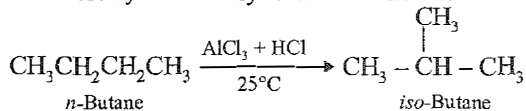


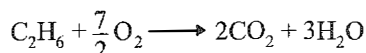
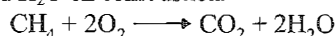
Hydrocarbons

- Isomerization** : In this reaction straight chain alkanes on heating in presence of AlCl_3 and dry HCl gas are converted into more symmetrically stable branched chain alkane.

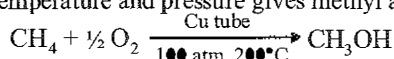


- Oxidation** : Oxidation of alkanes gives different products according to reaction conditions and catalyst used.

Complete oxidation (Combustion) : Alkanes produce CO_2 and H_2O on combustion.

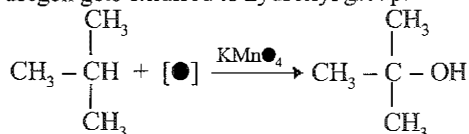


Incomplete combustion/controlled oxidation : A mixture of methane and oxygen on passing over a copper tube under high temperature and pressure gives methyl alcohol.

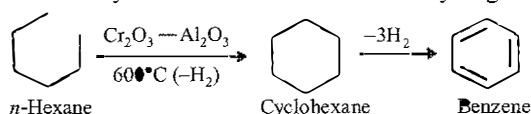


This method is used for industrial preparation of methyl alcohol.

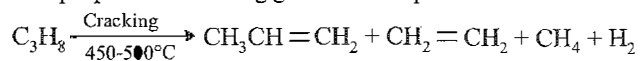
With potassium permanganate (KMnO_4) a tertiary hydrogen gets oxidised to hydroxyl group.



- Aromatization** : Alkanes containing six to ten carbon atoms are converted into benzene and its homologues at high temperature in the presence of catalyst. Aromatization involves cyclisation isomerisation and dehydrogenation.



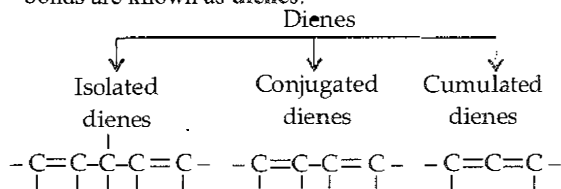
- Pyrolysis/Cracking/Thermal Decomposition** : Decomposition of a compound by application of heat is known as pyrolysis. But when applied to alkanes, the process is known as cracking and leads to formation of lower alkanes, alkenes and hydrogen. For example, propane on cracking gives various products.



Mechanism of cracking is believed to be free-radical mechanism.

ALKENES

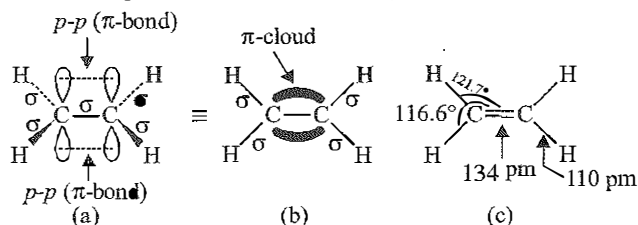
- Organic compounds containing $\text{C}=\text{C}$ are known as alkenes. General formula C_nH_{2n} . Alkenes with two double bonds are known as dienes.



Structure of Double Bond

- In ethene carbon atom having sp^2 hybridised orbitals, one of the p -orbitals remains unhybridised. The three

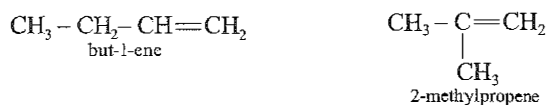
sp^2 hybrid orbitals are inclined to each other at an angle of 120° and lie in a plane. The unhybridised p orbital is at right angle to this plane. All the four ($3 sp^2$ -hybrid + 1 unused p -orbitals) orbitals are singly occupied. Two of the hybrid orbitals on each carbon atom overlap with $1s$ orbitals of two H-atoms to form $\text{C}-\text{H}$ bonds. The third sp^2 hybrid orbital of one carbon overlaps with the similar orbital of the other carbon to form a sigma $\text{C}-\text{C}$ bond. The two unutilised p -orbitals at right angles to the plane containing hybrid orbitals are parallel to each other and overlap sideways to form a pi (π) $\text{C}-\text{C}$ bond.



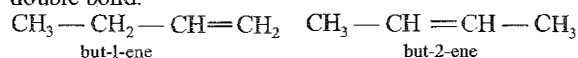
Isomerism

- Alkenes show four types of isomerisms, viz.,
 - Chain isomerism
 - Position isomerism
 - Geometrical isomerism
 - Functional isomerism
 These are described below :

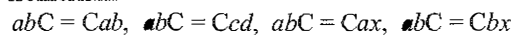
- Chain isomerism** : This is due to the difference in the structure of the carbon chain. For example, but-1-ene and 2-methylpropene are chain isomers.



