9. HYDROCARBONS

Organic compounds containing carbon and hydrogen atoms only are called hydrocarbons. Depending on the types of C-C bond, they can be classified into three – saturated, unsaturated and aromatic hydrocarbons. Saturated hydrocarbons are also called alkanes. They contain only C-C single bonds. Unsaturated hydrocarbons contain atleast one carbon-carbon double bond (alkene) or carbon-carbon triple bond (alkyne). Aromatic hydrocarbons are a special type of cyclic compounds. They are also called arenes.

ALKANES

Alkanes are saturated open chain hydrocarbons containing carbon-carbon single bonds. They form a homologous series. Their general molecular formula is C_nH_{2n+2}. In alkanes, all the C atoms are sp^3 hybridised. So each C atom has a regular tetrahedral shape.

Alkanes do not react with acids, bases and other reagents under normal conditions. So they are also called paraffins. (In Latin paraffin means little affinity).

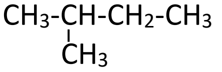
Isomerism in Alkanes

Alkanes show two types of structural isomerism – **chain isomerism** and **position isomerism**.

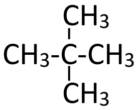
Chain isomers differ in the carbon skeleton. i.e arrangement of carbon atoms in the chain.

E.g.: The chain isomers of alkane with molecular formula C_5H_{12} are:

$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$ (n-pentane)



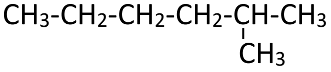
$CH_3\text{-}\underset{\underset{\displaystyle CH_3}{|}}{C}H\text{-}CH_2\text{-}CH_3$ (isopentane)



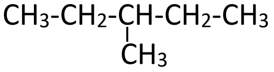
$CH_3\text{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\text{-}CH_3$ (neopentane)

Position isomers differ in the position of the side chain or branch.

E.g. The position isomers of alkane with molecular formula C_6H_{14} are:



$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\underset{\underset{\displaystyle CH_3}{|}}{C}H\text{-}CH_3$ (2-Methylpentane)



$CH_3\text{-}CH_2\text{-}\underset{\underset{\displaystyle CH_3}{|}}{C}H\text{-}CH_2\text{-}CH_3$ (3-Methylpentane)

Preparation of alkanes

1. **From unsaturated hydrocarbons**: Alkenes and alkynes add Hydrogen in presence of finely divided catalysts like Ni, Pd or Pt to form alkanes. This process is called ***hydrogenation***.

$$CH_2=CH_2+H_2\xrightarrow{Pt/Pd/Ni}CH_3-CH_3$$

Ethene Ethane

$$CH_3-C\equiv C-H+2H_2\xrightarrow{Pt/Pd/Ni}CH_3-CH_2-CH_3$$

Propyne Propane

2. **From alkyl halides**:
   a) Alkyl halides on reduction with zinc and dil. HCl, we get alkanes.

$$R\text{-}X + H_2 \xrightarrow{Zn/HCl} R\text{-}H + HX$$

$$CH_3-Cl+H_2\xrightarrow{Zn,\,H^+}CH_4+HCl$$

Chloromethane Methane

$$C_2H_5-Cl+H_2\xrightarrow{Zn,\,H^+}C_2H_6+HCl$$

Chloroethane Ethane

b) ***Wurtz reaction***:

Alkyl halides react with metallic sodium in dry ether to form alkanes. This reaction is known as Wurtz reaction. The alkane so formed contains double the number of C atoms than that present in the alkyl halide. Hence this method is used for the preparation of alkanes with even number of carbon atoms.

$$\text{R-X} + 2\,\text{Na} + \text{X-R} \xrightarrow{Dry\ ether} \text{R-R} + 2\,\text{NaX}$$

$$CH_3Br + 2Na + BrCH_3 \xrightarrow{\text{dry ether}} CH_3-CH_3 + 2NaBr$$

Bromomethane Ethane

$$C_2H_5Br + 2Na + BrC_2H_5 \xrightarrow{\text{dry ether}} C_2H_5-C_2H_5$$

Bromoethane n-Butane

When two different alkyl halides are used, we get a mixture of alkanes.

3. **From carboxylic acids**:

a) ***Decarboxylation***: Sodium salt of carboxylic acids (R-COONa) on heating with soda lime (a mixture of NaOH and CaO), we get an alkane containing one carbon atom less than that of the carboxylic acid. This process is known as decarboxylation, since it involves the elimination of a CO_2 molecule from the carboxylic acid (R-COOH).

$$\text{R-COONa} + \text{NaOH} \xrightarrow{\text{CaO}} \text{R-H} + Na_2CO_3$$

E.g. $CH_3COONa + NaOH \xrightarrow{\text{Cao}} CH_4 + Na_2CO_3$

Sodium acetate methane

b) ***Kolbe's Electrolytic method***: An aqueous solution of sodium or potassium salt of a carboxylic acid on electrolysis gives alkane containing even number of carbon atoms.

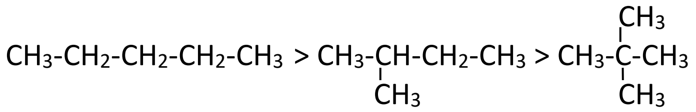
$$2CH_3COONa + 2H_2O \longrightarrow CH_3-CH_3 + 2CO_2 + 2NaOH + H_2$$

(Sod. Acetate) (Ethane)

Physical Properties

Boiling point of alkanes increase with increase of molecular mass (or with number of C atoms). This is because in alkanes there is only weak van der Waal's force of attraction between different molecules. As the molecular size increases, the surface area increases and hence van der Waal's force increases. So the boiling point increases.

The boiling point of isomeric alkanes decreases with branching. As the branching increases, the molecule attains the shape of a sphere. So the surface area decreases and hence the b.p. So among three isomeric pentane boiling point decreases in the order: n-pentane > isopentane > neopentane.



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

(n-pentane) (isopentane) (neopentane)

Chemical Properties

1. **Substitution reactions**

These are reactions in which hydrogen atom of an alkane is replaced by other atoms or atom groups. E.g. when an alkane is treated with halogen in the presence of diffused sunlight or uv light, we get haloalkane. This reaction is known as halogenation reaction.

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$

(monochloromethane or methyl chloride)

$$CH_3Cl + Cl_2 \xrightarrow{h\upsilon} CH_2Cl_2 + HCl$$

(dichloromethane or methylene chloride)

$$CH_2Cl_2 + Cl_2 \xrightarrow{h\upsilon} CHCl_3 + HCl$$

(trichloromethane or chloroform)

$$CHCl_3 + Cl_2 \xrightarrow{h\upsilon} CCl_4 + HCl$$

(tetrachloromethane or carbon tetrachloride)

Mechanism

Halogenations takes place by free radical chain mechanism and it involves three steps – initiation, propagation and termination.

i) *Initiation step*: The reaction is initiated by the homolysis of chlorine molecule in presence of sunlight.

$$Cl{-}Cl \xrightarrow[\text{homolysis}]{h\nu} \dot{C}l + \dot{C}l$$

Chlorine free radicals

ii) *Propagation step*: The chlorine free radical attacks the methane molecule and form methyl free radical and HCl.

$$CH_4 + \dot{C}l \xrightarrow{h\nu} \dot{C}H_3 + H{-}Cl$$

The methyl radical then attacks the second Cl_2 molecule to form CH_3Cl and Chlorine free radical.

$$\dot{C}H_3 + Cl - Cl \xrightarrow{h\nu} CH_3 - Cl + \dot{C}l$$

The above two steps repeat and thus the reaction propagates.

$$CH_3Cl + \dot{C}l \rightarrow \dot{C}H_2Cl + HCl$$

$$\dot{C}H_2Cl + Cl - Cl \rightarrow CH_2Cl_2 + \dot{C}l$$

iii) *Termination step*: The reaction stops after some time due to any one of the following reactions:

(a) $\dot{C}l + \dot{C}l \rightarrow Cl{-}Cl$

(b) $H_3\dot{C} + \dot{C}H_3 \rightarrow H_3C{-}CH_3$

(c) $H_3\dot{C} + \dot{C}l \rightarrow H_3C{-}Cl$

2. Combustion (Oxidation):

On combustion in presence of air or oxygen, alkanes give CO_2, H_2O and large amount of heat.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) + \text{heat}$$

The general combustion equation for any alkane is:

$$C_nH_{2n+2} + (3n+1)/2\ O_2 \longrightarrow nCO_2 + (n+1)\ H_2O$$

Incomplete combustion of alkanes with insufficient amount of air or O_2 gives carbon black.

