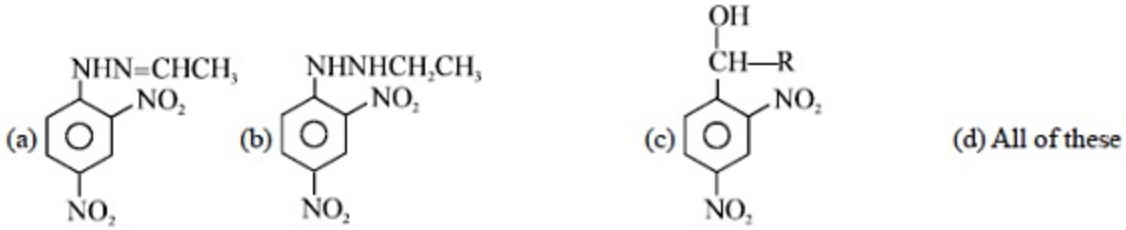
(a) RCH=NNH–Ph (b) RCH_2  (c) a, b both (d) $PhN_2-\underset{R}{\underset{|}{CH}}-OH$

32. $PhNHNH_2 \cdot HCl \xrightarrow[\text{solution}]{\text{Fehling's}}$ Positive. Which one/s are possible product/s ?

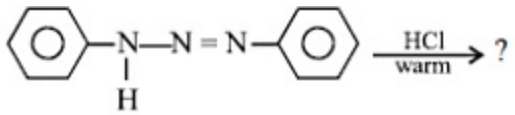
(a) C_6H_6 (b) CH_2O (c) N_2 (d) All of these

33. 

Product 'B' is

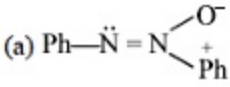
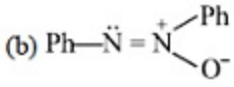


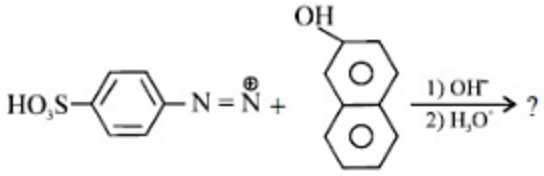
(d) All of these

34. 



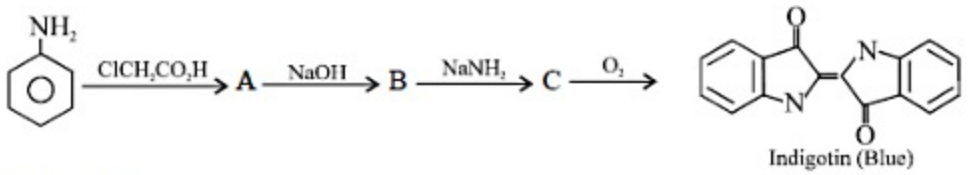
35. Which has more melting point (mp) ?

(a)  (b)  (c) $PhN(CH_3)_2$ (d) All of these.

36. 

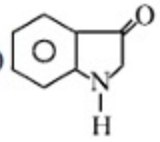
The product used as ?

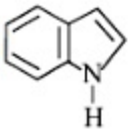
(a) dye (b) food (c) petroleum (d) None of these.

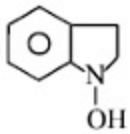
37. 

Indigotin (Blue)

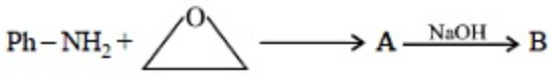
What is 'C' "

(a) 

(b) 

(c) 

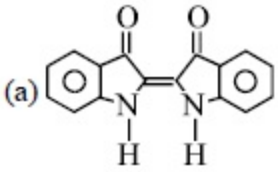
(d) None of these

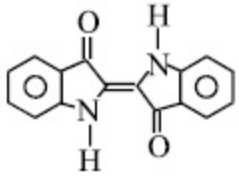
38. 

that is 'B' ?

(a) $PhNHCH_2CH_2ONa$ (b) $PhNHCH_2ONa$ (c) $PhNHCH_2CH_3$ (d) All of these

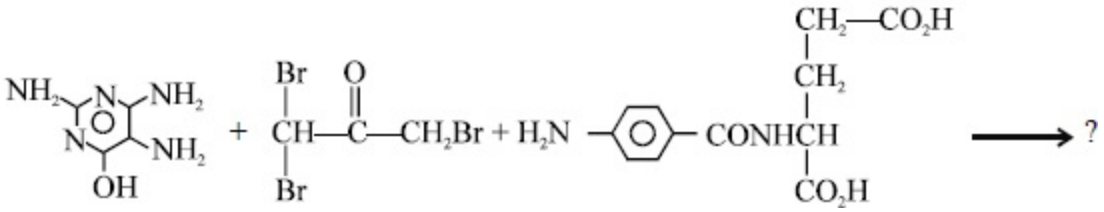
39. Which one is optically active ?

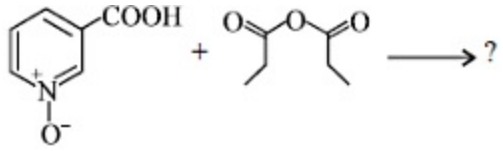
(a) 

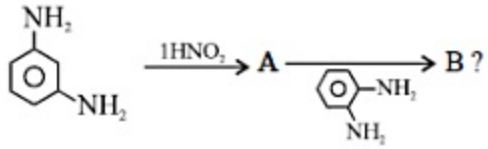
(b) 

(c) 

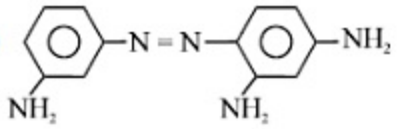
(d) All of these

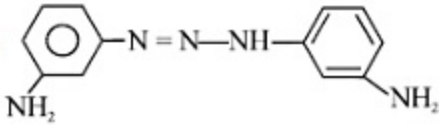
40. 

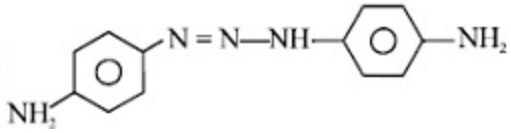
41. 

42. 

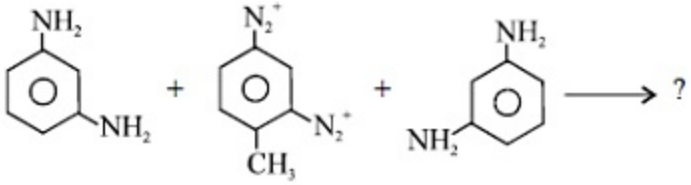
'B' can be

(a) 

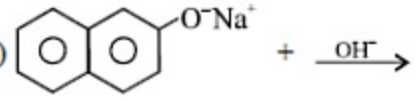
(b) 

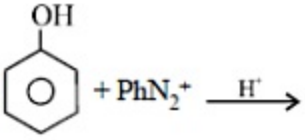
(c) 

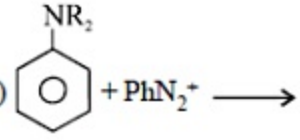
(d) All of these.

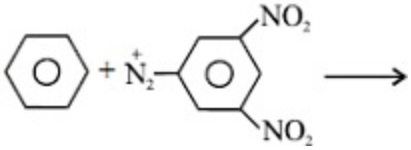
43. 

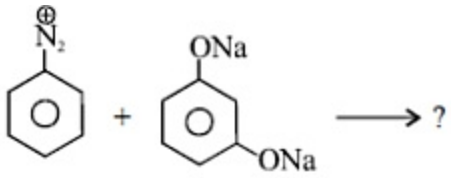
44. Which reaction should take place among the following –

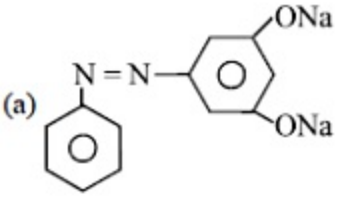
(a) 

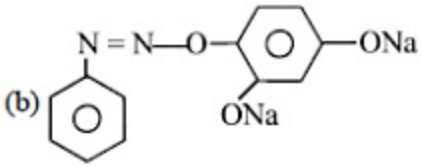
(b) 

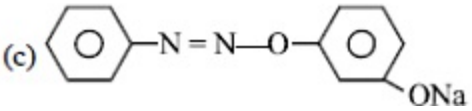
(c) 

(d) 

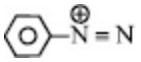
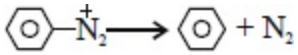
45. 

(a) 

(b) 

(c) 

(d) None of these

46. As we understand that  should not be very stable, as N_2 is a good leaving group. Therefore the  decomposition will be faster, when

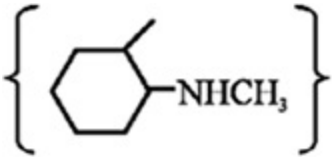
(a) OMe is at ortho or para

(b) $-NO_2$ or $-CO_2H$ is at orth or para

(c) $-CH_3$ is at ortho or para

(d) $-CH_3$ is at meta

Answer & Hints

1. 

2. (b)

3. (a) **Hint :** [Amides reduce to – CH_2NH_2]

4. (a)

5. (b)

6. (a)

7. (a) **Hint :** [As the Curtius rearrangement is completely intramolecular)

8. (d)

9. (a)

10. (c)

11. (b) **Hint :** [When cycloalkyl azides are heated ring expansion takes place]

12. (a)

13. (a)

14. (a)

15. (b)

16. (c)

17. (c)

18. (b) **Hint :** [This product (b) is called Mischler's ketone]

19. (b)

20. (b)

21. (a)

22. (b)

23. (c)

24. (b)

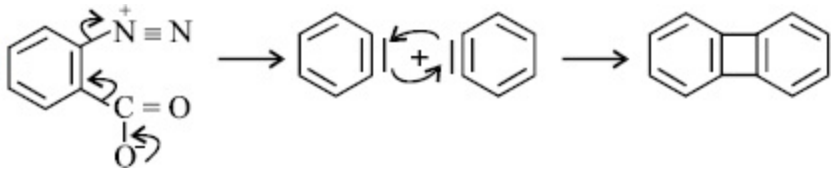
25. (a)

26. (c)

27. (b)

28. (b)

29. (b)

30. (a) **Hint :** 

31. (a) : **Hint :** $PhN_2^+Cl^- \xrightarrow{SnCl_2/HCl} PhNHNH_2$, HCl etc.

32. (d)

33. (a)

34. (b)

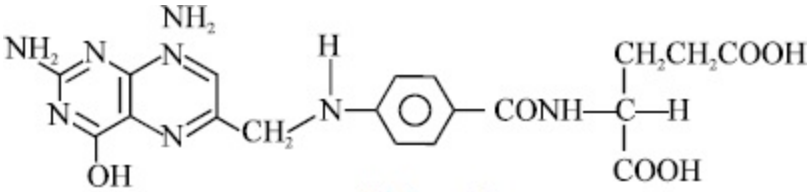
35. (a) **Hint :** [may be due to high dipole moment which causes stronger dipole-dipole attraction.]

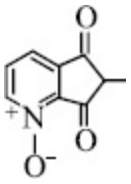
36. (a)

37. (a)

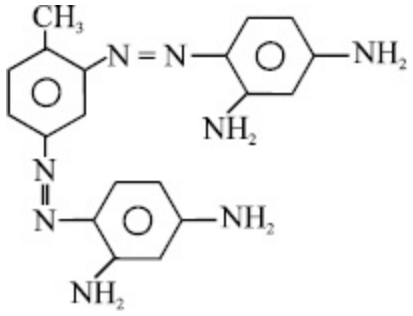
38. (a)

39. (b)

40. 
(Folic acid)

41. 

42. (a)

43. 

Hint : [We must understand that although $-NH_2$ (1°) gives N – N coupling when $-NH_2$ is alone but if there are two $-NH_2$ groups then due to large activation of benzene ring N – C coupling takes place].

44. (b), (d)

45. (b) **Hints :** [This is azodye]

46. Hint : [CH_3 at meta does not have hyperconj ugative effect reaching to C $-N^+ \equiv N$ bond to give C – N double bonding character. So, only +I effect operates which causes easy departure of electron towards $-N_2+$ group and therefore easy departure of $-N_2$, which needed the flow of electron, takes place].

Amino acid

1. N-terminus acid can be identified by

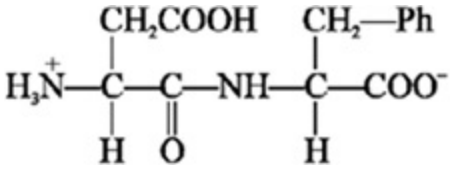
(a) Edman degradation

(b) Sanger's method

(c) Dansyl chloride method

(d) All of these

2. The artifical sweetner aspartame is obtained from naturally occuring amino acids, aspartaue is (S, S) which is given below ;



How many total optical isomers are possible ?

(a) 2

(b) 4

(c) 6

(d) 8

3. Match the following and which is/are correct options ?

(I)	**(II)**
A. Phosphoproteins	1. High density lipoprotein in blood.
B. Ghycoprotein	2. Casein of milk
C. Nucleoprotein	3. Haemoglobin
D. Metalloprotein	4. DNA, RNA

(a) (A-1)

(b) (B- 1)

(c) (D-3)

(d) (C– 4)

4. Asphixiation (i.e. transport of O_2 stops to the tissues) is caused by

(a) CO

(b) N_2

(c) NO_2

(d) CO_2

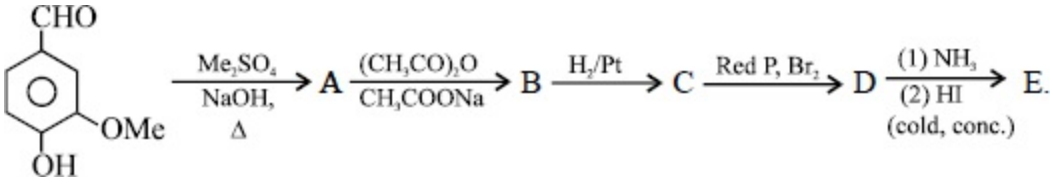
5. Denaturation (i.e. alternation or loss of unique three dimensional conformational state of a protein) is caused by

(a) Heat

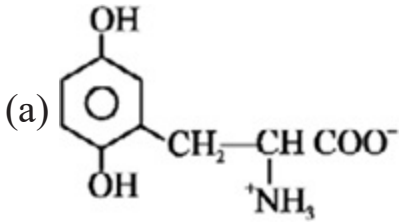
(b) Change in pH

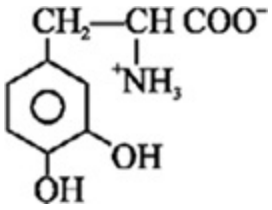
(c) Heavy metal ions, detergents

(d) All of these

6. 

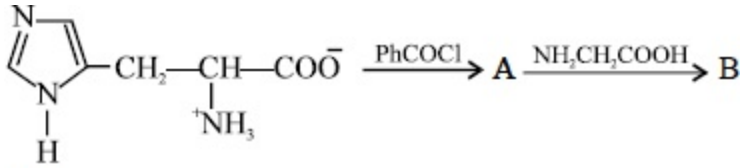
Structure E is

(a) 

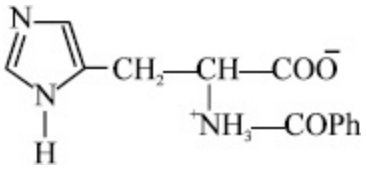
(b) 

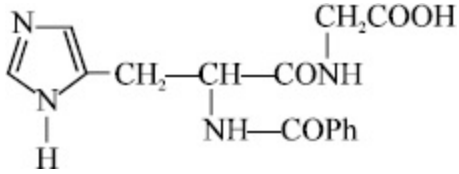
(c) (a, b) both

(d) none of these

7. 

'B' is

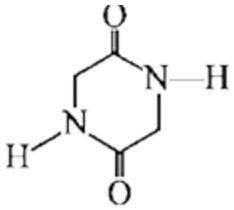
(a) 

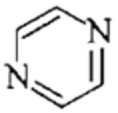
(b) 

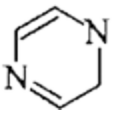
(c) (a, b) both.

(d) None of these

8. If NH_2COOH is heated, the product becomes,

(a) 

(b) 

(c) 

(d)None of these

9. Nylon 6 is a polymer of

(a) $NH_2(CH_2)_3$ COOH

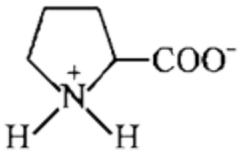
(b) $NH_2(CH_2)_5COOH$

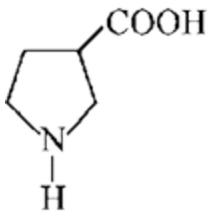
(c) $NH_2(CH_2)_4COOH$

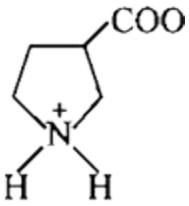
(d) All of these

10. $HOOC(CH_2)_4COOH \xrightarrow[NH_3]{SOCl_2} A \xrightarrow[\Delta]{\bar{O}Br} B \xrightarrow[Br_2]{Red\ P} C \xrightarrow{\Delta} D$

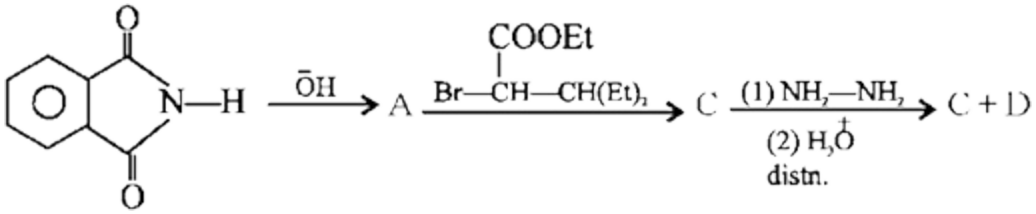
'D' is

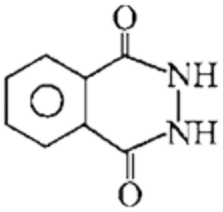
(a) 

(b) 

(c) 

(d) None of these

11. 

(a) C is 

(b) D is $\overset{+}{N}H_3—\underset{\underset{CH(Et)_2}{|}}{\overset{\overset{COOEt}{|}}{CH}}$

(c) D is $\overset{+}{N}H_3—\underset{\underset{CH—CH(Et)_2}{|}}{\overset{\overset{CO\bar{O}}{|}}{CH}}$

(d) All of these

12. Which one is the correct pH to separate all three amino acid at a time by electrophoresis? Given; glycine (pi = 5.9), aspartic acid (pi = 2.77), Histidine (7.5).

(a) 5.9

(b) 2.77

(c) 7.5

(d) None of these

13. At pi of amino acid, which one is the correct statement :

(a) Concentration of Zwitter ion is maximum

(b) Concentration of conjugate acid and conjugate base are equal and minimum.

(c) no movement towards electrodes

(d) All of these.

14. At pi, which is the correct statement related to Ka_1, Ka_2 of an amino acid (with proper meaning)

(a) $pi = 1/2(pKa_1 + pKa_2)$

(b) $pi = 1/2(pKa_1 - pKa_2)$

(c) $pi = pKa_1 + pKa_2$

(d) None of these

Answer & Hints

1. (d)

2. (b)

3. (b), (c), (d)

4. (a)

5. (d)

6. (b)

7. (b)

8. (a)

9. (b)

10. (a)

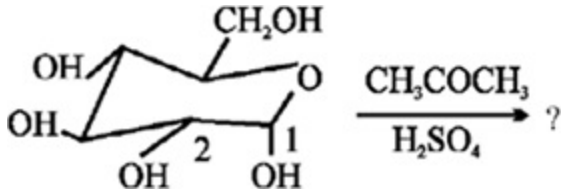
11. (a), (c)

12. (a)

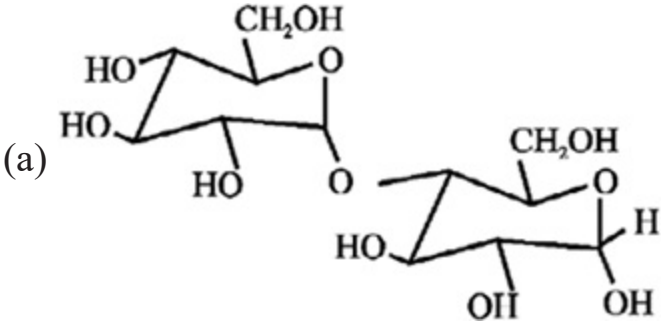
13. (d)

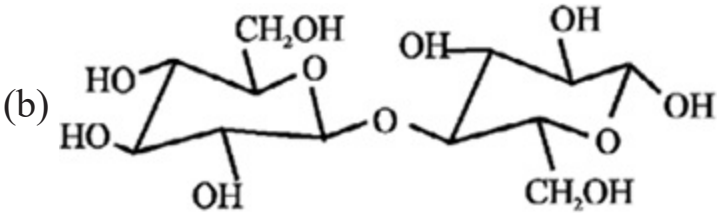
14. (a)

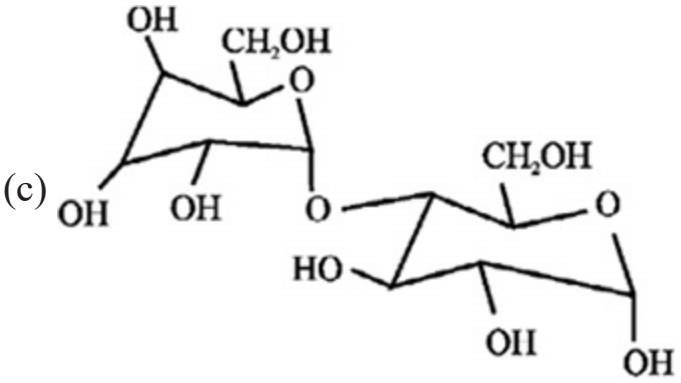
Carbohydrate

1. 

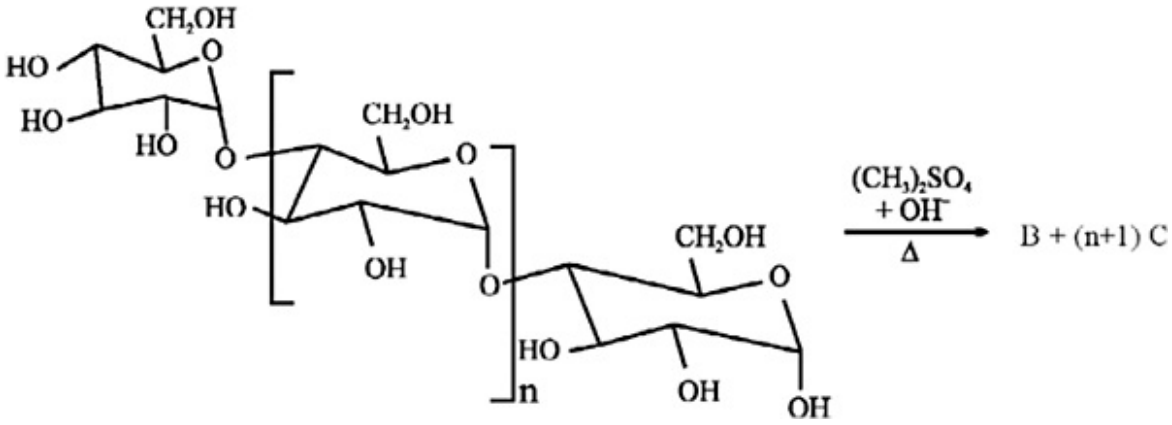
2. Identify cellobiose unit ?

(a) 

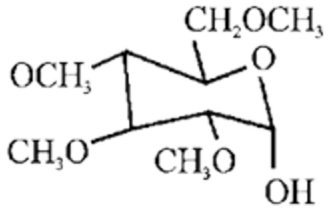
(b) 

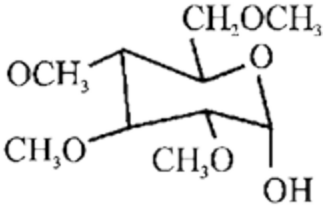
(c) 

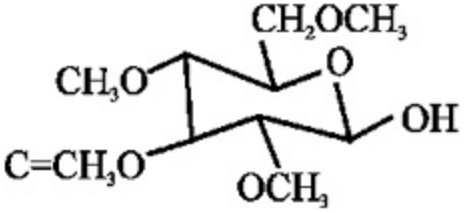
(d) None of these

3. 

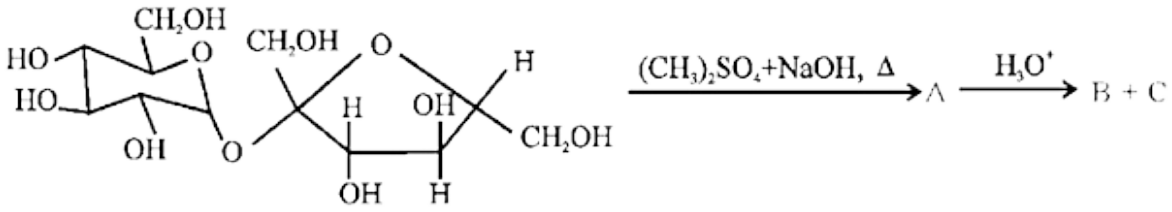
Which one/s is / are correct?

(a) B = 

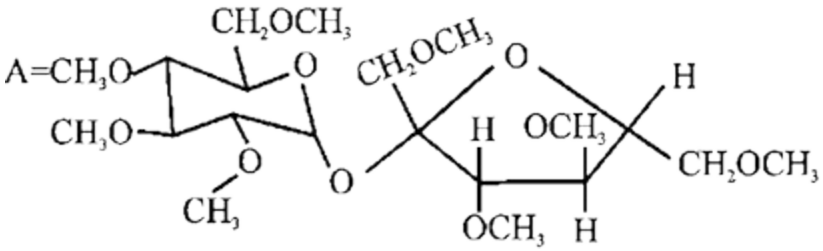
(b) C= 

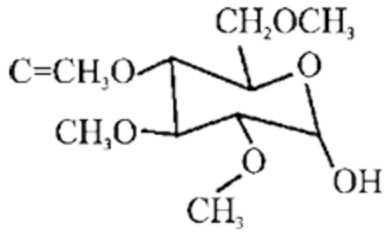
(c) 

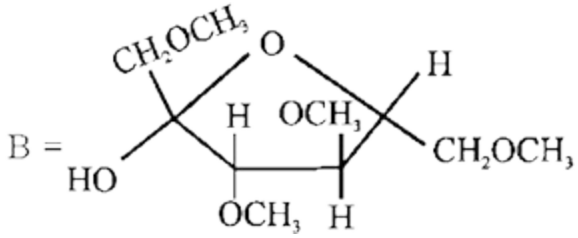
(d) only (b)

4. 

(a) , (B) and (C) are

(a) 

(b) 

(c) 

(d) All of these

5. Lactose is found in-

(a) adhesive

(b) milk

(c) rayon

(d) fibre

6. Amylopectin is

(a) soluble in water

(b) insoluble in water

(c) monomer of starch

(d) None of these

7. Maltose breaks

(a) α - glucoside linkage of maltose

(b) β - glucoside linkage of cellobiose

(c) α , β both glucosidic linkage

(d) None of these

8. $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$ D(+) glucose D(–) fructose

$[\alpha]_n = +66°$ $[\alpha]_D = +52°$ $[\alpha]_D = -92°$

In the above hydrolysis process the optical rotation of (+) sucrose (+66°) changes to net negative value
of optical rotation of the hydrolysed mixture. The phenomenon is called is-

(a) inversion of cane sugar

(b) epimerisation

(c) anomer formation

(d) all of these

9. Which enzyme can carryout the above hydrolysis ?

(a) xymase

(b) invertase

(c) cellulose

(d) lactose

10. Which one\s is\are non reducing ?

(a) sucrose

(b) lactose

(c) maltose

(d) cellobiose

11. In sucrose which units are present ?

(a) α - D glycopyranose

(b) β - D glucopyranose

(c) β -D fructofuranose

(d) σ -D fructofuranose

12. Which one/s is/ are true ?

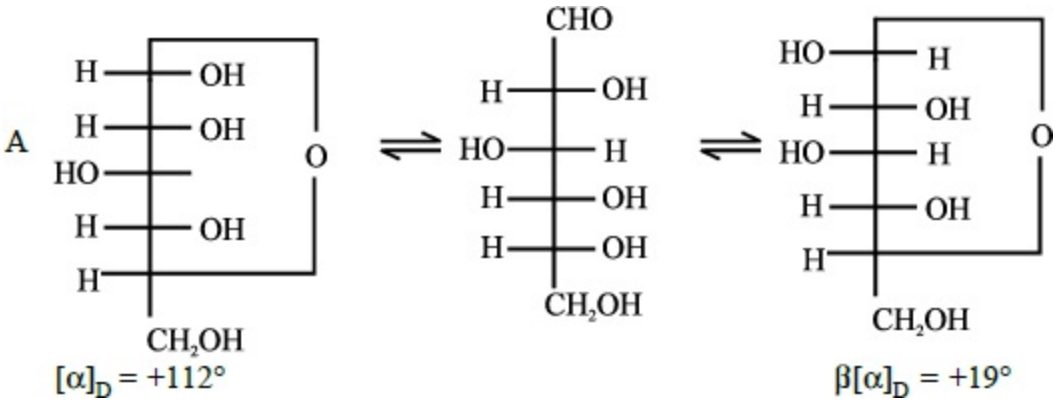
(a) Maltose $\xrightarrow{H_3O^+}$ 2glucose

(b) Lactose $\xrightarrow{H_3O^+}$ Glucose + galactose

(c) Sucrose $\rightarrow$ Glucose + Fructose

(d) All of these

13.



The above process in which α converts to β - form is called-

(a) Mutarotation

(b) Epimerisation

(c) Condensation

(d) Inversion

14. Mutarotation takes place in presence of

(a) only acid

(b) only base

(c) acid and base together

(d) None of these

15. D(+) glucose $\xrightarrow[HCl]{CH_3OH}$ A + B, A, B are-

(a) Methyl – α - D glucoside

(b) Methyl - β -D glucoside

(c) α - D- glucopyranoside

(d) β - D- glycopyranoside

16. In Lobry- de- Bruyn –Van Ekenstein rearrangement, which occurs-

(a) D- glucose $\rightleftharpoons$ D- fructose

(b) D glucose $\rightleftharpoons$ D- mannose

(c) D fructose $\rightleftharpoons$ D- mannose

(d) All of these

17. Epimers are-

(a) D- glucose, D- Mannose

(b) D- glucose, D- fructose

(c) D- fructose, D- mannose

(d) None of these

18. Epimers on treatment with 3 moles of $PhNHNH_2$, gives-

(a) same osazone

(b) different osazone

(c) only hydrazone derivative

(d) All of these

19. To step up for aldoses which method/s is/ are used?

(a) Killani synthesis

(b) Sowden's method

(c) Wohl's method

(d) Ruff's method

20. To step down in sugar series, we use-

(a) Wohl's method

(b) Ruff's method

(c) Killani synthesis (d) None of these

21. During osazone formation-

(a) 1 mole Ph NH_2 forms

(b) 1 mole of NH_3 forms

(c) no $PhNH_2$ comes out

(d) None of these

22. H- bonding occurs in-

(a) osazone

(b) amylopectin

(c) α -d glucose

(d) β -d glucose

23. Amadori rearrangement is involved-

(a) for oxime formation

(b) for acetylation of – OH groups

(c) for osazone formation

(d) None of these

24. Fructose is obtained from –

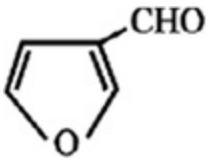
(a) insulin upon hydrolysis

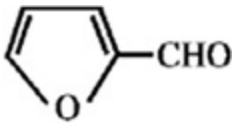
(b) polysaccharide which occurs in dahali tubers

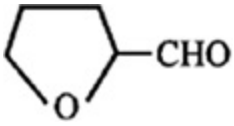
(c) maltose

(d) lactose

25. $C_5H_{10}O_5 \xrightarrow{HCl} \xrightarrow{?} + 3H_2O$. The product is-Aldopentose

(a) 

(b) 

(c) 

(d) None of these

26. Which one/s is/ are true ?

(a) oligosaccharides contain 2-10 monosaccharides

(b) polysaccharides contains more than 10 monosaccharides

(c) raffinose ($C_{18}H_{32}O_{16}$) is a disaccharide

(d) Sucurose is a trisaccharide

27. Which one/s is/ are true ?

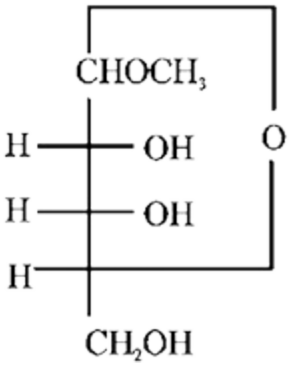
(a) α - amylose contains unbranched chain

(b) α - amylose gives blue colour with I_2 (due to inclusion complex)

(c) Amylopectin is soluble in water.

(d) Amylopectin i.e. β - amylose contains branched chain

28. How many moles of HIO_4 is required to break down the following molecule ?



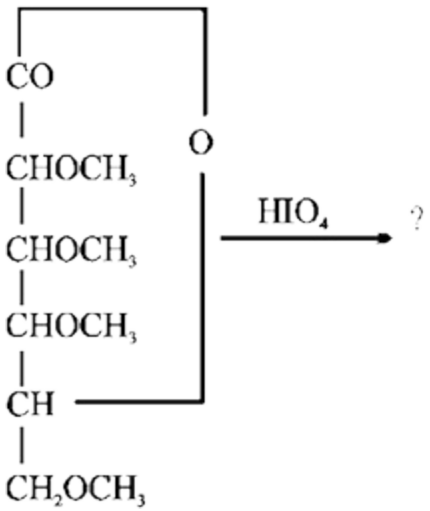
(a) 1

(b) 2

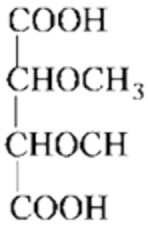
(c) 3

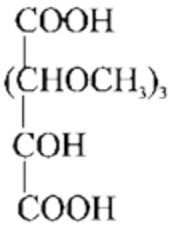
(d) 4

29. Which is the product of the following reaction ?

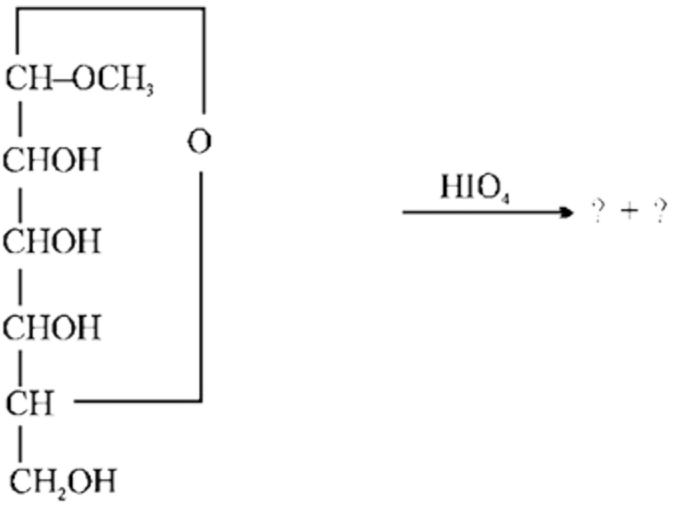


(a) 

(b) 

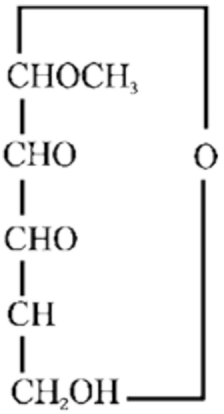
(c) 

(d) None of these

30. 

The no. of moles of HIO_4 required for the above reaction and products formed are

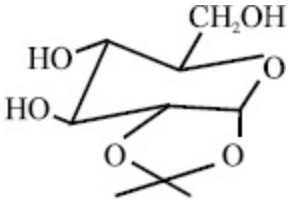
(a) 1

(b) 

(c) 2

(d) HCO_2

Answer & Hints

1. 

2. (b)

3. (a), (b)

4. (d)

5. (b)

6. (b)

7. (a)

8. (a)

9. (b)

10. (a)

11. (a), (c)

12. (d)

13. (a)

14. (c)

15. (a), (b)

16. (d)

17. (a)

18. (a)

19. (a), (b)

20. (a), (b)

21. (a), (b)

22. (a), (b)

23. (c)

24. (a), (b)

25. (b)

26. (a), (b)

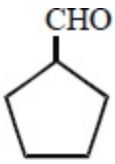
27. (a), (b), (c), (d)

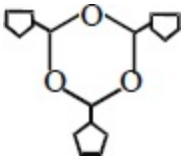
28. (a)

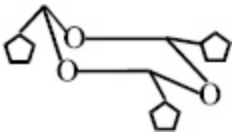
29. (a)

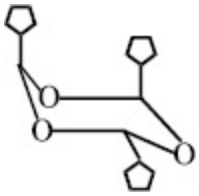
30. (b), (c), (d)

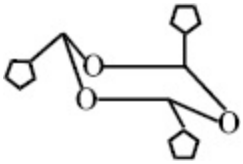
Polymers

1. 

forms trimer as  . Which one is the correct structure of the trimer ?

