

UNIT - I (A)

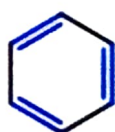
BENZENE AND ITS DERIVATIVES

Points to be covered in this topic

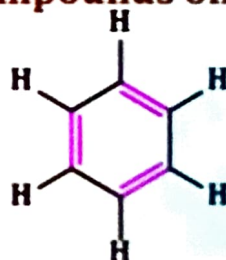
1. INTRODUCTION
2. NOMENCLATURE
3. METHODS OF PREPARATION
4. PHYSICAL PROPERTIES
5. CHEMICAL PROPERTIES

□ INTRODUCTION

- **Benzene** (also called cyclohexatriene) is an organic chemical compound with the **molecular formula C_6H_6**
- The benzene molecule is composed of **six carbon atoms** joined in a **planar ring** with **one hydrogen atom** attached to each
- Because it contains only carbon and hydrogen atoms, benzene is classed as a **hydrocarbon**
- Benzene and its homologues **occur chiefly in coal-tar** and **coal gas**
- They are also found to be present in **petroleum** which was formerly thought of as a mixture of aliphatic compounds only

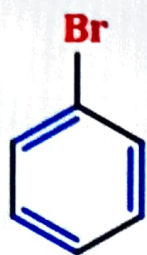


Benzene

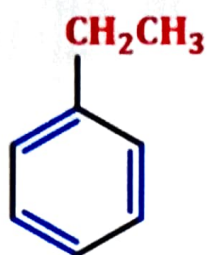


NOMENCLATURE

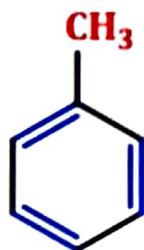
❖ Naming of mono substituted benzene



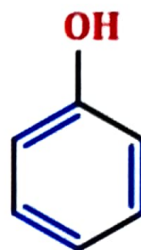
Bromo benzene



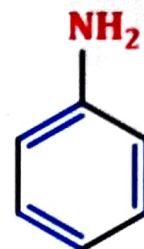
Ethylbenzene



Methylbenzene (Toluene)

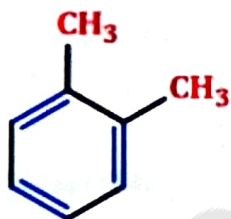


Hydroxy benzene (Phenol)

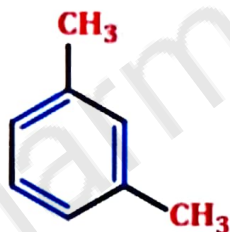


Amino benzene (Aniline)

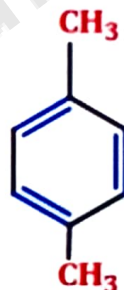
❖ Naming of di substituted benzene



o-dimethyl benzene



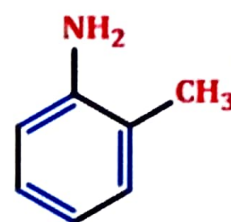
m-dimethyl benzene



p-dimethyl benzene



1-bromo-2-chloro benzene

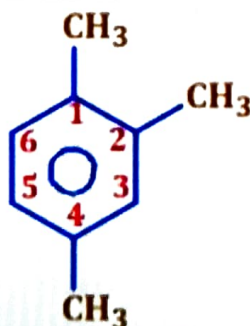


2-Methyl aniline

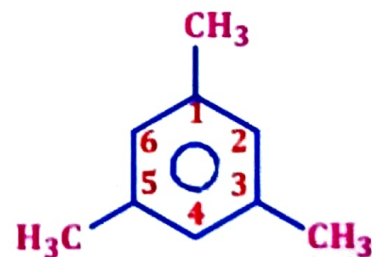
❖ Naming of poly substituted benzene



1,2,3-Trimethylbenzene



1,2,4-Trimethylbenzene

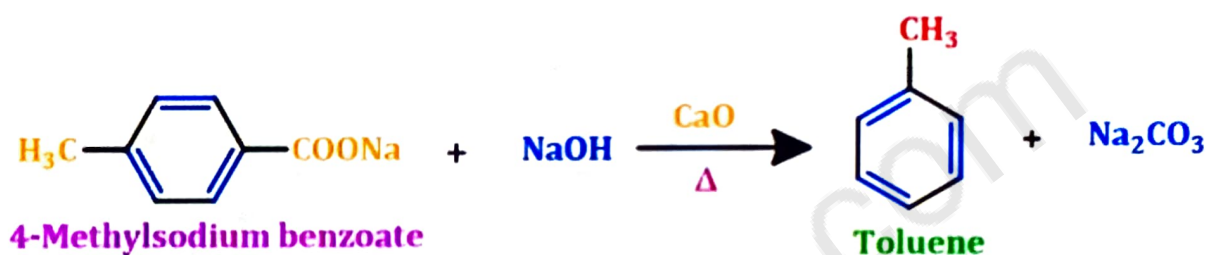
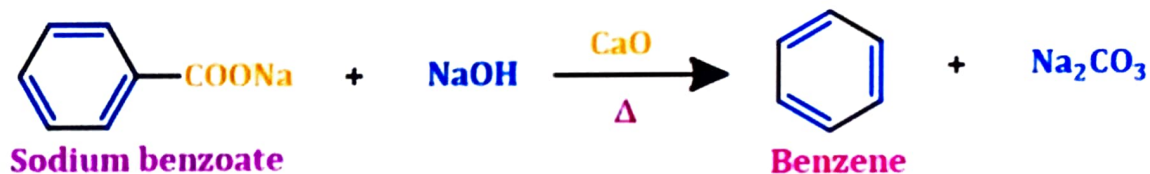


1,3,5-Trimethylbenzene

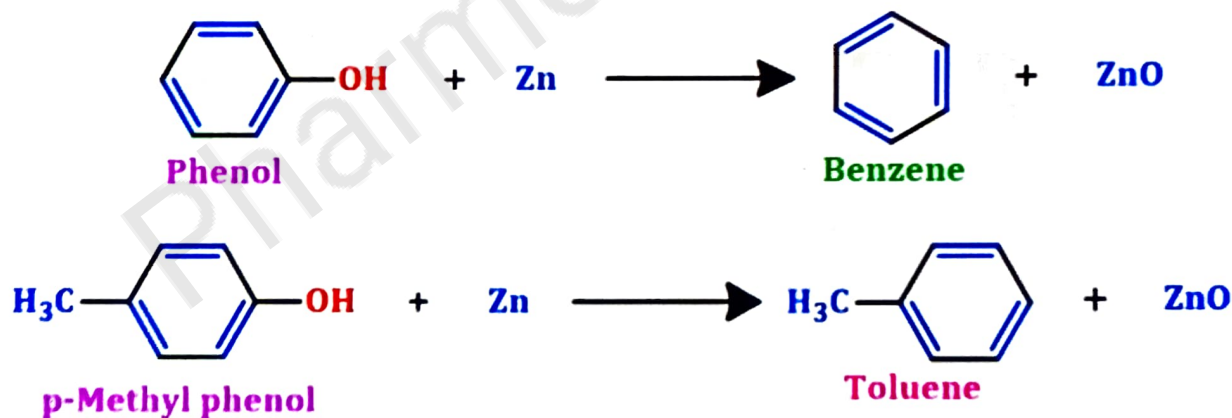
❑ METHODS OF PREPARATION

❖ LABORATORY PREPARATION

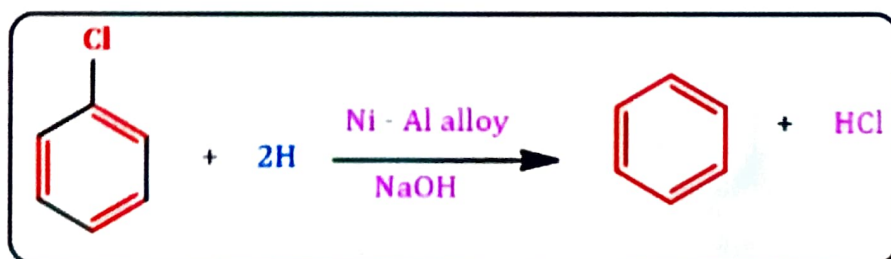
1. **From aromatic carboxylic acids:** Aromatic carboxylic acid (-COOH) and substituted acid or its sodium salt when **heated with soda lime** gives benzene or its analogues.



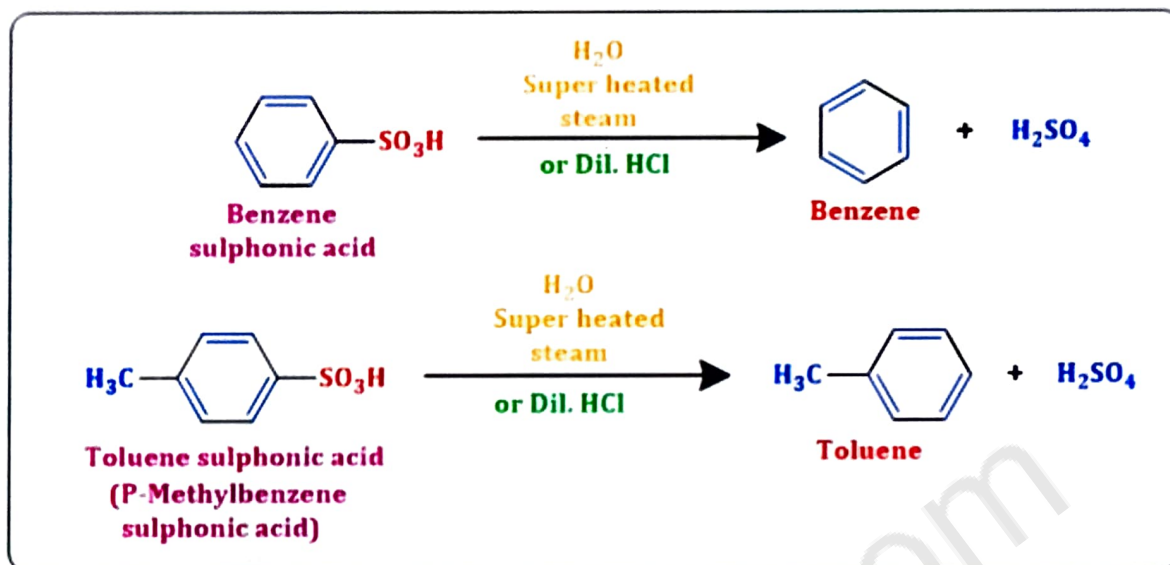
2. **Removal of -OH group:** Phenol and o/m/p-methyl phenol vapors are passed through **heated zinc dust to yield benzene** and toluene respectively.



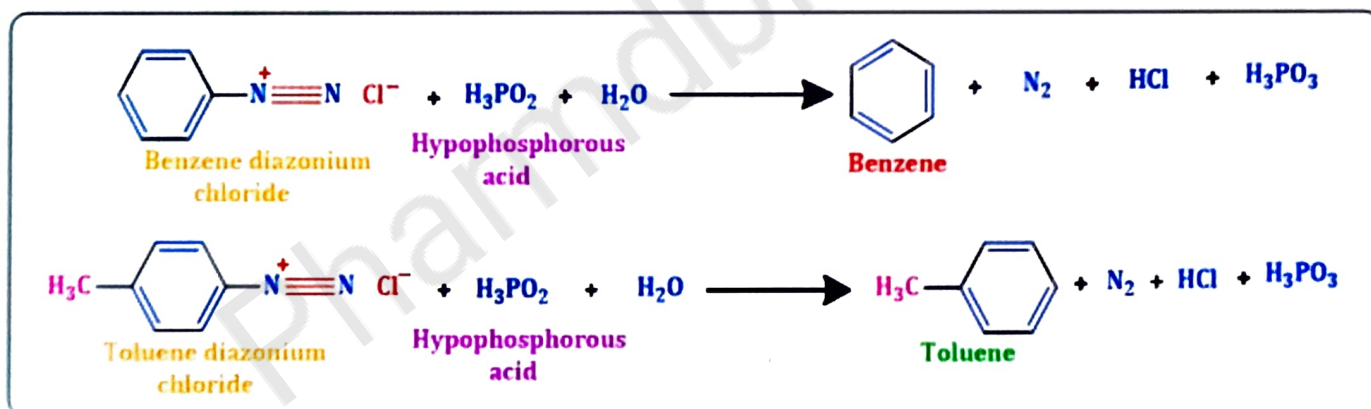
3. **From chlorobenzene:** Chlorine of the benzene substituted by **reduction with Ni-Al alloy and NaOH**.