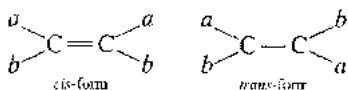
- Position isomerism** : Position isomerism in alkenes arises from the difference in the position of the double bond in the same chain. But-1-ene is a position isomer of but-2-ene because these differ only in the position of the double bond.



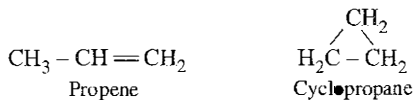
- Geometrical isomerism** : When two carbon atoms are joined by a double bond, they cannot rotate freely. As a result, the relative positions of the various groups attached to these carbon atoms get fixed and give rise to geometrical isomers. Such compounds which possess the same structural formula but differ in the spatial arrangement of the groups about a double bond are called geometrical isomers and the phenomenon is known as the geometrical isomerism. This type of isomerism is also known as *cis-trans isomerism*. The necessary and sufficient condition for a compound to exhibit geometrical isomerism is that the two groups attached to the same carbon must be different, i.e., alkenes of the following types show *cis-trans isomerism*.



- In the *cis*-form, the groups or atoms of higher priority lie on the same side of the double bond.
- In the *trans*-form, the groups or atoms of higher priority lie on the opposite sides of the double bond.



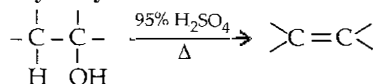
- Functional isomerism** : Alkenes and cycloalkanes have the same molecular formula (C_nH_{2n}). The cycloalkanes do not behave as unsaturated hydrocarbons. Therefore, alkenes and cycloalkanes are termed functional isomers. For example, propene is isomeric with cyclopropane (or trimethylene).



In alkenes, the functional group is the double bond, while in cycloalkanes, it is the closed ring which represents the functional group.

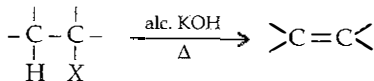
Methods of Preparation

- By dehydration of alcohols** :

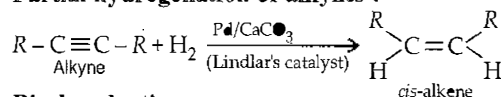


Saytzeff rule : If a single starting compound can yield two or more isomers then more substituted alkene is formed in greater amount.

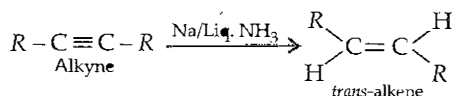
- By dehydrohalogenation of alkyl halides** :



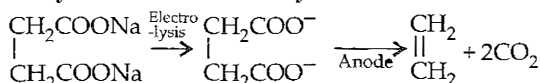
- Partial hydrogenation of alkynes** :



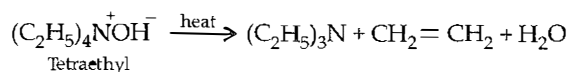
- Birch reduction** :



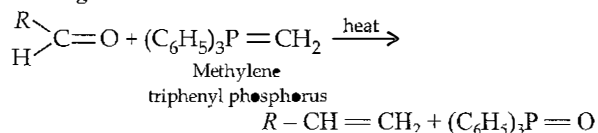
- Electrolysis of salt of dicarboxylic acids** :



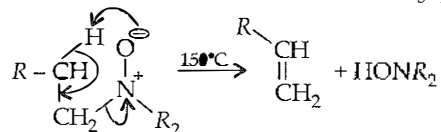
- Hofmann elimination** :



- Wittig reaction** :



- Cope reaction** :



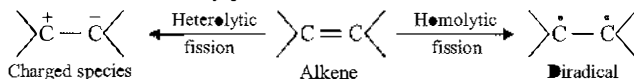
Physical Properties

- Physical State** : $C_2 - C_4$ gases, $C_5 - C_{17}$ liquids, C_{18} onwards solids.

- Colour and odour** : All are colourless, all are odourless except ethene. [Ethene : Pleasant odour]
- Solubility** : Insoluble in water, soluble in organic solvents.
- Boiling point and Melting point** : Gradual increase with increase in molecular mass. b.pt. of *cis*-isomer > b.pt. of *trans*-isomer.

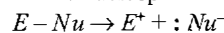
Chemical Properties

- The most important reactions of alkenes are the addition reactions. Alkenes are reactive due to the presence of double bond. The π -electrons are loosely held and are, therefore, easily polarisable.

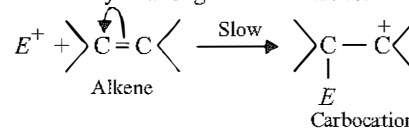


Ionic Mechanism

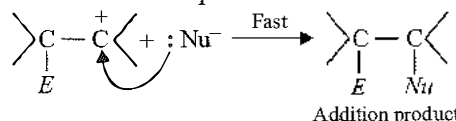
- 1st step** : The reagent $E - Nu$ ionises to give an electrophile and nucleophile.