3. Controlled Oxidation:

Alkanes on heating with O_2 at high pressure and in presence of suitable catalysts to form different products like alcohol, aldehyde or carboxylic acid.

$$2\ CH_4 + O_2 \xrightarrow{Cu/523K/100\ atm} 2\ CH_3OH$$

(Methanol)

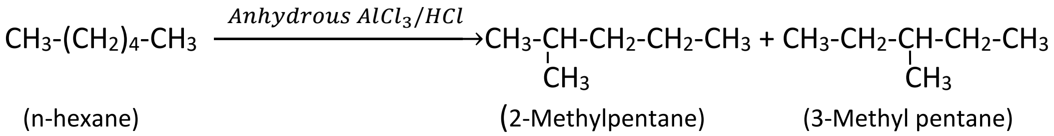
$$CH_4 + O_2 \xrightarrow{Mo_2O_3/\Delta} HCHO + H_2O$$

(formaldehyde)

$$2\ CH_3\text{-}CH_3 + 3\ O_2 \xrightarrow{(CH_3COO)_3Mn/\Delta} 2\ CH_3COOH + 2\ H_2O$$

(Acetic acid or ethanoic acid)

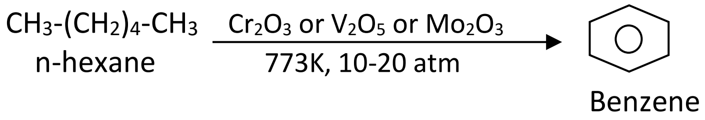
4. **Isomerisation**: n-Alkanes on heating in the presence of anhydrous aluminium chloride and hydrogen chloride gas isomerise to branched chain alkanes.



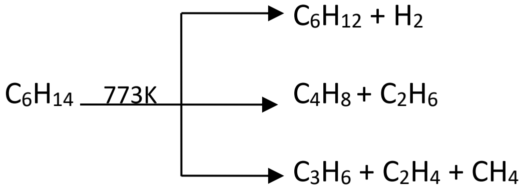
$$CH_3\text{-}(CH_2)_4\text{-}CH_3 \xrightarrow{Anhydrous\ AlCl_3/HCl} CH_3\text{-}\underset{\displaystyle CH_3}{\underset{|}{C}}H\text{-}CH_2\text{-}CH_2\text{-}CH_3 + CH_3\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{C}}H\text{-}CH_2\text{-}CH_3$$

(n-hexane) (2-Methylpentane) (3-Methyl pentane)

5. **Aromatization**: n-Alkanes having six or more carbon atoms on heating to 773K at 10 to 20 atmospheric pressure in the presence of oxides of vanadium, molybdenum or chromium supported over alumina, we get aromatic compounds. This reaction is known as aromatization or reforming.



6. **Pyrolysis**: Alkanes having six or more carbon atoms on heating at higher temperature decompose to form lower alkanes, alkenes etc. This reaction is known as pyrolysis.



Conformations of Alkanes

Alkanes contain carbon-carbon sigma (σ) bonds. Since, electron distribution of the sigma bonds is symmetrical around the bond axis, rotation around C–C bond is allowed. This rotation changes the spatial arrangements of atoms attached to C atoms. These different spatial arrangements of atoms arising due to free rotation around a *C-C* single bond are called conformations or conformers or rotamers.

Conformations of Ethane

Ethane contains a C-C σ bond and each carbon atom contains three hydrogen atoms. Due to free rotation of C atoms around the single bond, the spatial arrangement of hydrogen atoms attached to the C atoms change. Thus ethane can show an infinite number of conformational isomers.

If we fix one carbon atom and rotate the other, there arise two extreme cases called eclipsed and staggered conformations.

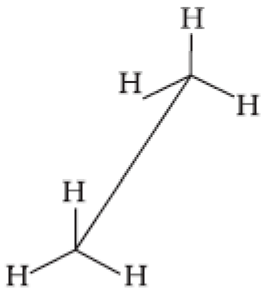
In *eclipsed conformation, the hydrogen atoms attached to each carbon atoms are closed together as possible. Or, here the hydrogen atoms of the 2nd carbon atoms are exactly behind that of the first.*

In staggered conformation, the hydrogen atoms are far apart as possible. Any conformations between eclipsed and staggered conformations are called **skew conformations**.

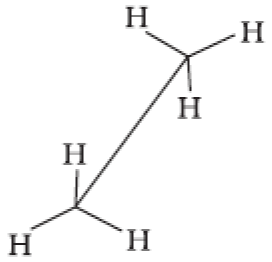
Staggered conformation is stabler than eclipsed form. This is because in staggered form, the electron clouds of carbon-hydrogen bonds are very far apart. So there is minimum repulsive forces, minimum energy and maximum stability. But in eclipsed form, the electron clouds are close to each other. So the repulsion is maximum and the stability is minimum. Eclipsed and staggered conformations can be represented by ***Sawhorse and Newman projection formulae.***

1. **Sawhorse projections**:

Here the molecule is viewed along the molecular axis. C–C bond is denoted by a longer straight line. The front carbon is shown at the lower end of the line and the back carbon is shown at the upper end. Each carbon has three lines at an angle of 120° corresponding to three hydrogen atoms .
Sawhorse projections of eclipsed and staggered conformations of ethane are as follows:



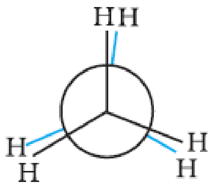
(i) Eclipsed



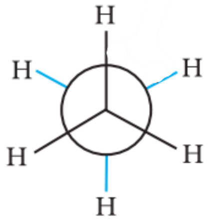
(ii) Staggered

2. **Newman projections**:

Here the molecule is viewed at the C–C bond head on (i.e. from the front side). The front carbon atom is represented by a point. Three hydrogen atoms attached to this carbon atom are shown by three lines drawn at an angle of 120° to each other. The back carbon atom is represented by a circle and the three hydrogen atoms are shown attached to it are denoted by shorter lines drawn at an angle of 120° to each other.
The Newman's projections for eclipsed and staggered conformations of ethane are as follows:



(i) Eclipsed



(ii) Staggered

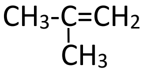
ALKENES

Alkenes are unsaturated hydrocarbons containing at least one C=C (carbon-carbon double bond). They are also known as *olefins* (oil forming) since the first member, ethylene or ethene (C_2H_4) forms an oily liquid on reaction with chlorine. The general formula for alkenes is C_nH_{2n}.

Isomerism in alkenes

Alkenes show *structural and stereo isomerism*. The important **structural isomerism** shown by alkenes are *chain isomerism and position isomerism*.

E.g. for chain isomers with molecular formula C_4H_8 are:

$CH_3\text{-}CH_2\text{-}CH{=}CH_2$	(Butene or Butylene)
 $CH_3\text{-}\underset{\displaystyle CH_3}{\underset{\mid}{C}}{=}CH_2$	(2-methylprop-1-ene or Isobutylene)

E.g. for position isomers with molecular formula C_4H_8 are:

$CH_3\text{-}CH_2\text{-}CH{=}CH_2$ and $CH_3\text{-}CH{=}CH\text{-}CH_3$
(but-1-ene) (but-2-ene)

The stereoisomers have same atom to atom bond but they differ only in the spatial arrangement of atoms or groups. The **stereoisomerism** shown by alkenes is geometrical isomerism.