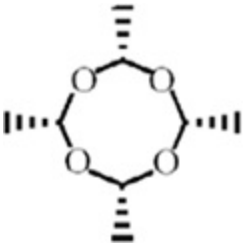
(a) 

(b) 

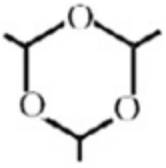
(c) 

(d) None of these

2. CH_3CHO forms metaldyhyde at < 0°C . The correct structure is ?

(a) 

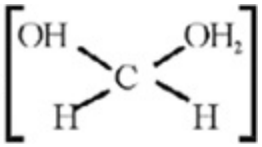
(b) 

(c) 

(d) None of these.

3. Among trioxan, polyoxymethylene, formalin bad source of HCHO is ?

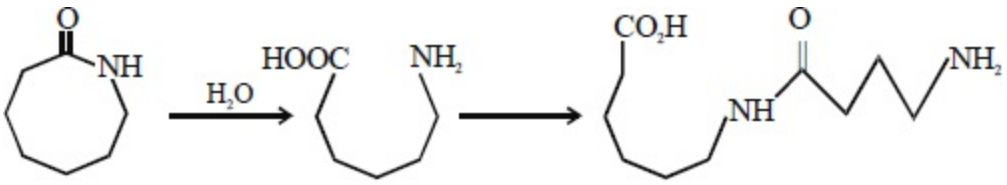
(a) trioxan 

(b) formalin 

(c) polyoxymethylene

(d) None of these

4. Nylon 6 form froms carprolactum. It goes on through which end of the hydrolysed compound ?



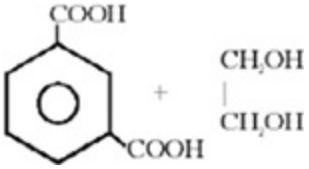
(a) $-NH_2$

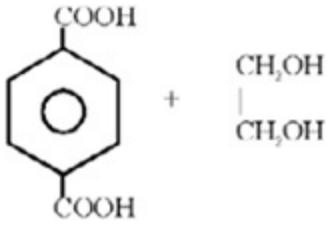
(b) –COOH

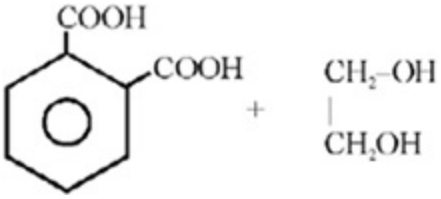
(c) Both

(d) None of these

5. Polyster is made up of the monomer

(a) 

(b) 

(c) 

(d) None of these

6. Bakelite is a polymer of

(a) PhOH + CH_3OHO

(b) PhOH + $(CH_3CO)_2O$

(c) PhOH+HCHO

(d) Ph–NO_2 + PhOH

7. Elastomers are made by using long chain aliphatic diols from parsly polymerised

(a) epoxides

(b) alcohols

(c) ethers

(d) aldehyde

8. Match the followings-

I. Atacitic A. Substituents can be in the any side

II. Isotactic B. All substituents in the same side

III. Diotactic C. All substituenents in the sameside of the diszag chain

9. Teflon or PTFE is formed by

(a) cationic polymerisation

(b) anionic polymerisation

(c) free radical polymerisation

(d) None of these

10. Zieglar Natta catalyst is

(a) $TiCl_4$, $AlCl_3$

(b) $TiCl_4$, AlR_3

(c) TiR_4, $AlCl_3$

(d) all of these

11. Natural rubber has the configuration

(a) E

(b) Z

(c) any one

(d) none of these

12. To have good fibre proparty polymer should have

(a) axial disymetry

(b) axial symetry

(c) ductility

(d) all of these

13. In dacron –

(a) intermolicular H-bonding exists

(b) intra molecular H-bonding exists

(c) Intermolecular dipole-dipole attraction force exists

(d) none of these

14. Branched structure of polymers are

(a) non crystaline

(b) arystatline

(c) strong mechanical properties

(d) none of these.

15. Novlak is made up of_____ +_____

16. Epoxy resins are used in

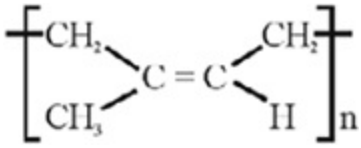
(a) electrial equipment

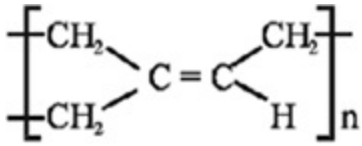
(b) flooring

(c) insulating form

(d) none of these

17. Natural rubber is

(a) 

(b) 

(c) $-[CH_2CH=CH-CH_2-]n$

(d) all of these

18. Rubber is

(a) Elastomeric

(b) Thermosetting

(c) Thermoplastic

(d) all of these

19. Vulcanisation imporves

(a) toughness

(b) resistance to heat

(c) brittleness

(d) water resistance property

Answer & Hints

1. (a)

2. (a)

3.

4. (a)

5. (b)

6. (c)

7. (a)

8. [1-A, II-C, III-B]

9. (c)

10. (b)

11. (b)

12. (a), (b)

13. (a), (c)

14. (a)

15. Phenol, formaldehyde

16. (a)

17. (a)

18. (a)

18. (a), (b), (d)

Practical organic chemistry

1. $RCOOH + KI + KIO_2 \rightarrow$ A(gas). What is the gas 'A', which gives blue colouration of starch solution?

(a) CO_2

(b) I_2

(c) CO

(d) None of these

2. Which compound(s) does/do not respond to Tollen's reagent?

(a) $\begin{matrix} CH_2—COCH_3 \\ | \\ OH \end{matrix}$

(b) $CH_2 = CH - CHO$

(c) HCOOH

(d) CH_3COCH_3

3. $KMnO_4 + H_2SO_4 + HCOOH \longrightarrow$ Products Products do not contain

(a) $MnSO_4$

(b) CO_2

(c) CO

(d) H_2O

4. Match the following :

A	B
a) Fehling's solution	1) (SO_2 + Rosaniline dye)
b) Benedict's solution	2) Ammonical $AgNO_3$ ie $[Ag(NH_3)_2]OH$
c) Tollen's reagent	3) (Cu^{+2} in $\begin{matrix} COO\bar{O}H^+ \\ \vert \\ CHOH \\ \vert \\ CHOH \\ \vert \\ COO^-Na^+ \end{matrix}$ solution)
d) Sclniff's reagent	4) Alkaline solution of Cu^{+2} in and trisodium citrate)

(a) (a-3, b-4, C–2, d-1)

(b) (a-2, b-4, C–3, d-1)

(c) (a-3, b-1, C–2, d-4)

(d) (a-1,b-4, C–2,d- 3)

5. When aldehyde reacts with Bendedict's solution, Cu^{+2} converts to

(a) Cu

(b) Cu_2C_2

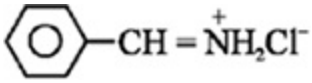
(c) Cu_2O

(d) CuO

6. Which all will respond to Fehling's solution test (directly or upon hydrolysis)

(a) $CH_3CH(OCH_3)_2$

(b) $CH_2 = CH(OCOCH_3)_2$

(c) 

(d) $HCOOCH_3$

7. Libermann's test is performed for

(a) Ph – NH_2

(b) Ph-OH

(c) PhCOOH

(d) Ph-Cl

8. Victor Meyer's test is performed for

(a) R – NH_2

(b) R_2NH

(c) R_3N

(d) All of these

9. Which one gives red colour finally when undergoes Victor Meyer's test

(a) 1° amine

(b) 2° amine

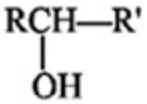
(c) 3° amine

(d) none of these

10. $(NH_4)_2Ce(NO_3)_6$ i.e. cerric ammonium test is used to identify

(a) R-OH

(b) R_3COH

(c) 

(d) All of these

11. $CH_3CH_2C \equiv C - H$ can be identified with acidic –H by

(a) $AgNO_3$(ammoniacal)

(b) Cu_2Cl_2 (ammoniacal)

(c) RMgx

(d) All of these

Answer & Hints

1. (b) [**Hint :** $6RCOOH + 5KI + 3KIO_3 \longrightarrow 6RCOOK + 3H_2O + 3I_2$]

2. (d) [**Hint:** $HCOOH + Ag^+ \longrightarrow Ag + CO_2 + H_2O$]

3. (c) **Note :** [In the above reactions we should understand that HCOOH is a reducing compound reduces Tollen's, Fehling's, Bendict's solution.]

4. (a)

5. (c)

6. (a), (b), (d)

7. (b)

8. (d)

9. (a)

10. (d)

11. (d)

IIT JEE

Questions and Answers

IUPAC Nomenclature

1. The correct IUPAC name of the compound is –

[IIT-90]

(a) 5,6-diethyl-8-methyl deC–6-ene

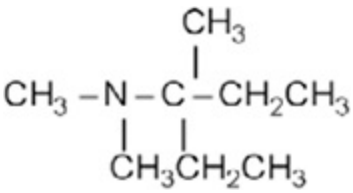
(b) 5,6-diethyl –3-methyl dec –4-ene

(c) 6-butyl-5-ethyl-3-methyl-oct-4-ene

(d) 2,4,5-triethyl-3-ene

2. IUPAC name of the compound is

[IIT-91]



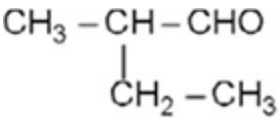
(a) 3-dimethyl amino-3-methyl pentane

(b) 3(N,N-trimethyl) 3 – amino pentane

(c) 3, N, N –trimethyl pentane

(d) 3, N, N- dimethyl amino-3-methyl pentane

3. Choose the correct IUPAC name for

 is-

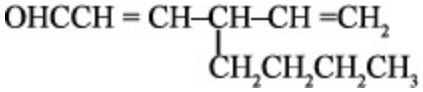
[IIT-93]

(a) Butan-2-aldehyde

(b) 2-Methylbutanal

(c) 3-Methylisobutyraldehyde

(d) 2-Ethylpropanal

4. The IUPAC name of 

(a) 5-Vinyloct-3-en-1- al

(b) 4-Butylhexa-2, 5-dien-1-al

(c) 5-Vinyloct-5-en-8-al

(d) 3-Butylhexa-1, 4-dien-8-al.

Isomerism

1. The enolic form of acetone contains

[IIT- 90]

(a) 9 σ bonds, 1 π bond & 2 lone pairs

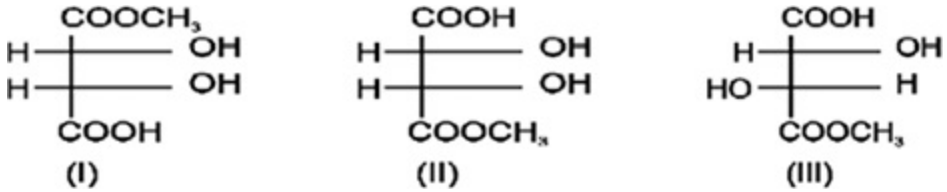
(b) 8 σ bonds , 2 π bonds & 2 lone pairs

(c) 10 σ bonds , 1 π bond & 1 lone pair

(d) 9 σ bonds , 2 π bonds & 1 lone pair

2. An organic molecule necessarily shows optical activity if it-

[IIT-93]



(a) Contains asymmetric carbon atoms

(b) is non –planar

(c) is non –superimposable on its mirror image

(d) is superimposable on its mirror image.

3. The compound which is not isomeric with diethyl ether is –

(a) butan-1-ol

(b) Butanone

(c) 2-methyl propan-2-ol

(d) n-propyl methyl ether

4. Ordinary light can be converted into plane polarized light with the help of a –

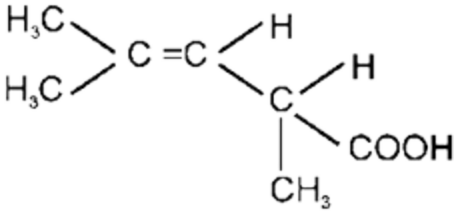
[IIT-93]

(a) Nickel prism

(b) Nicol prism

(c) Diffraction grating

(d) Quartz cell

5. The structure  shows :

[IIT-95]

(a) geometrical isomerism

(b) Optical isomerism

(c) geometrical & optical isomerism

(d) tautomerism

6. How many optically active stereoisomers are possible for butane –2, 3-diol ?

[IIT-97]

(a) 1

(b) 2

(c) 3

(d) 4

7. Isomers which can be interconverted through rotation around a single bond are –

[IIT-97]

(a) Conformers

(b) Diastereomers

(c) Enantiomers

(d) Positional isomers

8. The number of possible enantiomeric pairs that can be produced during monochlorination of 2-methyl- butane is-

[IIT-97]

(a) 2

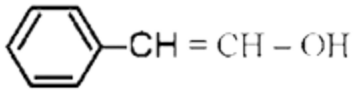
(b) 3

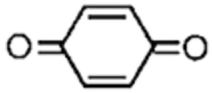
(c) 4

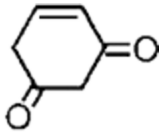
(d) 1

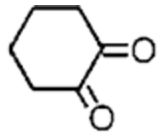
9. Tautomerism is exhibited by

[IIT-98]

(a) 

(b) 

(c) 

(d) 

10. Rotation of polarised light can be measured by-

[IIT-98]

(a) Monometer

(b) Galvanometer

(c) Polarimeter

(d) Viscometer

11. The optically active tartaric acid is named as D-(+)-tartaric acid because it has a positive-

[IIT-99]

(a) optical rotation and is derived from D-glucose

(b) pH in an organic solvent

(c) optical rotation and is derived from D-(+) –glyceraldehyde

(d) optical rotation only when substituted by deuterium

12. Which of the following compounds will exhibit geometrical isomerism ?

[IIT-2000]

(a) 1-phenyl-2-butene

(b) 3-phenyl-1-butene

(c) 2-phenyl-1-butene

(d) 1,1-diphenyl-1-propene

13. The number of isomers for the compound with molecular formula $C_2BrClFI$ is-

[IIT-2000]

(a) 3

(b) 4

(c) 5

(d) 6

14. Which of the following exhibits stereoisomerism-

[IIT-2000]

(a) 2-Methylbutene – 1

(b) 3-Methylbutyne –1

(c) 3-Methylbutanioc acid

(d) 2-Methylbutanoic acid

15. Which of the following compounds exhibits stereoisomerism ?

[IIT-2001]

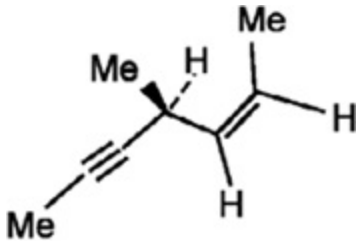
(a) 2-methylbutene-1

(b) 3-methylbutyne-1

(c) 3-methylbutanoic acid

(d) 2-methylbutanoic acid

16.



[IIT-2001]

Hydrogenation of the above compound in the presence of poisoned palladium catalyst gives

(a) optically active compound

(b) an optically inactive compound

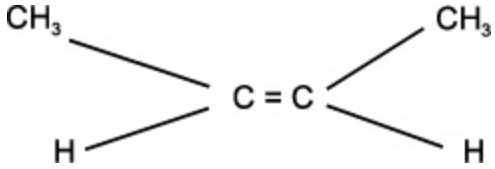
(c) a racemic mixture

(d) a diastereomeric mixture

17. Which of the following has the lowest dipole moment ?

[IIT-2002]

(a)



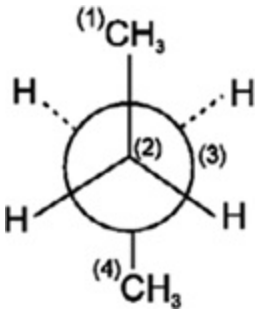
(b)CH_3-C = C–CH_3

(c) $CH_3CH_2C = CH$

(d) $CH_2 = CH – C = CH$

18. If C_2 in above compound is rotated by 120° angle in anticlockwise direction along C_2- C_3, which of the following form will be produced :

[IIT-2004]



(a) Partial eclipsed

(b) Perfectly eclipsed

(c) Perfeclty staggered

(d) Gauche conformation

19. D-Glucopyranose exist in two forms

[IIT-2005]

(a) Anomers

(b) Epimers

(c) Enantiomers

(d) Diastereoisomers

GOC, S_N , Elimination

1. Which one of the following has the smallest heat of hydrogenation per mole ?

[IIT-93]

(a) 1-Butene

(b) trans-2-Butene

(c) cis-2-Butene

(d) 1,3-Butadiene

2. Reaction of $R - CO - NH_2$ with a mixture of Br_2 and KOH gives $R - NH_2$ as the main product. The intermediates involved in this reaction are –

[IIT-92]

(a) R – CO – NHBr

(b) RNHBr

(c) R – Br

(d) $R.CO.NBr_2$

3. What is the decreasing order of strength of bases ?

[IIT-93]

$\overline{O}H$, $\overline{N}H_2$, $H-C\equiv C^-$, $CH_3-CH_2^-$

(a) $CH_3-CH_2^- > NH_2^- > H-C\equiv C^- > OH^-$ (b) $H-C\equiv C^- > CH_3-CH_2^- > NH_2^- > OH^-$

(c) $OH^- > NH_2^- > H-C\equiv C^- > CH_3-CH_2^-$ (d) $NH_2^- > H-C\equiv C^- > OH^- > H_3C-CH_2^-$

4. The kind of delocalization involving sigma bond orbitals is called

[IIT-94]

(a) Inductive effect

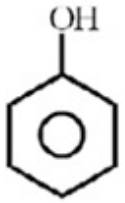
(b) Hyperconj ugation effect

(c) Electromeric effect

(d) Mesomeric effect

5. In the following compounds –

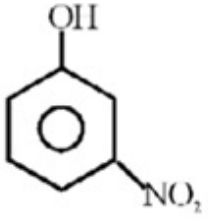
[IIT-96]



I



II



III



IV

The order of acidity is –

(a) III > IV > I > II

(b) I > IV > III > II

(c) II > I > III > IV

(d) IV > III > I > II

6. In the following groups :

[IIT-97]

–OAc (I) –OMe (II) $-OSO_2Me$ (III) $-OSO_2CF_3$ (IV) 3

the order of leaving group ability is

(a) I > II > III > IV

(b) IV > III > I > II

(c) III > II > I > IV

(d) II > III > IV > I

7. The intermediate during the addition of HCl to propene in the presence of peroxide is –

[IIT-97]

(a) $CH_3\dot{C}HCH_2Cl$

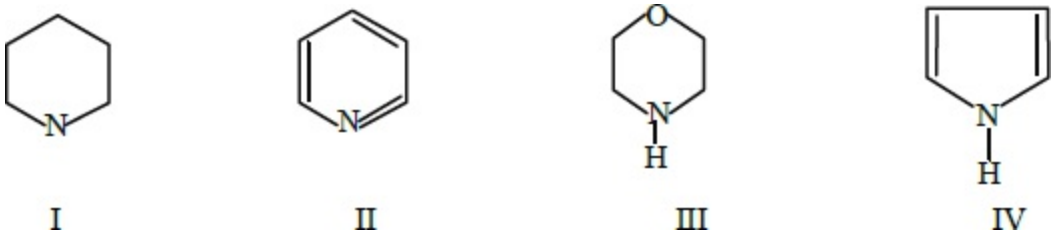
(b) $CH_3\overset{\oplus}{C}HCH_3$

(c) $CH_3CH_2\dot{C}H_2$

(d) $CH_3CH_2\overset{\oplus}{C}H_2$

8. In the following compounds, the order of basicity is –

[IIT-97]



I II III IV

(a) IV > I > III > II

(b) III > I > IV > II

(c) II > I > III > IV

(d) I > III > II > IV

10. The formation of cynohydrin from a ketone is an example of –

[IIT-98]

(a) Electrophilic addition

(b) Nucleophilic addition

(c) Nucleophilic substitution

(d) Electrophilic substitution

11. The most unlikely representation of resonance structure of p–Nitrophenoxide ion is –

[IIT-99]

(a) $\overset{\delta-}{C}H_2=CH-\overset{\delta+}{C}H=O$

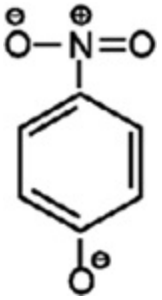
(b) $\overset{\delta-}{C}H_2=CH-CH=\overset{\delta+}{O}$

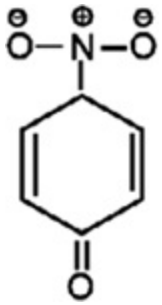
(c) $\overset{\delta-}{C}H_2=\overset{\delta+}{C}H-CH=O$

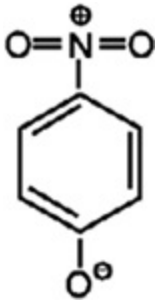
(d) $\overset{\delta+}{C}H_2=CH-CH=\overset{\delta-}{O}$

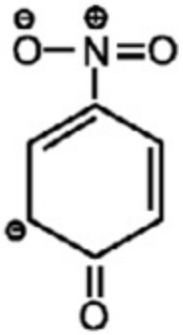
12. Polarisation of electrons in acrolein may be written as-

[IIT-98]

(a) 

(b) 

(c) 

(d) 

13. A solution of (+) – 2-chloro-2-phenylethane in toluene racemises slowly in the presence of small amount of $SbCl_5$ due to formation of –

[IIT-99]

(a) carbanion

(b) carbene

(c) free radical

(d) carbocation

14. An aromatic molecule will not –

[IIT-99]

(a) have 4n π electrons

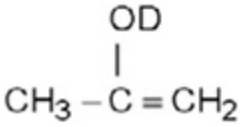
(b) have (4n + 2) π electrons

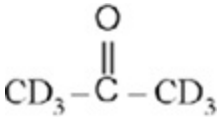
(c) be planar

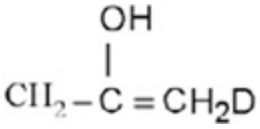
(d) be cyclic

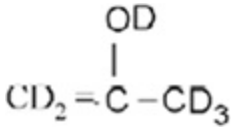
15. The enol form of acetone, after treatment with D_2O, gives –

[IIT-99]

(a) 

(b) 

(c) 

(d) 

16. Read the following statement and explanation and answer as per the option given below :

[IIT-2000]

Assertion : Phenol is more reactive than benzene towards electrophilic substitution reaction.

Reason : In the case of phenol, the intermediate cabocation is more resonance stabilised.

(a) If both assertion and reason are correct, and reason is the correct explanation of the assertion

(b) If both assertion and reason are correct, but reason is not correct

explanation of the assertion

(c) If assertion is correct but reason is incorrect

(d) If assertion is incorrect but reason is correct

17. Amongst the following, the most basic compound is –

[IIT-2000]

(a) $C_6H_5NH_2$

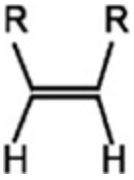
(b) p–NO_2 – $C_6H_4NH_2$

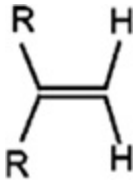
(c) m–NO_2 – $C_6H_4NH_2$

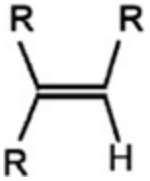
(d) $C_6H_5CH_2NH_2$

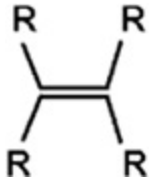
18. Which of the following alkenes will react fastest with H_2 under catalytic hydrogenation conditions ?

[IIT-2000]

(a) 

(b) 

(c) 

(d) 

19. Which of the following has the highest nucleophilicity ?

[IIT-2000]

(a) F^-

(b) OH^-

(c) CH_3^-

(d) NH_2^-

20. The reaction of propene with HOCl proceeds via the addtition of –

[IIT-2001]

(a) H^+ in the first step

(b) Cl^+ in the first step

(c) OH^- in the first step

(d) Cl^+ and OH^- in a single step

21. An SN^2 reaction at an assymetrical carbon of a compound always gives –

[IIT-2001]

(a) enantiomer of the substrate

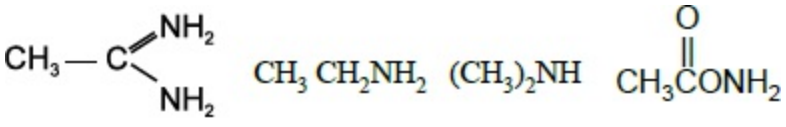
(b) a product with opposite optical rotation

(c) a mixture of diastereomeres

(d) a single stero isomers

22. The correct order of basicities of the following compounds is –

[IIT-2001]



1 2 3 4

(a) 2 > 1 > 3 > 4

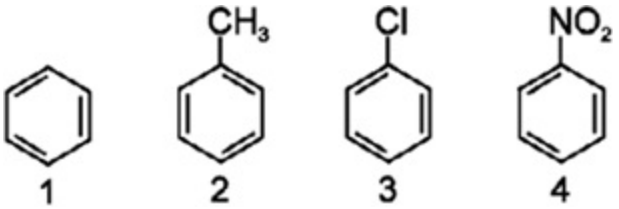
(b) 1 > 3 > 2 > 4

(c) 3 > 1 > 2 > 4

(d) 1 > 2 > 3 > 4

23. Identify the correct order of reactivity in electrophilic substitution reaction of the following compounds-

[IIT-2002]



(a) 1 > 2 > 3 > 4

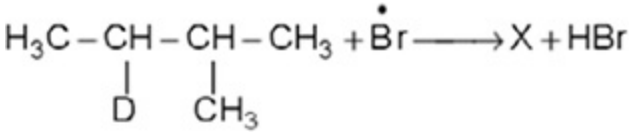
(b) 4 > 3 > 2 > 1

(c) 2 > 1 > 3 > 4

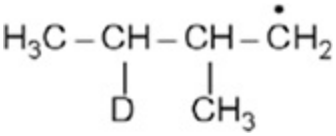
(d) 2 > 3 > 1 > 4

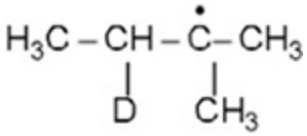
24. Consider the following reaction –

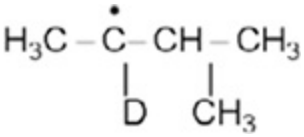
[IIT-2002]

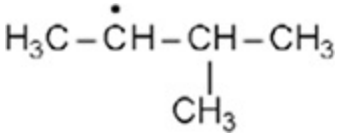


Indentify the structure of major product X

(a) 

(b) 

(c) 

(d) 

25. Left to right sp^2, sp^2, sp, sp hybridization is presnt in :

[IIT-2003]

(a) $H_2C = CH - C \equiv N$

(b) $H_2C = C = CH - CH_3$

(c) $HC \equiv C - C \equiv CH$

(d) $HC \equiv C - CH = CH_2$

26. Maximum dipole moment will be of :

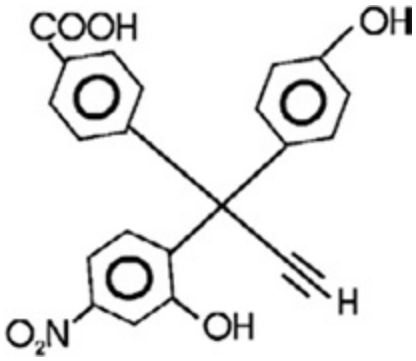
[IIT-2003]

(a) CCl_4

(b) $CHCl_3$

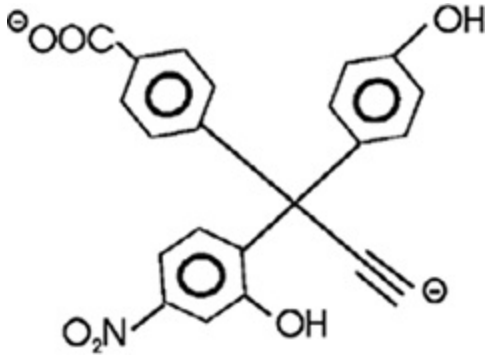
(c) CH_2Cl_2

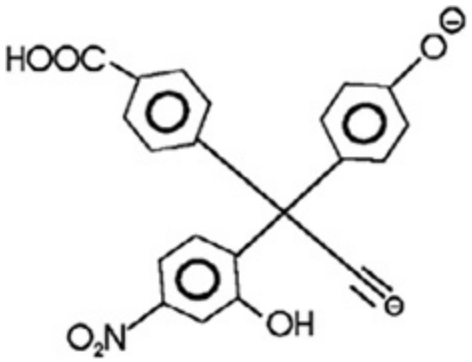
(d) CH_3Cl

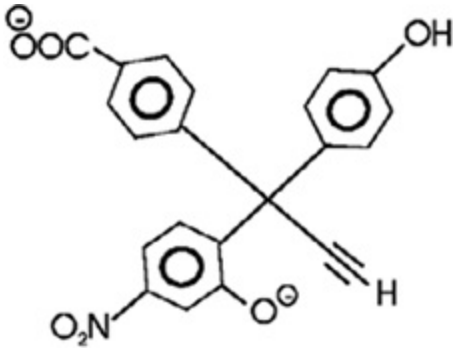
27. 

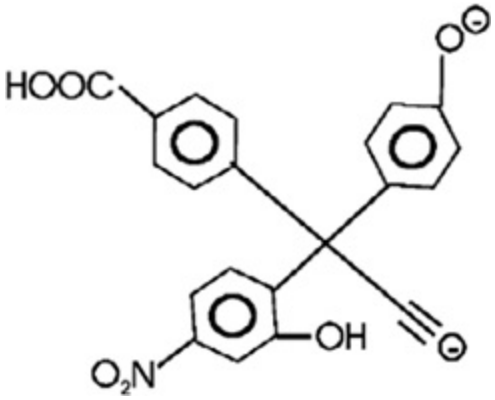
whenX is made to react with 2 eq. of$NaNH_2$ the product formed will be:

[IIT-2003]

(a) 

(b) 

(c) 

(d) 

28. Order of rate of reaction of following compound with phenyl magnesium bromide is :

[IIT-2004]

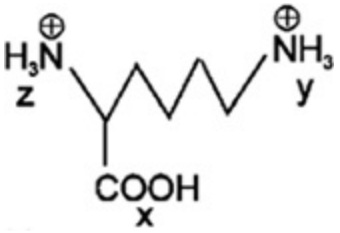
Ph - C - Ph	Me - C - H	Me - C - Me
‖	‖	‖
O	O	O
(I)	(II)	(III)

(a) I > II > III

(b) II > III > I

(c) III > I > II

(d) II > I > III

29. 

Correct order of acidic strength is :

[IIT-2004]

(a) x > y > z

(b) z > y > x

(c) y > z > x

(d) x > z > y

Alkane, Alkene, Alkye

1. Alcoholic solution of KOH is a specific reagent for –

[IIT Screening-90]

(a) Dehydration

(b) Dehydrogenation

(c) Dehydro halogenation

(d) Dehalogenation

2. Of the following, unsaturated hydrocarbons are –

[IIT-90]

(a) ethyne

(b) cyclohexane

(c) n-propane

(d) ethane

3. 1- chlorobutane on reaction with alcoholic potash gives –

[IIT-91]

(a) 1-butene

(b) 1-butanol

(c) 2-butene

(d) 2-butanol

4. The hybridisation of carbon atoms in C–C single bond of $HC \equiv C- CH = CH_2$ is –

[IIT-91]

(a) sp^3-sp^3

(b) sp^2-sp^3

(c) sp-sp^2

(d) sp^2-sp^2

5. The product(s) obtained via oxymercuation ($HgSO_4 + H_2SO_4$) of 1-butyne would be-

(a) $CH_3 - CH_2 - C - CH_3$

(b) $CH_3 - CH_2 - CH_2 - COOH$

(c) $CH_3 - CH_2 - CHO + HCHO$

(d) $CH_3 - CH_2 - COOH + HCOOH$

6. Which is the decreasing order of strength of bases : OH^-, NH_2^-, $HC \equiv C^-$ and $CH_3CH_2^-$?

(a) $CH_3CH_2^- > NH_2^- > HC \equiv C^- > OH^-$

(b) $HC \equiv C^- > CH_3CH_2^- > NH_2^- > OH^-$

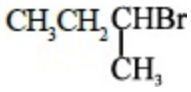
(c) $OH^- > NH_2^- > HC \equiv C^- > CH_3CH_2^-$

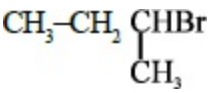
(d) $NH_2^- > HC \equiv C^- > OH^- > CH_3CH_2^-$

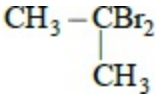
7. The chief reaction product of reaction between n-butane and bromine at 130°C is :

[IIT-95]

(a) $CH_3CH_2CH_2CH_2Br$

(b) 

(c) 

(d) 

8. $(CH_3)_3CMgCl$ on reaction with D_2O produces-

[IIT-97]

(a) $(CH_3)_3CD$

(b) $(CH_3)_3OD$

(c) $(cd_3)_3cd$

(d) $(cd_3)_3od$

9. When cyclohexane is poured on water, it floats, because –

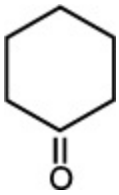
[IIT-97]

(a) Cyclohexand is in 'boat' form

(b) Cyclohexane is in 'chair' form

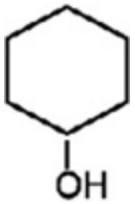
(c) Cyclohexane is in 'crown' form

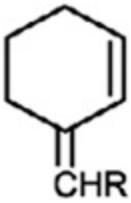
(d) Cyclohexane is less dense than water

10. When  reacts with, $Ph_3\overset{\oplus}{P} - \overset{\ominus}{C}HR$ the product is

[IIT-97]

(a) 

(b) 

(c) 

(d) 

11. Read the following statement and explanation and answer as per the

option given below :

[IIT-98]

Assertion : Addition of Br_2 to 1-butene gives two optical isomers.

Reason : The product contains one asymmetric carbon.

(a) If both assertion and reason are correct, and reason is the correct explanation of the assertion

(b) If both assertion and reason are correct, but reason is not correct explanation of the assertion

(c) If assertion is correct but reason is incorrect

(d) If assertion is incorrect but reason is correct

12. Which of the following compounds will show geometrical isomerism ?

[IIT-98]

(a) butane

(b) Propene

(c) 1-phenylpropene

(d) 2-methyl-2-butene

13. In the compound $CH_2 = CH - CH_2 - CH_2 - C \equiv CH$, the $C_2 - C_3$ bond is of the type –

[IIT-99]

(a) $sp - sp^2$

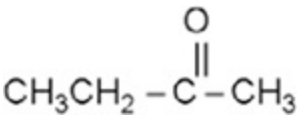
(b) $sp^3 - sp^3$

(c) $sp - sp^3$

(d) $sp^2 - sp^3$

14. The product(s) obtained via oxymercuration ($HgSO_4$+H_2SO_4) of 1 – butyne would give-

[IIT-99]

(a) 

(b) $CH_3CH_2CH_2$-CHO

(c) $CH_3CH_2CHO + HCHO$

(d) $CH_3CH_2COOH + HCOOH$

15. Read the following statement and explanation and answer as per the option given below :

[IIT-2000]

Assertion : 1 –Butene on reaction with HBr in the presence of a peroxide produces 1 –bromobutane
Reason : It involves the formation of a primary radical

(a) If both assertion and reason are correct, and reason is the correct explanation of the assertion

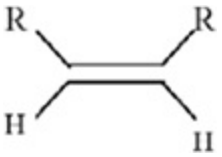
(b) If both assertion and reason are correct, but reason is not correct explanation of the assertion

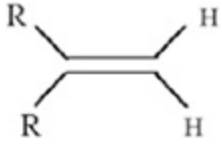
(c) If assertion is correct but reason is incorrect

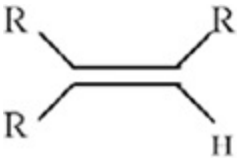
(d) If assertion is incorrect but reason is correct

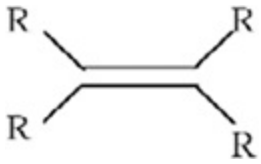
16. Which one of the following alkenes will react fastest with H_2 under catalytic hydrogenation condition

[IIT-2000]

(a) 

(b) 

(c) 

(d) 

17. Propyne and propene can be distinguished by –

[IIT-2000]

(a) conc. H_2SO_4

(b) Br_2 in CCl_4

(c) dil. $KMnO_4$

(d) $AgNO_3$ in ammonia

18. Read the following statement and explanation and answer as per the option given below :

[IIT-2001]

Assertion : Addition of bromine to trans-2-butene yields meso-2,3-dibromobutane

Reason : Bromine addition to an alkene is an electrophilic addition

(a) If both assertion and reason are correct, and reason is the correct explanation of the assertion

(b) If both assertion and reason are correct, but reason is not correct explanation of the assertion

(c) If assertion is correct but reason is incorrect

(d) If assertion is incorrect but reason is correct

19. In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti- Markovnikov addition to alkene because.

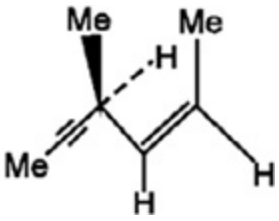
[IIT Screening-2001]

(a) both are highly ionic

(b) one is oxidising and the other is reducing

(c) one of the step is endothermic ion both the cases

(d) all the steps are exothermic in both cases.

