

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 at least 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.

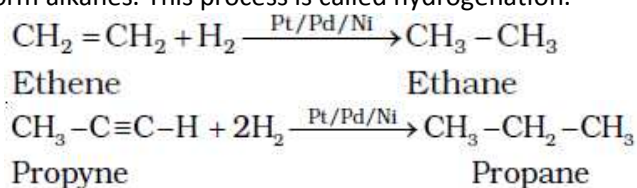
ALKANES

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).

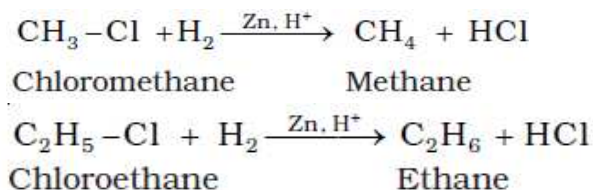
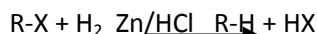
Preparation of alkanes

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.



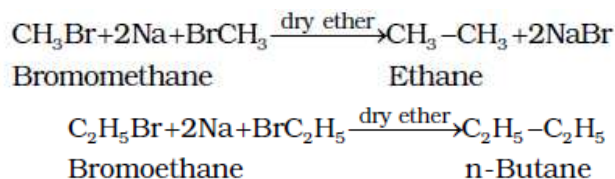
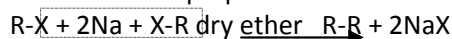
2. **From alkyl halides:**

- a) Alkyl halides on reduction with zinc and dil. HCl, we get alkanes.



- b) **Wurtz reaction:**

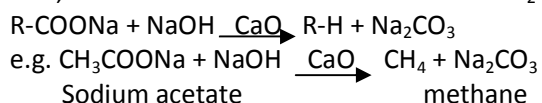
Alkyl halides react with metallic sodium in dry ether to form alkanes. This reaction is known as Wurtz reaction. The alkane formed contains double the number of C atoms than that present in the alkyl halide. So this method is used for the preparation of alkanes with even number of carbon atoms.



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

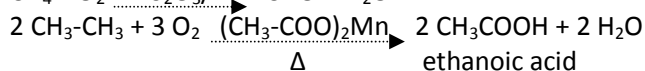
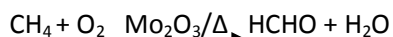
3. **From carboxylic acids:**

- 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.

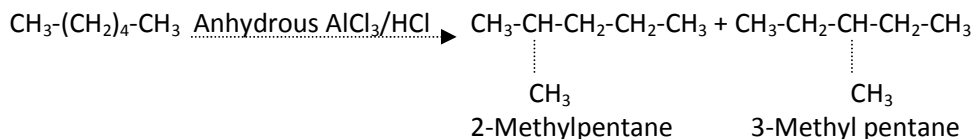


- b) **Kolbe's Electrolytic method:** An aqueous solution of sodium or potassium salt of a carboxylic acid on electrolysis gives alkane containing even number of carbon atoms.

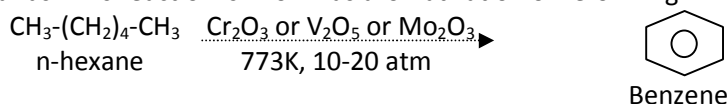
Alkanes on heating with O_2 at high pressure and in presence of suitable catalysts to form different compounds.



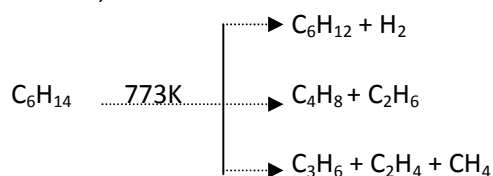
4. **Isomerisation:** n-Alkanes on heating in the presence of anhydrous aluminium chloride and hydrogen chloride gas isomerise to branched chain alkanes.



5. **Aromatization:** n-Alkanes having six or more carbon atoms on heating to 773K at 10-20 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.

