

## CLASS 11 Chemistry Chapter 13 Hydrocarbons

Hydrocarbons are the organic compounds containing carbon and hydrogen only. Based on the types of carbon-carbon bonds present, hydrocarbons can be classified into three categories- (i) Saturated (ii) Unsaturated (iii) Aromatic hydrocarbons.

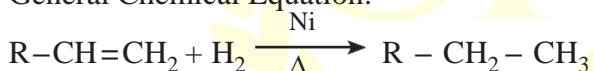
Saturated hydrocarbons contain carbon-carbon multiple bonds—double bonds, triple bonds or both.

**ALKANES:** Saturated open chain hydrocarbons containing carbon-carbon single bonds. These are inert under normal conditions i.e., do not react with acids, bases and other reagents. Alkanes exhibit Chain isomerism, Position isomerism and conformational isomerism.

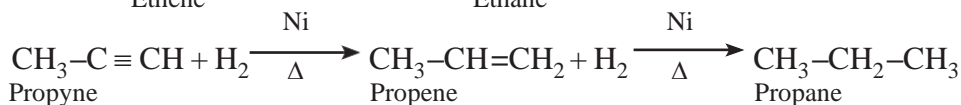
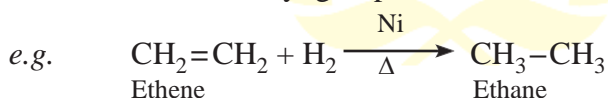
### General methods of preparation of alkanes:

- From Unsaturated hydrocarbons:** By hydrogenation in the presence of platinum, palladium or nickel as catalyst.

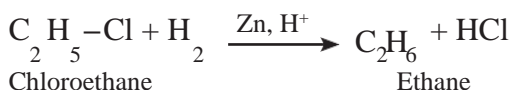
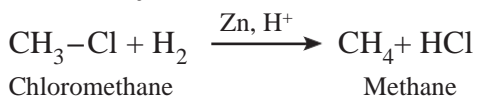
General Chemical Equation:

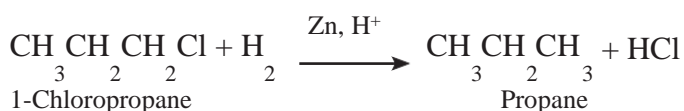


[Where R is H or Alkyl group]

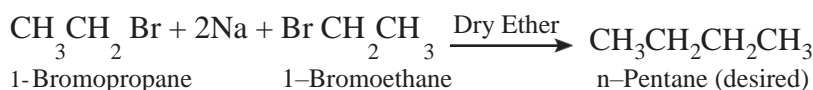
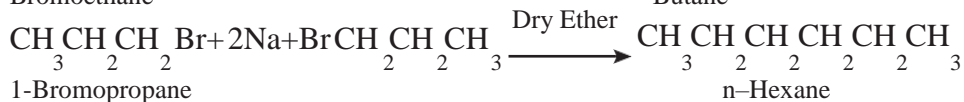
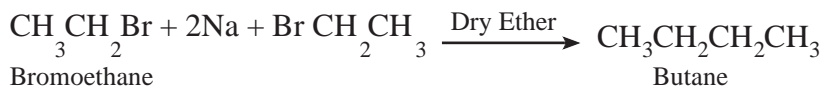


- From alkyl halides:** on reduction with Zinc and dilute hydrochloric acid

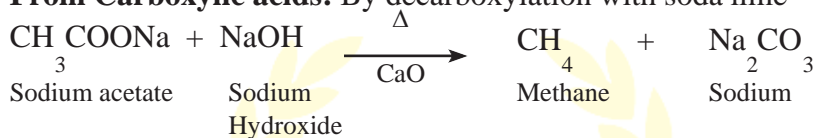




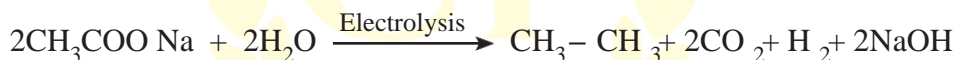
3. **From alkyl halides by Wurtz reaction:** Reaction of alkyl halide with sodium in dry ether, useful only for the preparation of symmetrical alkanes.



