HYDROCARBON

Hydrocarbons

1. **Aliphatic Hydrocarbons**
   - The word *aliphatic* comes from the Greek word *aleiphar*, meaning **oil**.
   - These hydrocarbons were originally obtained by the chemical degradation of fats.
   - **Definition:** All hydrocarbons that **do not contain a benzene ring** are classified as *aliphatic hydrocarbons*.
2. **Aromatic Hydrocarbons**
   - Hydrocarbons containing **at least one benzene ring** are called *aromatic hydrocarbons*.
   - In modern terminology, they are also called **arenes**.
   - The word *arene* is made up of:
     - **"ar"** → stands for aromatic
     - **"ene"** → taken from the last three letters of benzene, showing **unsaturation**

Historical Background of Benzene

- In **1825**, Michael Faraday isolated a hydrocarbon from oily residues found in London gas pipes. He called it **"bicarburet of hydrogen."**
- Later, in **1834**, Eilhardt Mitscherlich (University of Berlin) prepared the same substance by heating **benzoic acid** with lime.

$$C_6H_5COOH + CaO \rightarrow C_6H_6 + CaCO_3$$

- Benzoic acid was obtained from **gum benzoin**, a resin of the balsam tree (Java, Indonesia). The product was named **benzin**, which later became **benzene**.

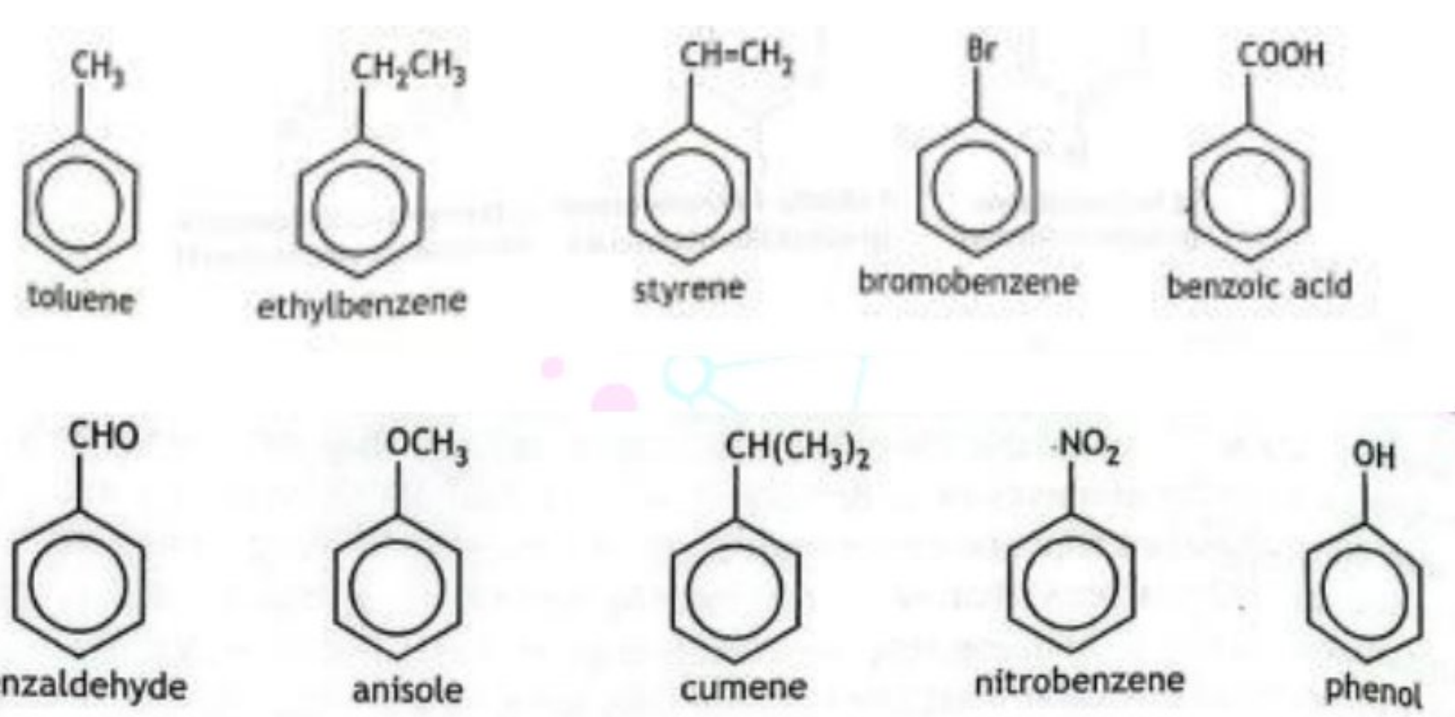
Aromatic Hydrocarbons

- All compounds related to **benzene** and **toluene** are classified as aromatic hydrocarbons.
- The word *aroma* comes from Latin, meaning **fragrance**.
- Interestingly, although aromatic hydrocarbons were first discovered from **pleasant-smelling plant extracts**, not all of them are fragrant. Some even have **harmful or unpleasant vapours**.
- The main reason for their classification as *aromatic* is their **unusual stability** due to the benzene ring.
- **Rule:** All aromatic compounds must contain **at least one benzene ring**.

Nomenclature of Benzene

1. Monosubstituted Benzenes

- These compounds have **only one substituent** attached to the benzene ring.
- **IUPAC rule reminder:**
  - Compound names are written in **lowercase** (except at the beginning of a sentence).
  - Element symbols always start with an **uppercase** letter (e.g., Cl, Br, NO_2).
- Examples:
  - Chlorobenzene (Cl–C_6H_5)
  - Nitrobenzene (NO_2–C_6H_5)
  - Methylbenzene (C_6H_5–CH_3, also called **toluene**).



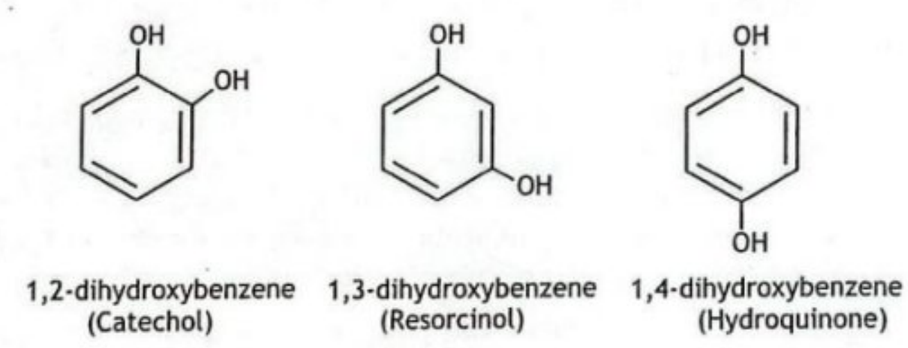
2. Disubstituted Benzenes

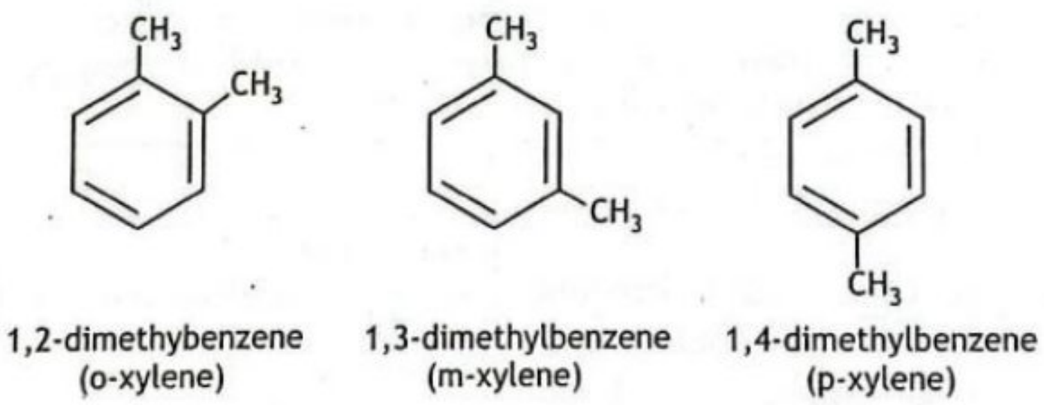
- These compounds have **two substituents** on the benzene ring.
- They can form **three positional isomers**:
  - **Ortho (o-) / 1,2-** → substituents on adjacent carbons.
  - **Meta (m-) / 1,3-** → substituents separated by one carbon.
  - **Para (p-) / 1,4-** → substituents opposite each other.

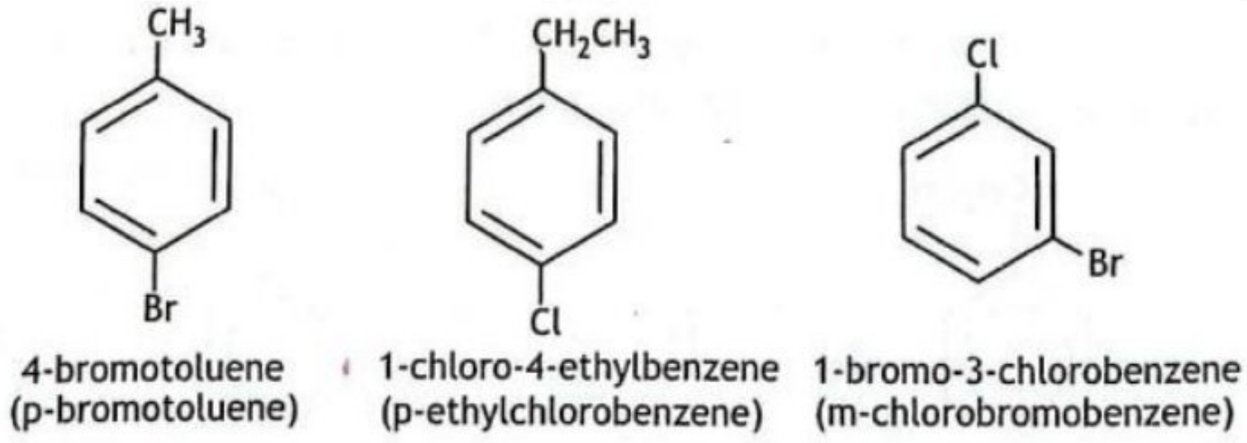
Examples:

- o-dichlorobenzene (1,2-dichlorobenzene)
- m-dinitrobenzene (1,3-dinitrobenzene)
- p-xylene (1,4-dimethylbenzene).
- **Special names rule:**
  - If one substituent gives a special name (like **toluene, phenol, aniline**), that group is placed at **position 1**, and the compound is named as a derivative of that parent.
  - Example: 2-nitrotoluene (not methyl nitrobenzene).

- **Xylene exception:**
  - The three isomeric **dimethylbenzenes** are collectively called **xylene** (ortho, meta, para forms).
- **No special group case:**
  - If no substituent provides a special name, list them in **alphabetical order** before the word *benzene*.
  - Example: 1-bromo-3-chlorobenzene.







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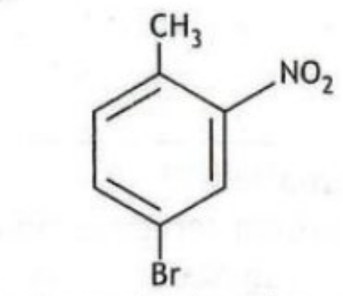
3. Polysubstituted Benzenes (3 or more substituents)

- **Numbering rule:** Assign numbers to give the **lowest possible set of locants**.
- **Special group case:** If one substituent provides a special name (e.g., toluene, phenol), the compound is named as its derivative.
- **No special group case:** List substituents in **alphabetical order** before "benzene."

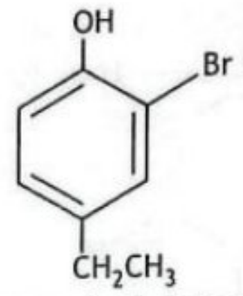
👉 Examples:

1. A derivative of **toluene**: 2,4-dinitrotoluene.

2. A derivative of **phenol**: 3-chloro-4-methylphenol.
3. No special name → 1-bromo-2-chloro-4-nitrobenzene.



4-bromo-2-nitrotoluene



2-bromo-4-ethylphenol

Discovery and Molecular Formula of Benzene

After the discovery of benzene in **1835**, the structure of the benzene molecule puzzled nineteenth-century chemists for about forty years. **Elemental analysis** proved that benzene has an unusually low hydrogen-to-carbon (H:C) ratio, with molecular formula **C_6H_6** and empirical formula **CH**. This suggested a **high degree of unsaturation**.

Early Proposed Structures of Benzene

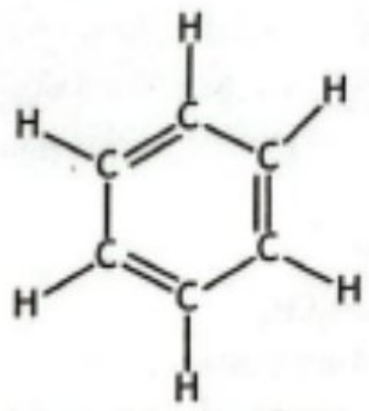
Considering this unsaturation, many chemists proposed different structures for benzene containing **carbon–carbon double and triple bonds**, such as:

- **CH_2=CH–C≡C–CH=CH_2**
- **HC≡C–CH_2–CH_2–C≡CH**

However, the observed **chemical properties of benzene** did not match with these open-chain structures. These proposals failed because they imagined benzene as a **linear (open) molecule**, whereas experimental evidence later showed that benzene is a **cyclic compound** with unique stability and resonance.

Kekulé's Dream and Proposal (1865)

In 1865, a German chemist **August Kekulé** was sitting near a fire on a cold night in his laboratory, struggling to determine the structure of the benzene molecule. Suddenly, he had a **dream** in which he saw atoms dancing around and forming chains. These chains turned into rings and appeared like **snakes biting their tails**.


Kekule's structure

This vision inspired Kekulé to propose that benzene is a **cyclic molecule with six carbon atoms** in a ring, each bonded to one hydrogen atom. This was the **first cyclic structural model** of benzene.

Importance of Kekulé's Ring Structure

The ring structure of benzene imagined by Kekulé was a **revolutionary idea in chemistry**. It encouraged chemists to consider **ring structures in other organic molecules** as well.

This cyclic model successfully explained the **unexpected stability** and many of the **observed chemical properties** of benzene, which open-chain structures could not.

The Concept of Resonance in Benzene

Kekulé further proposed that the benzene ring contains **three alternating carbon–carbon double bonds**. These double bonds **shift positions rapidly**, so the two possible Kekulé structures cannot be distinguished.

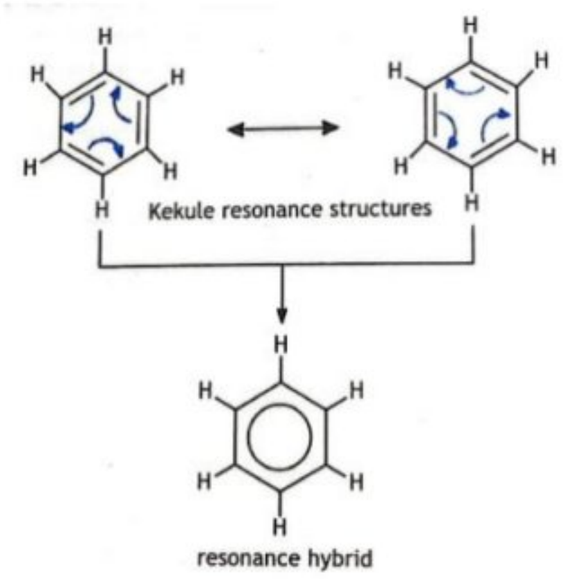
This movement occurs because the **π (pi) electrons are delocalized** and spread evenly over all six carbon atoms in the ring. Thus, the real structure of benzene is not either one of Kekulé's forms but rather a **resonance hybrid** of the two.

Limitations and Criticism of Kekulé's Model

Although Kekulé's proposal was consistent with many experimental results, it was later challenged because it could not answer some important questions:

1. If benzene has double bonds like alkenes, **why does it not react like an alkene?**
2. If benzene has three double bonds, **why can it not add three moles of bromine?**
3. Why does benzene show a preference for **substitution reactions instead of addition reactions**?

Due to these limitations, new and more refined models were developed to explain the true nature of the benzene molecule.



Introduction to the Molecular Orbital Model

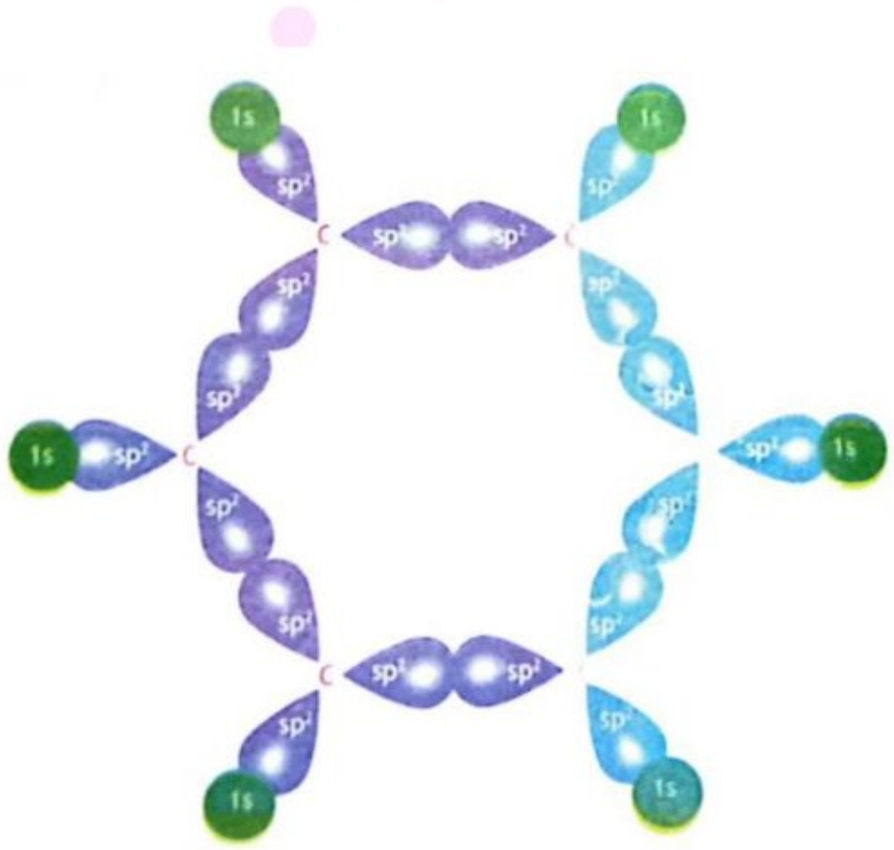
In the **1930s**, **Linus Pauling** developed the concepts of **hybridization** and **resonance theory**. These two ideas provided the first **adequate explanation of the structure of benzene**, improving upon Kekulé's model.

