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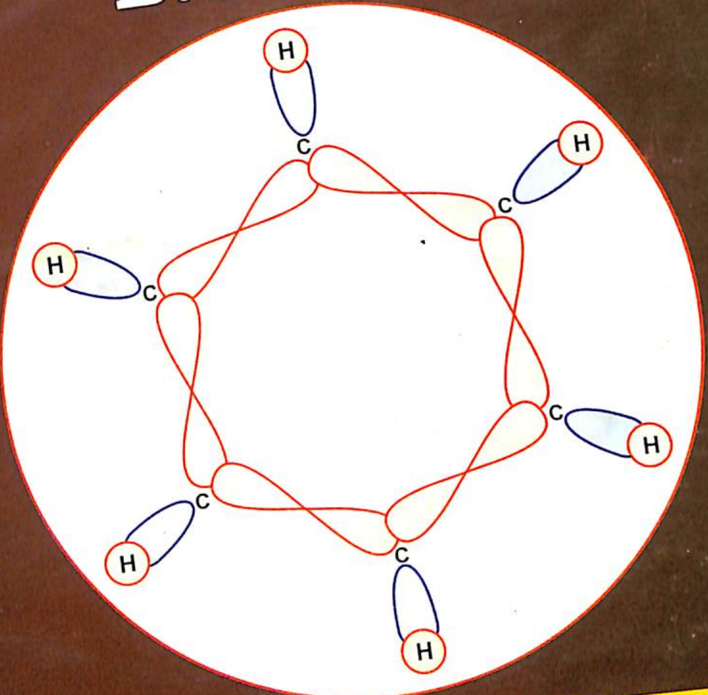

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PREFACE

We are happy to place in the hands of readers, **'A Text book of Organic Chemistry'** For **B.Sc. I. year.** This book has been written to feed the needs of **B.Sc. I. year** students of **Swami Ramanand Teerth Marathwada University, Nanded.**

This book is written in keeping this view in mind. the effort is made to present the topics in simple and lucid language and explained the same with suitable examples, structures and figures.

The topic **IUPAC Nomenclature of Organic Compounds** will help the students for giving the systematic names to **Organic Compunds** on the basis of structure. We hope that, simple and lucid explanation of the curriculum will help to understand and will not make the students perfect in **Organic Chemistry** paper.

We are greatful to **Principal Wamanrao Suryawansi, B.S. College, Basmath.** and **Principal Dr. Vaidya, N.S.B. College, Nanded.** for their encouragement and keen interest throughtout the work of this publication and moreover my freinds, Collegues of our college. and all members of family.

We express our thanks to our Publisher **Mr. Narendra Gatagat, Nikita Publication** for bringing out this book in present form I need suggestion for improvement of book but favourably welcome criticism which may modify book.

The authors wish to thanks all those in a valuable way, whose help in the making of this book is of great value.

● **Authors**

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UNIT - [I]

1.1 Nomenclature of Organic Compound

1.2 Organometallic Compounds

1.1 Nomenclature of Organic Compound

I] Types of organic compounds

There are millions of organic compounds. in dealing with such a large number of organic compounds some classification is essential. There fore organic compounds are classifieds into two types.

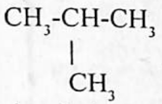
1) **Aliphatic compounds or open chain compounds.**

These Compounds contains chain of carbon atom which is open at the all ends. They have straight chain or branched chain of carbon atoms.

CH_3-CH_2-CH_2-CH_3
n- butane

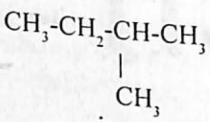
CH_3-CH_2-CH_2-CH2-CH_3
n-pentane

(Straight chain)



CH_3-$\underset{\displaystyle CH_3}{CH}$-$CH_3$

iso- butane



CH_3-CH_2-$\underset{\displaystyle CH_3}{CH}$-$CH_3$

iso-pentane

(Branched chain)

The organic compounds which contain only carbon and hydrogen are called hydrocarbons. Saturated hydrocarbons contain only carbon-carbon single bonds. And unsaturated hydrocarbons contains C=C or C ≡ C multiple bonds. For ex:

Ethane	CH_3-CH_3	It is saturated
Ethylene	CH_2=CH_2	It is unsaturated
Acetylene	CH ≡ CH	It is unsaturated

2) **Closed chain or cyclic compounds:**

The organic compounds with closed chain of atoms are called closed compounds or ring compounds.

These compounds are further classified into

i) Homocyclic or carbocyclic compounds

ii) Heterocyclic compounds

i) **Homocyclic or carbocyclic compounds**: Homocyclic compounds the ring structure is made up of only carbon atoms.

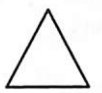
These compounds are further classified into

i) Alicyclic compounds and

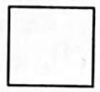
ii) Aromatic compounds

i) Alicyclic compounds:

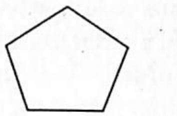
Cyclic compounds which consist of only carbon atoms are called alicyclic compounds or carbocyclic compounds. For ex:



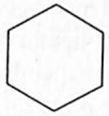
Cyclopropane



Cyclobutane



Cyclopentane

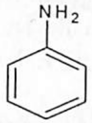


Cyclohexane

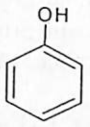
ii) Aromatic compounds.

a) These compounds containing at least one benzene ring. And the compounds that have structures and chemical properties resembling benzene are called aromatic compounds. For ex:

Benzene



Aniline

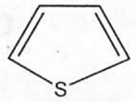


Phenol

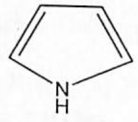
b) **Heterocyclic compounds.**

Cyclic compounds that contain at least one atom other than carbon as hetero atom within the ring are called heterocyclic compounds. Hetero atoms are generally N, O, S and P. for ex:

Furan



Thiophene



pyrrole

II) Characteristics of organic compounds: All organic compounds have the following characteristics properties

1) Many organic compounds are inflammable.
2) They are mostly covalent compounds.
3) They are generally soluble in non-polar solvent like carbon tetra chloride, benzene etc.
4) They have generally low boiling point and melting point.
5) They exhibit isomerism

III] Homologous series:

A group or class of organic compounds related to each other by a general molecular formula contributes homologous series.

Characteristics of homologous series:

Homologous series have the following Characteristics

1) All members of a series contain same elements and the same functional groups.
2) All members of a series can be prepared by similar methods

3) All members of a series can be prepared by a general formula
4) All members of a series usually under goes similar reactions.
5) Each member of series is differing by a $-CH_2$- group,
6) the physical properties of the members of a homologous series vary in a regular way

Down the series, for example, boiling point, melting point, and density of the alkane series vary in a regular way with increasing number of carbon atom.

IV] Functional group concept:

A functional group is an atom or group of atoms in a molecule that gives the characteristic properties of the molecule. Double or triple-bonds are the functional groups. Other examples are -Cl, -Br, -OH, $-NH_2$, -COOH groups

CH_3-CH_2-COOH -COOH is functional group.
R-COOH -COOH is functional group.

R-to represent hydrocarbon portion to which functional group is attached. Where R is any alkyl group. Some common functional groups and the corresponding class.

Class	Functional group	Example	Name
Alkene	$>C=C<$	$CH_2=CH_2$	ethylene
Alkynes	$-C\equiv C-$	$CH\equiv CH$	acetylene
Alcohol	$-OH$	CH_3-CH_2-OH	ethyl alcohol
Ether	$-\overset{\vert}{\underset{\vert}{C}}-O-\overset{\vert}{\underset{\vert}{C}}-$	CH_3-O-CH_3	dimethyl ether
Aldehyde	$-\underset{\overset{\Vert}{O}}{C}-H$	$CH_3-\underset{\overset{\Vert}{O}}{C}-H$	acetaldehyde
Ketones	$-\underset{\overset{\Vert}{O}}{C}-$	$CH_3-\underset{\overset{\Vert}{O}}{C}-CH_3$	acetone
Carboxylic acids	$-\underset{\overset{\Vert}{O}}{C}-OH$	$CH_3-\underset{\overset{\Vert}{O}}{C}-OH$	acetic acid
Esters	$-\underset{\overset{\Vert}{O}}{C}-OR$	$CH_3-\underset{\overset{\Vert}{O}}{C}-O\ C_2H_5$	ethyl acetate
Amines	$-\underset{\overset{\vert}{H}}{N}-H$	CH_3-NH_2	methyl amine
Amide	$-\underset{\overset{\Vert}{O}}{C}-NH_2$	$CH_3-\underset{\overset{\Vert}{O}}{C}-NH_2$	acetamide
Acid chloride	$-\underset{\overset{\Vert}{O}}{C}-Cl$	$CH_3-\underset{\overset{\Vert}{O}}{C}-Cl$	acetyl chloride
Halide	$-X$	CH_3-Cl	Methyl Chloride

(X= F,Cl, Br, I)

Each functional group undergoes characteristic reactions.

A molecule can contain more than one functional group. It is then said to be **Polyfunctional,**

V] Principals of Nomenclature:

In early days when a new organic compound was discovered, the chemist usually named it on the basis of its history, e.g., Formic acid was obtained by distillation of red ants (Latin, Formica = ants). Acetic acid derive its name from vinegar (Latin, acetum = vinegar).of which it is the chief constituent. These names are called **Common or Trivial name.**

IUPAC system of nomenclature:

With the rapid growth of organic chemistry, the number of compounds increased fantastically. It became impossible to give common names to such a large number of compounds.

In 1957, International Union of pure and applied chemistry evolved a scheme for giving systematic names to organic compounds on the basis of structure. And this is called as IUPAC system.

This system has set of rules for naming organic molecules from their structure .the systematic name of a compound derived from its structural formula by applying IUPAC rules, is referred to as its IUPAC names. One organic compound can have only one IUPAC name. Common names identify compounds only but IUPAC names represent structures.

IUPAC Nomenclature of Aliphatic compounds.

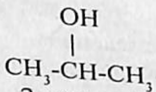
a) Root words or Root names b) Multiplier and c) Locants d) suffix e) prefix.

a) Root words or Root names: This defines the number of carbon atoms in the **longest continuous chain** that contains the principal functional group. Here is a list of the root names for naming the parent hydrocarbon chain of C_1 to C_{10} and few other biologically important chains. This list is very important as it provides the foundation for all IUPAC nomenclature.

CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}
Methane	Ethane	Propane	Butane	Pentane
C_6H_{14}	C_7H_{16}	C_8H_{18}	C_9H_{20}	$C_{10}H_{22}$
Hexane	Heptane	Octane	Nonane	Decane

b) Multiplier: If a group occurs more than once then, a simple multiplier such as di (for two), tri (for three), tetra (for four), etc. is used to indicate how many times it occurs.

c) Locants: Locants are the numbers that define the position of the principle functional group and substituents. For ex: (2-is the locant for the functional group –OH)



$$CH_3\text{-}\underset{}{\overset{OH}{\overset{|}{C}H}}\text{-}CH_3$$

2-propanol

d) Suffix: There are two types of suffixes i) primary suffix ii) secondary suffix.

A primary suffix is written after the Root word to indicate whether the parent chain is saturated or unsaturated. Some primary suffixes are:

Name of carbon chain	Primary suffixes
Saturated (C-C)	ane
Unsaturated (C=C)	ene
($C\equiv C$)	yne

Secondary suffix: secondary suffix is used to indicate the functional group in the organic compound. Secondary suffix is added to the primary suffix: i.e. written after the primary suffix. For ex:

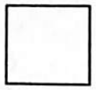
Class	functional Group	Secondary suffix	IUPAC name	Remarks
Carboxylic acid	-COOH	-oic acid	alkanoic acid	**e** of pri. Suffix is replaced.
Ester	-COOR	-ate	alkyl alkanoate	**e** of pri. Suffix is replaced.
Ketones	-CO	-one	alkanone	**e** of pri. Suffix is replaced.

e) Prefix: prefix is the part of name which appears before the root word. Prefix suggests the substituent(s) present in the organic compound. In IUPAC name system certain characteristics groups are not considered as functional groups. Such characteristics group are considered as the substituents. Each such group or substituents are denoted by a prefix. Some examples are.

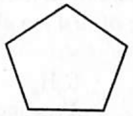
Substituent group	Prefix
-F	fluoro
-Cl	chloro
-Br	bromo
-I	iodo
$-CH_3$	methyl
$-CH_2\text{-}CH_2\text{-}CH_3$	n-propyl
$-CH(CH_3)_2$	iso- propyl
$-C(CH_3)_3$	t-butyl
-NO2	nitro
$-OCH_3$	methoxy
$-OC_2H_5$	ethoxy

Prefix is also used to distinguish between Alicyclic (aliphatic cyclic compounds) and acyclic (open chain) compounds. If the given compound is an alicyclic compound, then a prefix cyclo is used just before the root name. for ex:

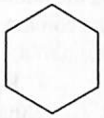
Cyclopropane



Cyclobutane



Cyclopentane



Cyclohexane

Cycloalkanes are often represented by simple geometrical figures. And in which each corner represent $-CH_2-$ group.

1] ALKANES:-

Alkanes are the simplest organic compounds made up of carbon and hydrogen only.

Alkanes are aliphatic saturated hydrocarbon containing carbon-carbon and carbon-hydrogen single covalent bond. They having general formula C_nH_{2n-2}. Some examples of alkanes are represented as:

CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}
Methane	Ethane	Propane	Butane	Pentane

Alkanes contain strong C-C and C-H bond; there fore this class of hydrocarbons is relatively inert. Hence they are also called as paraffin's. [Latin, parum affins = little affinity]

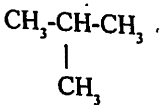
Alkanes are classifieds into two types depending upon the type of carbon chain that they contain in the molecule.

i) Normal alkanes (Prefix n) : In an alkane, if the carbon atoms are continuously attached to form a single chain, then it is called straight chain or normal alkanes. Normal alkanes denoted by Prefixing n before the name of alkanes for ex:

$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3$
n- Butane

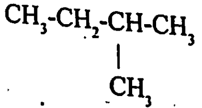
$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$
n-Pentane

ii) Branched chain alkanes: In an alkane, if the carbon atoms are not in a continuous chain or it has side chain, then it is called branched alkanes. For ex:



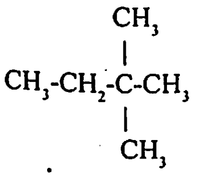
$CH_3\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}CH_3$

Iso-butane



$CH_3\text{-}CH_2\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}CH_3$

iso-pentane



$CH_3\text{-}CH_2\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{-}CH_3$

neo- pentane

NOMENCLATURE:-

There are two systems of naming alkanes.

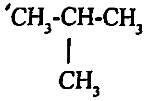
i) Common name system: The first four members of the series are called by their Common or trivial name. Methane, Ethane, propane, butane, from fifth on words, alkanes are named by prefixing the Greek numerals, pent-(5), Hex-(6), Hept-(7), Oct-(8),Non-(9), Dec-(10).etc. indicating the number of carbon atoms in the molecule. To the terminal -ane. The common name of first ten alkanes is:

CH_4 Methane	C_2H_6 Ethane	C_3H_8 Propane	C_4H_{10} Butane	C_5H_{12} Pentane
C_6H_{14} Hexane	C_7H_{16} Heptane	C_8H_{18} Octane	C_9H_{20} Nonane	$C_{10}H_{22}$ Decane

Meaning of Prefix iso and neo

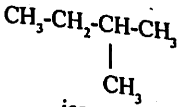
The alkanes, in which the carbon chain is branched, are called branched chain alkanes. Such alkanes which posse's one carbon branch on the second carbon of the basic normal chain are known as iso-hydrocarbons or **Prefix iso**. And if two branches on the same carbon atom are called neo- hydrocarbon **Prefix neo.**

For ex:



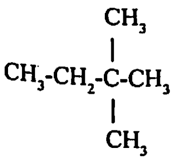
$CH_3\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}CH_3$

Iso-butane



$CH_3\text{-}CH_2\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}CH_3$

iso-pentane



$CH_3\text{-}CH_2\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{-}CH_3$

neo- pentane

Structural formula of alkanes contains four types of carbon atoms.

i) Primary carbon atom: A carbon atom attached to another only one carbon atom is called as Primary carbon atom.

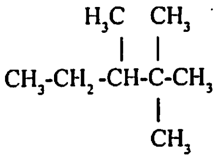
ii) Secondary carbon atom: A carbon atom attached to another two carbon atom is called as

secondary carbon atom.

iii) Tertiary carbon atom: A carbon atom attached to another three carbon atom is called as tertiary carbon atom.

iv) Quaternary carbon atom: A carbon atom attached to another three carbon atom is called as quaternary carbon atom.

Hydrogen atoms attached to the primary, secondary, tertiary carbon atom are called Primary, secondary, tertiary hydrogen atoms.



$CH_3\text{-}CH_2\text{-}\overset{\overset{H_3C}{|}}{CH}\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{-}CH_3$

Alkyl groups:

Alkyl groups are formed by the removing hydrogen atom of alkane.

$$R\text{-}H \xrightarrow{-H} R\text{-}$$

Alkyl group

$$CH_3\text{-}H \xrightarrow{-H} CH_3\text{-}$$

Methane methyl group

Alkyl groups are named by removing **–ane** from the name of the corresponding alkane, and adding the ending **–yl.**

Alkane – ane + yl = alkyl

For ex:

Structure of alkyl group	**name of alkyl group**
CH_3-	methyl
C_2H_5-	ethyl
C_3H_7-	propyl
$CH_3\text{-}\underset{\vert}{CH}\text{-}CH_3$	isopropyl
$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2$-	n-butyl
$CH_3\text{-}\underset{\vert}{CH}\text{-}CH_2\text{-}CH_3$	sec-butyl

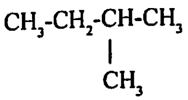
I] IUPAC Rules for Naming Alkanes:-

The IUPAC system is much the same for all classes of organic compounds.

Rules;-

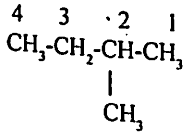
1) **Select the longest continuous chain of carbon atom.**

2) **Name the longest chain.** This is the parent name. The longest continuous chain has four carbons thus the compound is named as butane.

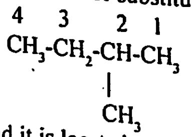


$CH_3\text{-}CH_2\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}CH_3$

3) Number the longest chain. The numbering is started from that end nearest of the Substituent so as to gives lowest possible number to carbon carrying Substituent.

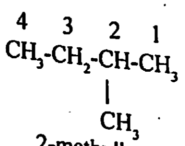

$\overset{4}{CH_3}-\overset{3}{CH_2}-\underset{\underset{CH_3}{|}}{\overset{2}{CH}}-\overset{1}{CH_3}$

4) Name the substituent. The position of substituent indicated to which it is attached.


$\overset{4}{CH_3}-\overset{3}{CH_2}-\underset{\underset{CH_3}{|}}{\overset{2}{CH}}-\overset{1}{CH_3}$

Methyl is the substituent and it is located at carbon -2.

5) Prefix the position number and name of the substistuent on to the parent name. The whole name is written as one word. i .e. 2-methylbutane


$\overset{4}{CH_3}-\overset{3}{CH_2}-\underset{\underset{CH_3}{|}}{\overset{2}{CH}}-\overset{1}{CH_3}$

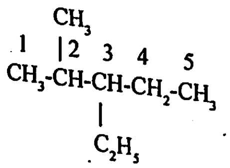
2-methylbutane

2- Position of alkyl group

methyl- substituent

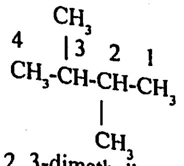
butane- longest chain

6) When two or more different substituent is present, their names are arranged in alphabetic order, along with respective numbers. And added to the name of the parent alkane. As one word.


$\overset{1}{CH_3}-\overset{\overset{CH_3}{|}\,2}{CH}-\underset{\underset{C_2H_5}{|}}{\overset{3}{CH}}-\overset{4}{CH_2}-\overset{5}{CH_3}$

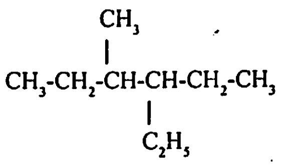
3- Ethyl and 2-methyl are the substituents, and parent alkane is pentane.
There fore the name of the compound is **3-Ethyl -2- methylpentane.**

7) If, there are two or more substituents or side chains are the same type, then prefix di, tri, tetra etc. position of each substituent is indicated by a separate number. These position numbers, separated by commas, are placed just before the name of the substituents, with the hyphen before and after the numbers when necessary. Which indicate the similar type of substituents.

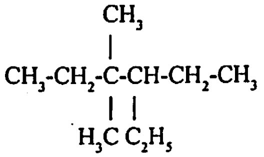

$\overset{4}{CH_3}-\overset{\overset{CH_3}{|}\,3}{CH}-\underset{\underset{CH_3}{|}}{\overset{2}{CH}}-\overset{1}{CH_3}$

2, 3-dimethylbutane

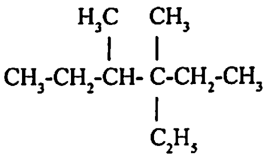
For example :-


$CH_3-CH_2-\overset{\overset{CH_3}{|}}{CH}-\underset{\underset{C_2H_5}{|}}{CH}-CH_2-CH_3$

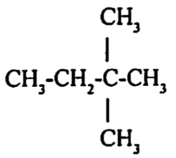
3-Ethyl-4-methylhexane


$CH_3-CH_2-\underset{\underset{H_3C}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{C_2H_5}{|}}{CH}-CH_2-CH_3$

4-Ethyl-3, 3-dimethylhexane


$CH_3-CH_2-\overset{\overset{H_3C}{|}}{CH}-\underset{\underset{C_2H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_3$

3-Ethyl-3, 4-dimethylhexane


$CH_3-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

2, 2-dimethylbutane

II] CYCLOALKANES:-

The carbocyclic or Homocyclic compounds having closed chains or rings of carbon atoms and bearing certain resemblance with aliphatic compounds these properties are called as Alicyclic compounds.

Simple saturated alicyclic hydrocarbons are known as Cycloalkanes.

Cycloalkanes having general formula C_nH_{2n}.

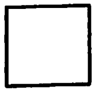
IUPAC rules for naming the Cycloalkanes.

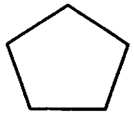
Rules;

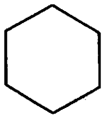
1) Cycloalkanes are named by prefixing the word **-cyclo** to the name of alkanes having same number of carbon as in the ring.

For ex:-


Cyclopropane


Cyclobutane


Cyclopentane


Cyclohexane

Cycloalkanes are often represented by simple geometrical figures. And in which each corner is equal to CH_2 group.