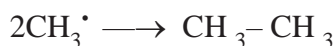
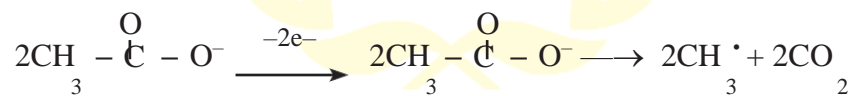
4. **From Carboxylic acids:** By decarboxylation with soda lime



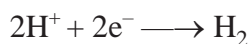
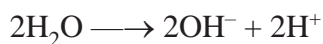
5. **By Kolbe's electrolytic method:** Electrolysis of an aqueous solution sodium or potassium salt of carboxylic acid. Alkane containing even number of carbon atoms is formed at anode.



**At Anode:** (Oxidation)



**At Cathode:** (Reduction)



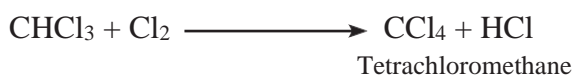
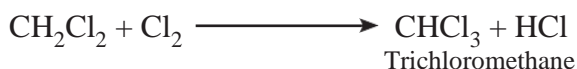
### Physical Properties of alkanes:

- Boiling point of alkanes decreases on branching due to decrease in surface area of molecule with branching which decreases magnitude of van der Waal's forces of attraction.
- Alkanes being non-polar in nature are soluble in non-polar solvents.

## Chemical properties of Alkanes:

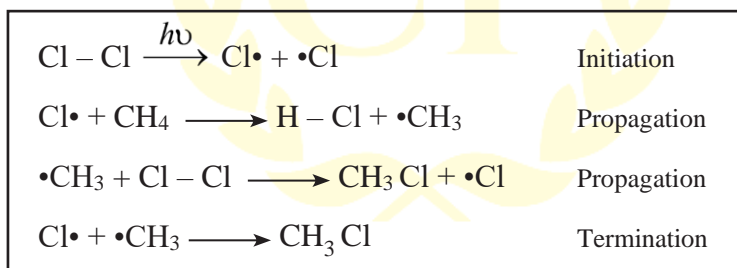
- Alkanes undergo substitution reactions.  
*e.g.*, Halogenation, Nitration, Sulphonation.

Halogenation: For example, Chlorination of methane



Rate of reaction of alkanes with halogens is  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$ . Rate of replacement of hydrogen in alkanes is  $3^\circ > 2^\circ > 1^\circ$ . Fluorination is too violent to be controlled. Iodination is reversible and it is therefore carried out in the presence of oxidising agent like  $\text{HNO}_3$ .

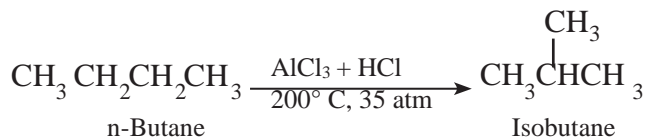
**Mechanism of halogenation:** Free radical mechanism



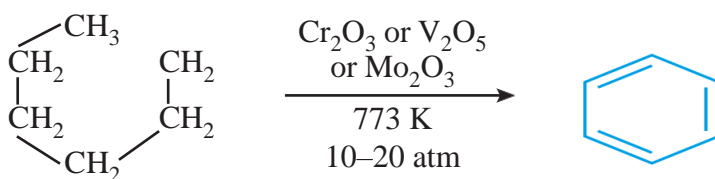
**Combustion:** Complete combustion gives carbon dioxide and water.