20. 

Hydrogenation of the above compound in the presence of poisoned pallodium catalyst gives.

[IIT Screening-2001]

(a) An optically active compound

(b) An optically inactive compound

(c) A racemic mixture

(d) A diastereomeric mixture.

21. The reaction of propene with HoCl proceeds via the addition of –

[IIT Screening-2001]

(a) H^+ in first step

(b) Cl^+ in first step

(c) OH^- in first step

(d) Cl^+ and OH^- in single step

22. The nodal plane in the π -bond of ethene is located in –

[IIT Screening-2002]

(a) the molecular plane

(b) a plane parallel to the molecular plane

(c) a plane perpendicular to the molecular plane which contains the carbon –Carbon σ -bond at right angle

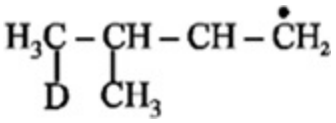
(d) a plane perpendicular to the molecular plane which contains the carboN–Carbon σ -bond

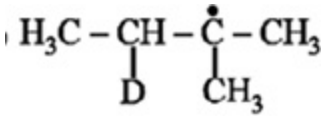
23. Consider the following reactions –

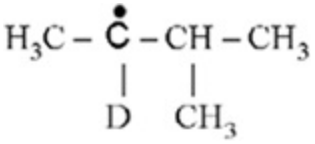
[IIT Screening-2002]

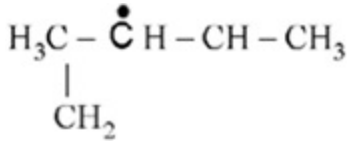
$$H_3C-\underset{D}{CH}-\underset{CH_3}{CH}-CH_3 + \dot{B}r \rightarrow 'X' + HBr$$

Identify the structure of the major product 'X'

(a) 

(b) 

(c) 

(d) 

24. Identify a reagent from the following list which can easily distinguish between 1-butyne and 2-butyne

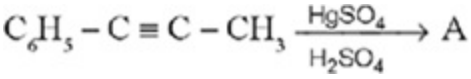
[IIT Screening-2002]

(a) bromine, CCl_4

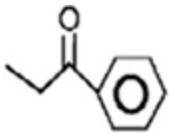
(b) H_2, Lindlar catalyst

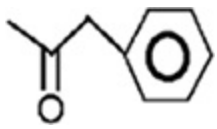
(c) dilute H_2SO_4, $HgSO_4$

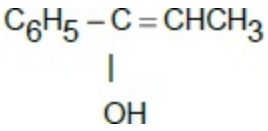
(d) ammoniacal Cu_2Cl_2 solution

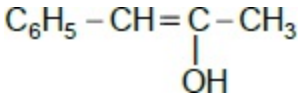
25. 

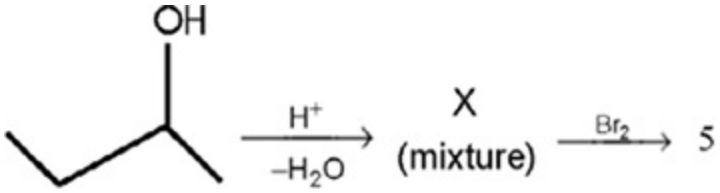
[IIT Screening-2003]

(a) 

(b) 

(c) 

(d) 

26.  compounds of molecular formula $C_4H_gBr_2$. No. of compounds in X will be :

[IIT Screening-2003]

(a) 2

(b) 3

(c) 4

(d) 5

27. 2–Hexyne can be converted into trans-2–Hexene by the action of :

[IIT Screening-2004]

(a) H_2-Pd-$BaSO_4$

(b) Li in Liquid NH_3

(c) H_2-PtO_2

(d) $NaBH_4$

28. On monochlorination 2-methyl butane , how many chiral compounds are formed

[IIT Screening-2004]

(a) 2

(b) 4

(c) 6

(d) 8

Alcohol? Ether and phenol

1. The products of combustion of an aliphatic thiol (RSH) at 298 K are –

[IIT-92]

$CO_2(\ell)$, H_2O (g) and SO_2 (g)

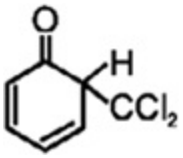
CO_2(g), H_2O (g) and SO_2 (g)

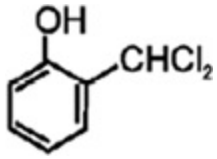
$CO_2(\ell)$, H_2O (ℓ) and SO_2 (g)

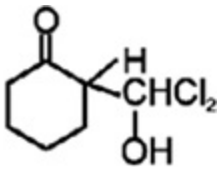
CO_2(g), H_2O (ℓ) and SO_2 (ℓ)

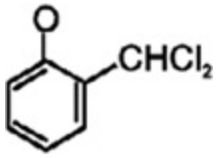
2. When phenol is reacted with $CHCl_3$ and NaOH followed by acidification, salicyladehyde is obtained which of the following species are involved in the above mentioned reaction as intermediates ?

[IIT-95]

(a) 

(b) 

(c) 

(d) 

3. An organic compound C_3H_6O does not give a precipitate with 2,4-dinitrophenyl hydrazine reagent and does not react with sodium metal. It could be –

[IIT-93]

(a) $CH_3 - CH_2 - CHO$

(b) $CH_3 - CO - CH_3$

(c) $CH_2 = CH - CH_2OH$

(d) $CH_2 = CH - OCH_3$

4. The reaction products of, $C_6H_5OCH_3 + HI \xrightarrow{\Delta}$ are –

[IIT-95]

(a)$C_6H_5OH + CH_3I$

(b)CIii + CH_3OH

(c) $C_6FLCH_3 + HOI$

(d)$C_6H_6 + CH_3OI$

5. The order of reactivity of the following alcohols –

[IIT-97]

(I) (II) (III) (IV)

towards conc. HCI is :

(a) I > II > III > IV

(b) I > III > II > IV

(c) IV > III > II > I

(d) IV > III > I > II

6. Among the following compounds , the strongest acid is –

[IIT-98]

(a) HC ≡ CH

(b) C_6H_6

(c) C_2H_6

(d) CH_3OH

7. Benzenediazonium chloride on reaction with phenol in weakly basic medium gives –

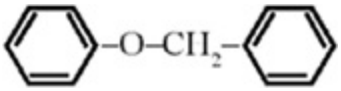
[IIT-98]

(a) Diphenyl ether

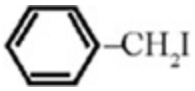
(b) p–Hydoroxyazobenzene

(c) Chlorobenzene

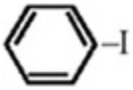
(d) Benzene

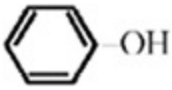
8. The ether  when treated with HI produces

[IIT-99]

(a) 

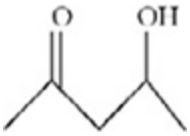
(b) 

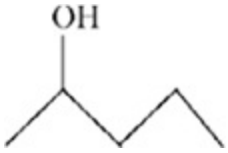
(c) 

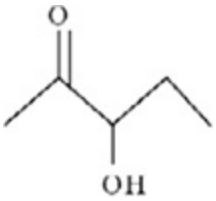
(d) 

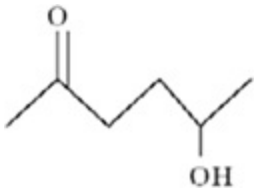
9. Which one of the following will most readily be dehydrated in acidic condition –

[IIT-2000]

(a) 

(b) 

(c) 

(d) 

10. 1-propanol & 2-propanal can be best distinguished by –

[IIT-2001]

(a) Oxidation with alkaline $KMnO_4$ followed by reaction with Fehling

solution

(b) Oxidation with acedic dichromate followed by reaction with Fehling solution

(c) Oxidation by heating with copper followed by reaction with Fehling solution

(d) Oxidation with cocentrated H_2SO_4 followed by reaction with Feheling

11. Identify the corect order of boiling point of the following compounds –

[IIT-2002]

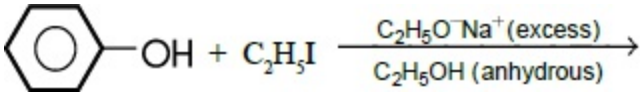
$\underset{1}{CH_3CH_2CH_2CH_2OH}$ $\underset{2}{CH_3CH_2CH_2CHO}$ $\underset{3}{CH_3CH_2CH_2COOH}$

(a) 1 > 2 > 3

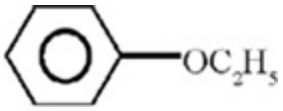
(b) 3 > 1 > 2

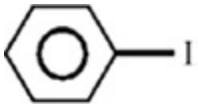
(c) 1 > 3 > 2

(d) 3 > 2 > 1

12. 

[IIT-2003]

(a) 

(b) 

(c) $C_6H_5OC_6H_5$

(d) $C_2H_5OC_2H_5$

13. Reaction of entainomerically pure acid with 1 chiral carbon and racemic alcohol with 1 chiral carbon gives an ester which is :

[IIT-2003]

(a) Meso

(b) Opticaly active

(c) Recemic mixure

(d) Enantionmerically pure

14. On acid catalysed hydration, 2-phenyl propene gives:

[IIT-2004]

(a) 3-phenyl-2-propanol

(b) 2-phenyl-1-propanol

(c) 1-phenyl-3-propanol

(d) 2-phenyl-2-propanol

15. Conversion of cyclohexanol into cyclohexene is most effective in

[IIT-2005]

(a) concentrated H_3PO_4

(b) concentrated HCl

(c) concentrated HCl / $ZnCl_2$

(d) concentrated HBr

–Aromatic compounds

1. The chlorination of toluene in presence of ferric chloride gives predominantly –

(IIT –1986)

(a) Benzyl chloride

(b) m-chlorotoluene

(c) Benzal chloride

(d) o-and- p-chlorotoluene

2. Aryl halides are less reactive towards nucleophilic substituion reaction as compared to alkyl halides due to-

[IIT-90]

(a) The formation of less stable carbonium ion

(b) Resonance stabilization

(c) Longer carbon – halogen bond

(d) The inductive effect

3. The most basic compound among the following is –

[IIT-90]

(a) Benzylamine

(b) Aniline

(c) Acetanilide

(d) p–Nitro aniline

4. Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives

[IIT-90]

(a) o-cresol

(b) p-cresol

(c) 2,4-dihydroxytoluene

(d) Benzoic acid

5. When nitrobenzene is treated with Br_2 in presence of $FeBr_3$ the maj or product formed is m-bromonitrobenzene. Statement which is related obtain the m-isomer is –

[IIT-92]

(a) The electron density on meta carbon is more than on ortho and para position.

(b) The intermediate carbonium ion formed after initial attack of Br+ attack the meta position is most destabilized

(c) Loss of aromaticity when Br+ attcks at the ortho and para positions and not at meta position.

(d) Easier loss of H+ to regain aromaticity from ortho and para positions than from meta positiion.

7. The maj or product of nitration of benzoic acid is –

[IIT-93]

(a) 3- nitrobenzoic acid

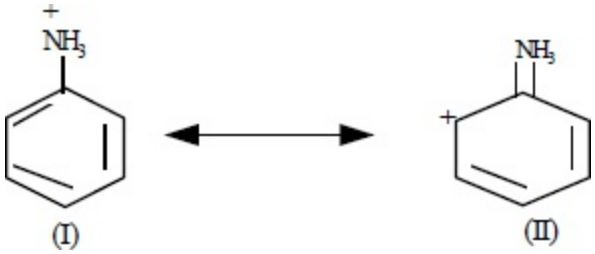
(b) 4- nitrobenzoic acid

(c) 2- nitrobenzoic acid

(d) 2,4- dinitrobenzoic acid

6. Choose the correct statement from the ones given below for two anilium in –

[IIT-93]



(a) II is not an acceptable canonical structure because carbonium ions

are less stable than ammonium ions

(b) II is not an acceptable canonical structure because it is non aromatic

(c) II is not an acceptable canonical structure because the nitrogen has 10 valence electrons

(d) II is an acceptable canonical structure

7. The major product of nitration of benzoic acid is –

(a) 3- nitrobenzoic acid

(b) 4- nitrobenzoic acid

(c) 2- nitrobenzoic acid

(d) 2,4- dinitrobenzoic acid

8. Most stable carbonium ion is –

[IIT-95]

(a) $p–NO_2 – C_6H_4 – {}^+CH_2$

(b) $C_6H_5{}^+CH_2$

(c) $p\text{-}Cl – C_6H_4 – {}^+CH_2$

(d) $p\text{-}CH_3O – C_6H_4 – {}^+CH_2$

9. Among the following statements on the nitration of aromatic compounds, the false one is –

[IIT-97]

(a) The rate of nitration of benzene is almost the same as that of hexadeuterobenzene

(b) The rate of nitration of toluene is greater than that of benzene

(c) The rate of nitration of benzene is greater than that of hexadeuterobenzene

(d) Nitration is an electrophilic substitution reaction

10. Arrange in order of decreasing trend towards S_E reactions,

Chlorobenzene ,	Benzene,	Aniline chloride,	Toluene
I	II	III	IV

[IIT-95]

(a) II > I > III > IV

(b) III > I > II > IV

(c) IV > II > I > III

(d) I > II > III > IV

11. Benzyl chloride ($C_6H_5CH_2Cl$) can be prepared from toluene by chlorination with –

(IIT-1998)

(a) SO_2Cl_2 hu

(b) $SOCl_2$

(c) PCl_5

(d) NaOCl

12. Nitrobenzene can be prepared from benzene by using a mixture of conc HNO_3 and conc. H_2SO_4. In the nitrating mixture HNO_3 acts as a –

[IIT-97]

(a) Base

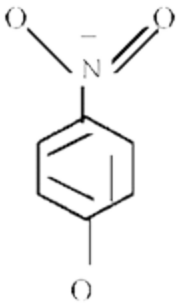
(b) Acid

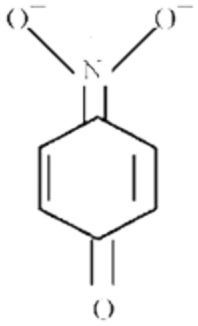
(c) Reducing agent

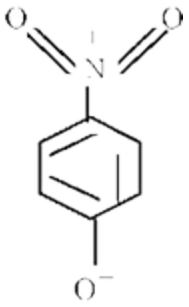
(d) Catalyst

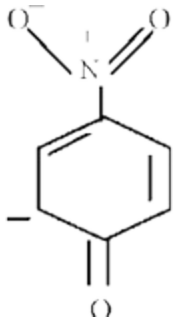
13. The most unlikely representation of resonace structure of p–Nitrophenoxide ion is –

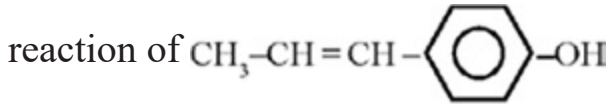
(IIT-1998)

(a) 

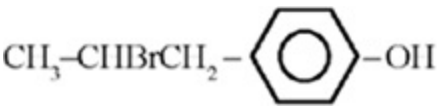
(b) 

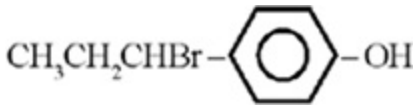
(c) 

(d) 

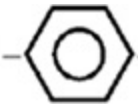
14. The reaction of  with HBr gives.

(IIT –1998)

(a) 

(b) 

(c) $CH_3CHBrCH_2$ –  – Br

(d) CH_3CH_2CHBr –  –Br

15. A new C – C bond is formed in

(IIT –98)

(a) Cannizzaro's reaction

(b) Friedel Crafts reaction

(c) Both (a) & (b)

(d) None of these

16. A solution of (+) – 2 – chloro-2-phenylethane in toluene racemises slowly in the presence of small amount of $SbCl_5$, due to the formation of –

(IIT-99)

(a) Carbanion

(b) Carbene

(c) Free–Radical

(d) Carbocation

17. Amongst the following the strongest base is –

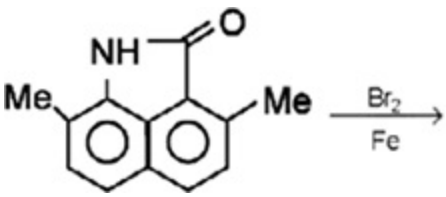
(IIT-2000)

(a) $C_6H_5NH_2$

(b) p-$O_2NC_6H_4NH_2$

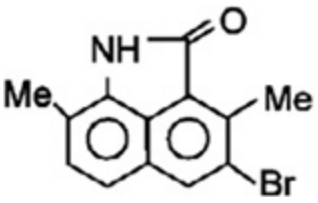
(c) m-$O_2NC_6H_4NH_2$

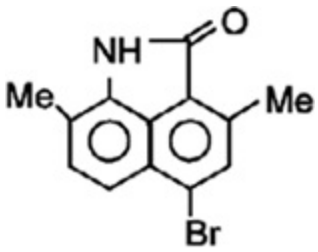
(d) $C_6H_5CH_2NH$

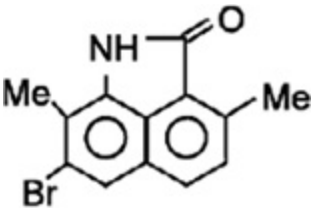
18. 

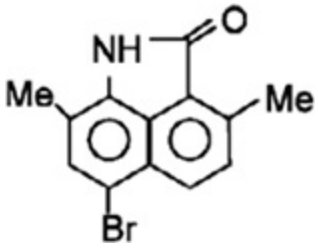
Major product of above reaction is :

(IIT-2004)

(a) 

(b) 

(c) 

(d) 

Alkyl and aryl halides

1. Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives

[IIT-90]

(a) o-cresol

(b) p-cresol

(c) 2,4-dihydroxytoluene

(d) Benzoic acid

2. Aryl halides are less reactive towards nucleophilic substituion reaction as compared to alkyl halides due to-

[IIT-90]

(a) The formation of less stable carbonium ion

(b) Resonance stabilization

(c) The inductive effect

(d) sp^2 hybridised carbon attached to the halogen.

3. 1–Chlorobutane on reaction with alcoholic potash gives –

[IIT-91]

(a) 1-butene

(b) 1-butanol

(c) 2-butene

(d) 2-butanol

4. The products of reaction of alcoholic silver nitrite with ethyl bromide are –

[IIT-91]

(a) Ethane

(b) methyl nitrite

(c) Nitroethane

(d) Ethyl alcohol

5. In the addition of HBr to propene in the absence of peroxides, the first step involves the addition of –

(IIT –93)

(a)H^+

(b)Br

(c) H"

(d) Br*

6. Arrange the following compounds in order of increasing dipole moment

[IIT-96]

Toluene	m- dichlorobenzene	o- dichlorobenzene	p-dichlorobenzene
I	II	III	IV

(a) I < IV < II < III

(b) IV < I < II < III

(c) IV < I < III < II

(d) IV < II < I < III

7. In the reaction of p-chloro toluene with KNH_2 in liq. NH_3, the major product is –

(IIT-1997)

(a) o-toluidine

(b) m-toluidine

(c) m-chloroaniline

(d) p-chloraniline

8. $(CH_3)_3CMgCl$ reaction with D_2O produces –

(IIT-1997)

(a) $(CH_3)_3CD$

(b) $(CH_3)_3OD$

(c) $(CD_3)_3CD$

(d) $(CH_3)_3OD$

9. The intermediate during the addition of HCl to propene in presence of peroxide is –

(IIT-1997)

(a) $CH_3\dot{C}HCH_2Cl$

(b) $CH_3\overset{+}{C}HCH_3$

(c) $CH_3\dot{C}HCH_2$

(d) $CH_3CH_2\dot{C}H_2$

10. The number of possible enantiomeric paris that can be produced during monochlorination of 2-methylbutane is-

(IIT-1997)

(a) 2

(b) 3

(c) 4

(d) 1

11. During debromination of meso-dibromobutane, the major compound formed is –

(IIT-1997)

(a) n-butane

(b) 1-butene

(c) cis-2-butene

(d) trans –2-butene

12. Which of the following react with water ?

(IIT-1998)

(a) $CHCl_3$

(b) Cl_3CCHO

(c) CCl_4

(d) $ClCH_2CH_2Cl$

13. Benzyl chloride ($C_6H_5CH_2Cl$) can be prepared from toluene by chlorination with –

(IIT-1998)

(a) SO_2Cl_2

(b) $SOCl_2$

(c) PCl_5

(d) NaOCl

14. Toluene , when treated with Br_2/Fe, gives p-bromotoluene as the major product, because the CH_3 group-

(IIT-1999)

(a) is para directing

(b) is meta directing

(c) deactivates the ring by hyperconjugation

(d) deactivates the ring.

15. $SbCl_5$ due to the formation of-

(IIT-99)

(a) Carbanion

(b) Carbene

(c) Free–Radical

(d) Carbocation

16. The order of reactivity of the following alkyl halides for a SN^2 reaction is –

(IIT-2000)

(a) R F > RCl > R-Br > R-I

(b) R-F > R-Br > R-Cl > R-I

(c) R-Cl > R-Br > RF > RI

(d) R-I > R Br > R-Cl > R-F

17. Which of the following has the highest nucleophilicity ?

(IIT-2000)

(a)F^-

(b)OH^-

(c) CH_3^-

(d) NH_2^-

18. The reaction of propene with HOCl proceeds through the addition of –

(IIT-2001)

(a) H^+ in the first step

(b) Cl^+ in the first step

(c) OH^- in the first step

(d) Cl^+ and OH^- in a singly step

19. An S_{N^2} reaction at an asymmetric carbon of a compound always gives-

(IIT-2001)

(a) an enantiomer of the substrate

(b) a product with opposite optical rotation

(c) A mixture of diastereomers

(d) a single stereoisomer

20. The number of isomers for the compound with molecular formula C_2BrCl FI is –

(IIT-2001)

(a) 3

(b) 4

(c) 5

(d) 6

21. In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markovnikov's addition to alkenes because

(IIT-2001)

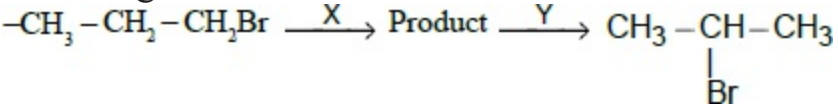
(a) both are highly ionic

(b) one is oxidising and the other is reducing

(c) one of the steps is endothermic in both the cases

(d) all the steps are exothermic in both the reactions.

22. Identify the set of reagents/ reaction conditions 'X' and 'Y' in the following set of transformations



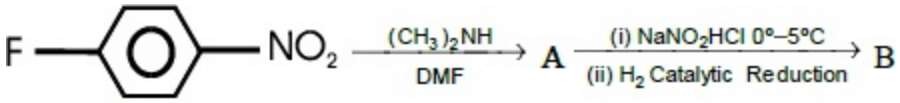
[IIT-2002]

(a) X = dilute aqueous NaOH, 20°C ; Y = HBr / acetic acid, 20°C

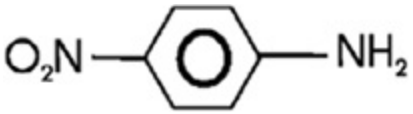
(b) X = concentrated alcoholic NaOH, 80°C ; Y = HBr / acetic acid, 20°

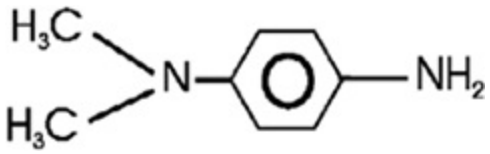
(c) X = dilute aqueous NaOH, 20°C ; Y = Br_2/ $CHCl_3$, 0°C

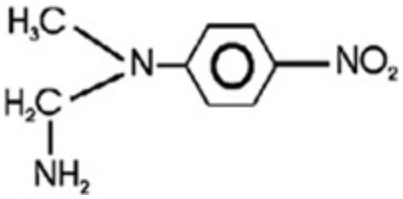
(d) X = concentrated alcoholic NaOH, 80°C ; Y = Br_2/$CHCl_3$, 0°C

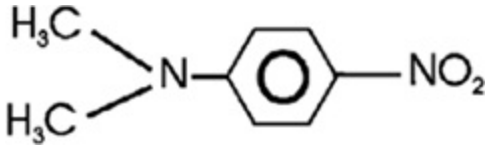
23. 

[IIT-2003]

(a) 

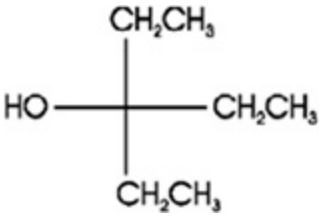
(b) 

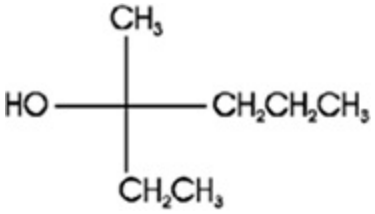
(c) 

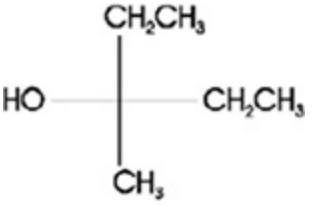
(d) 

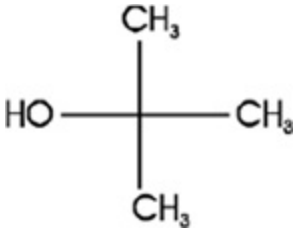
24. CH_3Mg Br + Ethyl ester $\rightarrow$ which can be formed as product.
(excess)

[IIT-2003]

(a) 

(b) 

(c) 

(d) 

Carboxylic acid and its derivatives

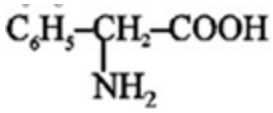
1. Which of the following carboxylic acids undergo decarboxylation easily –

[IIT-95]

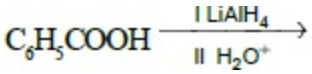
(a) $C_6H_5CO–CH_2COOH$

(b) $C_6H_5COCOOH$

(c) C_6H_5 – COOH

(d) 

2. The organic product formed in the reaction



[IIT-95]

(a) $C_6H_5CH_2OH$

(b) C_6H_5COOH & CH_4

(c) $C_6H_5CH_3$ & CH_3OH

(d) $C_6H_5CH_3$ & CH_4

3. The major product of nitration of Benzoic acid is –

[IIT-93]

(a) 3–Nitrobenzoic acid

(b) 4–Nitrobenzoic acid

(c) 2–Nitrobenzoic acid

(d) 2,4-Dinitrobenzoic acid

4. The molecular weight of benzoic acid ;in benzene as determined by depression in freezing point method corresponds to –

[IIT-96]

(a) Ionization of benzoic acid

(b) Dimerisation of benzoic acid

(c) Trimerisation of benzoic acid

(d) Solvation of benzoic acid

5. $CH_3CH_2COOH \xrightarrow[\text{Red P}]{Br_2} X \xrightarrow{NH_3(alc.)} Y$ Y in the above reactions is-

[IIT-96]

(a) Lactic acid

(b) Ethylamine

(c) Propylamine

(d) Alanine

6. Among the given compounds, the most susceptible to nucleophilic attack at the carbonyl group is –

(IIT-1997)

(a) MeCOCl

(b) MeCHO

(c) MeCOOMe

(d) MeCOOCOMe.

7. Read the following statement and explanation and answer as per the option given below :

(IIT- 1998)

Assertion : Acetic acid does not undergo haloform reaction.

Reason : Acetic acid has no alpha hydrogens

(a) If both assertion and reason are correct, and reason is the correct explanation of the assertion

(b) If both assertion and reason are correct, but reason is not correct explanation of the assertion

(c) If assertion is correct but reason is incorrect

(d) If assertion is incorrect but reason is correct

8. When propionic acid is treated with aqueous $NaHCO_3$, CO_2 is librated. The 'C' of CO_2 comes from –

(IIT-1999)

(a) Methyl group

(b) Carboxylic acid group

(c) methylene group

(d) bicarbonate

9. Benzoyl chloride is prepared from benzoic acid by –

(IIT- 2000)

(a) Cl_2, h**v**

(b) SO_2Cl_2

(c) $SOCl_2$

(d) Cl_2, H_2O

10. Which of the following acids has the smallest dissociation constant ?

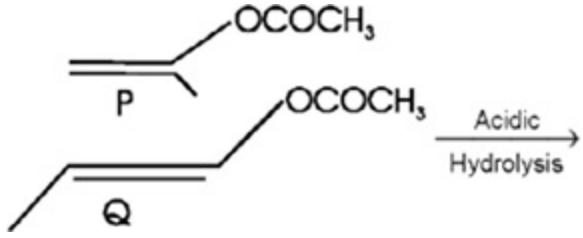
(IIT- 2002)

(a) $CH_3CHFCOOH$

(b) FCH_2H_2COOH

(c) $BrCH_2CH_2COOH$

(d) $CH_3CHBrCOOH$

11. 

Products formed by P & Q can be differentiated by

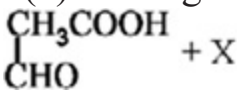
(IIT- 2003)

(a) 2 & 4 DNP

(b) Lucas reagent ($ZnCl_2$) conc. HCl

(c) $NaHSO_3$

(d) Fehlings solution

12.  + X

(IIT- 2005)

(a) CH_3COOH

(b) $BrCH_2 – COOH$

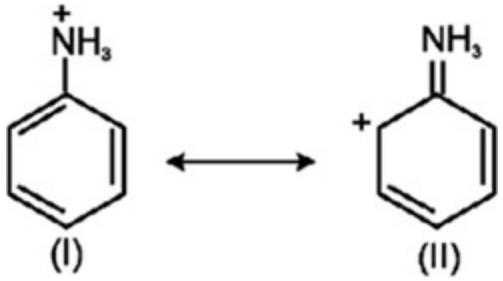
(c) $COOH\ (CH_3CO)_2O$

(d) $(CH_3CO)_2O$

Nitro and amines

1. Examine the following two structures for the anilinium ion and choose the correct statement from the ones given below

(IIT. 1993)



(a) II is not an acceptable canonical structure because carbonium ions are less stable than ammonium ions

(b) II is not an acceptable canonical structure because it is non-aromatic

(c) II is not an acceptable canonical sturcture because the nitrogen has ten valence electrons

(d) Both (a) & (c)

2. Read the following statement and explanation and answer as per the option given below :

(IIT- 1998)

Assertion : Benzonitrile is prepared by the raction of chlorobenzene with potassium cyanide

Reason : Cyanide (CN^-) is a strong nucleophile

(a) If both assertion and reason are correct, and reason is the correct explanation of the assertion

(b) If both assertion and reason are correct, but reason is not correct explanation of the assertion

(c) If assertion is correct but reason is incorrect

(d) If assertion is incorrect but reason is correct

(e)

3. Among the following compounds, which will react with acetone to give a product containing > C=N – ?

(IIT. 1998)

(a) $C_6H_5NH_2$

(b) $(CH_3)_3$ N

(c) $C_6H_5NHC_6H_5$

(d) $C_6H_5NHNH_2$

4. p-Chloroaniline and anilinium hydrochloride can not be distinguished by

(IIT. 1998)

(a) Sandmeyer reaction

(b) $NaHCO_3$

(c) $AgNO_3$

(d) Carbylamine test

5. A positive carbylamine test is given by

(IIT. 1999)

(a) N, N-Dimethylaniline

(b) 2,4 –Dimethylaniline

(c) N- Methyl-o-methylaniline

(d) o-Methylbenzylamine

6. Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and conc. H_2SO_4. In the nitrating mixture, nitric acid acts as a

(IIT. 1997)

(a) base

(b) acid

(c) reducing agent

(d) catalyst.

7. Allyl isocyanide contains σ and π bonds, as-

(IIT. 1995)

(a) 9 σ and 3 π

(b) 9 σ and 9 π

(c) 3 σ and 4 π

(d) 5 σ and 7 π

8. Among following statements on the nitration of aromatic compounds, the false one is-

(IIT. 1997)

(a) the rate of nitration of benzene is almost the same as that of hexadeuterobenzene

(b) the rate of nitration of toluene is greater than that of benzene

(c) the rate of nitration of benzene is greater than that of hexadeuterobenzene

(d) nitration is an electrophilic substitution reaction.

9. Benzenediazonium chloride on reaction with phenol in weakly basic medium gives-

(IIT. 1998)

(a) Diphenyl ether

(b) p–Hydroxyazobenzene

(c) Chlorobenzene

(d) Benzene

10. Among the following, the strongest base is-

(IIT. 2000)

(a) $C_6H_5NH_2$

(b) p–NO_2-$C_6H_4NH_2$

(c) m–NO_2-$C_6H_4NH_2$

(d) $C_6H_5CH_2NH_2$

11. Read the following statement and explanation and answer as per the option given below :

(IIT- 2001)

Assertion : In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagents.

Reason : The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance.

(a) If both assertion and reason are correct, and reason is the correct explanation of the assertion

(b) If both assertion and reason are correct, but reason is not correct explanation of the assertion

(c) If assertion is correct but reason is incorrect

(d) If assertion is incorrect but reason is correct

(e)

12. The compound that will react most readily with NaOH to form methanol is

(IIT. 2001)

(a) $(CH_3)_4N^+I^-$

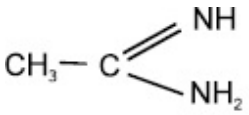
(b) CH_3OCH_3

(c) $(CH_3)_3S^+I^-$

(d) $(CH_3)_3CCl$

13. The correct order of basicities of the following compounds is

(IIT. 2001)



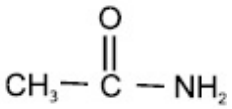
(1)

$CH_3CH_2NH_2$

(2)

$(CH_3)_2NH$

(3)



(4)

(a) 2 > 1 > 3 > 4

(b) 1 > 3 > 2 > 4

(c) 3 > 1 > 2 > 4

(d) 1 > 2 > 3 > 4

14. When benzamide is treated with $POCl_3$, the product formed is :

(IIT. 2004)

(a) Benzonitrile

(b) Aniline

(c) Chlorobenzene

(d) Benzylamine

15. On heating $(NH_4)_2\ C_2O_7$. $\rightarrow$ gas evolved is 'X'. In which of the following cases the same gas 'X' will be evolved

(IIT. 2004)

(a) NH_4NO_2

(b) NH_4NO_3

(c) $Mg_3N_2 + H_2O$

(d) $Na_2O_2 + H_2O$

Carbonyl Compounds

1. The formation of cyanohydrin from a ketone is an example of –

[IIT-90]

(a) Electrophilic addition

(b) Nucleophilic addition

(c) Nucleophilic substitution.

(d) Electrophilic substitution.

2. The enolic form of acetone contains –

(a) 9 sigma bonds, 1 pi bond and 2 lone pairs

(b) 8 sigma bonds, 2 pi bonds and 2 lone pairs

(c) 10 sigma bonds, 1 pi bond and 1lone pair

(d) 9 sigma bonds, 2 pi bonds and 1 lone pair

3. m-chlorobenzaldehyde on reaction with conc. KOH at room temperature gives –

[IIT-91]

(a) Potassium m-chlorobenzoate and m–Hydroxybenzaldehyde

(b) m–Hydroxy benzaldehyde and m-chlorobenzyl alcohol

(c) m-chlorobenzyl and m–Hydroxybenzyl alcohol.

(d) Potassium m-chlorobenzoate and m–Hydroxybenzyl alcohol.