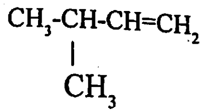
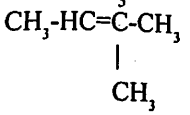
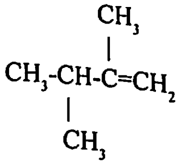
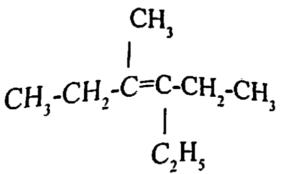
III] ALKENES:

Alkenes are aliphatic unsaturated hydrocarbons having carbon-carbon one double bond. They have general formula C_nH_{2n} They are also called as olefins. In the common name system of alkenes ane of alkane can be replaced by ylene. **(Alkane - ane + ylene)**

IUPAC rules for naming the alkenes:

Rules:

1) Select the longest continuous carbon chain containing the double bond. as a parent chain.
2) **Name the longest chain.** The name is obtained by removing the final ane of alkane by **ene.** And adding **ene** at the end. **(Alkane -ane + ene = alkene)**
3) **Number the longest chain**. Numbering is started from that end closer to the double bond.
4) **Indicate the position of double bond.** By the number of the first carbon atom involved in the double bond.
5) Substituent / side chain are numbered, named and placed as prefixes in alphabetic order. **For ex:**

STRUCTURE	**IUPAC Name**	**Common name**
$CH_2=CH_2$	Ethene	ethylene
$CH_3\text{-}CH=CH_2$	Propene	propylene
$CH_3\text{-}CH_2\text{-}CH=CH_2$	1-butene	butylene
$CH_3\text{-}CH=CH\text{-}CH_3$	2-butene	butylene
 $CH_3\text{-}\underset{\underset{CH_3}{\vert}}{CH}\text{-}CH=CH_2$	3-methyl-1-butene	
 $CH_3\text{-}HC=\underset{\underset{CH_3}{\vert}}{C}\text{-}CH_3$	2-methyl-2-butene	
 $CH_3\text{-}\underset{\underset{CH_3}{\vert}}{CH}\text{-}\overset{\overset{CH_3}{\vert}}{C}=CH_2$	2, 3-dimethyl-1-butene	
 $CH_3\text{-}CH_2\text{-}\overset{\overset{CH_3}{\vert}}{C}=\underset{\underset{C_2H_5}{\vert}}{C}\text{-}CH_2\text{-}CH_3$	3-ethyl-4methyl-3-hexene	

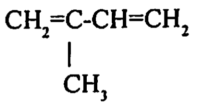
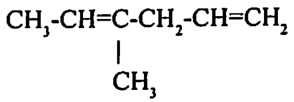
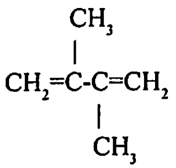
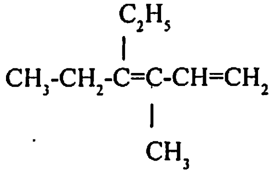
IV] DIENES:-

Dienes are aliphatic unsaturated hydrocarbons having two double bonds. They are having general formula C_nH_{2n-2}

IUPAC rules for naming dienes:

Rules:

1) Longest continuous chain of carbon atom containing two double bonds as a parent chain.
2) **Name the longest chain.** The name is obtained by removing the final **ne** of alkane by **diene.** And adding diene at the end. **(Alkane -ne + diene = alkadiene)**
3) **Number the longest chain.** Numbering is started from that end closer to the double bond.
4) **Indicate the position of double bond.** by the number of the first carbon atom involved in the double bond closer to the end.
5) Substituent / side chain are numbered, named and placed as prefixes in alphabetic order. **For ex:**

$CH_2=CH\text{-}CH=CH_2$	1, 3-butadiene
 $CH_2=\underset{\underset{CH_3}{\vert}}{C}\text{-}CH=CH_2$	2-methyl-1, 3-butadiene
 $CH_3\text{-}CH=\underset{\underset{CH_3}{\vert}}{C}\text{-}CH_2\text{-}CH=CH_2$	4-methyl-1, 4-pentadiene
 $CH_2=\overset{\overset{CH_3}{\vert}}{C}\text{-}\underset{\underset{CH_3}{\vert}}{C}=CH_2$	2, 3-dimethyl-1, 3-butadiene
 $CH_3\text{-}CH_2\text{-}\overset{\overset{C_2H_5}{\vert}}{C}=\underset{\underset{CH_3}{\vert}}{C}\text{-}CH=CH_2$	4-ethyl-3methyl-1, 3-hexadiene

V] ALKYNES:

Alkynes are aliphatic unsaturated hydrocarbons having carbon-carbon triple bond. They have general formula C_nH_{2n-2}. The simplest alkyne is acetylene. $CH\equiv CH$ and in the common name system higher members are considered to be the derivative of acetylene.

For ex: $CH_3\text{-}C\equiv CH$ Methyl acetylene, $CH_3\text{-}CH_2\text{-}C\equiv CH$ Ethyl acetylene.

IUPAC rules for naming the alkynes:

Rules:

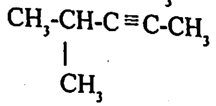
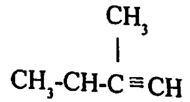
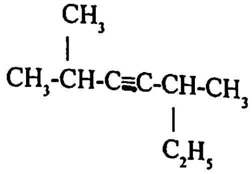
1) Select the longest continuous carbon chain containing the triple bond. As a parent chain.

2) **Name the longest chain.** The name is obtained by removing the final **ane** of alkane by **yne.** And adding yne at the end. **(Alkane -ane + yne = alkyne)**

3) **Number the longest chain.** Numbering is started from that end closer to the triple bond.

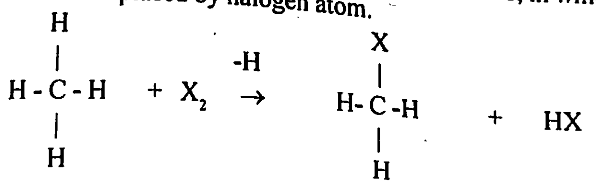
4) **Indicate the position of triple bond.** By the number of the first carbon atom involved in the triple bond.

5) Substituent / side chain are numbered, named and placed as prefixes in alphabetic order. For ex:

Structure	**IUPAC Name**	**Common name**
$CH\equiv CH$	Ethyne	Acetylene
$CH_3-C\equiv CH$	Propyne	Methyl acetylene
$CH_3-CH_2-C\equiv CH$	1-butyne	Ethyl acetylene
$CH_3-C\equiv C-CH_3$	2-butyne	Dimethyl acetylene
 $CH_3-\underset{CH_3}{\underset{\vert}{CH}}-C\equiv C-CH_3$	4-methyl-2-Pentyne	
 $CH_3-\overset{CH_3}{\overset{\vert}{CH}}-C\equiv CH$	3-methyl-1-butyne	
 $CH_3-\overset{CH_3}{\overset{\vert}{CH}}-C\equiv C-\underset{C_2H_5}{\underset{\vert}{CH}}-CH_3$	2-ethyl-5methyl-3-hexyne	

VI] ALKYL-HALIDES:

Alkyl halides are the halogen derivative of alkanes, in which hydrogen atom of alkane can be replaced by halogen atom.



$$H-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-H + X_2 \xrightarrow{-H} H-\underset{H}{\underset{|}{\overset{X}{\overset{|}{C}}}}-H + HX$$

In the common name system of alkyl halides, the word **halide** is attached after the name of **alkyl group.** And common names of alkyl halides are given in brackets.

IUPAC Name system

Rules:

1) Select the longest continuous carbon chain to which halogen is attached and give the name of corresponding alkanes.

2) **Name the longest chain.** By prefixing name chloro, bromo, iodo, or fluoro.

3) **Number the longest chain.** So as to give the smallest possible number carrying the halogen atom.

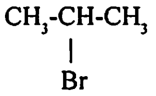
4) Substituent / side chain are numbered, named and placed as prefixes in alphabetic order.

5) If there are two or more identical halogen atoms as a substituent. Then prefix di, tri, tetra, etc.

For ex:

CH_3-Br
(Methyl bromide)
bromo-methane

CH_3-CH_2-Br
(ethyl bromide)
bromo-ethane

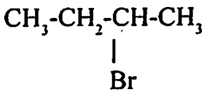


$CH_3-\underset{Br}{\underset{|}{CH}}-CH_3$

(iso-propyl bromide)
2-bromo-propane

$CH_3-CH_2-CH_2-Br$
(n- propyl bromide)
1-Bromo-propane

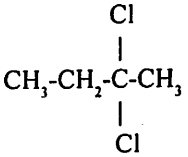
$CH_3-CH_2-CH_2-CH_2-Br$
(n- butyl bromide)
1-Bromo-butane



$CH_3-CH_2-\underset{Br}{\underset{|}{CH}}-CH_3$

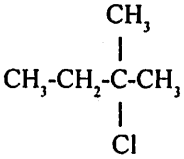
(sec-butyl bromide)

2- bromobutane



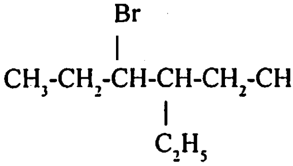
$CH_3-CH_2-\underset{Cl}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}-CH_3$

2, 2-dichlorobutane



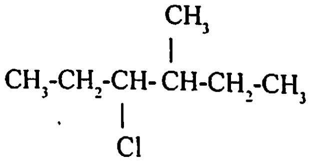
$CH_3-CH_2-\underset{Cl}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$

2-chloro-2-methylbutane



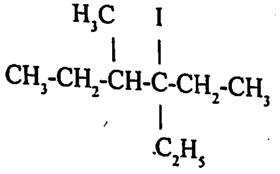
$CH_3-CH_2-\overset{Br}{\overset{|}{CH}}-\underset{C_2H_5}{\underset{|}{CH}}-CH_2-CH_3$

3- Bromo-4-Ethyl hexane



$CH_3-CH_2-\underset{Cl}{\underset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_3$

3-Chloro-4-Methyl Hexane



$CH_3-CH_2-\overset{\overset{H_3C}{|}}{C}H-\underset{\underset{C_2H_5}{|}}{\overset{\overset{I}{|}}{C}}-CH_2-CH_3$

3-ethyl-3-iodo-4-methylhexane

VII] ALCOHOL:—

Alcohols are the hydroxyl derivative of alkanes, in which hydrogen atom of alkane can be replaced by –OH group. Alcohols are also considered to be the derivative of water.

In the common name system of alcohol, the word **alcohol** suffixed to the name of **alkyl group.** For ex: methyl alcohol CH_3-OH, CH_3-CH_2-OH ethyl alcohol.

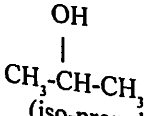
IUPAC rules for naming the alcohol

Rules:

1) Select the longest continuous carbon chain containing the hydroxyl group (OH), as a parent chain.
2) **Name the longest chain.** The name is obtained by removing the final e of alkane by ol. And adding ol at the end. **(Alkane -e + ol = alkanol)**
3) **Number the longest chain.** Numbering is started from that end closer to the hydroxyl group (OH).
4) **Indicate the position of hydroxyl group (OH).**
5) Substituent / side chain are numbered, named and placed as prefixes in alphabetic order. **For ex:**

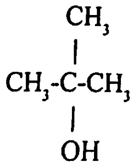
CH_3-CH_2-OH (Ethyl alcohol) Ethanol

CH_3-CH_2-CH_2-OH
(n-propyl alcohol)
1 -propanol



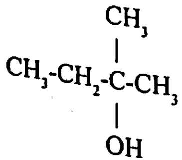
$CH_3-\overset{\overset{OH}{|}}{C}H-CH_3$

(iso-propyl alcohol)
2-propanol



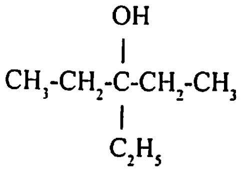
$CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

(t- butyl alcohol)
2-methyl-2-propanol



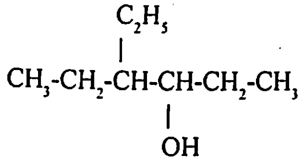
$CH_3-CH_2-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

(t-pentyl alcohol)
2-methyl-2-butanol



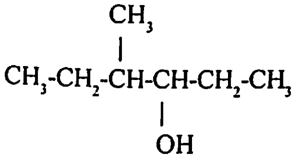
$CH_3-CH_2-\underset{\underset{C_2H_5}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2-CH_3$

3-Ethyl-3- pentanol



$CH_3-CH_2-\underset{\underset{OH}{|}}{C}H-\overset{\overset{C_2H_5}{|}}{C}H-CH_2-CH_3$

4 - ethyl-3-hexanol



$CH_3-CH_2-\underset{\underset{OH}{|}}{C}H-\overset{\overset{CH_3}{|}}{C}H-CH_2-CH_3$

4-methyl-3-hexanol

VIII] ETHERS :—

Ethers are the organic compounds in which divalent oxygen atom is attached to two same or different alkyl or aryl groups. Ethers having general formula $C_nH_{2n+2}O$. they are represented as R-O-R' or Ar-O-R or Ar-O-Ar

Structurally ethers may be considered to be derivative of water by replacement of hydrogen atom of water by alkyl or aryl groups. Also they are considered to be the derivative of alcohol in which hydrogen atom of alcohol replaced by alkyl or aryl groups.

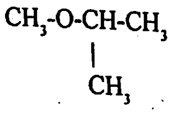
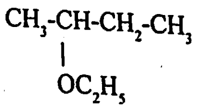
In the common name system of ethers two alkyl or two aryl groups attached to the oxygen atoms are different then they are placed in alphabetical order. If two alkyl or two aryl groups attached to the oxygen atoms are same then di, tri, can be used. And the word **Ether** is attached after the name of alkyl or aryl groups.

IUPAC rules for naming the ethers:

Rules:

1) Ethers are considered to be derivatives of alkoxy-alkanes.(smaller alkyl group of oxygen atom is called alkoxy Substituent.
2) Larger alkyl group is considered as parent alkane.
3) Prefix the name of alkoxy group to the name of parent alkane.
4) Substituent / side chain are numbered, named and placed as prefixes in alphabetic order. **For ex:**

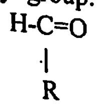
Structure	**IUPAC name**	**Common name**
CH_3-O-CH_3	methoxy methane	dimethyl ether

$CH_3\text{-}O\text{-}CH_2\text{-}CH_3$	methoxy ethane	Ethyl- methyl ether
$CH_3\text{-}O\text{-}C_2H_5$	methoxy ethane	Ethyl- methyl ether
$CH_3\text{-}O\text{-}C_3H_7$	methoxy propane	methyl- n-propyl ether
$C_2H_5\text{-}O\text{-}C_2H_5$	ethoxy ethane	diethyl ether
 $CH_3\text{-}O\text{-}\underset{CH_3}{CH}\text{-}CH_3$	2- methoxy propane	methyl- iso-propyl ether
 $CH_3\text{-}\underset{OC_2H_5}{CH}\text{-}CH_2\text{-}CH_3$	2- ethoxy butane	Ethyl- sec-butyl ether

IX] CARBONYL COMPOUNDS:-

Carbonyl group (>C=O) is the common functional group for aldehydes and ketones .In which oxygen atom is attached to a carbon atom by double bond. and the compound which having carbonyl group are known as carbonyl compounds.

ALDEHYDES:— In which one valency of carbonyl carbon can be satisfied by hydrogen atom and another by any alkyl or aryl group. Aldehydes having functional group –CHO or H-C=O


$H\text{-}\underset{R}{C}=O$

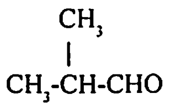
Common names of aldehydes are taken from those of corresponding carboxylic acids in which the suffix **ic acid** is replaced by **aldehyde.**
For ex: $CH_3\text{-}CHO$ acetaldehyde, $CH_3\text{-}CH_2\text{-}CHO$ propionaldehyde.

IUPAC rules for naming the Aldehyde:

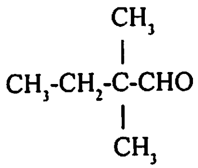
Rules :

1) Select the longest continuous carbon chain containing the aldehyde group (-CHO),as a parent chain.
2) **Name the longest chain.** The name is obtained by removing the final e of alkane by **al.** And adding **al** at the end. **(Alkane -e + al = alkanal)**
3) **Number the longest chain.** Number one is given the aldehyde group (-CHO), and number one is not used to indicate the position of aldehyde group (-CHO), since it is placed at the end of the chain.
4) Other substituent / side chain are numbered, named and placed as prefixes in alphabetic order. **For ex:**

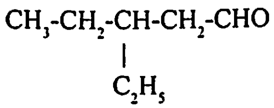
$CH_3\text{-}CHO$	$CH_3\text{-}CH_2\text{-}CHO$	$CH_3\text{-}CH_2\text{-}CH_2\text{-}CHO$
(Acetaldehyde)	(Propionaldehyde)	(butyralaldehyde)
ethanal	propanal	Butanal


$CH_3\text{-}\overset{CH_3}{CH}\text{-}CHO$

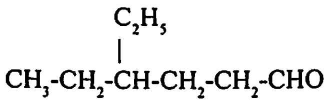
(iso-butyraldehyde)
2-methyl-2-propanal


$CH_3\text{-}CH_2\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}CHO$

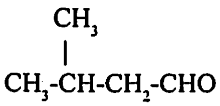
2, 2- dimethylbutanal


$CH_3\text{-}CH_2\text{-}\underset{C_2H_5}{CH}\text{-}CH_2\text{-}CHO$

3-Ethyl pentanal


$CH_3\text{-}CH_2\text{-}\overset{C_2H_5}{CH}\text{-}CH_2\text{-}CH_2\text{-}CHO$

4 -ethyl-hexanal


$CH_3\text{-}\overset{CH_3}{CH}\text{-}CH_2\text{-}CHO$

2-methyl-butanal

KETONES:- In which both valencies of carbonyl carbon can be satisfied by two alkyl or two aryl group or one alkyl and one aryl group.
ketones having functional group R-C=O


$R\text{-}\underset{R_1}{C}=O$

Ketones are commonly named on the basis of alkyl groups attached to the carbonyl carbon atom. In the common name system of ketones, the word **ketone** is attached after the name of alkyl groups and alkyl groups are placed in alphabetical order. Acetone is the trivial name which is the first member of series.

IUPAC rules for naming the ketenes:

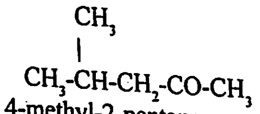
Rules:

1) Select the longest continuous carbon chain containing the keto group (>C=O), as a parent chain.
2) **Name the longest chain.** The name is obtained by removing the final **e** of alkane by —**one.** And adding -one at the end. **(Alkane -e + one = alkanone)**
3) **Number the longest chain.** Lowest number is given to the carbonyl carbon.
4) Other substituent / side chain are numbered, named and placed as prefixes in alphabetic order. **For ex:**

$CH_3\text{-}CO\text{-}CH_3$	$CH_3\text{-}CH_2\text{-}CO\text{-}CH_3$
(acetone) / (dimethyl ketone)	(ethyl methyl ketone)
Propanone	2-butanone

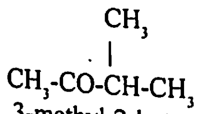
$C_2H_5-CO-C_2H_5$
(diethyl ketone)
3- pentanone

$CH_3-CO-C_3H_7$
(methyl propyl ketone)
2- pentanone



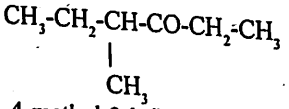
$\begin{array}{l} \quad CH_3 \\ \quad | \\ CH_3-CH-CH_2-CO-CH_3 \end{array}$

4-methyl-2-pentanone



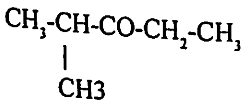
$\begin{array}{l} \qquad\quad CH_3 \\ \qquad\quad | \\ CH_3-CO-CH-CH_3 \end{array}$

3-methyl-2-butanone



$\begin{array}{l} CH_3-CH_2-CH-CO-CH_2-CH_3 \\ \qquad\qquad | \\ \qquad\quad CH_3 \end{array}$

4-methyl-3-hexanone



$\begin{array}{l} CH_3-CH-CO-CH_2-CH_3 \\ \qquad | \\ \quad CH3 \end{array}$

2-methyl-3- pentanone.

X] CARBOXYLIC ACIDS :-

Organic compounds which contain the carboxyl group (-COOH) as a functional group are called the carboxylic acids. They are represented as R-COOH. [Where R= H or R= alkyl group]

Common name system: common names are given by its original source.

For ex: i) formic acid	HCOOH	obtained from formica (red ant)
ii) acetic acid	CH_3-COOH	obtained from acetum (vinegar)
iii) propionic acid	CH_3-CH_2-COOH	obtained previously therefore it is called proipionic acid.
iv) butyric acid	$CH_3-CH_2-CH_2$-COOH	obtained from butter.
v) valeric acid	$CH_3-(CH_2)_3$-COOH	obtained from velar.etc.

In common name system Greek letters α, ß, γ, δ.are used to indicate the position of substituents and carbon atom adjacent to the carboxyl group is represented as α.

IUPAC rules for naming the carboxylic acid:

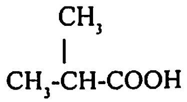
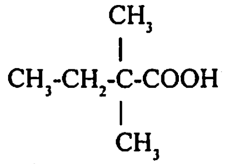
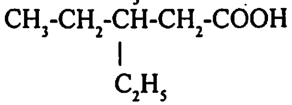
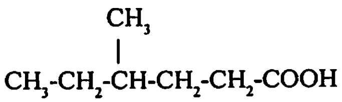
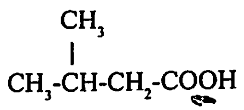
Rules:

1) Select the longest continuous carbon chain containing the carboxyl group (-COOH), as a parent chain.

2) **Name the longest chain.** The name is obtained by removing the final e of alkane by **-oic acid.** And adding **-oic acid** at the end. **(Alkane -e + -oic acid = alkanoic acid)**

3) **Number the longest chain.** Numbering one is given the carboxyl group (-COOH), and number one is not used to indicate the position of carboxyl group (-COOH), since it is placed at the end of the chain.

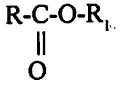
4) Other substituent / side chain are numbered, named and placed as prefixes in alphabetic order. **For ex:**

Structure	**IUPAC name**	**Common name**
HCOOH	Methanoic acid	formic acid
CH_3-COOH	Ethanoic acid	acetic acid
CH_3-CH_2-COOH	Propanoic acid	proipionic acid
$CH_3-CH_2-CH_2$-COOH	Butanoic acid	n-butyric acid
 $\begin{array}{l} \quad CH_3 \\ \quad \vert \\ CH_3-CH-COOH \end{array}$	2-methyl-propanoic acid	iso- butyric acid
$CH_3-(CH_2)_3$-COOH	pentanoic acid.	n-valeric acid
$CH_3-(CH_2)_4$-COOH	hexannoic acid.	n-caproic acid
 $\begin{array}{l} \qquad\qquad CH_3 \\ \qquad\qquad \vert \\ CH_3-CH_2-C-COOH \\ \qquad\qquad \vert \\ \qquad\qquad CH_3 \end{array}$	2, 2- dimethyl- butanoic acid	
 $\begin{array}{l} CH_3-CH_2-CH-CH_2-COOH \\ \qquad\qquad \vert \\ \qquad\qquad C_2H_5 \end{array}$	3-Ethyl- pentanoic acid.	
 $\begin{array}{l} \qquad\qquad CH_3 \\ \qquad\qquad \vert \\ CH_3-CH_2-CH-CH_2-CH_2-COOH \end{array}$	4 - methyl-hexannoic acid	
 $\begin{array}{l} \quad CH_3 \\ \quad \vert \\ CH_3-CH-CH_2-COOH \end{array}$	3-methyl-butanoic acid	

XI] ESTERS:

Esters are the alkyl derivatives of carboxylic acids and are obtained by replacing (hydroxyl group) –OH by -OR alkoxy group.

They are represented by



$\begin{array}{l} R-C-O-R_1 \\ \quad \| \\ \quad O \end{array}$

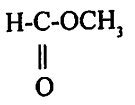
IUPAC rules for naming esters;

Rules:-

1) Prefix the name of alkyl group which is attached to the oxygen atom of the –**COOH** group.

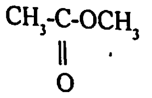
2) The name of the parent acid is obtained by removing **-ic acid** of acids by **-ate.**

For ex:

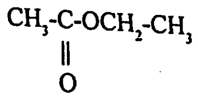


$\begin{array}{l} H-C-OCH_3 \\ \quad \| \\ \quad O \end{array}$

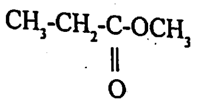
Methyl methanoate.



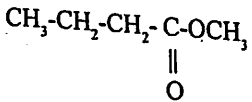
$CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}OCH_3$ Methyl ethanoate.



$CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}OCH_2\text{-}CH_3$ Ethyl ethanoate.



$CH_3\text{-}CH_2\text{-}\underset{\underset{O}{\|}}{C}\text{-}OCH_3$ Methyl propanoate.



$CH_3\text{-}CH_2\text{-}CH_2\text{-}\underset{\underset{O}{\|}}{C}\text{-}OCH_3$ Methyl butanoate.