4. Removal of $-SO_3H$ group: Benzene sulphonic acid or toluene sulphonic acid (p-methyl benzene sulphonic acid) is hydrolyzed with super heated steam or boiling with **dilute HCl under pressure at 400-447 K** to yield benzene and toluene respectively.



5. Removal of $N_2^+Cl^-$ group: Benzene diazonium salts or arene diazonium salts or toluene diazonium salts when reduced with **hypo phosphorous acid** yields benzene and toluene respectively.



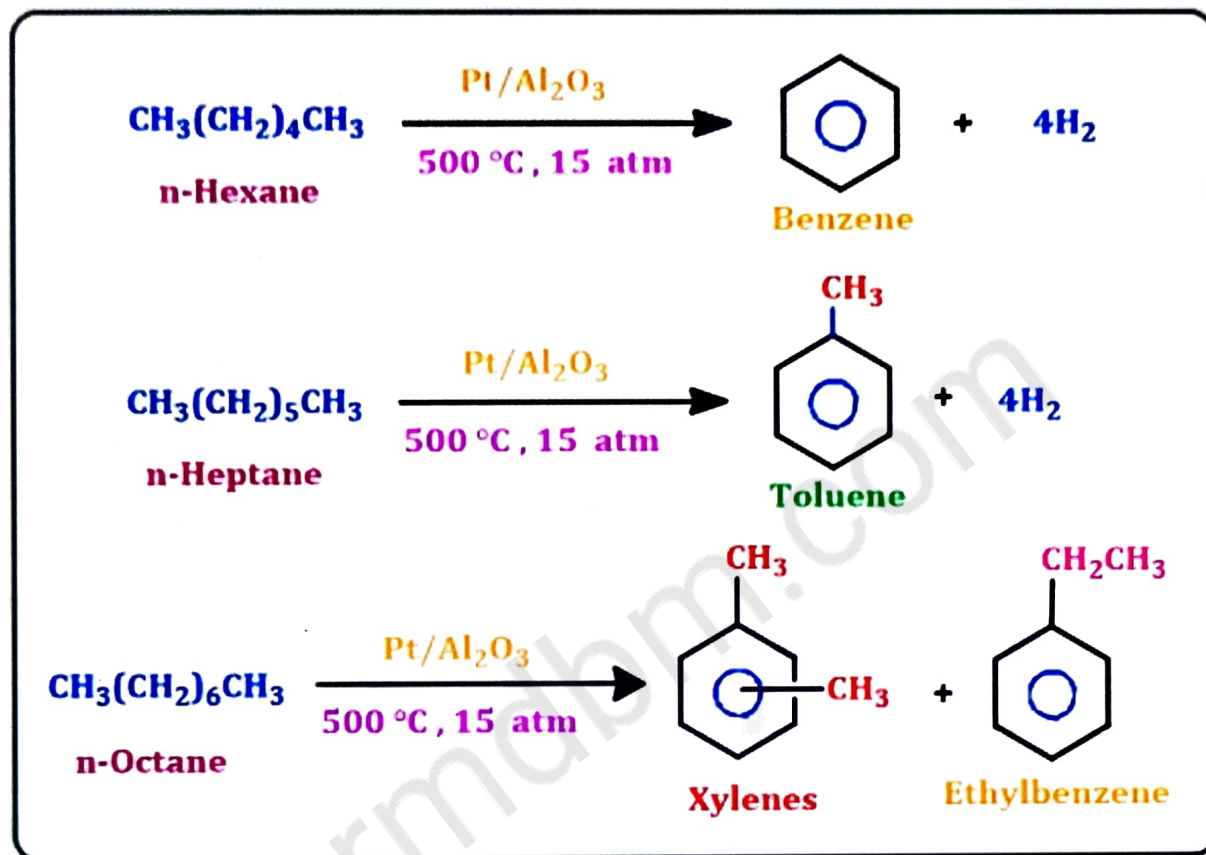
❖ SYNTHESIS

From acetylene: when acetylene is passed through a red hot metallic tube, cyclic polymerization takes place and benzene is formed



❖ MANUFACTURE

1. From Petroleum: Cyclization of **long chain alkanes** on heating at 500-500°C under high pressure in **presence of catalyst**.



- Benzene is recovered from the mixture by solvent extraction and fractional distillation.
2. From Light Oil Fraction of Coal-tar:
- The **distillation of coal-tar** gives the light oil fraction (up to 200°C).
 - This is **washed with concentrated sulfuric acid** to remove basic impurities (pyridine), and then with sodium hydroxide solution to remove acidic impurities (phenols).
 - The oil thus purified is **finally washed with water**; dried, and distilled.
 - The fraction **passing up to 110°C** contains benzene, some toluene, and thiophene ($\text{C}_4\text{H}_4\text{S}$).
 - This is refractionated and the fraction collected **between 80-82°C** is **almost pure benzene**.

☐ PHYSICAL PROPERTIES OF BENZENE

1. Benzene is a **colorless liquid**, bp 80.1°C , mp 5.5°C
2. It is **insoluble in water**, forming the upper of two layers when mixed. **It is miscible with alcohol, ether, and chloroform.**
3. Benzene itself is a **good solvent** for many organic and inorganic substances e.g., fat, resins, sulphur and iodine.
4. Its **vapors are highly toxic** which on inhalation produce loss of consciousness. Benzene poisoning in the long run can prove fatal, destroying the red and white blood corpuscles.
5. It **burns with a luminous, sooty flame**, in contrast to alkanes and alkenes which usually burn with a bluish flame.
6. Benzene and its derivatives show **characteristic IR spectrum**. The two bands near 1600 cm^{-1} and 1500 cm^{-1} have been correlated with the stretching of the carbon-carbon bonds of the aromatic ring. The sharp bands near 3030 cm^{-1} are caused by aromatic C-H bond

☐ CHEMICAL REACTIONS OF BENZENE

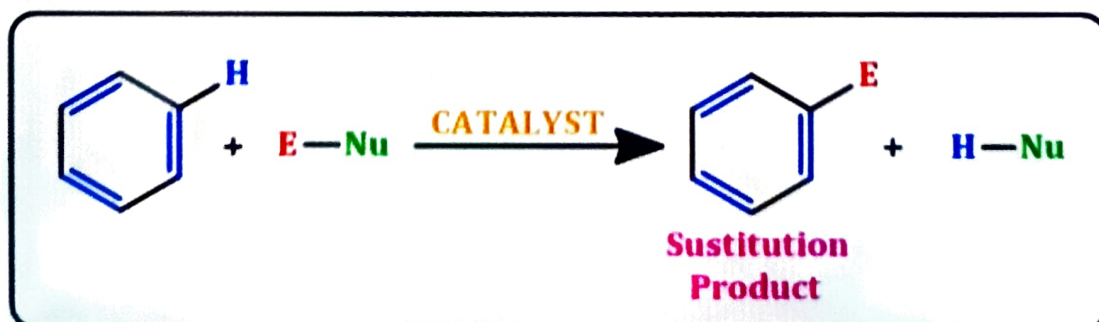
(I) Electrophilic aromatic substitution reactions

(II) Addition reactions of benzene

(III) Oxidation reactions

❖ ELECTROPHILIC SUBSTITUTION REACTIONS

- Benzene undergoes **electrophilic substitution reactions**
- The benzene ring with **its delocalized π electrons** is an electron-rich system
- It is **attacked by electrophiles**, giving substitution products



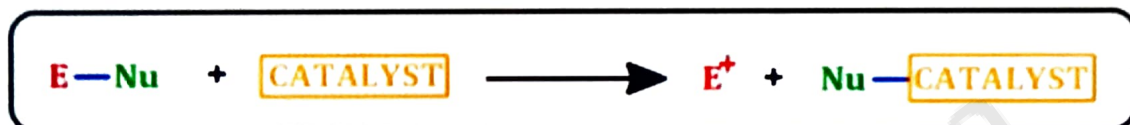
Where E^+ is any electrophile and Nu^- is a nucleophile.

➤ ELECTROPHILIC AROMATIC SUBSTITUTION REACTIONS

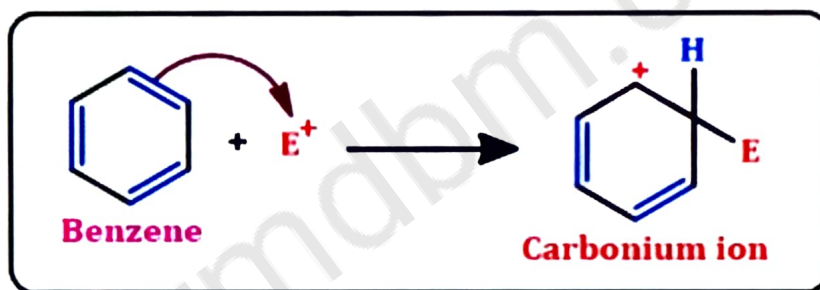
- Such reactions in which **hydrogen atom of the aromatic ring is replaced by an electrophile** are called **electrophilic aromatic substitution reactions**.

GENERAL MECHANISM: All electrophilic aromatic substitution reactions follow the same three-step mechanism :

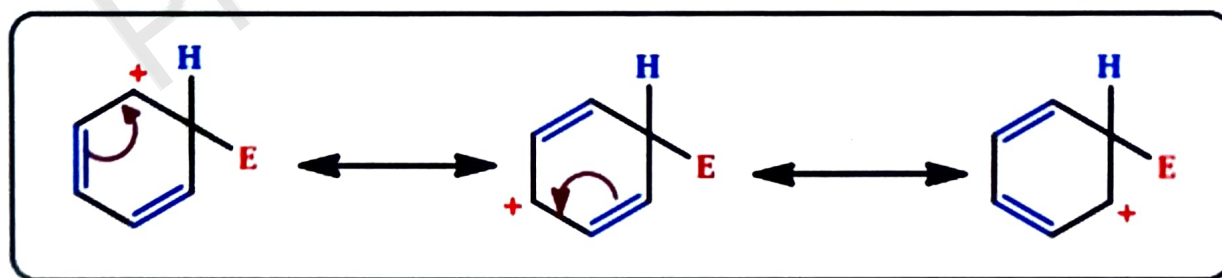
Step 1: Formation of an electrophile.



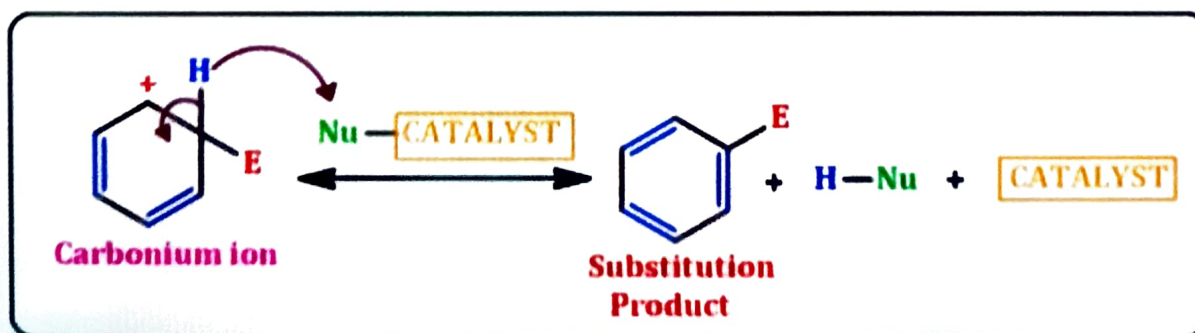
Step 2: The electrophile attacks the aromatic ring to form a carbonium ion.



The intermediate ion is resonance-stabilized. It is a hybrid of the following three structures :



Step 3: Loss of proton gives the substitution product.



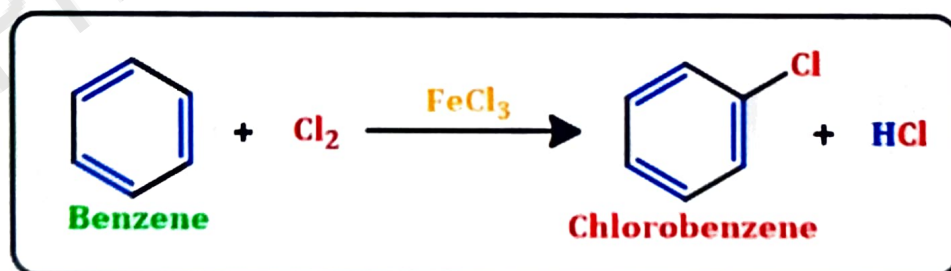
➤ Types of Electrophilic Aromatic Substitution Reactions

➤ In an electrophilic substitution reaction, an **electrophile (Y^+)** is put on the ring and H^+ removed from the ring.