4. Hydrogenation of benzoyl chloride in the presence of Pd on $BaSO_4$ gives –

[IIT-92]

(a) Benzyl alcohol

(b) Benzaldehyde

(c) Benzoic acid

(d) Phenol

6. Under Wolff Kishner reduction conditions, the conversions which may be brought about is ?

(IIT- 1995)

(a) Benzaldehyde into Benzyl alcohol

(b) Cyclohexanol into Cyclohexane

(c) Cyclohexanone into Cyclohexanol

(d) Benzophenone into Diphenylmethane

6. An organic compound C_3H_6O does not give a precipitate with 2,4-Dinitrophenyl hydrazine reagent and does not react with metallic sodium. It could be –

[IIT-93]

(a) CH_3CH_2CHO

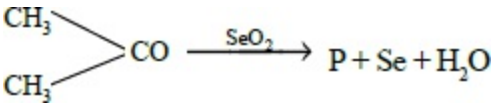
(b) CH_3COCH_3

(c) $CH_2 = CH - CH_2\,OH$

(d) $CH_2{=}CH - O - CH_3$

7. In the reaction , P is –

(IIT- 1995)



(a) CH_3COCHO

(b) CH_3COOCH_3

(c) CH_3COCH_2OH

(d) None

8. In the Cannizzaro reaction given below, $2Ph\text{-}CHO \xrightarrow{OH^-} Ph - CH_2OH + PhCO_2^-$ the slowest step is –

[IIT-96]

(a) the attack of OH^- at the carbonyl group

(b) the transfer of hydride to the carbonyl group

(c) the abstraction of proton from the carboxylic acid

(d) the deprotonation of Ph – CH_2OH

9. Which of the following will give yellow precipitate with I_2/NaOH ?

(IIT-1997)

(a) $ICH_2COCH_2CH_3$

(b) $CH_3COOCOCH_3$

(c) CH_3CONH_2

(d) $CH_3CH(OH)CH_2CH_3$

10. Among the given compounds, the most susceptible to nucleophilic attack at the carbonyl group is

(IIT-1997)

(a) MeCOCl

(b) MeCHO

(c) MeCOOMe

(d) MeCOOCOMe

11. $CH_3CHO + H_2NOH \rightarrow CH_3 - CH = N - OH$ .The above reaction occurs at –

(IIT- 1997)

(a) pH = 1

(b) pH = 4.5

(c) Any value of pH

(d) pH = 12

12. Among the following compounds, which will react with acetone to give a product containing >C=N–

[IIT-98]

(a) $C_6H_5NH_2$

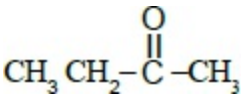
(b) $(CH_3)_3N$

(c) $C_6H_5NHC_6H_5$

(d) $C_6H_5NHNH_2$

13. The product obtained via oxymercuration ($HgSO_4 - H_2SO_4$) of 1-butyne would be –

[IIT-98]

(a) 

(b) $CH_3CH_2CH_2CHO$

(c) $CH_3CH_2CHO + HCHO$

(d) $CH_3CH_2COOH + HCOOH$

14. Which of the following will not undergo aldol condensation –

[IIT-98]

(a) Acetaldehyde

(b) Propanaldehyde

(c) Benzaldehyde

(d) Trideutero acetaldehyde

15. Which of the following will react with water –

[IIT-98]

(a) $CHCl_3$

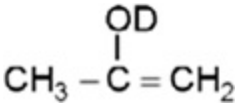
(b) Cl_3CCHO

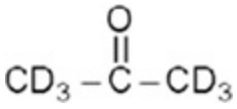
(c) CCl_4

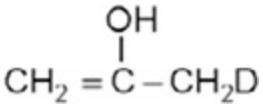
(d) $ClCH_2CH_2Cl$

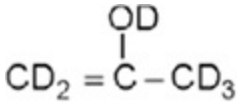
16. The enol form of acetone, after treatment with D_2O gives –

[IIT-99]

(a) 

(b) 

(c) 

(d) 

17. Which of the following has the most acidic hydrogen –

[IIT-2000]

(a) 3–Hexanone

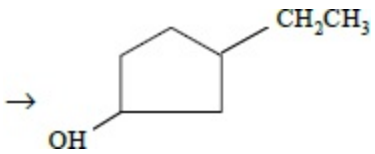
(b) 2,4–Hexanedione

(c) 2,5–Hexanedione

(d) 2,3–Hexandione

18. The appropriate reagent for the following transformation –

[IIT-2000]



(a) Zn (Hg), HCl

(b) NH_2NH_2, OH"

(c) H_2/Ni

(d) $NaBH_4$

19. Read the following statement and explanation and answer as per the option given below :

(IIT-2001)

Assertion : Dimethylsulphide is commonly used for the reduction of an ozonide of an alkene to get the carbonyl compounds

Reason : It reduces the ozonide giving water soluble dimethyl sulphoxide and excess of it evaporates.

(a) If both assertion and reason are correct, and reason is the correct explanation of the assertion

(b) If both assertion and reason are correct, but reason is not correct explanation of the assertion

(c) If assertion is correct but reason is incorrect

(d) If assertion is incorrect but reason is correct

20. A mixture of benzladehyde and formaldehyde on heating with aqueous NaOH solution gives –

[IIT-2001]

(a) benzyl alcohol and sodium formate

(b) sodium benzoate and methyl alcohol

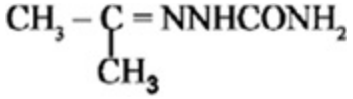
(c) sodium benzoate and sodium formate

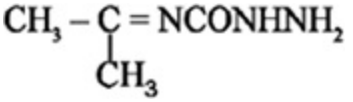
(d) benzyl alcohol and methyl alcohol

21. Compound A (molecular formula C_3H_8O) is treated with acidified potassium dichromate to from a product B (molecular formula C_3H_6O). B forms a shining silver mirror on warming with ammonical silver nitrate. B whne treated with an aqueous solution of $H_2NCONHNH_2$. HCl and sodium acetate gives a product C. Identify the structure of C –

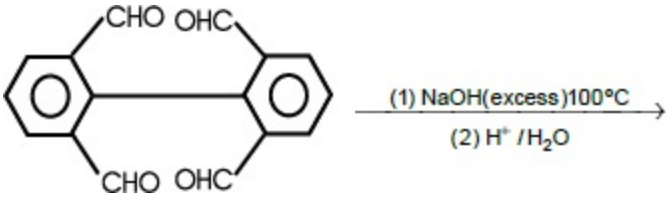
[IIT-2002]

(a) $CH_3CH_2CH = NNHCONH_2$

(b) 

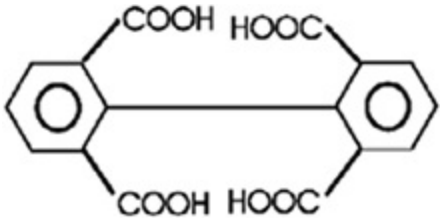
(c) 

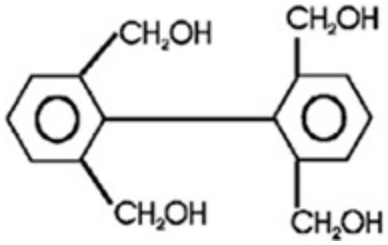
(d) $CH_3CH_2CH = NCONHNH_2$

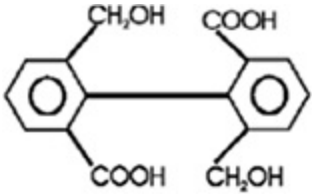
23. 

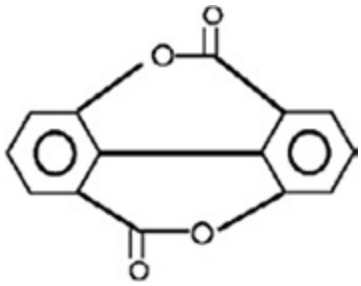
any one of the products formed is :

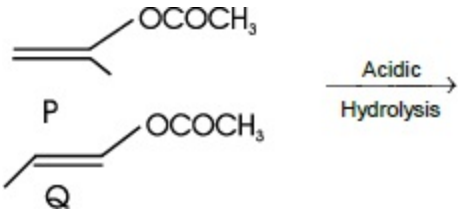
(IIT- 2003)

(a) 

(b) 

(c) 

(d) 

24. 

Products formedbyP&Q can be differentieted by :

(IIT-2003)

(a) 2, 4 DNP

(b) Lucas reagent ($ZnCl_2$) conc. HCl

(c) $NaHSO_3$

(d) Fehlings solution

25. Which of the reagent is used to convert 2-Butanone into propanoic acid ?

(IIT- 2005)

(a) NaOH , I_2 / H^+

(b) Tollen's reagent

(c) Fehling solution

(d) NaOH , NaI / H^+

IITJEE-2006

1. When benzene sulfonic acid and p–Nitrophenol are treated with $NaHCO_3$, the gases released respectively are

(a) SO_2 , NO_3

(b) SO_2 , NO

(c) SO_2 , CO_2

(d) CO_2 , CO_2

2. (I) 1,2-dihydroxy benzene (II) 1,3-dihydroxy benzene
(III) 1,4-dihydroxy benzene (IV) Hydroxy genzene
The increasing order of boiling points of above mentioned alcohols is –

(a) I < II < III < IV

(b) I < II < IV < III

(c) IV < I < II < III

(d) IV < II < I < III

3. The IUPAC name of C_6H_5COCl is –

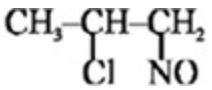
(a) Benzoyl chloride

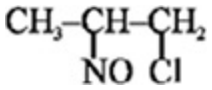
(b) Benzene chloro ketone

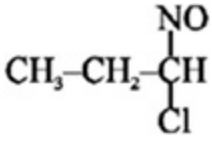
(c) Benzene carbonyl chloride

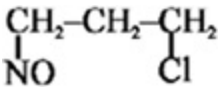
(d) Chloro phenyl ketone

4. CH_3-CH=CH_2+NOCl $\rightarrow$ P Identify the adduct –

(a) 

(b) 

(c) 

(d) 

5. $CH_3NH_2 + CHCl_3 + KOH \rightarrow$ Nitrogen containing compound + KCl + H_2O. Nitrogen containing compound is–

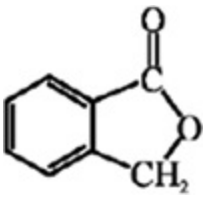
(a) $CH_3C{\equiv}N$

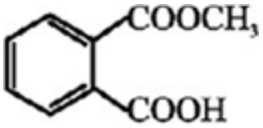
(b) $CH_3–NH\text{-}CH_3$

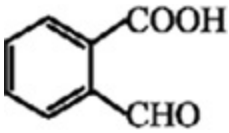
(c) $CH_3-\bar{N}H\equiv\overset{+}{C}H_3$

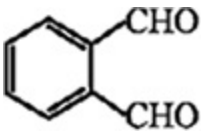
(d) $CH_3\overset{+}{N}\equiv\bar{C}$

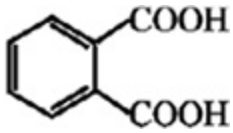
6. Which of the following reactants on reaction with conc. NaOH followed by acidification gives the following lactone as the only product

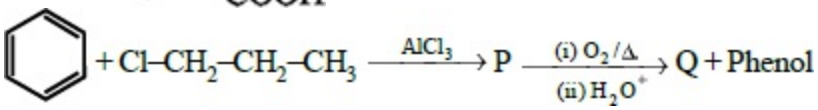


(a) 

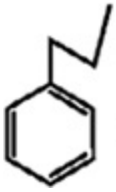
(b) 

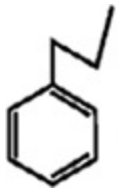
(c) 

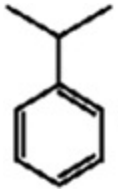
(d) 

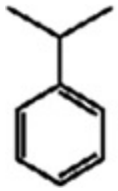
7. 

The major product P and Q are –

(a)  and CH_3CH_2CHO

(b)  and CH_3COCH_3

(c)  and CH_3COCH_3

(d)  and CH_3CH_2CHO

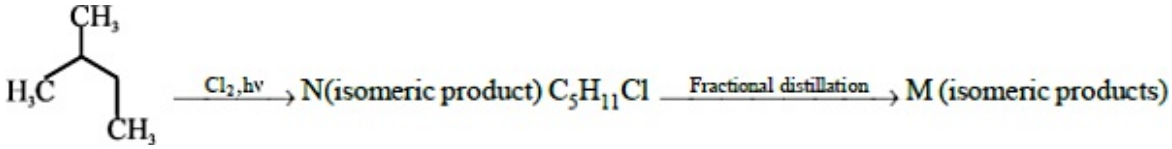
8. The smallest ketone and its next homologue are reacted with NH_2OH to form oxime –

(a) Two different oximes are formed

(b) Three different oximes are formed

(c) Two oximes are optically active

(d) All oximes are optically active

9. 

What are N and M –

(a) 6,6

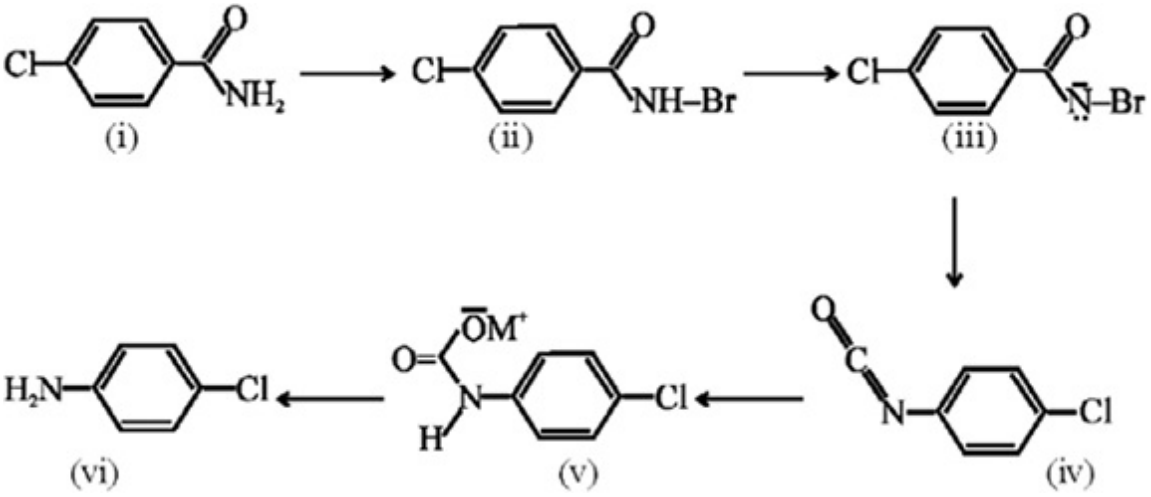
(b) 6, 4

(c) 4,4

(d) 3,3

$RCONH_2$ is converted into RNH_2 by means of Hoffmann bromide

degradation.



In this reaction, RCONHBr is formed from which this reaction has derived its name. Electron donating group at phenyl activates the reaction. Hofmann degradation reaction is an intramolecular reaction.

10. How can the conversion of (i) to (ii) be brought about –

(a) KBr

(b) KBr + CH_3ONa

(c) KBr + KOH

(d) Br_2 + KOH

11. Which is the rate determining step in Hoffmann bromamide degradation –

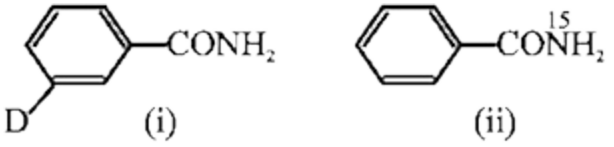
(a) Formation of (i)

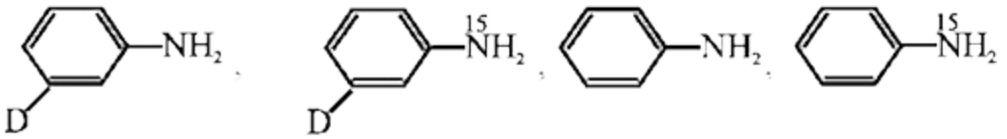
(b) Formation of (ii)

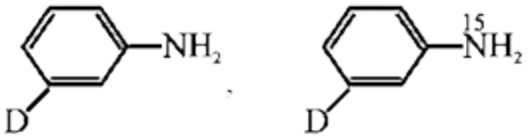
(c) Formation of (iii)

(d) Formation of (iv)

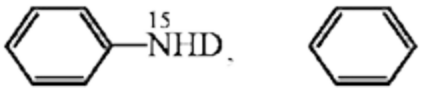
12. What are the constituent amines formed when the mixture of (i) and (ii) undergoes Hofmann bromamide degradation



(a) 

(b) 

(c) ‘ 

(d) 

13. Match the following –

Column-1	**Column-II**
(a) CH_3-CHBr-CD_3 on treatment with alc. KOH gives CEL=CH-CD,, as a major product	(P) E1 reaction
(b) Ph-CHBr-CH_3 reacts faster than Ph-CHBr-CD_3	(Q) E2 reaction
(c) Ph-CH_2-CH_2Br on treatment with $C_2H_5OH/C_2H_5O^-$gives Ph-CD=CH_2 as the major product	(R) E1 cb reaction
(d) $PhCH_2CH_2Br$ and $PhCD_2CH_2Br$ react with same rate	(S) First order reaction

ANSWER KEY

IUPAC Nomenclature

Q.	1	2	3	4
A.	(b)	(d)	(b)	(b)

Isomerism

Q.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
A.	(a)	(c)	(b)	(b)	(b)	(b)	(a)	(a)	(a)	(c)	(a)	(a)	(d)	(d)	(d)
Q.	16	17	18	19											
A.	(b)	(b)	(d)	(a)											

GOC, S_N, Elimination

Q.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
A.	(d)	(a)	(a)	(b)	(b)	(d)	(b)	(d)	(b)	(b)	(d)	(c)	(d)	(a)	(b)
Q.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
A.	(a)	(d)	(a)	(c)	(b)	(d)	(b)	(c)	(b)	(a)	(d)	(c)	(b)	(d)	(a)

Alkane, Alkene, Alkye

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

Alcohol, Ether and Phenol

Q.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
A.	(b)	(d)	(d)	(a)	(c)	(d)	(b)	(d)	(a)	(c)	(b)	(a)	(c)	(d)	(a)

Aromatic compounds

Q.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
A.	(d)	(b)	(a)	(d)	(a)	(c)	(a)	(d)	(c)	(c)	(a)	(a)	(c)	(b)	(b)
Q.	16	17	18	19											
A.	(d)	(d)	(d)	(a)											

Alkyl and aryl halides

Q.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
A.	(d)	(b)	(a)	(c)	(a)	(b)	(b)	(a)	(b)	(a)	(d)	(b)	(a)	(a)	(d)
Q.	16	17	18	19	20	21	22	23	24	25					
A.	(d)	(c)	(b)	(d)	(d)	(c)	(b)	(b)	(d)	(a)					

Carboxylic acid and its derivatives

Q.	1	2	3	4	5	6	7	8	9	10	11	12
A.	(a)	(a)	(a)	(b)	(d)	(a)	(c)	(d)	(c)	(c)	(d)	(d)

Nitro and amines

Q.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
A.	(d)	(d)	(a)	(d)	(b)	(a)	(a)	(c)	(b)	(d)	(d)	(a)	(b)	(a)	(a)

Carbonyl Compounds

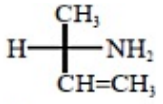
Q.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
A.	(b)	(a)	(d)	(b)	(d)	(d)	(a)	(b)	(d)	(a)	(d)	(b)	(d)	(a)	(c)
Q.	16	17	18	19	20	21	22	23	24	25					
A.	(b)	(a)	(b)	(b)	(a)	(a)	(a)	(c)	(d)	(a)					

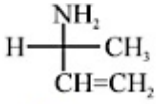
IIT-2006

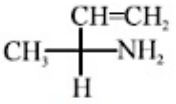
Q.	1	2	3	4	5	6	7	8	9	10	11	12
A.	(d)	(c)	(a)	(a)	(d)	(c)	(c)	(b)	(b)	(d)	(d)	(b)
Q.	13											
A.	(a)–Q; (b)–P,S; (c)–R ; (d)–Q											

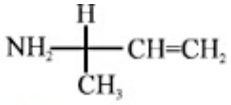
Miscellaneous

1. Which of the following combinations amongst the four Fischer projections represents the same absolute configurations ?


(I)


(II)


(III)


(IV)

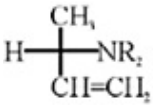
(a) (II) and (III)

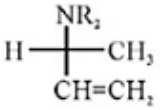
(b) (I) and (IV)

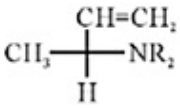
(c) (II) and (IV)

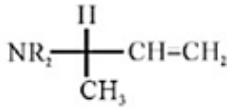
(d) (III) and (IV)

2. Which of the following combinations amongst the four Fischer projections represents the enantiomers?









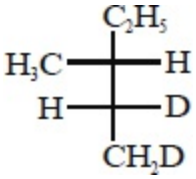
(a) (I) and (II)

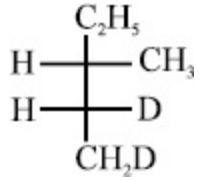
(b) (I) and (III)

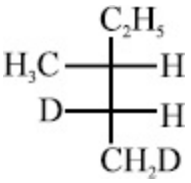
(c) (II) and (IV)

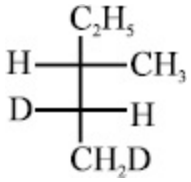
(d) None of these

3. The structure of (2R, 3S)-$C_2H_5CH(CH_3)CH(D)CH_2D$ is

(a) 

(b) 

(c) 

(d) 

4. From the following reactions

$$HC \equiv CH + NaNH_2 \rightleftharpoons NH_3 + HC \equiv CNa$$

$$H_2O + HC \equiv CNa \rightleftharpoons HC \equiv CH = NaOH$$

Predict which of the following facts regarding the base strength is correct?

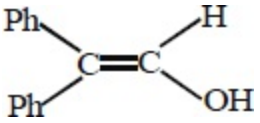
(a) $NaNH_2 > HC \equiv CNa > NaOH$

(b) $NaNH_2 > NaOH > HC \equiv CNa$

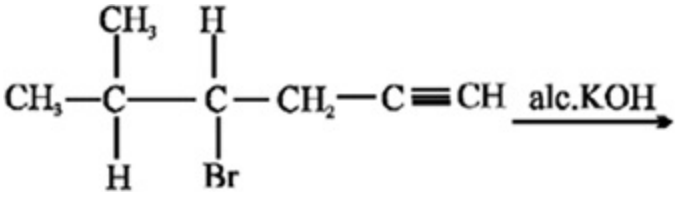
(c) $HC \equiv CNa > NaNH_2 > NaOH$

(d) $HC \equiv CNa > NaOH > NaNH_2$

5. Fill in the blanks :

(a) A structure  is known as.....structure.

(b) The product obtained in the reaction

 .....is

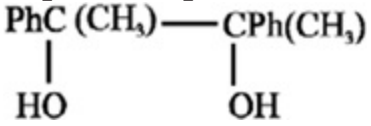
6. True or False :

(a) The number of isomers (including structural and stereoisomers) of alkynes C_6H_{10} is six.

(b) The addition of HBr to butadiene at –80° C to give 1,2 – adduct is

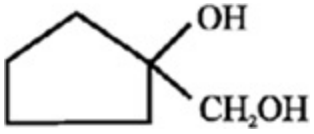
kinetically controlled while that at 40°C to give 1, 4- adduct is thermodyanamically controlled

(c) The decreasing order of reactivity of benzyle alcohol with HBr is p- $CH_3OC_6H_4CH_2OH$ > $C_6H_5CH_2OH$ > p-$ClC_6H_4CH_2OH$ > p-$O_2NC_6H_4CH_2OH$

(d) In pinacol- pinacolone rearrnagement reaction involving 

, the phenyl group migrates in preference to methyl group.

(e) Schiff base is N- substituted imine.

(f) An organic compound on treatment with HIO_4 gives cyclopentanone and formaldehyde. The compound is 

(g) As compared to RNH .$RCONH_2$ is more stabilised by delocalisation of the lone pair electrons of the carbonyl group.

(h) As compared to RNH_3^+, $RCONH_3^+$ is destabilised because the electron-withdrawing carbonyl group destablises the positive charge on nitrogen.

(i) Δ G° for the conversion of $RNH_2 \xrightarrow{H^+} RNH_3^+$ is more than that of the reaction

$$RCONH_2 \overset{H^+}{\rightleftharpoons} RCONH_3^+$$

(j) Peroxy acids, $CH_3\overset{\overset{O}{\|}}{C}OOH$, are much stronger than $CH_3\overset{\overset{O}{\|}}{C}OH$

(k) p- $NO_2C_6H_4COOH$ is more acidic than the meta isomer.

(l) H_2C = $CHCH_2COOH$ is more acidic than CH_3CH_2COOH

(m) Salycylic acid, o- HOC_6H_4COOH, is a stronger acid than o-$H_3COC_6H_4COOH$.

(n) Formic anhydride can be prepared by heating formic acid.

(o) The rate of esterification of Et_3CCOOH is slower than that of $(i\text{-}Pr)_2$ CHCOOH.

(p) Phthalimide is much more acidic than benzamide.

7. Benzyl chloride ($C_6H_5CH_2Cl$) can be prepared from toluene by chlorination with

(a) SO_2Cl_2

(b) $SOCl_2$

(c) Cl_2

(d) NaOCl

8. An industrial method of preparation of methanol is–

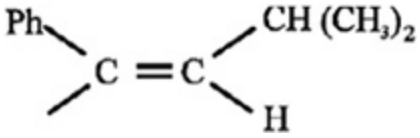
(a) catalytic reduction of carbon monoxide in presence of $ZnO\text{-}Cr_2O_3$

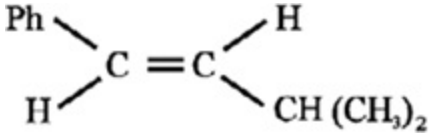
(b) by reacting methane with steam at 900°C with a nickel catalyst.

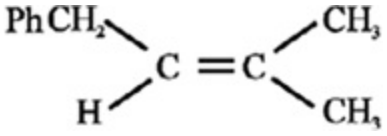
(c) by reducing formaldehyde with lithium aluminium hydride

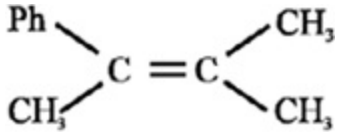
(d) by reacting formaldehyde with aqueous sodium hydroxide solution.

9. The major product in the reaction of $PhCH_2CH(OH)CH(CH_3)_2$ with concentrated H_2SO_4 is

(a) 

(b) 

(c) 

(d) 

10. Which of the alcohols does not give iodoform test ?

(a) $(CH_3)_2CH(OH)CH_3$

(b) PhCH $(OH)CH_2CH_3$

(c) 2- methylcyclohexanol

(d) $CH_3CH_2CH(OH)CH_3$

Multiple choice questions

11.1 The bond dissociation enthalpy C– X in CH_3X (where X is halogen) follows the order

(a) $CH_3 – Cl > CH_3 – Br > CH_3 –I$

(b) $CH_3 – Cl < CH_3 – Br < CH_3 – I$

(c) $CH_3 – Cl > CH_3 – Br < CH_3 –I$

(d) $CH_3 – Cl < CH_2 – Br > CH_3 –I$

11.2 Which of the following compounds will react with ehthanolic KCN?

(a) Ethyl chloride

(b) Acetyl chloride

(c) Chlorobenzene

(d) p-methoxy benzaldehyde

12. The enol form of acetone, after treatment with D_2O, gives

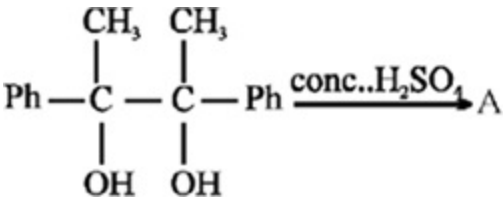
(a) $CH_3-\underset{\underset{OD}{|}}{C}=CH_2$

(b) $CH_3-\underset{\underset{O}{\|}}{C}-CH_3$

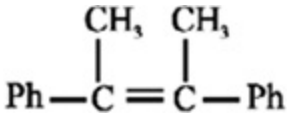
(c) $CH_2=\underset{\underset{OH}{|}}{C}-CH_2D$

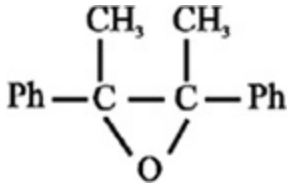
(d) $CD_2=\underset{\underset{OD}{|}}{C}-CD_3$

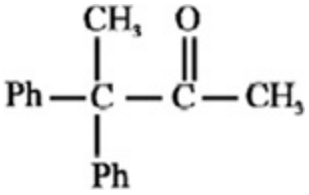
13. In the reaction

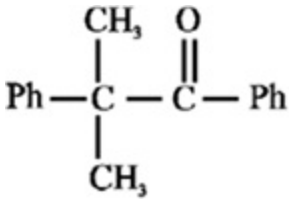


; The product A is–

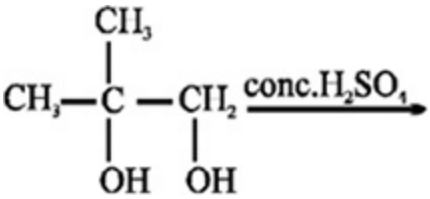
(a) 

(b) 

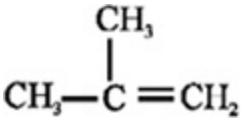
(c) 

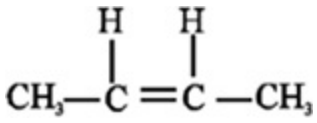
(d) 

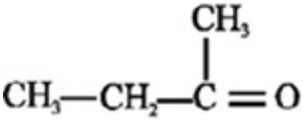
14. In the reaction

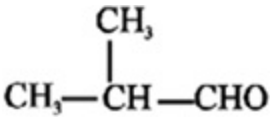


A ; The product A is –

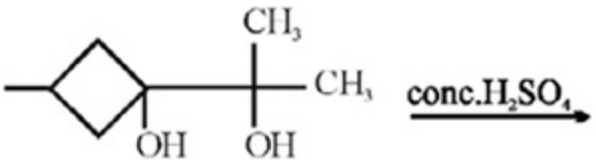
(a) 

(b) 

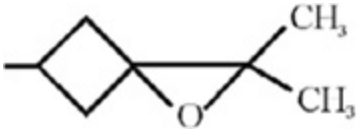
(c) 

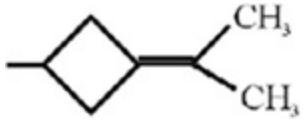
(d) 

15. In the reaction

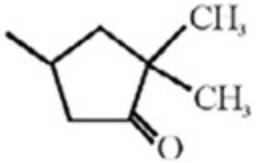


The product A is –

(a) 

(b) 

(c) 

(d) 

16. Which of the following sequences is correct ?

(a) pK_a (p-$O_2NC_6H_4COOH$) > pK_a (C_6H_5COOH)> pK_a (p–HOC_6H_4COOH)

(b) pK_a (p-$O_2NC_6H_4COOH$) < pK_a (C_6H_5COOH) < pK_a (p–HOC_6H_4COOH)

(c) pK_a (p-$O_2NC_6H_4COOH$) > pK_a (C_6H_5COOH) < pK_a (p–HOC_6H_4COOH)

(d) pK_a (p-$O_2NC_6H_4COOH$) < pK_a (C_6H_5COOH) > pK_a (p–HOC_6H_4COOH)

17. Which of the following sequences of rates of alkaline hydrolysis of esters is correct ?

(a) $CH_3CH_2CH_2COOCH_3 < (CH_3)_2 CHCOOCH_3 < (CH_3)_3CCOOCH_3$

(b) $CH_3CH_2CH_2COOCH_3 > (CH_3)_2 CHCOOCH_3 > (CH_3)_3CCOOCH_3$

(c) $CH_3CH_2CH_2COOCH_3 < (CH_3)_2 CHCOOCH_3 < (CH_3)_3CCOOCH_3$

(d) $CH_3CH_2COOCH_3 > (CH_3)_2\ CHCOOCH_3 > (CH_3)_3CCOOCH_3$

18. Which of the following orders of reactivity of acid derivatives towards a nucleophile is correct?

(a) acid chloride > anhydride > ester

(b) acid chloride < anhydride < ester

(c) acid chloride > ester > anhydride

(d) anhydride > acid chloride > ester

19. Which of the following orders regarding the base strength of a leaving group in a reaction of an acid with a nucleophile is correct ?

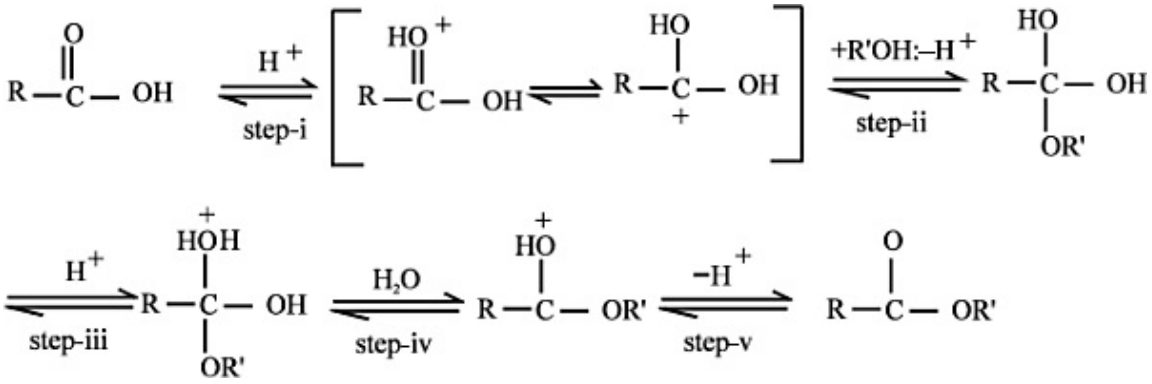
(a) $Br^- < RO^- < NH_2^-$

(b) $Br^- > NH_2^- > RO^-$

(c) $Br^- > Cl^- > NH_2^-$

(d) $RO^- > NH_2^- > Cl^-$

20. The mechanism of ester formation in acidic medium is as follows :



The slowest step in the above mechanism is–

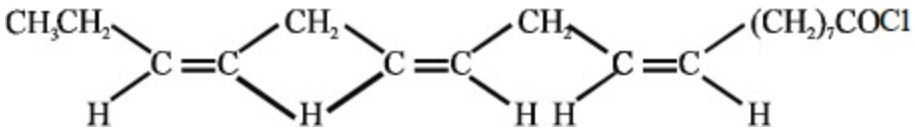
(a) step (i)

(b) Step (ii)

(c) Step (iii)

(d) Step (iv)

21. The IUPAC name of



22. The monomer of natural rubber is–

(a) butadiene

(b) chloroprene

(c) 2- methyl-1,2- butadiene

(d) 2- methyl-1,3- budadiene

23. Which of the following polymer is hard?

(a) Linear

(b) Cross- linked

(c) Branched-chain

(d) Thermoplastic

24. Which of the following polymers has esters linkages?

(a) nylon

(b) bakelite

(c) Terylene

(d) PVC

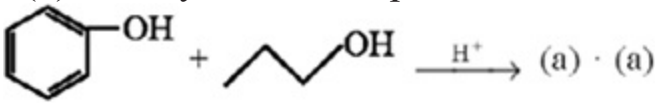
25. The monomers of Buna-S polymers are–

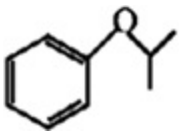
(a) Vinyl chloride and vinylidene

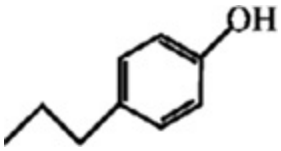
(b) Styrene and butadiene

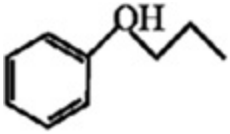
(c) Acrylonitrile and butadiene

(d) Isobutylene and isoprene

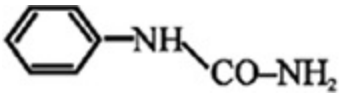
26. 

(a) 

(b) 

(c) 

(d) None of these

27.  "X" will be –

(a) p-isomer

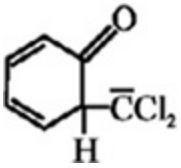
(b) o-isomer

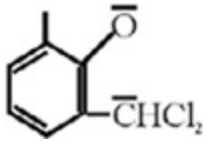
(c) m-isomer

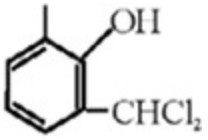
(d) (a) and

(b) both

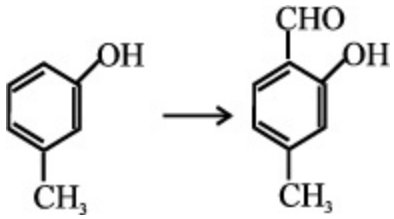
28. When phenol is treated with $CHCl_3$ and NaOH, followed by acidification, salicyladehyde is obtained. Which of the following species are involved in the above mentioned reaction as intermediate –

(a) 

(b) 

(c) 

(d) Both (a) and (b)

29. 