XII} AMINES:

Amines are nitrogen containing organic compounds; they are defined as alkyl derivatives of ammonia and are obtained by replacing by one, two, or all the three hydrogen atoms of ammonia by alkyl groups.

For ex:

CH_3NH_2	methyl amine
$(CH_3)_2NH$	dimethyl amine
$(CH_3)_3N$	trimethyl amine.

In the common name system of amines, amines are named by adding the suffix – amine to the name of alkyl group or groups. The entire name is written as one word. And the names of alkyl groups are arranged in alphabetic order. for ex:

$CH_3\text{-}NH_2$	methylamine
$(CH_3)_2NH$	dimethylamine
$(CH_3)_3N$	trimethylamine.
$CH_3\text{-}NH\text{-}C_2H_5$	ethyl,methylamine
$CH_3\text{-}N(C_2H_5)_2$	diethyl,methylamine

IUPAC rules for naming amines:

Rules:

1) Select the longest continuous carbon chain containing the amino group ($-NH_2$), as a parent chain.

2) **Name the longest chain.** The name is obtained by removing the final e of alkane by **amine.** And adding **amine** at the end. **(Alkane -e + amine = alkanamine)**

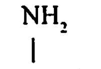
3) **Number the longest chain.** Numbering is started from that end closer to the amino group ($-NH_2$).

4) **Indicate the position of amino group ($-NH_2$).**

5) Substituent / side chain are numbered, named and placed as prefixes in alphabetic order. For ex:

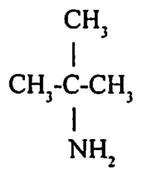
$CH_3\text{-}NH_2$
Methanamine

$CH_3\text{-}CH_2\text{-}NH_2$
Ethanamine



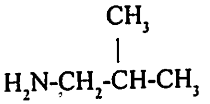
$CH_3\text{-}\overset{\overset{NH_2}{|}}{CH}\text{-}CH_3$

2- propanamine



$CH_3\text{-}\underset{\underset{NH_2}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}CH_3$

2-methyl-2-propanamine

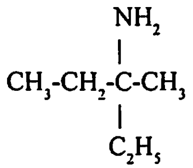


$H_2N\text{-}CH_2\text{-}\overset{\overset{CH_3}{|}}{CH}\text{-}CH_3$

2-methyl-1-propanamine

$(CH_3)_2NH$
Di-methanamine

$(CH_3)_3N$
Tri-methanamine



$CH_3\text{-}CH_2\text{-}\underset{\underset{C_2H_5}{|}}{\overset{\overset{NH_2}{|}}{C}}\text{-}CH_3$

3-methyl-3- pentanamine

$(CH_3)_2\text{-}N\text{-}CH_2\text{-}CH_2\text{-}CH_3$ N, N-dimethylpropanamine

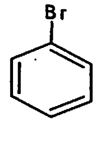
XIII] BENZENE DERIVATIVES:-

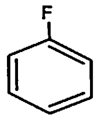
The term aromatic compounds were first used by Kekule to classify benzene and its derivatives, many of which possess fragrant odour or aroma. The term aromatic came to be associated with chemical stability rather than any aroma. The stable character of aromatic compounds was attributed to the presence of a ring structure specific of benzene. So that, the term aromatic compound stands for the whole series of compounds which contain one or more benzene rings in their molecule. With the introduction of the new name of **Arenes** for all aromatic hydrocarbons (Benzene, Naphthalene, Anthracene, etc.)

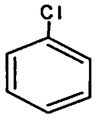
Nomenclature Of Benzenederivatives :-

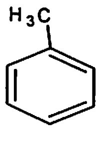
A) Naming of Mono-substituted Benzene:-

Benzene is represented by a regular hexagon with a circle inscribed in it. The mono- substituted derivatives of benzene are those in which hydrogen atom of ring is replaced by another substituent. These are named by prefixing the name of substituent to the word benzene. For ex: one hydrogen atom ring is replaced by bromine (Br). And the name becomes bromobenzene.

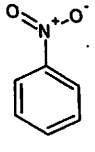

Bromobenzene

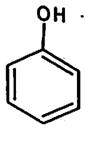

Fluorobenzene

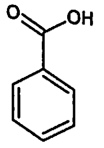

Chlorobenzene

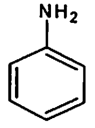

methyl benzene

Other mono-substituted benzene has common names

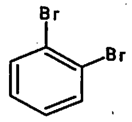

Nitrobenzene

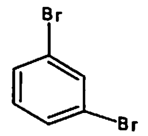

Phenol

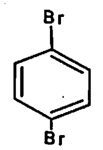

Benzoic acid

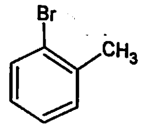

Aniline

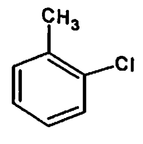
B) Naming of di- substituted benzene:


o-dibromobenzene

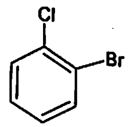

m- dibromobenzene

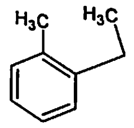

p-dibromobenzene


o-bromotoluene.


o-chlorotoluene.

If two substituents are different, they are usually put in alphabetical order

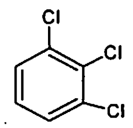

1-bromo-2-chlorobenzene

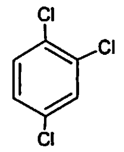

1-ethyl-2-methylbenzene

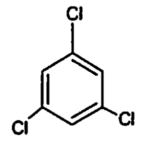
C) Naming of poly substituted benzene:-

When three or more substituents are placed on the the benzene ring, numbers must be used to designate their position.

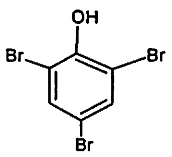
One of the substituent is put at the top of the ring and numbered 1.the numbering of the remaining position is done clock wise or anti-clock wise, i.e lowest number gets to other substituents.

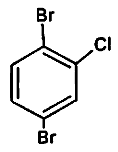

1, 2, 3-trichlorobenzene

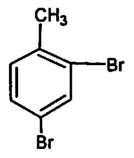

1, 2, 4- trichlorobenzene


1, 3, 5-trichlorobenzene

If one of the group present gives rise to a compound with special name, then only the remaining positions of substituents are mentioned.

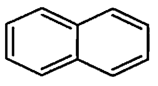

2, 4, 6-tribromophenol

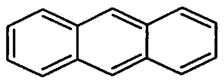

1,4-dibromo-2-chllorobenzene

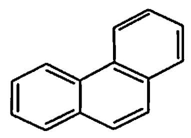

2,4-dibromotoluene

Fused polycyclic Arenes:-

In which aromatic hydrocarbons having one or more benzene rings fused together in ortho positions


Naphthalene

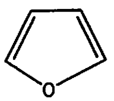

Anthracene

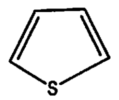

Phenanthrene

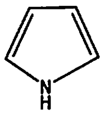
XIV] HETEROCYCLIC COMPOUNDS:-

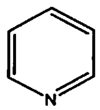
Cyclic compounds that contain at least one atom other than carbon as hetero atom within the ring are called heterocyclic compounds.

Hetero atoms are generally N, O, S and P. for ex:


Furan


Thiophene


Pyrrole


pyridine

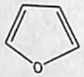
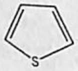
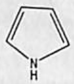
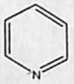
IUPAC rules for naming the heterocyclic compounds:-

1) Following prefixes are used for hetero atom oxa for oxygen, thia for sulphur, aza for nitrogen, phospha for phosphorous etc.

2) Last vowel of prefixes are replaced by the respective name ending words, depending upon the size of ring

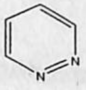
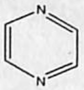
No. of atoms in rings	Name endings
3	-irine
4	-ele
5	-ole
6	-ine
7	-epine

For ex.

Structure	Trival name	IUPAC name
	Furan	oxole (a = ole)
	Thiophene	thiole
	Pyrrole	azole
	Pyridine	azine (a = ine)

3 In monocyclic compounds containing only-one heteroatom, numbering start from heteroatom.

4 when two or more same hetero atoms are presents the prefixes di,tri etc are used.

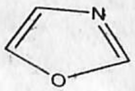
Structure	Trival name	IUPAC name
	pyrinine	1,3- di azine
	pyrazine	1,4-Di azine

3) When the ring contains more than one type of hetero atom, then the position 1 (first preference) is given to the element from the highest group number of the periodic table

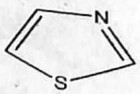
For ex : the preference is Oxyen (O) (gr. VI) before N and S (gr.VI) before N (gr. V) Similarly the preference is to N before Si (gr. IV) & P before Si.

The first preference is also given to the element of lowest atomic number is same group.

4) The direction of numbering round the ring is such that the numbers are kept to minimum.



1, 3-Oxazole



1, 3-Thiazole

1.2 Organometallic Compounds

Organometallic compounds are those compounds which having at least one carbon metal bond.

The nature of such bond depends largely upon the difference in electro-negativities of metal and carbon. Thus it may be purely ionic or purely covalent.

$$-\overset{|}{\underset{|}{C}}\text{-Metal} \quad \text{or} \quad -\overset{|}{\underset{|}{C}}\text{-M}$$

Where M = Mg, Li, Pb, Zn, Na.

For ex.:- i) R-MgX	Alkyl magnesium halide
ii) R_2Zn	Dialkyl zinc
iii) R_3Al	trialkyl aluminium.

Organometallic compounds are named by simply adding the name of the metal to that of the organic group bonded to metal. For ex:

CH_3-Mg-I Methyl magnesium iodide	CH_3-CH_2-Mg-I Ethyl magnesium iodide
CH_3-Li Methyl lithium	$(CH_3)_4$ Pb Tetra methyl lead

3

A] Organomagnesium compounds: - [Grignard reagent] R-Mg-X

The alkyl or aryl magnesium halides [(R) or (Ar) - MgX] are called Grignard reagent.

Formation / preparation: - A Grignard reagent is prepared by adding an alkyl or aryl halide to flask containing a suspension of magnesium turnings in the dry ether. A visible reaction takes place at the surface of magnesium, which shows down during the course of reaction.

$$R\text{-}X + Mg \xrightarrow{\text{ether}} RMgX$$

Alkyl magnesium halide

$$Ar\text{-}X + Mg \xrightarrow{\text{ether}} ArMgX$$

Aryl magnesium halide.

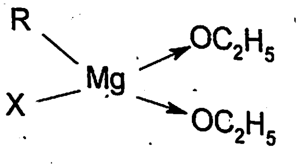
$$CH_3\text{-}I + Mg \xrightarrow{\text{ether}} CH_3Mg\,I$$

Methyl iodide → Methyl magnesium iodide

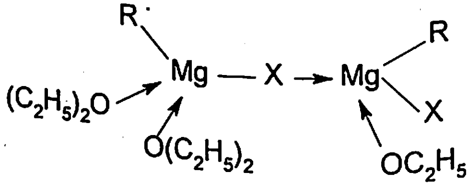
$$CH_3\text{-}CH_2\text{-}I \xrightarrow{\text{ether}} CH_3\text{-}CH_2MgI$$

Ethyl iodide → Ethyl magnesium iodide

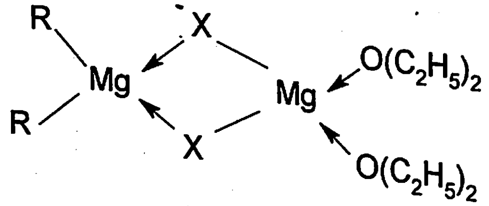
Structure: - Following three alternative formulations have been proposed; in which they may exist as monomers or dimers along with ether of crystallization.



I



II



III

Structure (I) shows the simplest structure of monomeric form which is solvated by coordinating with two molecules of ether.

The Structure (II) and (III) represent the dimeric forms solvated in ether. In Structure (II) halogen atom of one molecule coordinated with mg atom of the other .

Where as in Structure (III), the compound is considered as existing in a 1:1 complex of dialkyl magnesium and magnesium halide.the halogen atom of the magnesium halide coordinate with the magnesium atom of dialkyl magnesium.

Chemical reactions:-

The C-Mg bond in Grignard reagent is covalent but highly polar. The carbon atom is more electronegative than magnesium. There fore bonding electro pair of C-Mg bond is shifted to words the carbon atom. i. e. carbon atom has partial positive charge and magnesium atom has partial negative charge.

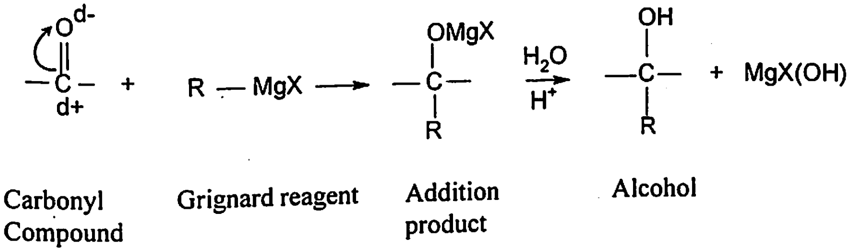
$$-C^{\delta-}\text{-}Mg^{\delta+}X \quad \text{or} \quad \overset{\delta-}{R}\,\overset{\delta+}{Mg}\,X$$

Thus the characteristic reaction of Grignard reagent is nucleophilic substitution and nucleophilic addition reactions.

Nucleophilic substitution reactions: The Grignard reagent undergoes substitution reaction by following general mechanism.

$$\overset{\delta-}{R}\,\overset{\delta+}{MgX} + A\text{-}B \rightarrow \mathbf{R\text{-}A} + MgX(B)$$

Nucleophilic addition reactions: Carbonyl compounds are attacked by Grignard reagent to form addition product which upon acid hydrolysis yield alcohols, acids, esters, amines, etc.



Grignard reagent reacts with a variety of substances produce the entire range of organic compounds.

Synthetic applications Grignard reagent:-

1) Synthesis of Hydrocarbons [Zerevatins method for active H-atom].

a) **Alkanes:** - When Grignard reagent undergoes double decomposition; they combine with water, alcohol & amines to form alkanes.

1. $H\text{-}OH + CH_3MgI \rightarrow CH_4 + Mg(OH)I$
2. $R\text{-}OH + CH_3MgI \rightarrow CH_4 + Mg(OR)I$
3. $R\text{-}NH_2 + CH_3MgI \rightarrow CH_4 + Mg(NH\text{-}R)I$

Higher alkanes can be prepared by treating with alkyl halides.

b) **Alkenes:** - Alkene are obtained by action of unsaturated halides on Grignard reagent

$$CH_3MgI + I\text{-}CH_2\text{-}CH{=}CH_2 \rightarrow CH_3\text{-}CH_2\text{-}CH{=}CH_2 + MgI_2$$

c) **Alkynes:** When lower alkynes treated with Grignard reagent to form higher alkynes.

$$CH_3\text{-}C\equiv CH + CH_3MgI \rightarrow CH_3\text{-}C\equiv C\text{-}MgI + CH_4$$

$$CH_3\text{-}C\equiv C\text{-}MgI + I\text{-}C_2H_5 \rightarrow CH_3\text{-}C\equiv C\text{-}C_2H_5 + MgI_2$$

2) Synthesis of alcohols:-

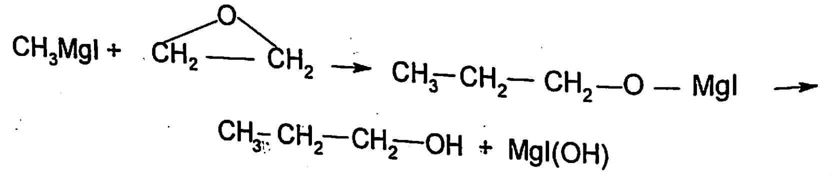
a) Primary alcohol

When methyl magnesium iodide reacts with formaldehyde it gives ethyl alcohol.

$$CH_3Mg\text{-}I + CH_2O \rightarrow CH_3\text{-}CH_2\text{-}O\text{-}MgI \rightarrow \underset{\text{ethanol}}{CH_3\text{-}CH_2\text{-}OH} + Mg(OH)I$$

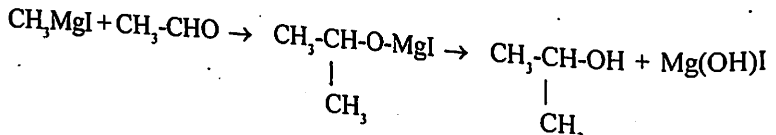
b) **Primary alcohol:**

When epoxides are treated with methyl magnesium iodide they undergo ring opening to form intermediate compound which on acid hydrolysis it gives alcohols.



c) Secondary alcohol:-

When methyl magnesium iodide reacts with acetaldehyde it gives isopropyl alcohol.

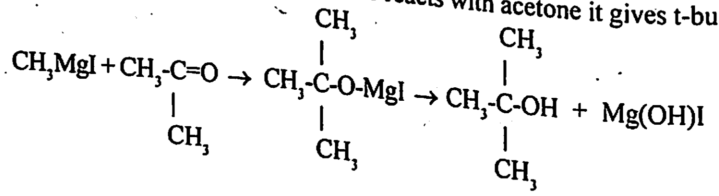


$$CH_3MgI + CH_3\text{-}CHO \rightarrow CH_3\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}O\text{-}MgI \rightarrow CH_3\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}OH + Mg(OH)I$$

2- propanol

d) Tertiary alcohol

When methyl magnesium iodide reacts with acetone it gives t-butyl alcohol.

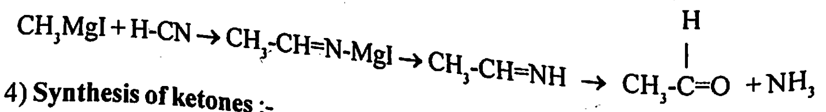


$$CH_3MgI + CH_3\text{-}\underset{\underset{CH_3}{|}}{C}{=}O \rightarrow CH_3\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{-}O\text{-}MgI \rightarrow CH_3\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{-}OH + Mg(OH)I$$

2-methyl-2-propanol

3) Synthesis of Aldehydes:-

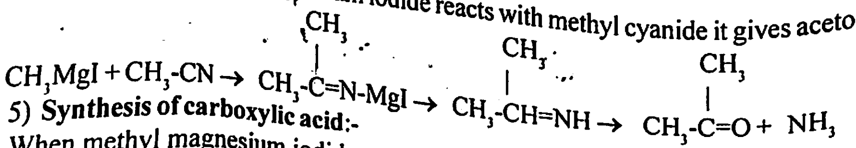
When methyl magnesium iodide reacts with hydrogen cyanide it gives acetaldehyde.



$$CH_3MgI + H\text{-}CN \rightarrow CH_3\text{-}CH{=}N\text{-}MgI \rightarrow CH_3\text{-}CH{=}NH \rightarrow CH_3\text{-}\overset{\overset{H}{|}}{C}{=}O + NH_3$$

4) Synthesis of ketones :-

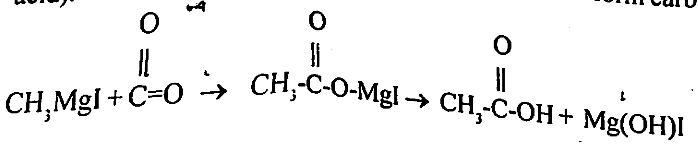
When methyl magnesium iodide reacts with methyl cyanide it gives acetone



$$CH_3MgI + CH_3\text{-}CN \rightarrow CH_3\text{-}\overset{\overset{CH_3}{|}}{C}{=}N\text{-}MgI \rightarrow CH_3\text{-}\overset{\overset{CH_3}{|}}{CH}{=}NH \rightarrow CH_3\text{-}\overset{\overset{CH_3}{|}}{C}{=}O + NH_3$$

5) Synthesis of carboxylic acid:-

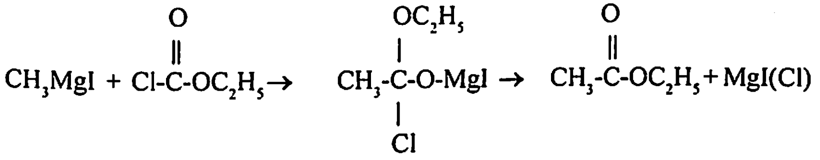
When methyl magnesium iodide reacts with solid CO_2 (dry ice) at 273k to form complex which on decomposition with HCl solution to form carboxylic acid.(acetic acid).



$$CH_3MgI + \overset{\overset{O}{||}}{C}{=}O \rightarrow CH_3\text{-}\overset{\overset{O}{||}}{C}\text{-}O\text{-}MgI \rightarrow CH_3\text{-}\overset{\overset{O}{||}}{C}\text{-}OH + Mg(OH)I$$

6) Synthesis of Esters:-

When methyl magnesium iodide react with ethyl chloroformate to form complex which on heating it decomposition to form ethyl acetate.



$$CH_3MgI + Cl\text{-}\overset{\overset{O}{||}}{C}\text{-}OC_2H_5 \rightarrow CH_3\text{-}\overset{\overset{OC_2H_5}{|}}{\underset{\underset{Cl}{|}}{C}}\text{-}O\text{-}MgI \rightarrow CH_3\text{-}\overset{\overset{O}{||}}{C}\text{-}OC_2H_5 + MgI(Cl)$$

7) Synthesis of acetonitrile:-

When methyl magnesium iodide reacts with cyanogens chloride to form methyl cyanide (acetonitrile)

CH_3MgI + CN-Cl → CH_3-CN + Mg(I)Cl
cyanogen chloride acetonitrile

8) Synthesis of methyl amine: - When methyl magnesium iodide reacts with chloramine to form methyl amine.

CH_3MgI + H_2N-Cl → CH_3-NH_2 + Mg(I)Cl
Chloramines Methyl amine

B] ORGANOLITHIUM COMPOUNDS:-

Organo lithium compounds are those compounds which contain C-Li bond.

For ex:

CH_3-Li	C_2H_5-Li	C_3H_7-Li
Methyl lithium	ethyl lithium	propyl lithium

Organo lithium compounds are most important reagents for organic synthesis.

Synthesis of Organo lithium compounds:-

1) **From alkyl or aryl halides:-** When alkyl halides (CH_3-I) reacts with methyl lithium at low temperature in a hydrocarbon solvent and in an atm. of N_2 or orgon. Methyl lithium compound is formed.

$$R\text{-}X + 2\,Li \rightarrow R\text{-}Li + Li\text{-}X$$

$$CH_3\text{-}I + 2\,Li \rightarrow CH_3\text{-}Li + Li\text{-}I$$

2) **By halogen metal exchange method:-**

Organo lithium compounds are obtained by treating alkyl or aryl halides with lithium alkyls.

For ex: When ethyl lithium react with methyl iodide to form methyl lithium

$$C_2H_5\text{-}Li + CH_3\text{-}I \rightarrow CH_3\text{-}Li + C_2H_5\text{-}I$$

Reactions of organo lithium compounds:

1) **Synthesis of methane.:**

Organo lithium compounds react with water to form alkane. When methyl lithium react with water to form methane.

$CH_3\text{-}Li + H\text{-}OH \rightarrow CH_4 + Li\text{-}OH$

methane.

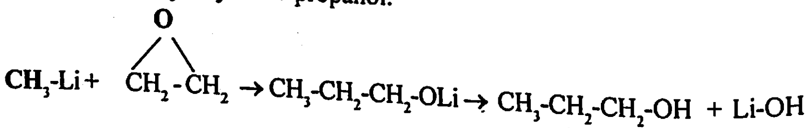
2) Synthesis of alcohols :-

a) **Primary alcohol:** When methyl lithium reacts with formaldehyde to give addition compound which on hydrolysis yield ethanol.

$CH_3\text{-}Li + CH_2O \rightarrow CH_3\text{-}CH_2\text{-}OLi \rightarrow CH_3\text{-}CH_2\text{-}OH + Li\text{-}OH$

Ethanol

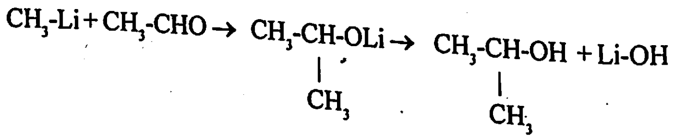
b) When methyl lithium react with ethylene oxide to give addition compound, which on hydrolysis yield 1-propanol.