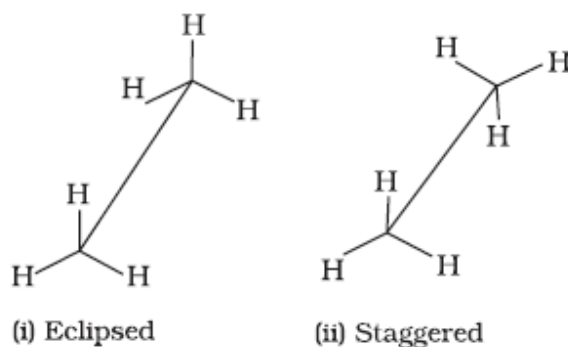
Eclipsed and staggered conformations can be represented by Sawhorse and Newman projection formulas.

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 attached to it corresponding to three hydrogen atoms.

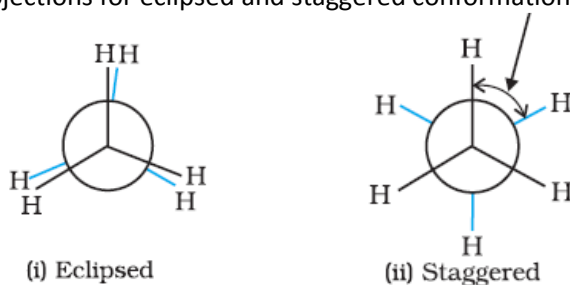
Sawhorse projections of eclipsed and staggered conformations of ethane are as follows:



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:



ALKENES

Alkenes are unsaturated hydrocarbons containing at least one double bond. They are also known as *olefins* (oil forming) since the first member, ethylene or ethene (C_2H_4) was found to form 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 isomerisms shown by alkenes are *chain isomerism* and *position isomerism*. The stereo isomerism shown by alkenes is geometrical isomerism.

Geometrical Isomerism

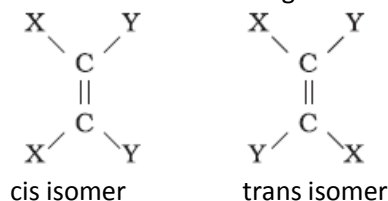
The isomerism arising due to the difference in the spatial arrangement of atoms around carbon-carbon double bond is called *geometrical isomerism*. Such isomers are called geometrical isomers. It is a type of stereo isomerism.

Geometrical isomerism arising due to the restricted rotation about carbon-carbon double bond.

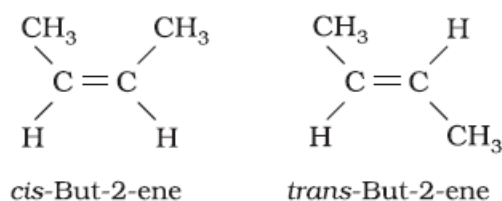
There are two types of geometrical isomers – **cis isomer** and **trans isomer**.

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 formula $YX C = C XY$ can show geometrical isomerism as follows:



e.g. But-2-ene

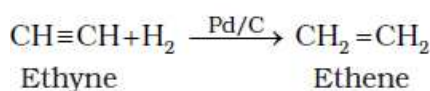
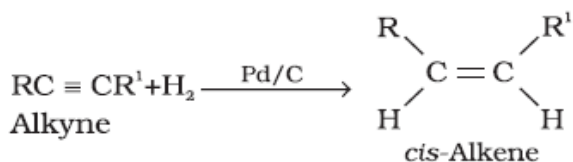


Due to different arrangement of atoms or groups in space, these isomers differ in their physical properties like melting point, boiling point, dipole moment, solubility etc

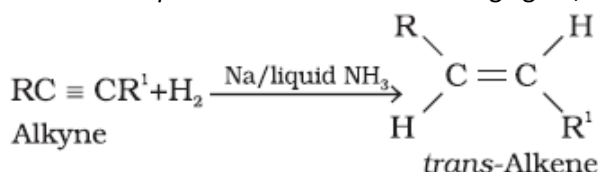
Cis form of alkene is found to be more polar than the trans form. In the case of solids, the trans isomer has higher melting point than the cis form.

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.

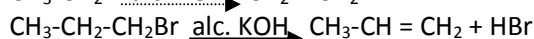
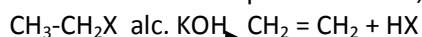


If we use *sodium in liquid ammonia* as the reducing agent, we get *trans* alkene.