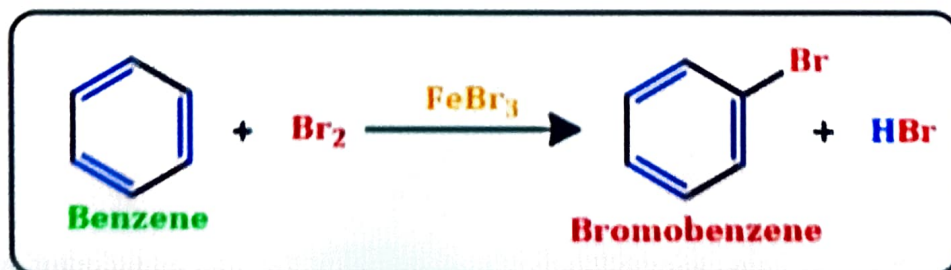
1. **Halogenations:** A bromine, chlorine or iodine substitutes for a hydrogen atom.
2. **Nitration:** A nitro ($-NO_2$) group substitutes for a hydrogen atom.
3. **Sulfonation:** A sulphonic acid ($-SO_3H$) group substitutes for a hydrogen atom.
4. **Friedel - Craft's acylation:** An acyl group substitutes for a hydrogen atom.
5. **Friedel - Craft's alkylation:** An alkyl group substitutes for a hydrogen atom.

1. **Halogenation of Benzene:** Benzene reacts with halogens (Br_2 or Cl_2 or I_2) in the presence of Lewis acid catalyst ($FeBr_3$ or $FeCl_3$) to give bromobenzene or chlorobenzene or iodobenzene respectively. Lewis acid is a compound that accepts a pair of electrons.

➤ Chlorination

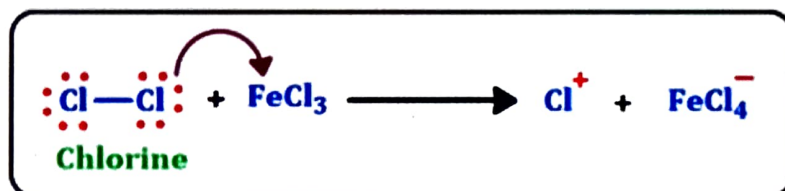


➤ Bromination

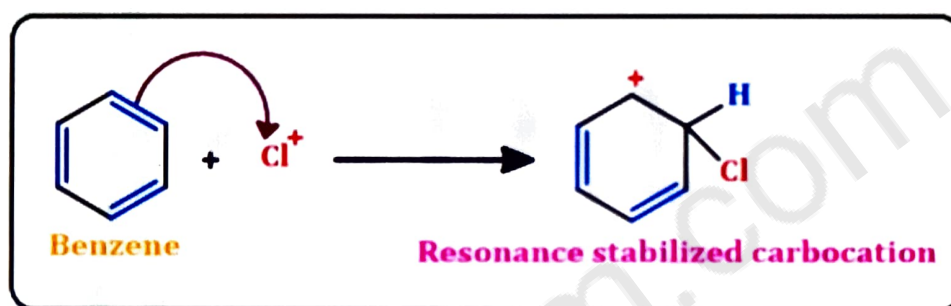


➤ Mechanism of Chlorination

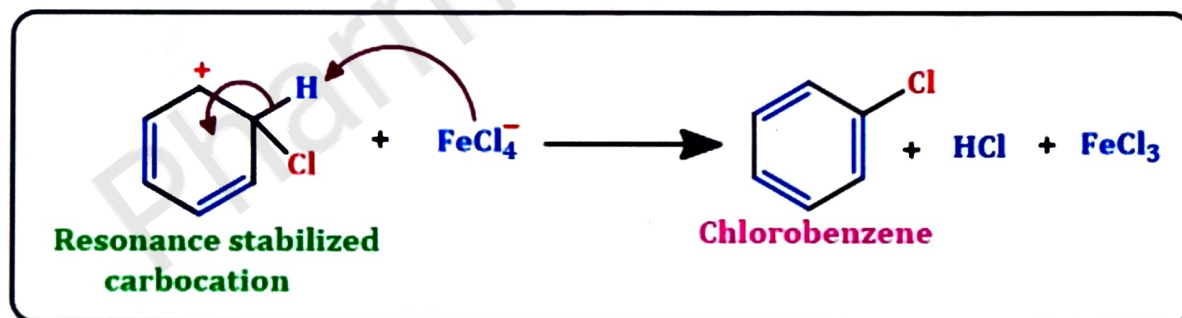
Step 1: Formation of electrophile: Formation of electrophile (Cl^+) takes place by heterolysis of chlorine molecule.



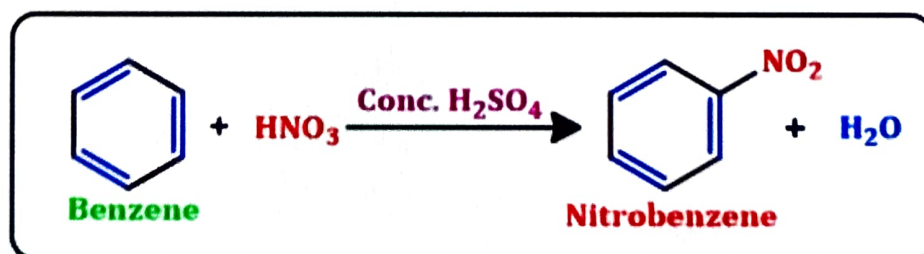
Step 2: Formation of carbocation intermediate: Electrophile (Cl^+) attacks the benzene nuclei and forms resonance stabilized carbocation intermediate.



Step 3: Loss of proton leads to the formation of substituted product: A base from the reaction mixture ($\text{FeCl}_4^- / \text{Cl}^-$ or the solvent) removes the proton from the carbocation to yield the product.



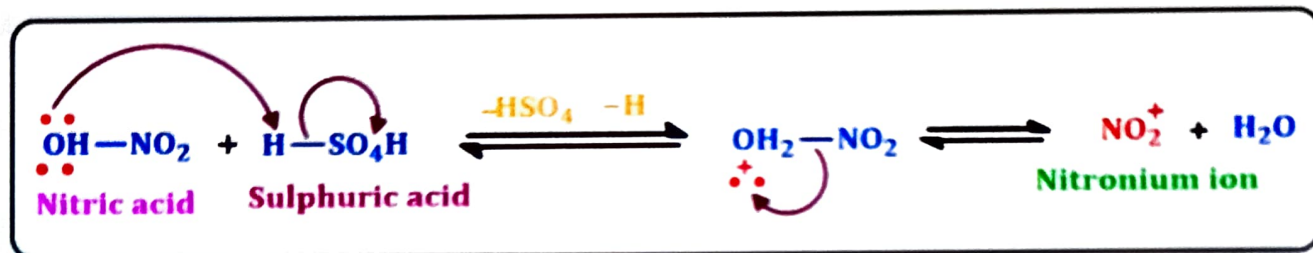
2. Nitration: Benzene reacts with Conc. HNO_3 acid and conc. H_2SO_4 (nitrating mixture) at 60°C to give nitrobenzene



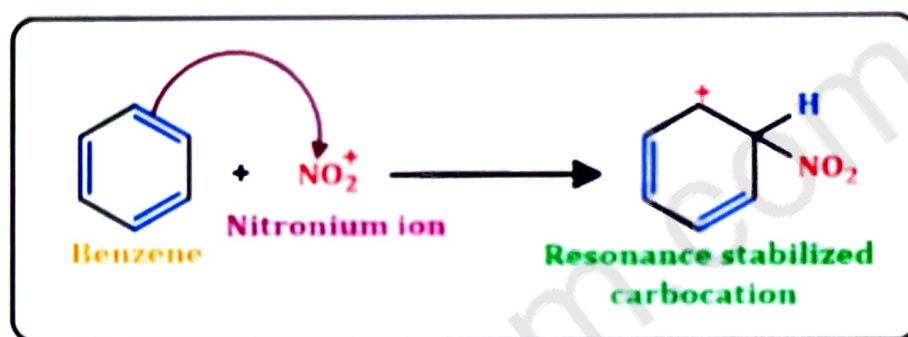
Nitration of benzene with HNO_3 required H_2SO_4 as a catalyst. Here sulphuric acid protonates HNO_3 which produces nitronium ion by the loss of water molecule. Nitronium ion acts as an electrophile which is needed for nitration.

➤ Mechanism of Nitration:

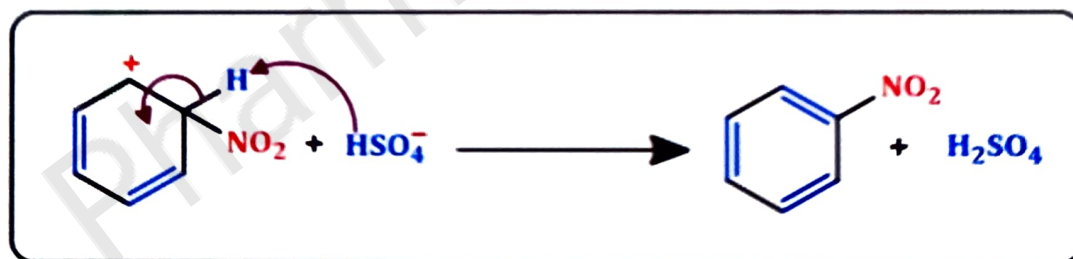
Step 1: Formation of electrophile: The electrophile (NO_2^+) is formed by the reaction between sulphuric acid and nitric acid. Here sulphuric acid protonates HNO_3 which produces nitronium ion by the loss of water molecule.



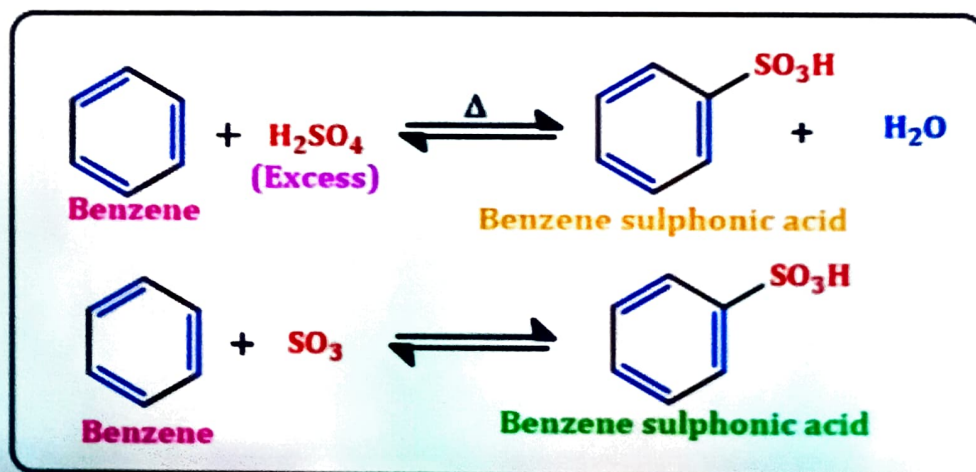
Step 2: Formation of carbocation intermediate: Electrophile (NO_2^+) attacks the benzene nuclei and forms resonance stabilized carbocation intermediate.



Step 3: Loss of proton leads to the formation of substituted product: A base from the reaction mixture removes the proton from the carbocation to yield the product.