1-propanol

II) Secondary alcohol:

When methyl lithium react with acetaldehyde to give addition compound, which on hydrolysis yield 2-propanol.

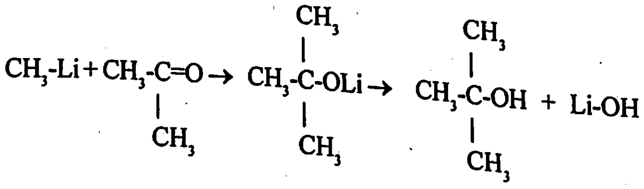


$$CH_3\text{-}Li + CH_3\text{-}CHO \rightarrow \underset{\displaystyle CH_3}{\underset{|}{CH_3\text{-}CH\text{-}OLi}} \rightarrow \underset{\displaystyle CH_3}{\underset{|}{CH_3\text{-}CH\text{-}OH}} + Li\text{-}OH$$

2- propanol

5) Tertiary alcohol:-

When methyl lithium react with acetone to give addition compound, which on hydrolysis yield 2-methyl-2-propanol.

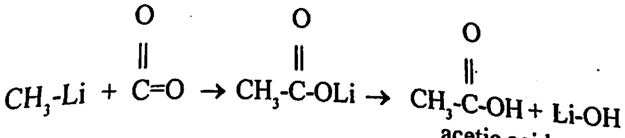


$$CH_3\text{-}Li + \underset{\displaystyle CH_3}{\underset{|}{CH_3\text{-}C{=}O}} \rightarrow \underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{CH_3\text{-}C\text{-}OLi}}}} \rightarrow \underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{CH_3\text{-}C\text{-}OH}}}} + Li\text{-}OH$$

2-methyl-2-propanol

6) Synthesis of acid :

When methyl lithium react with CO_2 to give addition compound, which on hydrolysis yield acetic acid.



$$CH_3\text{-}Li + \overset{\displaystyle O}{\overset{\|}{C}}{=}O \rightarrow \overset{\displaystyle O}{\overset{\|}{CH_3\text{-}C\text{-}OLi}} \rightarrow \overset{\displaystyle O}{\overset{\|}{CH_3\text{-}C\text{-}OH}} + Li\text{-}OH$$

acetic acid.

❖❖❖

UNIT - [II]

2.1 Mechanism of Organic Reaction

2.2 Alkenes, Dienes And Alkynes

2.1 MECHANISM OF ORGANIC REACTION

1) **Substrate and Reagent**:-

In a chemical reaction, the reacting molecule undergoing attack is referred to as the substrate. And the general term used to describe the attacking species is the reagent. The substrate and reagent interact to yield the product of the reaction.

SUBSTRTE + REAGENT → PRODUCTS

The carbon bonds in the substrate molecule are broken to form fragments which are very reactive and constitute transitory intermediates. At once they may react with other species present in the environment to form new bond to give the product.

The steps of an organic reactions showing the breaking and making of new bonds of carbon atoms in the substrate leading the formation of the final product through transitory intermediates, are often referred to as its **Mechanism.**

SUBSTRTE → INTERMEDIATES → PRODUCTS
(Transitory)

Most of the attacking reagents carry either positive or negative charge.

The positively charged reagents attack on the region of the high electron density in the substrate molecule. While the negatively charged reagents will attack on the region of low electron density in the substrate molecule.

2) **Types of reagents: Electrophiles and Nucleophiles**:-

Organic reactions fall into two main groups:-

i) Electrophiles or electrophilic reagents
ii) Nucleophiles or nucleophilic reagents

i) Electrophiles or electrophilic reagents (E^+)

A reagent which can accept an electron pair in a reaction is called as electrophiles or electrophilic reagents.

They can attack on high electron density centre in the substrate molecule. They are electron –deficient. They can be positively charged ions or neutral molecules with electron deficient centre. For ex: - H^+, NO_2^+, Br^+, R_3C^+, RN_2^+, SO_3H^+, $AlCl_3$, BF_3.

ii) Nucleophiles or nucleophilic reagents (Nu^-)

A reagent which can donate an electron pair in a reaction is called as nucleophiles or nucleophilic reagents.

They can attack on low electron density centre in the substrate molecule.

They are electron–rich centre. They are negatively charged ions or neutral molecules with free electron pairs.

For ex: - OH^-, Br^-, CN^-, $R-CH^-$, NH_3, RNH_2, H_2O, ROH.

4

3) **Types of breaking of bonds: Homolytic and Heterolytic fission**:-

Every reaction of organic compounds involves the breaking of at least one bond and the making of another bond. a covalent (σ bond) can undergo fission in two ways.

i) Homolytic fission. ii) Heterolytic fission.

i) Homolytic fission:

Symmetrical breaking of a covalent bond is known as homolytic fission. In this process each bonded atom acquires one of the bonding electrons.

A-B or A: B → • A + • B

When symmetrical breaking of a covalent bond takes place free radicals are obtained. **·A** and **·B** are called free radicals. They are electrically neutral and have unpaired electron. Free radicals are extremely reactive because of the tendency of this electron to become paired.

Homolytic reactions are usually initiated by heat, light or organic peroxides.

ii) Heterolytic fission:

Unsymmetrical breaking of a covalent bond is known as heterolytic fission. In this process one of the atom acquire both the bonding electron.

A-B or A: B → A+: B

When unsymmetrical breaking of a covalent bond takes place carbocations and carbanions are obtained. In which more electronegative atom acquire negative charge, while other atom carries positive charge. Heterolytic fission occurs most readily with polar compounds with polar solvent.

ELECTRON MOBILITY:-

1) **Inductive effect**: - Permanent polarization of a covalent bond due to the electronegativity difference between the atom joined by it, leading the fractional positive and negative charges on the respective atoms are called inductive effect.

When a covalent bond is formed between two atoms having different electronegativities, bonding electron pair is pulled by the more electronegative atom and acquire a small negative charge, while other atom having small positive of the same magnitude and bond become polar.

The atoms or group of atoms which pulls the bonding electron pair is said to be negative inductive effect [-I]. And the one which repels bonding electron pair is said to be positive inductive effect [+I].

This effect is transmitted along a chain of covalent bond.

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

-I Effect: electron withdrawing groups.

$NO_2 > F > Cl > Br > I > OCH_3 > C_6H_5$.

+I Effect: electron repelling groups.

$(CH_3)_3C > (CH_3)_2CH > C_2H_5 > CH_3$.

Strength of acids: - Inductive effect is related to strength of acid

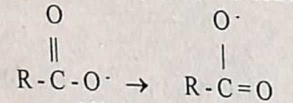
According to Bronsted-Lowry theory, an acid is a compound which gives a proton. The strength of acid can be determined by its capacity to lose proton.

Ex: $R\text{-}COOH \rightarrow R\text{-}COO^- + H^+$

An acid ionises the ions have tendency to recombine. If recombination is easy then acid is weak and if recombination is hard then acid is strong.

The recombination of proton (H^+) and carboxylate ion ($RCOO^-$) is mainly depends upon the electron density on oxygen atom

The carboxylate ion stabilized by resonance,



$$R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O^- \rightarrow R\text{-}\overset{\overset{O^-}{|}}{C}=O$$

If R is electron repelling group (+I effect) then electron density on oxygen increases, thus it has great tendency to combine with H^+ hence acid is weak. If R is electron withdrawing group (-I effect) then electron density on oxygen decreases, thus it has lower tendency to combine with H^+ hence acid is strong.

For ex: - Acetic-acid (CH_3COOH) is weaker acid than formic acid because in acetic acid the $-CH_3$ group is electron repelling group, thus electron density on oxygen increases and has great tendency to combine with H^+, hence acetic acid is weaker acid than formic acid.

$$CH_3COOH \longrightarrow CH_3COO^- + H^+$$

Similarly, monochloro acetic acid is stronger acid than acetic acid, in which Cl-atom is electron withdrawing group, then electron density on oxygen atom decreases there fore, it is stronger acid than acetic acid.

Strength of base:-

The strength of base is determined its to donate an electron.

Ammonia is basic in nature due to presence of lone pair of electrons on N-atom. If, H-atom of ammonia is replaced by alkyl group then electron density on N-atom increases due to +I effect of electron repelling group (alkyl group) hence basicity increases.

The order of basicity is,

$$NH_3 > RNH2 > R_2NH.$$

Field effect: - the inductive effect may be directly transmitted through space, solvent molecule or low dielectric cavity provided by organic solvent rather than along a chain . Such effect is called field effect. Both inductive and field effects operate in the same direction; it is, there fore difficult to separate them.

2) RESONANCE:-

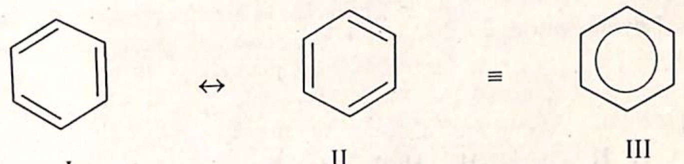
Whenever a molecule can be represented by two or more structures that differ only in the arrangement of electrons-that is by structures, that have the same arrangement of atomic nuclei-there is resonance.

When these contributing structures are of about the same stability, then resonance is important.

The phenomenon in which two or more structures can be written for a molecule, which involve identical positions of atom. But two structures differs only

in the position of atoms, is called resonance.

The actual structure of the molecule is said to be a resonance hybrid. The resonance hybrid structure is more stable than any of the contributing structures.



I

II

III

Resonance structure of benzene

resonance hybrid structure

Out of the two structures of benzene (I and II) none represent the actual structure. All the carbon-carbon bond distances in benzene are equal (1.39) and thus there can not be 3- single bonds (C-C, 1.48) and (C=C, 1.34) as is the case with either structure (I and II).thus in benzene pi- electrons (double bonds) are delocalized and actual structure is the resonance hybrid structure (III) the circle inside the ring showing delocalized pi- electrons, i. e. a cyclic sextet of delocalized pi-electrons.

Resonance involve only the movement of electron never atoms, and double headed arrow indicates resonance phenomenon, while pair of arrow indicates equilibrium.

Ex 1, 3 butadiene

$$CH_2=CH\text{-}CH=CH_2 \leftrightarrow CH_2^+-CH=CH-CH_2^- \leftrightarrow CH_2^--CH=CH-CH_2^+$$

Resonance structure of 1, 3 butadiene

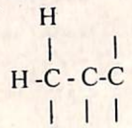
EX: 3) Vinyl chloride

$$CH_2=CH\text{-}\ddot{\underset{..}{Cl}}: \leftrightarrow \ddot{C}H_2\text{-}CH=\underset{+}{\ddot{Cl}}:$$

3) HYPERCONJUGATION:-

The relative stability of various classes of carbonium may be explained by the number of bond resonance structure that can be written for them.

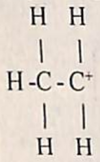
Baker and Nathan suggest that alkyl group with at least one hydrogen atom on the carbon atom, when attached to an unsaturated carbon atom, are able to release electron by a mechanism.



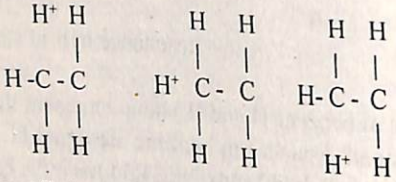
$$\begin{array}{c}H\\|\quad\;\;|\\H\text{-}C\text{-}C\text{-}C\\|\;\;|\;\;|\end{array}$$

Such type of electron release mechanism due to the presence the system H-C-C=C is called hyper conjugation.

Great will be number of C-H bond at α carbon atom to an unsaturated system greater would be the electron release to words the terminal carbon producing high electron density. It is also called as no-bond resonance. More hyperconjugation structures mean more stable species. Ethyl carbonium stabilized by three hyperconjugations



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C^+}}$$



$$H-\underset{H}{\overset{H^+}{C}}-\underset{H}{\overset{H}{C}} \qquad H^+\ \underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}} \qquad H-\underset{H^+}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}$$

4] Intermediates and its type:-

A great majority of organic reactions are multi step processes involving intermediates whose life is very short.

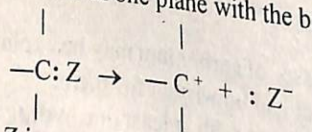
Homolytic and heterolytic bond fission results in the formation of short lived fragments called reaction intermediates.

Among the important reaction intermediates are carbonium ion, carbanion, carbon free radicals, cabenes, nitrenes, and arynes.

i) CARBONIUM ION:-

An organic species which has a positively charged carbon atom bearing six electrons in its outer most shell are called as carbocations. Carbocations are formed by heterolytic fission.

Carbon atom of the carbocation is SP^2 hybridised state and it uses the three hybrid orbits for single bond formation to three substituents, the remaining p-orbital is empty. The carbocation thus has flat structure having all the three covalent bonds in one plane with the bond angle 120^0 between them.



$$-\underset{|}{\overset{|}{C}}:Z \rightarrow -\underset{|}{\overset{|}{C^+}} + :Z^-$$

Where Z is more electro negative.

Formation: - Carbocations can be generated in a variety of ways. Some of the reactions, in which carbocations are formed as.

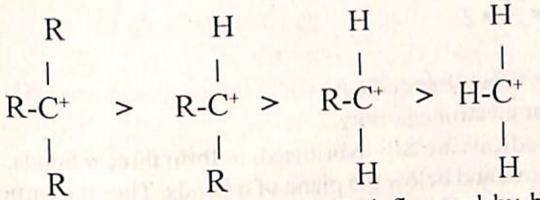
i) Solvolysis of C-X bond (X- is halogen)

$$R\text{-}X \rightarrow R^+ + X^-$$

ii) Determination of amines by nitrous acid.

$$R\text{-}NH_2 \rightarrow RN_2^+ \rightarrow R^+ + N_2$$

Stability : The alkyl group are more electron donating than hydrogen there fore it follow that when these groups are attached to the electron-deficient carbon of the carbocation, they tends to release electrons and partially compensate for all electron-deficiency of the positive carbon. Thus positive charge get dispersed over all the alkyl group and this dispersal of charge increase the stability of the whole system for ex:- tertiary carbocations are more stable than secondary and which is more stable than primary.



$$R-\underset{R}{\overset{R}{C^+}} > R-\underset{R}{\overset{H}{C^+}} > R-\underset{H}{\overset{H}{C^+}} > H-\underset{H}{\overset{H}{C^+}}$$

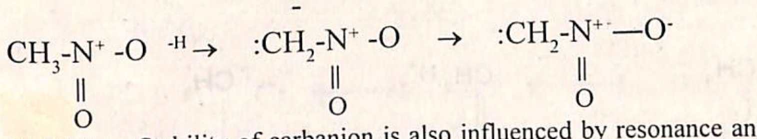
And stability of carbonium ion is influenced by both resonance and inductive effect.

ii) CARBANION :-

An organic species which has a negatively charged carbon atom bearing eight electron in its outer most cell are called as carbanions. Carbanions are formed by heterolytic fission.

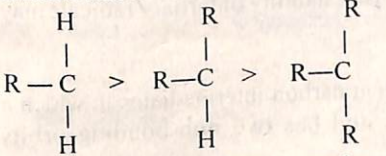
The negatively charged carbon atom in a carbanion is bonded to hydrogen or alkyl groups, it uses SP^3 hybrid orbits to form the three σ bonds

Formation:-The electronegativity of carbon and hydrogen (2.5and 2.1resply) the polarity of the C-H bond is very small heterolytic fission of this covalent bond to form carbanion and proton.



$$CH_3-\underset{\underset{O}{\|}}{N^+}-O \xrightarrow{-H} \overset{-}{:}CH_2-\underset{\underset{O}{\|}}{N^+}-O \rightarrow :CH_2-\underset{\underset{O}{\|}}{N^+}-O^-$$

Stability: - Stability of carbanion is also influenced by resonance and inductive effects. Stabilization of carbanions by inductive effects is the opposite direction from the carbonium ion. Electron releasing groups (+I groups) make the carbonion less stable. Thus a primary carbanion is more stable than secondary, while secondary is more stable than a tertiary. Because of the +I effect associated with alkyl groups.



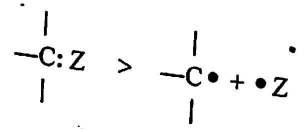
$$R-\underset{H}{\overset{H}{C}} > R-\underset{H}{\overset{R}{C}} > R-\underset{R}{\overset{R}{C}}$$

primary secondary tertiary

Also the stability of carbanion is the extent of S- character of the bonding orbits of the carbanionic carbon. Thus the stability of carbanion has been found to be in order to: $RCH_2 = > R_2CH > R_3C$

iii) FREE RADICALS:-

The fragments have no charge and are called free radicals. Free radicals are extremely reactive and yield a variety of products depending upon the experimental conditions.



$$-\overset{|}{\underset{|}{C}}:Z > -\overset{|}{\underset{|}{C}}\bullet + \bullet Z$$

Carbon free radical

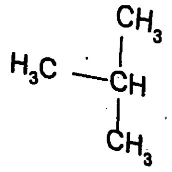
Here carbon and Z have similar electronegativity.

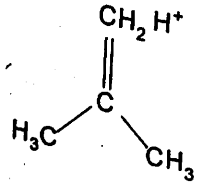
The carbon atoms in the free radicals are SP² hybridised, to form three σ bonds. A half filled p-orbital extends above and below the plane of σ bonds. Thus the carbon free radicals are electrically neutral and have one unpaired. Tendency of this electron to become paired at the earliest opportunity.

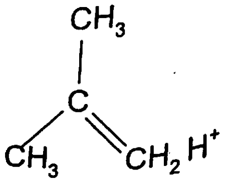
Formation: Free radicals are often produced when a molecule is supplied with sufficient energy-thermal or photochemical to cause homolysis of covalent bond. in addition oxidation reduction reaction involving the gain or loss of a single electron can also generate free radicals.

Stability The stability of the alkyl radicals is in the order. Tertiary > secondary > primary .the reason for the stabilizing influence of alkyl group is not for seek. if we consider that in going from methyl group to t-butyl group, there is increasing tendency for electron release due to hyper conjugation. The hyper-conjugative mechanism tends to fill this orbital and thus stabilize the radical to some extent.

For ex:







Another factor that is responsible for the increased stability of tertiary radicals may be steric effect .

iv) CARBENES:-

Carbenes are defined as neutral, divalent carbon intermediates in which a carbon is covalently bonded to two atoms and has two non-bonding orbits containing two electros between them.

For ex:- H— C: —H

Carbene are very reactive. They act as strong electrophile because they can accept a pair of electrons to complete their outer shell.

Singlet state carbene, carbon atom is presumed to approximate sp2 hybridization. Two of three hybrid sp2 orbital are utilized in forming two covalent bonds, where as third hybrid orbital contains the unshared pair of electrons. The unhybridised p-orbital remains vacant.

Formation: Carbenes are generated by number of ways:

1) By the reaction of chloroform in the presence of a strong alkali.

$$CHCl_3 + RO^- \rightarrow ROH + Cl_3C:^-$$

$$Cl_3C:^- \rightarrow \underset{\text{Carbene}}{Cl_2C:} + Cl:$$

2) By the decomposition of diazomethane ketene in the presence of UV light.

$$H_2C{=}N^+{=}N^- \rightarrow H_2C: + N_2$$

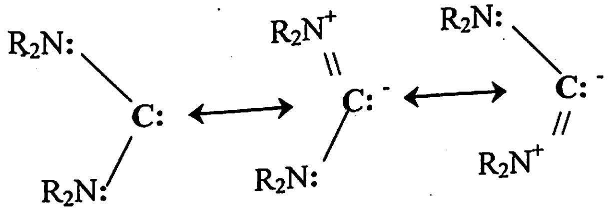
$$H_2C{=}C{=}O \rightarrow H_2C: + CO$$

The first carbene was detected in the alkaline hydrolysis of chloroform.

$$CHCl_3 + OH^- \rightarrow Cl_3C:^- + H_2O$$

$$Cl_3C:^- \rightarrow Cl_2C: + Cl^-$$

Stability: - Carbene in which the carbene carbon is attached to two atoms, **Each bearing an unshared pair of electrons is somewhat more stable due to resonance.**



NITRENES:-

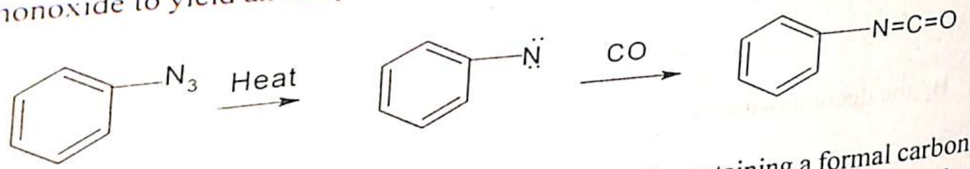
Nitrenes are electron-deficient monovalent nitrogen species in which the nitrogen atom has a sextet of electrons in its outer shell. Nitrenes are existing in two possible form i.e. singlet and triplet states.

Singlet Triplet

Formation: one of the most common source for the generation of nitrenes involves heating of azides.

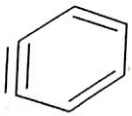
$$RN_3 \xrightarrow{\Delta} R\ddot{\underset{\cdot\cdot}{N}} + N_2$$

Stability: Nitrenes are extremely reactive species and are not isolable under normal reaction conditions. And nitrenes are trapped by its reaction with carbon monoxide to yield an isocyanate.



ARYNES:-

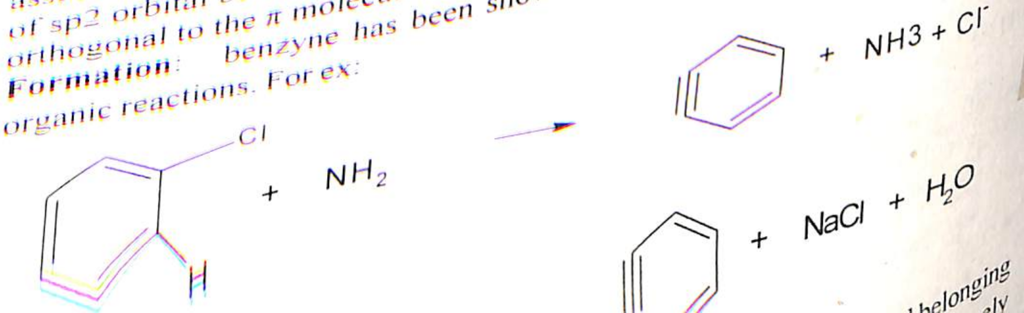
Arynes may be defined as aromatic compounds containing a formal carbon-carbon triple bond. The best known arynes is benzyne. Which may be regarded as the aromatic counter part of acetylene or in the other words, it is benzene minus two ortho hydrogen and it is also called dehydrobenzene.



Benzyne

Benzyne bond is not like the triple bond of acetylene, where the two carbon atom form a σ bond using sp orbits and the remaining p-orbit are used to form π bonds. Such structure is not possible in benzyne because the hexagonal geometry associated with benzene ring. And new bond of benzyne is formed by the overlap of sp2 orbital belonging to two neighbouring carbon atoms. These sp2 orbital are orthogonal to the π molecular orbital of the benzene ring.

Formation: benzyne has been shown to be intermediate in several important organic reactions. For ex:



reactive chemical species.

TYPES OF ORGANIC REACTIONS:-

The reactions of organic compounds can be classified into four main types

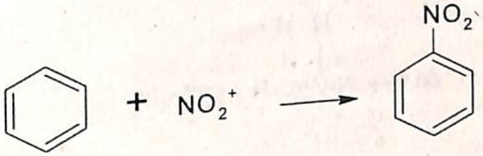
1) Substitution Reaction.
2) Addition Reaction.
3) Elimination Reaction.
4) Rearrangement Reaction.