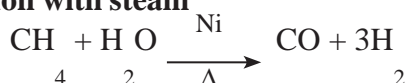
**Isomerisation:**



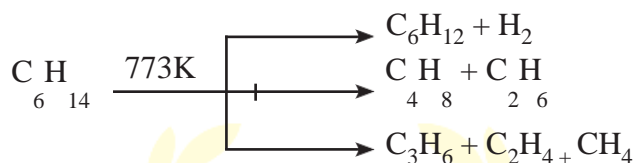
### Aromatisation:



(vi) **Reaction with steam**



**Pyrolysis:** Decomposition of higher alkanes to lower alkanes on heating.



### Conformations:

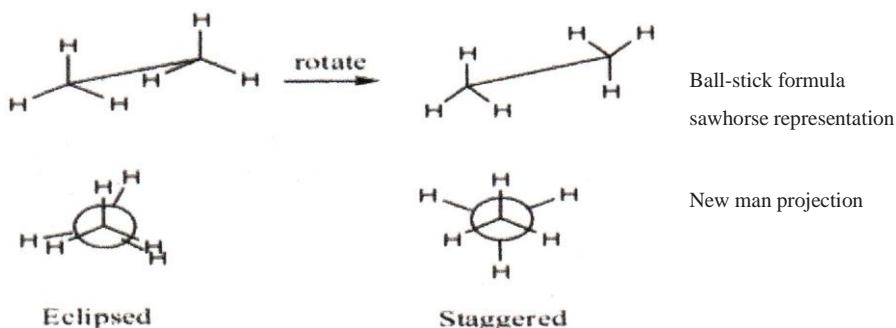
Different spatial arrangement of atoms arising due to rotation around C-C single bond.

#### Conformation of ethane, $\text{CH}_3\text{CH}_3$

Two conformational isomers or conformers.

**Eclipsed form** = all hydrogen atoms nearest to each other.

**Staggered form** = all hydrogen atoms are farthest apart.



Stability of eclipsed conformation is least while staggered conformation is most stable. The energy difference between two extreme forms is  $12.5\text{kJmol}^{-1}$ . Due to this small energy difference the two forms are easily inter-convertible at ordinary temperature and cannot be separated and isolated.

## ALKENES

These are unsaturated non-cyclic hydrocarbons which have  $sp^2$  -hybridisation with  $120^\circ$  bond angle.

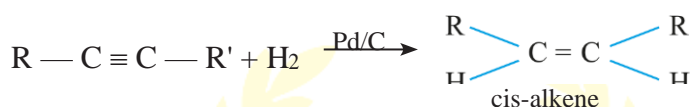
Alkenes are also called olefins [oil. Forming] which indicates their high reactive nature.

Alkenes have general formula  $C_n H_{2n}$ , where  $n = 2, 3, 4, \dots$

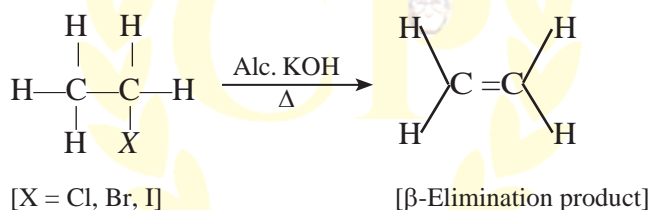
$C_2H_4$  (ethene),  $C_3H_6$  (propene), etc.

### • Methods of Preparation of Alkenes

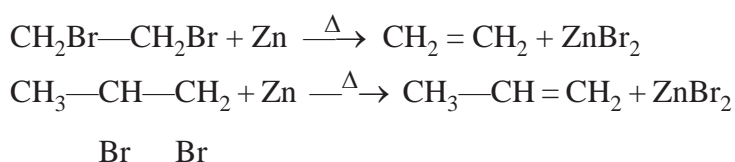
#### (i) From alkynes



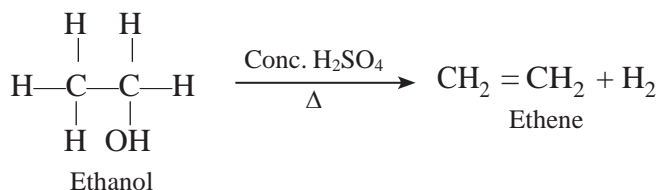
#### (ii) From alkyl halide [Dehydrohalogenation]