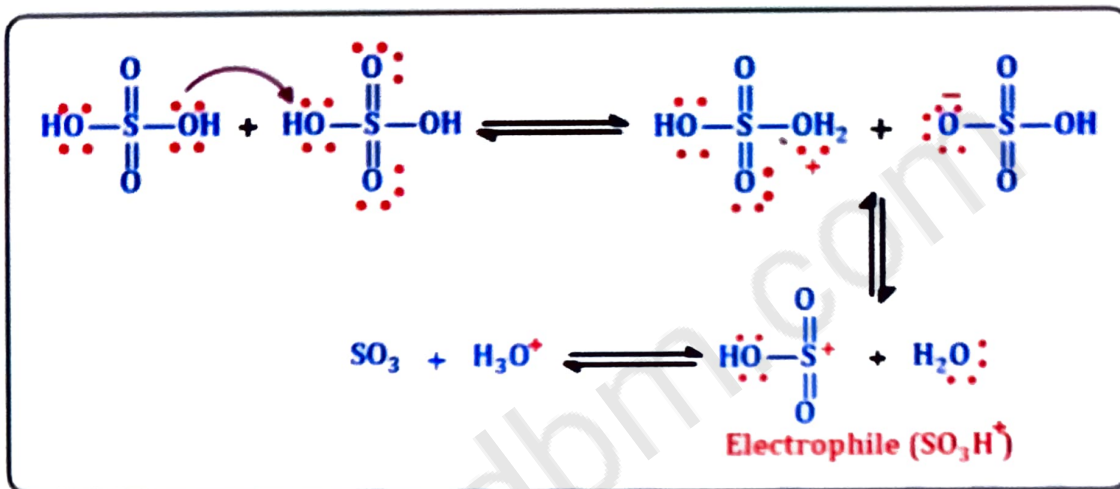


3. Sulphonation: Benzene reacts with fuming sulphuric acid (7% solution of SO_3 in H_2SO_4) or excess concentrated sulphuric acid to give benzene sulphonic acid.

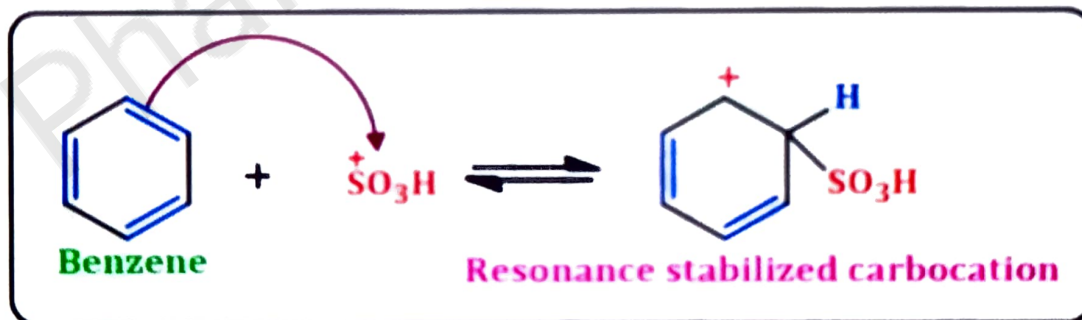


➤ Mechanism of Sulphonation

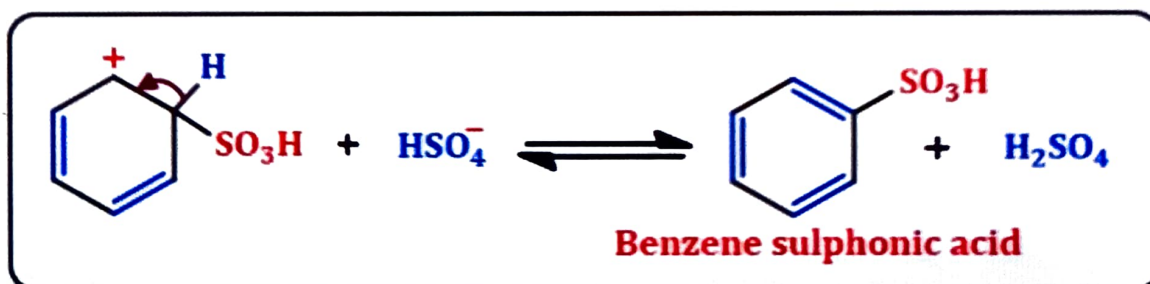
Step 1: Formation of electrophile: A substantial amount of electrophile (SO_3H^+) is formed on heating with conc. H_2SO_4 (loss of water molecule and a proton from H_2SO_4).



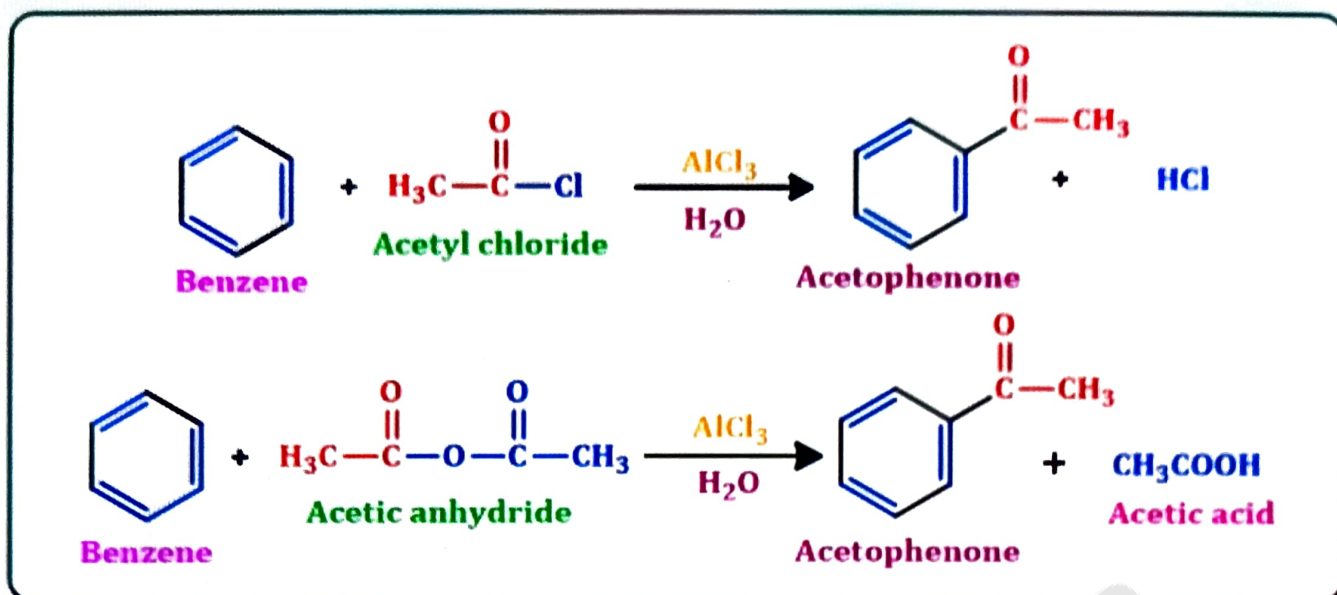
Step 2: Formation of carbocation intermediate: Electrophile attacks the benzene nuclei and forms resonance stabilized carbocation intermediate.



Step 3: Loss of proton leads to the formation of substituted product: A base from the reaction mixture removes the proton from the carbocation to yield the product.

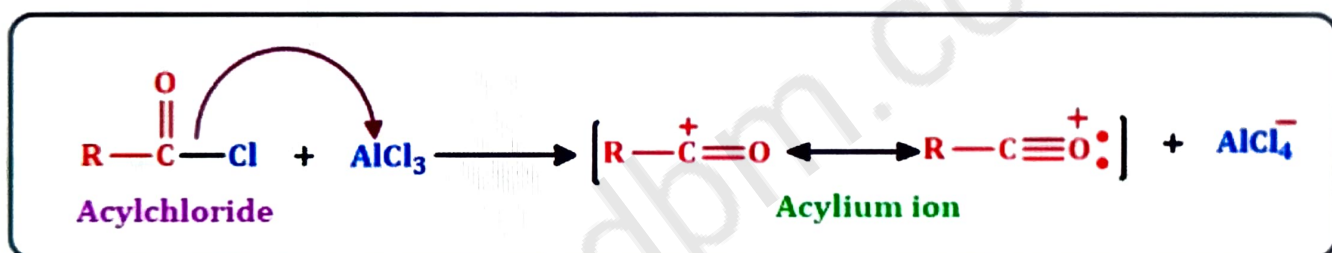


4. Friedel - Crafts Acylation: Benzene reacts with acid chlorides or acid anhydrides in the presence of AlCl_3 to give aromatic ketones.

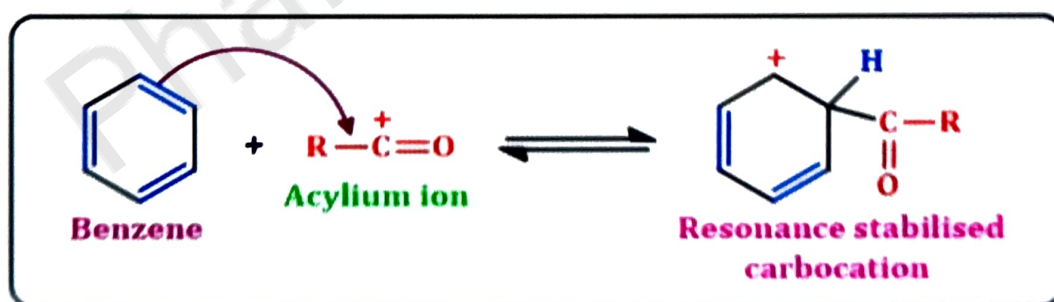


➤ Mechanism

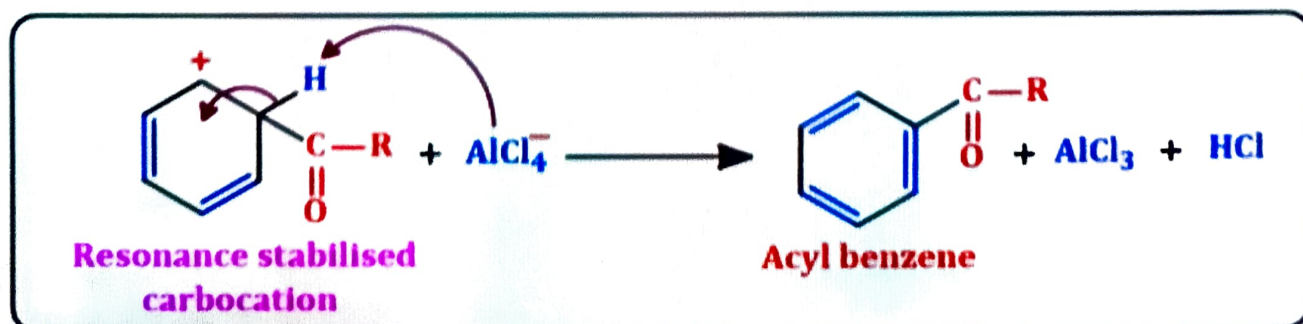
Step 1: Formation of electrophile:



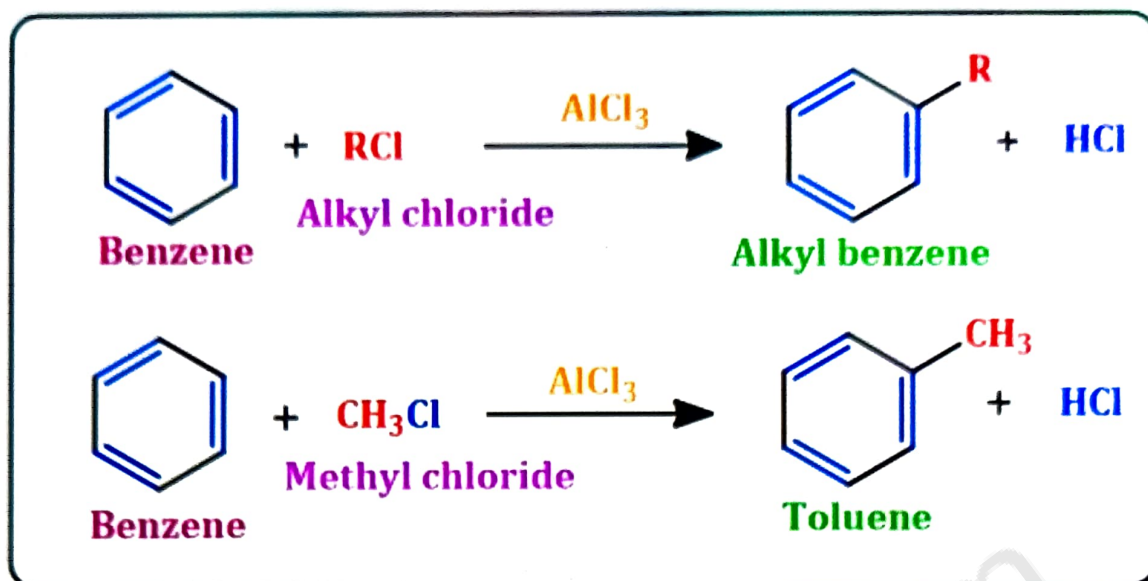
Step 2: Formation of carbocation intermediate: Electrophile (acylium ion) attacks the benzene nuclei and forms resonance stabilized carbocation intermediate.