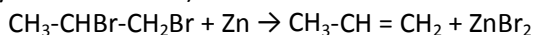
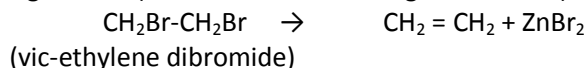
2. From Alkyl halides:

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. Since hydrogen atom is eliminated from the β carbon atom, the reaction is also known as **β -elimination reaction**.



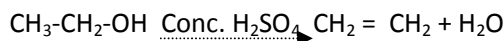
3. From vicinal dihalides:

Dihalides in which two 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).



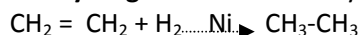
4. From alcohols:

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 $-\text{OH}$ group is eliminated from the β -carbon atom.

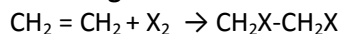


Chemical Properties

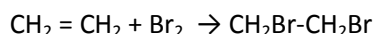
1. **Addition of hydrogen:** Alkenes add hydrogen in presence of finely divided Ni, Pd or Pt to form alkanes.



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



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.



3. **Addition of hydrogen halide:**

Alkenes add hydrogen halide to form alkyl halides.




$$\text{CH}_3-\text{CH}=\text{CH}_2 + \text{H}-\text{Br} \longrightarrow \begin{array}{l} \text{I} \left\{ \begin{array}{l} \text{CH}_3-\text{CH}-\text{CH}_3 \\ \quad | \\ \quad \text{Br} \end{array} \right. \\ \quad \quad \quad \text{2-Bromopropane} \\ \text{II} \left\{ \begin{array}{l} \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{Br} \end{array} \right. \\ \quad \quad \quad \text{1-Bromopropane} \end{array}$$

e.g. $\text{CH}_3\text{-CH=CH}_2 + \text{HBr} \xrightarrow{\text{Org. peroxide}}$ $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{Br}$
 Propene 1-bromopropane

$$\text{CH}_3\text{-CH=CH}_2 + \text{H}_2\text{O} \xrightarrow{\text{Conc. H}_2\text{SO}_4} \text{CH}_3\text{-CH(OH)-CH}_3$$

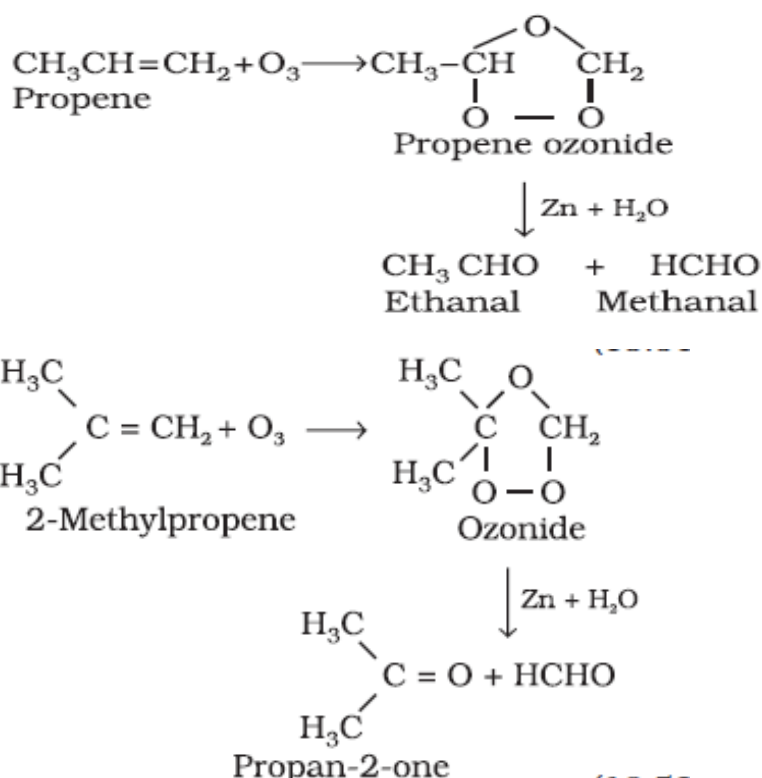
Propene2-propanaol

$$\text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} + \text{O} \xrightarrow[273 \text{ K}]{\text{dil. KMnO}_4} \begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ | \quad | \\ \text{OH} \quad \text{OH} \end{array}$$