1) Substitution Reaction: - A substitution reaction is the one in which atom or group of atom in a molecule is replaced by another atom or group of atom. The incoming group becomes attached to the same carbon to which the outing group attached. the substituting species may be either a nucleophile, an electrophile, or free radical.

a) In nucleophilic substitution, a nucleophile brings an electron pair to the substrate and the leaving group departs with an electron pair.

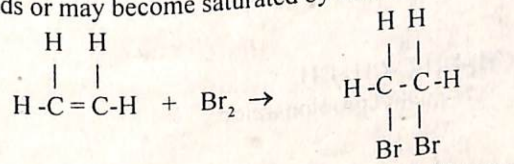
$$Nu:^- + R-X \rightarrow R-Nu + X:^-$$

b) In electrophilic substitution, the attacking species is an electrophile and the leaving group departs without the pair of bonding electrons. This type of reaction occurs mostly in aromatic system where the high electron density attracts electrophiles.



Benzene electrophile Nitro-benzene

Addition Reaction - Addition reaction is those in which atoms or group of atoms are simply added to a double or triple bond without the elimination of any atom or other molecule. In this reaction, at least one (pi) π bond is lost while two new σ-bonds are formed. Double bond becomes saturated, and triple bonds are converted into double bonds or may become saturated by further addition. For example.



$$H-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H + Br_2 \rightarrow H-\underset{Br}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{Br}{\underset{|}{\overset{H}{\overset{|}{C}}}}-H$$

Ethene 1, 2-dibromoethane

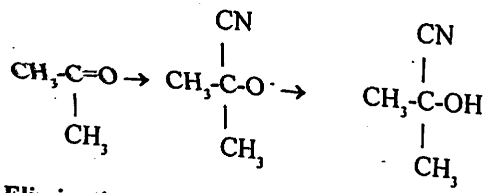
As with substitution reactions, here is also the attacking species may be electrophiles or nucleophiles.

a) In electrophilic addition, a positive species approaches a multiple bonds and at initial step π bond is converted into σ-bond and carbocation is formed. Which combine with nucleophile to form addition product.

$$CH_2{=}CH_2 + H^+ \rightarrow CH_3\text{-}CH_2^+ \xrightarrow{Br^-} CH_3\text{-}CH_2\text{-}Br$$

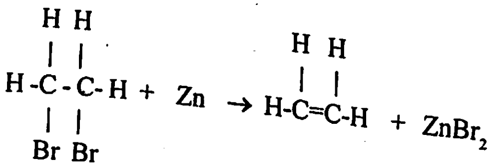
b) In nucleophilic addition, a negative species approaches to a multiple bonds to form carbanion, which combine with positive species.

$HCN \rightarrow H^+ + CN^-$



$$CH_3\text{-}\underset{\displaystyle CH_3}{C}{=}O \rightarrow CH_3\text{-}\overset{\displaystyle CN}{\underset{\displaystyle CH_3}{C}}\text{-}O^- \rightarrow CH_3\text{-}\overset{\displaystyle CN}{\underset{\displaystyle CH_3}{C}}\text{-}OH$$

Elimination Reaction: - an elimination reaction involves removal of atoms or group of atoms from the same molecule. In many such reactions, two atoms or group of atoms are removed from adjacent carbon atoms so that a new multiple bond is formed. Elimination reaction may be regarded as reverse of addition reaction. In this reaction two σ-bonds are lost and one π bond is formed. i. e. sutured compounds becomes unsaturated.

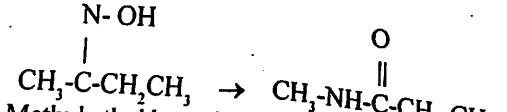


$$H\text{-}\overset{\displaystyle H}{\underset{\displaystyle Br}{C}}\text{-}\overset{\displaystyle H}{\underset{\displaystyle Br}{C}}\text{-}H + Zn \rightarrow H\text{-}\overset{\displaystyle H}{C}{=}\overset{\displaystyle H}{C}\text{-}H + ZnBr_2$$

1, 2-dibromoethane ethene

Rearrangement Reaction :- A rearrangement reaction is one in which an atom or group of atom migrate from one atom to another adjacent carbon atom within the molecule. The product is always the structural isomer of the original compound.

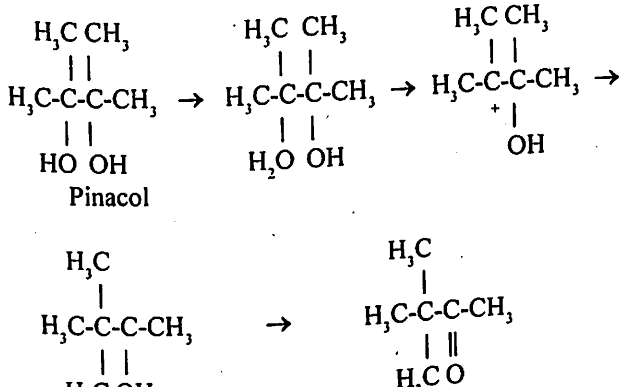
For ex: a)



$$CH_3\text{-}\overset{\displaystyle N\text{-}OH}{C}\text{-}CH_2CH_3 \rightarrow CH_3\text{-}NH\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}CH_2\text{-}CH_3$$

Methyl ethyl ketoxime N-methyl propionamide

b) Pinacol-pinacolone rearrangement reaction:



$$H_3C\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}\text{-}CH_3 \rightarrow H_3C\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle H_2O}{C}}\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}\text{-}CH_3 \rightarrow H_3C\text{-}\overset{\displaystyle CH_3}{\underset{+}{C}}\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}\text{-}CH_3 \rightarrow$$

$$H_3C\text{-}\overset{\displaystyle H_3C}{\underset{\displaystyle H_3C}{C}}\text{-}\underset{\displaystyle OH}{C}\text{-}CH_3 \rightarrow H_3C\text{-}\overset{\displaystyle H_3C}{\underset{\displaystyle H_3C}{C}}\text{-}\underset{\displaystyle O}{\underset{\|}{C}}\text{-}CH_3$$

Pinacol

Pinacolone

◆ ◆ ◆

2.2 ALKENES, DIENES AND ALKYNES

A) ALKENES:-

Alkenes are aliphatic, unsaturated hydrocarbon having one carbon-carbon double bond. They have general formula C_nH_{2n}. They are also called as olefins. Alkenes contain two hydrogen atoms less than alkanes.

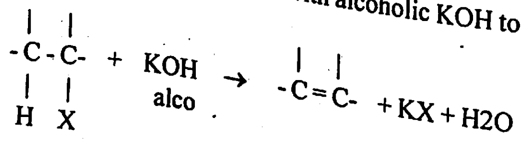
Ethylene is the first member of the series. And they are produced by cracking of petroleum. For ex:

Structure	Name of alkene
$CH_2=CH_2$	ethylene
$CH_3-CH=CH_2$	propylene
$CH_3-CH=CH-CH_3$	2-butene
$CH_3-CH_2-CH=CH_2$	1-butene.

Methods of preparations of alkenes:-

1) Dehydrogenation of alkyl halides:-

Alkyl halides heated with alcoholic KOH to form alkenes.



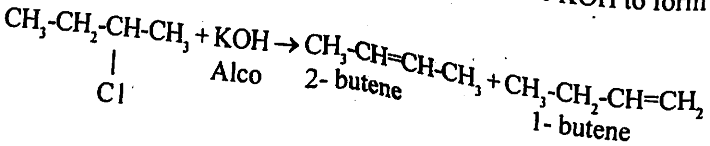
$$\underset{H\ \ X}{-\overset{|\ \ |}{C}-\overset{}{C}-} + \underset{alco}{KOH} \rightarrow -\overset{|\ \ |}{C=C}- + KX + H2O$$

For ex:-

i) When n- butyl chloride heated with alcoholic KOH to form 1- butene

$$CH_3-CH_2-CH_2-CH_2-Cl + \underset{Alco}{KOH} \rightarrow CH_3-CH_2-CH=CH_2 + KCl + H_2O$$

ii) When sec- butyl chloride heated with alcoholic KOH to form a mixture of 2- butene and 1- butene



$$CH_3-CH_2-\underset{Cl}{\underset{|}{CH}}-CH_3 + \underset{Alco}{KOH} \rightarrow \underset{2-\text{butene}}{CH_3-CH=CH-CH_3} + \underset{1-\text{butene}}{CH_3-CH_2-CH=CH_2}$$

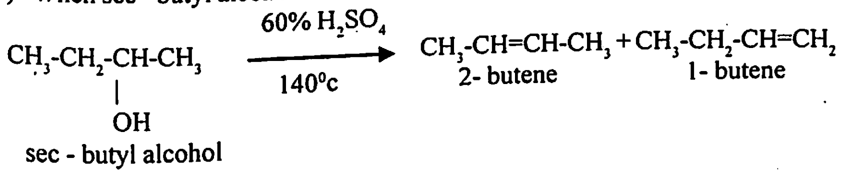
2) Dehydration of alcohol:-

An alcohol is converted into alkenes by dehydration. By eliminating a molecule of water. For ex:-

i) When n- butyl alcohol heated with 75% H_2SO_4 at 140°c to form 2- butane.

$$\underset{n-\text{butyl alcohol}}{CH_3-CH_2-CH_2-CH_2-OH} \xrightarrow[140^oc]{75\%\ H_2SO_4} \underset{2-\text{butene}}{CH_3-CH=CH-CH_3} + H_2O$$

ii) When sec - butyl alcohol heated with 60 % H2SO4 at 100°c to form 2- butane.



$$\underset{\text{sec - butyl alcohol}}{CH_3-CH_2-\underset{OH}{\underset{|}{CH}}-CH_3} \xrightarrow[140^oc]{60\%\ H_2SO_4} \underset{2-\text{butene}}{CH_3-CH=CH-CH_3} + \underset{1-\text{butene}}{CH_3-CH_2-CH=CH_2}$$

Chemical properties of alkenes:-

I]

1) Electrophilic addition of HBr to ethene.

When ethene adds with HBr to form ethyl bromide.

$$\underset{\text{Ethene}}{CH_2=CH_2} + HBr \rightarrow \underset{\text{ethyl bromide}}{CH_3-CH_2-Br}$$

Mechanism:-

i) HBr dissociate as follows

$$HBr \rightarrow H^+ + Br^-$$

ii) Electrophile (H+) combines with ethylene molecule to form carbonium ion.

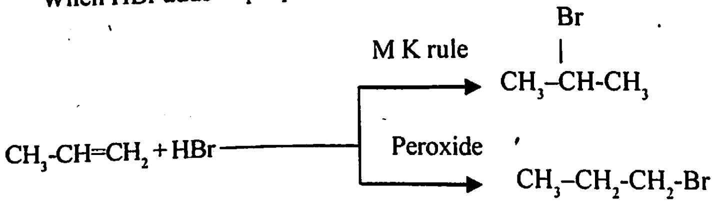
$$\underset{\text{Ethene}}{CH_2=CH_2} \rightarrow CH2^+-CH_2^- + H^+ \rightarrow \underset{\text{ethyl carbonium ion}}{CH_3-CH_2^+}$$

iii) Ethyl carbonium ion combines with Br^- (bromide ion) to form ethyl bromide.

$$\underset{\text{Ethyl carbonium ion}}{CH_3-CH_2^+} + Br^- \rightarrow \underset{\text{ethyl bromide.}}{CH_3-CH_2-Br}$$

2) Electrophilic addition of HBr to propene.

When HBr adds to propene to form n-propyl bromide and isopropyl bromide.



Mechanism :- a) electrophilic addition of HBr to propene.

i) HBr dissociate as follows

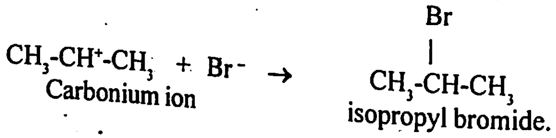
$HBr \rightarrow H^+ + Br^\cdot$

ii) Electrophile (H+) combines with propene molecule to form carbonium ion.

$CH_3\text{-}CH_2\text{=}CH_2 \leftrightarrow CH_3\text{-}CH^+\text{-}CH_2^{\cdot} + H^+ \rightarrow CH_3\text{-}CH^+\text{-}CH_3$

propene carbonium ion

iii) Carbonium ion combines with Br^- (bromide ion) to form isopropyl bromide.



$$\underset{\text{Carbonium ion}}{CH_3\text{-}CH^+\text{-}CH_3} + Br^- \rightarrow \underset{\text{isopropyl bromide.}}{CH_3\text{-}\overset{\overset{Br}{|}}{CH}\text{-}CH_3}$$

3) Free radical addition of HBr to ethene: -

When ethene adds with HBr in the presence of peroxide to form ethyl bromide.

i) Peroxide dissociates to form alkoxy free radical.

$R\text{-}O\text{-}O\text{-}R + \rightarrow 2RO^\cdot$

Alkoxy free radical

ii) Alkoxy free radical combines with HBr to form bromide free radical.

$RO^\cdot + H^\cdot\text{-}Br^\cdot \leftrightarrow R\text{-}OH + Br^\cdot$

Alkoxy free radical

iii) free bromide radical combine with ethylene to form free radical.

$CH_2\text{=}CH_2 \leftrightarrow CH_2^{\cdot}\text{-}CH_2^{\cdot} + Br^\cdot \rightarrow CH_2^{\cdot}\text{-}CH_2\text{-}Br$

Free radical.

iv) Free radical combine with HBr to form ethyl bromide.

$CH_2^{\cdot}\text{-}CH_2\text{-}Br + H^\cdot\text{-}Br^\cdot \rightarrow CH_3\text{-}CH_2\text{-}Br_{\Omega} + Br^\cdot$

Free radical.

v) $Br^\cdot + Br^\cdot \rightarrow Br_2$

4) Free radical addition of HBr to propene: -

When propene adds with bromine in the presence of inert solvent (carbon tetra chloride) to form 1-bromo propane.

i) Peroxide dissociates to form alkoxy free radical.

$R\text{-}O\text{-}O\text{-}R + \rightarrow 2RO^\cdot$

Alkoxy free radical

ii) Alkoxy free radical combine with HBr to form bromide free radical.

$RO^\cdot + H^\cdot\text{-}Br^\cdot \rightarrow R\text{-}OH + Br^\cdot$

Alkoxy free radical (ii)

iii) free bromide radical combine with ethylene to form free ethyl radical.

$CH_3\text{-}CH\text{=}CH_2 \leftrightarrow CH_3\text{-}CH^\cdot\text{-}CH_2^{\cdot} + Br^\cdot \rightarrow CH_3\text{-}CH^\cdot\text{-}CH_2\text{-}Br$

(ii) free radical. (iii)

iv) Free radical combines with HBr to form 1-bromo propane

$CH_3\text{-}CH^\cdot\text{-}CH_2\text{-}Br + H^\cdot\text{-}Br^\cdot \rightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}Br + Br^\cdot$

Free radical. (iii)

V) $Br^\cdot + Br^\cdot \rightarrow Br_2$

[II] **Electrophilic addition of Br_2 to ethene.**

When ethene adds with Br_2 to form 1,2-dibromoethane.

$CH_2\text{=}CH_2 + Br_2 \rightarrow Br\text{-}CH_2\text{-}CH_2\text{-}Br$

Ethene 1, 2-dibromoethane

Mechanism:-

i) Br_2 dissociate as follows

$Br_2 \rightarrow Br^+ + Br^-$

ii) electrophile (H+) combine with ethylene molecule to form carbonium ion.

$CH_2\text{=}CH_2 \leftrightarrow CH_2^{+}\text{-}CH_2^{\cdot} + Br^+ \rightarrow Br\text{-}CH_2\text{-}CH_2^+$

Ethene carbonium ion

iii) Carbonium ion combines with Br^- (bromide ion) to form ethyl bromide.

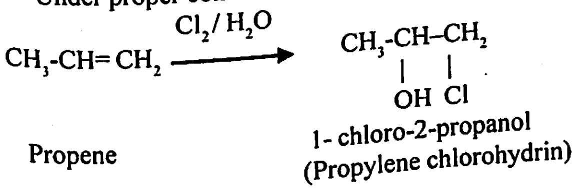
$Br\text{-}CH_2\text{-}CH_2^+ + Br^- \rightarrow Br\text{-}CH_2\text{-}CH_2\text{-}Br$

Carbonium ion 1, 2-dibromoethane

III) Halohydrin formation reaction (reaction of propene with Cl_2/H_2O):-

Addition of chlorine in the presence of water can yield compounds containing halogen and hydroxyl group on the adjacent carbon atom. These compounds are thus chloro-alcohols. They are commonly called as halohydrins. (Chlorohydrins)

Under proper conditions they can produce major product.



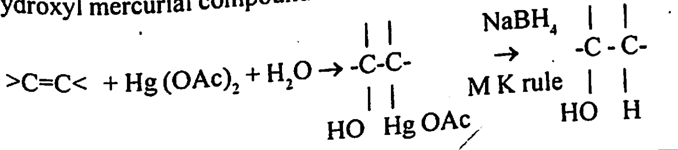
$$\underset{\text{Propene}}{CH_3\text{-}CH\text{=}CH_2} \xrightarrow{Cl_2/H_2O} CH_3\text{-}\underset{OH}{\underset{|}{CH}}\text{-}\underset{Cl}{\underset{|}{CH_2}}$$

1- chloro-2-propanol

(Propylene chlorohydrin)

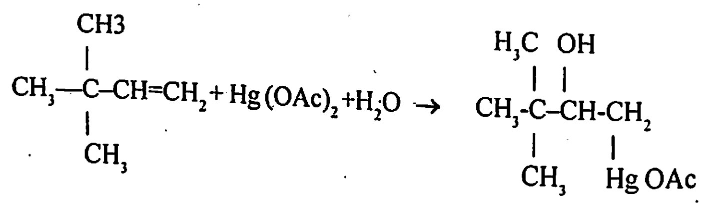
IV) Oxymercuration- demercuration:-

Alkenes react with mercuric acetate in the presence of water to give hydroxyl mercurial compounds which on reduction yield alcohols.



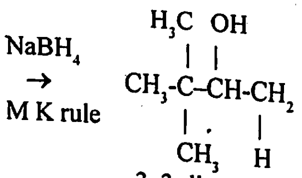
$$>C\text{=}C< + Hg(OAc)_2 + H_2O \rightarrow \underset{HO}{\overset{|}{\underset{|}{\text{-}C}}}\underset{Hg\,OAc}{\overset{|}{\underset{|}{\text{-}C\text{-}}}} \xrightarrow[\text{M K rule}]{NaBH_4} \underset{HO}{\overset{|}{\underset{|}{\text{-}C}}}\underset{H}{\overset{|}{\underset{|}{\text{-}C\text{-}}}}$$

3, 3-dimethyl-1-butene reacts with mercuric acetate in the presence of water to give hydroxyl mercurial compounds which on reduction yield 3, 3-dimethyl-2-butanol.



$$CH_3-\underset{CH_3}{\overset{CH3}{C}}-CH=CH_2 + Hg(OAc)_2 + H_2O \rightarrow CH_3\text{-}\underset{CH_3}{\overset{H_3C}{C}}\text{-}\overset{OH}{CH}\text{-}\underset{Hg\,OAc}{CH_2}$$

3, 3-dimethyl-1-butene



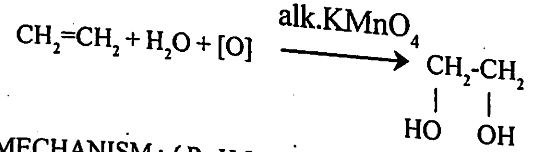
$$\xrightarrow[\text{M K rule}]{NaBH_4} CH_3\text{-}\underset{CH_3}{\overset{H_3C}{C}}\text{-}\overset{OH}{CH}\text{-}\underset{H}{CH_2}$$

3, 3-dimethyl-2-butanol.

v) Cis-Hydroxylation using alkaline $KMnO_4$:-

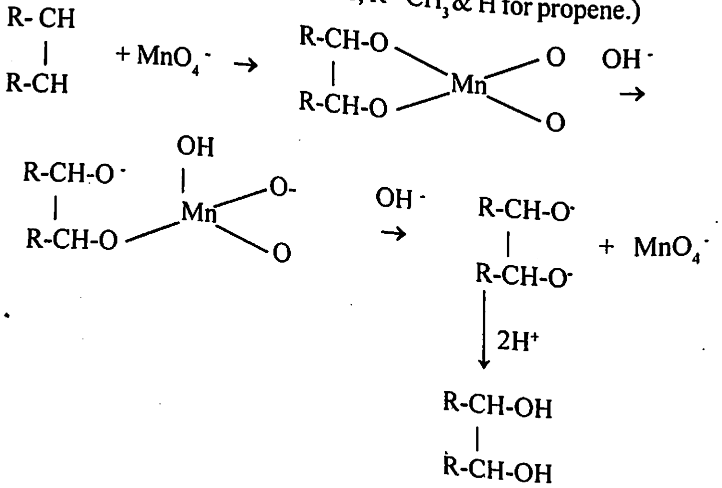
Alkene on treatment with dil alkaline $KMnO_4$ solution readily gets hydroxylated and gives Cis-glycol.

For ex: when ethylene treated with dil alkaline $KMnO_4$ solution to form cis-1, 2-ethylene glycol.



$$CH_2=CH_2 + H_2O + [O] \xrightarrow{alk.KMnO_4} \underset{HO}{CH_2}\text{-}\underset{OH}{CH_2}$$

MECHANISM :-(R=H for ethane, R= CH_3 & H for propene.)



$$\begin{matrix}R\text{-}CH\\ |\\ R\text{-}CH\end{matrix} + MnO_4^- \rightarrow \begin{matrix}R\text{-}CH\text{-}O\\ |\\ R\text{-}CH\text{-}O\end{matrix}>Mn<\begin{matrix}O\\ \\ O\end{matrix} \xrightarrow{OH^-}$$

$$\begin{matrix}R\text{-}CH\text{-}O^-\\ |\\ R\text{-}CH\text{-}O\end{matrix}-\overset{OH}{Mn}<\begin{matrix}O^-\\ \\ O\end{matrix} \rightarrow \begin{matrix}R\text{-}CH\text{-}O^-\\ |\\ R\text{-}CH\text{-}O^-\end{matrix} + MnO_4^- \xrightarrow{2H^+} \begin{matrix}R\text{-}CH\text{-}OH\\ |\\ R\text{-}CH\text{-}OH\end{matrix}$$

Cis-1, 2-glycol.

B) DIENES

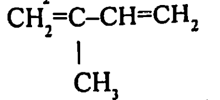
Introduction:-Dienes are unsaturated hydrocarbons; they containing two carbon-carbon double bonds are called dienes or alkadienes. They having general formula

C_nH_{2n-2}. They are also called as diolefins.

Another important member of this series is isoprene or 2-methyl butadiene.

For ex:-

i) $CH_2=CH-CH=CH_2$ 1, 3-butadiene



ii) $CH_2=\underset{CH_3}{C}-CH=CH_2$ 2-methyl, 1, 3-butadiene

iii) $CH_3-CH_2-CH=CH-CH=CH_2$ 1, 3- hexadiene

iv) $CH_3-CH=CH-CH=CH_2$ 1, 3- pentadiene

Classification:-Dienes are classifieds as follows.

i) **Isolated dienes:**-In which double bonds are separated by more than one single bonds or in which the position of double bond is not specific.

For ex; $CH_2=CH-CH_2-CH=CH_2$ 1, 4- pentadiene

$CH_2=CH-CH_2-CH_2-CH=CH_2$ 1, 5- Hexadiene

ii) **Conjugated dienes:**-In which double bonds are separated by one single bonds or alternate double or single bonds are present in the molecule.

For ex;- $CH_2=CH-CH=CH_2$ 1,3-butadiene

$CH_3-CH=CH-CH=CH_2$ 1, 3- pentadiene

$CH_3-CH_2-CH=CH-CH=CH_2$ 1, 3- hexadiene

iii) **Comulated dienes** - If the double bonds are adjacent to each other or two double bonds are attached to same carbon atom.