#### (iii) From vicinal dihalides

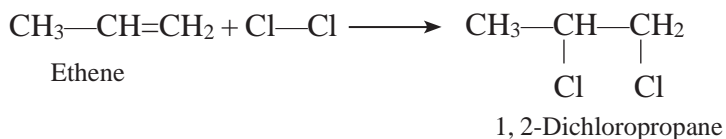
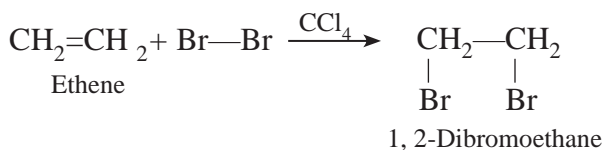


#### (iv) From alcohols by acidic dehydrogenation



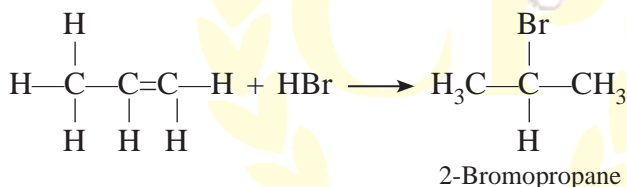
## • Chemical Properties of Alkenes:

### 1. Addition of Halogens:

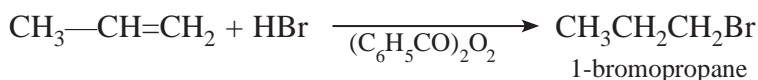


### 2. Addition of hydrogen halides HCl, HBr, HI: Add up to alkenes to form alkyl halides as per their reactivity order in $\text{HI} > \text{HBr} > \text{HCl}$ .

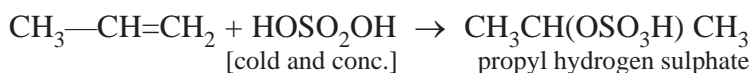
Addition reaction of HBr to unsymmetrical alkenes (Markownikov's rule)  
According to Markownikov's rule, the negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms.



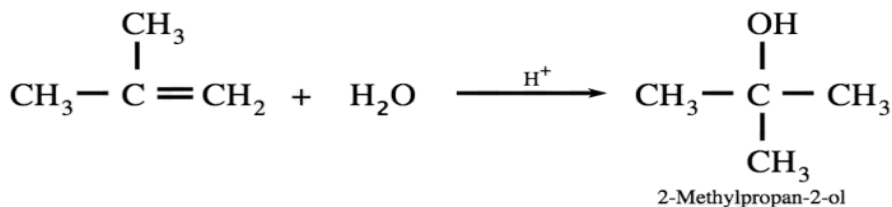
Anti Markownikov addition or peroxide effect or Kharasch effect in the presence of organic peroxide, addition of only HBr molecule on unsymmetrical alkene takes place contrary to the Markownikov's rule. Peroxide effect is not observed in case of HF, HCl and HI.



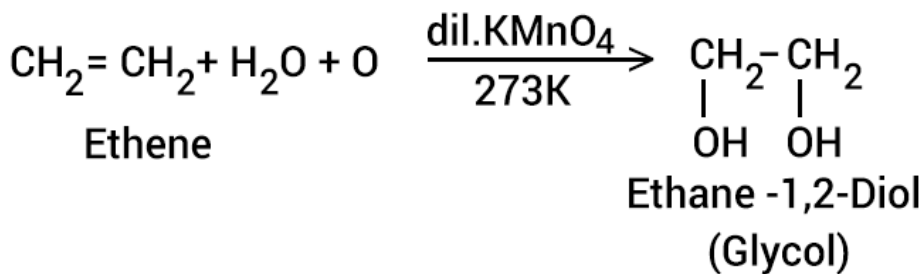
### 3. Addition of sulphuric acid



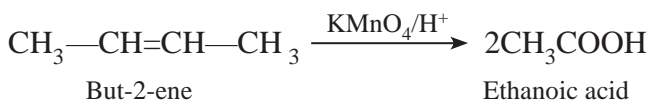
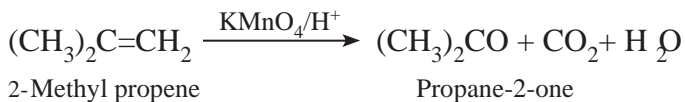
#### 4. Addition of water