Carbon Skeleton and Hybridization

The carbon atoms in benzene form a **regular hexagon** with bond angles of **120° (C–C–C and H–C–C)**. Each carbon atom is **sp^2 hybridized**:

- Two sp^2 orbitals overlap with neighboring carbon atoms to form **sigma (σ) bonds**.
- One sp^2 orbital overlaps with the **1s orbital of hydrogen** to form a **σ bond with hydrogen**.

Thus, every carbon in benzene is bonded to **two carbons and one hydrogen**.

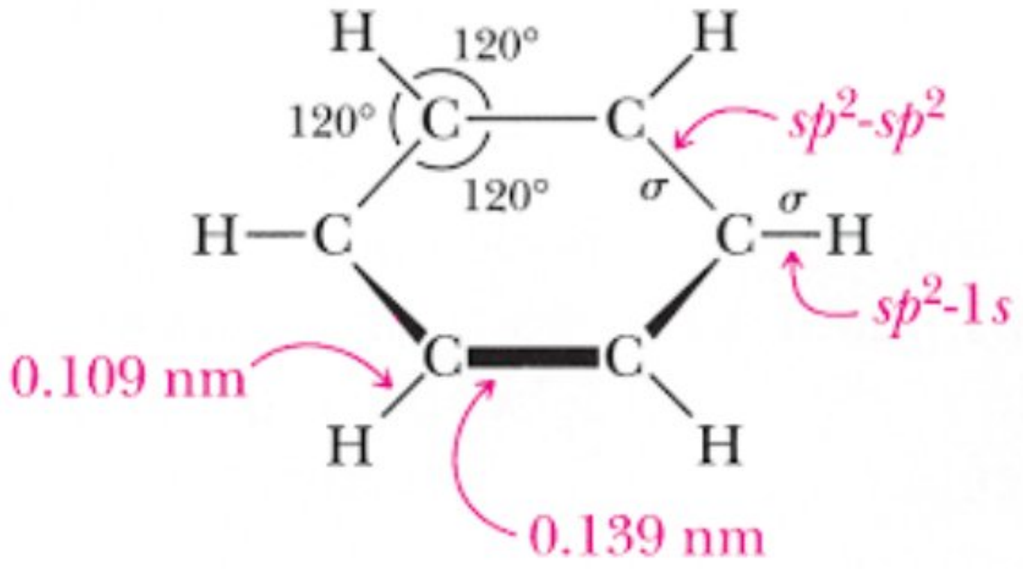


Experimental Bond Length Evidence

Experimental studies determined that the **C–C bond length in benzene** is **1.39 Å**, which lies between:

- The single bond length (**1.54 Å**)
- The double bond length (**1.30 Å**)

This indicates that the carbon–carbon bonds in benzene are **neither purely single nor purely double**, but instead **partial double bonds** due to electron delocalization.



Delocalized π-Electron Cloud

Each carbon atom has an **unhybridized 2p orbital** containing one electron. These six p orbitals lie **perpendicular to the ring plane** and overlap sideways to form a **continuous delocalized π-electron cloud**.

- This π-electron system extends **above and below the plane of the ring**.
- The electron density forms two **toroidal (doughnut-shaped) regions** surrounding the benzene ring.

This delocalization explains the **stability, uniform bond lengths, and unique chemical behavior** of benzene.

Resonance Energy of Benzene

The **resonance energy** (or delocalization energy) of benzene is defined as the **difference in energy between benzene and the hypothetical 1,3,5-cyclohexatriene**. This extra stability arises due to the **delocalization of π-electrons** over all six carbon atoms in the ring.

Basis of Calculation

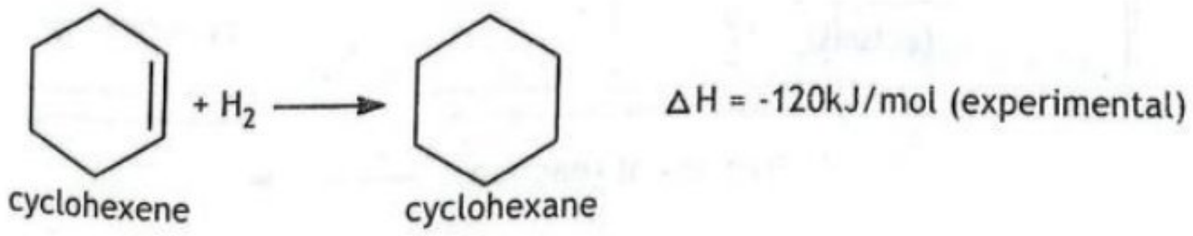
To determine the resonance energy, the **enthalpies of hydrogenation** of the following compounds are compared:

1. **Cyclohexene** (one double bond)
2. **Hypothetical 1,3,5-cyclohexatriene** (three isolated double bonds)
3. **Benzene** (delocalized π system)

Step 1: Cyclohexene

Hydrogenation of cyclohexene (one C=C bond) gives:

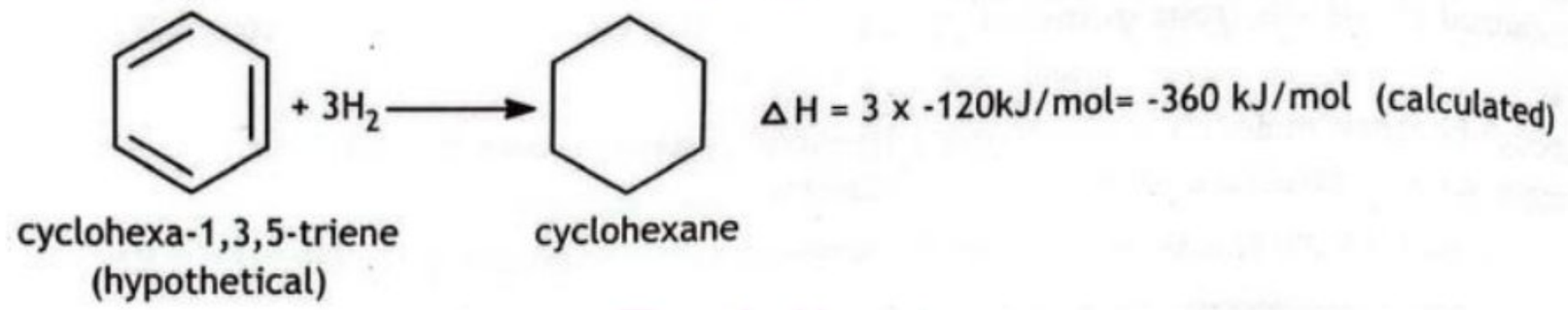
$$\Delta H = -120 \text{ kJ mol}^{-1} \text{ (experimental)}$$



Step 2: Hypothetical Cyclohexa-1,3,5-triene

If benzene were a compound with three localized double bonds, the expected enthalpy of hydrogenation would be:

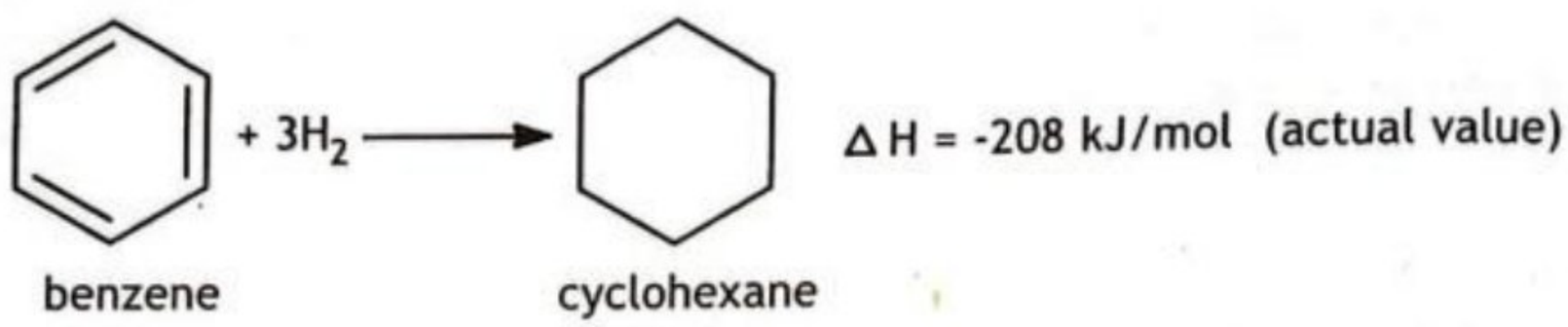
$$3 \times (-120) = -360 \text{ kJ mol}^{-1} \text{ (calculated)}$$



Step 3: Actual Benzene

Experimentally, benzene hydrogenates very slowly under normal conditions and requires **high temperature and pressure**. Its enthalpy of hydrogenation is:

$$\Delta H = -208 \text{ kJ mol}^{-1} \text{ (actual value)}$$

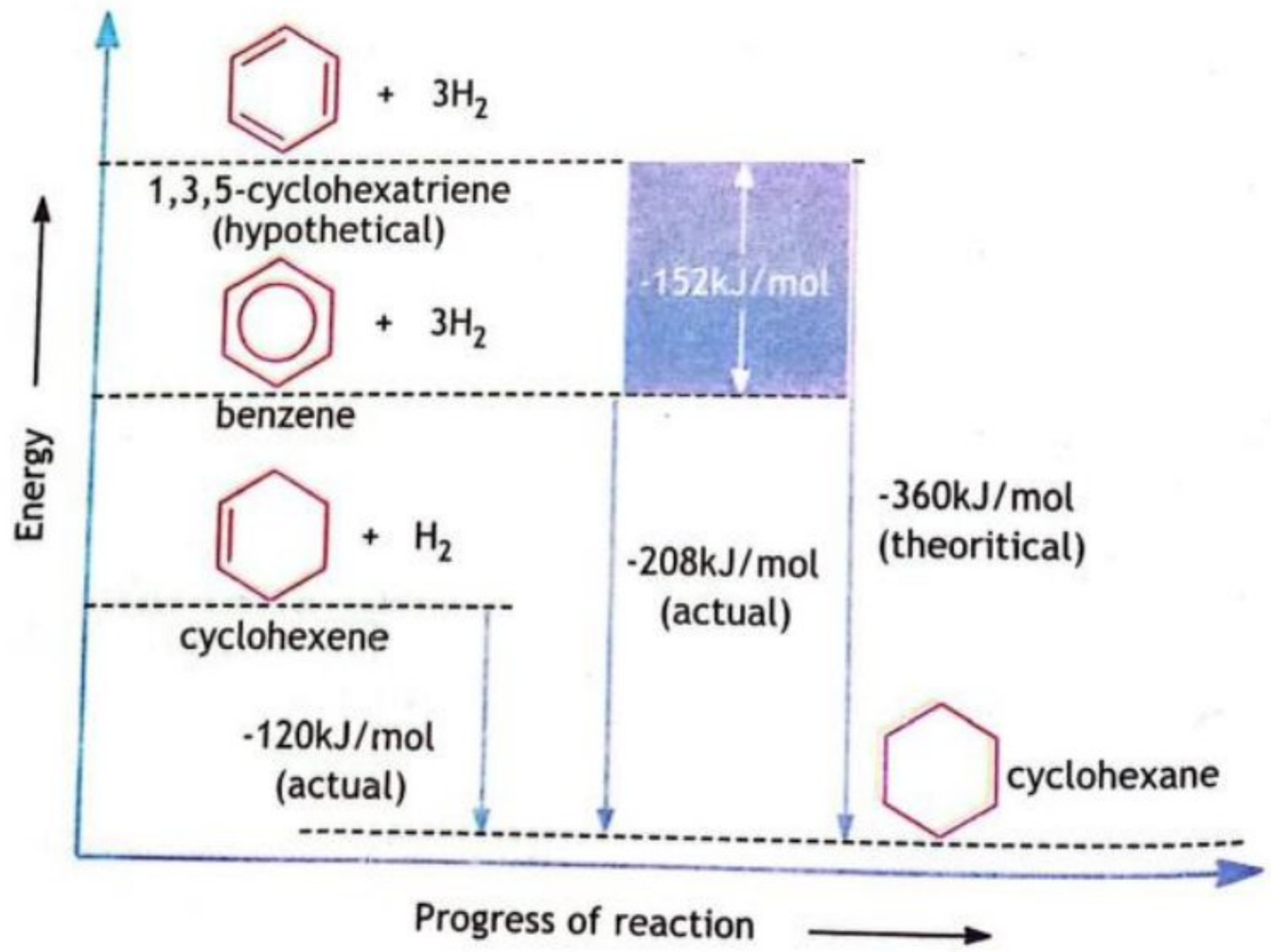


Resonance Energy Value

The difference between the expected and observed enthalpy values is the **resonance energy**:

$$\text{Resonance Energy} = (-360) - (-208) = 152 \text{ kJ mol}^{-1}$$

Thus, benzene is about **152 kJ mol^{-1} more stable** than the hypothetical localized triene due to resonance stabilization.



Reactivity of Benzene

Benzene has a highly stable **delocalized π-electron ring**, which remains intact in most chemical reactions. Due to this stability, benzene resists addition reactions (which would disrupt its aromaticity) and instead usually undergoes **substitution reactions**.

The common reactions of benzene include:

- **Addition reactions**
- **Oxidation reactions**
- **Electrophilic substitution reactions**

We will study these reactions one by one.

8.3.1 Electrophilic Aromatic Substitution (EAS) Reactions

Electrophilic aromatic substitution is the **most characteristic reaction of benzene**. In these reactions, an electrophile attacks the electron-rich aromatic ring, substituting one of its hydrogen atoms, while the stability of the delocalized π-system is largely preserved.

Steps of the Reaction Mechanism:

Ch#8: Hydrocarbons **By: Sir Amjad (Lecturer Chemistry)**

1. **Attack of Electrophile**
   - The high electron density of the delocalized π-electrons in benzene is attacked by an electrophile (electron-loving species).
   - This causes **partial disruption of aromaticity**.
2. **Formation of Arenium Ion**
   - An unstable, positively charged intermediate called the **arenium ion (or carbocation intermediate)** is formed.
3. **Restoration of Aromaticity**
   - The intermediate loses a proton ($\mathbf{H^+}$), which is replaced by the electrophile.
   - The delocalized π-electron system is restored, making the benzene ring stable again.

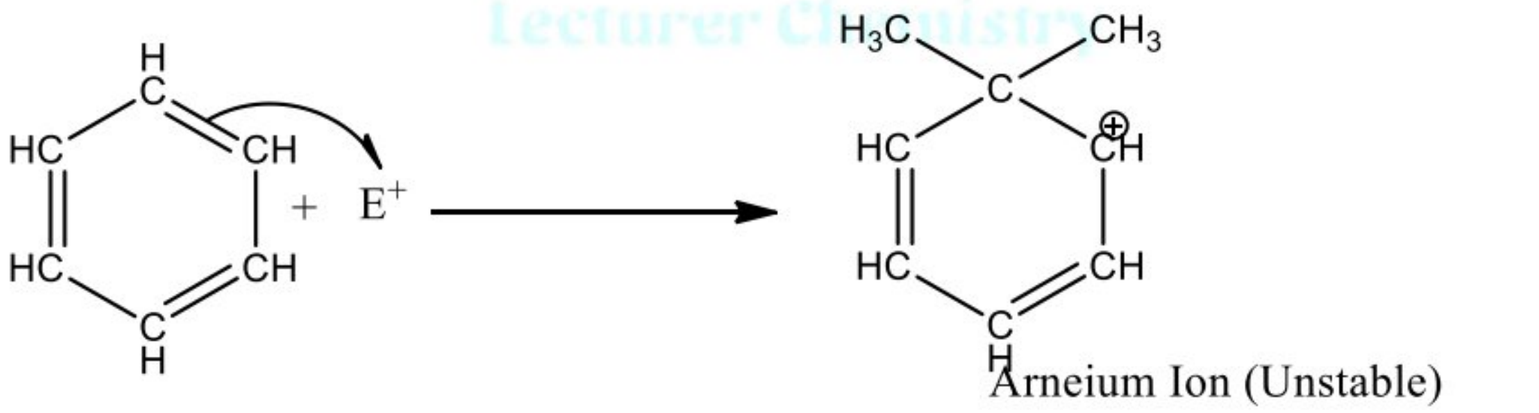
Mechanism

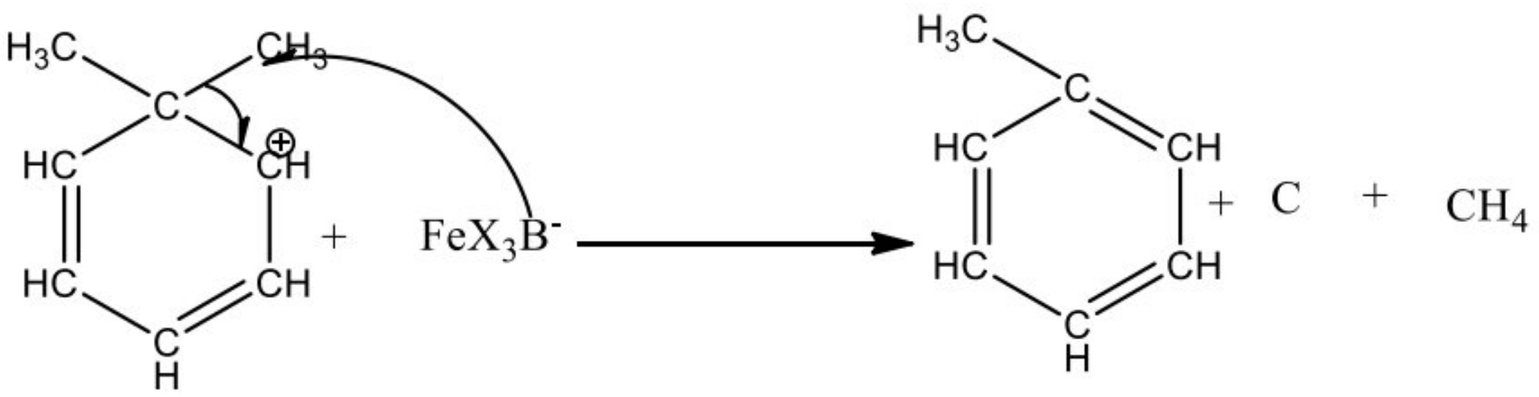
i. Generation of the electrophile. An electrophile is generated first from a suitable reagent with the help of a Lewis acid catalyst, like FeX3.

ii. Reaction of electrophile with benzene. The pi (π) electrons of benzene molecule attack on electrophile to make a cation intermediate called arenium ion. In this intermediate the aromatic ring is partially broken.

iii. Removal of hydrogen by a base.