For ex:- $CH_2=C=CH_2$ 1,3-propadiene

$CH_3-CH=C=CH-CH_3$ 2, 3- pentadiene

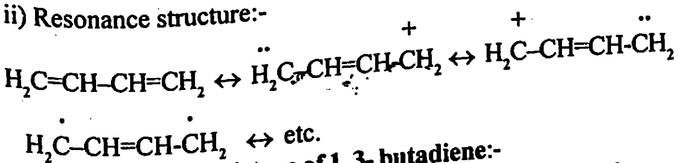
Resonance structure and Molecular orbital structure of 1, 3-butadiene

Resonance structure: -

i) Bond length: C-C bond length in 1, 3 butadiene is 1.48 A^0

And C=C bond length is 1.37 A^0.

ii) Resonance structure:-

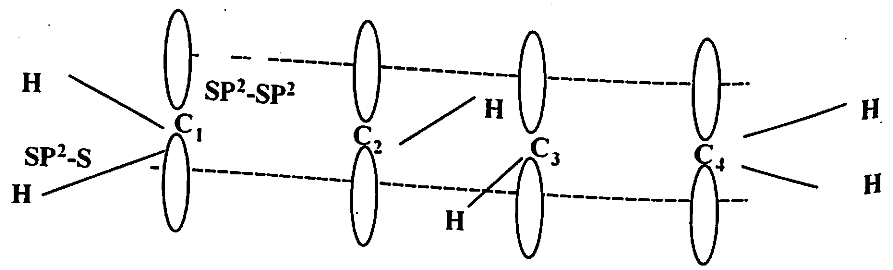


$$H_2C=CH-CH=CH_2 \leftrightarrow H_2\ddot{C}-CH=CH-\overset{+}{C}H_2 \leftrightarrow H_2\overset{+}{C}-CH=CH-\ddot{C}H_2$$

$$H_2\dot{C}-CH=CH-\dot{C}H_2 \leftrightarrow \text{etc.}$$

Molecular Orbital picture of 1, 3- butadiene:-

In 1,3 butadiene all carbon atoms are in SP^2 hybridised state, sp2-hybrid orbital of each carbon atom overlap with sp^2-hybrid orbital of another carbon atom to form a σ bond between carbon-carbon by sp^2-sp^2 Overlap. Similarly sp^2-hybrid orbital of each carbon can overlap with 1s-orbital of hydrogen atom to form σ bond between carbon-hydrogen by sp^2-S Overlap. And all these carbon atoms and hydrogen atoms lie in one plane.



(Orbital Picture of 1,3-butadiene)

Also each carbon atom containing unhybridised 2Pz orbital, which are perpendicular to the plane of σ bond

2Pz orbital of C_2 carbon can overlap with 2Pz orbital of C_1 or C_3. Similarly 2Pz orbital of C_3 carbon can overlap with 2Pz orbital of C_2 or C_4. i.e. all four 2Pz orbital overlap to form a large π molecular orbital and each pair of electrons thus attracted by all four carbon atoms.

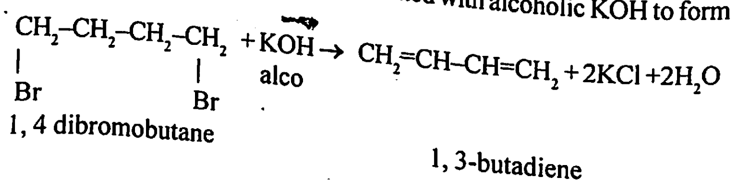
The overlap of 2Pz orbital of C_2 and C_3 in both direction and due to these π electrons to be spread over a large area referred to as delocalization and due to this delocalization of π electrons 1, 3-butadiene becomes stable.

Methods of preparations of 1, 3-butadiene:-

1) From 1, 4 dibromobutane:-

When 1, 4 dibromobutane heated with alcoholic KOH dehydrohalogenation takes place. i. e. hydrogen and halogen from adjacent carbon are removed and form 1, 3-butadiene.

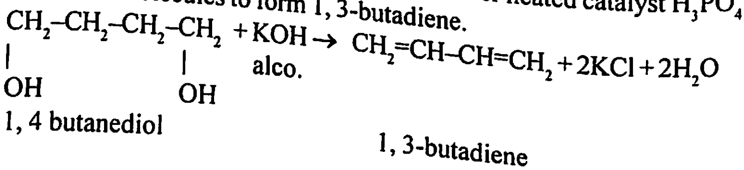
For ex:- when 1,4-dibromobutane heated with alcoholic KOH to form 1,3-butadiene.



$$\underset{\text{1, 4 dibromobutane}}{\underset{Br}{CH_2}-CH_2-CH_2-\underset{Br}{CH_2}} + \underset{\text{alco}}{KOH} \rightarrow \underset{\text{1, 3-butadiene}}{CH_2=CH-CH=CH_2} + 2KCl + 2H_2O$$

2) From 1, 4 butanediol:-

When 1, 4 butanediol passed over heated catalyst H_3PO_4, it eliminates two water molecules to form 1, 3-butadiene.

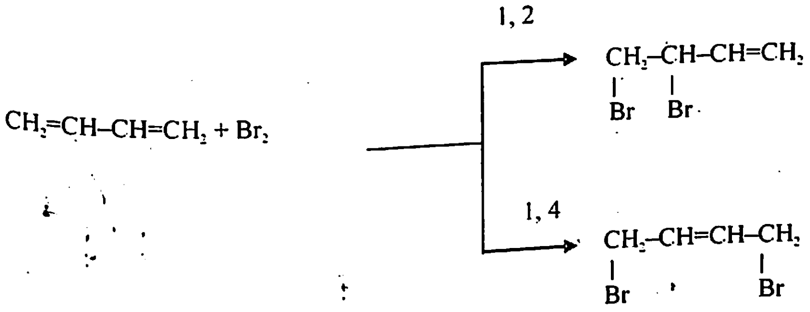


$$\underset{\text{1, 4 butanediol}}{\underset{OH}{CH_2}-CH_2-CH_2-\underset{OH}{CH_2}} + \underset{\text{alco.}}{KOH} \rightarrow \underset{\text{1, 3-butadiene}}{CH_2=CH-CH=CH_2} + 2KCl + 2H_2O$$

Chemical reaction of 1, 3 Butadiene:-

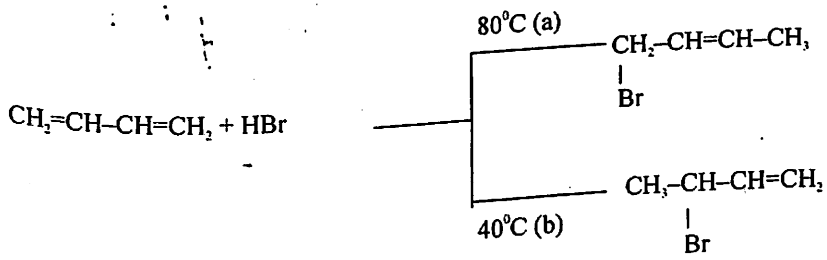
i) 1, 2 and 1,4 addition of Br2 :-

when 1,3 butadiene reacts with halogen in the presence of inert solvent CCl_4 to give a mixture of (a) 3,4-dibromo-1-butene by 1,2 addition and (b) 1,4-dibromo-2-butene by 1,4-addition



ii) 1, 2 and 1, 4 addition of HBr:-

when 1,3 butadiene reacts with HBr to form a mixture of (a) 1-bromo-2-butene by 1,4 addition (b) 3-bromo-1-butene by 1,2 addition.



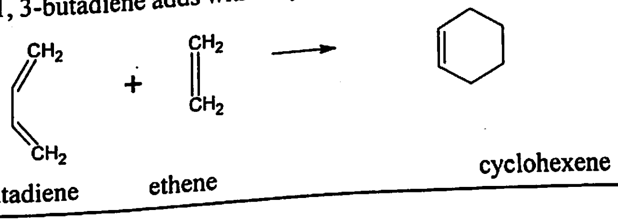
iii) Diel's Alder reaction:-[4+2 cycloaddition]

i) Conjugated dienes adds to alkenes by 1, 4 additions to form a cyclic compound, this reaction is called Diel's Alder reaction.

ii) In this reaction, alkenes or alkynes are called donophiles and obtained product is called adduct.

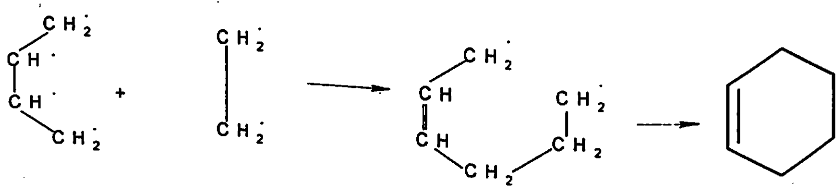
iii) This reaction does not require any catalyst, and yield six members ring compound.

For ex:-when 1, 3-butadiene adds with ethylene to form cyclohexene.

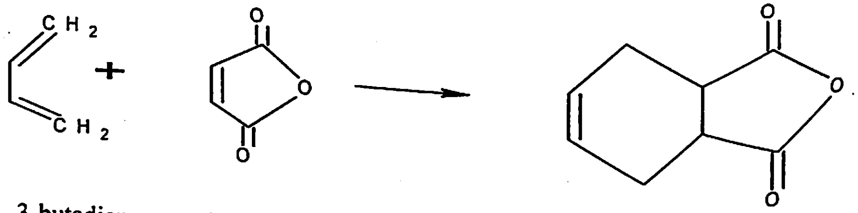


Mechanism:-

Diel's Alder reaction does not involve ionic or free radical intermediate.



For ex:- when 1,3-butadiene adds with maleic anhydride to form adduct.



1, 3-butadiene maleic anhydride tetrahydro-2-benzofuran-1,3-dione

ALKYNES

Introduction:- Alkynes are aliphatic unsaturated hydrocarbons having one Carbon-carbon triple bond. They having general formula C_nH_{2n-2}. Alkynes contain four hydrogen atoms less than alkanes. And two hydrogen atom less than alkenes.

The simplest and most important member of this series is acetylene $CH \equiv CH$ and carbon-carbon triple bond is called acetylene.

For ex:-

$H-C\equiv C-H$	acetylene.
$CH_3-C\equiv C-H$	methyl acetylene
$CH_3-C\equiv C-CH_3$	dimethyl acetylene

Methods of preparations of alkynes (acetylene):-

1) From Iodoform:-

When two molecules of iodoform heated with silver powder to form acetylene and silver iodide.

$$CHI_3 + 6Ag + I_3CH \rightarrow H-C\equiv C-H + 6Ag-I$$

2) From Methane:-

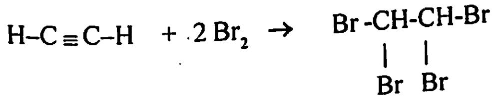
Acetylene is prepared by the controlled, high–temperature partial oxidation of methane.

$$6CH_4 + O_2 \rightarrow 2H-C\equiv C-H + 2CO + 10H_2$$

Chemical reactions of Acetylene (with mechanism)

1) Electrophilic addition of Br_2 to ethyne (acetylene):-

When acetylene adds with liquid bromine, it gives 1, 1, 2, 2-tetrabromo ethane.



$$H-C\equiv C-H + 2Br_2 \rightarrow Br-\underset{\displaystyle Br}{\underset{|}{CH}}-\underset{\displaystyle Br}{\underset{|}{CH}}-Br$$

Acetylene liquid bromine 1, 1, 2, 2-tetrabromo ethane

Mechanism:-

i) Br_2 dissociate as follows

$$Br_2 \rightarrow Br—Br \rightarrow Br^+ + Br^-$$

ii) Br^+ (bromonium ion) combines with acetylene to molecule to form carbonium ion.

$$H-C\equiv C-H \rightarrow CH^+=CH^- + Br^+ \rightarrow Br-CH=CH^+$$

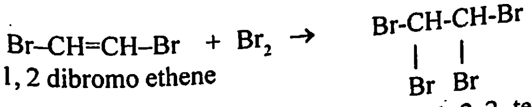
ethyne carbonium ion

iii) Carbonium ion combine with Br^- (bromide ion) to form 1,2 dibromo ethene.

$$Br-CH-CH^+ + Br^- \rightarrow Br-CH=CH-Br$$

carbonium ion 1,2 dibromo ethene

iv) 1 , 2 dibromo ethene combine with second molecule of Br2 to form 1, 1, 2, 2- tetrabromo ethane.



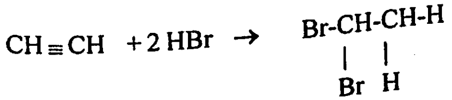
$$Br-CH=CH-Br + Br_2 \rightarrow Br-\underset{\displaystyle Br}{\underset{|}{CH}}-\underset{\displaystyle Br}{\underset{|}{CH}}-Br$$

1, 2 dibromo ethene 1, 1, 2, 2- tetrabromo ethane

2) Electrophilic addition of HBr to ethyne;-

In symmetrical alkynes addition of halogen acid takes place in two stages. In which second molecule of halogen acid add according to M.K rule i.e. both halogen atoms adds to the same carbon atom. (Markownikov rule = M.K rule)

For ex: When acetylene adds with HBr, it gives 1, 1-dibromo ethane.



$$CH\equiv CH + 2HBr \rightarrow Br-\underset{\displaystyle Br}{\underset{|}{CH}}-\underset{\displaystyle H}{\underset{|}{CH}}-H$$

1, 1-dibromo ethane

Mechanism:-

i) HBr dissociate as follows

$$HBr \rightarrow H^+ + Br^-$$

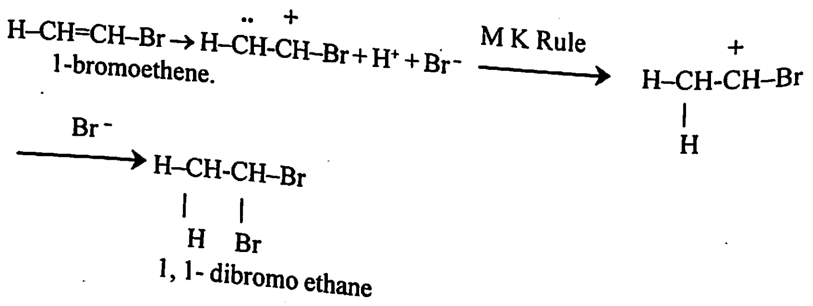
ii) H^+ combines with acetylene to molecule to form carbonium ion.

$$\underset{\text{ethyne}}{H{-}C\equiv C{-}H} \rightarrow CH^+{=}CH_2^{\cdot} + H^+ \rightarrow \underset{\text{carbonium ion}}{H{-}CH_2{=}CH_2^+}$$

iii) Carbonium ion combines with Br^- (bromide ion) to form 1-bromo ethene.

$$\underset{\text{carbonium ion}}{H{-}CH_2{=}CH_2^+} + Br^- \rightarrow \underset{\text{1-bromo ethene.}}{H{-}CH{=}CH{-}Br}$$

iv) 1-bromo ethene combines with second molecule of HBr to form 1, 1- dibromo ethane (addition of HBr takes place according to M.K.rule)



$$\underset{\text{1-bromoethene.}}{H{-}CH{=}CH{-}Br} \rightarrow H{-}\overset{\cdot\cdot}{C}H{-}\overset{+}{C}H{-}Br + H^+ + Br^- \xrightarrow{\text{M K Rule}} H{-}\underset{\displaystyle H}{\underset{|}{C}H}{-}\overset{+}{C}H{-}Br$$

$$\xrightarrow{Br^-} \underset{\text{1, 1- dibromo ethane}}{H{-}\underset{\displaystyle H}{\underset{|}{C}H}{-}\underset{\displaystyle Br}{\underset{|}{C}H}{-}Br}$$

3) Free radical addition of HBr to ethyne: -

When ethyne adds with HBr in the presence of inert solvent (carbon tetra chloride) to form 1, 2-bromo ethane.

i) Peroxide dissociates to form alkoxy free radical.

$$R{-}O{-}O{-}R + \rightarrow \underset{\text{Alkoxy free radical}}{2\,RO^{\cdot}}$$

ii) Alkoxy free radical combines with HBr to form bromide free radical.

$$\underset{\text{Alkoxy free radical}}{RO^{\cdot}} + H^{\cdot}{-}Br^{\cdot} \rightarrow R{-}OH + \underset{\text{(ii)}}{Br^{\cdot}}$$

iii) Free bromide radical combine with ethylene to form free ethyl radical.

$$CH\equiv CH \rightarrow CH^{\cdot}{=}CH^{\cdot} + Br^{\cdot} \rightarrow \underset{\text{free radical. (iii)}}{CH^{\cdot}{=}CH{-}Br}$$

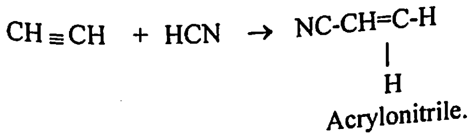
iv) Free radical combine with $H^{\cdot}$ to form 1-bromo ethane.

$$\underset{\text{free radical. (iii)}}{CH^{\cdot}{=}CH{-}Br} + H^{\cdot} \rightarrow \underset{\text{vinyl bromide}}{CH_2{=}CH{-}Br} + Br^{\cdot}$$

V) $CH_2{=}CH{-}Br + H^{\cdot}{-}Br^{\cdot} \rightarrow \underset{\text{1, 2-bromo ethane}}{Br{-}CH_2{-}CH_2{-}Br}$

4) Nucleophilic substitution reaction of Acetic acid and hydrocyanic acid:-

i) Addition of HCN: - Alkynes adds to hydrocyanic acid in the presence of barium cyanide catalyst it gives acrylonitrile.



$$CH\equiv CH + HCN \rightarrow \underset{\text{Acrylonitrile.}}{NC{-}CH{=}\underset{\displaystyle H}{\underset{|}{C}}{-}H}$$

Mechanism:-

i) HCN dissociates as follows

$$HCN \rightarrow H^+ + CN^-$$

ii) Cyanide ion (CN^-) combine with ethyne to form vinyl carbanion

$$\underset{\text{Ethyne}}{CH\equiv CH} \rightarrow \overset{+}{C}H{=}\overset{\cdot\cdot}{C}H + CN^- \rightarrow \underset{\text{vinyl carbanion}}{NC{-}CH{=}\overset{\cdot\cdot}{C}H}$$

iii) Vinyl carbanion combines with (H^+) proton to form acrylonitrile.

$$NC{-}CH{=}\overset{\cdot\cdot}{C}H + H^+ \rightarrow \underset{\text{Acrylonitrile}}{NC{-}CH{=}CH_2}$$

ii) Addition of CH_3COOH;-

Alkynes add to acetic acid in the presence of mercurous cyanide catalyst it gives first vinyl acetate and then Ethylidine acetate.

$$\underset{\text{Ethyne}}{CH\equiv CH} + \underset{\text{acetic acid}}{2\,CH_3COOH} \rightarrow \underset{\text{Ethylidine acetate}}{(H_3COCO)_2\,CH{-}CH_3}$$

Mechanism:-

i) CH_3COOH dissociates as follows

$$CH_3COOH \rightarrow H^+ + CH_3{-}COO^-$$

ii) Acetate ion combines with acetylene molecule to form vinyl carbanion

$$\underset{\text{Ethyne}}{CH \equiv CH} \rightarrow \overset{+}{C}H=\overset{..}{C}H + CH_3\text{-}COO^- \rightarrow \underset{\text{vinyl carbanion}}{\overset{..}{C}H=CH\,(OCOCH_3)}$$

iii) Vinyl carbanion combines with (H^+) proton to form vinyl acetate.

$$\underset{\text{vinyl carbanion}}{\overset{..}{C}H=CHOCOCH_3} + H^+ \rightarrow \underset{\text{vinyl acetate}}{CH_2=CH\,(OCOCH_3\,)}$$

iv) Vinyl acetate combines with second molecule of acetic acid to form ethylidine acetate. [Addition of second molecule of acetic acid takes place according to M.K.rule]

$$\underset{\text{vinyl acetate}}{CH_2=CH\,(OCOCH_3)} + CH_3COOH \rightarrow \underset{\text{ethylidine acetate}}{CH_3\text{-}CH\,(OCOCH_3)_2}$$

❖❖❖

UNIT - [III]

3.1 **Aromatic Compounds**

1.2 **Phenols**

3.1 AROMATIC COMPOUNDS

1) **Introduction, Industrial source of aromatic compounds.**

The term aromatic compounds were first used by Kekule to classify benzene and its derivatives. Many of which possessed fragrant odour or aroma.

Now the term aromatic compounds stands for the whole series of compounds which contain one or more benzene rings in their molecules. with the introduction of arenes for all aromatic compounds (Benzene Naphthalene, Anthracene.) a precise definition of aromatic compounds may be given as arenes and their derivatives.

2) **Industrial source of aromatic compounds:-**

The parent compound, benzene, was first discovered by Faraday in 1825from the gas obtained by the pyrolysis of whale oil. Later in1845, Hofmann discovered benzene in coal-tar which constitutes a major source of benzene with and its derivatives even to date. Petroleum is another important source of aromatic compounds. The alkane fraction of petroleum is being used for the manufacture of aromatic compounds.

Distillation of Coal; - On heating to 1000-1300, in absence of air, coal is converted into coke a useful fuel for smelting of iron and steel. In addition to coke, the following three fractions are obtained.

i) **Coal gas**:-It is a mixture of methane and hydrogen and is used as a fuel as well as for illumination purpose.

ii) **Coal-tar**:-It is a mixture of aromatic hydrocarbons (benzene, naphthalene, anthracene, toluene, xylene, etc.) their oxygenated derivatives (phenols) and some heterocyclic compounds such as pyridine, and quinoline.

iii) **Ammonical liquor**:-It is the aques layer containing ammonia. On distillation of coal tar, first fraction coming up to 110°c. Is known as 90% benzol (70% benzene, 24% toluene, and some xylene) careful fraction of 90% benzol gives benzene, toluene, and xylene. Further separation of xylene is difficult.

The second fraction collected between 110-140°c is called 90% toluol and consist of xylene and small amounts of benzene and toluene.

The third fraction is collected between 140-170°c and mainly consist of xylene and cumene, it is used as solvent for varnishes and paints.

The fourth fraction, consist of heavy naphtha it will be distilled between 170-200°C. And it is used as a solvent or is mixed with middle oil .naphthalene crystallizes

out from the middle oil fraction. On cooling middle oil fraction consist of naphthalene, phenol, cresol, and xylenols.

Heavy oil fraction consists of naphthols and quinoline, from anthracene oil on cooling gives anthracene oil, Phenanthrene and carbazol.

Structure of benzene:-

Molecular formula;-from elemental analysis molecular weight determination, the molecular formula of benzene has been found to be C_6H_6. Since carbon to hydrogen ratio in this compound is much less than corresponding alkanes C_6H_{14}. There fore benzene is expected to be highly unsaturated, i.e. it under goes addition reaction likes alkene, and alkynes. And following reactions shows presence of double bonds and a six membered. Carbo cyclic ring

1) it adds with six halogen atoms to form benzene hexachloride

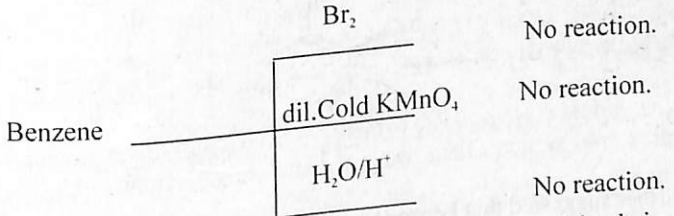
$C_6H_6 + 3X2 \rightarrow C_6H_6X_6$.

2) it can be hydrogenated catalitically, by adding a maximum of six hydrogen atoms to produce cyclohexane.

$C_6H_6 + 3H2 \rightarrow C_6H_{12}$.