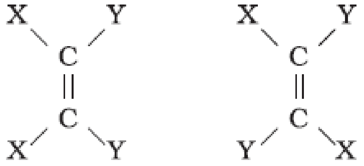
Geometrical Isomerism

The isomerism arising due to the difference in the spatial arrangement of atoms around carbon-carbon double bond is called *geometrical isomerism*. Such isomers are called geometrical isomers. It is a type of stereo isomerism.

Geometrical isomerism arising due to the restricted rotation about carbon-carbon double bond. There are two types of geometrical isomers – *cis isomer and trans isomer*.

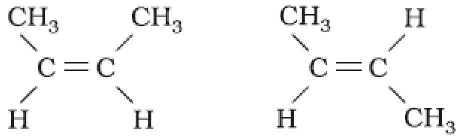
Isomer in which *identical atoms or groups are on the same side of the double bond is called* ***cis isomer***. *If the identical groups or atoms are on the opposite side of the double bond, it is called* ***trans isomer***.

Compounds with general formula YX C = C XY can show geometrical isomerism as follows:



cis isomer trans isomer

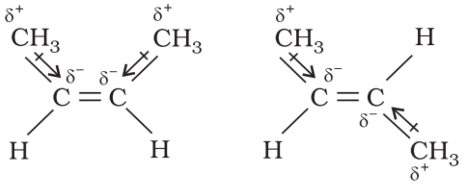
E.g. But-2-ene



cis-But-2-ene *trans*-But-2-ene

Due to different arrangement of atoms or groups in space, these isomers differ in their physical properties like melting point, boiling point, dipole moment, solubility etc.

Cis form of alkene is found to be more polar than the trans form. In trans form, the bond dipoles are in opposite directions and so they get cancelled each other.

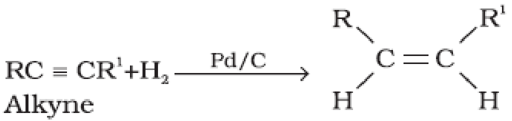


cis-But-2-ene (μ = 0.33D) *trans*-But-2-ene (μ = 0)

In the case of solids, the trans isomer has higher melting point than the cis form.

PREPARATION OF ALKENES

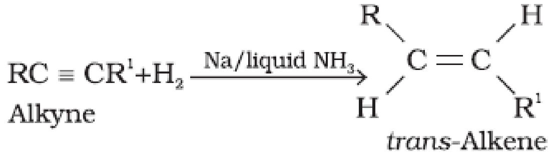
1. **From Alkynes**: Alkynes on partial reduction with dihydrogen in the presence of *palladised charcoal partially deactivated with sulphur compounds or quinoline* give alkenes. Partially deactivated palladised charcoal is known as Lindlar's catalyst. Alkenes thus obtained are having ***cis*** **geometry**.



cis-Alkene

$$\underset{\text{Ethyne}}{CH\equiv CH+H_2} \xrightarrow{Pd/C} \underset{\text{Ethene}}{CH_2=CH_2}$$

If we use *sodium in liquid ammonia* as the reducing agent, we get *trans* alkene.



2. **From Alkyl halides**:

Alkyl halides (R-X) on heating with alcoholic potash, eliminate one molecule of hydrogen halide to form alkenes. This reaction is known as dehydrohalogenation (i.e., removal of hydrogen halide from a compound). Since hydrogen atom is eliminated from the β carbon atom, the reaction is also known as ***β-elimination reaction***.

$CH_3\text{-}CH_2X \xrightarrow{\text{Alc.KOH}} CH_2 = CH_2 + HX$

$CH_3\text{-}CH_2\text{-}CH_2Br \xrightarrow{\text{Alc.KOH}} CH_3\text{-}CH = CH_2 + HBr$

3. **From vicinal dihalides**:

Dihalides in which halogen atoms are attached to two *adjacent carbon atoms* are known as *vicinal* (vic) dihalides. Vicinal dihalides on treatment with zinc metal lose a molecule of ZnX_2 to form an alkene. This reaction is known as dehalogenation (i.e. elimination of halogen molecule from a compound).

$CH_2Br\text{-}CH_2Br + Zn \longrightarrow CH_2 = CH_2 + ZnBr_2$

(vic-ethylene dibromide) (ethene)

$CH_3\text{-}CHBr\text{-}CH_2Br + Zn \longrightarrow CH_3\text{-}CH = CH_2 + ZnBr_2$

(1,2-Dibromopropane) (Propene)

4. **From alcohols**:

Alcohols when heated with concentrated sulphuric acid undergo dehydration (elimination of water molecule) to form alkenes. This reaction is also the example of β-elimination reaction since –OH group is eliminated from the β-carbon atom.

$CH_3\text{-}CH_2\text{-}OH \xrightarrow{\text{Conc.}H_2SO_4} CH_2 = CH_2 + H_2O$

Chemical Properties

1. **Addition of hydrogen**: Alkenes add hydrogen in presence of finely divided Ni, Pd or Pt to form alkanes.

$CH_2 = CH_2 + H_2 \xrightarrow{\text{Ni}} CH_3\text{-}CH_3$

2. **Addition of halogen**: Alkenes add halogen (Cl_2 or Br_2) to form vicinal dihalides.

$CH_2 = CH_2 + X_2 \longrightarrow CH_2X\text{-}CH_2X$

When Br_2 dissolved in CCl_4 (carbon tetrachloride) is added to unsaturated compounds (alkenes or alkynes), the reddish orange colour of bromine solution is discharged. This reaction is used as a test for unsaturation.

$CH_2 = CH_2 + Br_2 \longrightarrow CH_2Br\text{-}CH_2Br$

3. **Addition of hydrogen halide**:

Alkenes add hydrogen halide to form alkyl halides.

$CH_2 = CH_2 + HX \longrightarrow CH_3\text{-}CH_2X$

$CH_2 = CH_2 + HBr \longrightarrow CH_3\text{-}CH_2Br$

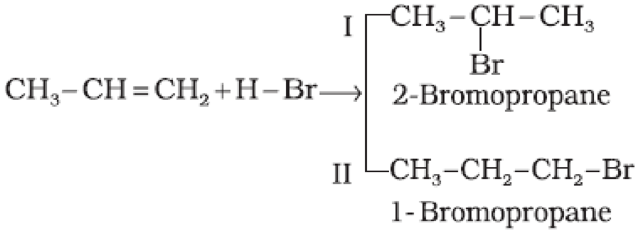
(ethene) (Bromoethane)

$CH_3\text{-}CH = CH\text{-}CH_3 + HBr \longrightarrow CH_3\text{-}CH_2\text{-}CHBr\text{-}CH_3$

(But-2-ene) (2-Bromobutane)

Addition of HBr to unsymmetrical alkenes (Markovnokov's Rule)

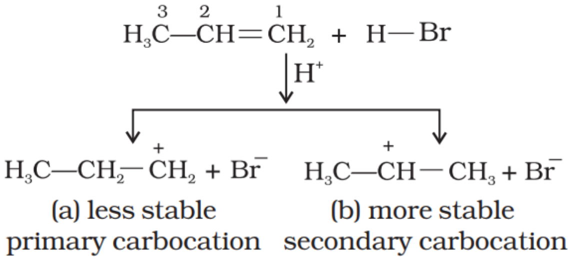
When HBr is added to propene, we get 2 products – 1-bromopropane and 2-bromopropane.