A Lewis base takes the hydrogen from the arenium ion, resulting in the formation of a mono. substituted benzene. This restores the delocalized n-electron ring of benzene molecule.

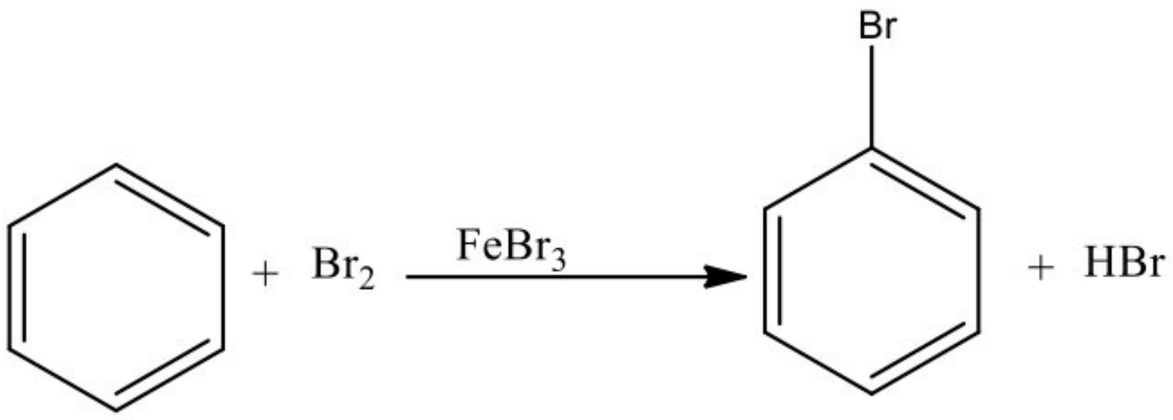




Some important electrophilic aromatic substitution reactions of benzene are given here.

Halogenation

Halogenation is a reaction in which a halogen molecule reacts with benzene molecule, resulting in substitution of a hydrogen atom on the benzene ring with a halogen atom. This reaction takes place in the presence of a catalyst, typically iron (III) halide. General Reaction:



For example, when a benzene molecule reacts with bromine in the presence of the catalyst iron (III) bromide ($FeBr_3$), bromobenzene is formed.

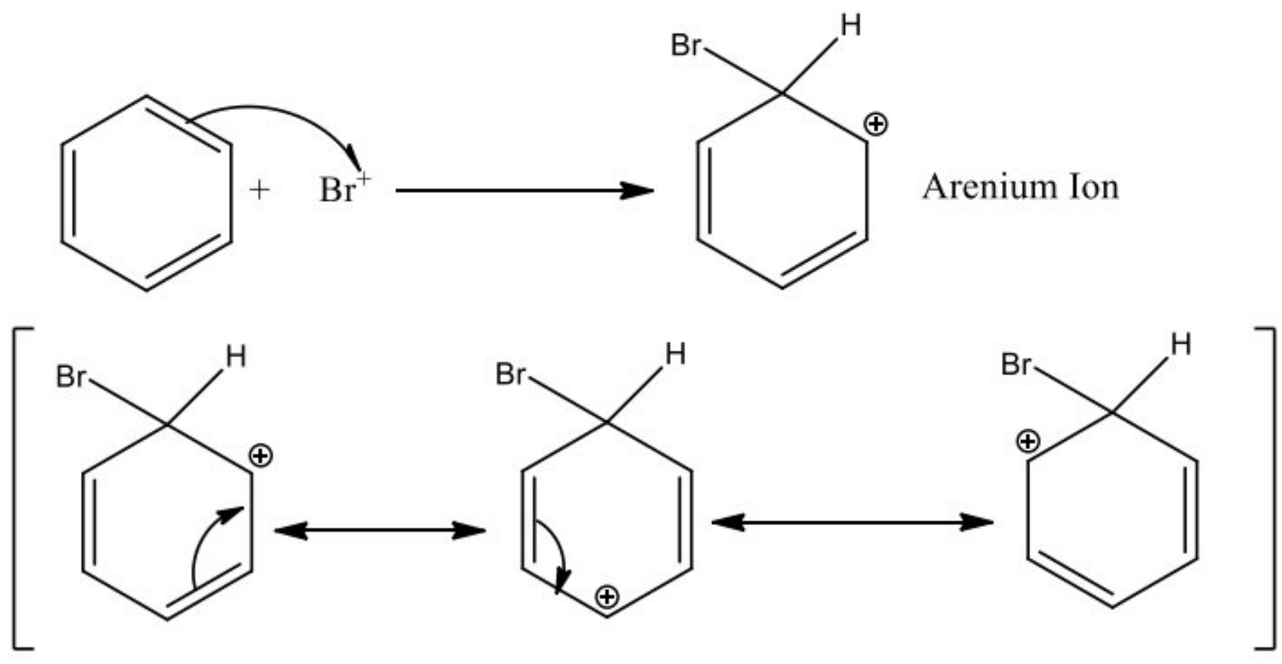
Mechanism of Bromination of Benzene:

In this reaction, On the bromine molecule (Br_2) acts as a Lewis base because it donates a pair of electron pair. One the other hand, iron (III) bromide ($FeBr_3$) acts as a Lewis acid as it accepts an electron pair

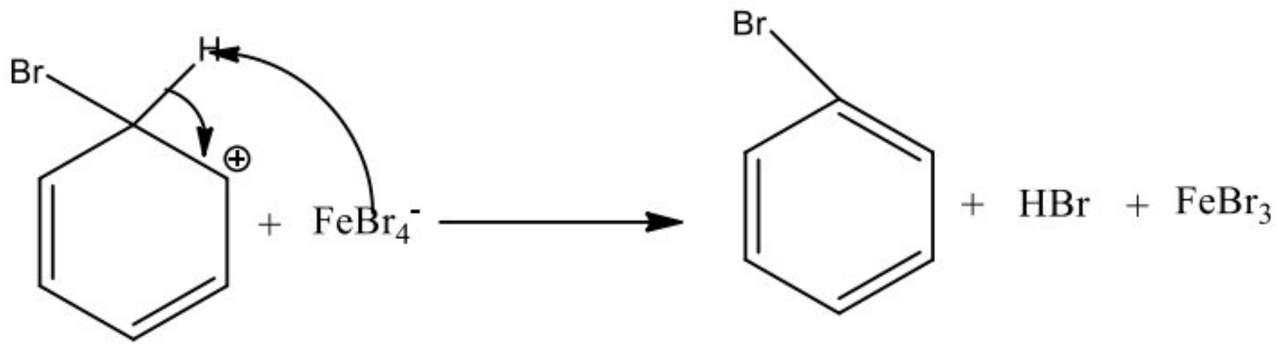
Step 1: Generation of Electrophile.

The Br^+ cation (bromonium ion) attacks on benzene ring to form an intermediate called arenium ion. Remember that the curly arrows show the movement of a pair of electrons.

Step 2: Generation of Arenium Ion/Sigma (0) Complex.

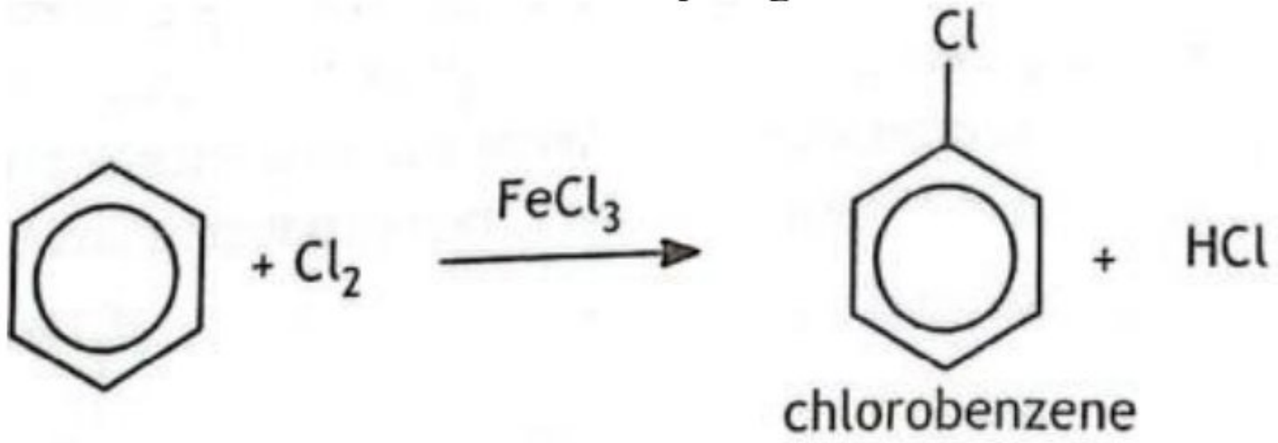


Step 3: Deprotonation/Regeneration of Catalyst.



Chlorination of Benzene:

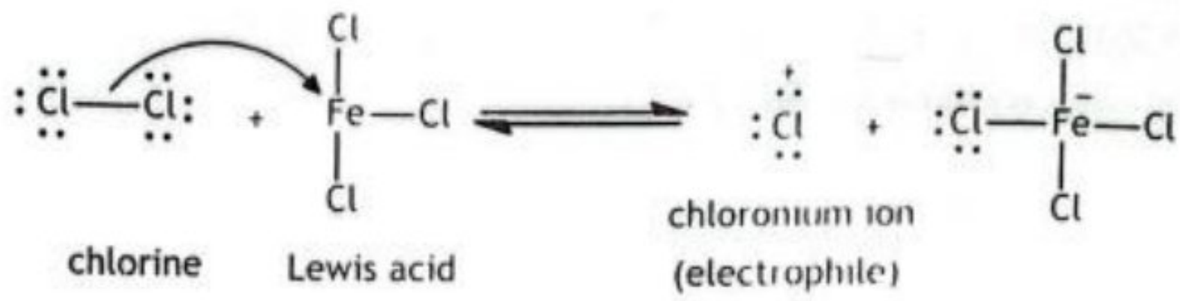
A similar reaction happens when chlorine gas is bubbled through benzene at room temperature in the presence of a catalyst, such as aluminium chloride. The products of this electrophilic substitution are chlorobenzene and hydrogen chloride.



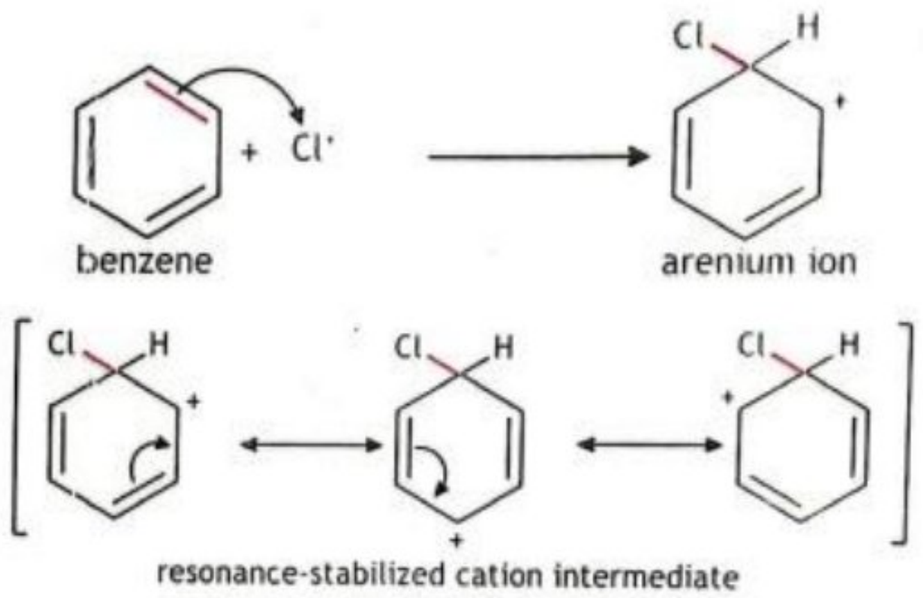
Mechanism of Chlorination of Benzene.

It follows the same pattern as bromination of benzene as shown.

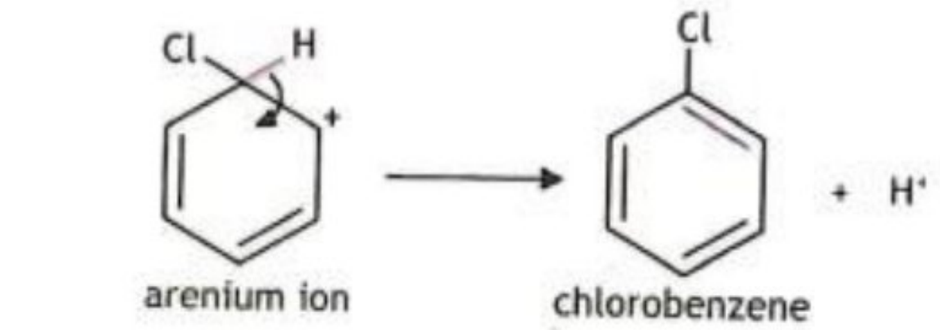
Step 1:



Step 2:

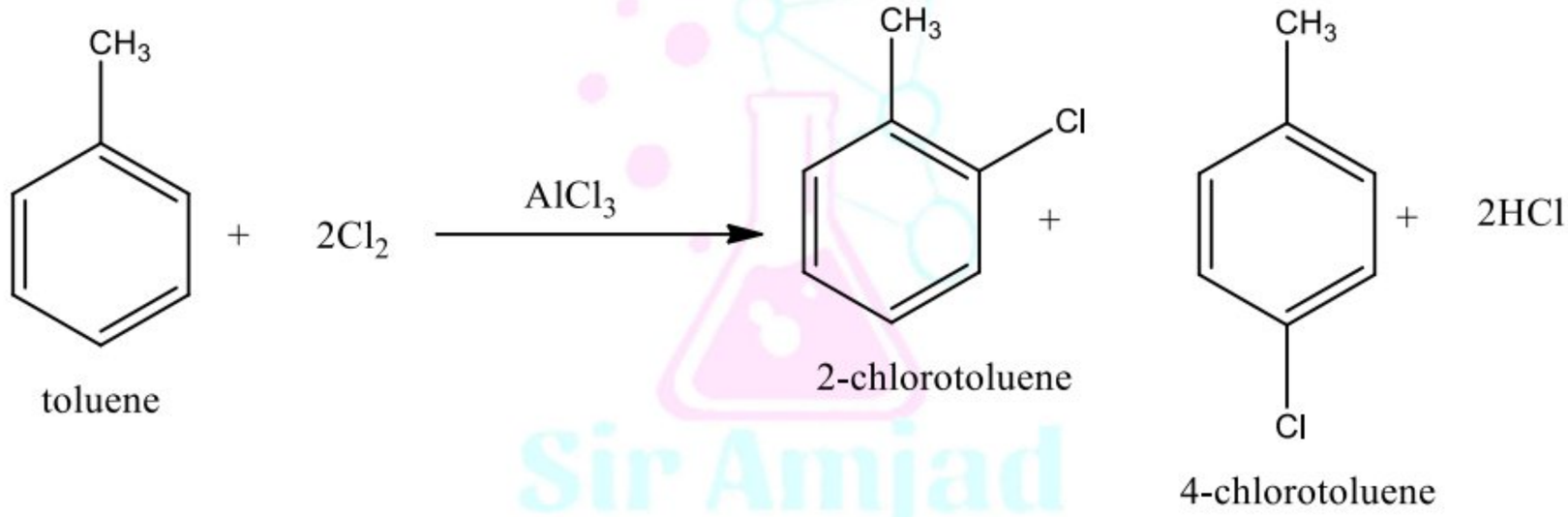


Step 3:



Halogenation of methylbenzene

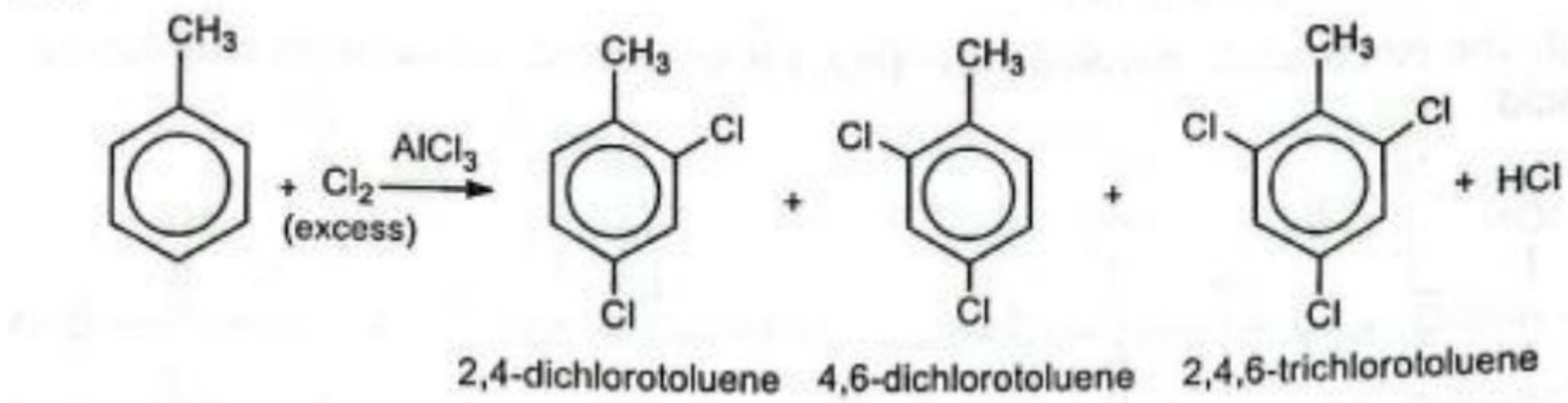
Halogenation of methylbenzene or other alkylarenes involved electrophilic attack at positions 2 or 4. The alkyl substituents are ring activating and increase electron cloud at position 2 and 4 in benzene ring.