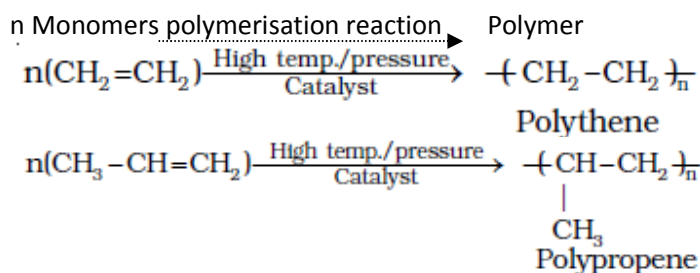
Ethane-1, 2-diol
(Glycol)

$$\begin{array}{lcl} \text{CH}_3\text{-CH=CH}_2 & \xrightarrow{\text{KMnO}_4/\text{H}^+} & \text{CH}_3\text{-COOH} + \text{CO}_2 + \text{H}_2\text{O} \\ \text{Propene} & & \text{Acetic acid} \\ \text{CH}_3\text{-CH=CH-CH}_3 & \xrightarrow{\text{KMnO}_4/\text{H}^+} & 2\text{CH}_3\text{-COOH} \\ \text{But-2-ene} & & \text{Ethanoic acid (acetic acid)} \\ (\text{CH}_3)_2\text{C=CH}_2 & \xrightarrow{\text{KMnO}_4/\text{H}^+} & \text{CH}_3\text{-CO-CH}_3 + \text{CO}_2 + \text{H}_2\text{O} \\ \text{ethylpropene} & & \text{Propanone (acetone)} \end{array}$$

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



- 7. 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.



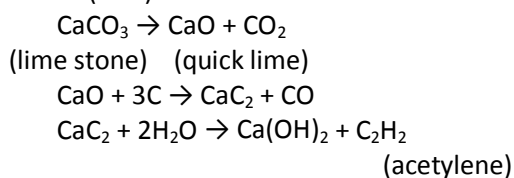
ALKYNES

They are unsaturated hydrocarbons containing at least one C≡C bond. Their general formula is $\text{C}_n\text{H}_{2n-2}$. 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.

PREPARATION

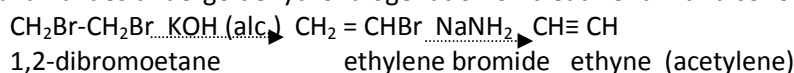
1. From Calcium carbide (CaC_2):

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



2. From vicinal dihalides:

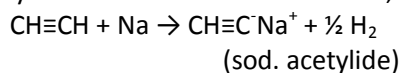
Vicinal dihalides undergo dehydrohalogenation on treatment with alcoholic KOH to form alkenes.



Chemical Properties

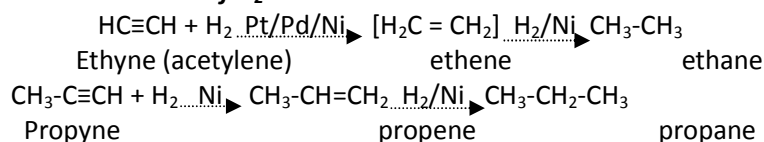
- 1. Acidic character:** 1-alkynes are acidic in nature. This is because in alkynes, the triple bonded carbon atoms are sp hybridized. Due to the greater s character (50%), the sp hybridised orbitals of carbon atoms in ethyne molecules have highest electronegativity. So they attract the shared electron 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 and H_2 .

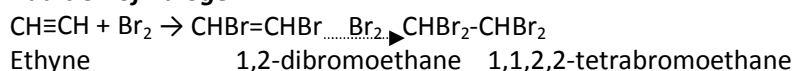


- ## 2. Addition reactions:

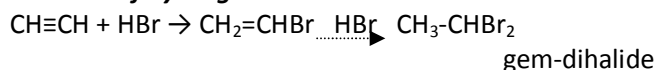
i. Addition of H_2 :



ii. Addition of halogen:

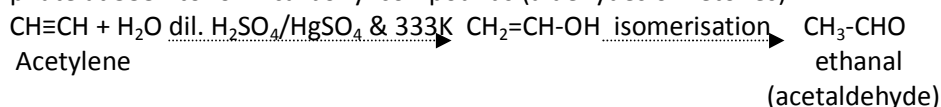


iii. Addition of hydrogen halide:



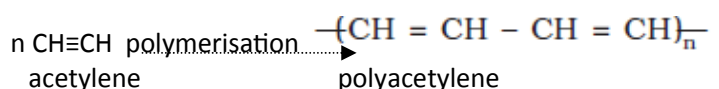
iv. Addition of water:

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).