Step 3: Loss of proton leads to the formation of substituted product: A base from the reaction mixture removes the proton from the carbocation to yield the product.



5. Friedel - Crafts Alkylation: Benzene reacts with alkyl halides in the presence of AlCl_3 or FeCl_3 to give alkyl benzene.

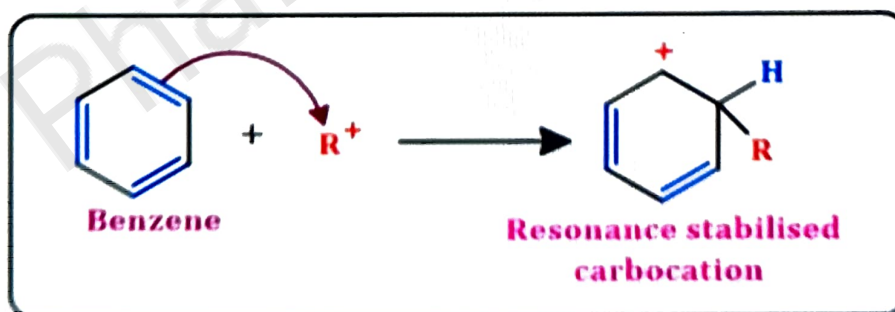


➤ Mechanism

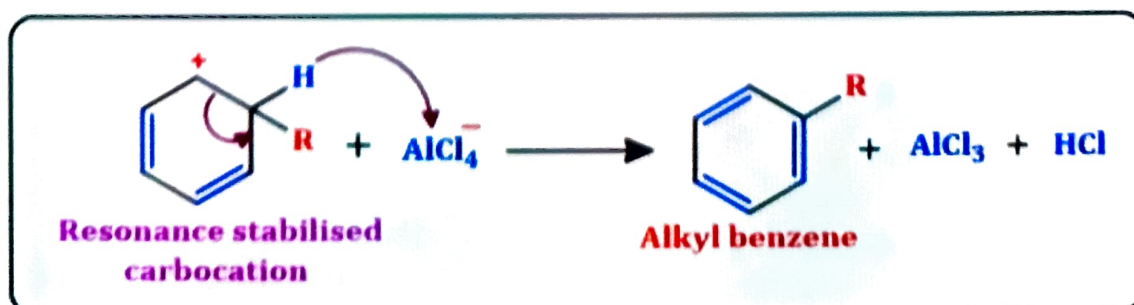
Step 1: Formation of electrophile (R^+):



Step 2: Formation of carbocation intermediate: Electrophile (R^+) attacks the benzene nuclei and forms resonance stabilized carbocation intermediate.



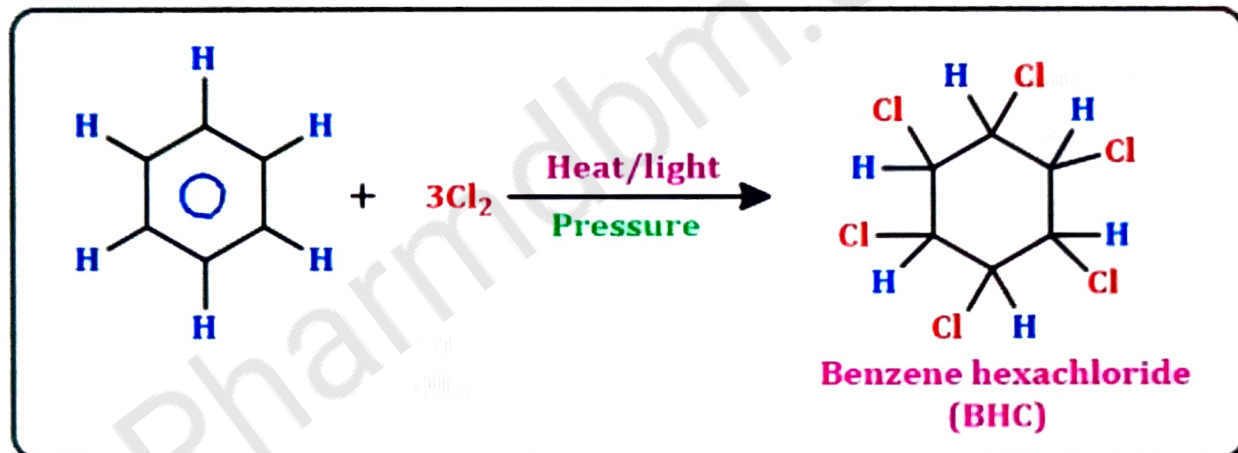
Step 3: Loss of proton leads to the formation of substituted product: A base from the reaction mixture removes the proton from the carbocation to yield the product.



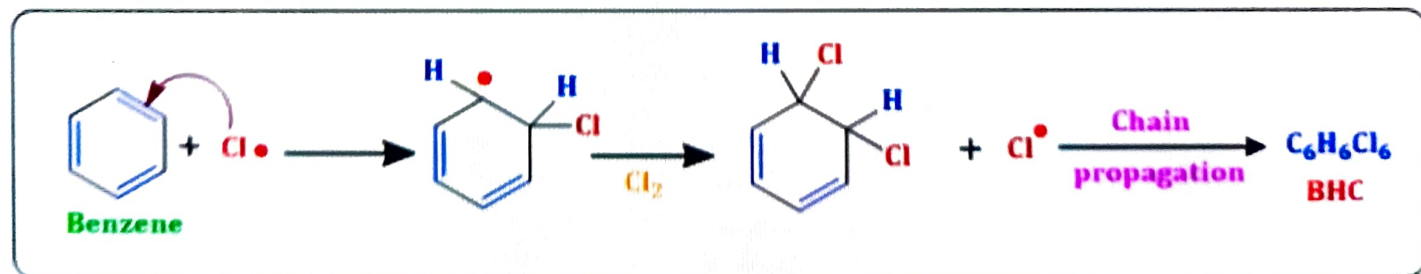
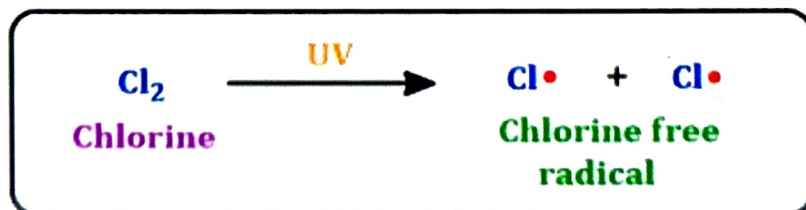
❖ ADDITION REACTIONS OF BENZENE

- Benzene more commonly undergoes substitution reaction, but it may undergo addition reaction under drastic conditions.
- Following reactions are the examples of addition reactions of benzene.

1. **Halogenation:** When **benzene molecule is treated with** an excess amount **of chlorine in the presence of heat** under pressure or irradiation with light gives benzene hexa chloride (BHC). During this reaction, three π bonds of the **benzene ring is substituted with 6 chlorine atoms** (1,2,3,4,5,6-hexa chloro cyclohexane).

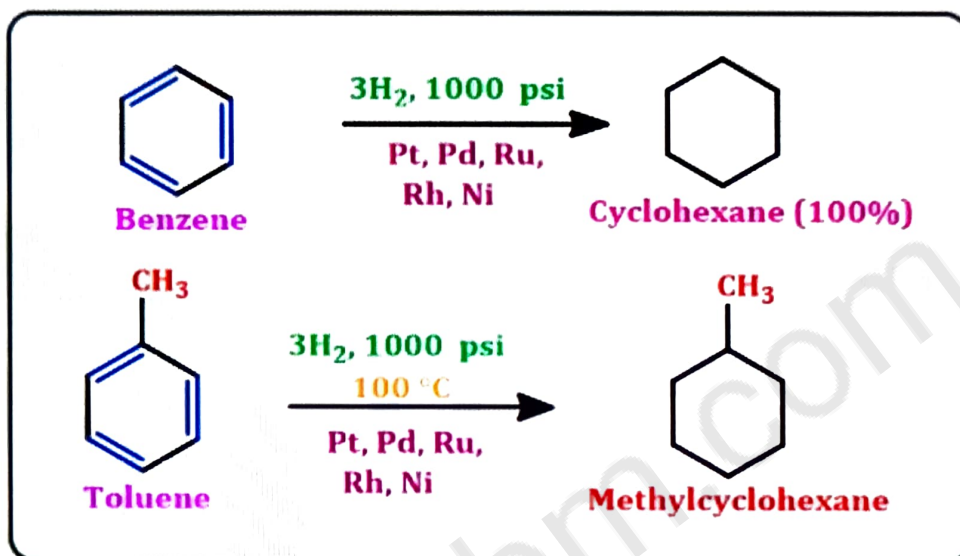


- **Mechanism:** The reaction takes place via the formation of chlorine free radical.



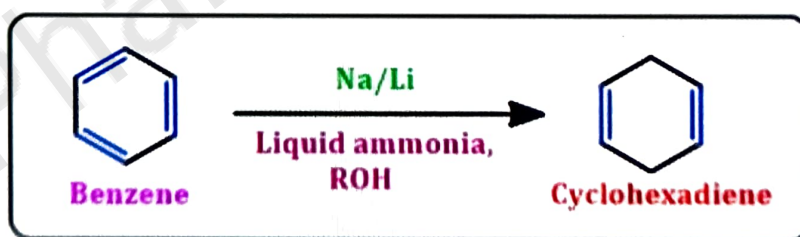
2. Catalytic Hydrogenation or Addition of Hydrogen to the Benzene:

- Benzene undergoes **reduction or hydrogenation at elevated temperature** and pressure or in the **presence of Pt or Pd or Ni, Ru, or Rhodium (Rh)**.
- **Substituted benzene** gives **substituted cyclohexane**.
- This reaction is the **commercial method** for the preparation of **cyclohexane and substituted cyclohexane derivatives**.



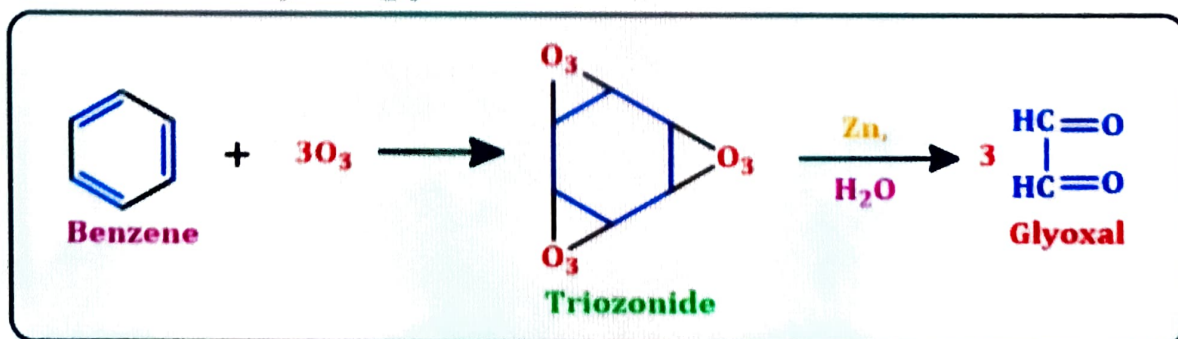
3. Birch reduction:

- **Reduction of benzene** or its derivatives with **sodium or lithium** in a mixture of **liquid ammonia** and **alcohol** gives **1,4 cyclohexadiene**.
- This reaction is known as **Birch reduction**.