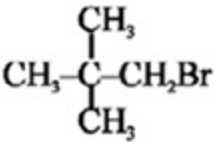
The above conversion can be done by –

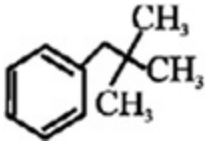
(a) $CO + HCl/AlCl_3$

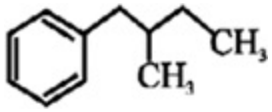
(b) $HCN/HCl/AlCl_3$

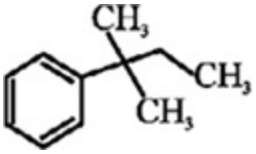
(c) $CHCl_3/NaOH$

(d) All the above

30. When benzene reacts with neopentyl bromide  in presence of $AlBr_3$ is formed –

(a) 

(b) 

(c) 

(d) All of these

31. Which of the following alcohol will undergo acid catalysed dehydration with greatest ease by E_1 mechanism –

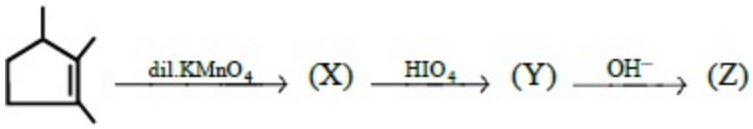
(a) $CH_2=CH-OH$

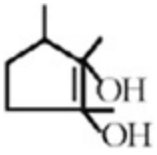
(b) 

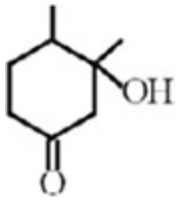
(c) 

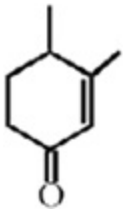
(d) Me_2CHOH

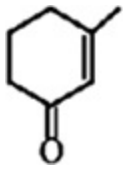
32. Identify the final product (Z) in the following sequence of reactions

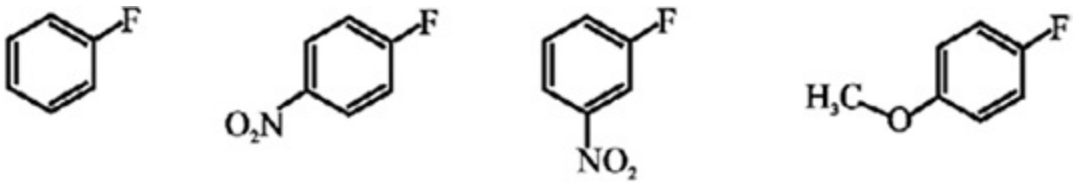


(a) 

(b) 

(c) 

(d) 

33. 

(i) (ii) (iii) (iv)

Ease of nucleophilic substitution among these compounds will be in the order –

(a) (i) > (iii) > (iv) > (i)

(b) (i) > (ii) > (iii) > (iv)

(c) (ii) > (iii) > (i) > (iv)

(d) (iv) > (iii) > (ii) > (i)

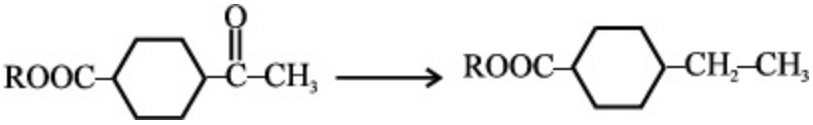
34. Formaldehyde is used in the manufacture of –

(a) Teflon

(b) Bakelite

(c) Gammaxene

(d) Dynamite

35. The transformation  can be best carried out by –

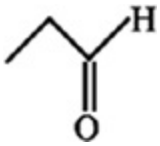
(a) Wolff-Kishner reduction

(b) Clemmensen's reduction

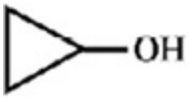
(c) Raney Ni reduction of cyclic thioacetal

(d) All the three

36. $\underset{C_3H_5O}{\overset{A}{}} \xrightarrow[H_2SO_4]{NaCN}$ cyanohydrin of (a). If the cyanohydrin is optically active, then the possible structure of

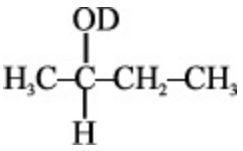
(a) 

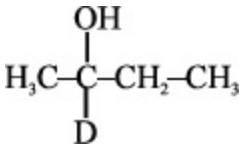
(b) 

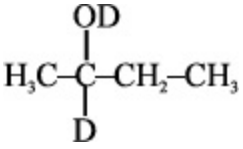
(c) 

(d) 

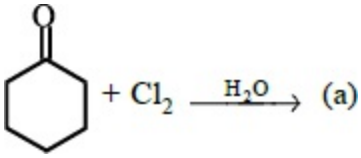
37. $H_3C-CH_2-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[D_2O]{NaBH_4}$ Product ?

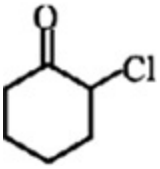
(a) 

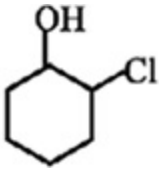
(b) 

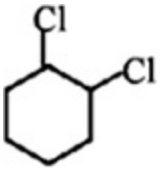
(c) 

(d) None

38. 

(a) 

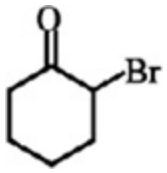
(b) 

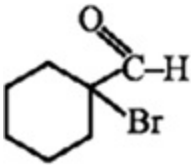
(c) 

(d) None

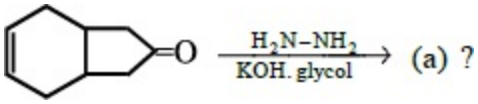
39. Greatest amount of hydration is in –

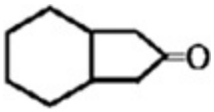
(a) 

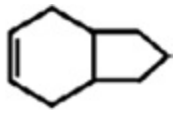
(b) 

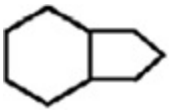
(c) 

(d) All are equal

40. 

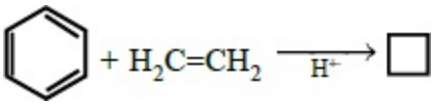
(a) 

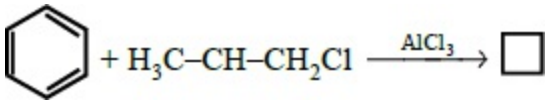
(b) 

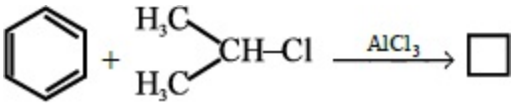
(c) 

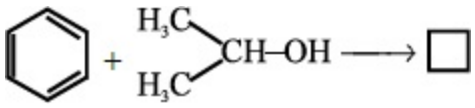
(d) None

41. Isopropyl benzene can not be obtained by –

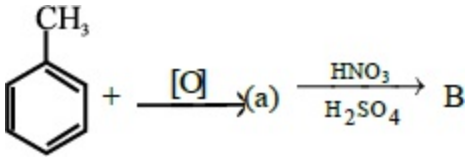
(a) 

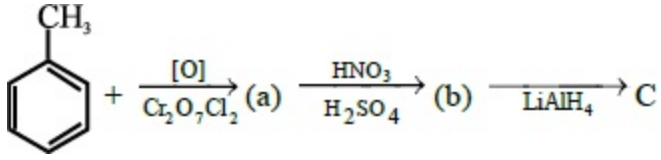
(b) 

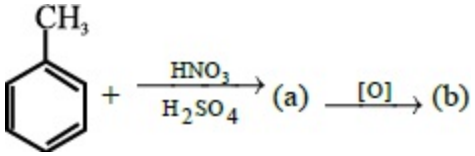
(c) 

(d) 

42. m–Nitro benzoic acid can be obtained by –

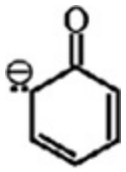
(a) 

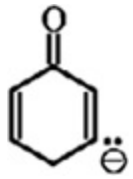
(b) 

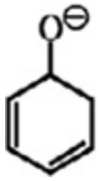
(c) 

(d) None of these

43. Resonating structure of phenoxide ions are –

(a) 

(b) 

(c) 

(d) None of these

44. Electrolysis of CH_3COOK gives –

(a) C_2H_6

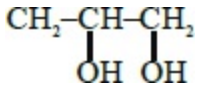
(b) CH_4

(c) C_2H_2

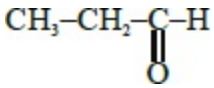
(d) C_2H_4

45. CH_3-CH=CH_2 reacts with B_2H_6 in presence of H_2O_2 to give –

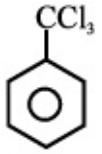
(a) CH_3COCH_3

(b) 

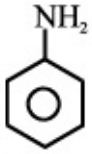
(c) CH_3-CH_2-CH_2-OH

(d) 

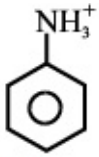
46. Electrophile $N0_2$ attacks the following : ($HN0_3$ is the source)



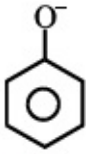
(I)



(II)



(III)



(IV)

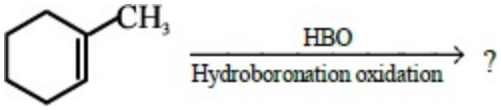
In which cases $\overset{+}{N}O_2$ will be meta-position –

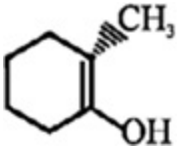
(a) (II) and (IV)

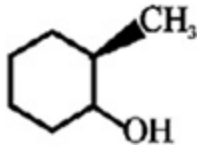
(b) (I), (II) and (III)

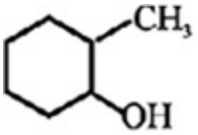
(c) (II) and (III) only

(d) (I) only

47. 

(a) 

(b) 

(c) 

(d) None

48. Which of the following has the higherst potential energy for pentane ?

(a) Anti conformation

(b) Eclipsed conformation

(c) Gauche conformation

(d) All have same potential energy

49. Compound A is chiral and has the molecular formula $C_8H_{11}N$. When A reacts with nitrous acid there occurs a brisk evolution of N_2 gas. A dissolves in aqueous HCl. What is the identity of A?

(a) 2-phenylethanamine

(b) 1-phenylethanamine

(c) 1–Cyclohexylethanamine

(d) N-ethylaniline

50. If 2-pentanone is reacted with $NaBH_4$ followed by hydrolysis with D_2O the product will be

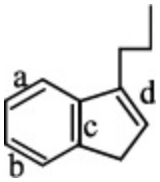
(a) $CH_3CH(OD)CH_2CH_2CH_3$

(b) $CH_3CD\ (OH)CH_2CH_2CH_3$

(c) $CH_3CH(OH)CH_2CH_2CH_3$

(d) $CH_3CD\ (OD)CH_2CH_2CH_3$

51. If 1 mole H_2 is reacted with 1 mol of the following compound.



Which double bond will be hydrogenated ?

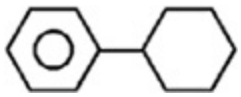
(a) c

(b) b

(c) a

(d) d

52. Which of the following is a correct for the following compound



(a) cyclohexylbenzene

(b) biphenyl

(c) hexylbenzene

(d) phenylbenzene

53. Which of the following is true about the cycloheptatrienyl free radical?

(a) It is an isolatable stable free radical

(b) It is an aromatic free radical

(c) If has $4n + 2$ π electrons

(d) none of these

54. The enthalpy of hydrogenation for 1-pentene is + 126 Kj/mol. The enthalpy of hydrogenation for 1: 3-pentadiene is + 230 Kj/mol. Hence estimate the resoance (delocalization) energy of 1 : 3 –pentadiene

(a) 22 Kj

(b) 104 Kj

(c) 252 Kj

(d) Cannot be calculated from this information.

55. What simple laborattory test could be performed to distinguish between 1-pentyen and 2-pentyne?

(a) the addition of Ag^{+} in ammonia

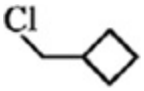
(b) the addition of H_2SO_4 in Hg^{+2}

(c) the addition of Br_2 in CCl_4

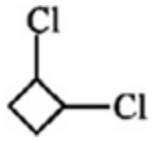
(d) the addition of H_2 on a Pt catalyst.

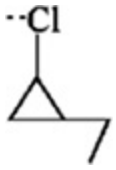
56. A compound A has the molecular formula C_5H_9Cl. It does not react with bromine is carbon tetrachloride. On treatement with a strong base it produces a single compound B. B has a molecular formula C_5H_8 and reacts with bromien in carbon tetrachloride. Ozonolysis of B produces a

compound C which has a molecular formula $C_5H_8O_2$. Which of the following structures is that of A?

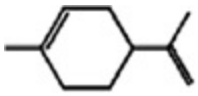
(a) 

(b) 

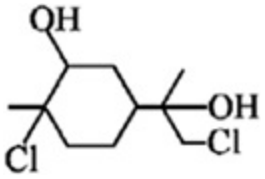
(c) 

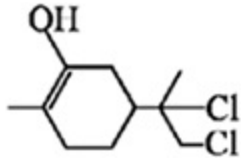
(d) 

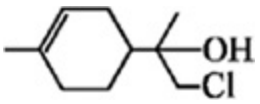
57. The alkene limonene has the following structure.

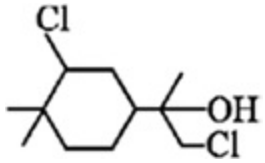


Which product results from the reaction of limonene and chlorine water?

(a) 

(b) 

(c) 

(d) 

58. Which of the following does not exist as geometric isomers?

(a) 3-bromo-2-methyl-2-butene

(b) cyclodecene

(c) 3-bromo-1–Chloro-1-pentene

(d) 3-methyl-2-pentene

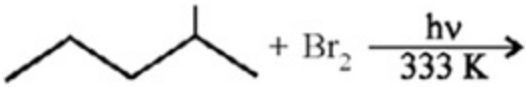
59. Which of the following most readily undergoes E2 elimination with a strong base?

(a) 2-bromopentane

(b) 2-bromo-2-methylbutane (c) 1-bromo-2, 2-dimethylpropane

(d) 2-bromo-3-methylbutane

60. Which of the following is the major product of the following reaction?



(a) 3-bromo-2-methylpentane

(b) 2-bromo-2-methylpentane

(c) 1-bromo-2-methylpentane

(d) 4-bromo-2-methylpentane

61. Which of the following is the strongest base?

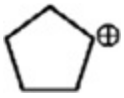
(a) $HC = C^-$

(b) $CH_2 = CH^-$

(c) $CH_3CH_2^-$

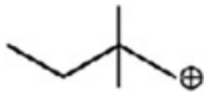
(d) NH_2^-

62. Select the most stable carbocation from amongst the following :

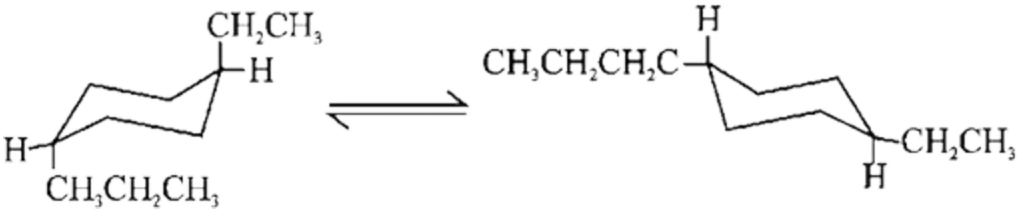
(a) 

(b) 

(c) 

(d) 

63. Consider the following equilibrim



Which of the followinb best describes the equilibirum constant K of this interconversion?

(a) $K < 1$

(b) $K > 1$

(c) $K = 1$

(d) K cannot be deduced from this information

64. Which of the following best desbribes the stability of the cis and trans isomers of 1, 1, 3, 5-tetraethylcyclohexane?

(a) The trans isomer is more stable than the cis.

(b) The cis isomer is more stable than the trans.

(c) Both have the same stability

(d) The information given is not sufficient to deduce the stability of the isomers.

65. Which of the following has the greatest angle strain?

(a) methyl cyclobutane

(b) methyl cyclopentane

(c) methyl cyclohexane

(d) methyl cycloprpane

66. Which would be the most stable conformatikon of trans-1-ethyl-3-methylcyclohexane?

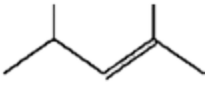
(a) equatorial (methyl)-equatorial (ethyl)

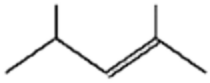
(b) axial(methyl)-equatorial(ethyl)

(c) axial (methyl)-axial(ethyl)

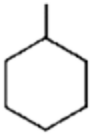
(d) axial (ethyl)-equatorial(methyl)

67. Which of the consitutional isomer of the compound



(a) 

(b) 

(c) 

(d) both (a) and (b)

68. Which of the following has the highest boiling point?

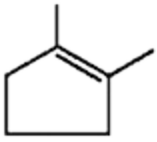
(a) 2, 2-dimethylbutane

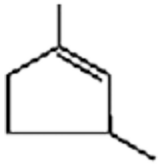
(b) 2, 3-dimethylbutan e

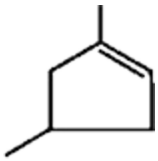
(c) 2-methylpentane

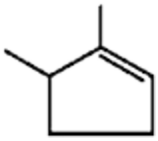
(d) pentane

69. The compound that would yield a oxo-2-methyl thexanal on ozonolysis is

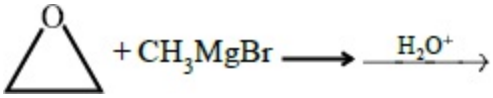
(a) 

(b) 

(c) 

(d) 

70. The following sequence of reactions gives



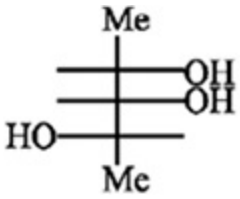
(a) 1-butanol

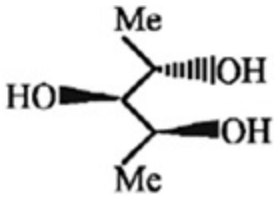
(b) 2-butanol

(c) 3,4–Hexamediol

(d) 3-methyl-3-pentanol

71. The following steroisomers are





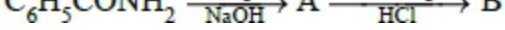
(a) Enantiomers

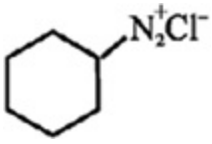
(b) epimers

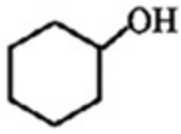
(c) diastereomers

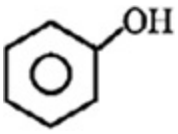
(d) None of these

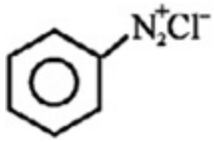
72. The product B of the following sequence of reactions is



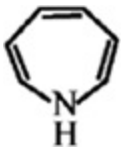
(a) 

(b) 

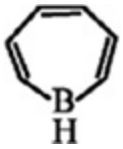
(c) 

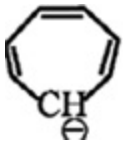
(d) 

73. The aromatic compound would be

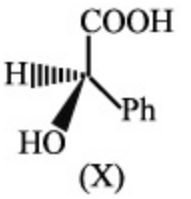
(a) 

(b) 

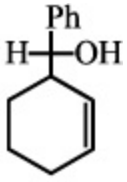
(c) 

(d) 

74. The configurations of the asymmetric centres in (X) and (Y) molecules are respectively



(X)



(Y)

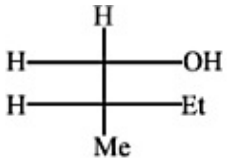
(a) S, S

(b) S, R

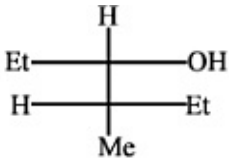
(c) R, R

(d) R, S

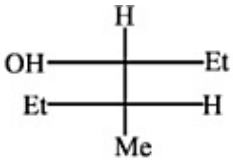
75. Among the following, the pair of enantiomers is



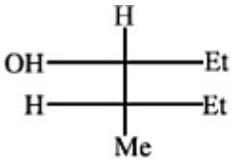
(I)



(II)



(III)



(IV)

(a) I and III

(b) II and IV

(c) II and III

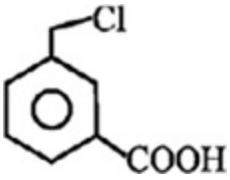
(d) III and IV

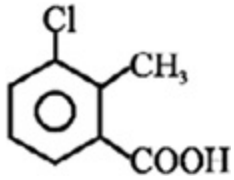
76. A compound undergoes the following sequence of reactions and gives the product ($C_gH_4O_3$)

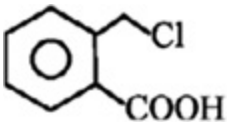
(i) Reaction with dilute aq. NaOH (ii) Acidification

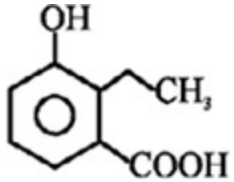
(iii) Treatment with acidic $Na_2Cr_2O_7$ (iv) Heating

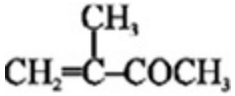
Hence the compound is

(a) 

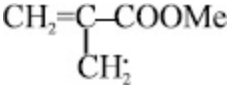
(b) 

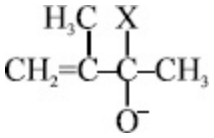
(c) 

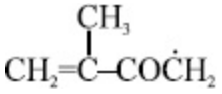
(d) 

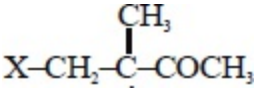
77. The most probable reaction of a radical X with 

would give

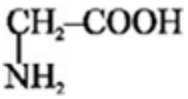
(a) 

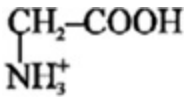
(b) 

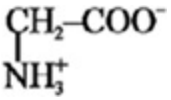
(c) 

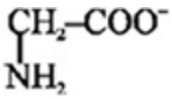
(d) 

78. The structure representing the zwitter ion form of glycine is

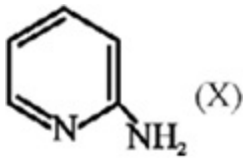
(a) 

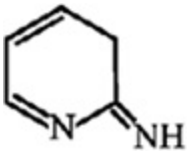
(b) 

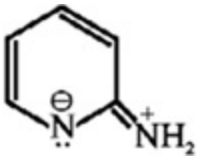
(c) 

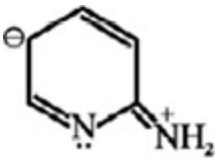
(d) 

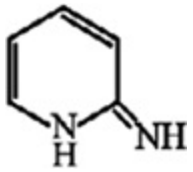
79. The proper tautomeric structure for 2-aminopyridine (X) is


(X)

(a) 

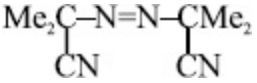
(b) 

(c) 

(d) 

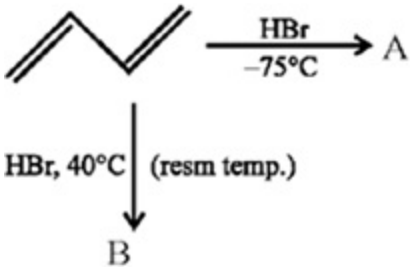
80. The compound, which can be used to initiate a radical polymerisation is

(a) Ph–N=N-Ph

(b) 

(c) $C_6H_{12}COCl$

(d) $C_6H_5COCOOH$

81. 

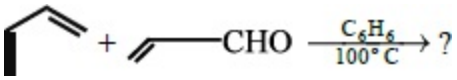
'A' and 'B' are –

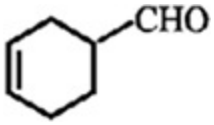
(a) KCP, TCP

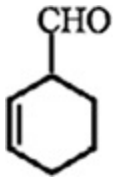
(b) TCP, KCP

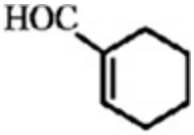
(c) both are KCP

(d) both are TCP

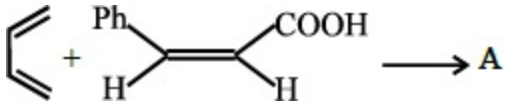
82. 

(a) 

(b) 

(c) 

(d) none of these

83. 

'A' is –

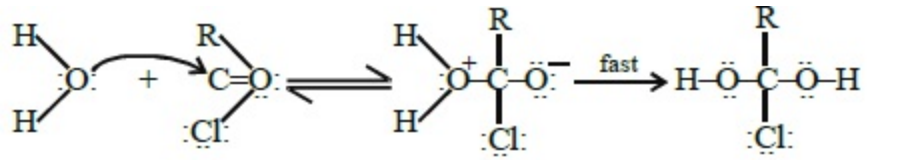
(a) cis product

(b) trans product

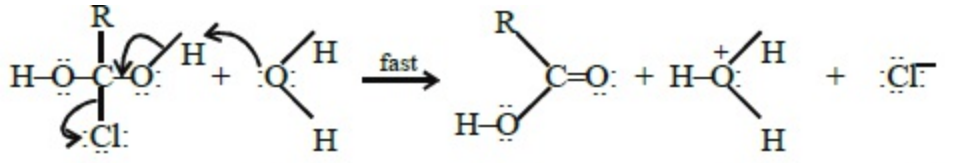
(c) both form

(d) none of these

84. First stage : Formation of the tetrahedral intermediate by nucleophilic addition of water to the carbonyl group.



Second stage : Disscociation of the tetrahedral intermediate by dehydrohalogenation.



84.1 Which will hydrolyse fast ?

(a) $CH_3COOC_2H_5$

(b) $HCOONH_2$

(c) CH_3COCl

(d) HCOCl

84.2 Which one is the rds ?

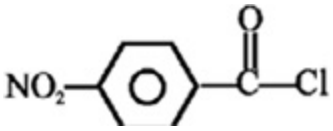
(a) I

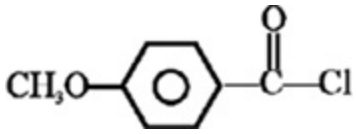
(b) II

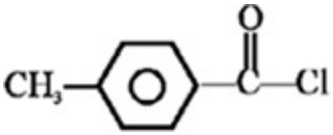
(c) III

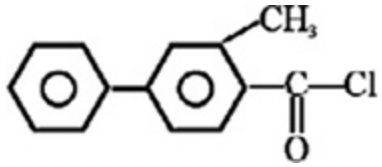
(d) none of these

84.3 Which will show the fastest rate of hydrolysis ?

(a) 

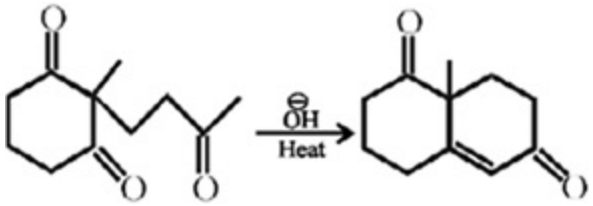
(b) 

(c) 

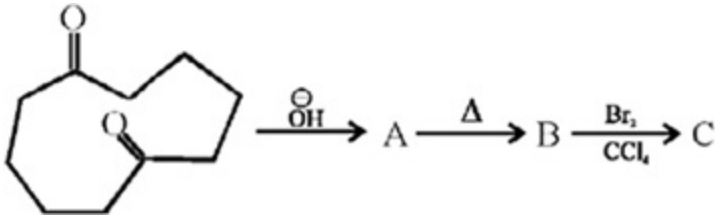
(d) 

85.1 ***Assertion:-*** $RCOCl > (RCO)_2O > RCOOR' > RCONH_2$ is the reactivity order for SN2 (Th)

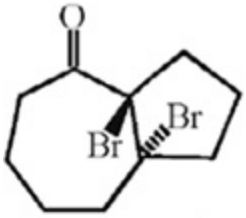
Reason :- Resonance stabilisation by N is maximum and by Cl (3p) is leasts.

85.2 ***Assertion:–*** 

Reason :- The product occurs due to aldol condensation.

86. 

Product 'C' is –

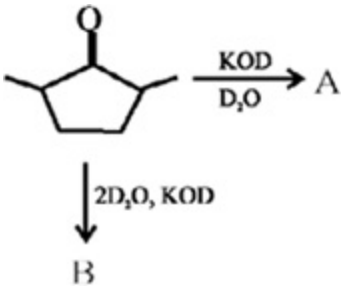
(a) 

(trans isomer)

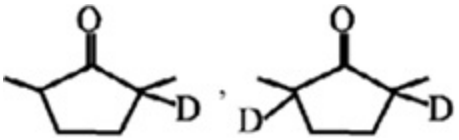
(b) cis isomer

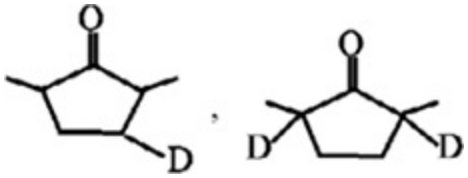
(c) both

(d) none of these

87. 

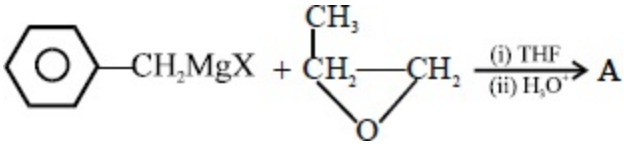
'A' and 'B' are

(a) 

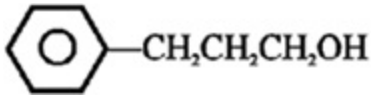
(b) 

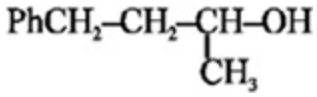
(c) All of these

(d) none of these

88. 

Product 'A' is –

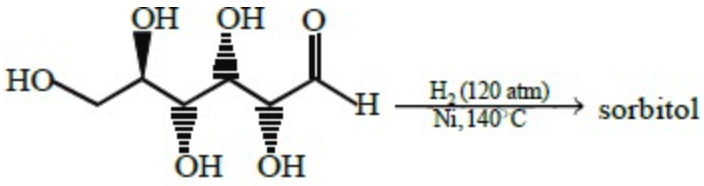
(a) 

(b) 

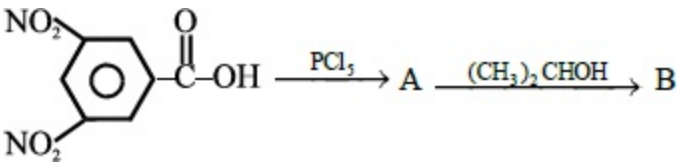
(c) all of these

(d) none of these

89. Sorbital is a sweetner often substituted for cane sugar, because it is better tolerated by diabetics. It is also an intermediate in the commercial synthesis of vitamin c. Sorbital is prepared by high-pressure hydrogenation of glucose over a nickel catalyst. What is the structure (including stereochemistry) of sorbitol ?



Glucose

90. 

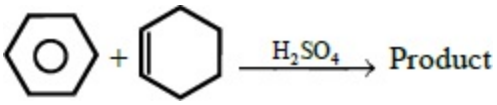
'B' is –

(a) ester

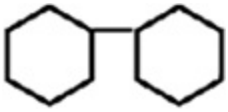
(b) acid

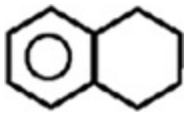
(c) alcohol

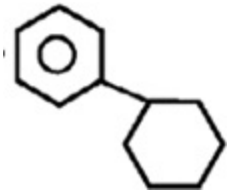
(d) none of these

91. 

Product is –

(a) 

(b) 

(c) 

(d) none of these

92. Which one is the most form in your opinion for calicene 

(a) 

(b) 

(c) 

(d) none of these

93. (C) Chemoselectivity : Which functional group will react.

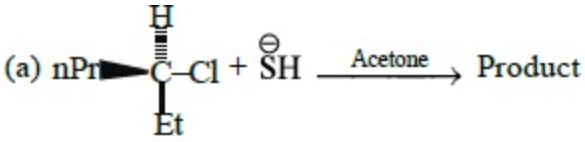
(R) Regioselectivity : Where it will react

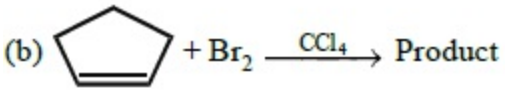
(S) Stereoselectivity : How it will react (Stereoselectivity of the products)

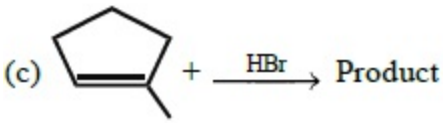
(St) Stereospecifity : How it will react (Stereochemistry of the reactants and products both)

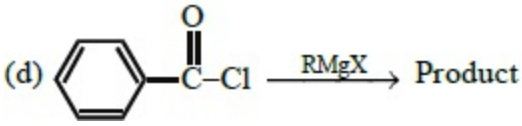
Match the following based on above definitions.

(A) Reactions

(a)  (i) S

(b)  (ii) C

(c)  (iii) St

(d)  (iv) R

94. Read the following passage carefully and answer the followings ;

Case – I : When a compound has total 'n' asymmetric 'C' atoms (i.e. stereomers) then total number of optically active isomers = 2^n

Case – II : If a molecule is divisible into two identical halves, and n=even, then the

(a) number of optically active isomers = 2^{n-1}

(b) number of meso forms = $2^{(n/2\ -1)}$

So total number of configurational isomers = $2^{n-1} + 2^{n/2-1}$

Case – III : "If a molecule is divisible into two identical halves, and n= odd, then

number of optically active isomers = $2^{n-1} - 2^{(n-1)/2}$

number of meso form = $2^{(n-1)/2}$

So total number of configurational isomers = 2^{n-1}

94.1 The total no. of meso forms of the compound COOH-(CHOH)COOH is –

(a) 2

(b) 2^2

(c) 2^3

(d) 2^4

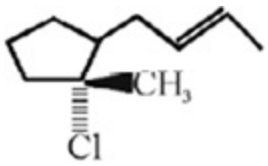
94.2 The total number of optical isomers for the above compound is –

(a) 10

(b) 12

(c) 8

(d) 6

94.3 

Total number of stereoisomers is –

(a) 2^2

(b 2^3

(c) 2^4

(d) none of these

94.4 $COOH\ (CHOH)_5COOH$ has total number of enantiomeric pairs –

(a) 6

(b) 4

(c) 5

(d) 7

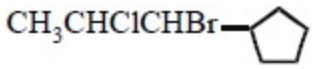
94.5 For the compound given in (Q. 4), total number of meso forms –

(a) 2^2

(b) 2^3

(c) 2

(d) $2^{3/2}$

94.6  has total optically inactive isomer is –

(a) 1

(b) 0

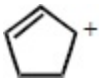
(c) 2

(d) 4

95. Which one is maximum stable out of the following –

(a) $CH_2=CH-\overset{+}{C}H_2$

(b) $CH_3-CH=CH-\overset{+}{C}HCH_3$

(c) 

(d) $CH_2=CH-\overset{CH_3}{\underset{CH_3}{C\oplus}}$

96. $CH_2=CH\text{-}CH_3$ has

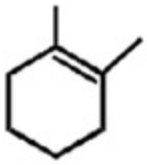
(a) 3 vinylic and 3 allylic H

(b) 2 vinylic, 3 allylic H

(c) 1 vinylic and 3 allylic H

(d) none of these

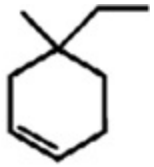
97. Which one/s will give same carbenium ion upon protonation ?



I



II



III

(a) I, III

(b) II, III

(c) I, II

(d) all of these

98. Which one is most stable –

(a) $CH_2=C=CH_2$

(b) $CH_3CH=CH_2$

(c) $CH_3CH=CH_2$

(d) $CH_2=C=C(CH_3)_2$

99. Which one is having least bond length from the shown bonds –

$CH_3CH_2–CH_3$ (I) $\quad$ $CH_3–CH=CH_2$ (II) $\quad$ $CH_2=CH–CH=CH_2$ (III)

(a) I

(b) II

(c) III

(d) none of these

100. Boiling point order is



I II III IV

(a) I > II > III > IV

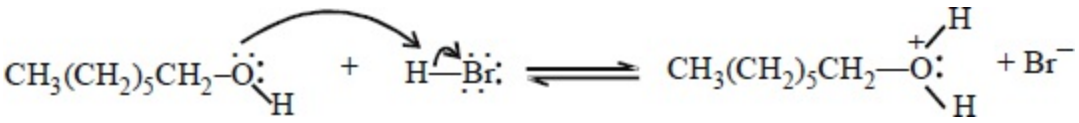
(b) IV > III > II > I

(c) I > III > II > IV

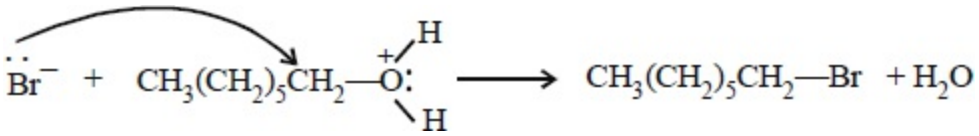
(d) IV > III > I > II

101. [Passage]

Step 1 : Protonation of 1-butanol to give the corresponding alkyhloxonium ion:



Step-2 Nucleophilic attack on the alkyloxonium ion by bromide ion:



101.1 Which one is the solwest or rds?

(a) Step-1

(b) step-2

(c) step-1 and step-2 both

(d) None of these

101.2 Which acid can make the halide formation fastest?

(a) HI

(b) HBr

(c) HCl

(d) HF

101.3 The mechanism of step-2 is:

(a) **V**

(b) **Sn2**

(c) E

(d) **V**

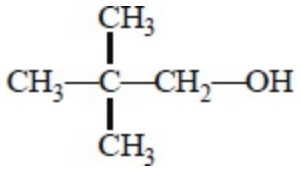
101.4 Is the rearranged prodcut possible for the substrate?