- 2nd step** : The electrophile attacks the carbon-carbon double bond and forms a covalent bond with one of the carbon atoms by utilising the π -electrons.

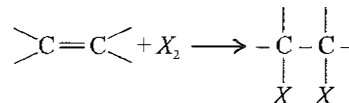


- 3rd step** : The nucleophile now attacks the carbocation to form an addition product.

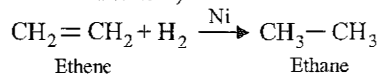


As the addition reaction is initiated by an electrophile, the reaction is termed as electrophilic addition.

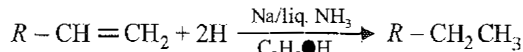
- Addition of halogens** : Alkenes readily add on the halogens in the presence of an inert solvent to form 1, 2 or vicinal dihalides.



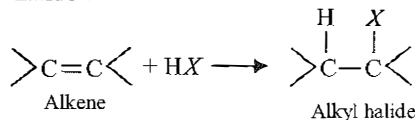
- Addition of dihydrogen (H_2) (Hydrogenation)** : Alkenes undergo hydrogenation in presence of catalyst like Ni, Pt, Pd, etc., to form corresponding alkane. (Sabatier and Sandereen's reduction.)



- Birch reduction** :

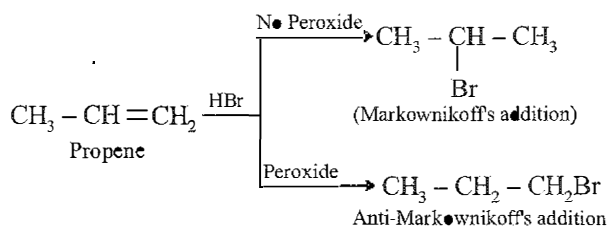


- Addition of hydrogen halide** : Alkenes react with hydrogen halides or halogen acids to give corresponding alkyl halides.

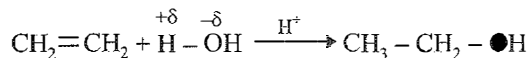


Hydrocarbons

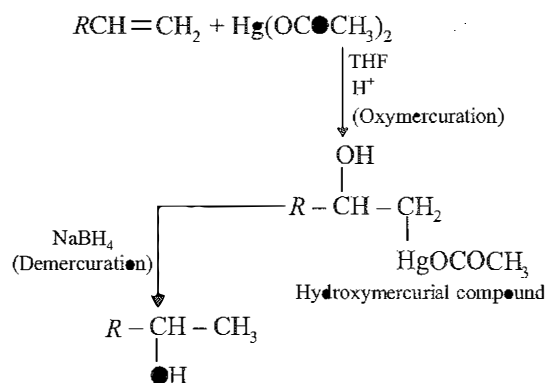
- **Markownikoff's rule** : It states that during the addition of unsymmetrical reagent such as HX, HOH, HOX, etc. to unsymmetrical alkene, the positive part of the addendum (i.e., molecule to be added) goes to less substituted carbon atom of double bond i.e. carbon atom of the double bond which carries greater number of hydrogen atoms.
- **Peroxide effect or Kharasch effect** : Kharasch and Mayo in 1933 observed that addition of HBr to an unsymmetrical alkene in presence of peroxides such as benzoyl peroxide gives the product contrary to Markownikoff's rule. It is known as anti-Markownikoff's addition.



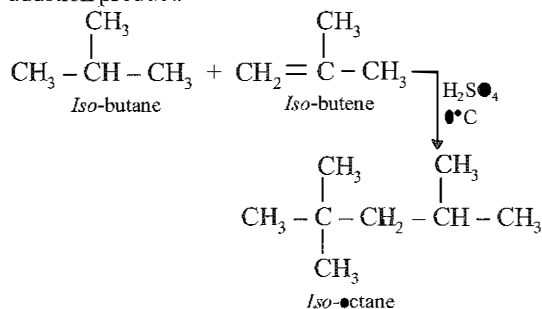
- **Addition of water** :
 - ♦ **Direct hydration of alkenes** : Water molecule adds up to the alkene in presence of some mineral acid, to yield alcohol. Addition takes place in accordance with Markownikoff's rule.



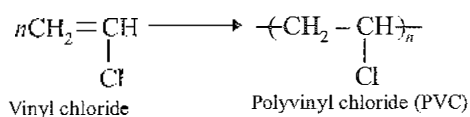
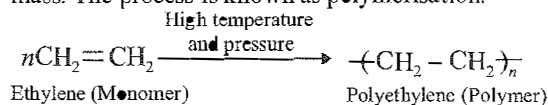
- ♦ **Oxymercuration-demercuration** : Reaction of alkenes with mercuric acetate in presence of water followed by reduction with sodium borohydride also results in hydration of alkene according to Markownikoff's rule.