Sirnilarly, hydroxyl group and amino groups also activate the benzene ring by pumping electrons in it through p-orbitals bridge. When methylbenzene is reacted with chlorine gas, using an anhydrous aluminium chloride catalyst, two products can be formed.

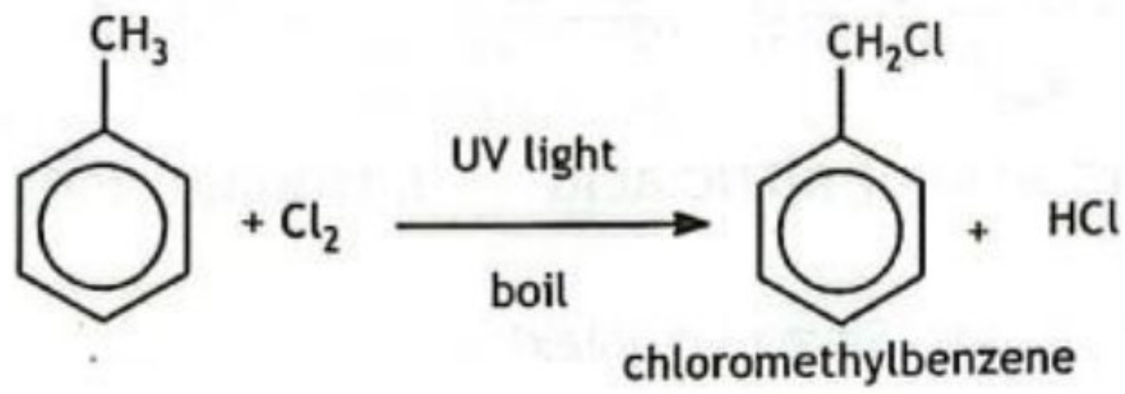
When Excess Chlorine is used:

If excess chlorine gas is used, we get a mixture of 2,4-dichlorotoluene, 2,6- dichlorotoluene and 2,4,6-trichlorotoluene.



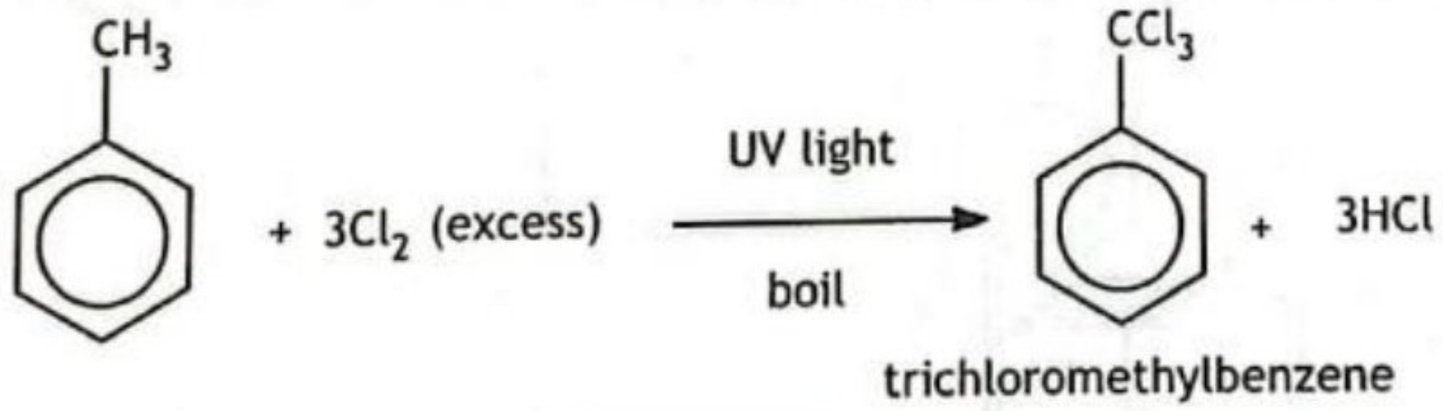
Side Chain Halogenation

When chlorine will react with alkyl side chain of alkylbenzene in the presence of ultraviolet (UV) light or strong sunlight. This reaction follows free-radical substitution mechanism. When chlorine gas is passed over boiling methylbenzene in the presence of UV light, the following reaction takes place.



Remember that there is no substitution into the benzene ring under these conditions.

In excess of chlorine

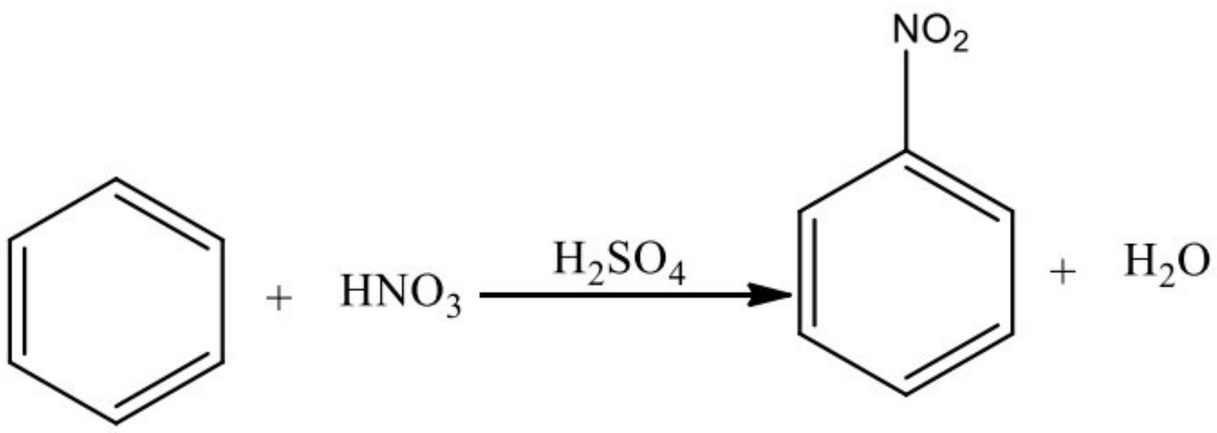


In excess of chlorine, eventually all three of the hydrogen atoms on the methyl side-chain will be replaced by chlorine atoms.

Nitration of Benzene (Electrophilic Substitution Reaction)

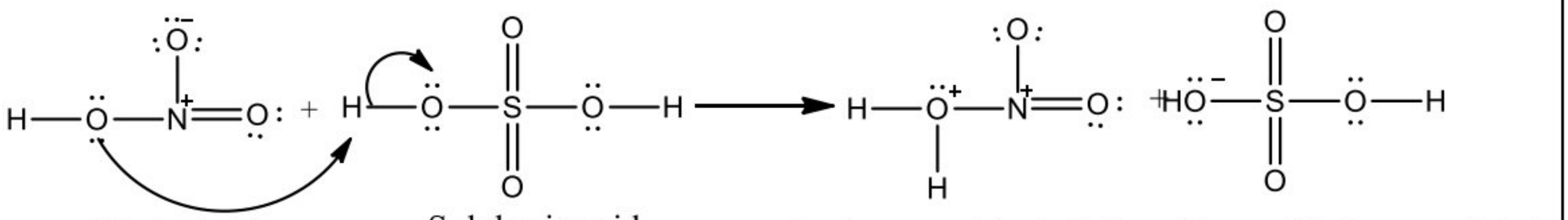
Nitration means introducing a **–NO_2 group** into the benzene ring. The reaction is carried out using a mixture of concentrated **HNO_3** and **H_2SO_4** (called nitrating mixture).

The **electrophile** in this reaction is the **nitronium ion (NO_2^+)**.

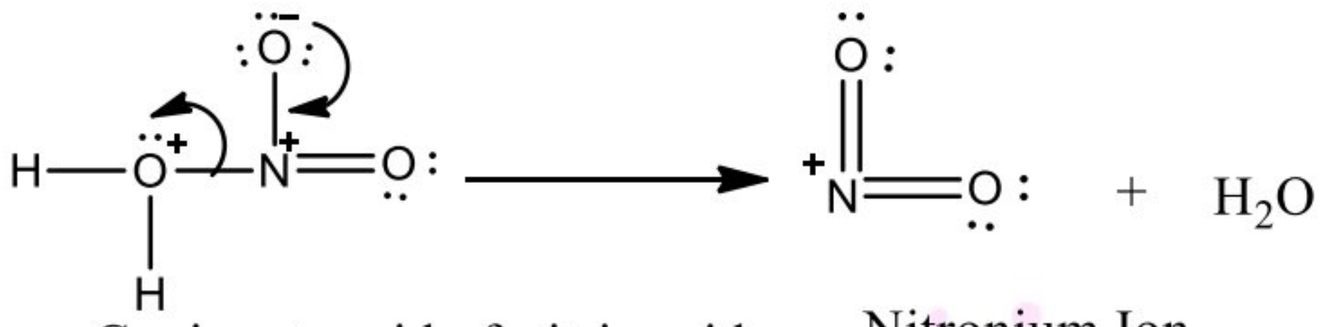


Step 1: Generation of Electrophile (Nitronium Ion, NO_2^+)

Concentrated sulfuric acid protonates nitric acid, producing the nitronium ion:



Nitric Acid Sulphuric acid Conjugate acid of nitric acid Hydrogensulphate

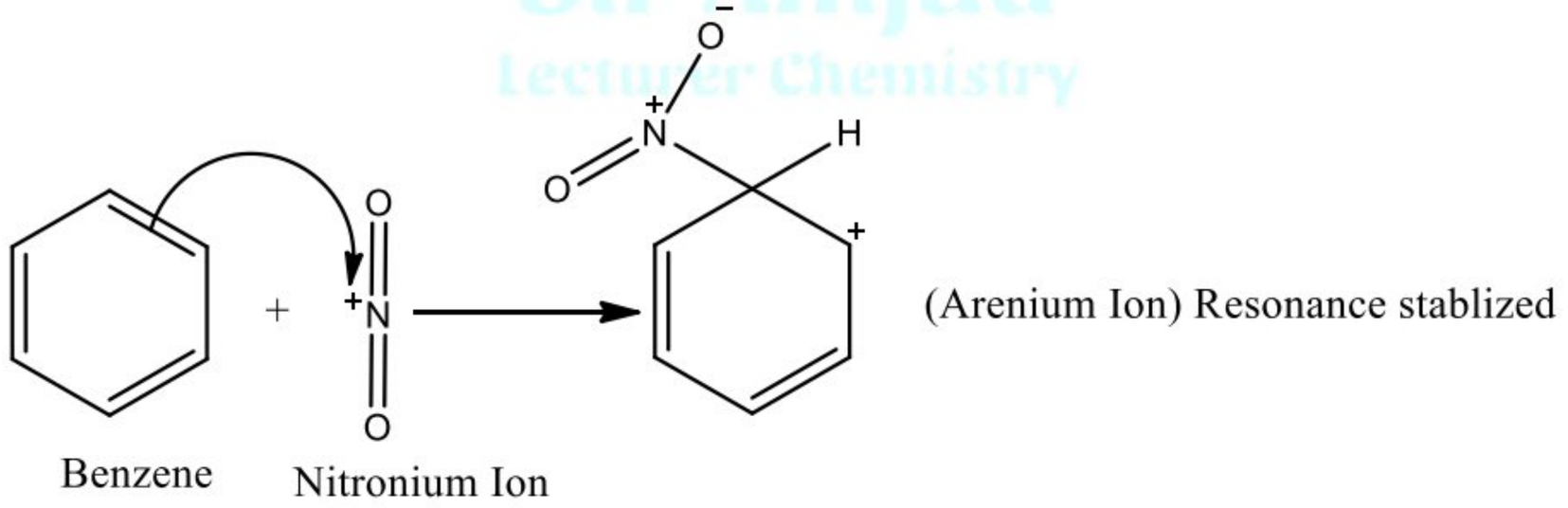


Conjugate acid of nitric acid Nitronium Ion

Thus, NO_2^+ is formed, which acts as the attacking species (electrophile).

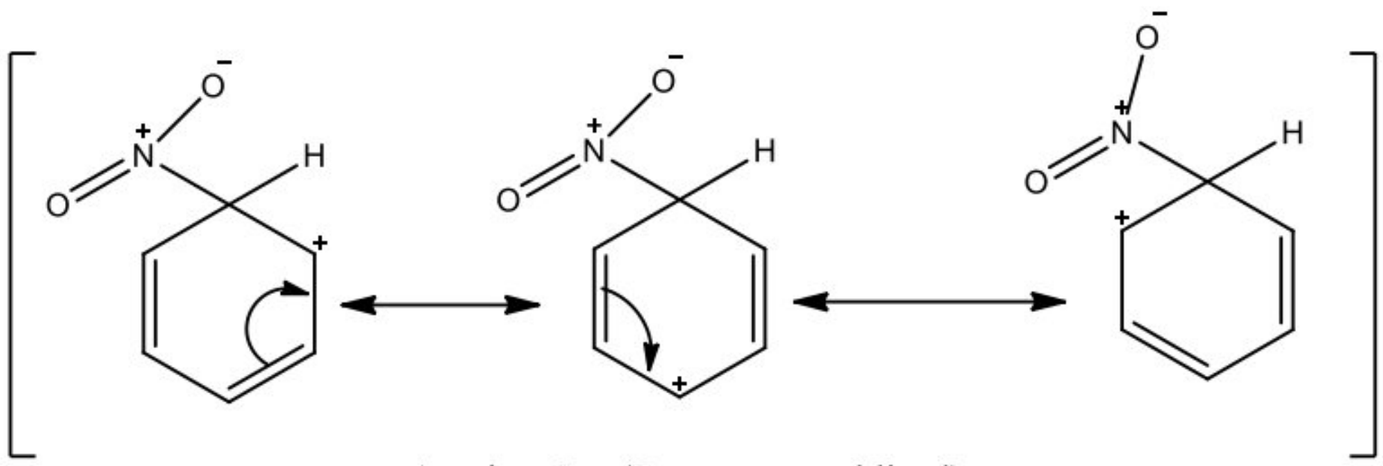
Step 2: Attack on Benzene Ring (Formation of Arenium Ion / σ-complex)

- The **π-electrons** of the benzene ring are donated to the nitronium ion.
- A new **C–NO_2 bond** is formed.
- The aromatic ring temporarily loses delocalization, giving an **unstable arenium ion (σ-complex)**.



Benzene Nitronium Ion (Arenium Ion) Resonance stablized

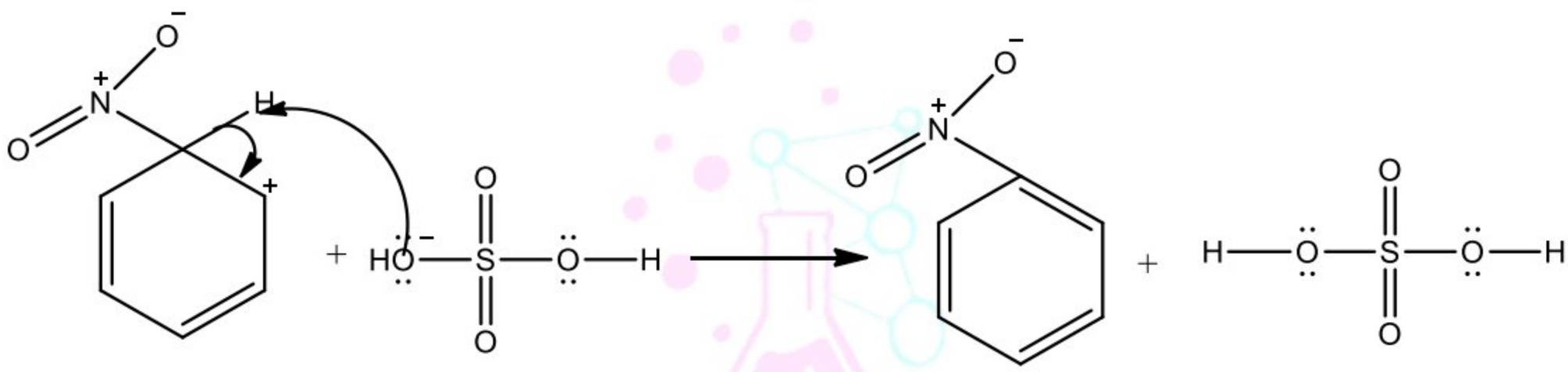
The arenium ion has four pi (π) electrons and a positive charge delocalized over five carbon atoms. It undergoes resonance stabilization as follows:



Arenium Ion (Resonance stablized)

Step 3: Restoration of Aromaticity

- The arenium ion loses a **proton (H^+)** from the carbon atom where substitution occurred.
- The electrons from the broken C–H bond return to the ring.
- **Aromaticity is restored**, and **nitrobenzene ($C_6H_5NO_2$)** is formed.