Straight chain structure is not possible

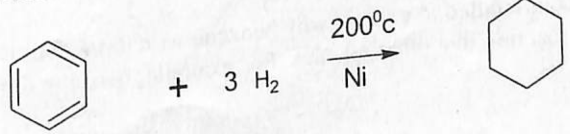
Benzene could be constructed as a straight chain or ring compound having double (C=C) or triple (C ≡ C) bonds but benzene did not behave like alkenes or alkynes. It does not delocalize bromine in carbon tetrachloride or cold aq. Potassium permanganate. Also it did not add water in the presence of acids.



From the above reaction it is clear that, it does not having straight chain structure.

Evidence of cyclic structure: - .

a) Benzene adds with hydrogen in the presence of catalyst Ni, Pt/ pd: At 200°, it gives cyclohexane.



b) Substitution reaction of benzene:-

Benzene reacts with bromine in the presence of $FeBr_3$ (catalyst) to form mono bromobenzene.

$$C_6H_6 + Br_2 \xrightarrow{FeBr_3} C_6H_5\text{-}Br + HBr$$

In which only-one mono bromine is formed but not isomeric product are formed. Which indicate that all six hydrogen atoms in benzene were indicated. This could be possible only, if benzene had a cyclic structure of six carbon and each carbon attached to one hydrogen.

Kekule structure of benzene:-

In 1865, August Kekule suggested that structure of benzene.

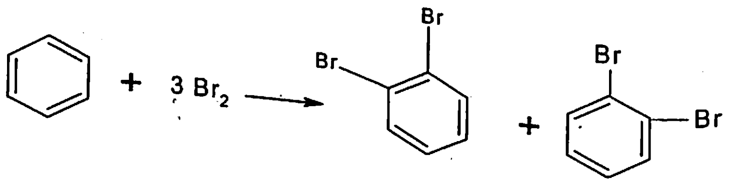
1) Benzene consist of a cyclic planner structure, it contains six carbon atoms and six hydrogen atoms [M..F C_6H_6]

2) All six carbon atoms are joined by a single covalent bond to one another, to form flat or hexagonal ring.

3) each carbon atom of ring is joined by a single covalent bond with hydrogen atom.

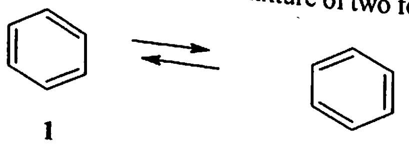
4) To account for tetravalency of carbon, double bonds are placed alternately.

5) There are two objections (a) If Kekule structure was correct their should be two isomers of dibromo benzene. In one isomer, the two bromine atoms should be on carbons that are connected by double bond, as shown in structure (1). in structure (2)bromine should be on carbon connected by a single bond. In fact only-one ortho dibromo benzene could be prepared.



1 2

Kekule further suggested that benzene was a mixture of two form (1) and (2).



1 2

6) Kekule structure failed to explain why benzene with three double bonds did not give addition reaction like other alkenes. For example, benzene did not react with HBr or Br_2 in CCl_4.

Carbon- carbon bond length in benzene:-

In benzene 1) carbon-carbon single bond length = 1.54 A°

2) carbon-carbon double bond length = 1.34 A°

3) Benzene having the bond angle = 120°c

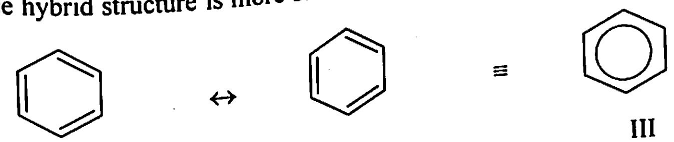
RESONANCE STRUCTURE OF BENZENE

Whenever a molecule can be represented by two or more structures that differ only in the arrangement of electrons-that is by structures, that have the same arrangement of atomic nuclei-there is resonance.

When these contributing structures are of about the same stability, then resonance is important.

The phenomenon in which two or more structures can be written for a molecule, which involve identical positions of atom. But two structures differs only in the position of atoms, is called resonance.

The actual structure of the molecule is said to be a resonance hybrid. The resonance hybrid structure is more stable than any of the contributing structures.



I , II III

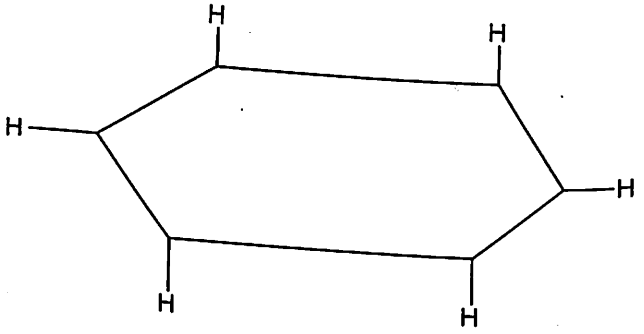
Resonance structure of benzene resonance hybrid structure

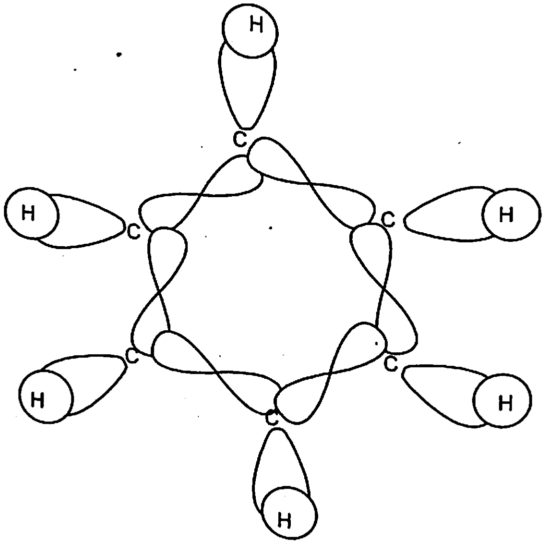
Out of the two structures of benzene (I and II) none represent the actual structure. All the carbon-carbon bond distances in benzene are equal (1.39) and thus there can not be 3- single bonds (c-c, 1.48) and (c=c, 1.34) as is the case with either structure (I and II).thus in benzene pi- electrons (double bonds) are delocalized and actual structure is the resonance hybrid structure (III) the the circle inside the ring showing delocalized pi- electrons, i.e a cyclic sextet of delocalized pi- electrons.

Resonance involve only the movement of electron never atoms, and double headed arrow indicates resonance phenomenon, while pair of arrow indicates equilibrium.

Molecular orbital picture of benzene:-

In benzene all six carbon atoms are in sp2 hybridized state, sp2 hybrid orbital of each carbon can overlap with sp2 hybrid orbital of another carbon atom to form a σ bond between two carbon atoms by sp2-sp2 overlap.

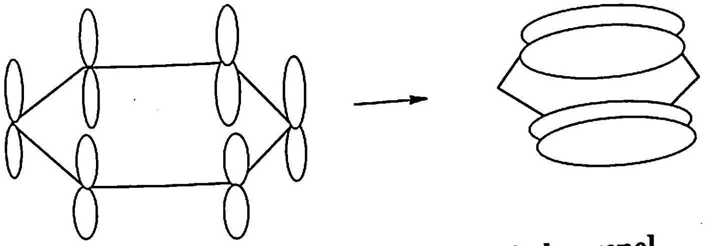




[Formation of σ bonds in benzene is as shown in fig]

Similarly, sp2 hybrid orbital of each carbon can overlap with half filled 1s orbital of hydrogen atom to form an σ bond between carbon and hydrogen atom by sp2-s overlap.

Since all σ bonds formed by the overlap of sp2 orbital of all carbon atoms and hydrogen atoms in benzene lie in one plane and C-C-H bond angle is 120°. Also, each carbon in benzene possesses one unhybridised 2Pz orbital containing one electron to each and these 2Pz orbital are perpendicular to the plane of σ bonds. These 2Pz orbital laterally overlap and produces a π (bond) molecular orbital lies above and below the plane of the σ bonds (ring).



[Formation of π molecular orbital in benzene]

These six electrons of p-orbital cover six carbon atoms and are said to be delocalized, due to delocalization a stronger π bond is formed and becomes more stable.

MODERN THEORY OF AROMATICITY : -

- An aromatic compound is a flat or planner, having alternate double bond And single bonds in cyclic structures and resembles benzene in a chemical behavior, also they under go substitution reaction than addition reaction. For this characteristic behavior is called Aromaticity or aromatic character.

Aromaticity is, in fact, a property of the sp2 hybridized planner ring in which the p-orbital (one in each atom) allow cyclic delocalization of π electrons.

Criteria for Aromaticity:-

The following criteria help to knowing whether a particular compound is aromatic or non-aromatic.

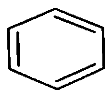
i) An aromatic compound is cyclic and planner.

ii) Each atom in an aromatic ring has p-orbital. These p-orbital must be parallel so that a continuous overlap is possible around the ring.

iii) the cyclic π molecular orbital (electron cloud) formed by overlap of p-orbital must contain (4n+2) π electrons.

Where n is whole integer, 1, 2, 3, 4……and this is known as Huckel rule.

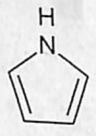
For ex : i) Benzene is a cyclic and planner compound, it contains six π electrons.



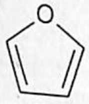
$4n + 2 = 6$

$4n = 4$, $n = 1$.

ii) Heterocyclic compounds also behave as aromatic compound; they obey the aromatic rule (Huckel rule).

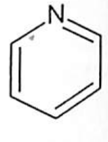


Pyrrole



Furan

Thiophene



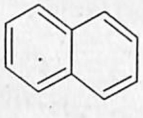
Pyridine

Each contains six electrons i.e. n = 1, there fore these are aromatic compounds.

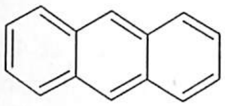
iii) Naphthalene and Anthracene

They contains 10 and 14 π electrons n = 2 for naphthalene.

n = 3 for anthracene.



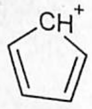
Naphthalene



Anthracene

iv) cyclopenta-2, 4-dienylium:

it contain five π electrons there fore n = not whole integer i.e. 1,2,3,...etc.

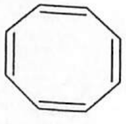


v) Cyclopentadienyl anion:-

it contain six π electrons there fore n = 1 , there fore it is aromatic compound .

Annulene:-The name Annulene has been proposed as a general name for monocyclic compounds having alternate double bond and single bond. The ring size of an annulene is indicated by a number in bracket. Thus benzene is [6] annulene. And cyclo-octatetrane is [8] annulene.

Benzene
[6] annulene



cyclo-octatetrane
[8] annulene

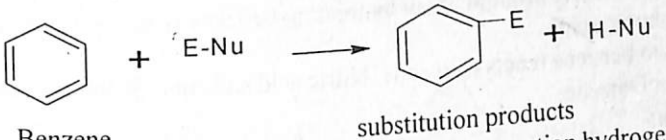
Chemical reactions of benzene:-

The principal type of reactions of benzene is

i) Electrophilic substitution reaction.
ii) Addition reaction.
iii) Oxidation reaction

Electrophilic substitution reaction:-

Benzene undergoes electrophilic substitution reactions. The benzene ring with its delocalized π electrons is an electron rich system. It is attacked by electrophile, giving substitution products. Reaction can be represented as follows.



Benzene

substitution products

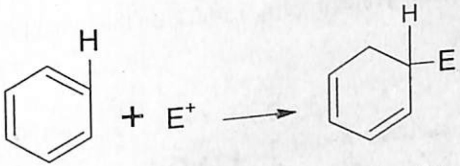
Where E- is electrophile and Nu- is nucleophile in this reaction hydrogen-atom of benzene ring is replaced by an electrophile are called electrophilic aromatic substitution reactions.

General Mechanism: - All electrophilic aromatic substitution reactions follow the same three step mechanism.

1] Formation of an electrophile.

$$\textbf{E-Nu} + \textbf{catalyst} \longrightarrow \underset{\text{Electrophile}}{E^+} + \text{H-Nu}$$

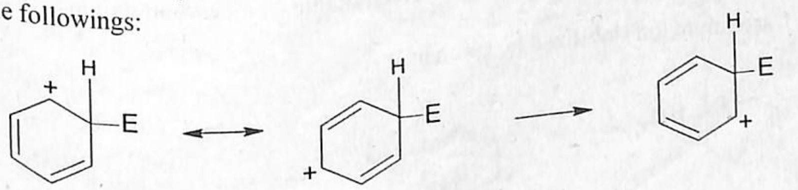
2] An electrophile attack on the aromatic ring to form a carbonium ion (intermediate compound)



Benzene

carbonium ion

3] Carbonium ion (intermediate compound) is resonance stabilized. It is a hybrid of the followings:



Me
grea
elec
stru
hyp
H
H -
]
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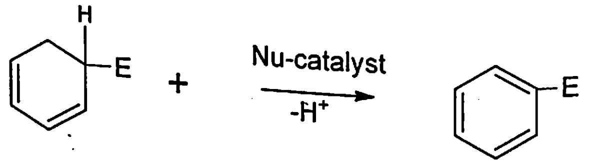
4] Carbonium ion (intermediate compound) loses a proton (H^+), to form substitution product.



Carbonium ion

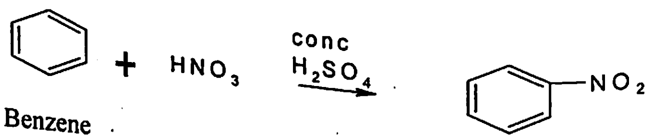
substitution product.

Nitration of Benzene:-

Nitration is usually brought about by treating benzene with a mixture of nitric acid and sulphuric acid.

Ex: - when benzene reacts with conc. Nitric acid and conc. Sulphuric acid at 60°c to form nitrobenzene.

Reaction;-



Benzene

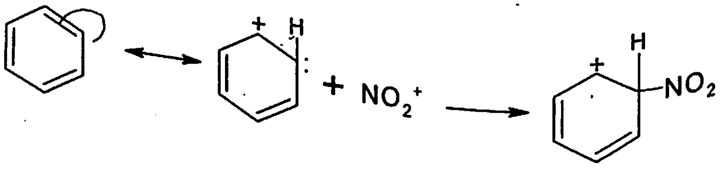
nitrobenzene

Mechanism:-

1) Formation of nitronium ion (NO_2^+) as a electrophile

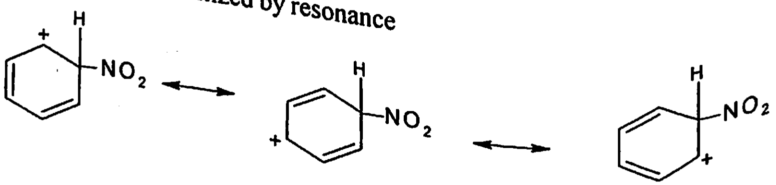
$$2\,H_2SO_4 + HNO_3 \rightarrow NO_2^+ + 2\,HSO_4^- + H_3O^+$$

2) nitronium ion (NO_2^+) (electrophile) attack on the benzene ring to form carbonium ion.

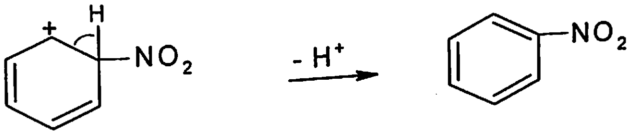


electoophile carboniumion.

3) Carbonium ion stabilized by resonance



4) Carbonium ion (intermediate compound) loses a proton (H^+), to form nitro benzene.

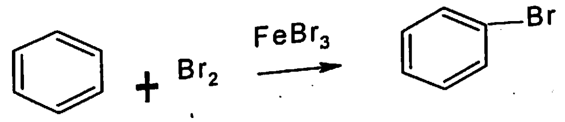


nitrobenzene

II] Bromination of benzene:-

When benzene reacts with liquid bromine in the presence of ferric bromide ($FeBr_3$) to form bromo benzene.

Reaction:-



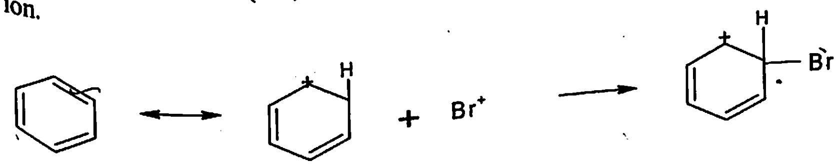
Benzene liq Bromo benzene

Mechanism:-

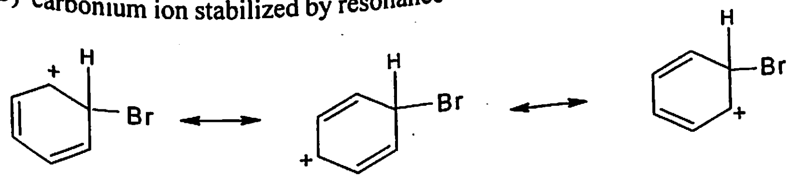
1) Formation of bromonium ion (Br^+) as a electrophile.

$$Br_2 \leftrightarrow Br\text{—}Br + FeBr_3 \leftrightarrow Br^+ + FeBr_4^-$$

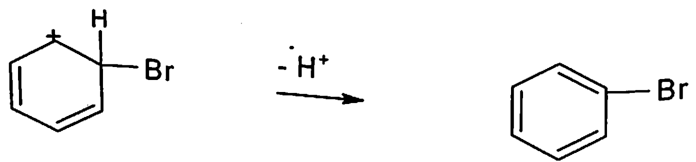
2) Bromonium ion (Br^+) electrophile attack on benzene ring to form carbonium ion.



3) carbonium ion stabilized by resonance



4) Carbonium ion (intermediate compound) loses a proton (H^+), to form bromo benzene



Carbonium ion

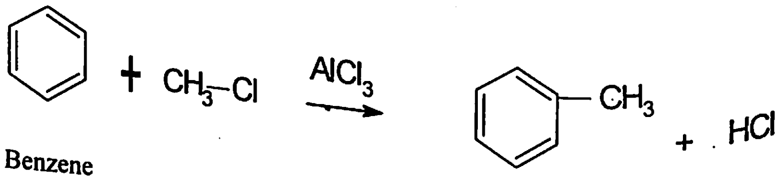
Bromobenzene

III) Friedel Craft Reaction:-

a) Friedel Craft alkylation reaction

Benzene reacts with alkyl halide in the presence of aluminium chloride to form alkyl benzene; this reaction is called Friedel Craft alkylation's reaction.

Reaction: - Benzene reacts with methyl iodide in the presence of aluminium chloride to form methyl benzene.



Benzene

methyl benzene.

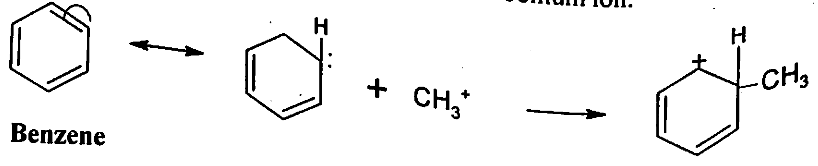
Mechanism:-

1) Formation of an electrophile.

Electrophile is formed by the reaction between methyl chloride and aluminium chloride.

$$_3\text{-Cl} + AlCl_3 \rightarrow CH_3^+ + AlCl_4^-$$

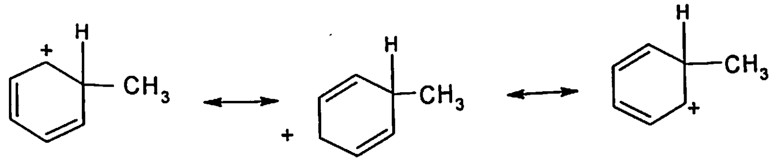
2) Electrophile attack on benzene ring to form carbonium ion.



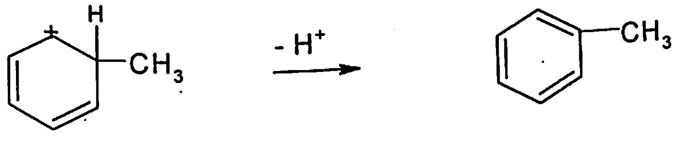
Benzene

Carbonium ion.

3) Carbonium ion stabilized by resonance



4) Carbonium ion (intermediate compound) loses a proton (H^+), to form methylbenzene

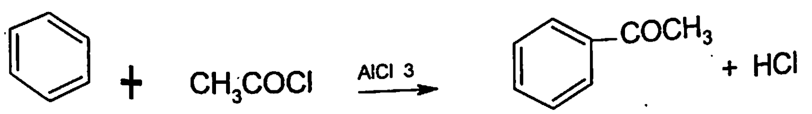


Carbonium ion

Methylbenzene

b) Friedel Acylation reaction:-

Reaction: - Benzene reacts with acid chloride or acid anhydride in the presence of aluminium chloride to form acetophenone. And this reaction is called as Friedel Craft Acylation reaction.



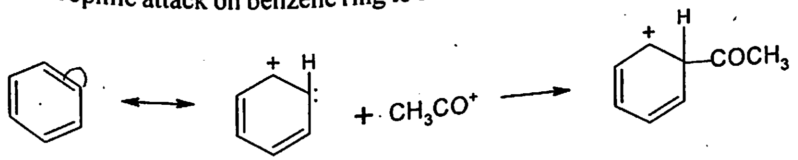
Mechanism:-

1) Formation of an electrophile.

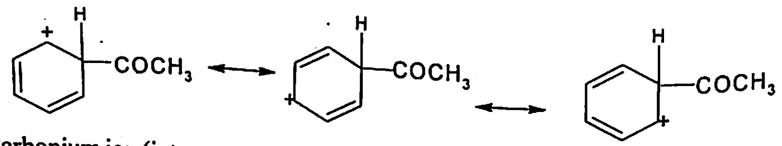
Electrophile is formed by the reaction between acetyl chloride and aluminium chloride.

$$CH_3COCl + AlCl_3 \rightarrow CH_3CO^+ + AlCl_4^-$$

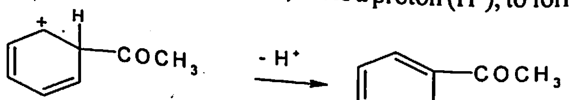
2) Electrophile attack on benzene ring to form carbonium ion.



3) Carbonium ion stabilized by resonance



4) Carbonium ion (intermediate compound) loses a proton (H⁺), to form acetophenone.

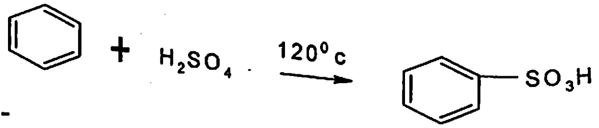


Carbonium ion

Acetophenone.

IV) Sulphonation reaction:-

Benzene reacts with conc H_2SO_4 at 120°c or fuming H_2SO_4 at room temperature to give benzene sulphonic acid.

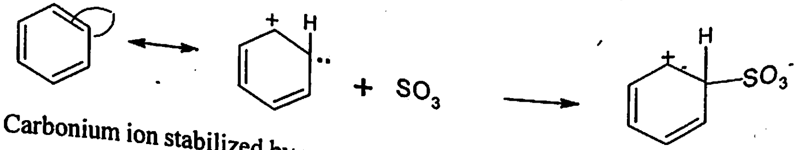


Mechanism:-

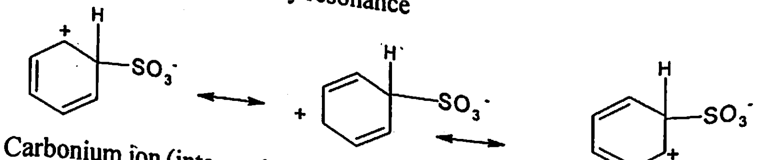
1) In this reaction electrophile is sulphur trioxide (SO_3) In conc. H_2SO_4. SO3 is produced as follows:

$$H_2SO_4 \rightleftharpoons SO_3 + H_3O^+ + HSO_4^-$$

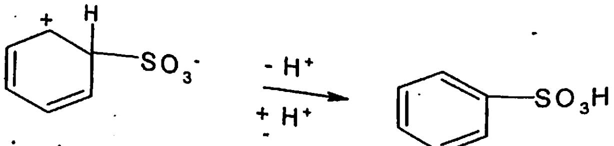
2) Electrophile attack on benzene ring to form carbonium ion.