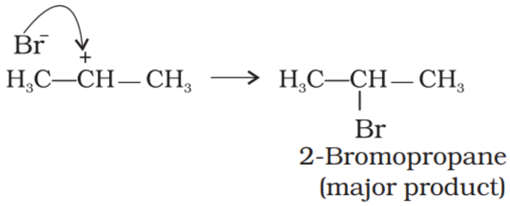
Here the major product is determined by a rule called ***Markovnikov rule***. The rule states that "when an unsymmetrical reagent is added to an unsymmetrical alkene, the negative part of the addendum (adding molecule) gets attached to the double bonded carbon with lesser number of hydrogen atoms". Thus in the above reaction 2-bromopropane is the major product.

Mechanism:

(i) Hydrogen bromide provides an electrophile H^+, which attacks the double bond to form carbocation.



(ii) Since secondary carbocation (b) is more stable than the primary carbocation (a), it is attacked by Br^- ion to form the product as follows :



Anti Markovnikov addition or peroxide effect or Kharash effect

In presence of organic peroxide (e.g. acetyl peroxide [$(CH_3-CO)_2O_2$], benzoyl peroxide [$(C_6H_5CO)_2O_2$] etc.), addition of HBr to unsymmetrical alkenes takes place against Markovnikov rule. i.e. in such cases, the negative part of the reagent gets attached to the double bonded carbon atom with greater number of hydrogen atom. This is known as ***peroxide effect or Kharash effect or anti-Markovnikov addition reaction***.

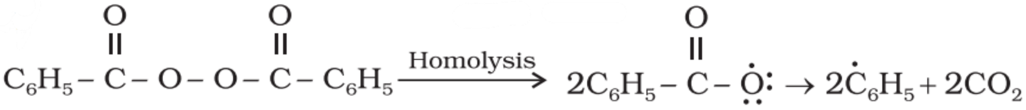
e.g. $CH_3\text{-}CH= CH_2 + HBr \xrightarrow{(C_6H_3CO)_2O_2} CH_3\text{-}CH_2\text{-}CH_2Br$

Propene 1-bromopropane

Mechanism:

Peroxide effect proceeds via *free radical chain mechanism* as follows:

(i) Homolysis of benzoyl peroxide produces phenyl free radical.

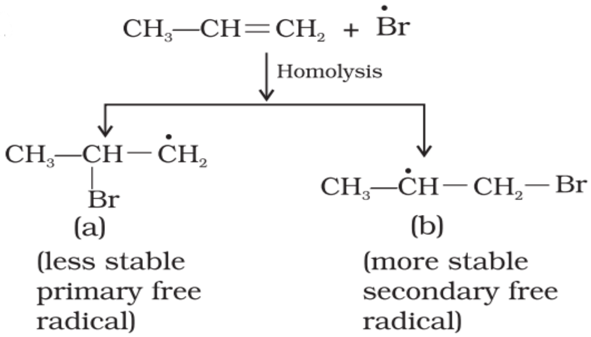


$$C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5 \xrightarrow{\text{Homolysis}} 2C_6H_5-\overset{O}{\overset{\|}{C}}-\dot{\underset{\cdot\cdot}{O}}\colon \rightarrow 2\dot{C}_6H_5+2CO_2$$

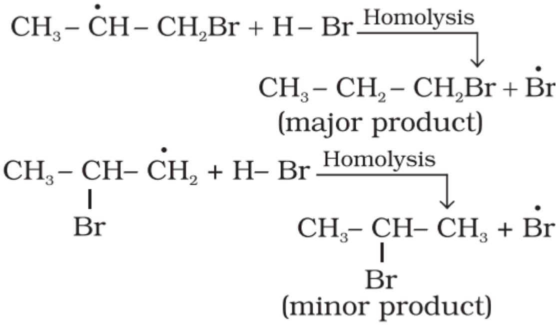
(ii) Phenyl free radical reacts with HBr to form Bromine free radical.

$$\dot{C}_6H_5+H-Br \xrightarrow{\text{Homolysis}} C_6H_6+\dot{B}r$$

(iii) Bromine free radical attacks propene to form a primary and secondary free radicals. Since secondary free radical is stabler, it will be the major one.



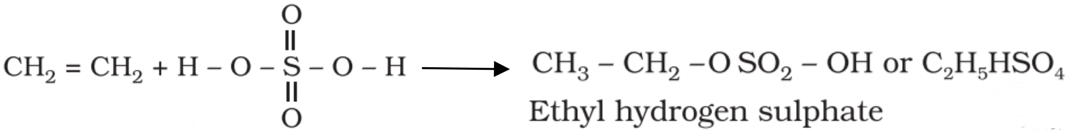
(iv) These free radicals react with H-Br to form the products and Bromine free radical.



$$CH_3-\dot{C}H-CH_2Br + H-Br \xrightarrow{\text{Homolysis}} \underset{\text{(major product)}}{CH_3-CH_2-CH_2Br} + \dot{B}r$$

$$CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-\dot{C}H_2 + H-Br \xrightarrow{\text{Homolysis}} \underset{\text{(minor product)}}{CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3} + \dot{B}r$$

4. **Addition of sulphuric acid**: Cold concentrated sulphuric acid adds to alkenes and form alkyl hydrogen sulphate. The reaction takes place in accordance with Markovnikov rule.



$$CH_2=CH_2 + H-O-\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle O}{\underset{\|}{S}}}}-O-H \longrightarrow \underset{\text{Ethyl hydrogen sulphate}}{CH_3-CH_2-OSO_2-OH \text{ or } C_2H_5HSO_4}$$

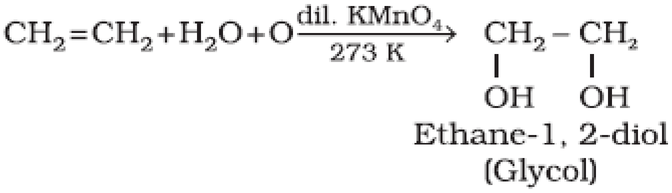
5. **Addition of water:**

Alkenes add water in presence of a few drops of concentrated sulphuric acid to form alcohols. The reaction occurs according to the Markovnikov rule.

$$\underset{\text{Propene}}{CH_3\text{-}CH=CH_2 + H_2O} \xrightarrow{\text{Conc.}H_2SO_4} \underset{\text{2-propanaol}}{CH_3\text{-}CH(OH)\text{-}CH_3}$$

6. **Oxidation**:

i) When oxidised using cold and dilute aqueous solution of potassium permanganate ($KMnO_4$) [commonly called Baeyer's reagent], alkenes give vicinal glycols.



$$CH_2=CH_2+H_2O+O \xrightarrow[273\text{ K}]{\text{dil. }KMnO_4} \underset{\text{Ethane-1, 2-diol (Glycol)}}{\underset{\displaystyle OH}{\underset{|}{CH_2}}-\underset{\displaystyle OH}{\underset{|}{CH_2}}}$$

When $KMnO_4$ is added to alkene, its pink colour gets discharged. So this reaction is also used as a test for unsaturation.

ii) Acidified potassium permanganate ($KMnO_4$) or acidified potassium dichromate ($K_2Cr_2O_7$) oxidises alkenes to ketone or acids depending on the nature of the alkene.

$$\underset{\text{(Propene)}}{CH_3\text{-}CH=CH_2} \xrightarrow{KMnO_4/H^+} \underset{\text{(Acetic acid)}}{CH_3\text{-}COOH} + CO_2 + H_2O$$

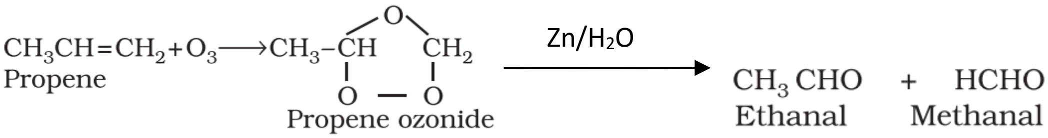
$$CH_3\text{-}CH{=}CH\text{-}CH_3 \xrightarrow{KMnO_4/H^+} 2\ CH_3\text{-}COOH$$

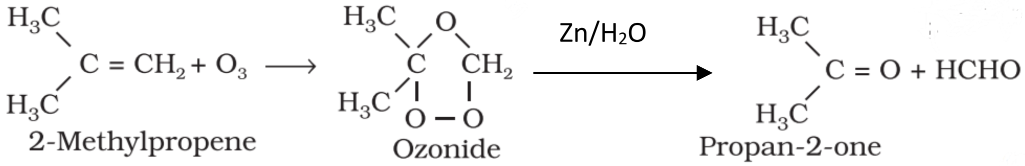
(But-2-ene) [Ethanoic acid (acetic acid)]

$$(CH_3)_2C = CH_2 \xrightarrow{KMnO_4/H^+} CH_3\text{-}CO\text{-}CH_3 + CO_2 + H_2O$$

(2- Methylpropene) [Propanone (acetone)]

7. **Ozonolysis**: Alkenes add ozone to form an ozonide which on hydrolysis in presence of Zn to form carbonyl compounds (Aldehydes or ketones).