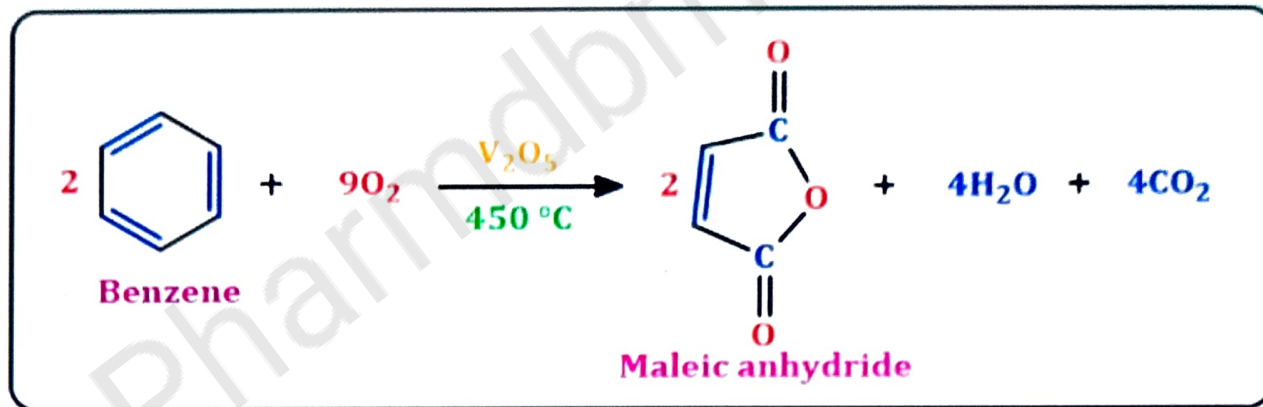


❖ OXIDATION REACTION

1. Ozonolysis: Benzene reacts with ozone to yield a triozone which upon hydrolysis with zinc yield glyoxal.

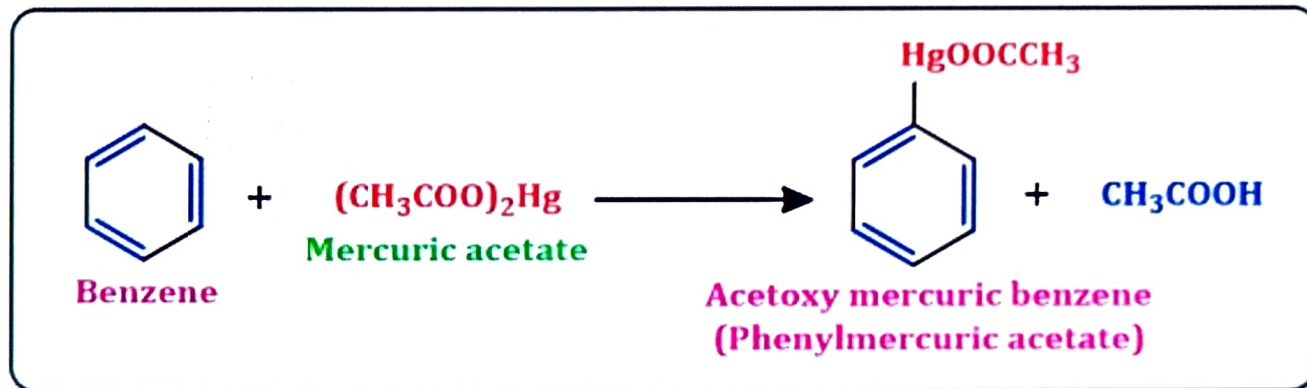


2. Vapour phase oxidation: **Benzene oxidizes with air or oxygen** in the presence of **vanadium pentoxide** at **450 °C** to yield maleic anhydride.



3. Mercuriation:

- When **benzene is heated with mercuric acetate**, one of the hydrogen atom of benzene ring is **replaced by acetoxy mercuric group** (HgCOOCH_3).



UNIT - I (A)

BENZENE AND ITS DERIVATIVES

Points to be covered in this topic

- ANALYTICAL EVIDENCE
- SYNTHETIC EVIDENCE
- EVIDENCES IN THE DERIVATION OF STRUCTURE
- MOLECULAR ORBITAL STRUCTURE OF BENZENE
- RESONANCE IN BENZENE
- AROMATIC CHARACTERS (HUCKEL'S RULE)

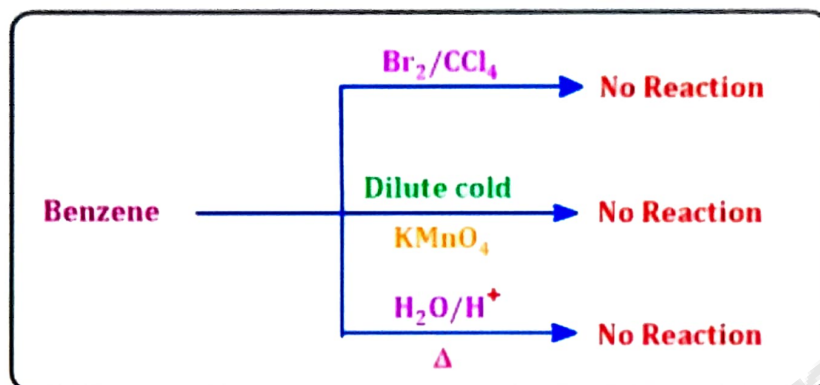
ANALYTICAL, SYNTHETIC AND OTHER EVIDENCES IN THE DERIVATION OF STRUCTURE OF BENZENE

❖ Analytical evidence:

- **Molecular Formula:** Elemental analysis and molecular weight determination showed that benzene had the molecular formula C_6H_6 .
- This indicated that benzene was a highly unsaturated compound (compare it with *n*-hexane, C_6H_{14}).

❖ Synthetic evidence:

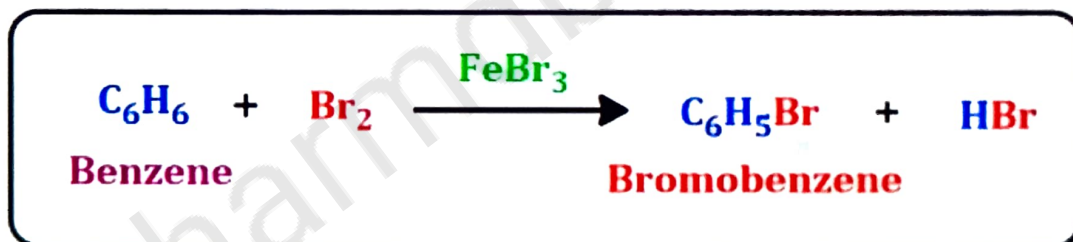
- ✓ **Straight-Chain Structure Not Possible:** Benzene could be constructed as a straight-chain or ring compound having double (C=C) and/or triple bonds. But benzene did not behave like alkenes or alkynes.
- ✓ It did not decolorize bromine in carbon tetrachloride or cold aqueous potassium permanganate. It did not add water in the presence of acids.



❖ Other evidences:

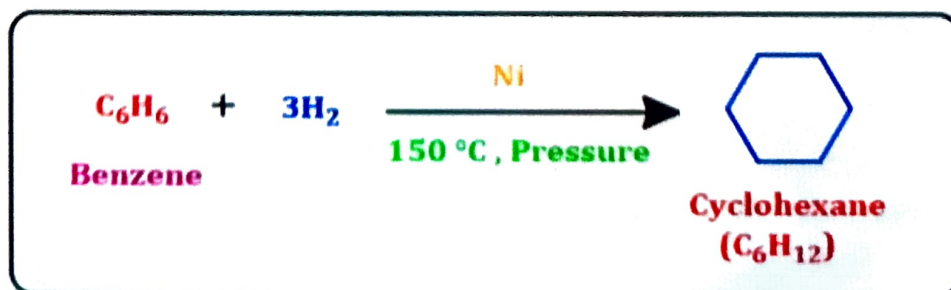
1. Evidence of Cyclic Structure:

- (a) **Substitution of Benzene:** Benzene reacted with bromine in the presence of FeBr_3 (catalyst) to form monobromobenzene.



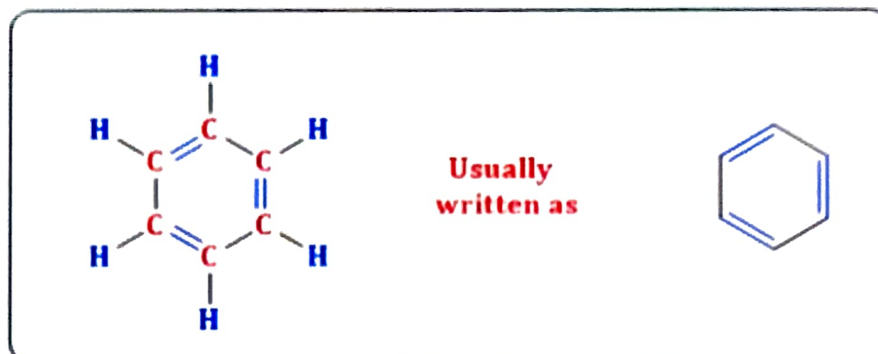
The fact that only one monobromo and no isomeric products were obtained indicated that all six hydrogen atoms in benzene were identical. This could be possible only if benzene had a cyclic structure of six carbons and to each carbon was attached one hydrogen.

- (b) **Addition of Hydrogen:** Benzene added three moles of hydrogen in the presence of nickel catalyst to give cyclohexane.



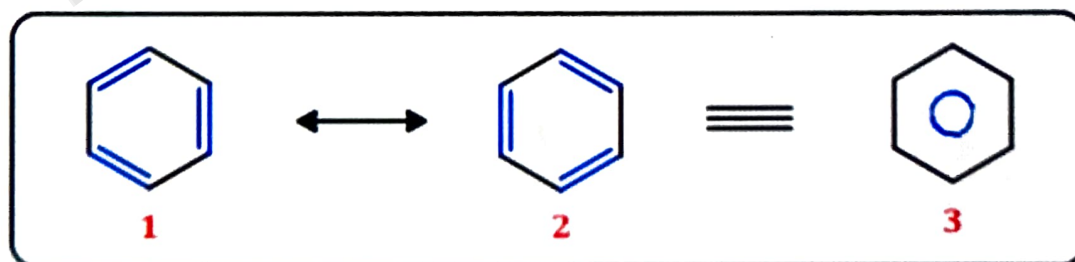
This confirmed the cyclic structure of benzene and also showed the presence of three carbon-carbon double bonds.

2. Kekule's Structure for Benzene: August Kekule suggested that benzene consisted of a cyclic planar structure of six carbons with alternate double and single bonds. To each carbon was attached one hydrogen. Benzene according to this proposal, was simple, 1,3,5-cyclohexatriene.



☐ Resonance Description of Benzene

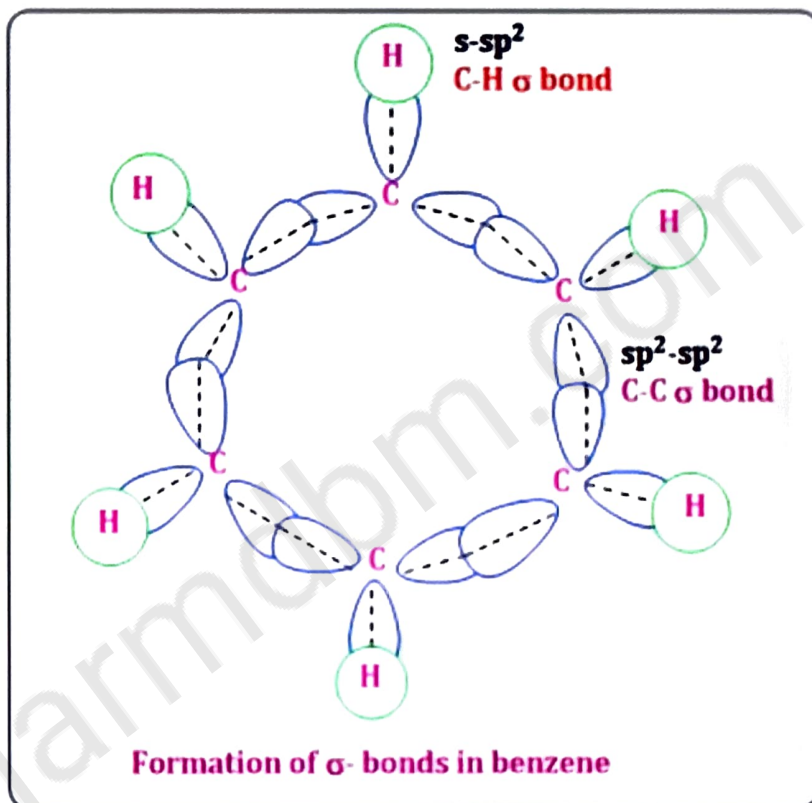
- The phenomenon in which two or more structures can be written for a substance which involve **identical positions of atoms** is called **Resonance**.
- The actual structure of the molecule is said to be **Resonance Hybrid** of various **possible alternative structures**.
- The alternative structures are referred to as the **Resonance Structures or Contributing Forms**.
- A **double headed arrow (\leftrightarrow)** between the resonance structures is used to represent the **resonance hybrid**.