- **Addition of alkanes** : Alkanes add on to alkenes in presence of acid catalyst such as H₂SO₄ or HF to give addition product.

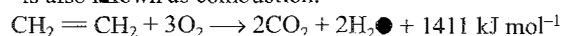


- **Self addition or polymerization** : Alkene molecules link together in presence of acid catalyst at high temperature and pressure to give new bigger molecule with high molecular mass. The process is known as polymerisation.



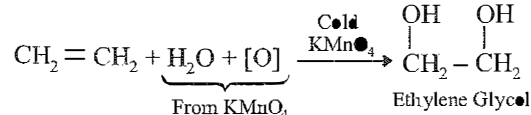
- **Oxidation reactions of alkenes** : Oxidation of alkenes yields different products under different conditions.

- ♦ **Complete oxidation (combustion)** : Alkenes oxidise completely in air to yield CO₂ and H₂O. The reaction is also known as combustion.



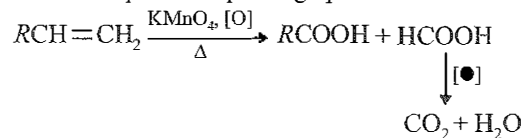
- ♦ **Oxidation with potassium permanganate** : On oxidation with KMnO₄, different products are obtained depending upon reaction conditions.

Oxidation with cold dilute neutral or alkaline KMnO₄ : Alkenes on reaction with cold dilute neutral or alkaline KMnO₄ get hydroxylated to form 1, 2 glycols or 1, 2-diols.

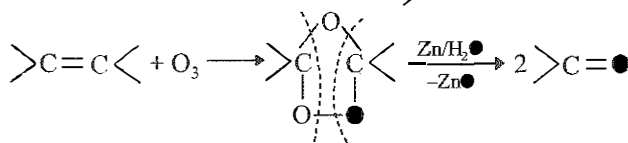


Cold alkaline KMnO₄ is known **Baeyer's reagent** and the test is known as **Baeyer's test**.

Oxidation with hot KMnO₄ : On reaction with hot alkaline KMnO₄ or higher conc. of KMnO₄ or acidic KMnO₄, alkenes are oxidatively cleaved leading to the formation of different compounds depending upon structure of alkene.



- **Ozonolysis of alkenes** : Ozone on passing through a solution of alkenes in an inert solvent like CCl₄ or CHCl₃ at low temperature oxidises the alkene to a cyclic product called ozonide which is unstable and on reduction with reducing agents like zinc and water or hydrogen in presence of palladium gives aldehydes and or ketone depending upon structure of alkene, i.e. >C = part of the alkene which get converted to >C = O.

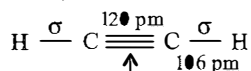


ALKYNES

- Alkynes are unsaturated hydrocarbons which contain a carbon-carbon triple bond (C ≡ C). The general formula of alkynes is C_nH_{2n-2}, where n is 1, 2, Alkynes were earlier called *acetylenes*.

Structure of Triple Bond in Alkynes

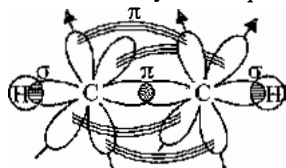
- Alkynes can be described by the condensed formula $R-C\equiv C-R$ where R may be an alkyl group or H. The simplest member of this homologous series (putting, $n = 2$) has the molecular formula C_2H_2 .



one σ -bond + two π -bonds

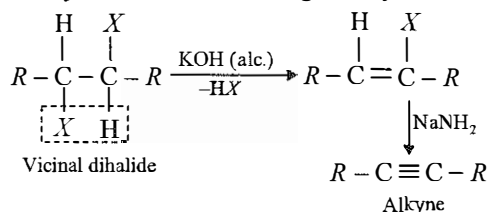
The triple bond present in alkynes $-C\equiv C-$ is the functional group for alkynes. The properties of alkynes are largely determined by the triple bond ($-C\equiv C-$). In ethyne (or in alkynes in general), the triple-bonded carbon atoms exhibit sp hybridisation. Therefore, ethyne molecule is a linear molecule.

In ethyne (acetylene, C_2H_2 or $HC\equiv CH$), atomic orbitals of carbon are sp hybridised. The two hybrid orbitals are inclined to each other at an angle of 180° . The other two unused p -orbitals lie at right angles to the hybrid orbitals and also to each other. Each of the four orbitals (two hybrid and two unused p -orbitals) contains only one electron. The unused p -orbitals lying parallel to each other give rise to two π bonds due to sideways overlap.