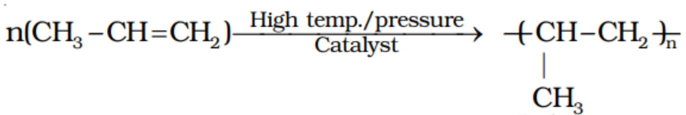


8. **Polymerisation**: The complex organic molecules formed by the combination of simple molecules are called polymers (macromolecules) and the reaction is called polymerisation reaction. The simple molecule from which a polymer is formed is called monomer.

$$\text{n Monomers} \xrightarrow{\text{Polymerisation reaction}} \text{Polymer}$$

$$n(CH_2{=}CH_2) \xrightarrow[\text{Catalyst}]{\text{High temp./pressure}} \left(CH_2{-}CH_2 \right)_n$$

Polythene



$$n(CH_3{-}CH{=}CH_2) \xrightarrow[\text{Catalyst}]{\text{High temp./pressure}} \left(\underset{\substack{| \\ CH_3}}{CH}{-}CH_2 \right)_n$$

Polypropene

ALKYNES

They are unsaturated hydrocarbons containing at least one $C \equiv C$ bond [carbon-carbon triple bond]. Their general formula is C_nH_{2n-2}. The first member of alkyne series is ethyne commonly called acetylene (C_2H_2). Other members are considered as the derivatives of acetylene and so alkynes are also called Acetylenes. In alkynes, the triple bonded carbon atoms are ***sp*** hybridized and hence are linear.

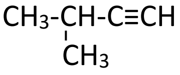
Isomerism in Alkynes

Alkynes show two types structural isomerism – Position isomerism and chain isomerism.
Position isomers of C_4H_6 are:

$CH_3\text{-}CH_2\text{-}C{\equiv}CH$ and $CH_3\text{-}C{\equiv}C\text{-}CH_3$
(but-1-yne) (but-2-yne)

Chain isomers of C_5H_8 are:

$CH_3\text{-}CH_2\text{-}C{\equiv}C\text{-}CH_3$ and



$CH_3\text{-}\underset{\substack{| \\ CH_3}}{CH}\text{-}C{\equiv}CH$

(pent-2-yne) (2-methylbut-1-yne)

Preparation of alkynes

1. **From calcium carbide (CaC_2):** On large scale, ethyne is prepared by treating calcium carbide with water. Calcium carbide is prepared by heating quick lime (CaO) with coke.

$$\underset{\text{(lime stone)}}{CaCO_3} \xrightarrow{\quad} \underset{\text{(quick lime)}}{CaO} + CO_2$$

$$CaO + 3C \xrightarrow{\quad} CaC_2 + CO$$

$$\underset{\text{(calcium carbide)}}{CaC_2 + 2H_2O} \xrightarrow{\quad} \underset{\text{(acetylene)}}{C_2H_2} + Ca(OH)_2$$

2. **From vicinal dihalides:** Vicinal dihalides undergo dehydrohalogenation on treatment with alcoholic KOH to form alkenyl halide which on treatment with sodamide ($NaNH_2$) to form alkyne.

$$\underset{\text{1,2-dibromoetane}}{CH_2Br\text{-}CH_2Br} + KOH\ (alc.) \xrightarrow{\quad} \underset{\text{Ethylene bromide}}{CH_2 = CHBr} \xrightarrow{NaNH_2} \underset{\text{Ethyne (acetylene)}}{CH \equiv CH}$$

$$\underset{\text{(1,2-Dichloropropane)}}{CH_3\text{-}CHCl\text{-}CH_2Cl + KOH\ (alc.)} \xrightarrow{\quad} \underset{\text{(1-chloroprop-1-ene)}}{CH_3\text{-}CH{=}CHCl} \xrightarrow{NaNH_2} \underset{\text{(propyne)}}{CH_3\text{-}C{\equiv}CH}$$

Chemical Properties

1. **Acidic character**: 1-alkynes are acidic in nature. This is because in alkynes, the triple bonded carbon atoms are sp hybridized. Due to the greater s-character (50%), the sp hybridised orbitals of carbon atoms in ethyne molecules have highest electronegativity. So they attract the shared electron pair of the C-H bond to a greater extent and hence the hydrogen atom is removed as **H^+**. So 1-alkynes are acidic in nature.

   E.g. Acetylene on reaction with Na metal, we get sodium acetylide (monosodium ethynide) and hydrogen gas.

$$HC \equiv CH + Na \rightarrow \underset{\substack{\text{Monosodium}\\ \text{ethynide}}}{HC \equiv C^{-}Na^{+}} + ½H_2$$

   This on further reacts with Na metal to form disodium acetylide (disodium ethynide) and H_2.

$$HC \equiv C^{-}Na^{+} + Na \rightarrow \underset{\text{Disodium ethynide}}{Na^{+}C^{-} \equiv C^{-}Na^{+}} + ½H_2$$

   This reaction is not shown by alkenes and alkanes. Hence it is used for distinction between alkynes and alkenes or alkanes. Also this reaction is used to distinguish 1-alkynes from other isomeric alkynes. E.g. 1-butyne and 2-butyne can be distinguished by using this reaction.

2. **Addition reactions**:
   - *i.* ***Addition of H_2:***

$$\underset{\text{Ethyne (acetylene)}}{HC{\equiv}CH + H_2} \xrightarrow{Ni/Pt/Pd} \underset{\text{Ethene}}{[H_2C = CH_2]} \xrightarrow{H_2/Ni} \underset{\text{Ethane}}{CH_3\text{-}CH_3}$$

$$\underset{\text{Propyne}}{CH_3\text{-}C{\equiv}CH + H_2} \xrightarrow{Ni} \underset{\text{Propene}}{CH_3\text{-}CH{=}CH_2} \xrightarrow{H_2/Ni} \underset{\text{Propane}}{CH_3\text{-}CH_2\text{-}CH_3}$$

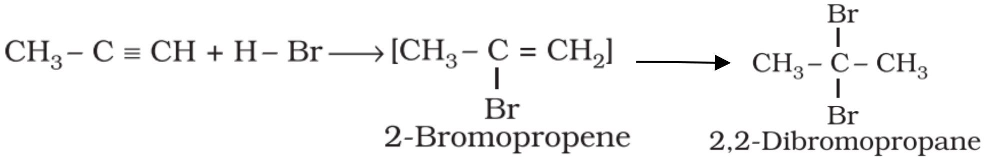
   - *ii.* ***Addition of halogen:***

$$\underset{\text{Ethyne}}{CH{\equiv}CH} + Br_2 \xrightarrow{CCl_4} \underset{\text{1,2-dibromoethane}}{CHBr{=}CHBr} \xrightarrow{Br_2/CCl_4} \underset{\text{1,1,2,2-tetrabromoethane}}{CHBr_2\text{-}CHBr_2}$$

Reddish orange colour of the solution of bromine in carbon tetrachloride is decolourised. This is used as a test for unsaturation.