(a) Yes

(b) No

(c) can't be said

(d) none of these

101.5 For the substrate  , what would be the mechanism of halide formation?

(a) S_N1

(b) S_N2

(c) S_N1'

(d) S_N2'

102. In biological systems, biopolymers degrade mainly by enzymatic hydrolysis and to some extent by oxida- tion. In view of the disposal problem of polymer waste and for developing polymers for other safe uses in human system, biodegradable synthetic polymers have been developed. These synthetic polymers mostly have functional groups prevalent in biopolymers and lipids.

Which one among the followings is not an example of biodegradable synthetic polymers –

(a) Poly (β –Hydroxy butyrate) and (β –Hydroxy valerate)

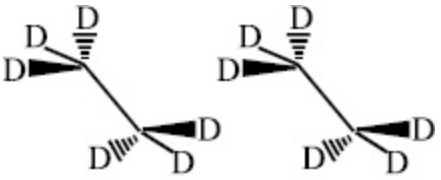
(b) Poly (glycolic acid) and poly (lactic acid)

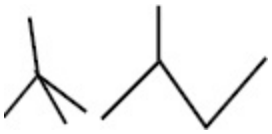
(c) Polyamide co-polymer of glycine and amino caproic acid (nylon-2, nylon-6)

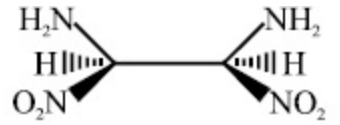
(d) All of these

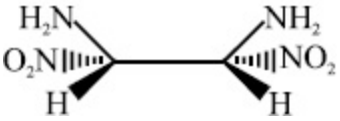
103. The spatial arrangement of atoms or groups of atoms in a molecule is the subject matter of Stereochemistry. Stereoisomers are compounds that have same sequence of covalent bonds but differ in the relative dispositions of their atoms in space. Conformational and configurational isomers are the two main sub-classes of stereoisomers. Conformational isomers can be introconverted simply by **o**-bond rotations, while configuratonal isomers can be interconverted only by breaking and reforming of bonds. Geometrical and optical isomers are the two important types of configurational isomers. The optical isomers rotate the plane of plane-polarised light. A sp^3–Hybridised carbon atom bearing four different types of substituents is called an asymmetric centre or chiral centre. Chiral molecules donot possess any of the elements of symmetry. A chiral object or molecule cannot be superimposed on its mirror image. Molecules that have or a centre of symmetry are superimpossable on their mirror images and are achiral. Stereoisomers that are mirror images of each other are called enantiomers. The stereoisomers that are not mirror images of each other are called

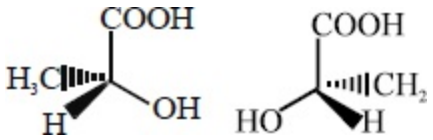
diastereomers. Which are enantiomers among the following structures.

(a) 

(b) 

(c) 



(d) 

104. Match the following –

(a) basic dye	(i) these are directly applied to fabric from aq. solution
(b) direct dye	(ii) the dyes get attached to anionic sides present on the fabrics
(c) vat dye	(iii) these act as ligand which coordinates to the metal ions
(D) mordant dye	(iv) on reduction converts to leuco form which is applied for dying and printing

105. Match the following –

(A) Talcom powder	(i) $(C_{17}H_{35}COO)_2Zn$
(b) Deodorant	(ii) $Mg_3(OH)_2Si_4O_{10}$

(c) Anti oxidant	(iii) Aspartame
(D) Artificial sweetener	(iv) these retard the action of oxygen on the food

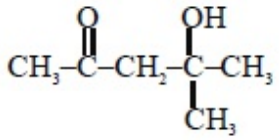
106. Match the following –

(A) Cationic detergent	(i) Alkylbenzene sulphonate
(b) Anionic detergent	(ii) Carbon Fibre Reinforced Carbon (CFRC)
(c) Carbon fibre	(iii) Cetyl trimethylammonium chloride
(D) Non ionic detergent	(iv) Esters formed from polyethylene glycol and stearic acid

107. Match the following –

(A) Analgesic	(i) Equanil
(b) Tranquilizer	(ii) Ibuprofen
(c) Anticeptic	(iii) Not safe for living tissues when used (Cl_2 in point to ppm)
(D) Disinfectant	(iv) Used to living tissues to kill microorganisms (soframycin)

108. Match List –I and List –II and select the correct answer from the code given below the list–

List– I (Name of reaction)	List – II (Product)
(i) Perkin reaction	(A) $CH_3–COCH_2–COOC_2H_5$
(ii) Claisen condensation	(B) 
(iii) Aldol condensation	(C) $C_6H_5–CH=CH–COOH$
(iv) Tischenko reaction	(D) $C_6H_5–CH=CH–CHO$

Codes

	(a)	(b)	(c)	(d)
(i)	(C)	(B)	(C)	(A)
(ii)	(A)	(B)	(A)	(C)
(iii)	(B)	(D)	(A)	(C)
(iv)	(A)	(D)	(C)	(B)

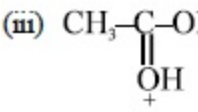
109. Match List –I and List –II and select the correct answer from the code given below the list–

List– I (Substances)	List – II (Value of 'a')
(i) $C_6H_6(g)$	(A) 0.217
(ii) $C_6H_5CH_3(g)$	(B) 5.464
(iii) Ne(g)	(C) 18.00
(iv) $H_2O(g)$	(D) 24.06

Codes

	(a)	(b)	(c)	(d)
(i)	(A)	(B)	(B)	(D)
(ii)	(D)	(A)	(C)	(C)
(iii)	(C)	(D)	(A)	(B)
(iv)	(B)	(C)	(D)	(D)

110. Match List –I and List –II and select the correct answer from the code given below the list–

List– I (Compounds)	List – II (pK_a value)
(i) $CH_3–CH_2–\overset{+}{O}H_2$	(A) 15.9
(ii) $CH_3–CH_2–\overset{+}{N}H_3$	(B) –6.1
(iii) 	(C) 11
(iv) $CH_3–CH_2–OH$	(D) –2.4

Codes

	(a)	(b)	(c)	(d)
(i)	(B)	(D)	(D)	(A)
(ii)	(D)	(C)	(B)	(C)
(iii)	(C)	(B)	(A)	(D)
(iv)	(D)	(A)	(B)	(A)

111. Match List –I and List –II and select the correct answer from the code given below the list–

List– I (Reagents)	List – II (Reactions involved)
(i) OsO_4 , $NaHSO_3 \cdot H_2O$	(a) Reduction of carbonyl group
(ii) BH_3 ,THF ; CH_3CO_2H	(b) Hydration of alkene
(iii) $Hg(OAc)_2$, $THF–H_2O$; $NaBH_4$, OH^-	(c) Reduction of alkene
(iv) $LiAlH_4$ ether ; H_2O	(d) Hydroxylation of alkene

Codes

	(a)	(b)	(c)	(d)
(i)	(D)	(C)	(A)	(B)
(ii)	(C)	(D)	(B)	(A)
(iii)	(C)	(D)	(A)	(B)
(iv)	(D)	(C)	(B)	(A)

112. Match List –I and List –II and select the correct answer from the code given below the list–

List– I (Intermediates)	List – II (Reactions involved)
(i) Meishenheimer	(a) Riemer – Tiemann reaction
(ii) Whenland intermediate	(b) Toluene with NBS (N-Bromosuccinamide)
(iii) Dichlorocarbene	(c) Nucleophilic aromatic substitution
(iv) Free radicals	(d) Nitration of benzene

Codes

	(a)	(b)	(c)	(d)
(i)	(C)	(A)	(D)	(B)
(ii)	(C)	(D)	(A)	(B)
(iii)	(B)	(A)	(D)	(C)
(iv)	(B)	(C)	(D)	(A)

113. Match List –I and List –II and select the correct answer from the code given below the list–

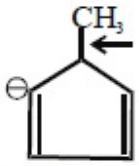
List– I (Catalyst/Reagent)	List – II (Used for)
(i) Jones reagent	(a) Homogeneous hydrogenation of alkene
(ii) Zeigler Natta catalyst	(b) Polythene production
(iii) Wilkinson's catalyst	(c) 'syn' hydrogenation of alkene
(iv) Lindlar catalyst	(d) Oxidizing alcohol to aldehyes

Codes

	(a)	(b)	(c)	(d)
(i)	(D)	(D)	(A)	(C)
(ii)	(D)	(B)	(C)	(A)
(iii)	(C)	(A)	(D)	(A)
(iv)	(B)	(C)	(D)	(A)

114. Match List –I and List –II and select the correct answer from the code given below the list–

List– I (Bond marked by ←) **List – II (Bond formed by)**

(i) 

(ii) $F\overset{\ominus}{=}CF_2$

(iii) $CH_3–CH_2–O–H$

(iv) $H_3C–O–H$

(A) $sp^3 - sp^3$ overlap

(B) $sp^2 - p$ overlap

(C) $sp^3 - s$ overlap

(D) $sp^3 - sp^3$ overlap

Codes

	(a)	(b)	(c)	(d)
(i)	(D)	(C)	(A), (D)	(B)
(ii)	(B)	(D)	(B)	(A)
(iii)	(B)	(D)	(C)	(C)
(iv)	(D)	(C)	(A), (D)	(A)

115. Match List –I and List –II and select the correct answer from the code given below the list–

List– I (Compound) **List – II (pK_a value)**

(i) $CH_2(NO_2)_2$

(ii) $CH_2(COMe)_2$

(iii) CH_3COCH_3

(iv) $CH_2(CO_2Et)_2$

(A) 13.3

(B) 4

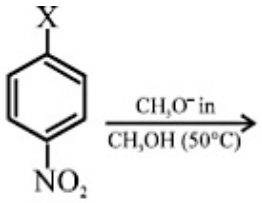
(C) 8.8

(D) 20

Codes

	(a)	(b)	(c)	(d)
(i)	(B)	(C)	(D)	(A)
(ii)	(C)	(B)	(B)	(C)
(iii)	(D)	(D)	(C)	(A)
(iv)	(A)	(A)	(A)	(D)

116. Match List –I and List –II and select the correct answer from the code given below the list–



List– I **List – II (Relative reactivity)**

(i) X = F

(ii) X = Cl

(iii) X = Br

(iv) X = I

(a) 0.8

(b) 312

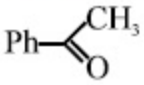
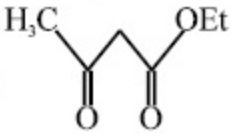
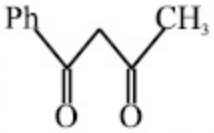
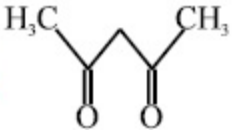
(c) 1

(d) 0.4

Codes

	(a)	(b)	(c)	(d)
(i)	(D)	(C)	(A)	(B)
(ii)	(B)	(C)	(A)	(C)
(iii)	(B)	(A)	(C)	(A)
(iv)	(D)	(A)	(C)	(D)

117. Match List –I and List –II and select the correct answer from the code given below the list–

List– I (Compound)	**List – II (Enol content)**
(i) 	(a) 89.2
(ii) 	(b) 1.1×10^{-6}
(iii) 	(c) 80
(iv) 	(d) 8.4

Codes

	(a)	(b)	(c)	(d)
(i)	(B)	(B)	(A)	(C)
(ii)	(B)	(D)	(C)	(A)
(iii)	(B)	(A)	(C)	(D)
(iv)	(D)	(C)	(A)	(B)

118. Unsaturation responds to Bayer's test and bromine water test. If bromine is added the red color of bromine decolourises due to stereoselective addition of bromine molecule to double bond. Answer the following accordingly ;

118.1 If 1 mole of Br_2 is added the product will be

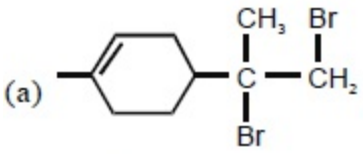
(a) Stereoselective

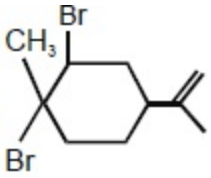
(b) stereospecific

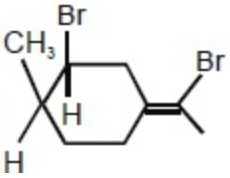
(c) (a, b) both

(d) none of these

118.2 Brominated product will be

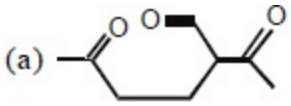
(a) 

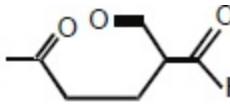
(b) 

(c) 

(d) none of these

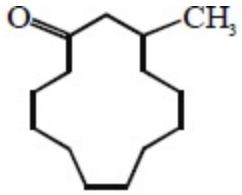
118.3 Bayer's test and Lemieux reagent (OsO_4 + $NaIO_4$) all introduce oxygen in the molecule. Products after the reaction with Lemieux reagent are

(a)  + HCOOH

(b)  + HCHO

(c) (a, b) both

(d) none of these

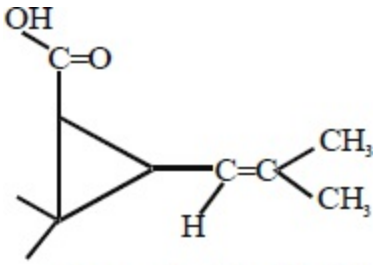
119.1 

Muscone

Can muscone add to HCN ?

119.2 If Muscone is to be produced from an alkyne then what should be the reagent to add to alkyne?

119.3 How many products you expect by reduction of muscone with $LiAlH_4$?

120. 

Chrysanthemic acid (A)

Crysanthemic acid upon treatment with cholic acid in presence of conc. H_2SO_4 (warming) by one mole each, gives a compound (A)

Answer the following ;

120.1 Will A respond to $NaHCO_3$ test ?

120.2 Will A respond to Lucas test ?

121. Epoxide ring cleaves in presence of aq. acid to give diol. Also olefinic n-bond gets polarised by electrophile like H^+ and give further nucleophilic addition products.

If (X) reacts with H^+/H_2O

121.1 Which one will react, epoxide or double bond ?

121.2 Can (X) under go 1, 4 addition anywhere with RMgX ?

121.3 Protonated (X) means protonation at ester or at double bond or at epoxide-O ?

121.4 Can (X) under go any attack by N – of streptimidone ?

121.5 How many stereoisomers streptimidone can show ?

122. Among purine, adenine, nicotine shown in the adjacent diagram all show basic character. Among them purine can show very little acidic character. Now answer the followings

122.1 Which one has maximum pk_{bi} value ?

122.2 Which one is non aromatic ?

123. In biological systems, biopolymers degrade mainly by enzymatic hydrolysis and to some extent by oxida- tion. In view of the disposal problem of polymer waste and for developing polymers for other safe uses in human system, biodegradable synthetic polymers have been developed. These synthetic polymers mostly have functional groups prevalent in biopolymers and lipids.

Which one among the followings is not an example of biodegradable synthetic polymers –

(a) Poly (β –Hydroxy butyrate) and (β –Hydroxy valerate)

(b) Poly (glycolic acid) and poly (lactic acid)

(c) Polyamide co-polymer of glycine and amino caproic acid (nylon-2, nylon-6)

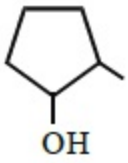
(d) All of these

124. Match the followings :

(A) $CH_3\underset{\underset{OH}{|}}{CH}(CH_2)_5CH_3 + SO_2Cl_2 \xrightarrow{K_2CO_3}$ product (i) S_N2

(B) $(CH_3CH_2)_2CHCH_2OH \xrightarrow[Pyridine]{SOCl_2}$ product (ii) S_Ni

(C) $CH_3(CH_2)_3CH_2OH \xrightarrow{HBr}$ product (iii) S_N2'

(D)  $\xrightarrow{PBr_3}$ product (iv) S_N1

(a) (A)-(i), (B)-(i), (C)-(iv), (D)-(ii) (b) (A)-(ii), (B)-(i), (C)-(iv), (D)-(iii)

(c) (A)-(ii, iii), (B)-(i), (C)-(iv), (D)-(iii) (d) (A)-(ii), (B)-(iii, i), (C)-(iv), (D)-(iii)

125. Match the followings according to the bond dissociation energy (k Cal/mole) for the indicated bonds given below:

(A) $CH_3\underset{\uparrow}{—}CH_3$ (i) 83

(B) $CH_3CH_2\underset{\uparrow}{—}CH_2CH_3$ (ii) 81

(C) $(CH_3)_2CH\underset{\uparrow}{—}CH_2CH_3$ (iii) 88

(D) $(CH_3)_3C\underset{\uparrow}{—}C(CH_3)_3$ (iv) 86

(a) A-(iii), B-(iv), C-(i), D-(ii) (b) A-(ii), B-(iv), C-(i), D-(iii)

(c) A-(i), B-(ii), C-(iii), D-(iv) (d) A-(iv), B-(iii), C-(ii), D-(i)

126. Match the followings according to the bond dissociation energy (k Cal/mole) for the indicated bonds given below:

(A) $CH_3CH_2CH_2$—Cl (i) 70

(B) CH_3—Br (ii) 82

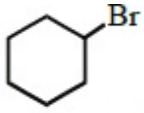
(C) $(CH_3)_2CH$—Cl (iii) 79

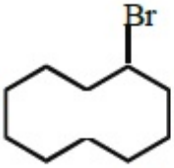
(D) $(CH_3)_3C$—Cl (iv) 81

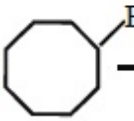
(a) A-(iii), B-(iv), C-(i), D-(ii) (b) A-(ii), B-(i), C-(iv), D-(iii)

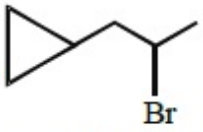
(c) A-(i), B-(ii), C-(iii), D-(iv) (d) A-(iv), B-(iii), C-(ii), D-(i)

127. Match the followings

(A)  $\xrightarrow[\Delta]{KOtBu}$ product/s (i) 2 geometrical isomers

(B)  $\xrightarrow[\Delta]{KOtBu}$ product/s (ii) No geometrical isomers

(C)  $\xrightarrow[\Delta]{KOtBu}$ product/s (iii) trans product is major

(D)  $\xrightarrow[\Delta]{CH_3\overset{-}{O}\overset{+}{K}}$ (iv) cis product is major

(a) A-(i, iii), B-(iv), C-(i, iv), D-(ii) (b) A-(ii, i), B-(i), C-(iii, iv), D-(iii)

(c) A-(i), B-(ii, iv), C-(iii, iv), D-(iv) (d) A-(ii), B-(i, iv), C-(i, iv), D-(i, iii)

128. (a) (A), (B) both are correct (b) (A) correct (B) is wrong

(c) (A), (B) both are correct but (B) is improper (d) both (A), (B) are wrong

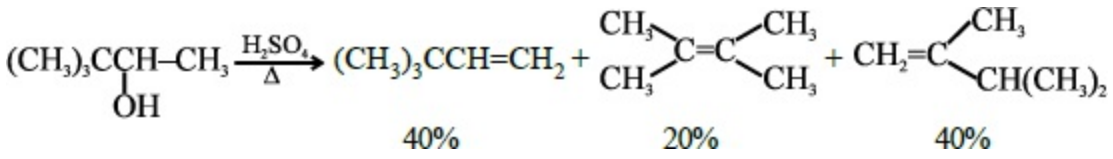
128.1 ***Assertion :-*** 2–bromo–2–methyl butane upon treatment with KOC_2H_5 at 70°C yields cis product.

Reason:- It follows Sayetzeff's elimination.

128.2 ***Assertion:–*** $CH_3(CH_2)_3OH \xrightarrow[170°C]{H_2SO_4}$ 1–butene + but–2–ene (major).

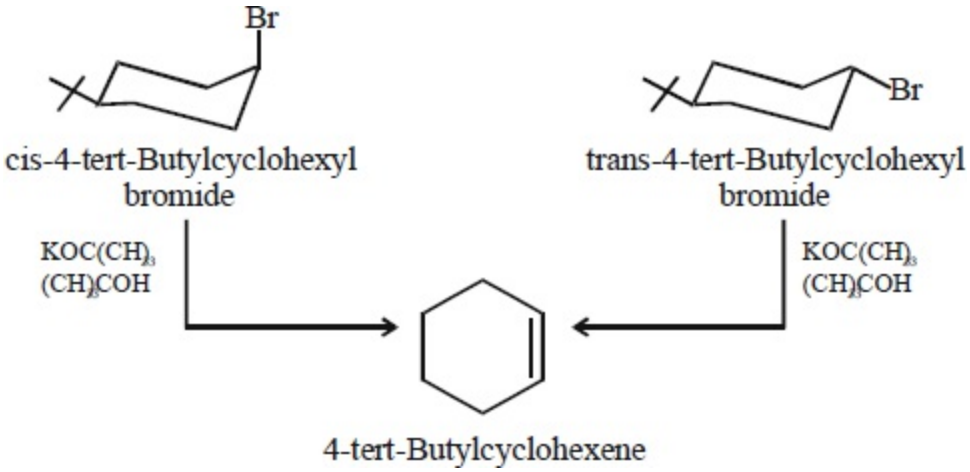
Reason :- The mechanism followed is E1.

128.3 ***Assertion:–***



Reason :- It follwos Hofamann's elimination by E2.

129. If we look into the E2 mechanism stereochemical features immediately comes into picture. One such experiment compares the rates of elimination of the cis and trans iosmers of 4–tert-butyl–cyclohexyl bromide.

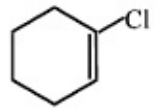


Altohugh both stereoisomers yield 4-tert-butylcyclohexene as the only alkene, they do so at quite different rates. The cis isomer reacts over 500 times faster than the trans. The difference in reaction rate results from different degrees of n bond development in the E2 transition state. Since p overlap of p orbitals requires their axes to be parallel, n bond formation is best achieved when the four atoms of the H–C–C–X unit lie in the same plane at the transition state. The two conformations that allow this are termed as syn coplanar and anti coplanar .

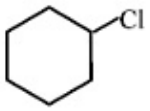
129.1 What is your conclusion regarding the rate of elimination of the followings –



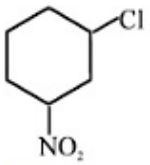
(a) I > II > III > IV (b) I > III > II > IV (c) IV > III > II > IV (d) None of these

129.2 

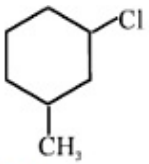
(I)



(II)

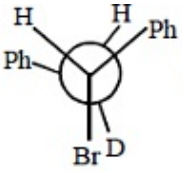


(III)



(IV)

(a) I > II > III > IV (b) I > III > II > IV (c) I > III > II > IV (d) None of these

129.3  can yield upon treatment with C_5H_5ONa

(a) cis product (b) trans product (c) both (d) none of these

130. Match the following considering the rate of SN reaction –

	Rate
(A) $PhCH_2CD_2Br$	(i) 20
(B) $Ph\,CD_2\,CH_2\,Br$	(ii) 19.5
(C) $Ph_2\,CD\,CH_2\,Br$	(iii) 30
(D) $Ph_2C\,CH_2\,Br$	(iv) 40

(a) (A)–(i), (B)–(iii),(C)–(iv), (D)–(iv) (b) (A)–(ii), (B)–(i),(C)–(iii), (D)–(iv)

(c) (A)–(ii), (B)–(iv),(C)–(iii), (D)–(i) (d) None of these

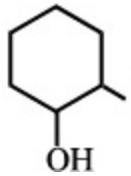
131. Match the following when R_1 , R_2 are the rates –

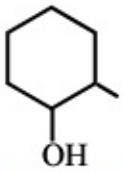
	Mechanism
(A) $CH_3OCH_2Cl \xrightarrow[R_1]{H_2O}$ Product	(i) SN 2
$CH_3SCH_2–Cl \xrightarrow[R_2]{H_2O}$ Product	
Result is $R_1 = R_2$	
(B) $CH_3CH_2–Cl \xrightarrow[CH_3COCH_3]{KOH}$ Product	(ii) SN 1
$CH_3CHD–Cl \xrightarrow[CH_3COCH_3]{KOH}$ Product	
Result is $R_1 \simeq R_2$	

(C) $(CH_3)_3CCH_2–Cl \xrightarrow[CH_3COCH_3]{NaHS}$ Product (iii) SN1

$(CH_3)_3C–Cl \xrightarrow[CH_3COCH_3]{NaHS}$ Product

Result is $R_1 \simeq R_2$

(D)  $\xrightarrow{PCl_5}$ Product (iv) SN1′

 $\xrightarrow{PCl_5}$ Product

(a) (A)–(ii), (B)–(i),(C)–(iii), (D)–(iv) (b) (A)–(i), (B)–(ii),(C)–(iii), (D)–(iv)

(c) (A)–(ii), (B)–(iv),(C)–(iii), (D)–(i) (d) None of these

132. Match the followings

(A)	Alkane molecules	(i)	Vander Waal's radii
(B)	Alcohol molecules	(ii)	London's dispersion force
(C)	Ketones molecules	(iii)	Dipole-dipole attraction
(D)	Amide molecules	(iv)	H-bonding

(a) (A)–(i) (ii), (B)–(iv),(C)–(iii), (D)–(iv) (b) (A)–(ii), (B)–(i),(C)–(iii), (D)–(iv)

(c) (A)–(ii), (B)–(iv),(C)–(iii), (D)–(i) (d) None of these

133. Match the followings

(a)	H_2O	(i)	1.7
(b)	CH_3OH	(ii)	1.8
(c)	CH_3Cl	(iii)	0
(d)	$CH_3CH_2CH_3$	(iv)	1.9

(a) (A)–(ii), (B)–(i),(C)–(iv), (D)–(iii) (b) (A)–(ii), (B)–(i),(C)–(iii), (D)–(iv)

(c) (A)–(ii), (B)–(iv),(C)–(iii), (D)–(i) (d) None of these

134. Which has highest boiling points of the following compounds –

(a) CH_3Cl, CH_2Cl_2 , $CHCl_3$, CCl_4

(b) $\underset{(I)}{CH_3CH_2F}$, $\underset{(II)}{CH_3CHF_2}$, $\underset{(III)}{CH_3CF_3}$, $\underset{(IV)}{CF_3CF_3}$

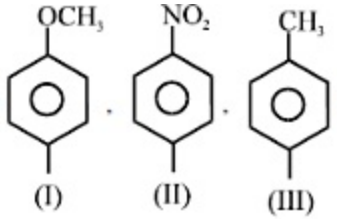
135. Alkene synthesis via alcohol dehydration is complicated by carbocation

rearrangements. A less stable carbo cation can rearrange to a more stable one by an alkyl group migration or by a hydride shift, opening the possibility for alkene formation from two different carbocations.



Secondary carbocation Tertiary carbocation

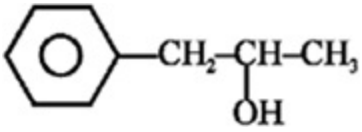
(G is a migrating group; it may be either a hydrogen, an alkyl group or aryl group)

135.1 If G =  (Hypothetically)

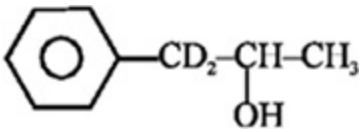
(I) (II) (III)

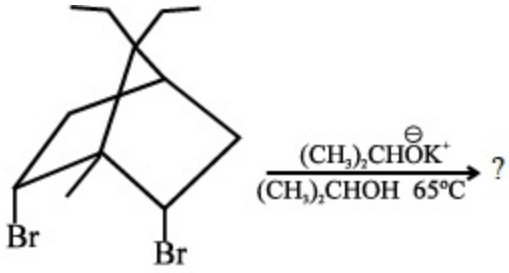
Which one should migrate fastest –

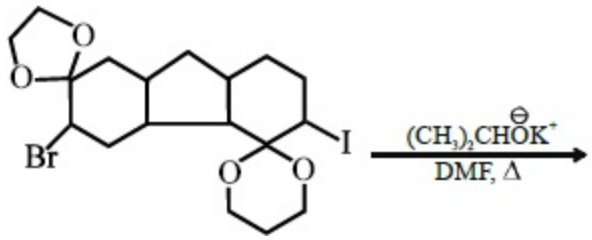
(a) I (b) II (c) (III) (d) Can't be said

135.2 Write the product for 

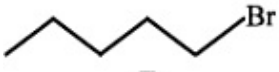
135.3 Will there be any change of rate in comparision to (ii) when we take

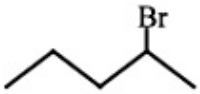


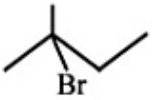
136. 

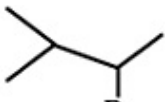
137 

138. The structural isomers of the halide $C_5H_{11}Br$ are shown as follows –


(I)


(II)


(III)


(IV)

138.1 Which one will show fastest E2 ?

138.2 Which one will show fastest E1 ?

138.3 Which one will show fastest E_1CB ?

138.4 Which one will show fastest Ei ?

139. Match the following –

	A		**B (major product)**
(A)	$CH_2=CHCH(CH_3)_2+HCl \longrightarrow$	(i)	$CH_3\underset{\displaystyle Cl}{\underset{\vert}{C}}HCH(CH_3)_2$
(B)	$CH_2=CCl\,CH(CH_3)_2+H_2 \longrightarrow$	(ii)	$CH_3CH_2\text{–}\underset{\displaystyle Cl}{\underset{\vert}{C}}(CH_3)_2$
(C)	$CH_2=CHCH_2CH_3+HBr \xrightarrow{(RCO)_2O_2}$	(iii)	$CH_3\underset{\displaystyle Br}{\underset{\vert}{C}}HCH_2CH_3$
(D)	$CH_2=CBrCH_2\,CH_3+H_2 \longrightarrow$	(iv)	$\underset{\displaystyle Br}{\underset{\vert}{C}}H_2CH_2CH_2CH_3$

(a) A–(ii), B–(i), C–(iv), D–(iii)

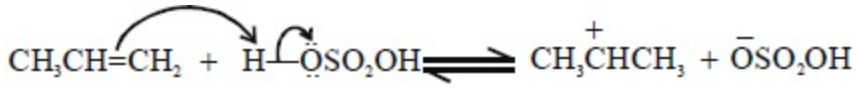
(b) A–(i), B–(ii), C–(iv), D–(iii)

(c) A–(iv), B–(i), C–(iii), D–(ii)

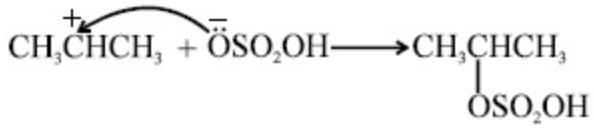
(d) A–(iii), B–(i), C–(iv), D–(ii)

140. Mechanism for the addition of H_2SO_4 to alkene is shown as follows ;

Step–1 : Protonation of the carboN–Carbon double bond in the direction that leads to the more stable carbocation, as shown below ;



Step–2 : Carbocation–anion combination



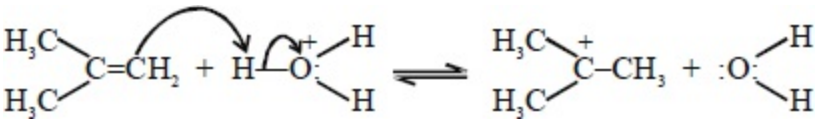
140.1 What is the regioselectivity ?

140.2 Can there be any rearrangement ?

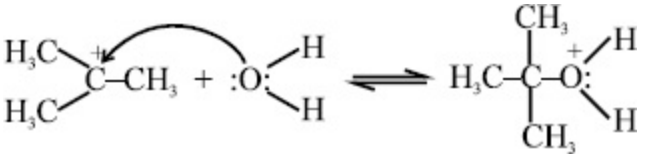
140.3 Which one should be the rds ?

140.4 Will more be any change of rate if $CD_3CH=CH_2$ is taken ?

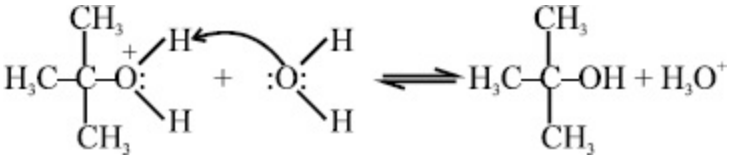
141. Step–I : Protonation of the carbon–carbon double bond in the direction that leads to the more stable carbocation.



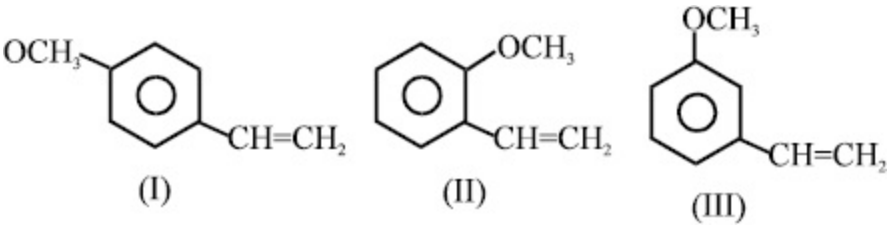
Step–II : Water acts as a nucleophile to capture tert-butyl cation :



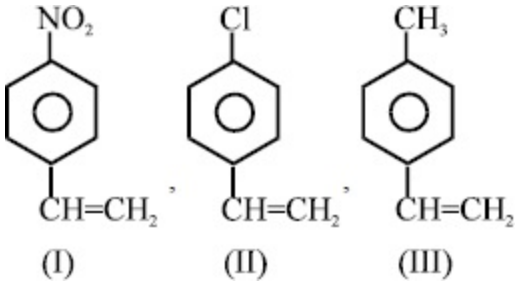
Step–III : Deprotonation of tert-butyloxonium ion. Water acts as a Bronsted base :



141.1 Which one will show fastest hydration ?



(I) (II) (III)

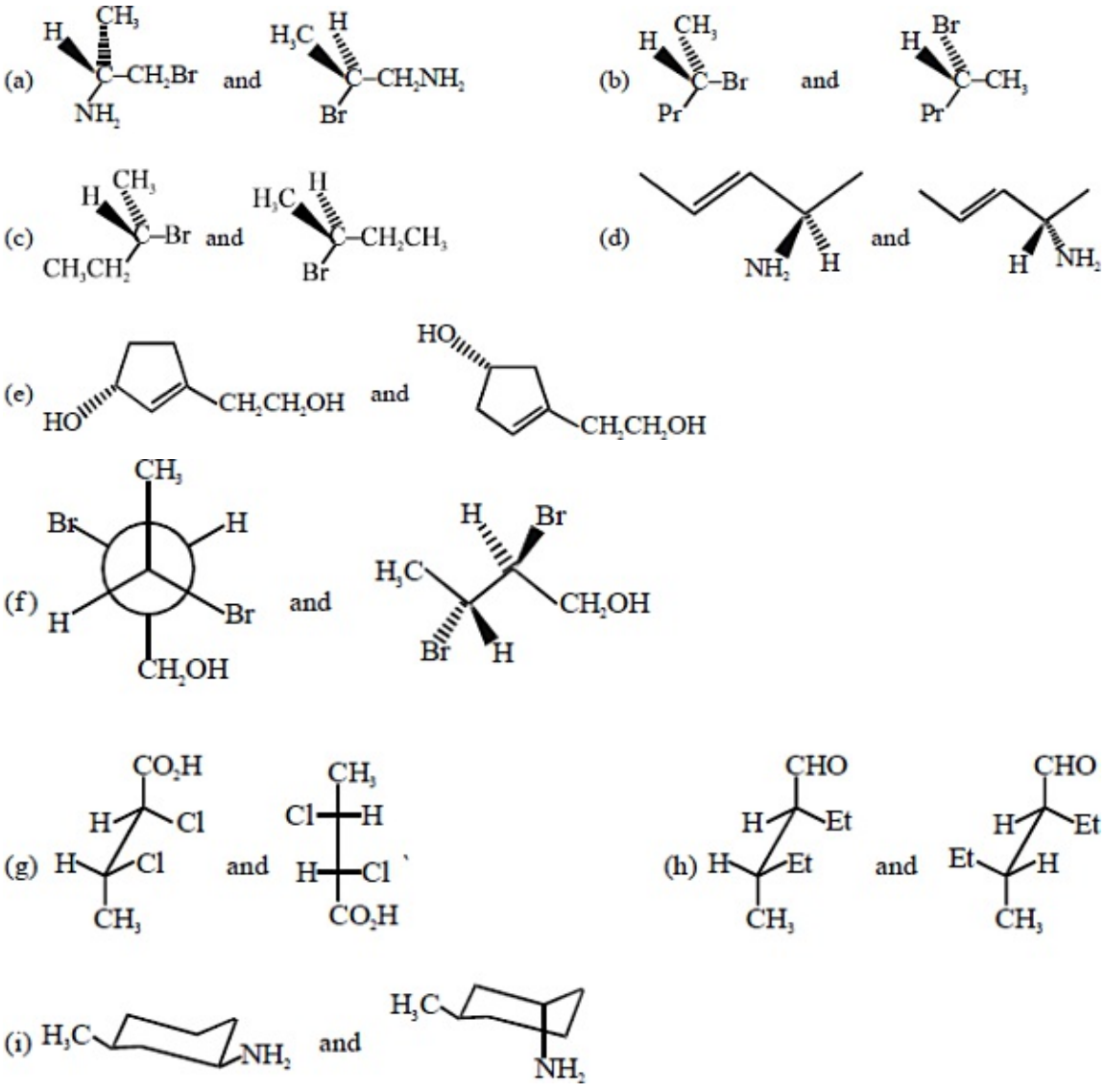
141.2 Among  which will show fastest rate of hydration.