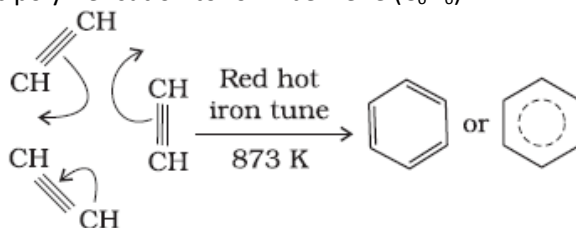


3. Polymerisation

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



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



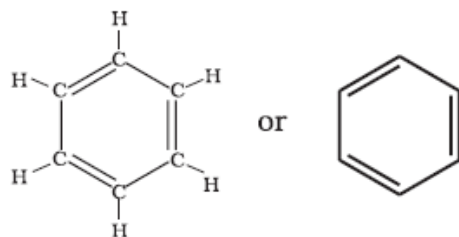
AROMATIC HYDROCARBONS (ARENES)

Most of the aromatic compounds have pleasant smell (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.

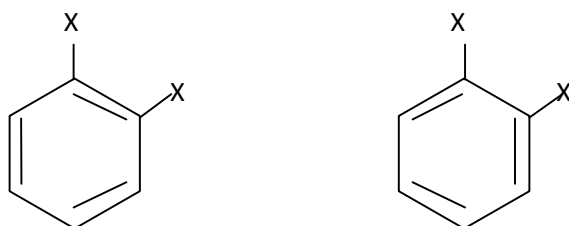
Structure of Benzene

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 benzene forms only one 1,2-disubstituted derivative.



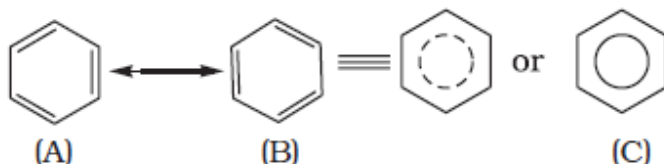
In order to overcome this problem, Kekule suggested the concept of oscillating nature of double bonds in benzene.



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.

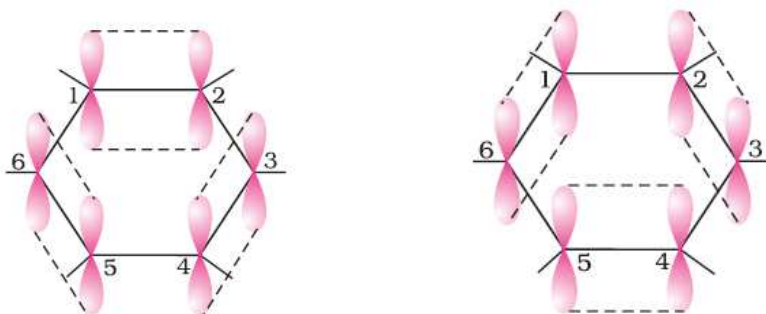


The actual structure of benzene is not A or B. It is in between these two resonating structures. So benzene is denoted by a hexagon with a dotted circle, which represents the delocalised π -electrons.

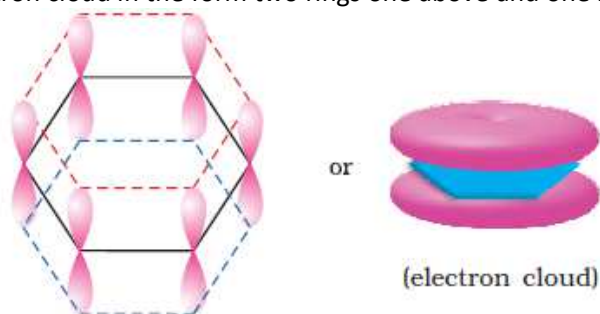
Orbital Overlap Concept of Benzene

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 a hydrogen atom to form six C—H sigma bonds.