iii. Addition of hydrogen halide:

$$CH\equiv CH + HBr \rightarrow CH_2=CHBr \xrightarrow{HBr} \underset{\text{(gem-dihalide)}}{CH_3\text{-}CHBr_2}$$



$$CH_3-C\equiv CH + H-Br \longrightarrow \underset{\text{2-Bromopropene}}{[CH_3-\underset{Br}{C}=CH_2]} \longrightarrow \underset{\text{2,2-Dibromopropane}}{CH_3-\overset{Br}{\underset{Br}{C}}-CH_3}$$

iv. Addition of water:

On warming with water, alkynes add one molecule of water in presence of dil. H_2SO_4 and mercuric sulphate at 333K to form carbonyl compounds (aldehydes or ketones). Acetylene gives acetaldehyde, while all other alkynes give ketones during this reaction.

$$\underset{\text{Acetylene}}{CH\equiv CH + H_2O} \xrightarrow{\text{Dil.}H_2SO_4/HgSO_4/333\text{ K}} CH_2=CH\text{-}OH \xrightarrow{\text{Isomerisation}} \underset{\text{Ethanal (Acetaldehyde)}}{CH_3\text{-}CHO}$$

$$\underset{\text{(Propyne)}}{CH_3\text{-}C\equiv CH + H_2O} \xrightarrow{HG^{2+}/H^{+}/333\ K} \underset{\text{(Propanone or acetone)}}{CH_3\text{-}CO\text{-}CH_3}$$

3. **Polymerisation**

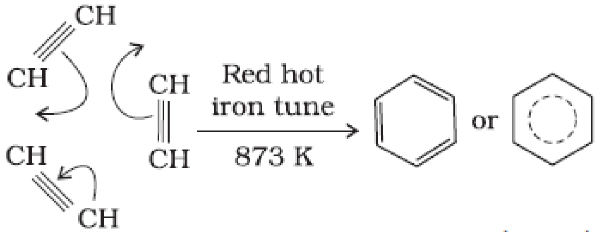
a) ***Linear polymerisation***: Ethyne undergoes linear polymerisation under suitable conditions to form polyethyne or polyacetylene.

$$\underset{\text{acetylene (Ethyne)}}{n\ CH\equiv CH} \xrightarrow{\text{Polymerisation}} \underset{\text{Polyacetylene (Polyethyne)}}{-\!\!\left(CH=CH-CH=CH\right)_n\!\!-}$$

Under special conditions, this polymer conducts electricity. Thin film of polyacetylene can be used as electrodes in batteries. These films are good conductors, lighter and cheaper than the metal conductors.

b) ***Cyclic polymerisation***: Ethyne (acetylene) on passing through red hot iron tube at 873K, undergoes cyclic polymerisation to form benzene (C_6H_6).

$$3\ C_2H_2 \xrightarrow{\text{Red hot Iron tube/873 K}} C_6H_6 \quad \text{OR,}$$



AROMATIC HYDROCARBONS (ARENES)

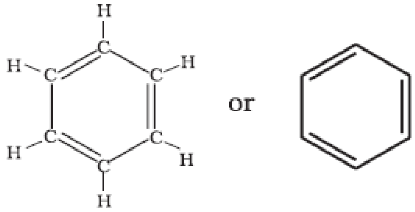
Most of the aromatic compounds have pleasant smell (In Greek aroma means pleasant smelling) and most of them contain benzene ring. *Aromatic compounds containing benzene ring are called* ***benzenoid compounds*** *and those which do not contain benzene ring are called* ***non-benzenoid compounds***.

Structure of Benzene

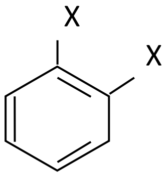
Benzene was first isolated by Michael Faraday and its structure was first deduced by August Kekulé.

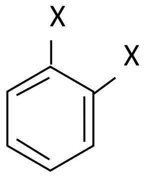
The molecular formula of benzene is C_6H_6, which indicates a high degree of unsaturation. But benzene was found to be a stable molecule and form a triozonide which indicates the presence of three double bonds. Also it produces only one monosubstituted derivative which indicates that all the six carbon and six hydrogen atoms of benzene are identical.

On the basis of these observations, *August Kekulé* proposed the following structure for benzene having cyclic arrangement of six carbon atoms with alternate single and double bonds.



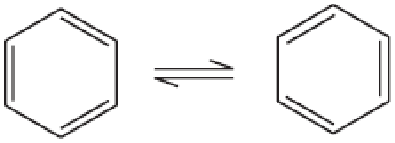
The *Kekule structure* indicates the possibility of two isomeric 1,2-disubstituted derivatives.





But actually these two structures are identical or, benzene forms only one 1,2,-disubstituted derivative.

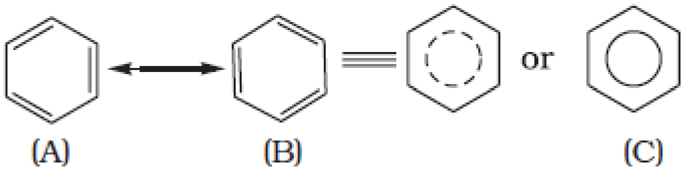
In order to overcome this problem, Kekule suggested the concept of oscillating nature of double bonds in benzene.



Kekule structure could not explain the stability of benzene and the preference of benzene to substitution reaction rather than addition reaction.

Resonance concept of Benzene

According to this concept, benzene is a hybrid of the following two resonance structures.

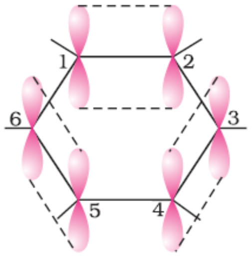


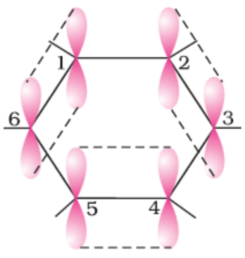
The actual structure of benzene is not A or B. It is in between these two resonating structures. So benzene is denoted by a hexagon with a dotted circle, which represents the delocalised π-electrons.

Orbital Overlap Concept of Benzene

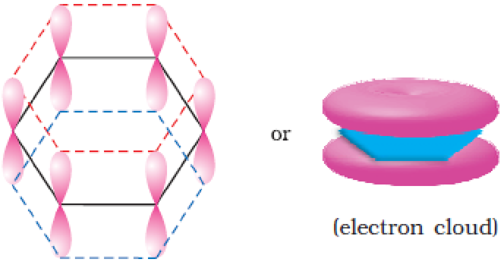
In Benzene all the six carbon atoms are sp^2 hybridized. Two sp^2 hybrid orbitals of each carbon atom overlap with sp^2 hybrid orbitals of adjacent carbon atoms to form six C—C sigma bonds which are in the hexagonal plane. The remaining one sp^2 hybrid orbital of each carbon atom overlaps with 1s orbital of hydrogen atom to form six C—H sigma bonds.

Now each carbon atom contains one unhybridised p orbital perpendicular to the plane of the ring. They overlap laterally to form three π-bonds. There are two possible overlapping.