(I) (II) (III)

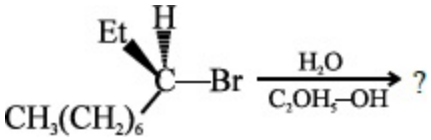
141.3 Which one is the stronger acid ?

H_3O+ or $(CH_3)_3C+$

142. Identify the relationship in each of the following pairs.



143. Write the nature of the products



(a) Racemic mixture

(b) More inversion of configuration

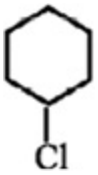
(c) More retention of configuration

(d) All of these

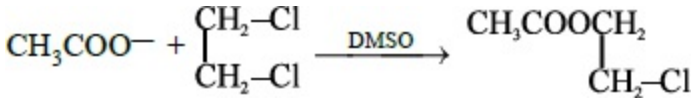
144. Out of the followings which are more reactive through SN1

(a) $CH_3(CH_2)_3CH_2Cl$

(b) 

(c) 

(d) CH_3CD_2Cl

145. 

The above reaction occurs by –

(a) SN2

(b) Through NGP

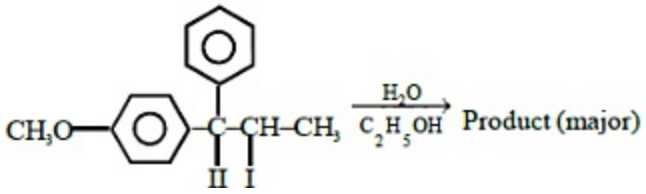
(c) SN1

(d) SN1'

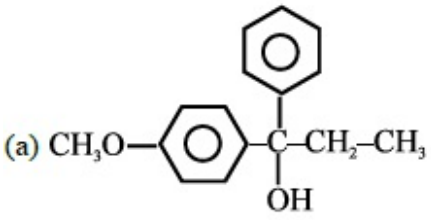
146. $(CH_3)_2\underset{Br}{CH}-CH-CH_3 \xrightarrow[C_2H_5OH]{H_2O}$ Product (major)

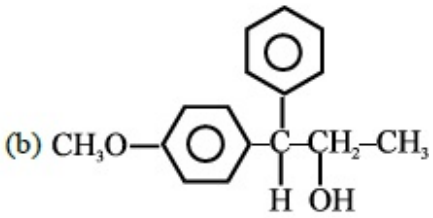
Product (major) is

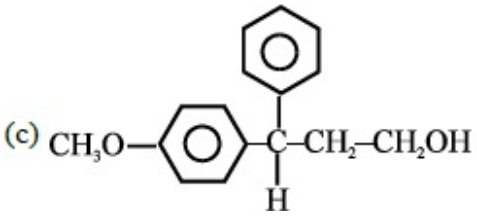
(a) $(CH_3)_2CH-\underset{OH}{CH}-CH_3$ (b) $(CH_3)_2\underset{OH}{C}-CH_2CH_3$ (c) $(CH_3)_2\underset{OC_2H_5}{CH}-CH-CH_3$ (d) All of these

147. 

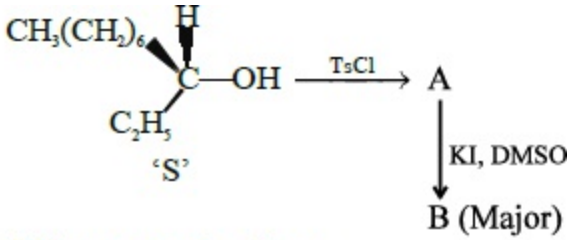
Major product is –

(a) 

(b) 

(c) 

(d) None of these

148. 

'B' has stereochemistry –

(a) R

(b) S

(c) R, S both

(d) None of these

149. $HC\equiv\overset{\ominus}{C} + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br \rightarrow$ product

Product is –

(a) a SN2 product

(b) an E1product

(c) an E2 product

(d) an E1CB product

150. $CH_3CH_2CH_2C\equiv C\,CH_2CH_2CH_3 + H_2O \xrightarrow[Hg^{+2}]{H^+} X$

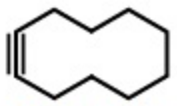
$H\text{–}C\equiv C - (CH_2)_5CH_3 \xrightarrow[H_2O]{Hg^{+2},\,H^+} Y$

(a) 4 octanone, 2–octanone

(b) 5 octanone, 2–octanone

(c) 4 octanone, 3–octanone

(d) None of these

151. 

X and Y are –

(a) cis, trans

(b) trans, cis

(c) cis, cis

(d) trans, trans

152. Match the following –

[Compounds]	[Boiling Point]
(A) $C_6H_4NH_2$	(i) 351
(B) $(C_2H_5)_2NH$	(ii) 329
(C) $C_2H_5N(CH_3)$	(iii) 311
(D) C_4H_9OH	(iv) 390

(a) (A)–(ii); (B_{MO} ; (C)–(iii); (D)–(iv)

(b) (A)–(i); (B)–(ii) ; (C)–(iii); (D)–(iv)

(c) (A)–(iv); (B)–(i) ; (C)–(iii); (D)–(ii)

(c) (A)–(i); (B)–(ii) ; (C)–(iv); (D)–(iii)

153. Match the following –

[Compounds]	[Boiling Point]
(A) CH_3CN	(i) 354.6
(B) C_2H_5CN	(ii) 370
(C) $CH_3C{\equiv}CH$	(iii) 295

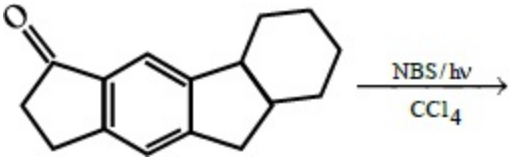
(a) (A(–i); (B)–(ii) ; (C)–(iii)

(b) (A)–(ii); (B)–(i) ; (C)–(iii)

(c) (A)–(ii); (B)–(iii) ; (C)–(i)

(c) (A)–(iii); (B)–(i) ; (C)–(ii)

154. Number of monobromo derivatives in the given reaction would be –



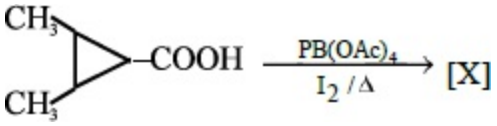
(a) One

(b) Two

(c) Three

(d) Five

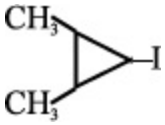
155. In the given reaction



[X] is –

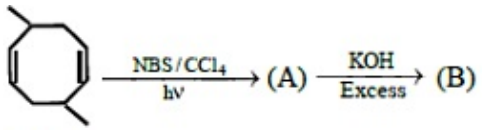
(a) $CH_2I\text{-}CH_2\text{-}CHI\text{-}COOH$

(b) $CH_3–CHI–CHI–COOH$

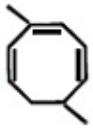
(c) 

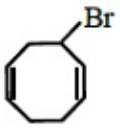
(d) $CH_2I–CH_2–CH_2I$

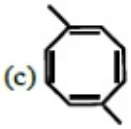
156. Product of the given reaction

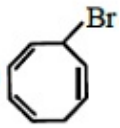


(B) is –

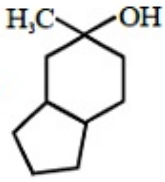
(a) 

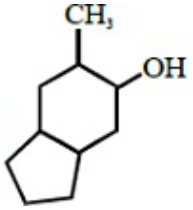
(b) 

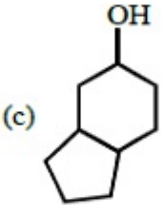
(c) 

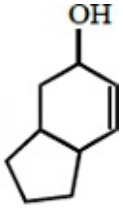
(d) 

157. Which one among the following alcohols show maximum rate of reactivity during dehydration reaction ?

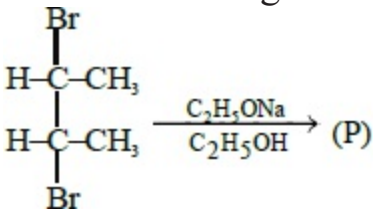
(a) 

(b) 

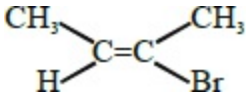
(c) 

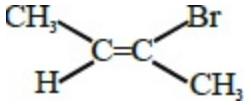
(d) 

158. In the following reaction –



(P) will be –

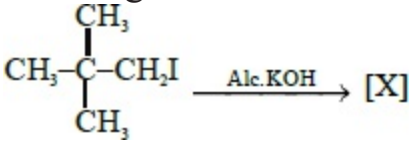
(a) Only 

(b) Only 

(c) 1 : 1 mixture of (a) and (b)

(d) 2 : 1 mixture of (a) and (b)

159. In the given reaction



[X] will be –

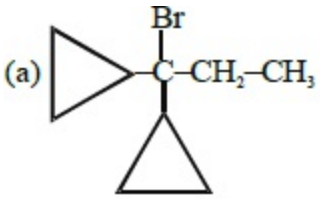
(a) 3–methyl–1–butene

(b) 2–methyl–2–butene

(c) 2–butene

(d) 1–butene

160. Which one of the following will be the most reactive for E1 reactions ?

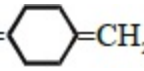
(a) 

(b) $C_6H_5–\underset{Br}{\underset{|}{CH}}–C_2H_5$

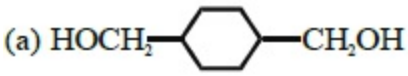
(c) $CH_2=CH–\underset{Br}{\underset{|}{CH}}–C_2H_5$

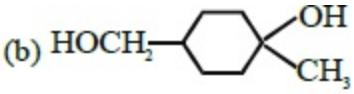
(d) $CH_2=CH–\underset{\underset{CH_3}{|}}{\overset{Br}{\overset{|}{C}}}–C_2H_5$

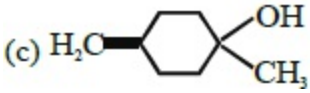
161. In the following reaction

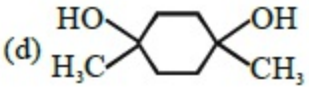
$H_2C=$  $=CH_2 \xrightarrow[(ii)\ H_2O_2/OH^-]{(i)\ B_2H_6/THF\ (excess)}$

the product formed will be –

(a) 

(b) 

(c) 

(d) 

162. Match List-I with List-II and select the correct answer using the codes given below the lists –

List–I (Reactions)	List–II (Reagents)
(A) $C_2H_5–CH=CH_2 \rightarrow C_2H_5–CHBr–CH_3$	(1) HBr
(B) $C_2H_5–CH=CH_2 \rightarrow C_2H_5–CH_2–CH_2Br$	(2) Br_2
(C) $C_2H_5–CH=CH_2 \rightarrow CH_3CHBr–CH=CH_2$	(3) HBr/H_2O_2
(D) $C_2H_5–CH=CH_2 \rightarrow CH_3–CH_2CHBr–CH_2Br$	(4) NBS

	A	B	C	D
(a)	1	3	2	4
(b)	1	3	4	2
(c)	3	1	4	2
(d)	3	1	2	4

163. Match List–I with List–II and select the correct answer using the codes given below the lists –

List–I (Reactions)

(A) $C_2H_5–CH=CH_2 + HCl \rightarrow C_2H_5–\underset{Cl}{CH}–CH_3$

(B) $C_2H_5–CH=CH_2 + HBr \xrightarrow{H_2O_2} C_2H_5–CH_2–CH_2–Br$

(C) $CH_3–\underset{CH_3}{\overset{CH_3}{C}}–CH_2OH \xrightarrow{ZnCl_2/HCl} CH_3–\underset{CH_3}{\overset{Cl}{C}}–CH_2–CH_3$

(D) $C_2H_5–CH=CH_2 + \ddot{C}H_2$ (Singlet) $\rightarrow C_2H_5–CH\overset{CH_2}{\diagdown\diagup}CH_2$

List–II (Reagents)

(1) S_N1

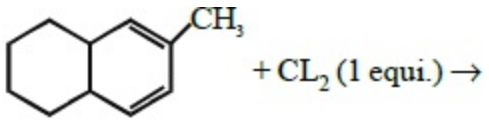
(2) Electrophilic addition

(3) Free radical addition

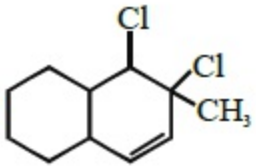
(4) Concerted addition

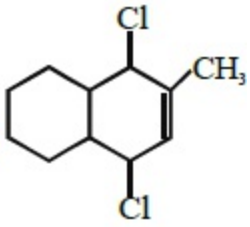
	A	B	C	D
(a)	3	2	1	4
(b)	2	3	1	4
(c)	1	3	2	4
(d)	4	3	2	1

164. The product (s) of the given reaction

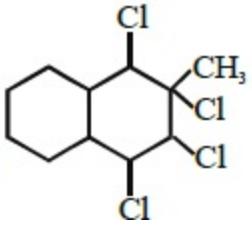


is –

(a) Only 

(b) Only 

(c) Mixture of (a) and (b)

(d) 

165. Read the passage carefully and answer the following :

Alkenes undergo electrophilic addition reacton with $Hg(OCOCH_3)_2$, BH_3 and H_2O_2/OH^- , H_2O/H^+ . In all these cases reaction is regioselective reaction. BH_3 gives addition reaction through formation of four centred cyclic transition state. $Hg(OCOCH_3)_2$ gives addition reaction through formation of bridge carbocation as reaction intermediate whereas water gives addition reaction through formation of classical carbocation in presence of acid catalyst.

165.1 Alkene can be converted into alcohol by which of the following reagents :

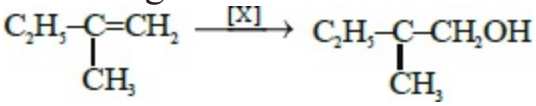
(a) H_2O/H_2SO_4

(b) BH/THF followed by H_2O_2/NaOH

(c) $Hg(OCOCH_3)_2$ / H_2O followed by $NaBH_4$

(d) All of these

165.2 In the given reaciton :



[X] is –

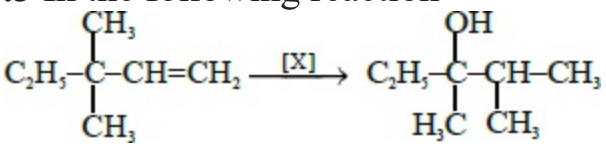
(a) $Hg(OCOCH_3)_2$ / H_2O followed by $NaBH_4$

(b) BH_3 followed by H_2O_2/NaOH

(c) H_2O/H_2SO_4

(d) All of these

165.3 In the following reaction –



[X] is –

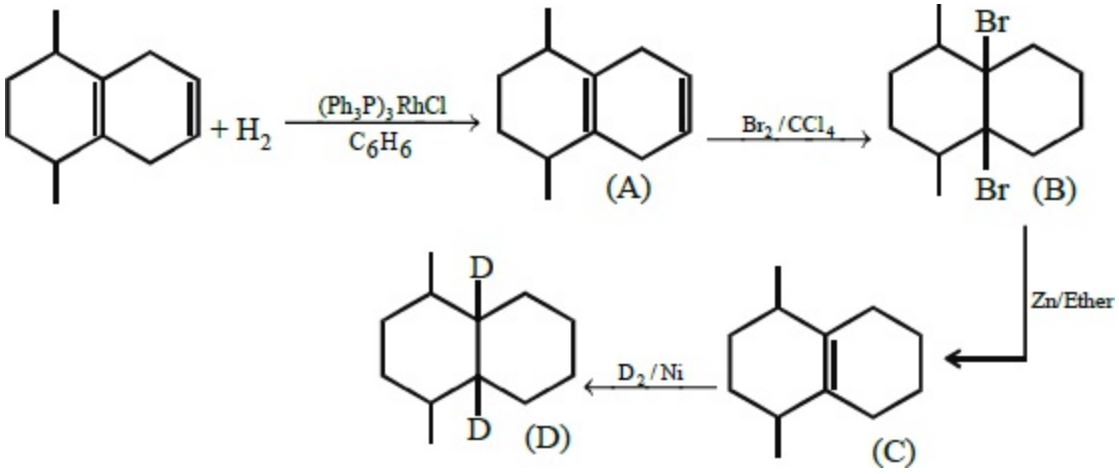
(a) H_2O/H_2SO_4

(b) $Hg(OCOCH_3)_2$ / H_2O followed by $NaBH_4$

(c) BH_3 followed by H_2O_2/NaOH

(d) All of these

166. In the given reaction sequence



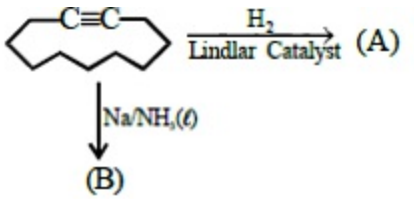
Which one of the products is not correct –

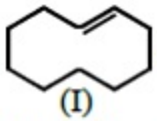
(a) A

(b) C

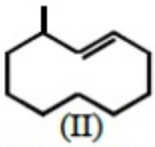
(c) D

(d) B

167. 

(a)  in both cases

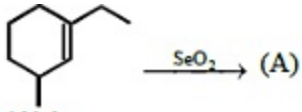
(I)

(b)  in both cases

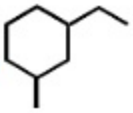
(II)

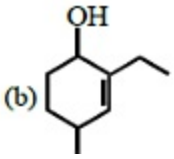
(c) (A) is (I) and (B) is (II)

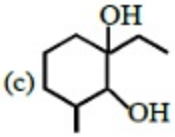
(d) Only (B) is correct

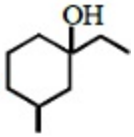
168. 

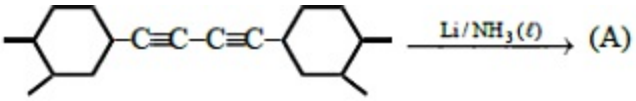
(A) is –

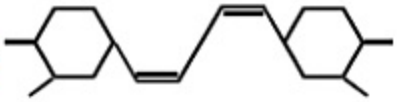
(a) 

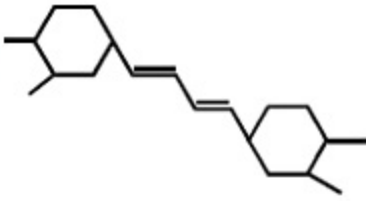
(b) 

(c) 

(d) 

169. 

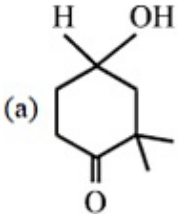
(a) 

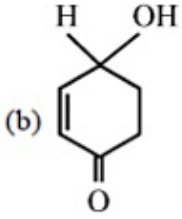
(b) 

(c) Both (a) and (b)

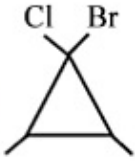
(d) None

170. Which one of the following compounds has a chiral centre :

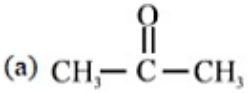
(a) 

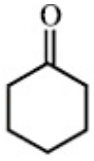
(b) 

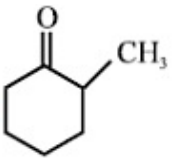
(c) 

(d) 

171. Which of the compound will show tautomerism?

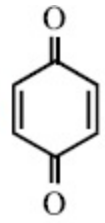
(a) 

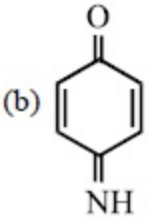
(b) 

(c) 

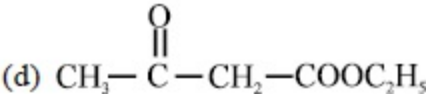
(d) All of these

172. Which of the following compounds does not exist in the enol form ?

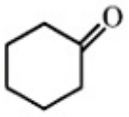
(a) 

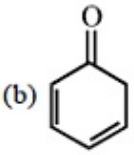
(b) 

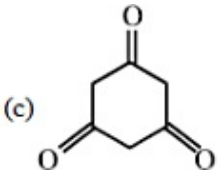
(c) both (a) and (b)

(d) 

173. Which of the compounds exist mainly in the enol form ?

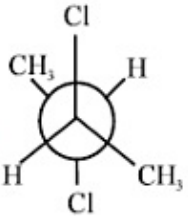
(a) 

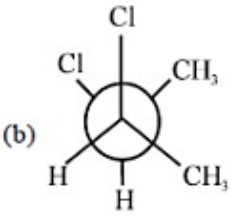
(b) 

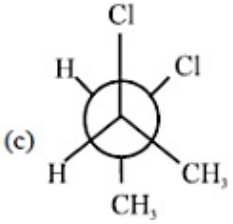
(c) 

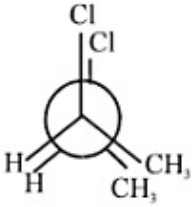
(d) All of these

174. Which of the following is most stable conformer ?

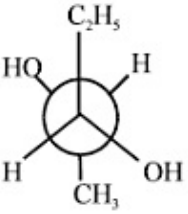
(a) 

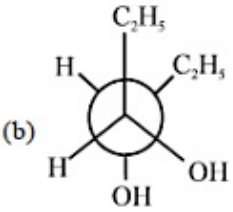
(b) 

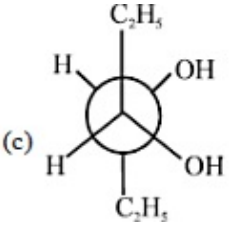
(c) 

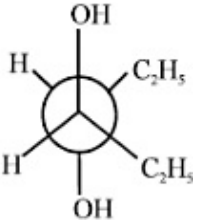
(d) 

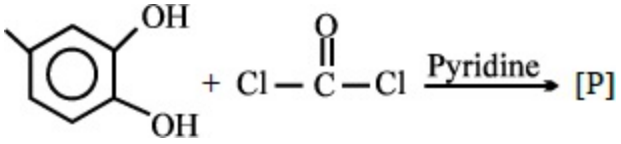
175. Which of the following is the most stable conformer ?

(a) 

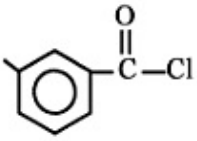
(b) 

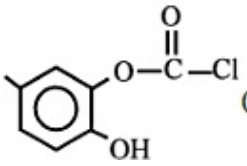
(c) 

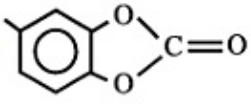
(d) 

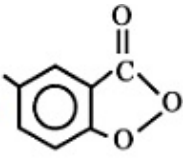
176. In the given reaction 

[P] will be :

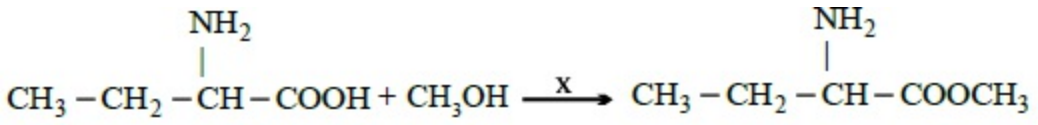
(a) 

(b) 

(c) 

(d) 

177. In the given reaction



(x) will be-

(a) $H^{\oplus}$ (b) $\overset{\ominus}{O}H$ (c) $CH_3\overset{\ominus}{O}$ (d) HOH

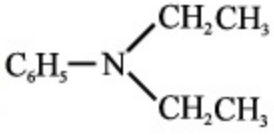
178.1 ***Assertion :-*** Treatment of phenol with nitrous acid yields p-benzoquinone monoxime.

Reason :- p- nitrosophenol and p- benzoquinone monoxime are tautomers.

178.2 ***Assertion :-*** Alkylation of benzene by Friedel –Crafts reaction gives polyalkylated benzene

Reason :- The ring gets activated for further substitution after the introduction of one alkyl group.

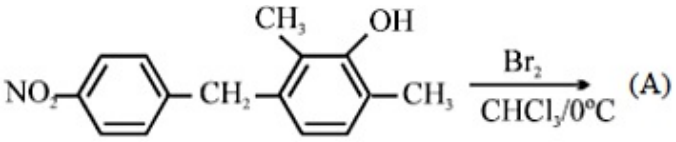
179. Match List-I with List-II and select the correct answer from the codes given below the lists :

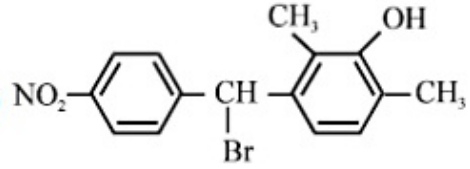
List -I (Compounds)	**List- II (rate of bromination)**
(A) $C_6H_5-OCH_3$	(1) 10^9
(B) 	(2) 10
(C) $C_6H_5-CH_2CH_3$	(3) 1
(D) C_6H_6	(4) 10^{14}

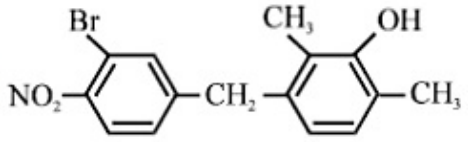
Codes :

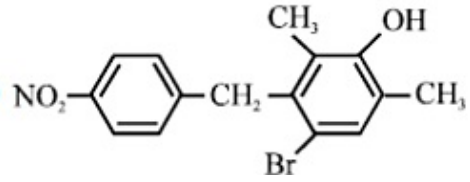
	A	B	C	D
(a)	3	1	1	2
(b)	1	4	2	3
(c)	1	2	2	3
(d)	4	3	2	3

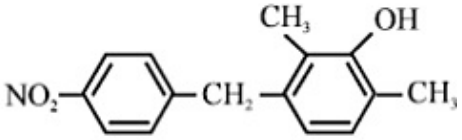
180. Identify the product obtained in the following reaction :



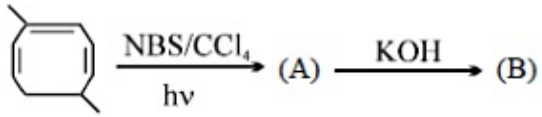
(a) 

(b) 

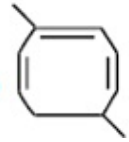
(c) 

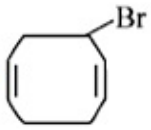
(d) 

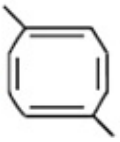
181. Product of the given reaction

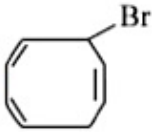


(B) is :

(a) 

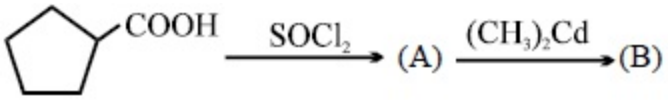
(b) 

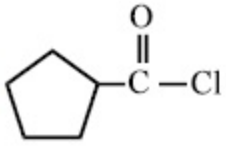
(c) 

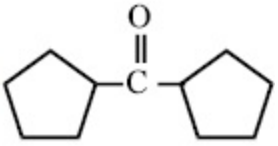
(d) 

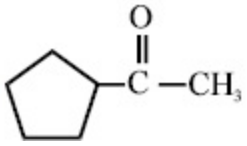
182. In the given reaction sequence

(b) will be:



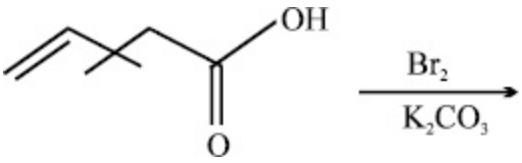
(a) 

(b) 

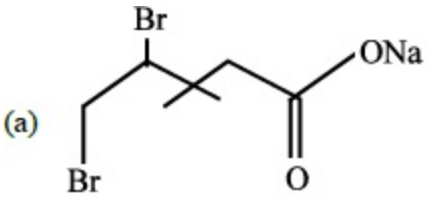
(c) 

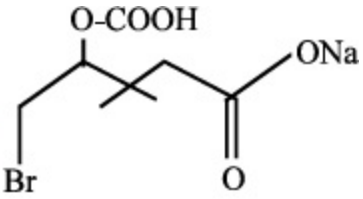
(d) All of these

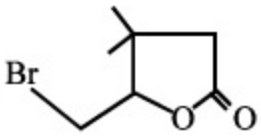
183. In the following reaction

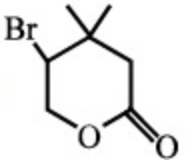


the major product formed is :

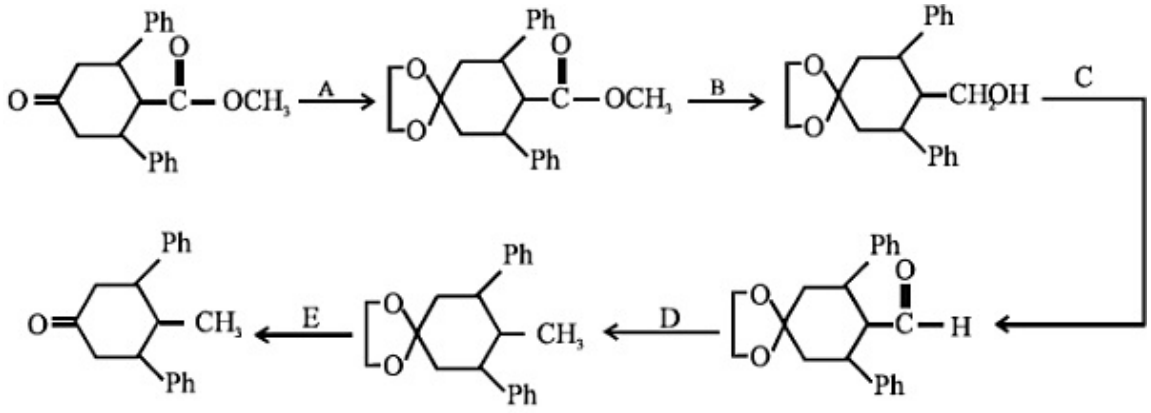
(a) 

(b) 

(c) 

(d) 

184. Match the reaction and reagent used and select the correct answer from the codes given below the list:



(1) CH_2OH | CH_2OH

(2) $LiAlH_4$/ether/ $H_3O^{\oplus}$

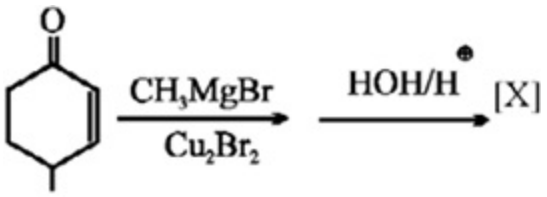
(3) $NH_2 - NH_2$/ KOH

(4) H_3O^+

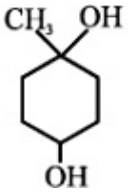
(5) $Br_2 + H_2O$

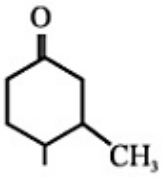
	A	B	C	D	E
(a)	1	2	5	3	4
(b)	1	3	4	5	2
(c)	1	5	4	3	2
(d)	5	4	3	2	1

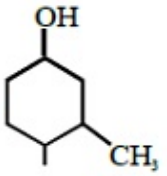
185. In the given reaction :

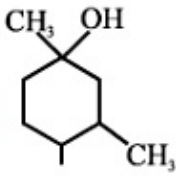


[X] will be :

(a) 

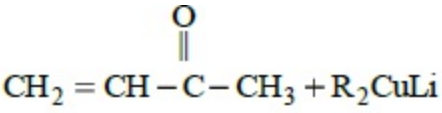
(b) 

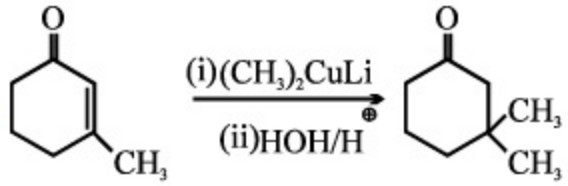
(c) 

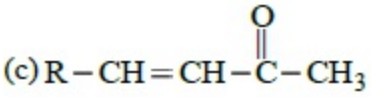
(d) 

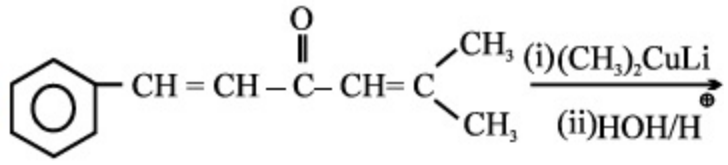
186. Lithium organocuprate does not react with aldehydes and ketones. α , β - unsaturated aldehydes and ketones give conjugate addition with this reagent. If carbonyl group is conjugated with two carbon- carbon double bonds, then conjugate addition takes place on the conjugate carbon which is less substituted.

Which reaction is possible?

(a) 

(b) 

(c) 

(d) 

(e) All of these

187. Look at the following series of reactions and answer the following questions.

187.1 Among the following reactions which will follow the SN1 reaction ?

187.2 Among the following reactions which will follow the SN2 reaction ?

187.3 Among the following reactions which will not occur ?

187.4 Among the following reactions which will follow the bimolecularity ?

187.5 Among the following reactions which will follow the unimolecularity ?

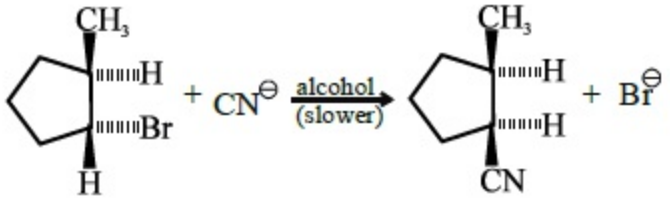
187.6 Among the following reactions which will follow the SNi reaction ?

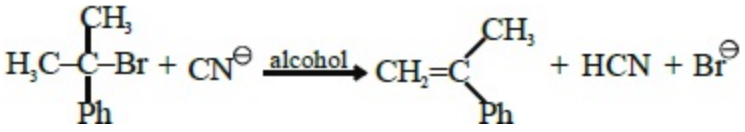
187.1 In reaction 6, if we change the solvent to aqueous alcohol, then what will be the change in the rate of the reaction ?

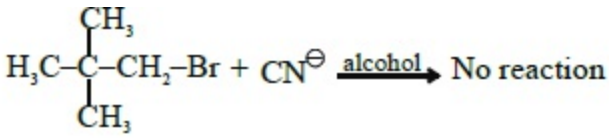
187.1 How many optical isomers of the product are possible in reaction 2 ?

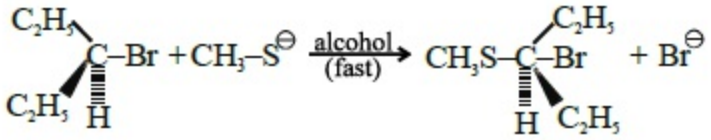
187.9 In reaction (1) if the solvent is changed to dimethyl ether then what will be the change in the reaction rate ?

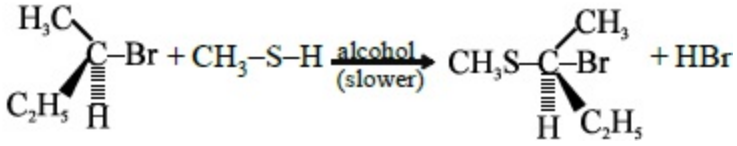
1. $CH_3CH_2CH_2Br + CN^{\ominus} \xrightarrow[\text{(fast)}]{\text{alcohol}} CH_3CH_2CH_2CH_2CN + Br^{\ominus}$

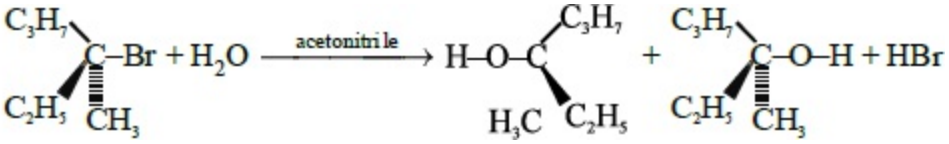
2. 