Friedel–Crafts Reaction

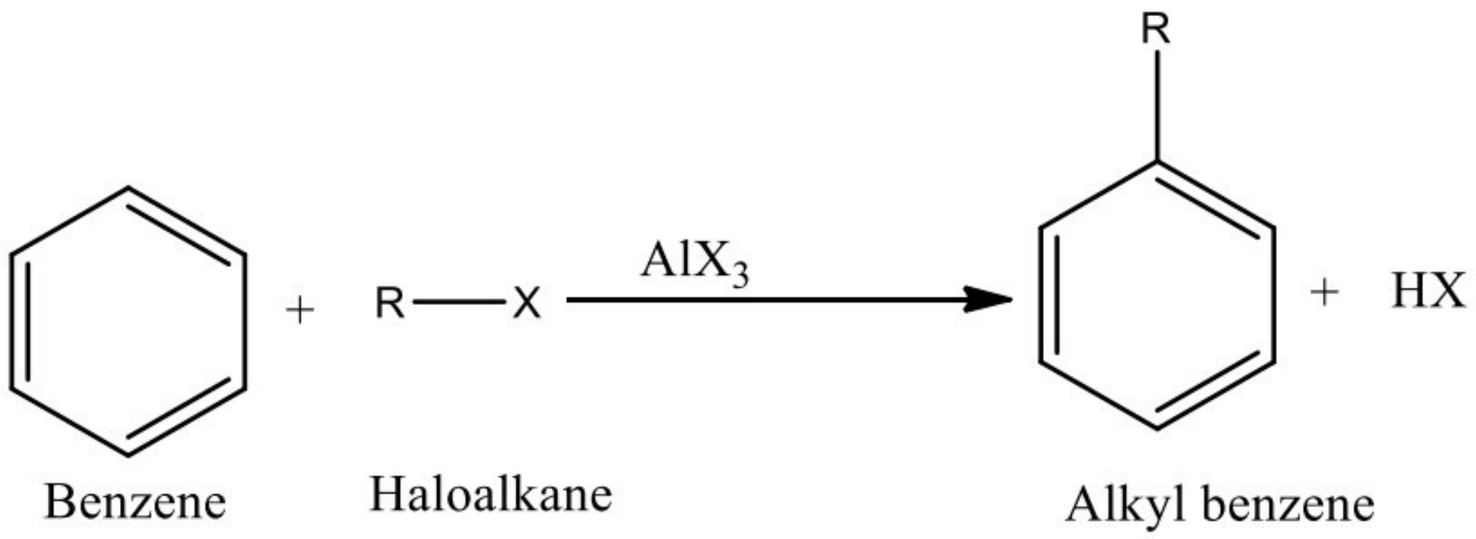
Discovered in **1877** by **Charles Friedel** and **James Crafts**, this reaction involves the substitution of a hydrogen atom in benzene with an **alkyl group** (alkylation) or an **acyl group** (acylation).

- **Reagents:**
  - **Alkyl halide** + Benzene → Alkylbenzene
  - **Acyl halide** + Benzene → Phenyl ketone
- **Catalyst: $AlCl_3$** (Lewis acid)

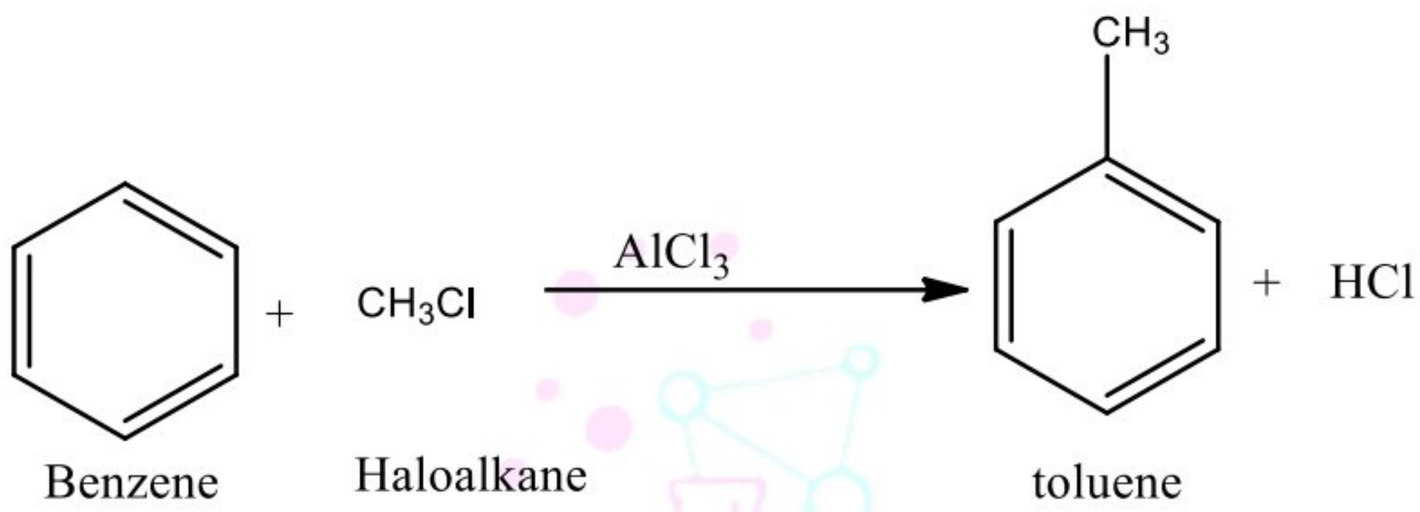
(i) Friedel–Crafts Alkylation

Definition:
The introduction of an **alkyl group (-R)** into the benzene ring when benzene is treated with an alkyl halide in the presence of **$AlCl_3$ catalyst** is called **Friedel–Crafts alkylation**.

General Reaction:



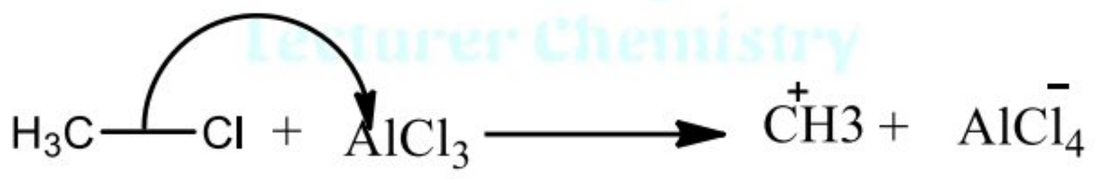
Example:



Mechanism of Friedel–Crafts Alkylation

Step 1: Generation of Electrophile (Carbocation, R^+)

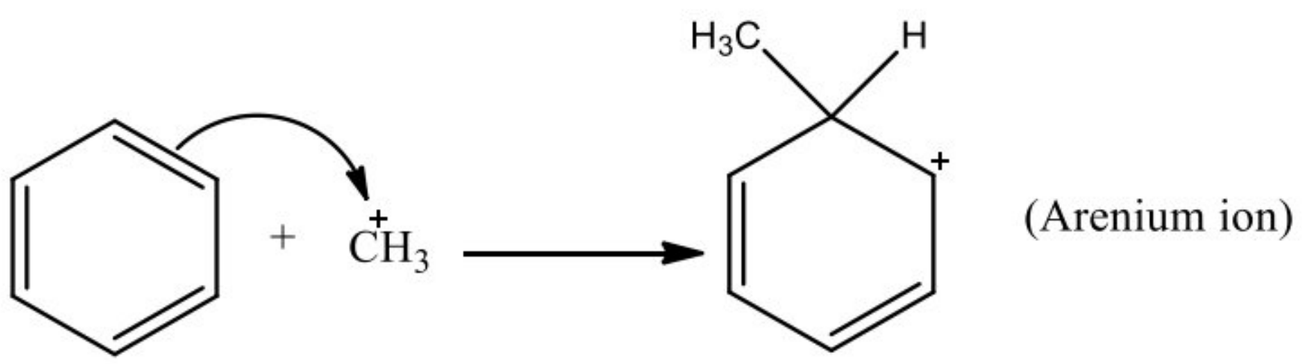
The alkyl halide reacts with $AlCl_3$ (a Lewis acid) to form a carbocation (alkyl cation):



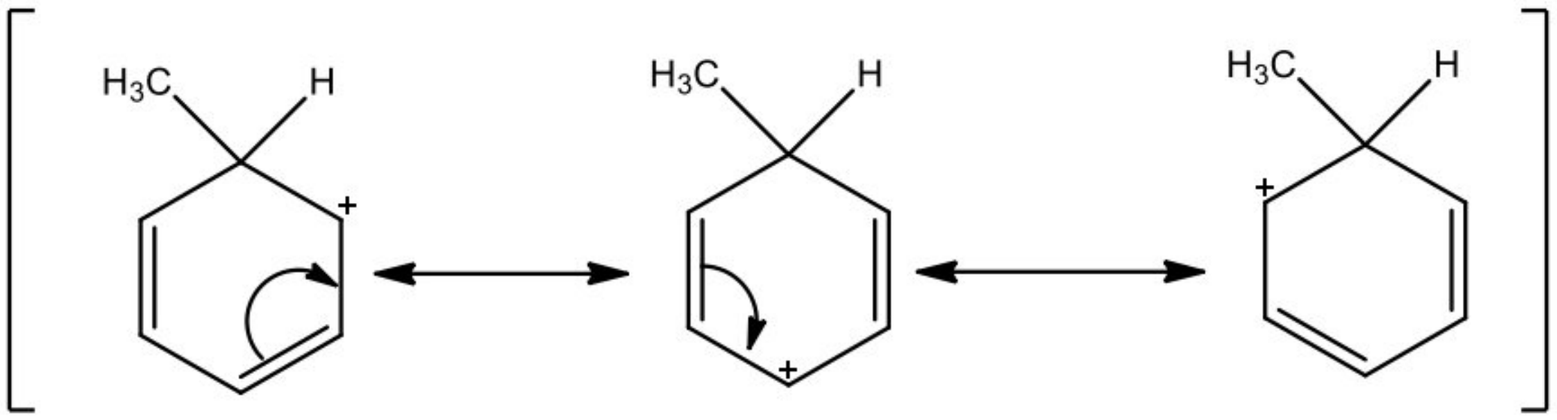
Here, **CH_3^+** is the electrophile.

Step 2: Attack on Benzene Ring (Formation of Arenium Ion)

- The **π-electrons** of benzene attack the electrophile (CH_3^+).
- This forms a temporary **arenium ion (σ-complex)**, in which the aromaticity is lost.



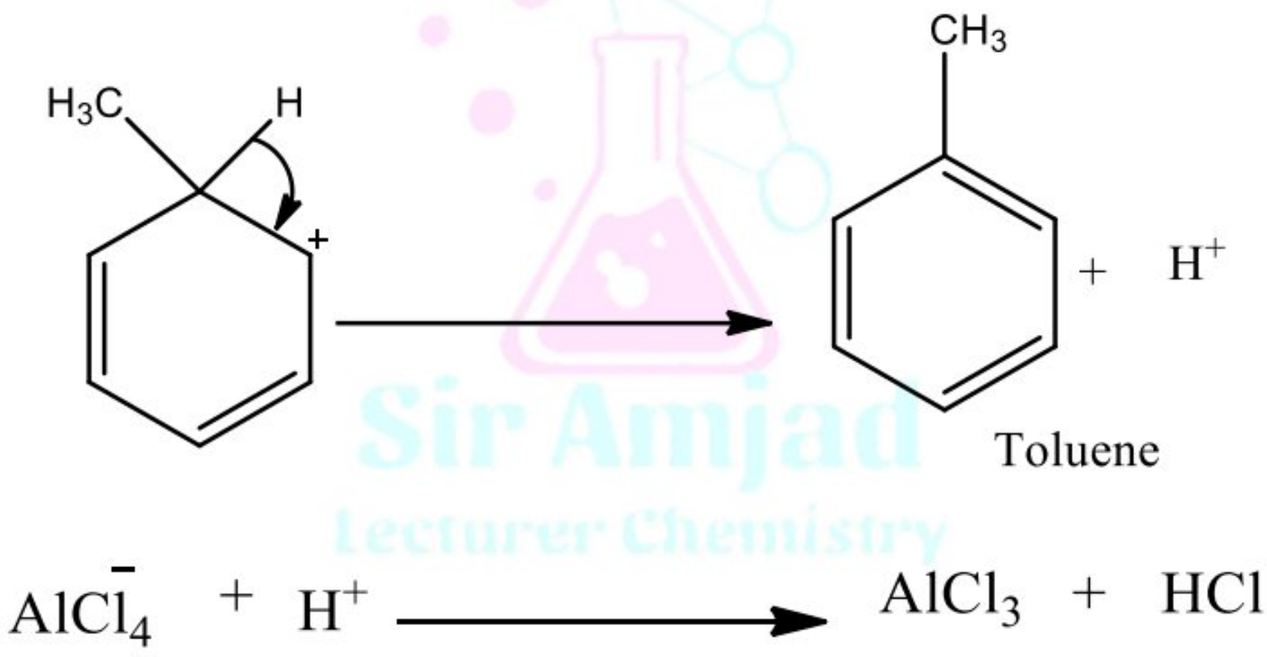
The arenium ion undergoes resonance stabilization as follows:



Arenium Ion (Resonance stablized)

Step 3: Deprotonation and Restoration of Aromaticity

- The arenium ion loses a **proton (H^+)**.
- The electron pair from the C–H bond restores the aromatic π-system.
- **$AlCl_4^-$** abstracts the proton, regenerating **$AlCl_3$ catalyst** and releasing **HCl**.

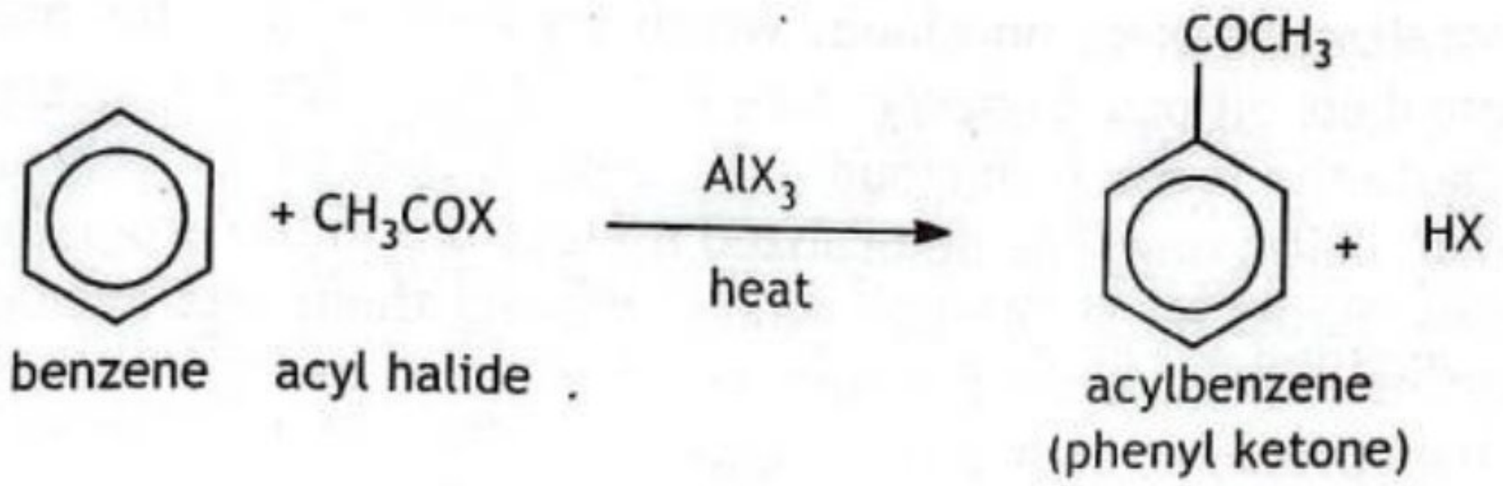


Friedel–Crafts Acylation

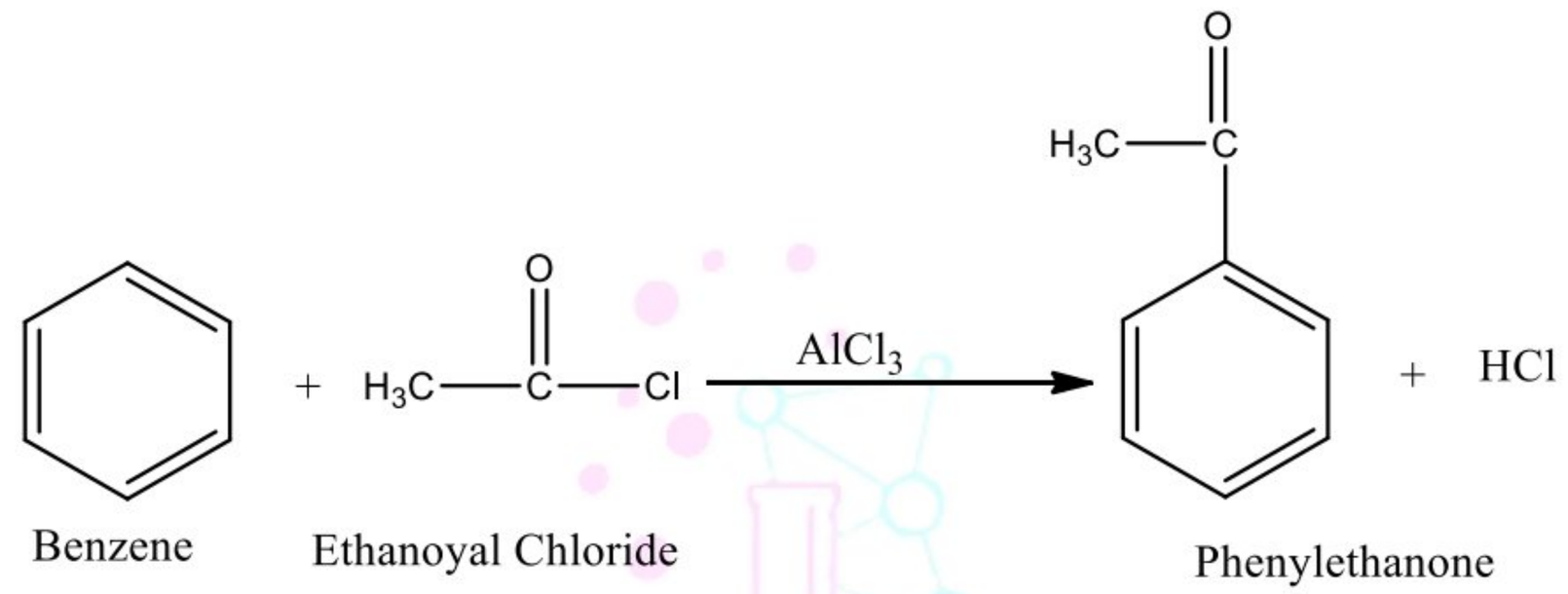
Definition:
The reaction in which an **acyl group (R–CO–)** is introduced into the **benzene ring** using an **acyl halide (RCOCl)** in the presence of a **Lewis acid catalyst** like **$AlCl_3$** is called **acylation**.