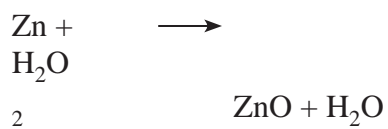
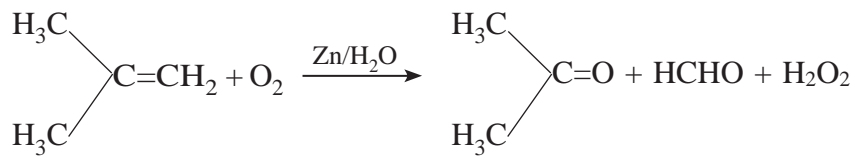
5. **Oxidation:** Alkenes decolourise cold dilute aqueous solution potassium permanganate (Baeyer's reagent). It is used as a test for unsaturation.



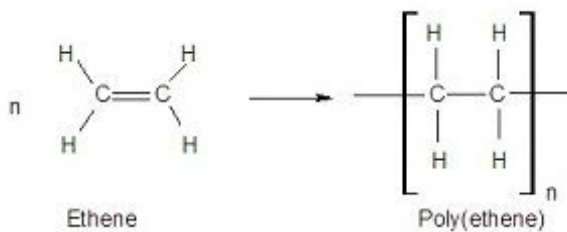
Acidic  $\text{KMnO}_4$  or acidic  $\text{K}_2\text{Cr}_2\text{O}_7$  oxidises alkenes to ketones and/or acids depending upon the nature of alkene and the experimental conditions.



6. **Ozonolysis:** Reaction of ozone with alkene to form ozonide which on subsequent reductive cleavage with zinc dust and water give carbonyl compounds (aldehydes & ketones).



## 7. Polymerization





## ALKYNES

These are unsaturated hydrocarbons with general formula  $C_nH_{2n-2}$  e.g.,  $C_2H_2$  (ethyne),  $C_3H_4$  (propyne).

Alkynes also exhibit electrophilic addition reaction but less reactive than alkenes because the dissociation of  $\pi$ -electron cloud requires more energy.

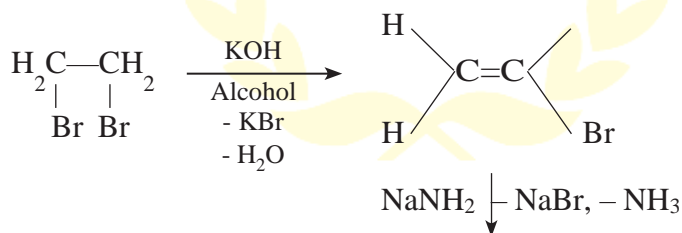
$H-C\equiv C-H$  contains  $3\sigma$  and  $2\pi$  -bonds and bond length is 120 pm. In acetylene.  $H-C-C$  bond angle is  $180^\circ$ .

### • Methods of Preparation of Alkynes

#### 1. From calcium carbide



#### 2. From vicinal dihalides

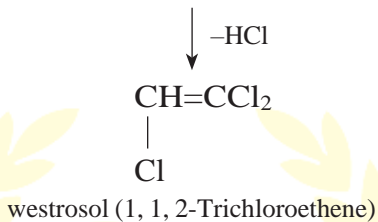
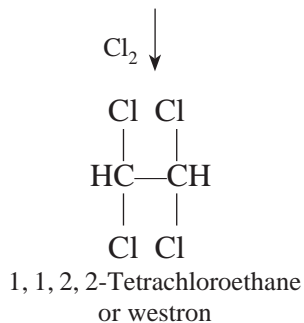