3. 

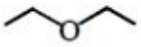
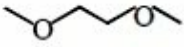
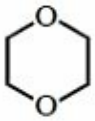
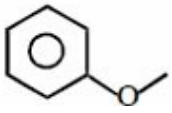
4. 

5. 

6. 

7. 

188. State True or False –

(A)	The smallest cyclic ether	(i)	
(B)	An aerosol spray propellant	(ii)	
(C)	A common low boiling solvent	(iii)	
(D)	A high boiling solvent	(iv)	
(E)	Dioxane, a cyclic ether and high boiling solvent	(v)	
(F)	One of the most polar simple ethers that is used as a solvent	(vi)	
(G)	Anisole (methoxy benzene), a major constituent of the essential oil of anise seed.	(viii)	

189. State True or False :–

Diethyl ether peroxides can be detected with potassium iodide (KI) solution or potassium iodide / starch paper. A positive test results in the

formation of iodine (I_2) that causes a pink color of the ether phase or a dark bluish spot on the paper strip.

190. State True or False :–

An aromatic compound contains a set of covalently-bound atoms with specific characteristics:

a) A delocalized conjugated pi system, most commonly an arrangement of alternating single and double bonds

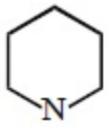
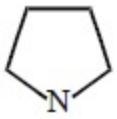
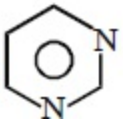
b) Coplanar structure, with all the contributing atoms in the same plane

c) Contributing atoms arranged in one or more rings

d) A number of pi delocalized electrons that is even but not a multiple of 4. This is known as Huckel's rule. Permissible numbers of pi electrons include 6, 10, 14, and so on.

e) special reactivity in organic reactions for example electrophilic aromatic substitution and nucleophilic aromatic substitution [all are true]

191. Match the following :

Base	pKa
(A) 	(i) 5.2
(B) 	(ii) 11
(C) 	(iii) 11.2

(a) (A)–(iii); (B)–(ii); (C)–(i)

(a) (A)–(ii); (B)–(iii); (C)–(i)

(c) (A)–(iii); (B)–(i); (C)–(ii)

(d) (A)–(i); (B)–(ii); (C)–(iii)

192. Elimination reactions are important as a method for the preparation of alkenes. The term ***"elimination"*** describes the fact that a small molecule

is lost during the process. A **1,2-elimination** indicates that the atoms that are lost come from adjacent C atoms. The two most important methods are:

(a) Dehydration ($-H_2O$) of alcohol, and

(b) Dehydrohalogenation (–HX) of alkyl halides.

There are three fundamental events in these elimination reactions:

(c) removal of a proton

(d) formation of the C=C pi bond

(e) breaking of the bond to the leaving group

Depending on the relative timing of these events, different mechanisms are possible:

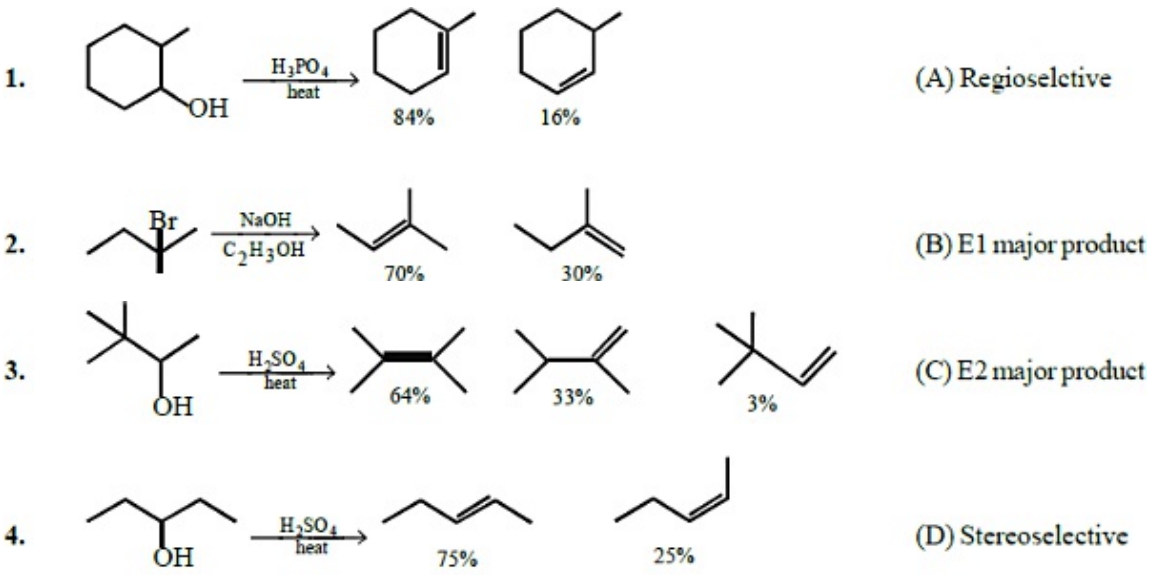
(f) Loss of the **LG** to form a carbocation, removal of H^+ and formation of C=C bond : E1 reaction

(g) Simultaneous H^+ removal, C=C bond formation and loss of the **LG** : E2 reaction

(h) Removal of H^+ to form a carbanion, loss of the **LG** and formation of C=C bond (E1cb reaction)

In many cases the elimination reaction may proceed to alkenes that are constitutional isomers with one formed in excess of the other. This is described as **regioselectivity.** Sayetzeff's rule, based on the dehydration of alcohols, describes the preference for eliminations to give the highly substituted (more stable) alkene, which may also be described as the **Sayetzeff product.** The rule is not always obeyed, some reactions give the anti-Zaitsev product. **Regioselectivity** (products are constitutional isomers): **Sayetzeff's rule,** based on experimental observations of the dehydration of alcohols, expresses the preference for eliminations to give the highly substituted **(more stable)** alkene, which may also be described as the **Sayetzeff product. Similarly,** eliminations often the more stable trans-product over the cis-product **(stereoselectivity)** . **Stereoselectivity (products are stereoisomers)**

Match the following considering the above passage.



(a) 1–A; 2–A,C ; 3–A,B, 4–B,D
(b) 1–B; 2–A,C ; 3–A,B, 4–B,D
(c) 1–A; 2–A,C ; 3–B, 4–B,D
(d) 1–C; 2–A,C ; 3–A,B, 4–B,D

194. The key concepts of resonance are:

Resonance occurs because of the overlap of orbitals. Double bonds are made up of pi bonds, formed from the overlap of 2p orbitals. The electrons in these pi orbitals will be spread over more than two atoms, and hence are delocalized.

Both paired and unshared electrons may be delocalized, but all the electrons must be conjugated in a pi system.

If the orbitals do not overlap (such as in orthogonal orbitals) the structures are not true resonance structures and do not mix.

Molecules or species with resonance structures are generally considered to be more stable than those without them. The delocalization of the electrons lowers the orbital energies, imparting this stability. The resonance in benzene gives rise to the property of aromaticity. The gain in stability is called the **resonance energy.**

All resonance structures for the same molecule must have the same sigma framework (sigma bonds form from the "head on" overlap of hybridized orbitals). Furthermore, they must be correct Lewis structures with the same number of electrons (and consequent charge) as well as the same number of unpaired electrons. Resonance structures with arbitrary separation of charge are unimportant, as are those with fewer

covalent bonds. These unimportant resonance structures only contribute minimally (or not at all) to the overall bonding description; however, they are important in some cases such as for a carbonyl group From the above theory of resonance answer the followings;

194.1 The correct resonating structure of 1,3-butadiene is –

(a) $\overset{+}{C}H_2–\overset{-}{C}H–CH=CH_2$ (b) $\overset{-}{C}H_2–\overset{+}{C}H–CH=CH_2$ (c) $\overset{-}{C}H_2–CH–CH=\overset{+}{C}H_2$ (d) None of these

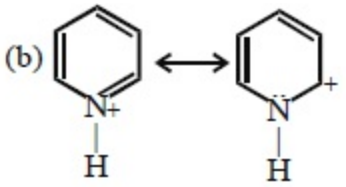
194.2 The correct resonating structure of benzene is –

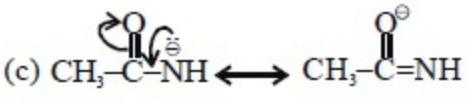


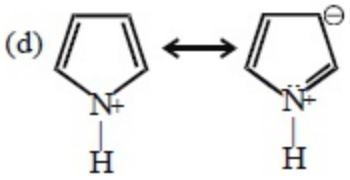
(d) None of these

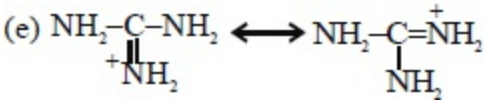
194.3 Which resonating structure is contributing are for the following structures –

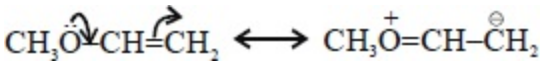
(a) $CH_2=CH–\overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2–CH=CH_2$









194.4 ***Assertion :–***  is correct resonating structure.

Reason :- Opposite charge separation is energetically unfavourable.

195. The Inductive effect in chemistry is an experimentally observable effect of the transmission of charge through a chain of atoms in a molecule by electrostatic induction (IUPAC definition). ***'Electrostatic induction'*** is a method by which an electrically charged object can be used to create an electrical charge in a second object, without contact between the two objects. The electron cloud in a a-bond between two unlike atoms is not uniform and is slightly displaced towards the more

electronegative of the two atoms. This causes a permanent state of bond polarization, where the more electronegative atoms has a slight negative charge(8-) and the other atom has a slight positive charge(8+).If the electronegative atom is then joined to a chain of atoms, usually carbon, the positive charge is relayed to the other atoms in the chain. This is the electron-withdrawing inductive effect, also known as the **-I effect. Some** groups, such as the alkyl group are less electron-withdrawing than hydrogen and are therefore considered as electron–Releasing. This is electron releasing character is indicated by the **+I effect. As** the induced change in polarity is less than the original polarity, the inductive effect rapidly dies out, and is significant only over a short distance. The inductive effect is permanent but feeble, as it involves the shift of strongly held a-bond electrons, and other stronger factors may overshadow this effect.

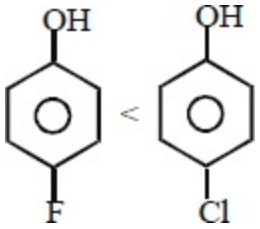
On the above facts explain the followings;

195.1 $-\overset{+}{N}R_3$ is stronger –I than $-\overset{+}{N}R_3$ due to –

(a) –N has less 's' character on N–C bond

(b) –N has more 's' character on N–C bond (c) both (a) and (b)

(d) None of these

195.2  according to acidic strength

This is due to –

(a) Stronger –I effect of Cl

(b) Stronger +I effect of F

(c) Stronger +R effect of F

(d) F doesnot bond d-orbital

195.3 Which one is convert according to the +I, –I effects –

(a) $-COOH > -COO^-$

(b) $-O^{\ominus}$

(c) $-NO_2 > -CN$

(d) None of these

195.4 Inductive effect is –

(a) Permanent phenomenon

(b) Operates from large distance

(c) It operates field effect

(d) all of these

196. Hyperconjugation is the stabilising interaction that results from the interaction of the electrons in a σ -bond (usually **C–H** or **C–C)** with an adjacent empty (or partially filled) p-orbital or a π -orbital to give an extended molecular orbital that increases the stability of the system. Based on the valence bond model of bonding, hyperconjugation can be described as "double bond – no bond resonance".

A higher-order bonding interaction between electron orbitals on three or more contiguous atoms in a molecule, which leads to characteristic changes in physical properties and chemical reactivity. One participant in this interaction can be orbital of a multiple (that is, double or triple) bond between two atoms, or a single electron or electron pair or electron vacancy on a single atom. The second component will be the pair of π electrons in an adjacent multiple bond in the case of conjugation, and in the case of hyperconjugation it will be the pair of π electrons in an adjacent polarized a bond (that is, σ bond where the electrons are held closer to one atom than the other due to electronegativity differences between the two atoms.

Based on the above answer the followings ;

196.1 In CH_3-C $\equiv$ C–H the effects which determine the chemical behaviour are –

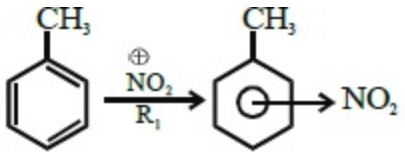
(a) Hyperconjugation

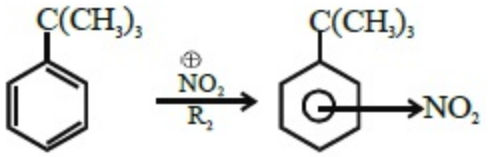
(b) Conjugation

(c) +I effect

(d) –I effect

196.2





(a) $R_1 > R_2$ (b) $R_1 \simeq R_2$ (c) $R_1 < R_2$ (d) All of these

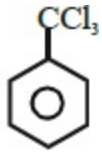
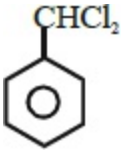
196.3 $\mu_{CH_3COCH_2CH_3} > \mu_{HCHO}$ may be due to –

(a) +I effect

(b) Hyperconjugation

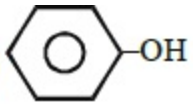
(c) No-bond resonance or sacrificial conjugation

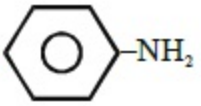
(d) None of these

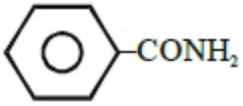
196.4 ***Assertion :***  is less reactive towards electrophile compound to  ***Reason :-*** If is due to Me participation of Cl– atoms into hyperconjugation (reverse hyperconjugation i.e.–H)

197. Between two elements when a bond length is experimentally found to be less than expected then we say bond order and 's' character of the central element is increased. If the opposite one happens to the above one then we say 's' character of the central element is decreased. This above phenomenon has greater importance on the observed bond angle. If 's' character is increased for the central element bond angle will increase (also can be explained on the basis of V SERR theory).

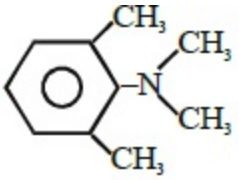
197.1 Match the following –

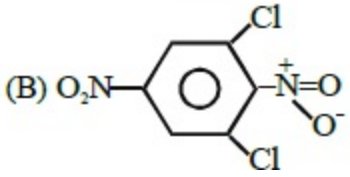
(A)  (I) C–N bond length is much decreased

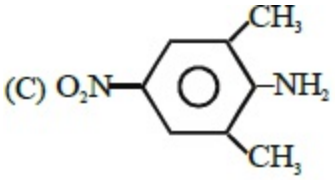
(B)  (II) C–O bond length is unchanged

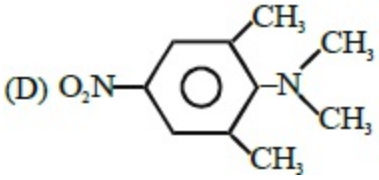
(C)  (III) C–N bond length is decreased

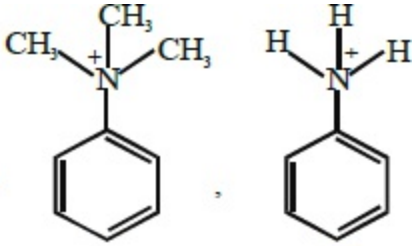
(D) $CH_3O–H$ (IV) C–OH bond angle is increased from 109°28′

197.2 (A)  (I) μ is more

(B)  (II) μ is less

(C)  (III) Larger C–N compared to $C–NO_2$

(D)  (IV) Larger C–N bond larger compared to aniline

197.3 Between  ,

(I) (II)

(a) N (I) has more ‘s’character in $N–CH_3$ bonds

(b) N (II) has more ‘s’character in N–H bonds

(c) N (I) has less 's'character in $N–CH_3$ bonds

(d) None of these

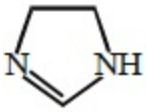
197.4 (a) $\angle$ $CH_3–N-CH_3$ is less than expected

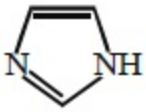
(b) $\angle$ $CH_3–N–CH_3$ is more than expected

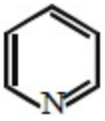
(c) $\angle$ H–N–H is same

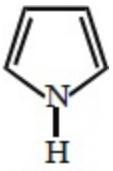
(d) None of these

197.5 Acid strength of the conjugate acids of the followings are –


(I)


(II)


(III)


(IV)

(a) I > II > III > IV

(b) III > II > I > IV

(c) IV > III > II > I

(d) None of these

197.6 The acidic strength of the conjugate acids of the following bases are –

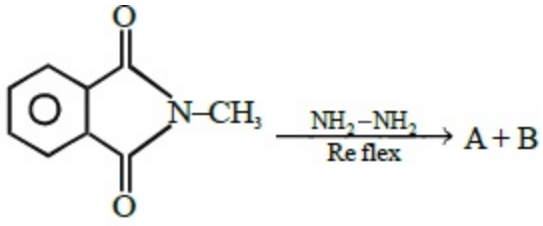
$CH_3COH=C(NH_2)_2$ (I) $PhOH=C(NH_2)_2$ (II) $MeOH=C(NH_2)_2$ (III)

(a) II > I > III

(b) I > II > III

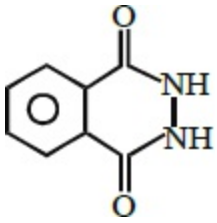
(c) III > II > I

(d) None of these

198. 

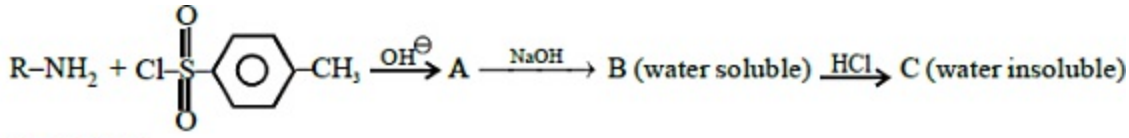
A and B cannot be –

(a) $C_2H_5 - NH_2$

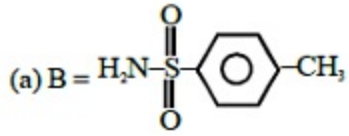
(b) 

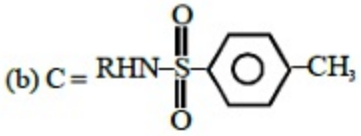
(c) CH_3NH_2

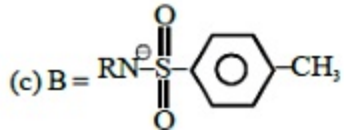
(d) All of these

199. 

Identify 'B'

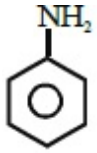
(a) B = 

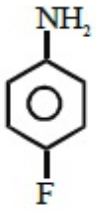
(b) C = 

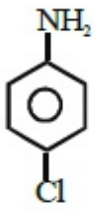
(c) B = 

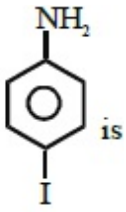
(d) None of these

200. Basicity order among –


(1)


(2)


(3)


is

(4)

(a) (1) < (2) < (3) < (4)

(b) (2) < (1) < (3) < (4)

(c) (2) < (3) < (1) < (4)

(d) (3) < (1) < (4) < (2)

Answer & Hints

1. (c)

2. (b)

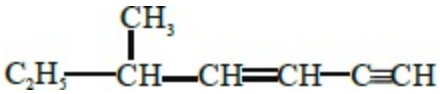
3. (c)

4. (a)

Hint : Weaker : $HC{\equiv}CH + NH_2^- \rightleftharpoons HC \equiv C^- + NH_3$

Stronger acid Weaker acid

5. (a) [Enol]

(b) 

The product obtained is cojugated diene and hence is more stable.

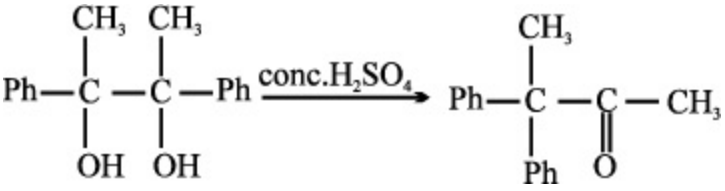
6. (a) True

(b) True

(c) True

(d) True

The reaction is



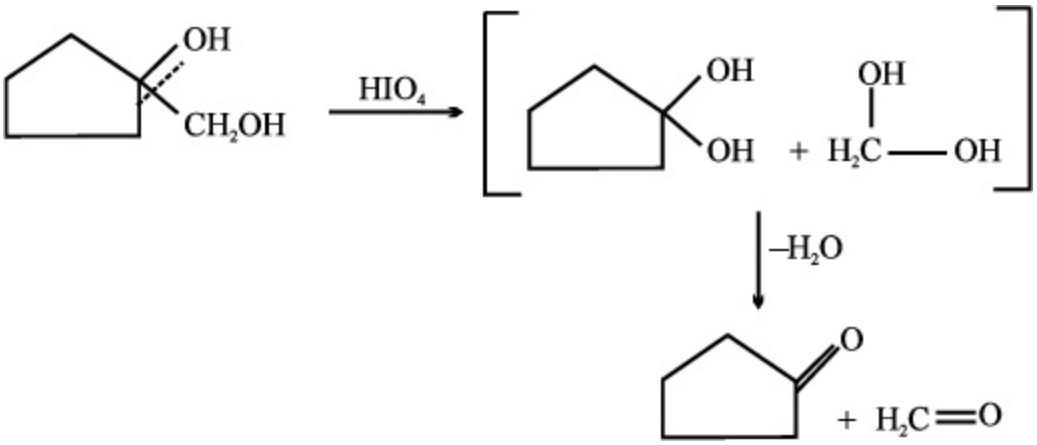
(e) True

The general reaction for the formation of a Schiff base is

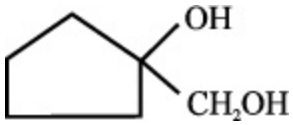
$RCHO + R'NH_2 \xrightarrow{-H_2O} RCH = N - R'$

(f) True

The reaction is



(g) True;

(h) True 

(i) True

(j) True;

Hint : Increased stability of $RCONH_2$ relative to RNH_2 and decreased stability of $RCONH_3^+$ relative to RNH_3^+ make amines more basic than amides. (j) False

(k) True

(l) True

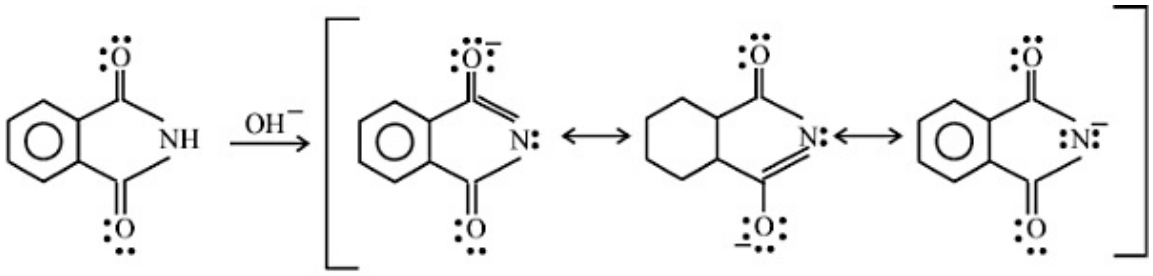
(m) True

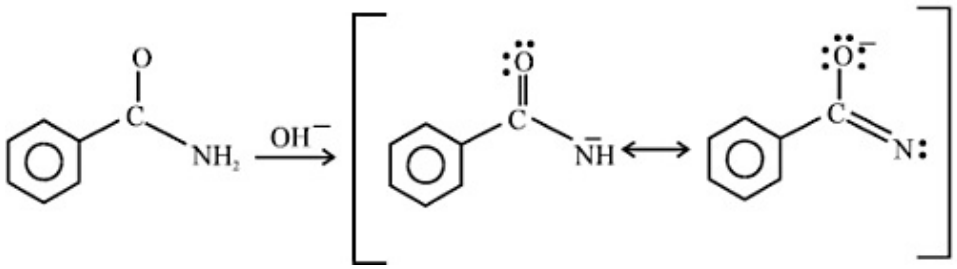
(n) True

(o) True

(p) True

Hint: Phthalimide has two carbonyl groups to stabilise the imide while benzamide has only one. There is more destabilisation in phthalimide.





7. (c)

8. (a)

9. (c)

10. (b)

11.1 (a)

11.2 (d)

12. (a)

13. (c)

14. (d)

15. (d)

16. (d)

17. (b)

18. (b)

19. (a)

20. (a)

21. (a)

22. [is t, t, t-3, 6, 9 octadecatrien-18-oic acid.

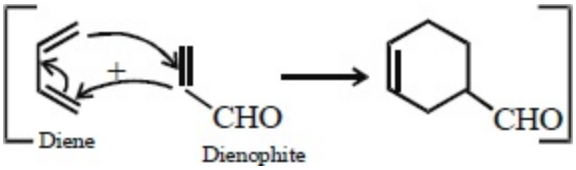
23. (c)

24. (c)
25. (c)
26. (b)
27. (a)
28. (a)
29. (a)
30. (d)
31. (d)
32. (d)
33. (c)
34. (a)
35. (b)
36. (b)
37. (a)
38. (a)
39. (a)
40. (c)
41. (b)
42. (a)
43. (a)
44. (a)
45. (a)
46. (b)
47. (c)
48. (b)
49. (b)
50. (a)
51. (d)

52. (a)
53. (d)
54. (a)
55. (a)
56. (b)
57. (d)
58. (c)
59. (b)
60. (b)
61. (c)
62. (b)
63. (b)
64. (d)
65. (d)
66. (b)
67. (d)
68. (c)
69. (b)
70. (a)
71. (c)
72. (d)
73. (c)
74. (c)
75. (c)
76. (c)
77. (c)
78. (c)
79. (a)

80. (b)

81. (b) [**This is Diel's alder reaction**]



82. (b)

83. (a)

84.1 (d)

84.2 (a)

84.3 (a)

85.1 (a)

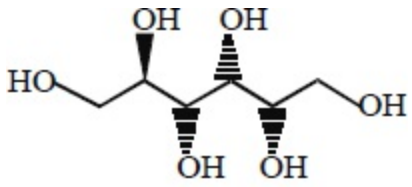
85.2 (a)

86. (a)

87. (a)

88. (b)

89.



Sorbitol

90. (a)

91. (a)

92. (a)

93. (a) (i, ii, iii)

(b) i, ii, iii, iv

(c) ii, iv

(d) ii, iv

94.1 (a)

94.2 (a)

94.3 (a)
94.4 (a)
94.5 (a)
94.6 (b)
95. (d)
96. (a)
97. (a)
98. (c)
99. (c)
100. (b)
101.1 (b)
101.2 (a)
101.3 (b)
101.4 (b)
101.5 (a)
102. (d)
103. (d)
104. (a)
105. (a)
106. (a)
107. (a)
108. (a)
109. (c)
110. (b)
111. (d)
112. (a)
113. (b)
114. (c)

115. (a)

116. (d)

117. (b)

118.1 (c)

118.2 (a)

118.3 (b)

119.1 Yes

119.2 [Hg^{+2}, H^{+}, H_2O]

119.3 2

120.1 Yes

120.2 No

121.1 epoxide

121.2 No

121.3 epoxide-O

121.4 No

121.5 2^5

122.1 Adenine

122.2 None

123. (d)

124. (a)

125. (a)

126. (a) Hint : [According to steric and stability of Me resultant free radicals.]

127. (d)

128.1 (c)

128.2 (b)

128.3 (d)

129.1 (c)

129.2 (c)

129.3 (b)

130. (b)

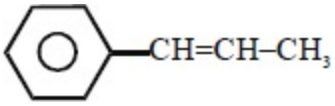
131. (a)

132. (a)

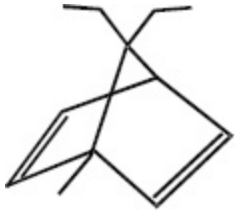
133. (a)

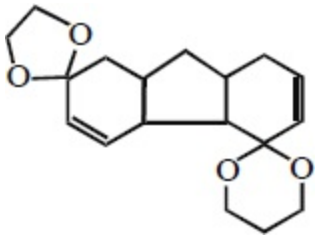
134. [$CCl_4 > CHCl_3 > CH_2Cl_2 > CH_3Cl$]

135.1 (a)

135.2 

135.3 [Yes, PKIE will be observed as C–D is stronger than C–H bond.]

136. 

137. 

138.1 (IV)

138.2 (III)

138.3 None

138.4 None

139. (a)

140.1 Markownikoff's addn.

140.2 Yes

140.3 Step–II

140.4 Slower compared to initial one

141.1 (I)

141.2

141.3 H_3O^+

142. (a) Structural isomer

(b) Enantiomers

(c) Identical

(e) Structural isomer

(d) Enantiomers

(f) Identical

(g) Identical

(h) Diastereomer

(i) Diastereomer

143. (b)

144. (a)

145. (a)

146. (b)

147. (a)

148. (a)

149. (c)

150. (a)

151. (a)

152. (b)

153. (a)

154. (c)

155. (c)

156. (c)

157. (d)

158. (a)
159. (b)
160. (a)
161. (a)
162. (b)
163. (b)
164. (c)
165.1 (d)
165.2 (b)
165.3 (a)
166. (a)
167. (d)
168. (b)
169. (b)
170. (b)**,** (d)
171. (d)
172. (c)
173. (b)
174. (a)
175. (a)
176. (c)
177. (a)
178.1 (b)
178.2 (a)
179. (b)
180. (c)
181. (c)
182. (c)

183. (c)
184. (a)
185. (b)
186. (e)
187.1 3
187.2 1,2,5,6
187.3 4
187.4 1,2,5,6
187.5 3
187.6 None
187.8 2
187.9 Faster
188. All are true
189. True
190. All are true
191. (a)
192. All are true
193. (a)
194.1 (c)
194.2 (d)
194.3 (a), (c), (e)
194.4 (c)
195.1 (a)
195.2 (c), (d)
195.3 (a), (b), (c)
195.4 (a), (c)
196.1 (a), (c)
196.2 (a)

196.3 (a), (b), (c)

196.2 (a)

197.1 (A)-(IV); (B)-(III); (C)-(I); (D)-(II)

197.2 (A)-(IV); (B)-(III); (C)-(I); (D)-(II)

197.3 (a)

197.4 (c)

197.5 (c) **Hint :** Consider the hybridisation of N-atoms are stability of protonated base

197.6 (a)

198. (a)

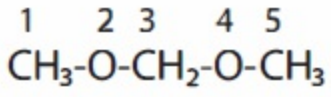
199. (b), (c)

200. (b)

Appendix

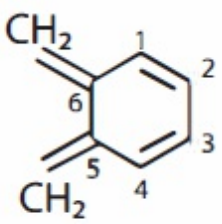
IUPAC Nomenclature

1



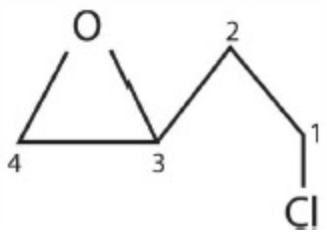
2, 4 - Dioxapentane

2



Bis(methylenecyclohexa-1,3-diene)

3

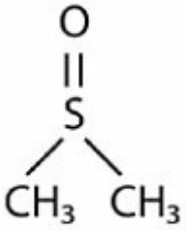


1-chloro-3,4-epoxybutane

Nucleophilic Substitution and Elimination

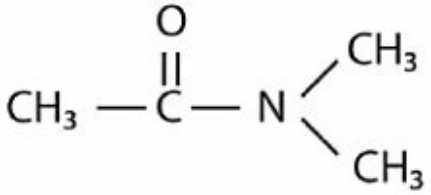
Chapter:

Some Polar Aprotic Solvents



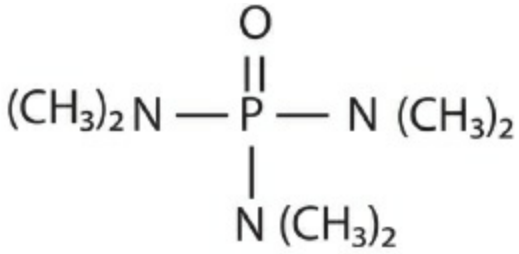
DMSO

(Dimethyl sulphoxide)



DMA

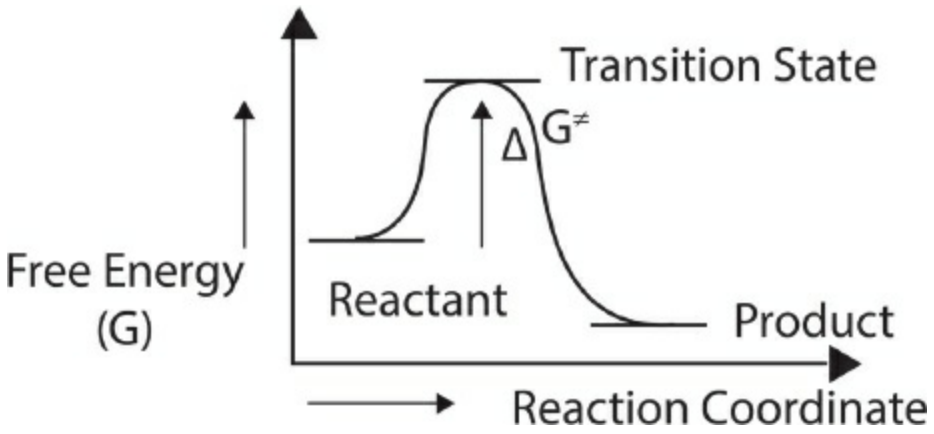
(Dimethyl acetamide)



HMPA

(Hexamethyl phosphoramide)

In terms of Gibb's free energy, the energy profile for S_N2 is as the following:



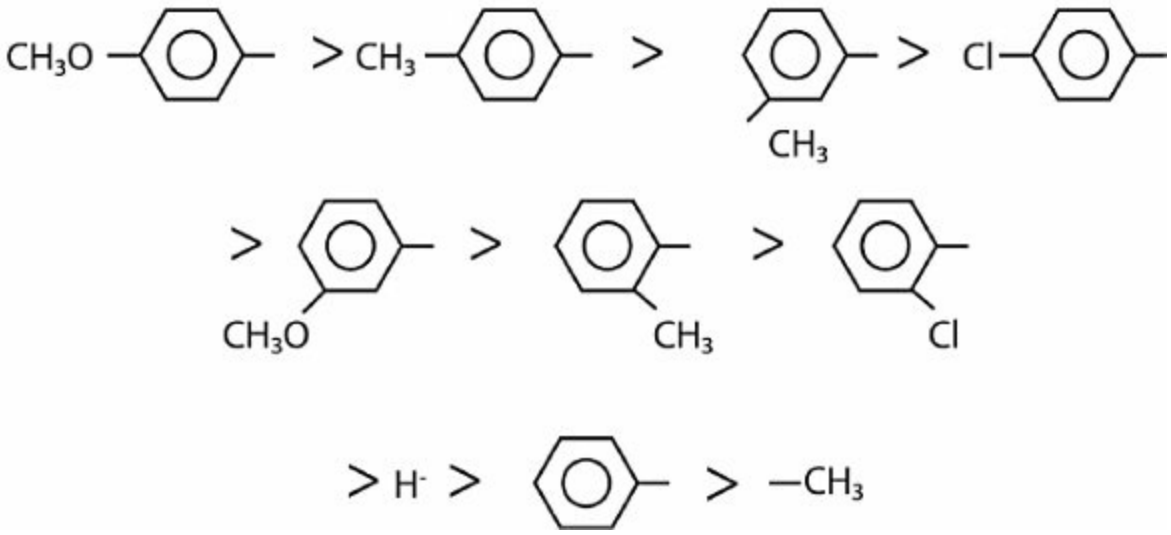
Chapter name: **Grignard's Reagent (RMgX)**

Active -H > -COCL > -CHO > -CO > - CO_2R > -CH_2X

Chapter name: **Alcohols**

Pinacol Pinacolone Rearrangement

The migratory order is,



Chapter name: **Carbonyl Compounds**

Migratory order in Baeyer– Villiger Reaction:

H^- > t – Bu – > isopropyl – > ph – > Et – > Me –

About the Author



Amitava Mazumder holds a BSc (Chemistry Hons.) from University of Burdwan, B E (Metallurgical Engineering, NIT, Durgapur) Masters of Engineering (Jadavpur University, Kolkata) and worked as Senior Research Fellow during his post graduation in a project of BOC, India. He has more than twenty years teaching experience and currently runs his own academy, Mazumder Classes, in Mumbai. Amitava presented his thesis at the International Conference for Manufacturing in Dhaka. He intends for this book to keep on evolving and welcomes comments and suggestions from students and members of the teaching community in India