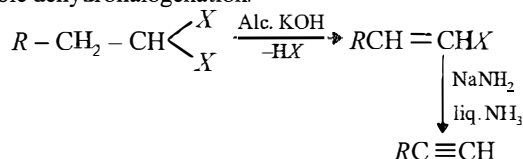


Methods of Preparation

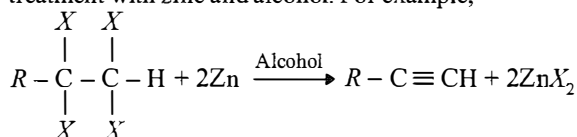
- Dehydrohalogenation of vicinal dihalides** : Alkynes can be prepared from vicinal dihalides by treatment with a base so that two molecules of hydrogen halide get eliminated from adjacent carbon atoms to give alkynes.



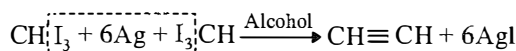
- Dehydrohalogenation of geminal dihalides** : Geminal dihalides on treatment with base also give alkyne, by double dehydrohalogenation.



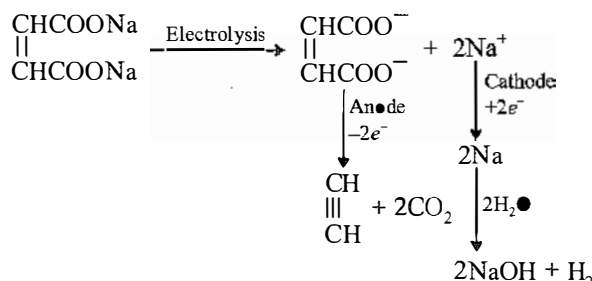
- Dehalogenation of tetrahalides** : Alkynes may also be prepared by dehalogenation of 1,1,2,2-tetrahalides on treatment with zinc and alcohol. For example,



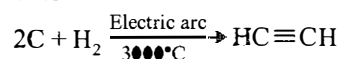
- Reaction of iodoform with silver** : Iodoform on heating with silver powder gives pure acetylene.



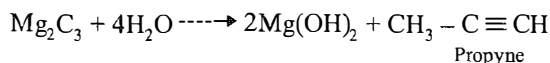
- Kolbe's electrolysis** : Electrolysis of concentrated solution of sodium or potassium salt of maleic or fumaric acid gives acetylene at anode.



- Synthesis from C and H₂ (Berthelot's synthesis)** : Acetylene can also be prepared by passing a stream of hydrogen through electric arc between carbon electrodes.



- Industrial preparation of acetylene (Wohler's reaction)** : Acetylene is prepared by action of water on calcium carbide.



Physical Properties

- Physical State** : $C_2 - C_4$ colourless gases
 $C_5 - C_{13}$ liquid, C_{14} onwards solids
- Polarity** : Weakly polar and lighter than water.
- Solubility** : Insoluble in water but highly soluble in organic solvents.
- Melting point and Boiling point** : Higher than corresponding alkane and alkene. Boiling points and melting points increases with increase in molecular mass.
- Order of B.pt, M.pt** : Alkynes > Alkenes > Alkanes

Chemical Properties

- Acidic nature** : Acetylene is acidic in nature. The acidity can be explained on the basis of percentage s -character of the hybrid orbitals. As s -character increases acidic nature increases.

Acidic nature : Alkyne > Alkene > Alkane

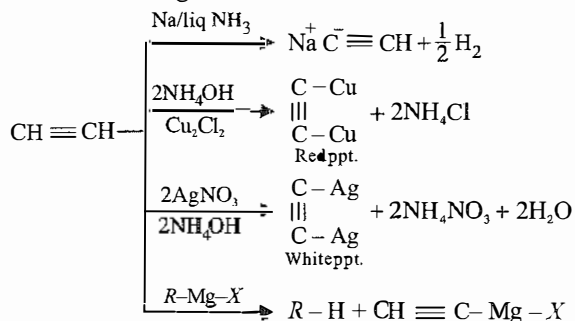
Hybridisation : sp sp^2 sp^3

s -character : 50% > 33.3% > 25%

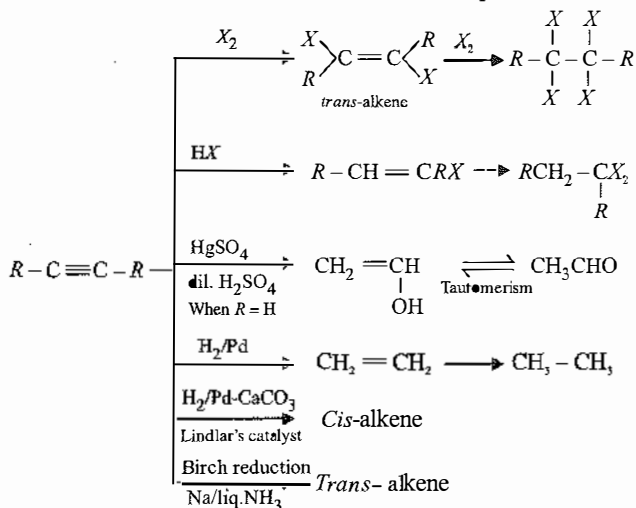
The electrons of the $C-H$ bond in acetylene are strongly held by carbon nuclei. This facilitates removal of H-atom.