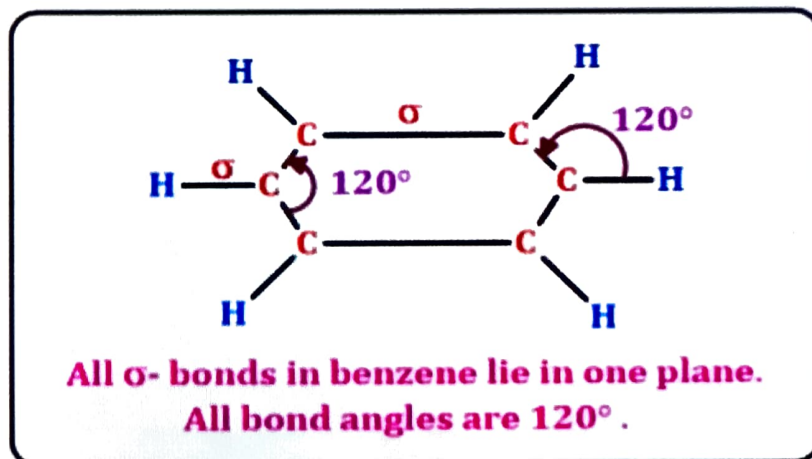
- ✓ **Resonance hybrid is more stable than any of its contributing structures.**
- ✓ **For benzene, the stability due to resonance is so great that π -bonds of the molecule will normally resist breaking.**
- ✓ **This explains lack of reactivity of benzene towards addition.**

MOLECULAR ORBITAL STRUCTURE OF BENZENE

- The structure of benzene is best described in terms of the modern molecular orbital theory.
- All six carbon atoms in benzene are sp^2 hybridized.
- The sp^2 hybrid orbitals overlap with each other and with s orbitals of the six hydrogen atoms forming C-C and C-H σ bonds.



- ✓ Since the σ -bonds result from the overlap of planar sp^2 orbitals, all carbon and hydrogen atoms in benzene lie in the same plane.
- ✓ All σ -bonds in benzene lie in one plane and all bond angles are 120°



□ AROMATIC CHARACTERS (HUCKEL'S RULE)

- The aromatic compounds apparently contain alternate double and single bonds in a cyclic structure, and resemble benzene in chemical behavior.
- They undergo substitution rather than addition reactions.
- This characteristic behavior is called **Aromatic Character or Aromaticity**.
- **Aromaticity is, in fact, a property of the sp^2 hybridized planar rings in which the p orbitals (one on each atom) allow cyclic delocalization of π electrons.**

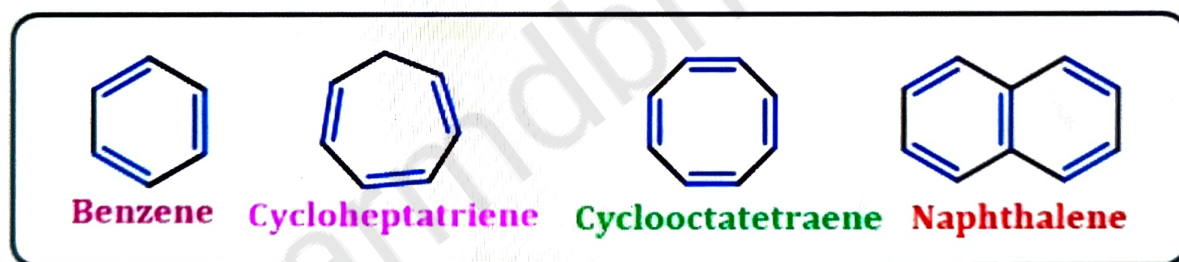
❖ Criteria for Aromaticity

Rule 1: An aromatic compound is **cyclic and planar**.

Rule 2: Each atom in an aromatic ring has a **p orbital**. These p orbitals must be parallel so that a continuous overlap is possible around the ring.

Rule 3: The cyclic π molecular orbital (electron cloud) formed by overlap of p orbitals must **contain $(4n+2)$ π electrons**, where $n =$ integer 0, 1, 2, 3 etc.

This is known as **Huckel's Rule**.



Benzene

Cycloheptatriene

Cyclooctatetraene

Naphthalene

- ❖ **Benzene:** It is a cyclic and planar compound. It has a p orbital on each carbon of the ring involved in a double bond. It has three double bonds and six π electrons, which is in accordance with Huckel's rule.

$$4n + 2 = 6 \quad \text{or} \quad 4n = 6 - 2$$

$$\therefore 4n = 4 \quad \text{and} \quad n = 1$$

- ❖ **Cycloheptatriene:** It is cyclic and planar. It has three double bonds and six π electrons. But one of the carbons is saturated and does not possess a p orbital. Hence a continuous overlap around the ring is not possible. This compound is, therefore, **non-aromatic**.
- ❖ **Cyclooctatetraene:** It is cyclic and has a p orbital on each atom of the ring. The Huckel's rule is not satisfied, since there are 8π electrons. The compound is non-aromatic.

UNIT - I (C)

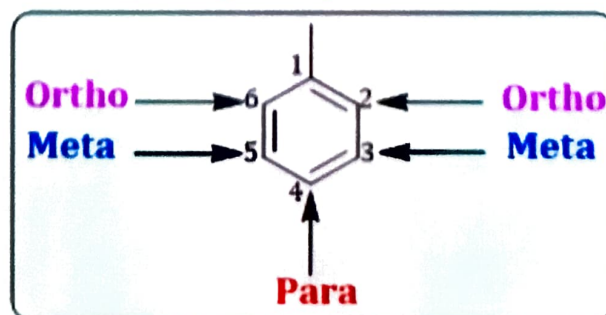
BENZENE AND ITS DERIVATIVES

□ EFFECT OF SUBSTITUENTS ON REACTIVITY AND ORIENTATION OF MONO SUBSTITUTED BENZENE COMPOUNDS TOWARDS ELECTROPHILIC SUBSTITUTION REACTION

- Benzene has **six hydrogen** which all are equal.
- If we replace any **one 'H' atom by a substituent** it gives a **monosubstituted derivative** of benzene.
- When **monosubstituted** benzene is converted into **di-substituted** in derivative, then **three isomers (ortho, meta and para)** are possible.
- The substituent which is **already present in the ring determines the position of the incoming group.**
- The **ability of a group** already present in the ring **to direct the incoming group** is called directive influence of groups.
- The already present group **not only decides the orientation of further substitution** but also affects the **reactivity of the benzene nucleus** towards further **electrophilic substitution reactions.**

□ Effect of Substituents on Orientation

- A **second substituent** can occupy any of the remaining five positions in monosubstituted benzene. The **position 2 & 6 are equivalent & gives Ortho product**
- **Position 3 & 5** are equivalent and gives **Meta product**
- **Position 4** is unique and gives **para product**

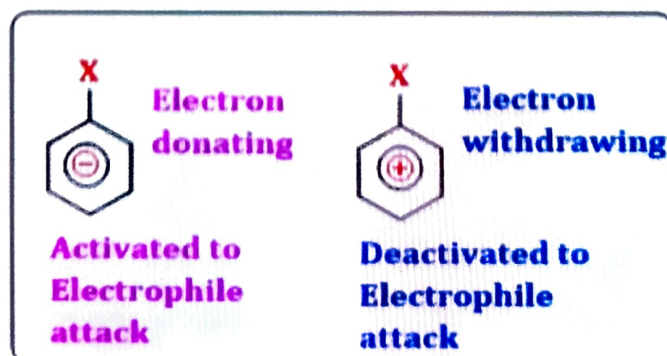


□ EFFECT OF SUBSTITUENTS ON REACTIVITY

Activating groups / ortho/para directing group	<ul style="list-style-type: none">• These groups increase electron density at ortho- and para-positions, which means that these groups are ortho- and para-directing.• These are highly ring activating groups so electrophilic substitution occurs at a very fast rate.• Some activating groups in decreasing order are given below: $-\text{NH}_2$, $-\text{NHR}$, $-\text{NR}_2$, $-\text{OH}$, $-\text{OR}$, $-\text{NHCOR}$, $-\text{SH}$, $-\text{OCOR}$, $-\text{CH}_3$, $-\text{CH}_2\text{CH}_3$, $-\text{CH}(\text{CH}_3)_2$
Deactivating groups / Meta directing	<ul style="list-style-type: none">• These groups are meta-directing and deactivate benzene ring, that is, they decrease electron density at ortho- and para-positions thereby making electrophilic substitution slower and occur only at the meta-position• Some deactivating groups in decreasing order are shown below: $-\text{NR}_3$, $-\text{NO}_2$, $-\text{CN}$, $-\text{COOH}$, $-\text{COOR}$, $-\text{SO}_3\text{H}$, $-\text{CHO}$, $-\text{COR}$

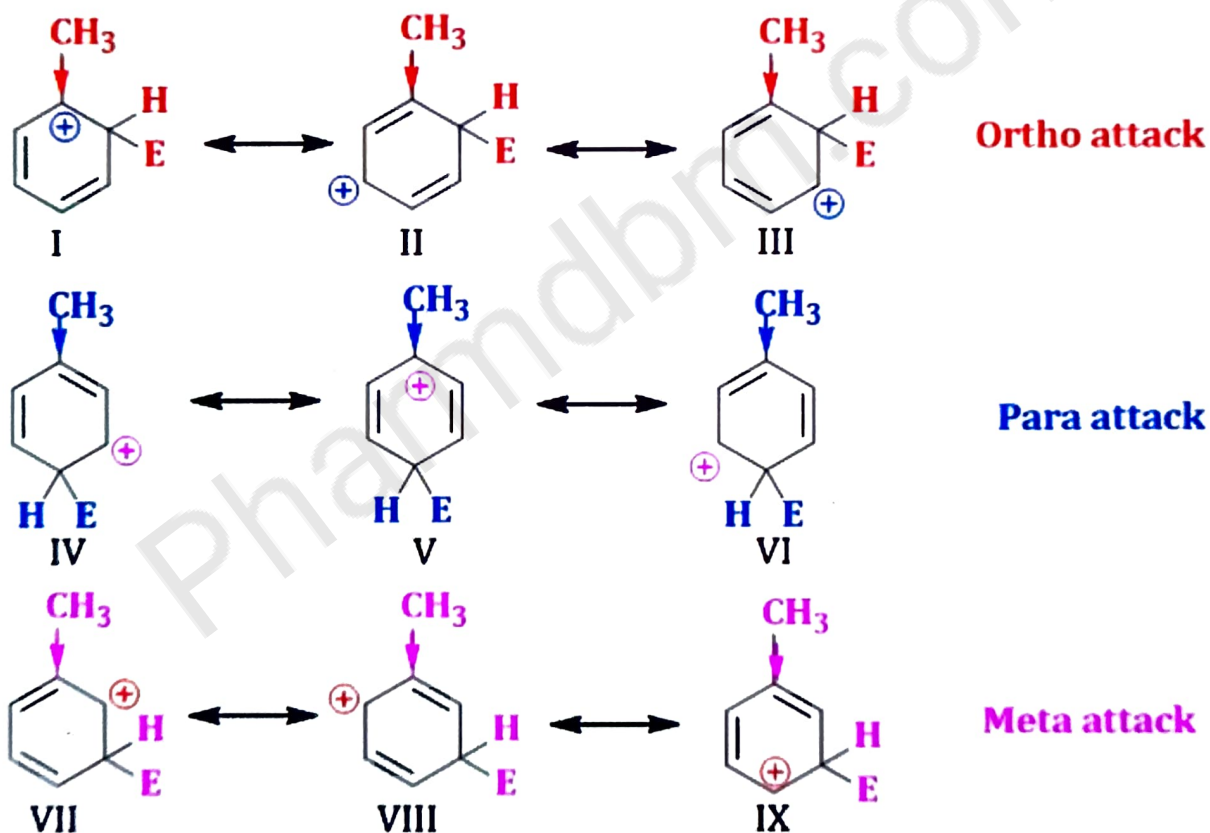
□ Theory of Reactivity

- The rate of **electrophilic substitution reactions** depends upon the **energy of activation** i.e. difference in energy of the transition state and ground state of reactants.
- So, the **rate depends on the availability of electrons** in the benzene ring.
- If the **ring is electron rich (-ve)**, the **electrophilic attack is faster**
- If the **ring is electron deficient (+ve)** the **attack is slower**
- So, an **electron donating substituent will activate** the aromatic ring while an **electron withdrawing substituent will deactivate** it.