- **Catalyst:** Aluminium chloride (**$AlCl_3$**)
- **Product:** Aromatic ketone (e.g., phenylethanone)

General Reaction:



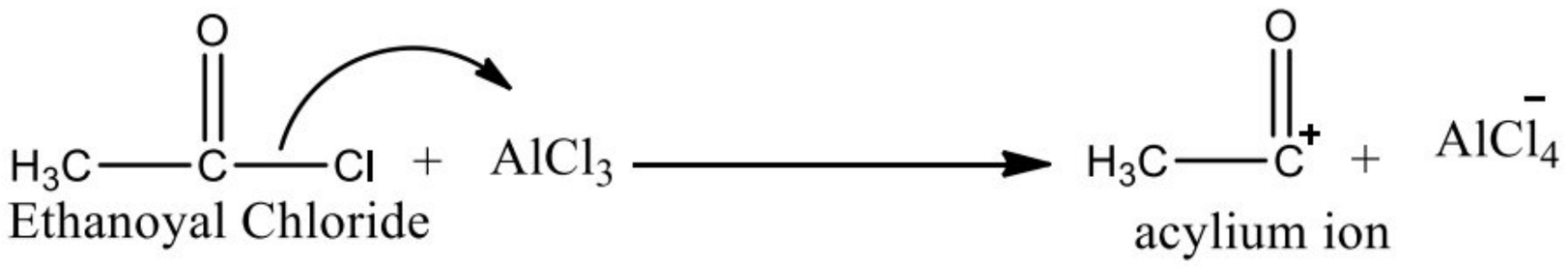
Example:



Mechanism

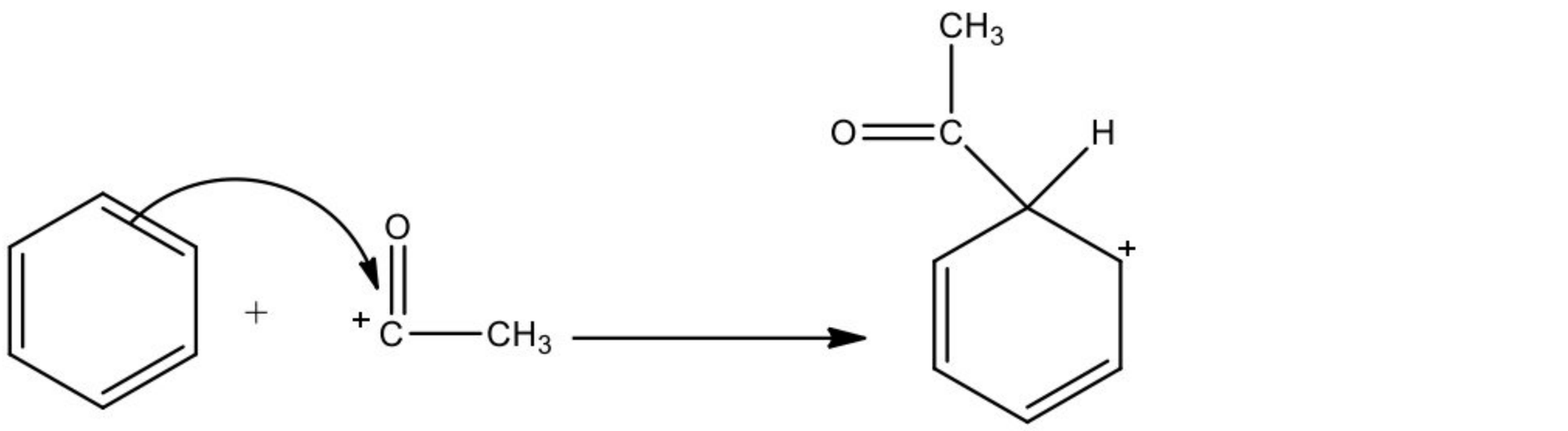
Step 1: Generation of Electrophile (Acylium Ion)

- The acyl halide reacts with aluminium chloride to form the **acylium ion (RCO^+)**:
- The **acylium ion (RCO^+)** is a strong **electrophile**.



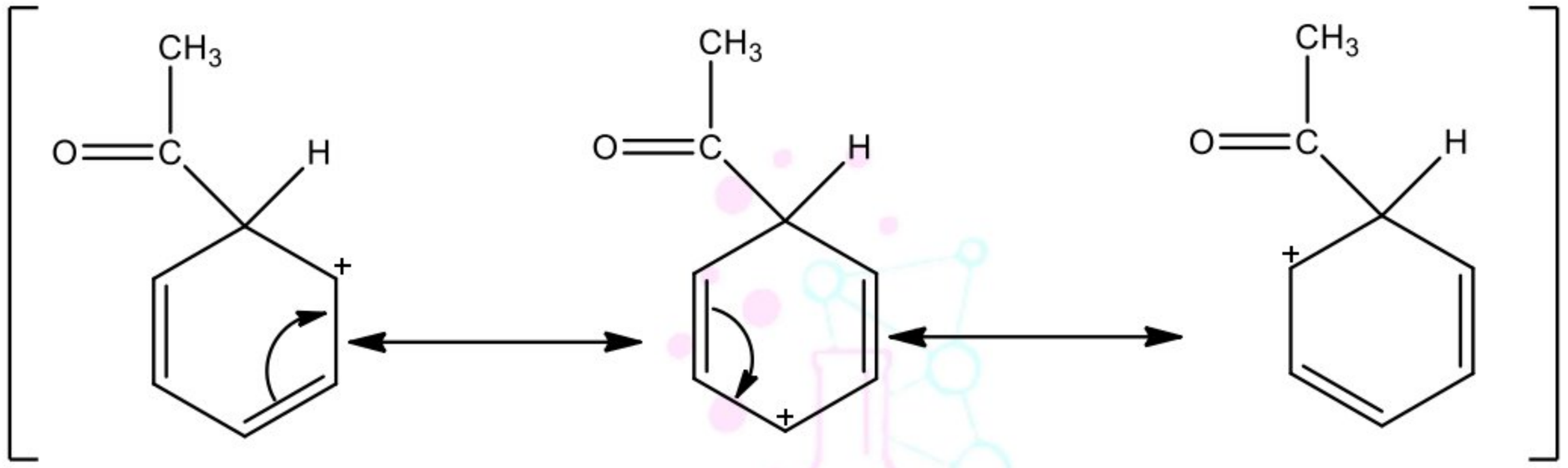
Step 2: Formation of Arenium Ion

- The benzene ring donates a pair of **π-electrons** to the acylium ion.
- This results in the formation of an **unstable intermediate** called the **arenium ion** (or σ-complex).
- Aromaticity is temporarily lost.



Benzene acylium ion Arenium Ion (Resonance stablized)

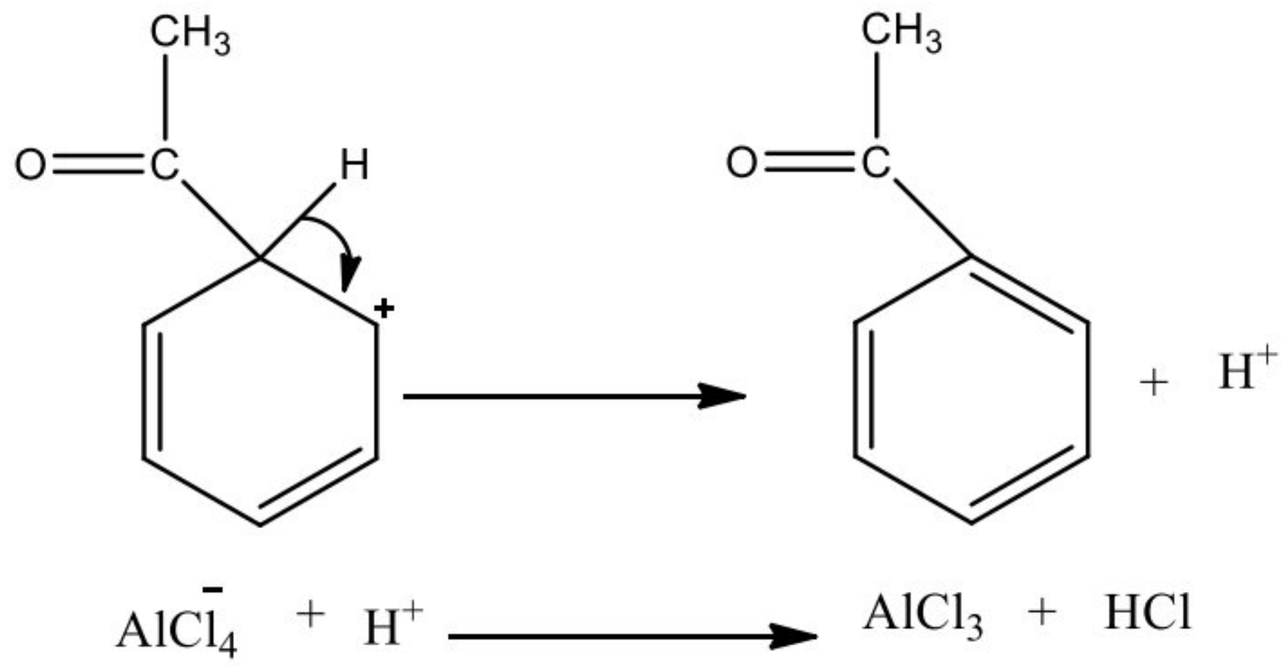
The arenium ion undergoes resonance stabilization as follows:



Arenium Ion (Resonance stablized)

Step 3: Deprotonation and Restoration of Aromaticity

- The arenium ion loses a **proton (H^+)**.
- The π-electron cloud is restored, regaining the aromatic structure.
- The **$AlCl_4^-$** ion abstracts the H^+ to form **HCl** and regenerate **$AlCl_3$**:



$$AlCl_4^- + H^+ \longrightarrow AlCl_3 + HCl$$

Addition Reactions of Benzene

Benzene has a **delocalized π-electron cloud**, which makes it more stable than ordinary alkenes.

- Under **normal conditions**, benzene does **not undergo addition reactions** readily because breaking the aromatic system requires destroying its **aromatic stability (resonance energy)**.
- Therefore, addition reactions of benzene only occur under **vigorous conditions** (high temperature, high pressure, or strong reagents).

In Friedel–Crafts reactions, **$AlCl_3$** acts as a **halogen carrier**, helping halogen atoms attach to benzene.

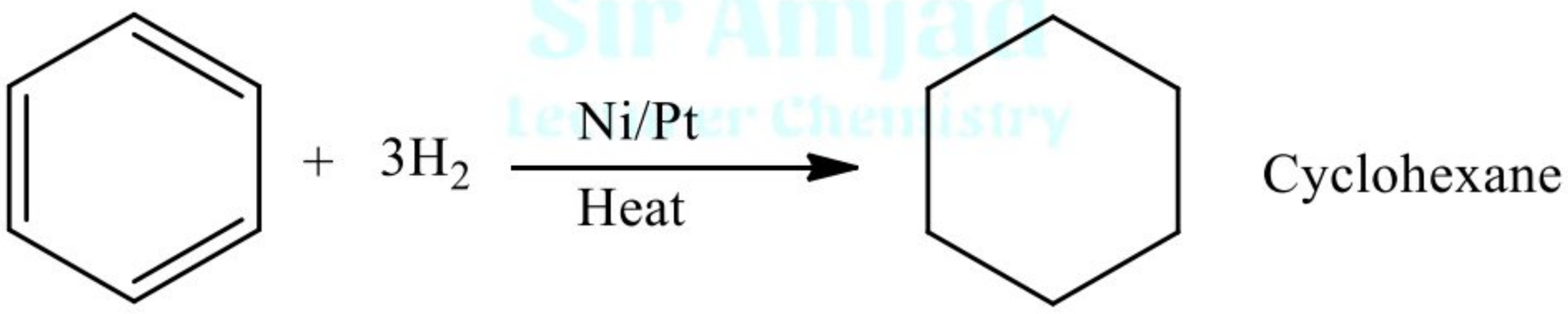
Hydrogenation of Benzene

Definition:
Hydrogenation is the **addition of hydrogen atoms** across the carbon atoms of benzene, converting it into **cyclohexane**.

Reaction Conditions:

- **Catalyst:** Nickel (Ni), Platinum (Pt), or Palladium (Pd)
- **Temperature:** 150–200 °C
- **Pressure:** 20–30 atm

General Reaction:



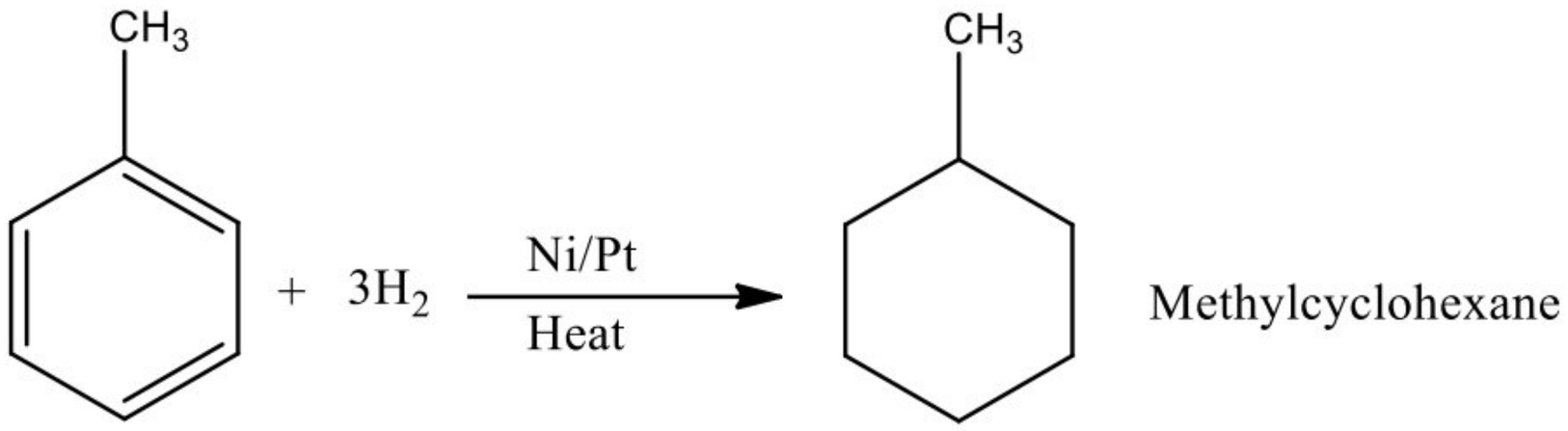
(Benzene → Cyclohexane)

Role of Catalyst

- The catalyst provides a **large surface area** for the reaction.
- Hydrogen molecules adsorb on the catalyst surface and break into individual hydrogen atoms.
- The catalyst weakens the **π-electron system** of benzene, making it more reactive.
- Six hydrogen atoms then add to the six carbon atoms of benzene, breaking its aromaticity.
- The **product cyclohexane** is released, while the catalyst remains unchanged and can be reused.

Example with Substituted Benzene

- **Methylbenzene** (Toluene) undergoes hydrogenation under the same conditions to form **methylcyclohexane**.



toluene

Difference Between Addition Reactions and Electrophilic Substitution Reactions

1. Addition Reactions (like in alkenes / hydrogenation of benzene)

- **Mechanism:**
  - An **electrophile** attacks the π-electrons of the double bond (or aromatic ring).
  - A **positively charged intermediate** (like a carbocation or bridged ion) is formed.
  - In the next step, a **nucleophile (anion)** attacks this intermediate.
  - Result: The **double bond (π-bond)** is lost, giving a **saturated product**.
- **Effect on Benzene:**
  - Benzene resists addition reactions because they **destroy aromaticity** (loss of resonance stabilization).
  - Only under **harsh conditions** (high temperature/pressure, strong catalysts) does benzene undergo addition (e.g., hydrogenation → cyclohexane).