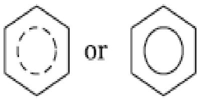




These give two Kekule structures with localized π electrons. But in benzene all the C-C bonds are identical and the bond length is 139 pm. To explain this, it is suggested that the p-orbitals of all the C atoms overlap each other. Thus in benzene, there is an electron cloud in the form two rings one above and one below the hexagonal ring as follows:



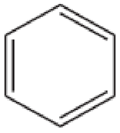
So the six π electrons are delocalised and can move freely about the six carbon nuclei. Presence of delocalised π electrons in benzene makes it more stable. The delocalised π electrons can be denoted by a circle inside a hexagonal ring.
So benzene is best represented as:



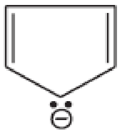
Aromaticity – Huckel Rule

Aromaticity is defined by a rule called 'Huckel rule'. According to this rule, "cyclic, planar systems containing (4n+2) delocalised π electrons are aromatic". Where n is an integer. n may be 0,1,2,3,……

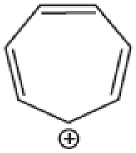
For benzene n = 1, so it should contain 6 delocalised π electrons. If n = 2, the number of delocalised π electrons =10 and so on. Example for some aromatic compounds are:



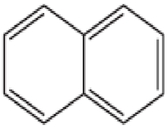
Benzene



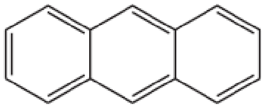
Cyclopentadienyl anion



Cycloheptatrienyl cation



Naphthalene

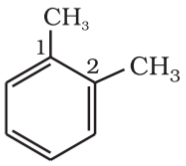


Anthracene

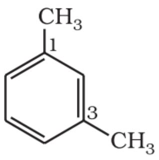
Isomerism in Disubstituted benzene

There are three position isomers for disubstituted benzene. It can be 1,2 or 1,3 or 1.4 isomers. 1,2 disubstituted isomer is called ortho isomer, 1,3 isomer is called meta isomer and 1,4 isomer is called para isomer.

E.g. xylene (Dimethyl benzene)



1,2-Dimethylbenzene
(*o*-Xylene)



1,3 Dimethylbenzene
(*m*-Xylene)

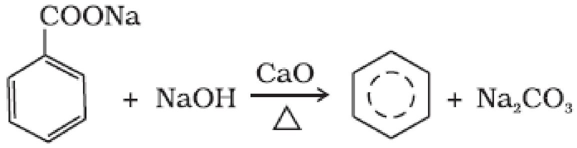
1,4-Dimethylbenzene
(*p*-Xylene)

Preparation of Benzene

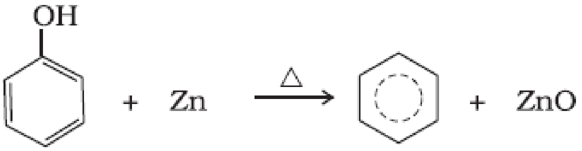
1. ***Cyclic polymerisation of ethyne (acetylene):*** When acetylene gas is passed mthrough red hot iron tube at 873 K, we get benzene.

$$3\ C_2H_2 \xrightarrow{\text{Red hot Iron tube/873 K}} C_6H_6$$

2. ***Decarboxylation of aromatic acids:*** Sodium salt of benzoic acid on heating with sodalime gives benzene.



3. ***Reduction of phenol:*** Phenol vapours are passed over heated zinc dust, it is reduced to benzene.



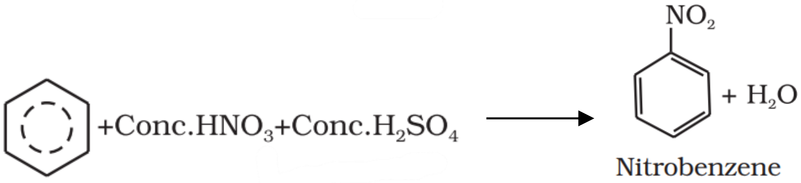
Chemical Properties

Aromatic compounds generally undergo electrophilic substitution reactions. Under special conditions, they can also undergo addition and oxidation reactions.

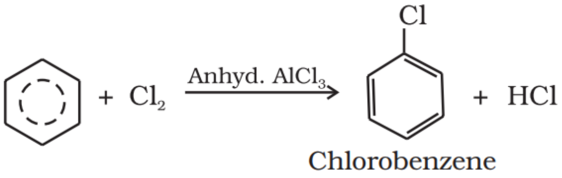
I) Electrophilic Substitution Reactions

These are reactions in which a weak electrophile is replaced by a strong electrophile. The important electrophilic substitution reactions are Nitration, Sulphonation, Halogenation and Friedel-Crafts alkylation and acylation.

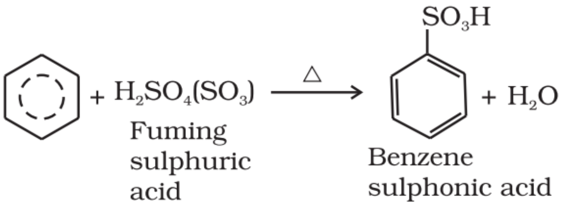
1. ***Nitration***: It is the introduction of nitro (-NO_2) group to a benzene ring. For this benzene is heated with a mixture of conc. HNO_3 and conc. H_2SO_4 (nitrating mixture).



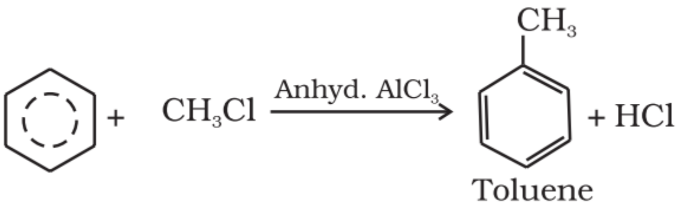
2. ***Halogenation***: It is the introduction of halo (-X) group to a benzene ring. For this benzene is treated with a halogen (Cl_2 or Br_2) in presence of Lewis acids like anhydrous $FeCl_3$, $FeBr_3$ or $AlCl_3$.



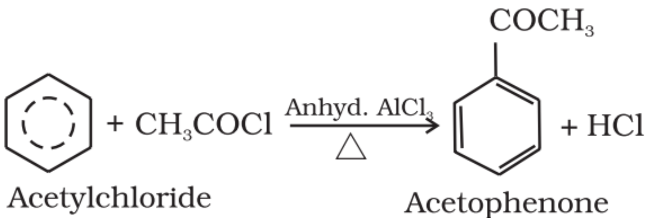
3. ***Sulphonation***: It is the introduction of sulphonic acid (-SO_3H) group to a benzene ring. It is carried out by heating benzene with fuming sulphuric acid ($H_2S_2O_7$ or oleum).

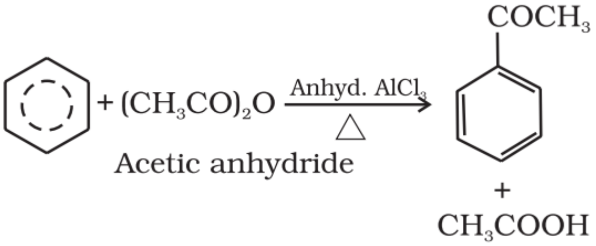


4. ***Friedel-Craft's reaction***: It is the introduction of alkyl (-R) group or acyl (-CO-R) group to a benzene ring. It is of two types:
   a) ***Friedel-Craft's Alkylation reaction:*** It is the introduction of alkyl (-R) group to a benzene ring. Here the reagents used are alkyl halide in presence of anhydrous $AlCl_3$.

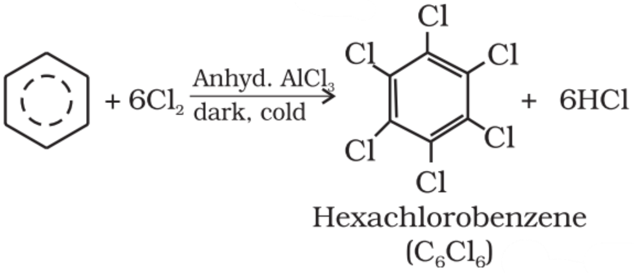


   b) ***Friedel-Craft's Acylation reaction***: It is the introduction of acyl (-CO-R) group to a benzene ring. Here the reagents used are acyl halide in presence of anhydrous $AlCl_3$.



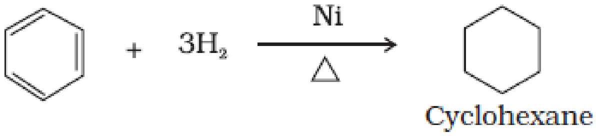


5. Benzene on treatment with excess of chlorine in the presence of anhydrous $AlCl_3$ in dark to form hexachlorobenzene (C_6Cl_6).