Acidic nature : $\text{HOH} > \text{ROH} > \text{HC}\equiv\text{CH} > \text{NH}_3 > \text{RH}$

Reactions showing acidic nature :



- **Addition Reactions :** Reactions are electrophilic addition.



AROMATIC HYDROCARBONS

- Aromatic hydrocarbons are now called arenes. Benzene is the simplest aromatic hydrocarbon.
- Arenes are the aromatic hydrocarbons which contain one or more benzene rings. Benzene ring is a six-membered ring containing carbon atoms linked to each other with an alternate single and double bonds. Arenes contain higher proportion of carbon as compared to the aliphatic hydrocarbons and constitute a unique class of unsaturated hydrocarbons.
- Arenes can be described by the general formula $\text{C}_n\text{H}_{2n-6m}$, where n is the number of carbon atoms and m is the number of benzene rings.

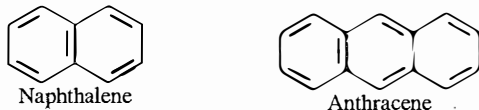
For monocyclic arenes, $m = 1$ and $n = 6$, or more.

e.g.



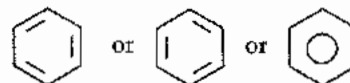
For bicyclic arenes, $n = 10$, $m = 2$

e.g.



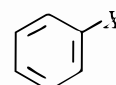
- **Nomenclature of aromatic compounds :** The aromatic compounds has two main parts :

Nucleus : It is benzene ring where all the six carbon atoms are in sp^2 hybridized state as there is alternate double and single bond. It is represented as

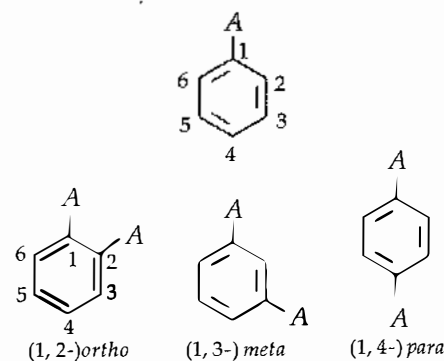


Side chain : Alkyl or any other aliphatic group attached to benzene nucleus is called side chain. This is obtained by replacing one or more hydrogen atoms in the ring by alkyl groups.

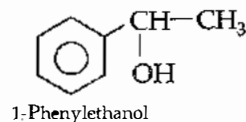
Monosubstituted derivatives : If one of the hydrogen atom of ring is substituted by an alkyl radical or a group then it is called as monosubstituted derivative.



Disubstituted derivatives : The position of second substituent with respect to first one will form different forms. For example 2nd and 6th positions of a ring with respect to first are called *ortho*-positions. 3rd and 5th positions of a ring with respect to first one are called *meta*-positions and 4th position of ring is called as *para*-position.

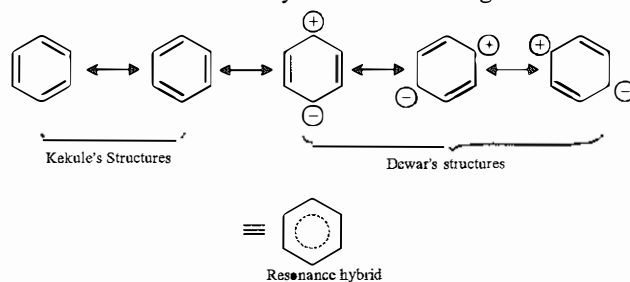


If side chain contains a functional group, then these are said to be phenyl derivatives of the corresponding aliphatic compounds.

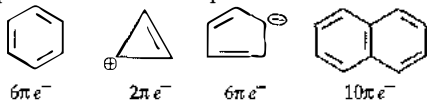


- **Resonance :** When a molecule can be given several molecular structures but none of them represents it completely, the molecule is said to be a resonance hybrid of those structures and the phenomenon is called resonance.

Benzene is a resonance hybrid of the following five structures:

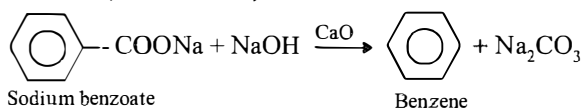


- **Aromaticity or Huckel rule** : A compound is said to be aromatic if it meets all of the following criteria.
 - ♦ Aromatic compounds contain one or more rings that have a cyclic arrangement of p -orbitals.
 - ♦ Aromatic rings are planar.
 - ♦ Aromatic systems are conjugated cyclic systems.
 - ♦ Aromatic systems must contain $(4n + 2)\pi$ electrons used in delocalisation, where $n = \text{integer } (0, 1, 2, \dots)$.
 - ♦ Examples of aromatic compounds :