2. Electrophilic Aromatic Substitution (EAS) Reactions

- **Mechanism:**
  - An **electrophile** attacks benzene, forming a **positively charged intermediate** (called the arenium ion or σ-complex).
  - Instead of a nucleophile attacking, the intermediate loses a **proton (H^+)**.
  - This regenerates the **aromatic π-electron system**.
- **Effect on Benzene:**
  - Aromaticity is **preserved** in the final product.
  - Hydrogen is replaced by another group (e.g., halogen, nitro group, alkyl group).

Key Contrast

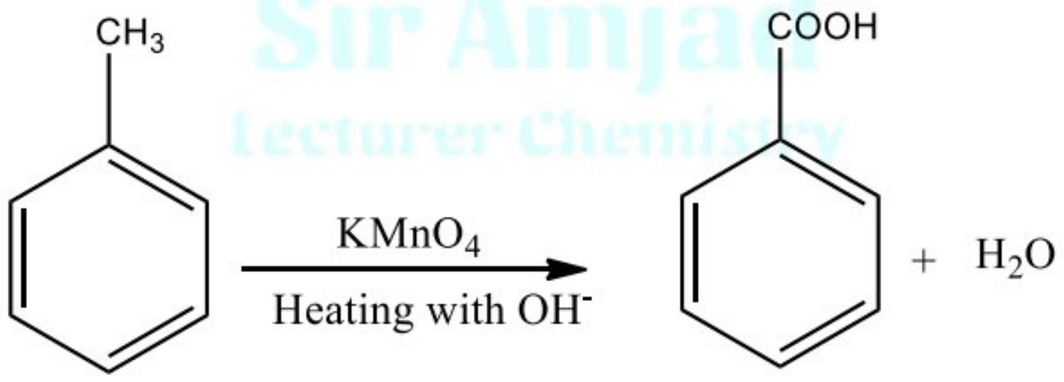
Feature	Addition Reaction	Electrophilic Aromatic Substitution (EAS)
Intermediate	Carbocation / halonium ion	Arenium ion (σ-complex)
Second Step	Nucleophile (anion) attacks	Loss of proton (H^+)
Final Product	Saturated compound (no aromaticity)	Substituted aromatic compound (aromaticity retained)
Conditions	Harsh (high T, high P, catalyst)	Milder, often at room temp with catalyst ($AlCl_3$, H_2SO_4)
Effect on Benzene	Destroys aromaticity	Preserves aromaticity

Oxidation Reactions of Benzene and Alkylbenzenes

1. Oxidation of Benzene

- Benzene itself is **very resistant** to oxidation.
- Ordinary oxidizing agents (like $KMnO_4$ or $K_2Cr_2O_7$) under normal conditions do **not affect benzene**.
- To oxidize the benzene ring, **vigorous conditions** such as high temperature, high pressure, and strong oxidants are required.
- Even then, the oxidation generally destroys the aromatic ring, giving **carbon dioxide (CO_2) and water (H_2O)** as end products.

Oxidation Reactions:



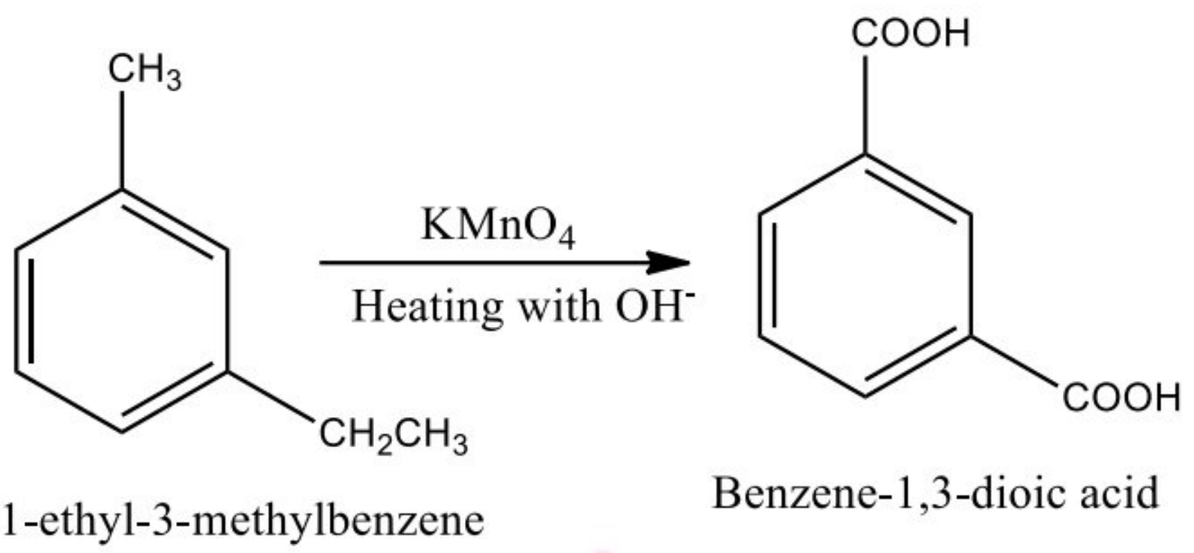
toluene benzoic acid

2. Oxidation of Alkylbenzenes (Side Chain Oxidation)

- In **alkylbenzenes** (e.g., methylbenzene / toluene), the **side-chain (alkyl group)** is much more reactive towards oxidation than the aromatic ring.
- Regardless of the length of the side chain, the **carbon atom directly attached to the benzene ring** is oxidized completely to a **–COOH group**.
- The result is always a **benzoic acid (C_6H_5COOH)** derivative.

Reason for Side Chain Oxidation

- The **benzene ring activates the side chain**, making the benzylic carbon (the carbon directly attached to the ring) more reactive.
- This benzylic position can form a **stabilized benzylic radical or carbocation**, which makes oxidation easier compared to normal alkanes.



1-ethyl-3-methylbenzene

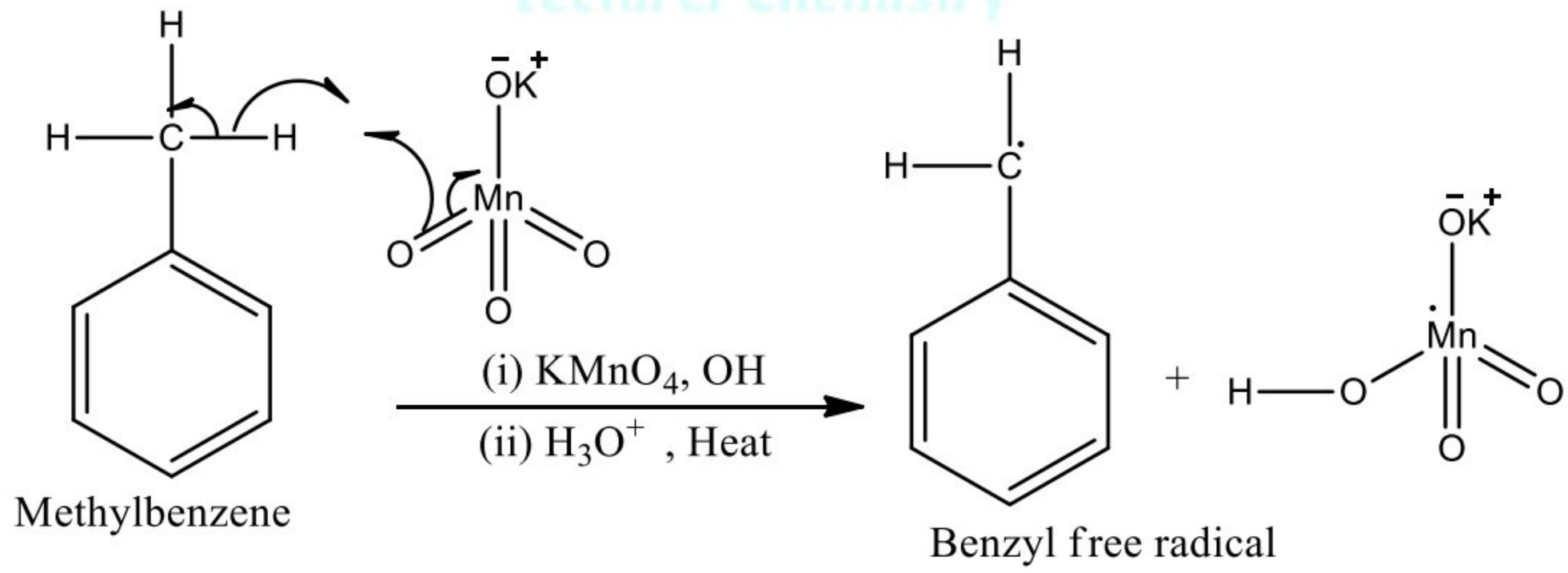
Benzene-1,3-dioic acid

Mechanism of Side Chain Oxidation of Alkylbenzenes

(using hot alkaline potassium manganate (VII), $KMnO_4$)

Step 1: Abstraction of Benzylic Hydrogen

- **Hot alkaline $KMnO_4$** abstracts a **benzylic hydrogen atom** (hydrogen on the carbon directly attached to benzene).
- This forms a **benzyl free radical ($C_6H_5–CH_2•$)**.

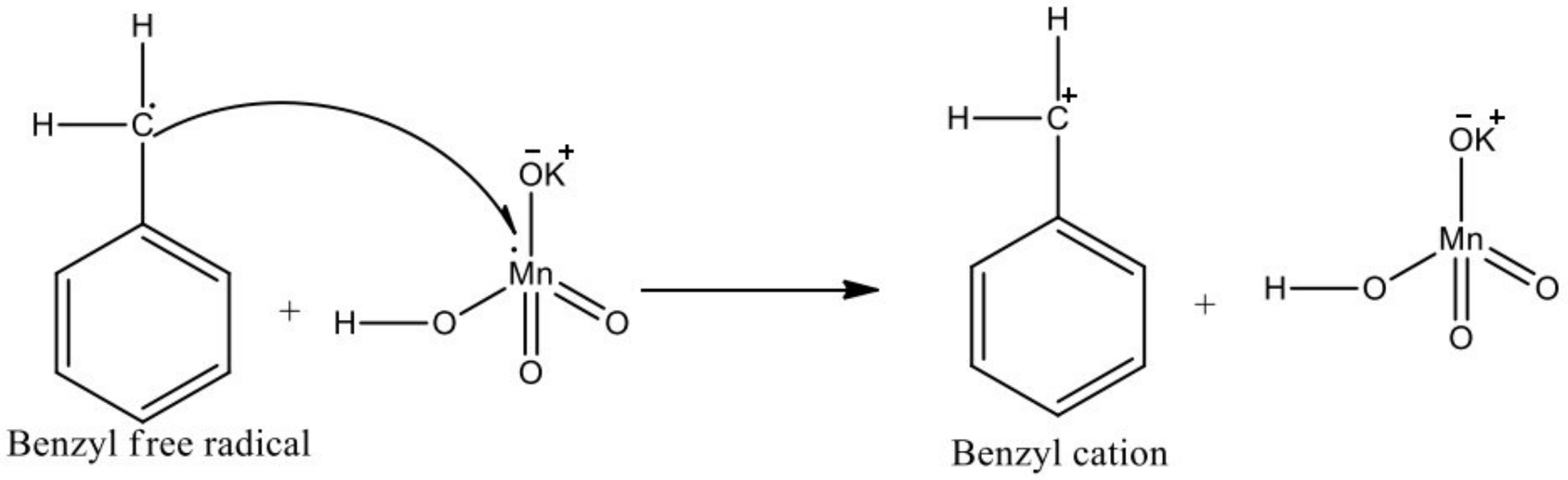


Methylbenzene

Benzyl free radical

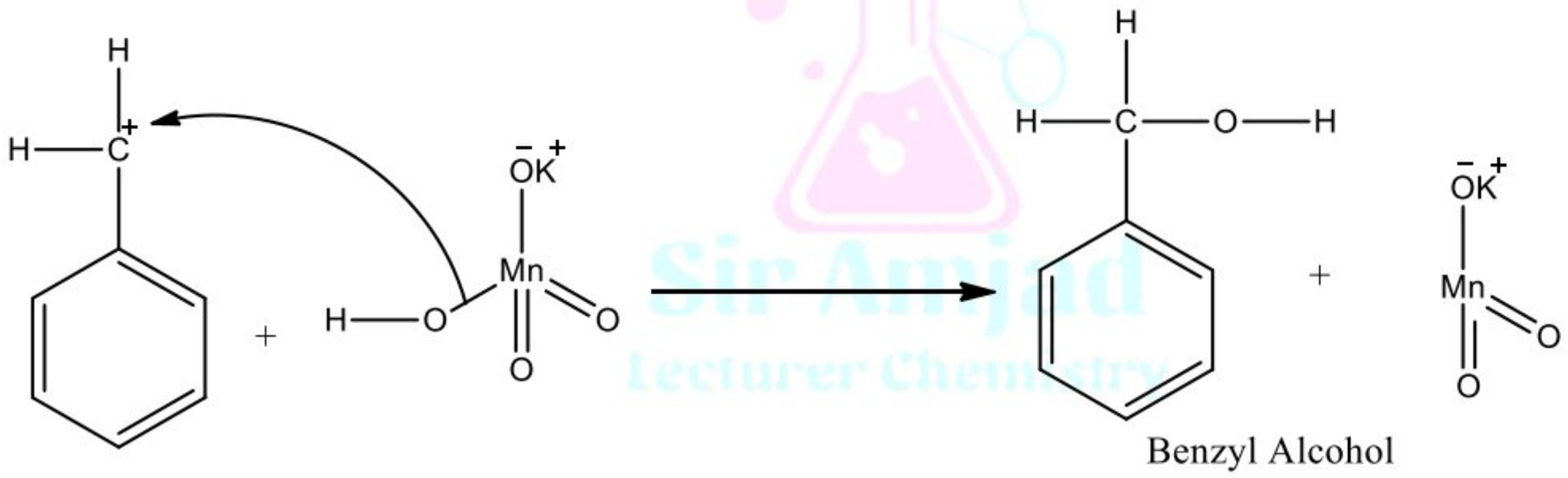
Step 2: Formation of Benzyl Cation and Hydroxylation

- The benzyl radical reacts with the **odd-electron intermediate** of $KMnO_4$.
- It converts into a **benzyl cation ($C_6H_5–CH_2^+$)**.
- This benzyl cation then abstracts a **–OH group** from unstable potassium hydrogenmanganate, forming **benzyl alcohol ($C_6H_5–CH_2OH$)**.

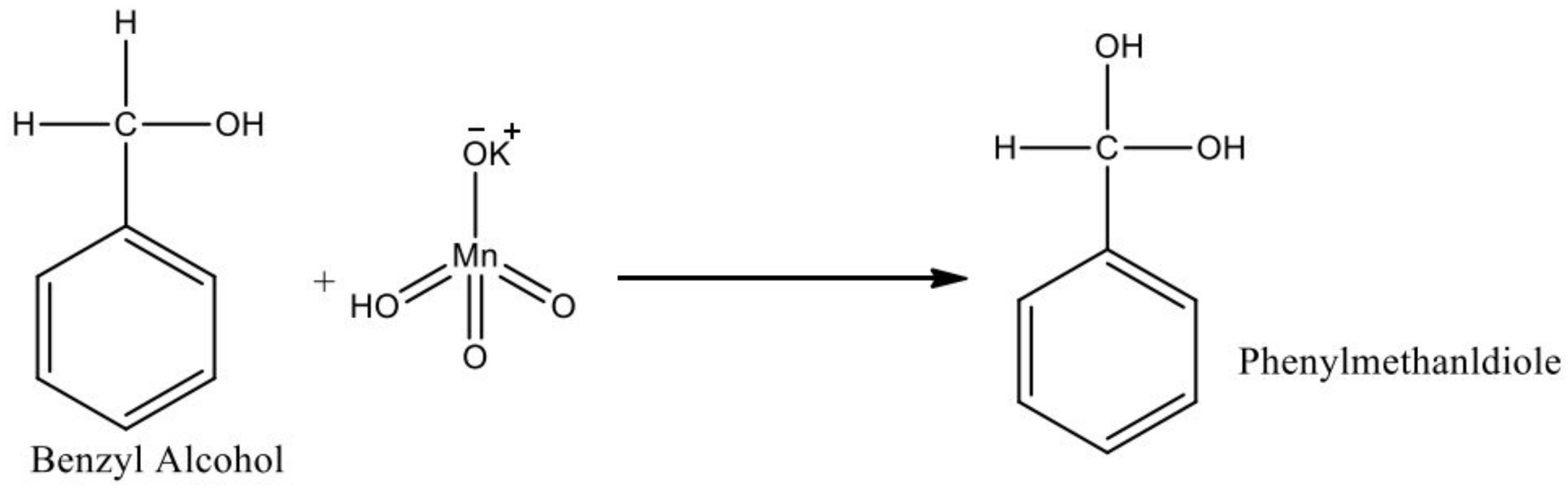


Step 3: Further Oxidation

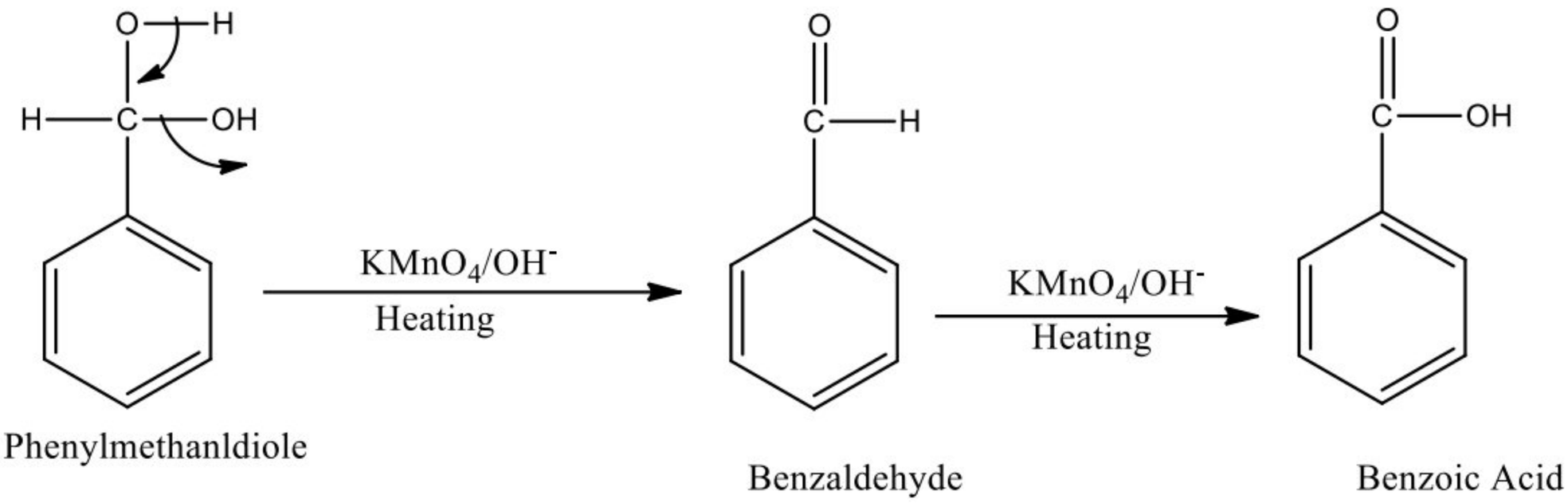
- The benzylic carbon undergoes successive oxidations:
  1. **Benzyl alcohol ($C_6H_5–CH_2OH$)** → oxidized to **phenylmethanediol ($C_6H_5–CH(OH)_2$)**.