### Physical Properties of Alkynes:

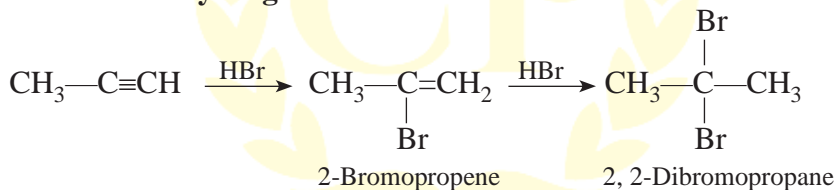
1. The first two members are gases next eight members ( $C_5 - C_{12}$ ) are liquids and higher members are solids.
2. They are all colorless and odorless with the exception of acetylene which has slightly garlic odour due to the presence of  $PH_3$  and  $H_2S$  as impurities.
3. Alkynes are insoluble in water but soluble in organic solvents like ethers, carbon tetrachloride and benzene.
4. Melting point, boiling point and density increase with increase in molar mass.



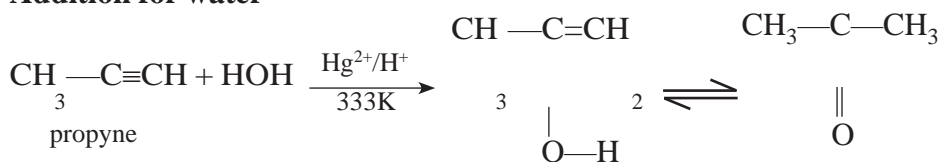
### Addition of halogens



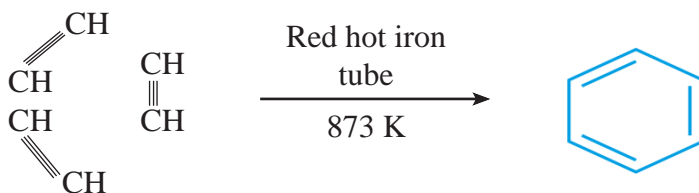
### Addition of hydrogen halides



### Addition for water



### (iii) Cyclic polymerization of ethyne

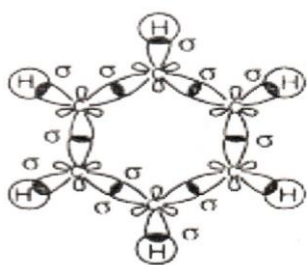


## AROMATIC HYDROCARBONS

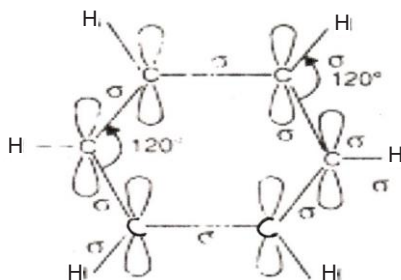
These hydrocarbons are also known as arenes. The parent member of the family aromatic hydrocarbons is benzene.

Aromatic compounds containing benzene ring are known as benzenoids.

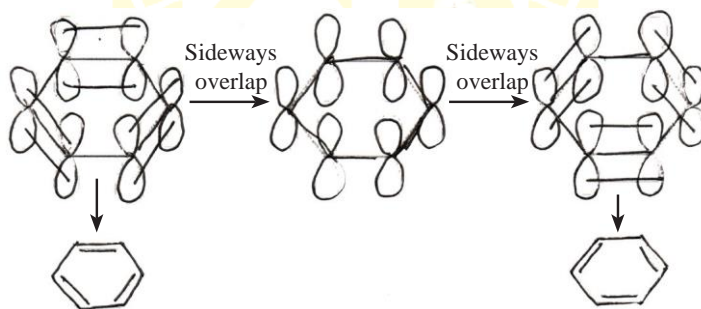
**Structure of benzene:** Hexagonal ring of carbon atoms with alternate single and double bonds. Each carbon atom is  $sp^2$  hybridized. Planar ring, bond angle  $120^\circ$ . All C-C bond lengths are equal due to complete delocalization of  $\pi$  electrons.