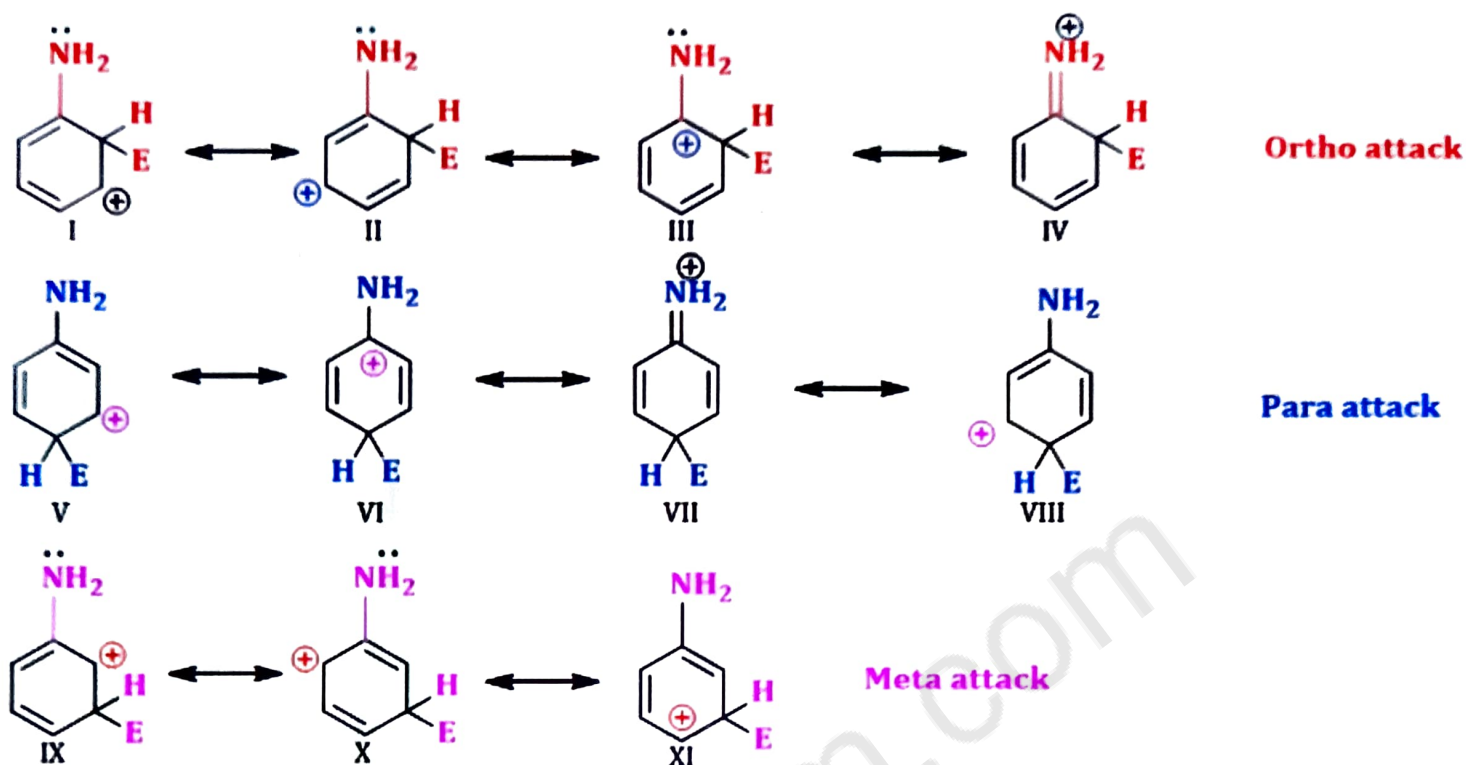
□ Theory of Orientation

- **Orientation or directive effect** can be explained by studying all the **possible resonance structures** of the a **complex formed** as a result of the **attack of the electrophile** at Ortho, meta and para positions for **different types of substitutions**
- **Ortho-para directing groups**
- **Ortho-para directing groups** having **electron releasing inductive effect** (+I effect)
- For example, **alkyl groups** has **+I effect** i.e. electron releasing inductive effect.
- Let us study the a complexes or the **carbocation intermediates** formed by attacked of E^+ at **ortho, para and meta positions** of toluene



- **Alkyl group has electron releasing effect** so it disperse the **positive charge** and thus stabilizes the carbocation.
- This **effect is maximum** in case of **structure I & V** as **+ve charge** is located on **the carbon atom to which methyl group is attached**.
- So, the structure I & V resulting from **ortho & para attack** are more, **stable than resulting from meta attack**.
- As a result of this, **electrophilic substitution occurs faster in toluene** than **in benzene**.

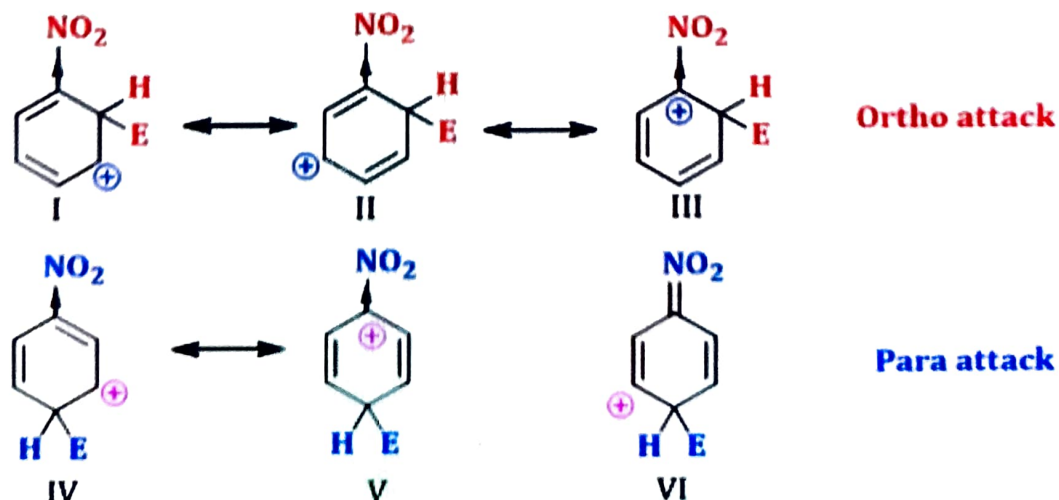
❖ **Ortho-para directing groups having electron withdrawing (-I effect) and electron releasing (+R or +M effect):** For example, $-\text{NH}_2$, group.

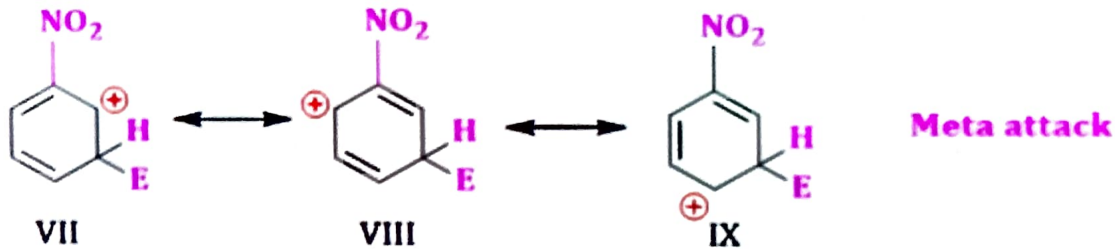


- σ complex obtained from ortho and para attack is a resonance hybrid of four structures while from meta attack is a resonance hybrid of only three structures.
- **Structure IV and VII are more stable as +ve charge is delocalised on the nitrogen atom** as well as the ring carbon atoms.
- No such structure is possible in case of meta attack.

❑ **Meta directing groups**

- All **meta directing groups are electron withdrawing** in nature.
- They have both electron withdrawing **inductive and resonance effect** i.e. -I & -R effect.
- For example, $-\text{NO}_2$, $-\text{CN}$, $-\text{COOH}$, $-\text{CHO}$, $-\text{SO}_2\text{H}$ etc.





- Structures III & V are **highly unstable** as **electron withdrawing nitro group is linked to the carbon atom carrying the +ve charge**.
- So, a **complex intermediates from ortho & para attack** are resonance hybrid of **only two structures**.

UNIT - I (D)

BENZENE AND ITS DERIVATIVES

Points to be covered in this topic

→ DICHLORO DIPHENYL TRICHLOROETHANE

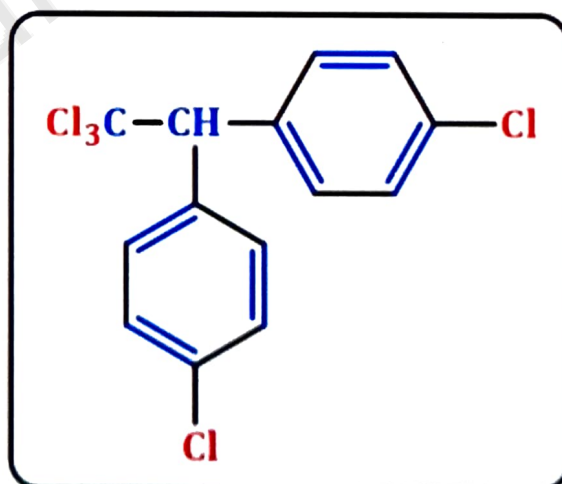
→ SACHHARIN/SACCHARIN SODIUM

→ BENZENE HEXACHLORIDE (BHC)

→ CHLORAMINE-T

DICHLORO DIPHENYL TRICHLOROETHANE (DDT)

STRUCTURE

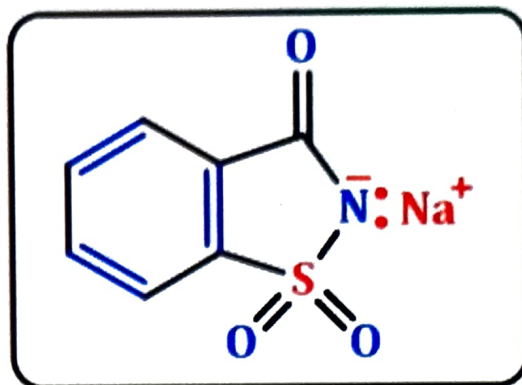


USES:

1. It is used as an effective insecticide and pesticide especially for mosquitoes.
2. It is used to completely destroy the malarial parasite but it is genotoxic to human beings.

□ SACHHARIN/SACCHARIN SODIUM

STRUCTURE

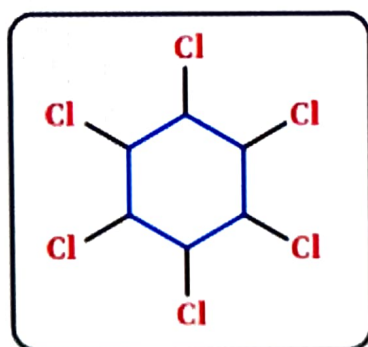


USES:

1. The soluble salt of saccharin is known as saccharin sodium.
2. It is used as sweetening agent in toothpaste and aerated drinks.

□ BENZENE HEXACHLORIDE (BHC) (HEXA CHLORO BENZENE)

STRUCTURE

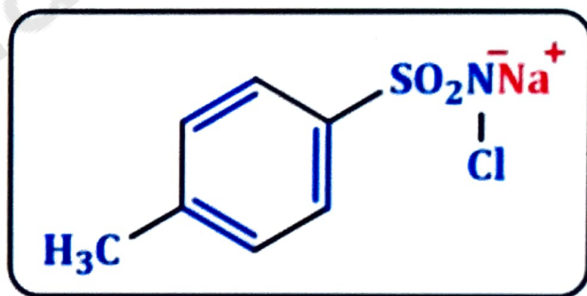


USES:

1. Benzene hexachloride is used as an insecticide on crops, in forestry, for seed treatment.
2. It is used in the treatment of head and body lice.
3. It is used in pharmaceuticals.
4. It is used to treat scabies.

□ CHLORAMINE-T (SODIUMSALT OF TOSYLCHLORAMIDE)

STRUCTURE



USES:

1. It is used as an algicide, bactericide, virucide & fungicide.
2. It is also effective against myco-bacterium tuberculosis, foot & mouth diseases and avian influenza.
3. It is also used for drinking water disinfection and used to destroy parasite.