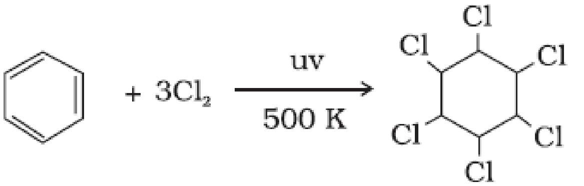


II) **<u>Addition Reactions</u>**

1. ***Addition of H_2***: Benzene add hydrogen in presence of nickel catalyst at high temperature and pressure to form cyclohexane.



2. ***Addition of halogen***: Benzene adds chlorine in presence of uv light or at 500K to form benzene hexachloride (BHC). It is also known as Gammaxane or Lindane or 666.

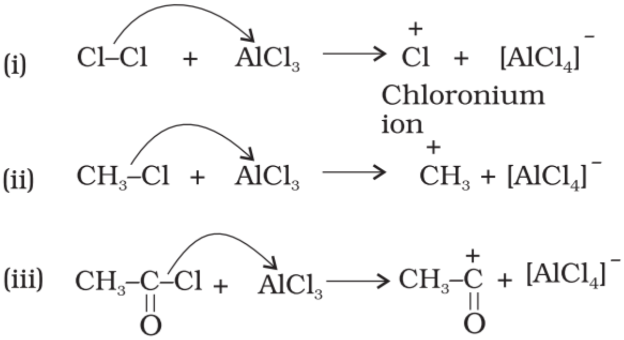


Benzene hexachloride,
(BHC)

Mechanism of Electrophilic substitution reactions

Electrophilic substitution reactions proceed through three steps: (a) Generation of the eletrophile (b) Formation of carbocation intermediate (c) Removal of proton from the carbocation intermediate.

(a) **Generation of the Electrophile**: In chlorination, alkylation and acylation of benzene, anhydrous $AlCl_3$ helps in the generation of the electrophile Cl^+(chloronium ion) , R^+ (carbocation), RCO^+ (acylium ion) respectively by combining with the attacking reagent.



(i) $Cl{-}Cl + AlCl_3 \longrightarrow \overset{+}{Cl} + [AlCl_4]^-$

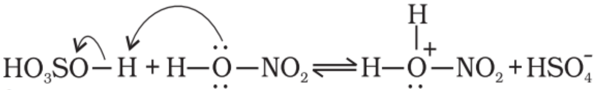
Chloronium ion

(ii) $CH_3{-}Cl + AlCl_3 \longrightarrow \overset{+}{C}H_3 + [AlCl_4]^-$

(iii) $CH_3{-}\underset{\underset{O}{\|}}{C}{-}Cl + AlCl_3 \longrightarrow CH_3{-}\underset{\underset{O}{\|}}{\overset{+}{C}} + [AlCl_4]^-$

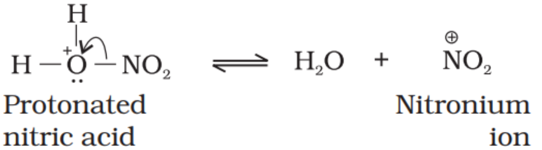
In the case of nitration, the electrophile, nitronium ion (NO_2^+) is produced by the transfer of a proton (from sulphuric acid) to nitric acid in the following manner:

Step I



$HO_3SO{-}H + H{-}\ddot{O}{-}NO_2 \rightleftharpoons H{-}\overset{\overset{H}{|}}{\overset{+}{O}}{-}NO_2 + HSO_4^-$

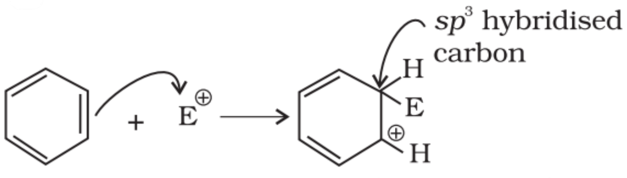
Step II



$H{-}\overset{\overset{H}{|}}{\overset{+}{O}}{-}NO_2 \rightleftharpoons H_2O + \overset{\oplus}{N}O_2$

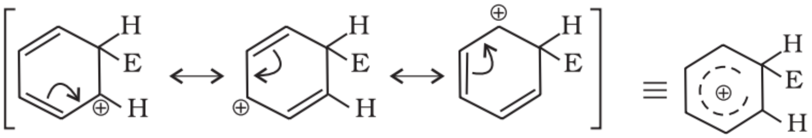
(b) **Formation of Carbocation (arenium ion):**

Attack of electrophile results in the formation of σ-complex or arenium ion.

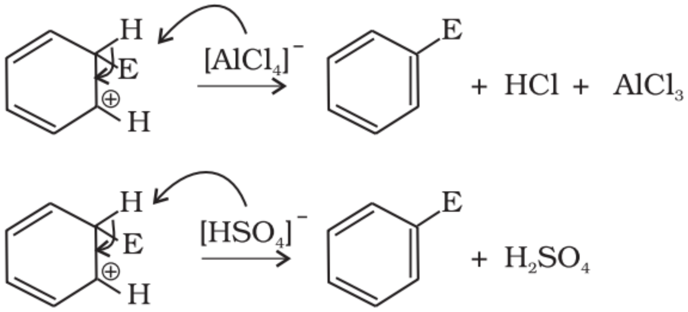


sigma complex (arenium ion)

The arenium ion gets stabilised by resonance:



(c) Removal of proton: To restore the aromatic character, σ -complex releases proton.



Directive influence of a functional group in mono-substituted benzene

When monosubstituted benzene undergoes further substitution, two types of products are formed - either ortho and para products or meta product. This behaviour depends on the nature of the substituent already present in the benzene ring. This is known as directive influence of substituents.

Based on the directive influence, there are two types of substituents – **ortho and para directing groups and meta directing groups**.

1. ***Ortho and para directing groups***: The groups which direct the incoming group to ortho and para positions are called ortho and para directing groups.

Example for such groups are -X, –OH, –NH_2, –NHR, -$NHCOCH_3$, –OCH_3, –CH_3, –C_2H_5 etc.

Generally, ortho-para directing groups are **activating groups**, since they increases the electron density on benzene ring. Or, they activate the benzene ring for the attack by an electrophile.

Halogens are deactivating eventhough they are ortho-para directing. This is because of their strong –I effect.

2. ***Meta direcing groups***: The groups which direct the incoming group to meta position are called meta directing groups. They are generally deactivating groups, since they reduces the electron density on benzene ring.

Examples are –NO_2, –CN, –CHO, –COR, –COOH, –COOR, –SO_3H, etc.

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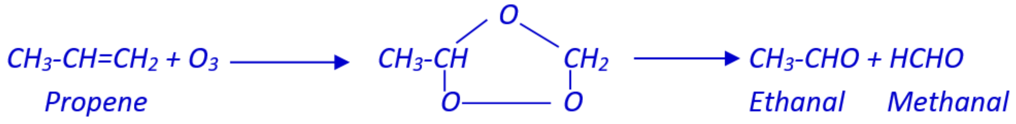
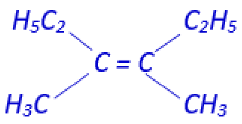
Q1) *An alkene on ozonolysis followed by reduction of the ozonide formed with zinc and water gave a mixture of ethanal and methanal. Identify the alkene. Illustrate the above mentioned reaction using the chemical equation.*

Ans: Propene

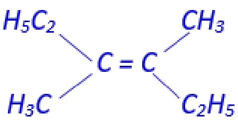


Q2) *Draw the cis and trans isomers of the following compound: C_2H_5-$C(CH_3) = C(CH_3)$-C_2H_5.*

Ans:



Cis-isomer



Trans-isomer

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