Formation of C-C and C-H sigma bonds



Sigma skeleton of benzene molecule



## HUCKEL'S RULE

- **Huckel's rule, (based on calculations):** a planar cyclic molecule with alternating double and single bonds has aromatic stability if it has  $(4n + 2\pi)$  electrons ( $n$  is 0, 1, 2, 3, 4)
- For  $n = 1$  :  $4n+2 = 6$ ; benzene is stable and electrons are delocalized.

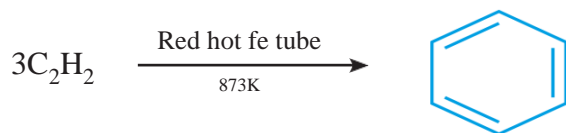
### Benzene



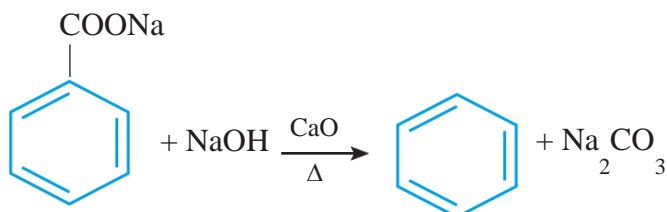
Three double bonds;  
six  $\pi$  electrons

## ● METHODS OF PREPARATION

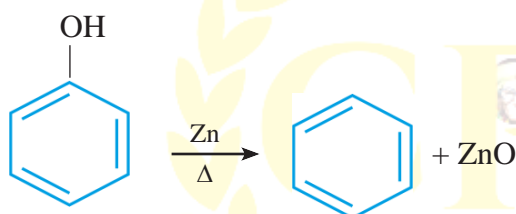
### 1. Cyclic polymerization of ethyne



### 2. Decarboxylation of aromatic acids



### 3. Reduction of phenol



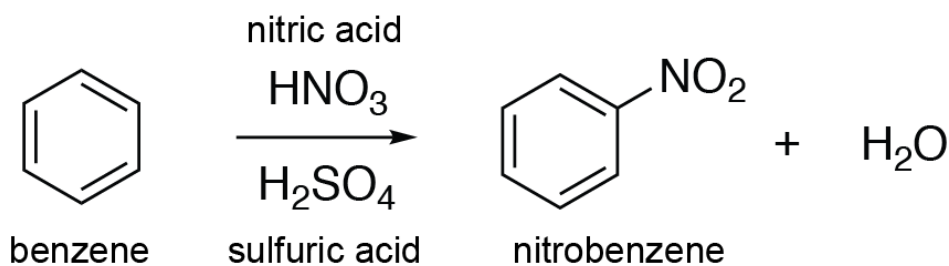
### Physical Properties of Benzene:

- (i) Aromatic hydrocarbons are non-polar molecules and are usually colourless liquids or solids with a characteristic aroma.
- (ii) Aromatic hydrocarbons are immiscible with water but readily miscible with organic solvents.
- (iii) Aromatic compounds burn with sooty flame.

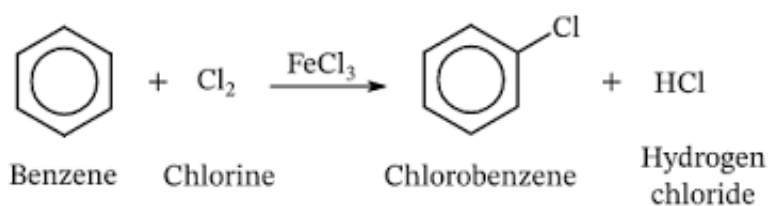
### Chemical Reactions of Benzene:

- (i) Benzene gives electrophile substitution reactions.
- (ii) According to experimental evidences, electrophile substitution reaction involve following three steps:
  - Generation of electrophile
  - Formation of carbocation intermediate.
  - Removal of proton from the carbocation intermediate.