3) Carbonium ion stabilized by resonance



4) Carbonium ion (intermediate compound) loses a proton (H⁺), to form benzene sulphonic acid.



Carbonium ion

Benzene sulphonic acid .

Activation and Deactivation effect: (a) observed in nitration of phenol (b) and nitration of nitrobenzene:-

When an electrophilic reagent attacks a substituted aromatic ring. It is the group already attached to ring that determines how readily the attack occurs and at which position of the ring it occurs. In other words, the group attached to the ring not only affects the reactivity but also determines the orientation of substitution.

Orientation or Directive effects:-

The first Substituent (S) may be direct the next incoming group or substituents (E) to ortho, Meta, or Para. Positions depend upon the nature of the first Substituent. This is called as directive or orientation effect.

These directive effects are divided into two categories.

(1) Activating group or Substituent / Ring activators:

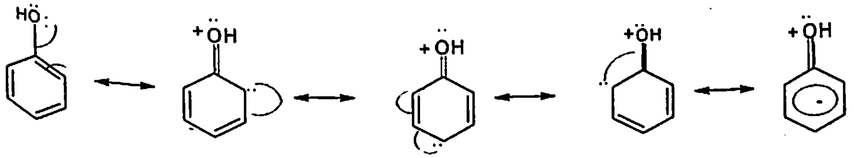
A Substituent which activates the aromatic ring to further substitution is called Activating substituent or Ring activators. Ex: -OH, $-CH_3$, - Cl, etc.

(2) Deactivating group or Substituent / Ring deactivators:-

Substituent which deactivates the aromatic ring to further substitution is called deactivating substituent or Ring deactivators. Ex: $-NO_2$, COOH, -C=N, $-^+NH_3$ etc.

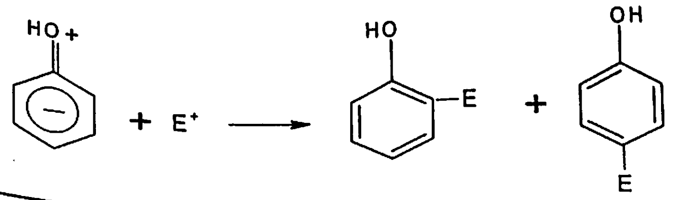
Ortho-Para Directing effects:-

Ortho-para directors activate the ring to words electrophilic substitution. For ex: In phenol, -OH group is strongly ortho-para directing, the resonance theory clearly explain this effect.



Resonance Hybrid.

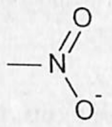
There are two non bonding electron pairs on the oxygen atom attached to the ring. One of the pair is distributed in the ring by interaction with (pi) π system as shown above, in the above resonance ortho and Para positions have a greater electron density than meta position and there fore negative charge in the ortho and Para positions with electron delocalization, there fore electrophile naturally attack at the electron rich centers, and forms ortho-Para directing effect.



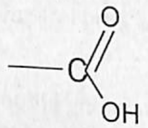
Similarly, the ortho-para directing effects occurred by –Cl, and explained by resonance.

Meta directing effect :-

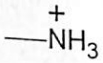
Structure of some common Meta directing groups:



Nitro



Carboxylic acid



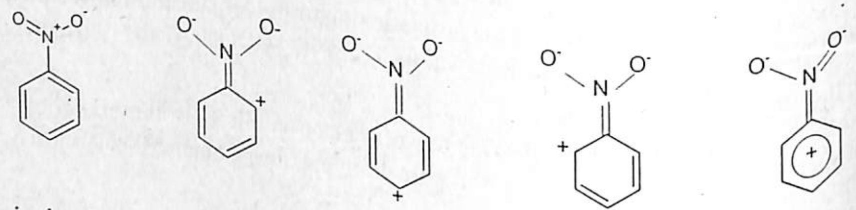
$-NH_3^+$

ammonium ion

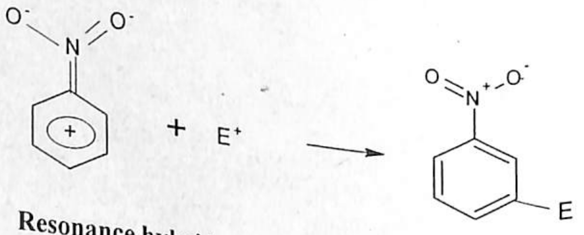
$-C \equiv N$

cyano

The key atom in the substituents is bonded to another highly electronegative atom by a double bond or triple bond. The electronegative atom pulls the electron pair of the multiple bonds and key atom in turn with-draws electrons from the benzene ring causing resonance thus nitrobenzene is a resonance hybrid of the following canonical form



in the above resonance structure ortho and para positions having positive charges and there fore, there is no scope of electrophile (E+) attack at ortho and para positions . Thus electrophile attack at Meta positions.



Resonance hybrid

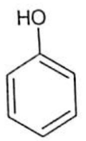
Meta product ·

⁂

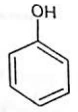
3.2 PHENOLS

1) Introduction and classification of phenol:-

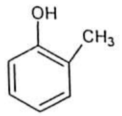
Introduction: phenols are aromatic hydroxy compounds in which –OH group is directly attached to benzene nucleus. i. e. H- atom of benzene ring can be replaced by –OH group. They are represented as R-OH. They are also called as carbolic acid.



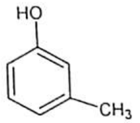
Nomenclature of phenol:-C_6H_5-OH and compounds with additional substituents are named as derivative of phenol, with carbon carrying the –OH group is numbered one(1) For ex:-



phenol



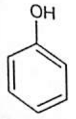
o-cresol / 2-methyl phenol



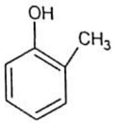
m-cresol / 3- methyl phenol

Classification of phenol :- phenols are classifieds as follows:

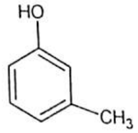
Monohydric phenol:-In which only one –OH group is attached to the benzene nucleus. For ex:-



phenol

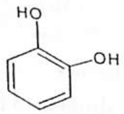


o-cresol / 2-methyl phenol

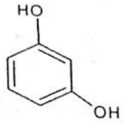


m-cresol / 3- methyl phenol

Dihydric phenol:-In which two –OH group is attached to the benzene nucleus. For ex:-



Catechol
[1,2 dihydroxy benzene]

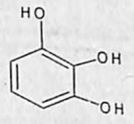


Resorcinol
[1, 3 dihydroxy benzene]

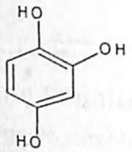
Quinol
[1, 4 dihydroxy benzene]

Trihydric phenol:-In which two –OH group is attached to the benzene nucleus.

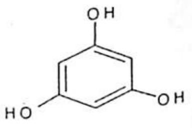
For ex:-



1, 2, 3 trihydroxy benzene



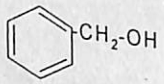
1, 2, 4 trihydroxy benzene



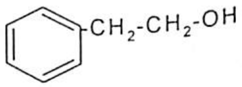
1,3,5 trihydroxy benzene

The compounds which contain an –OH group in side chain attached to an aromatic ring are not phenols. They are called aromatic alcohols.

For ex:



Benzyl alcohol

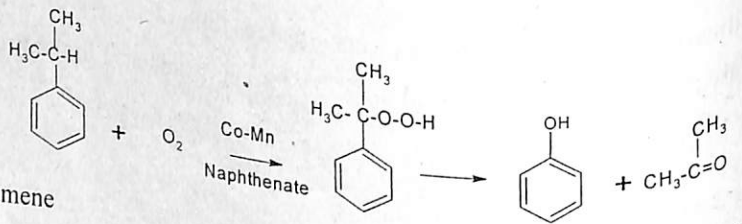


2- phenyl ethanol

2) Methods of preparation of phenols:-

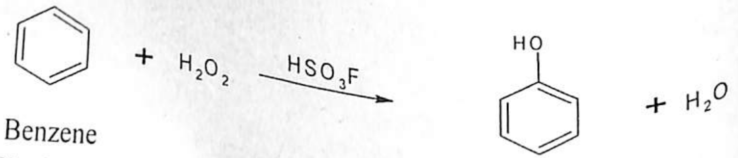
1) **From cumene:**- [Isopropyl benzene]

When cumene oxidized with air or oxygen in the presence of Cobalt-Naphthenate at 400°k to form cumene hydro peroxide, which is decomposed by an acid to form phenols.



Cumene cumene peroxide phenol acetone

2) From benzene:- when benzene reacts with hydrogen peroxide in the presence of fluorosulphonic acid to form phenol.



Benzene Phenol

3) Acidic character, comparative acidic strength of alcohols and phenols:

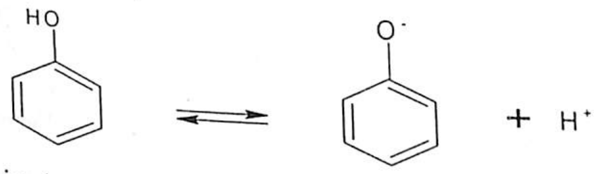
When phenol reacts with sodium hydroxide to form sodium phenoxide.

Phenol **Sodium phenoxide**

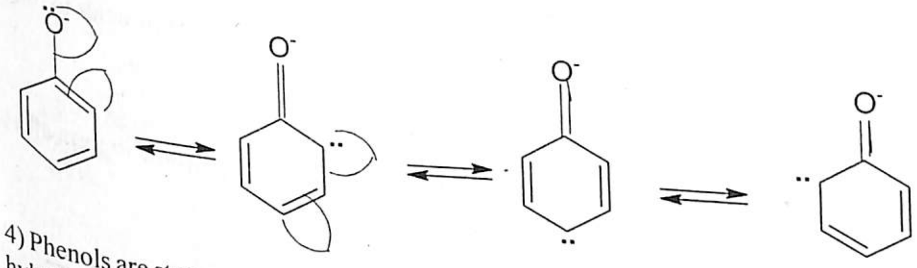
Phenols are weaker acids than carboxylic acids; it does not react with sodium carbonate and sodium bicarbonate.

1) Phenols are stronger acids than alcohols; the acidic character of phenol is due to powerful electron withdrawing mesomeric effect.

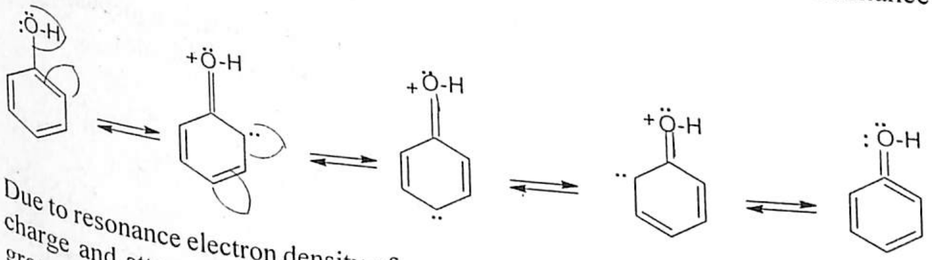
2) Phenols are acidic due to formation of stable phenoxide ion in aq. Solution.



3) Phenoxide ion is stable due to resonance. More stable phenoxide ions cause the dissociation of phenol and such type of resonance is not formed in alcohol therefore phenols are acidic in nature.



4) Phenols are stronger acids than the alcohol is that the phenols exists as resonance hybrid as shown below.



Due to resonance electron density of oxygen decreases and oxygen carries positive charge and attract a pair of electron between oxygen and hydrogen of the –OH group and facilates the release of proton (H^+) and causes ionises of phenol.

Comparative acidic strength of alcohols and phenols:-

The following six reactions describe the basic difference in the reactivity of phenol and ethyl alcohol.

1) Reaction with NaOH: - Phenol reacts with sodium hydroxide to form sodium phenoxide; Ethyl alcohol does not react with NaOH. There fore phenol is more acidic than alcohol.

$C_2H_5\text{-OH} + \text{--NaOH} \rightarrow$ NO Reaction

$C_6H_5\text{-OH} + NaOH \rightarrow C_6H_5\text{-ONa} + H_2O$

2) Catalytic reduction: - phenol under goes reduction with H2 / Ni to form cyclohexanol, ethyl alcohol does not give reaction.

$C_2H_5\text{-OH} + H_2/Ni \rightarrow$ NO Reaction

$C_6H_5\text{-OH} + H_2/Ni \rightarrow C_6H_{11}\text{-OH}$

3) Reaction with diazonium salts: - phenol reacts with benzene diazonium chloride to give a dye. Ethyl alcohol does not give reaction.

$C_6H_5\text{-OH} + C_6H_5N{=}N\text{-Cl} \rightarrow C_6H_5N{=}NC_6H_4\text{-OH}$

4) Reaction with $FeCl_3$:- Phenol gives purple coloration with ferric chloride solution, ethyl alcohol does not react.

5) Reaction with carboxylic acids:- ethyl alcohol reacts with carboxylic acids to form esters. Phenol does not give this reaction.

$C_2H_5\text{-OH} + HO\text{-O-C-}CH_3 \rightarrow C_2H_5\text{-O-O-C-}CH_3$

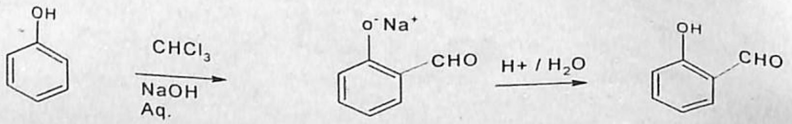
6) Reaction with halogen acids:-Ethyl alcohol reacts with halogen acid to form alkyl halides. Phenol does not give this reaction.

$C_2H_5\text{-OH} + H\text{-Br} \rightarrow C_2H_5\text{-Br} + H_2O$

4) Reactions of phenols:-

1) Reimer- Tiemann reaction with mechanism:-

This reaction involves the reaction of phenol with chloroform in aqueous sodium hydroxide solution to form O-hydroxy benzaldehyde (salicylaldehyde).



Mechanism:-

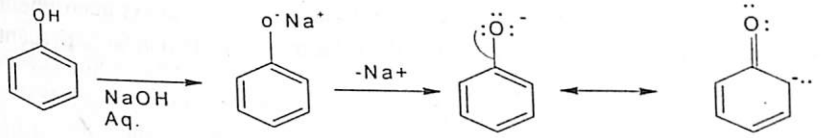
i) Formation of dichloro carbene from chloroform.

$H\text{-}CCl_3 + OH^- \rightarrow :CCl_3 + H_2O$

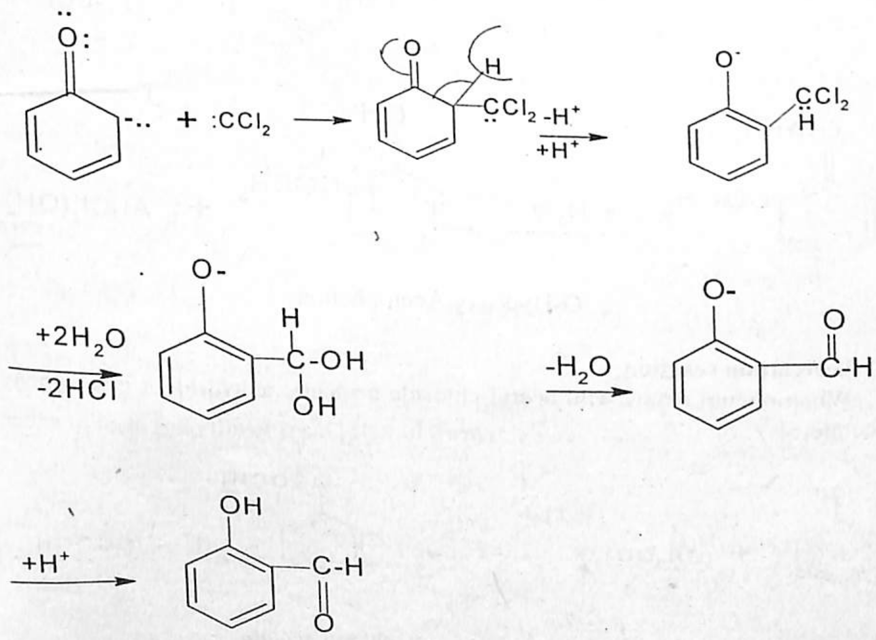
$:CCl3 \rightarrow :CCl_2 + Cl^-$

Dichloro carbene

ii) Formation of phenoxide ion:-



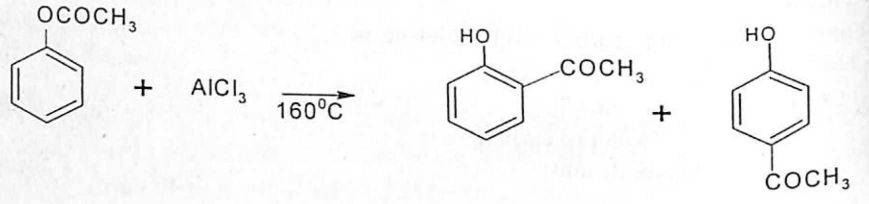
iii) Dichlorocarbene attack on phenoxide ion to form salisylaldehyde.



Salicylaldehyde

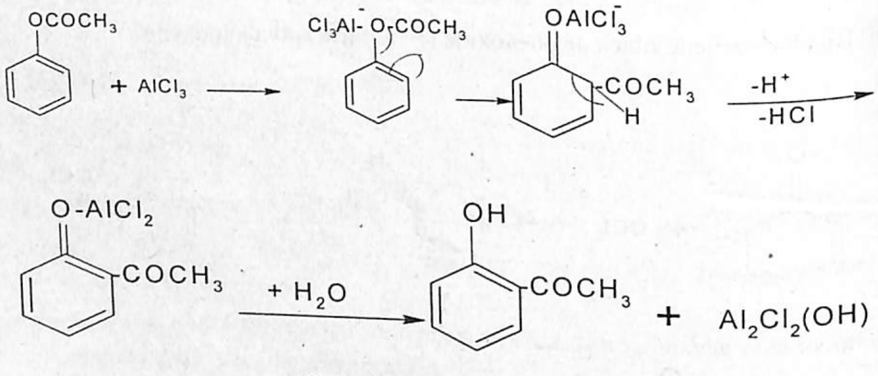
2) Fries Rearrangement reaction with mechanism:-

When phenyl acetate treated with anhydrous aluminium chloride at 160°c, it gives a mixture of ortho and Para hydroxy acetophenone.



Acetophenone o- hydroxy acetophenone. P-hydroxy acetophenone.

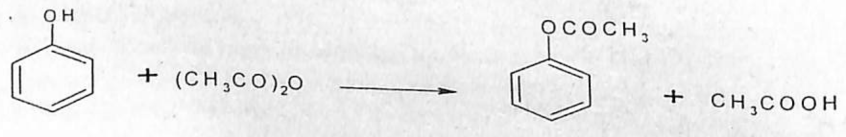
Mechanism:- At temperature below 60°c the P-isomer is formed in large percentage and at 160°c the O- isomer predominates.



O-Hydroxy Acetophenone

3) Acetylation reaction:-

When phenol reacts with acetyl chloride or acetic anhydride it gives phenyl acetate.

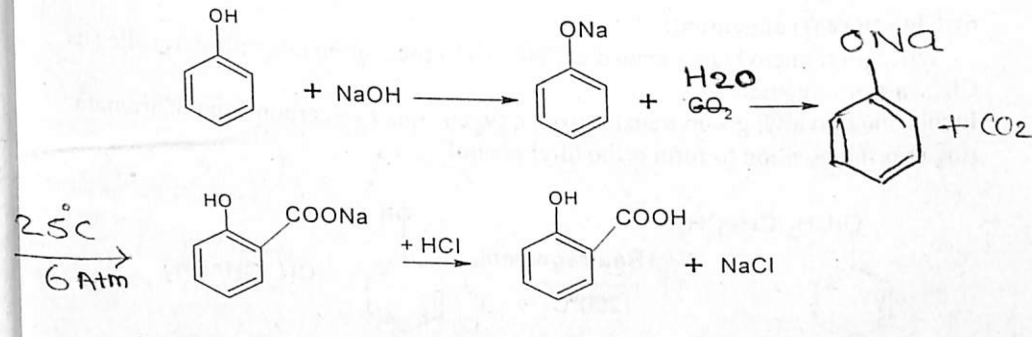


Phenol acetic anhydride phenyl acetate

Phenol acetyl chloride phenyl acetate

4) Carboxylation:-[Kolbe's Schmitt reaction]

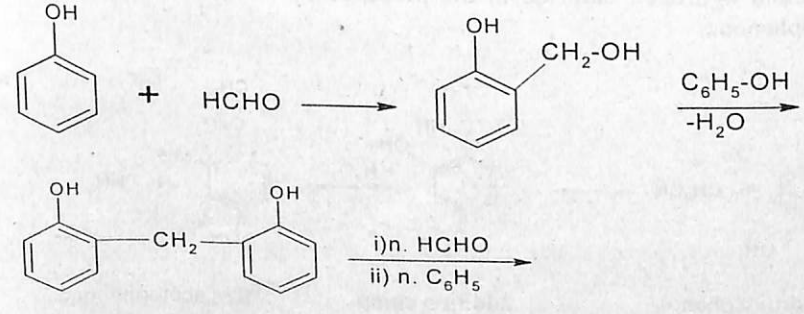
When sodium phenoxide reacts with carbon dioxide at 125°c under 6 atm.pressure to form sodium salicylate, which on acid hydrolysis it gives salicylic acid.

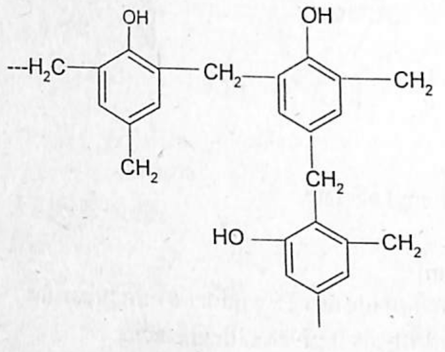


Sod. Salicylate Salicylic acid

5) Lederer Manase reaction:-

When phenol reacts with formaldehyde in the presence of dil.acid or alkali as a catalyst to form Bakelite or resin [phenol formaldehyde resin]



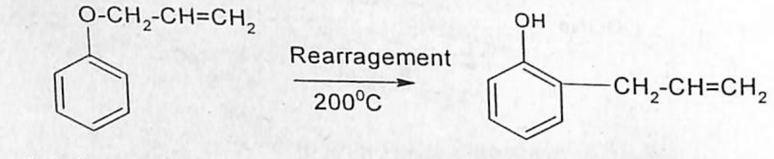


[Phenol formaldehyde resin] Bakelite

6) Claisen rearrangement:-

When allyl phenyl ether heated at 200°c as isomerisation takes place is called as Claisen rearrangement.

In this reaction allyl group transfer from oxvgen atom to a carbon atom of aromatic ring at ortho position to form ortho allyl phenol.

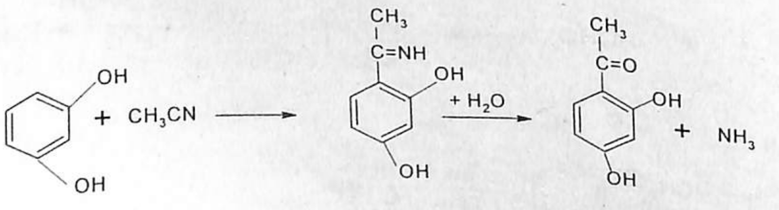


Allyl phenyl ether

Ortho- allyl phenol

7) Hauben- Hoesch reaction:-

When poly-hydroxy phenol [1,3- dihydroxy phenol] treated with acetonitrile (CH_3CN) and hydrogen chloride in the presence of $ZnCl_2$ or $AlCl_3$ to form Res.acetophenone.



1, 3- dihydroxy phenol

addition comp.

Res.acetophenone

Similarly, 1,3,5- trihydroxy phenol treated with acetonitrile (CH_3CN) and hydrogen chloride in the presence of $ZnCl_2$ or $AlCl_3$ to form Res.acetophenone.

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