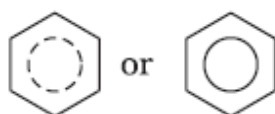
Now each carbon atom contains one unhybridised p orbital perpendicular to the plane of the ring. They overlap laterally to form three π -bonds. There are two possible overlapping.



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:

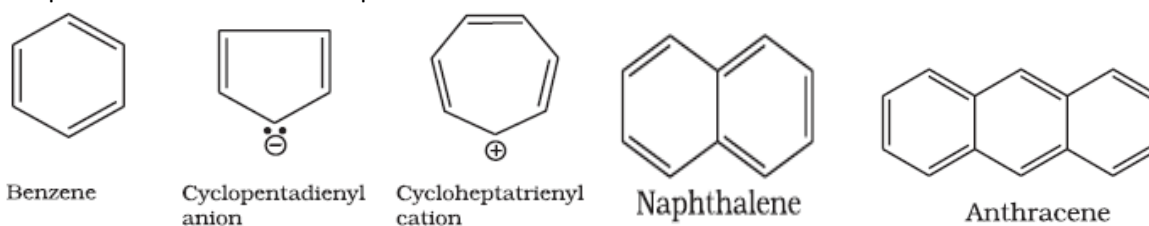


So the six π electrons are delocalised and can move freely about the six carbon nuclei. Presence of delocalised π electrons in benzene makes it more stable. The delocalised π electrons can be denoted by a circle inside a hexagonal ring. So benzene is best represented as:



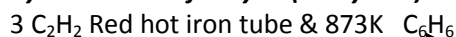
Aromaticity

Aromaticity is defined by a rule called 'Huckel rule'. According to this rule, "cyclic, planar, conjugated systems containing $(4n+2)$ π electrons are aromatic". Where n is the number of rings. n may be 1,2,3,... For benzene $n = 1$, so it should contain 6 delocalised π electrons. If $n = 2$, the no. of delocalised π electrons =10 and so on. Example for some aromatic compounds are:

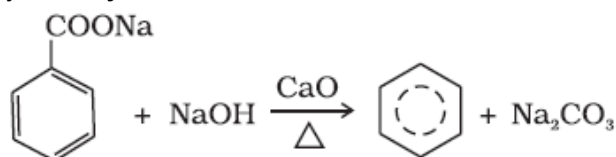


Preparation of Benzene

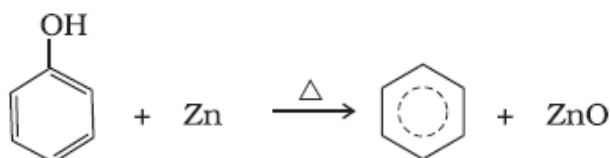
1. Cyclic polymerisation of ethyne (acetylene):



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



3. Reduction of phenol: Phenol is reduced to benzene by passing its vapours over heated zinc dust.



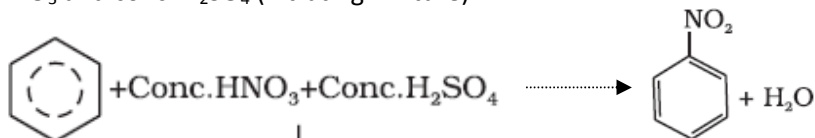
Chemical Properties

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

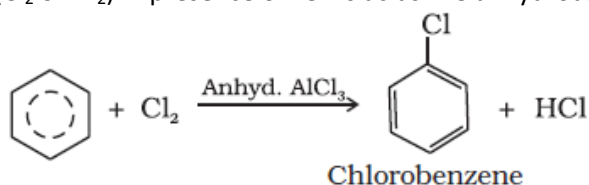
I) Electrophilic Substitution Reactions

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.

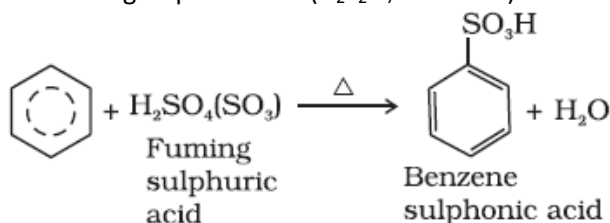
1. **Nitration:** It is the introduction of nitro ($-\text{NO}_2$) group to a benzene ring. For this benzene is heated with a mixture of conc. HNO_3 and conc. H_2SO_4 (nitrating mixture).