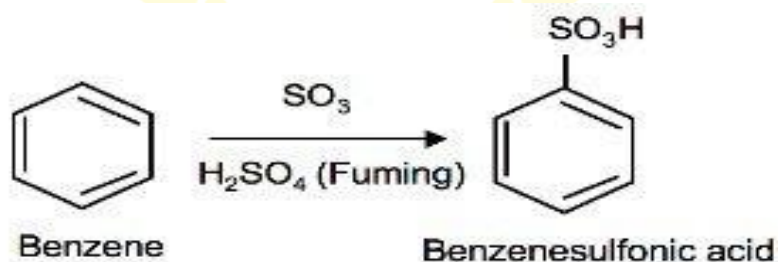
(i) Nitration



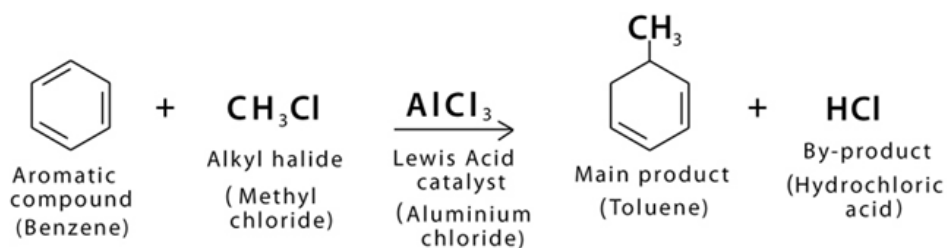
(ii) Halogenation



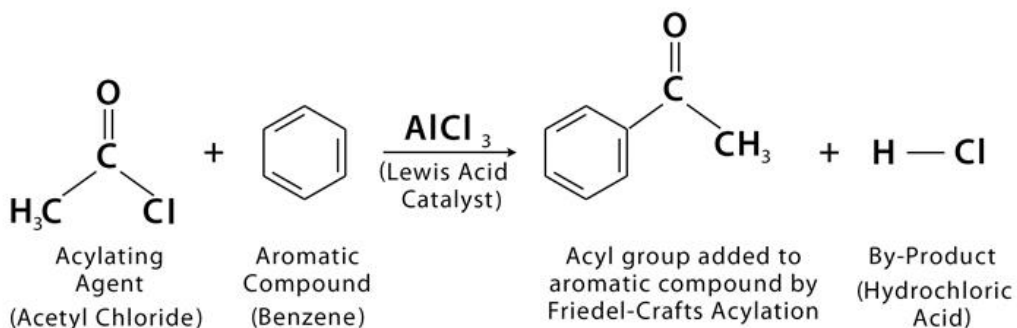
(iii) Sulphonation



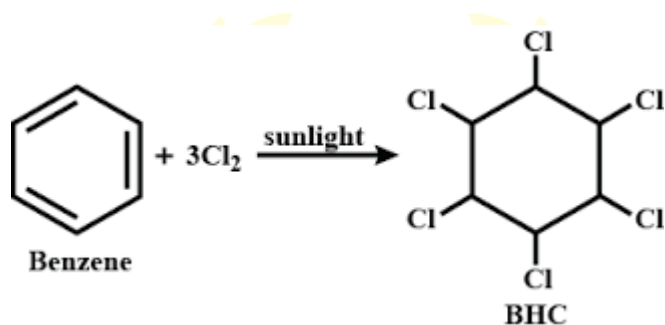
(iv) Friedel-Craft's alkylation reaction



(v) **Friedel-Crafts acylation reaction**



**Benzene also undergoes addition reactions e.g.**



**benzene hexachloride or 666  
(BHC or Gammexane or lindane)**

• **COMBUSTION**



**Directing influence of substituents in monosubstituted benzene**

- (i) **Ortho and para directing groups:** Ring activating groups  
*e.g.*, NH<sub>2</sub>, -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub>, -OCH<sub>3</sub> etc. (+ R effect)
- (ii) **Meta directing groups:** Ring deactivating groups  
*e.g.* -NO<sub>2</sub>, -CN, -CHO, -COOH, -SO<sub>3</sub>H (- R effect)