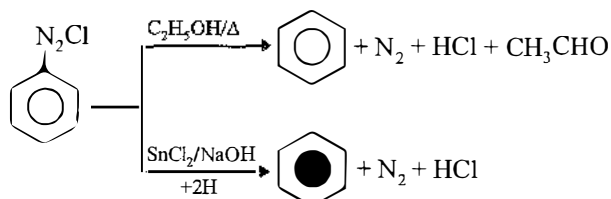
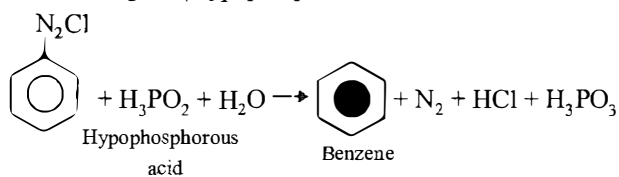


Methods of Preparation

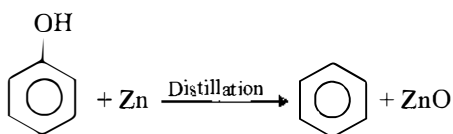
- **Decarboxylation of aromatic acids** : This is a convenient method to prepare benzene in laboratory in which aromatic acids or their sodium or potassium salts are heated with sodalime ($\text{NaOH} + \text{CaO}$).



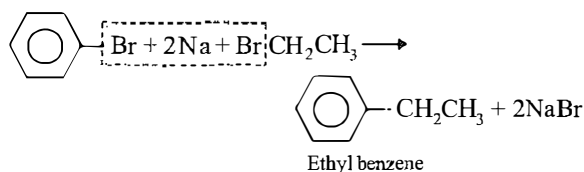
- **Reduction of diazonium salts** : Aryl diazonium salt can be reduced by number of reagents but most powerful one is heating with hypophosphorus acid.



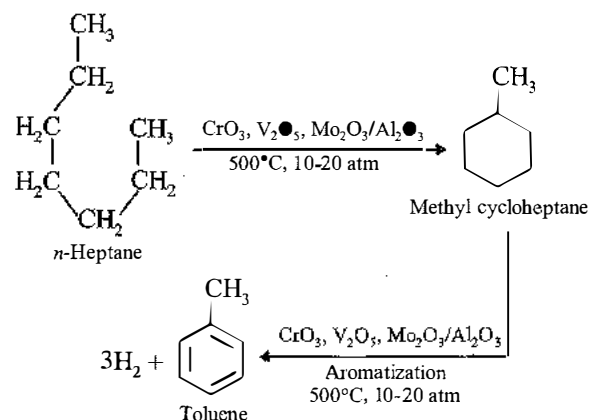
- **Deoxygenation of phenols** : Phenol or derivatives of phenol on distillation with zinc dust yield aromatic hydrocarbons.



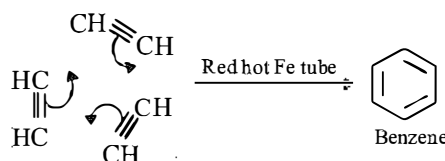
- **Wurtz - Fittig reaction** : In this reaction substituted aromatic hydrocarbons are obtained by the action of sodium metal on a mixture of alkyl halide and aryl halide in ether solution.



- **Cyclisation of long chain alkanes** : Long chain alkanes (C_6 - C_9) on passing over a catalyst generally metal oxide (Cr , V and Mo) supported over alumina at 500°C under pressure get converted into aromatic hydrocarbons. The reaction involves cyclisation followed by aromatization.



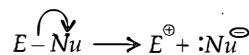
- **Polymerization of alkynes** : Alkynes on passing through red hot iron tube at high temperature undergo polymerization to yield aromatic hydrocarbons.



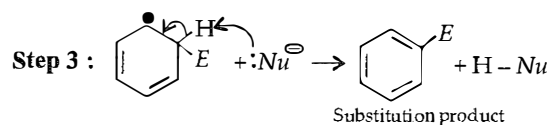
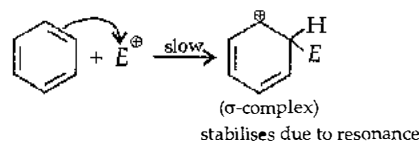
Chemical Properties