2. **Halogenation:** It is the introduction of halo ($-\text{X}$) 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 .

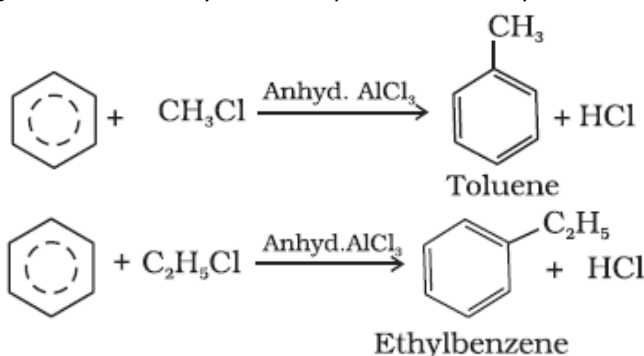


3. **Sulphonation:** It is the introduction of sulphonic acid ($-\text{SO}_3\text{H}$) group to a benzene ring. It is carried out by heating benzene with fuming sulphuric acid ($\text{H}_2\text{S}_2\text{O}_7$ or oleum).

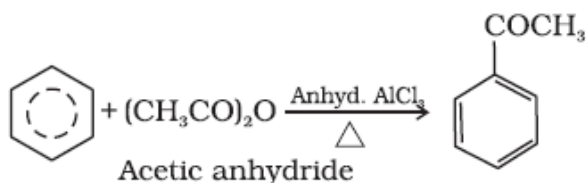


4. **Friedel-Craft's reaction:** It is the introduction of alkyl ($-\text{R}$) group or acyl ($-\text{CO}-\text{R}$) group to a benzene ring. It is of two types:

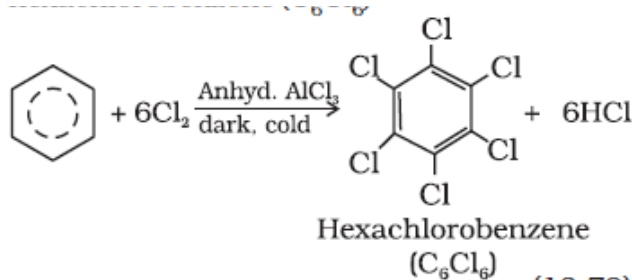
- a) **Friedel-Craft's Alkylation reaction:** It is the introduction of alkyl ($-\text{R}$) group to a benzene ring. Here the reagents used are alkyl halide in presence of anhydrous AlCl_3 .



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

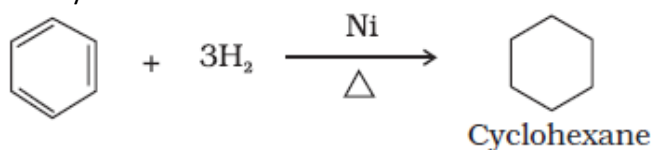


5. Benzene on treatment with excess of chlorine in the presence of anhydrous AlCl_3 in dark to form hexachlorobenzene (C_6Cl_6).

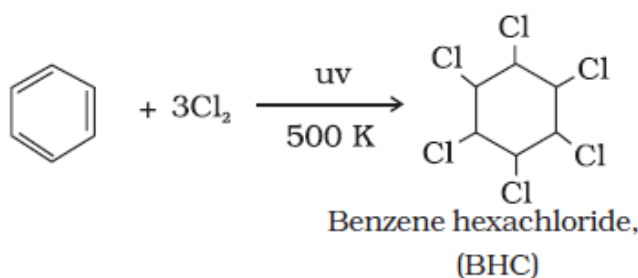


II) Addition Reactions

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 to form benzene hexachloride (BHC). It is also known as Gammexane or Lindane or 666.



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.

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 $-\text{OH}$, $-\text{NH}_2$, $-\text{NHR}$, $-\text{NHCOCH}_3$, $-\text{OCH}_3$, $-\text{CH}_3$, $-\text{C}_2\text{H}_5$ 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 $-\text{I}$ 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 $-\text{NO}_2$, $-\text{CN}$, $-\text{CHO}$, $-\text{COR}$, $-\text{COOH}$, $-\text{COOR}$, $-\text{SO}_3\text{H}$, etc.