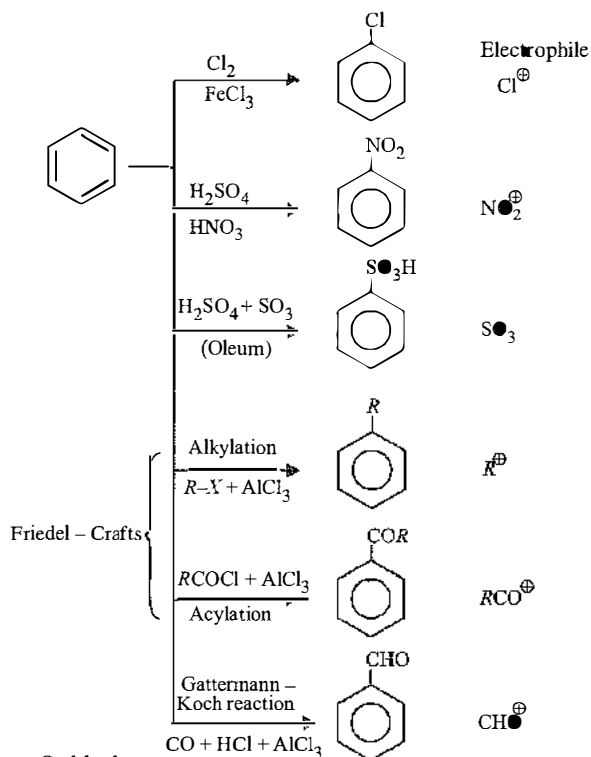
- Aromatic hydrocarbons are less reactive than alkenes and alkynes because their π -electrons are involved in delocalisation and not available for addition reactions. But the benzene ring is electron rich so the electrophile can replace H-atom of the benzene ring. Thus aromatic hydrocarbons undergo electrophilic substitution reactions.
- **Mechanism of electrophilic substitution reactions** : Benzene undergoes substitution because it is an electron rich system due to delocalised π -electrons.

Step 1 : Formation of an electrophile



- **Step 2** : Electrophile attacks on aromatic ring to form σ -complex.



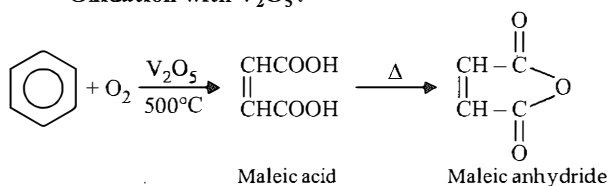


- Oxidation :**

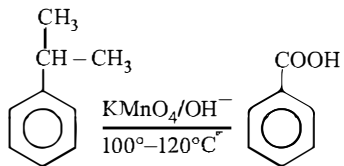
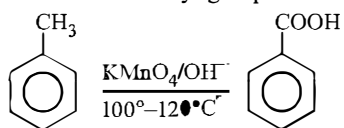
- **Combustion (complete oxidation) :**



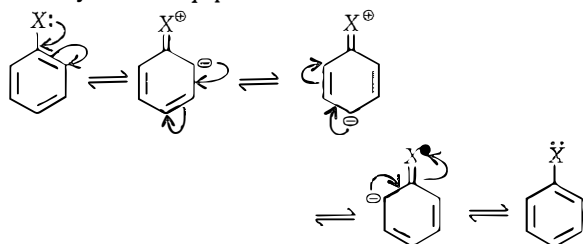
- **Oxidation with V_2O_5 :**



- **Oxidation with KMnO_4 :** Only side chains are oxidised to carboxyl groups.


Directive Influence

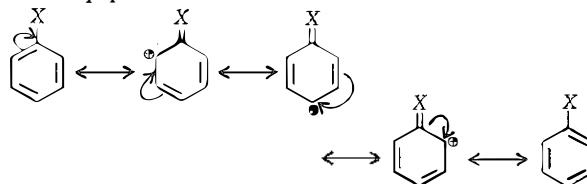
- Groups with positive mesomeric effect ($+M$) increases electron density on *o*- and *p*-positions due to delocalisation.



here X may be $-\text{OH}$, $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$.

Thus electrophile attacks on *o*- and *p*-positions because these are electron rich positions while nucleophile will attack on *meta* position because *m*-position is less electron rich.

- Groups with negative mesomeric effect ($-M$) decreases electron density on *o*- and *p*-positions so electrophile will attack on *meta* position and nucleophile will attack on *o*- and *p*-positions.



Here, X may be $-\text{NO}_2$, $-\text{SO}_3\text{H}$, $-\text{CN}$.

Carcinogenicity and toxicity

- PAH's generally have a low degree of acute toxicity to humans. (Polycyclic Aromatic Hydrocarbons).
- The most significant endpoint of PAH toxicity is cancer.
- Increased incidences of lung, skin and bladder cancers are associated with occupational exposure to PAHs. Data for other sites is much less persuasive.
- PAH's toxicity is very structurally dependent, with isomers (PAHs with the same formula and number of rings) varying from being non-toxic to being extremely toxic.
- One PAH compound, benzo[a]pyrene, is notable for being the first chemical carcinogen to be discovered (and is one of many carcinogens found in cigarette smoke).
- High prenatal exposure to PAH is associated with lower IQ and childhood asthma.
- Some PAH's known for their carcinogenic, mutagenic and teratogenic properties are

| | |
|-------------------------|--|
| Benzo[<i>a</i>]pyrene | |
| Chrysene | |
| Coronene | |
| Pyrene | |
| Triphenylene | |
| Ovalene | |