  2. Phenylmethanediol is unstable and loses water, giving **benzaldehyde ($C_6H_5–CHO$)**.



  3. Benzaldehyde is further oxidized by $KMnO_4$ to **benzoic acid ($C_6H_5–COOH$)**.



Phenylmethanldiole Benzaldehyde Benzoic Acid

Step 4: Effect on Longer Side Chains

- If the side chain is **longer than one carbon** (e.g., ethylbenzene, propylbenzene), **all extra carbons beyond the benzylic carbon are oxidized to CO_2**.
- The product is still **benzoic acid**, regardless of side-chain length.

Electrophilic Aromatic Substitution in Substituted Arenes

1. Monosubstituted Benzene

- In **benzene**, all six carbon atoms are **equivalent**, so the first substituent can attach at any carbon.
- Example: Nitration of benzene gives only **one product: nitrobenzene**.

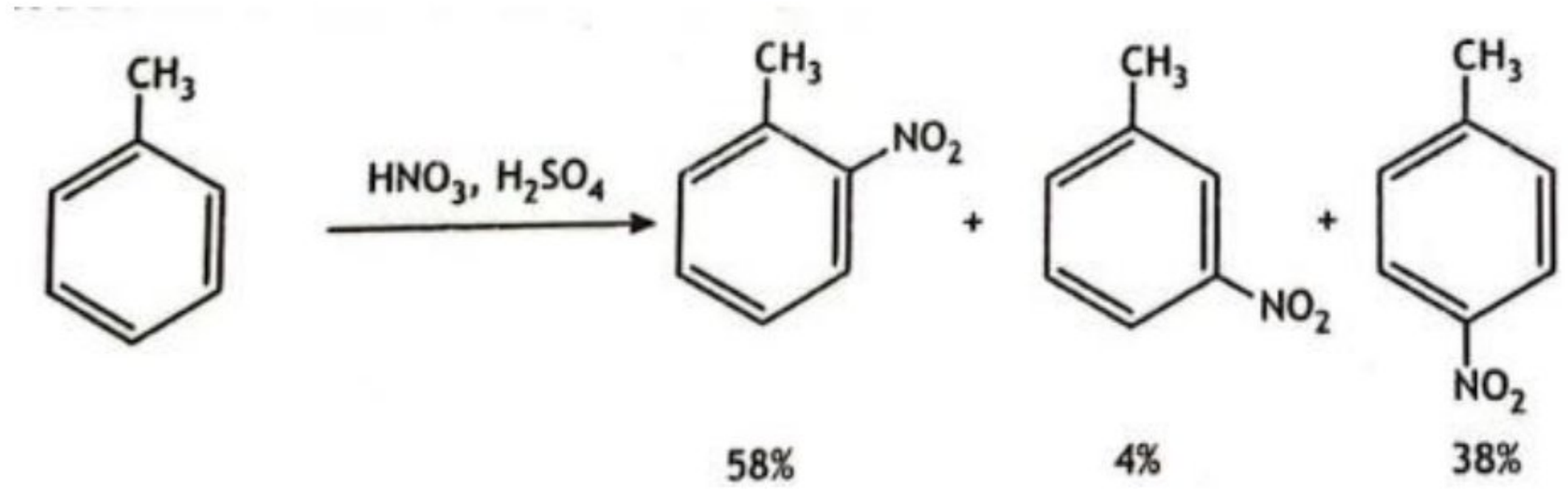
---

2. Disubstitution in Benzene

- When a **second electrophile** reacts with a **monosubstituted benzene**, three different **disubstituted isomers** are possible:
  - **Ortho (2-position)**
  - **Meta (3-position)**
  - **Para (4-position)**

Example:
Methylbenzene (toluene) on nitration can form:

- 2-nitromethylbenzene (ortho)
- 3-nitromethylbenzene (meta)
- 4-nitromethylbenzene (para)



3. Experimental Ratio (Random Substitution)

If nitration happened at random, we would expect:

- 2 parts ortho (40%)
- 2 parts meta (40%)
- 1 part para (20%)

This shows three possible positions for substitution, but the actual ratio depends on the nature of the first substituent**.**

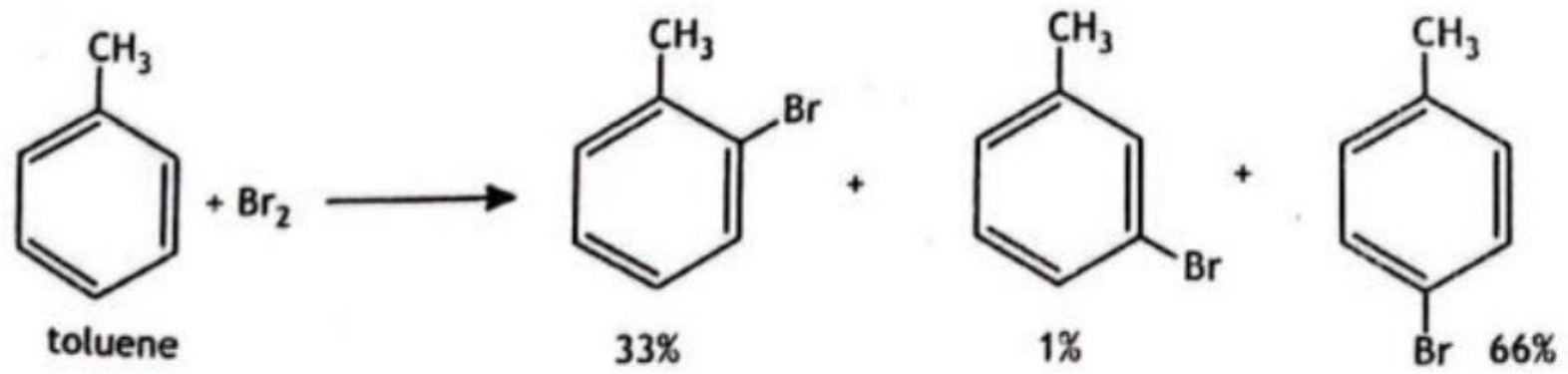
4. Orientation Effect of Substituents

From experiments, it is concluded:

1. The orientation of the incoming electrophile is controlled by the group already present on the benzene ring **(**not by the electrophile itself**).**
2. Substituents are divided into two categories based on where they direct the incoming group**:**

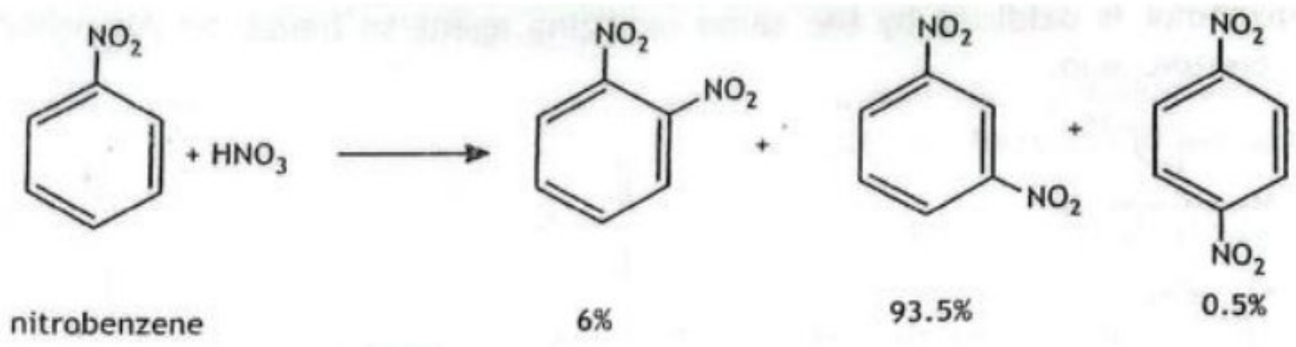
(i) Ortho/Para Directing Groups

- These groups activate the benzene ring by increasing electron density at the ortho and para positions.
- Common examples: **–CH_3, –OH, –NH_2, –OCH_3, –Cl, –Br**
- Example: Nitration of methylbenzene → mixture of **ortho-** and **para-nitrotoluene**.



(ii) Meta Directing Groups

- These groups deactivate the benzene ring by **withdrawing electrons** from the ring, especially at ortho and para positions, leaving meta as the most favorable site.
- Common examples: **–NO_2, –COOH, –SO_3H, –CN, –CHO**
- Example: Nitration of nitrobenzene → **meta-dinitrobenzene**.



Ring-Activating or Ortho/Para Directing Substituents

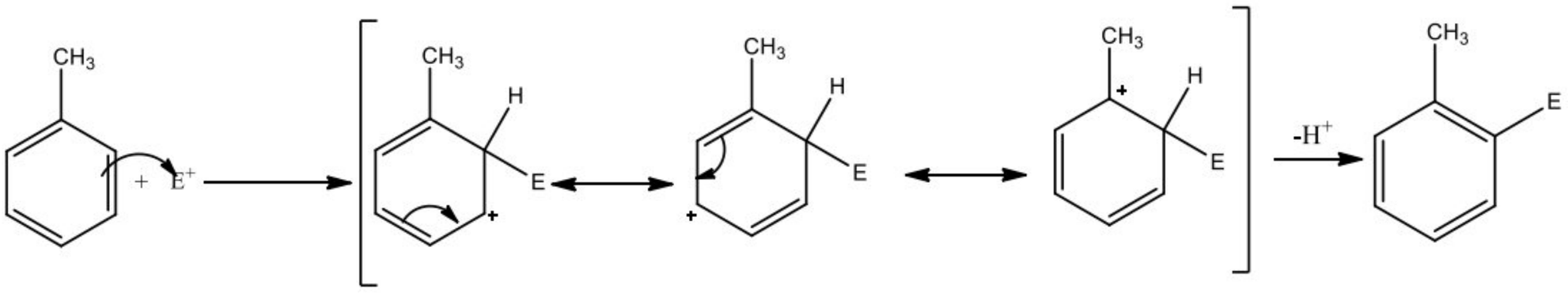
1. Definition

- Substituents that **increase the reactivity** of the benzene ring (compared to benzene itself) are called **ring-activating substituents**.
- They **donate electrons** to the ring (mostly by **resonance**), which increases electron density, especially at the **ortho (2-position)** and **para (4-position)**.
- This makes the ring more reactive toward incoming **electrophiles**.

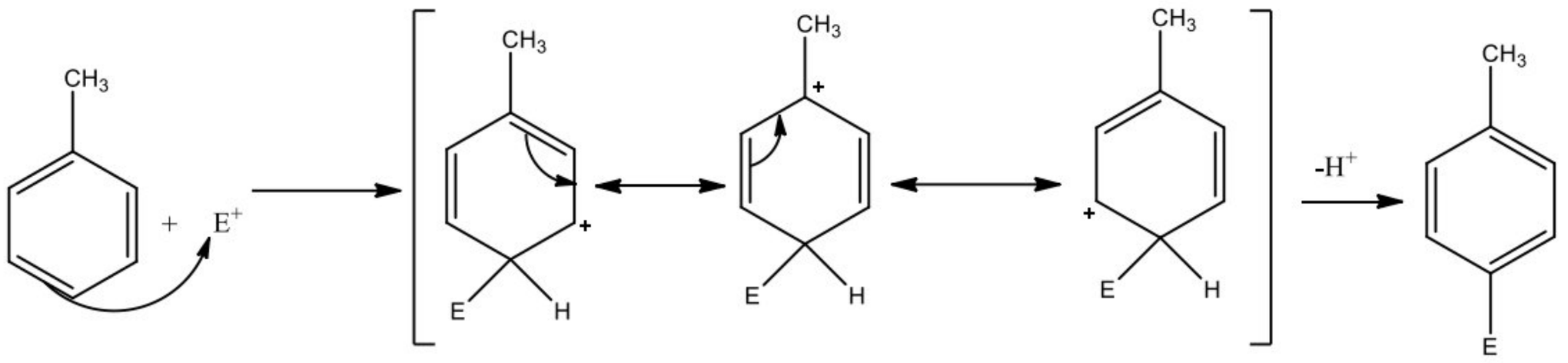
2. Why Are They Ortho/Para Directing?

- In **electrophilic aromatic substitution (EAS)**, an **arenium ion (σ-complex)** intermediate is formed.
- When the electrophile attacks at **ortho or para positions**, one resonance form places the **positive charge on the carbon directly bonded to the substituent**.
- If the substituent has electron-donating ability, it stabilizes this carbocation via **resonance** or **inductive donation**.
- In **meta attack**, no resonance structure places the positive charge next to the substituent, so **stabilization is weaker**, making meta products less favorable.

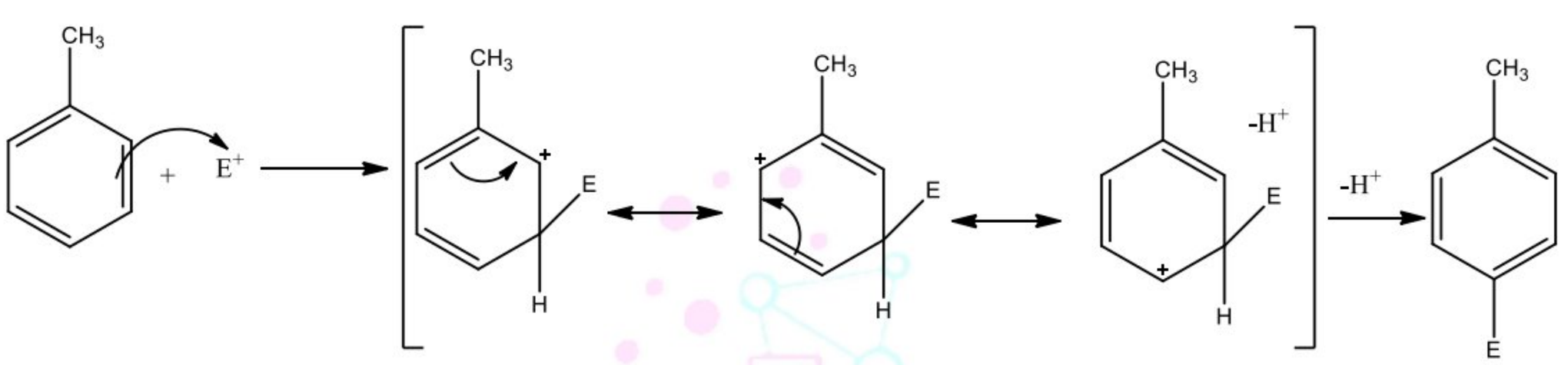
Ortho attack:



Para attack:



Meta attack:



3. Special Case: Halogens (-X)

- Halogens are **electron-withdrawing** by their strong **–I (inductive)** effect. → This tends to deactivate the ring.
- But, they also have **lone pairs** that can be donated into the ring by **resonance** → This makes ortho and para positions more stable than meta.
- **Result**: Halogens are **deactivating but ortho/para directing**.

---

4. Examples of Ortho/Para Directing Substituents

- **Strong activators** (very powerful electron donors):
  - –OH (hydroxyl)
  - –NH_2 (amino)
  - –OR (alkoxy)
- **Moderate activators**:
  - –R (alkyl groups, e.g., –CH_3)
- **Deactivating but still ortho/para directing**:
  - –X (halogens: –F, –Cl, –Br, –I)

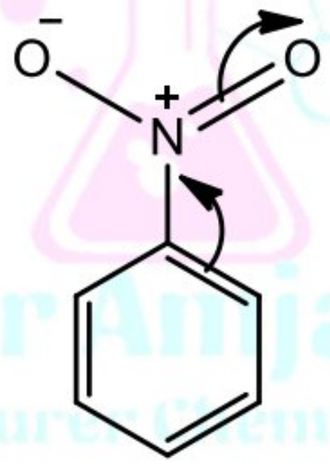
Summary Table

Substituent	Effect on Ring Reactivity	Directing Effect	Reason
–OH, –NH_2, –OR	Strongly activating	Ortho/Para	Strong resonance donation
–R (alkyl)	Moderately activating	Ortho/Para	Inductive electron donation
–X (halogens)	Deactivating	Ortho/Para	–I effect (deactivation) but +R effect (ortho/para directing)

Ring-Deactivating or Meta-Directing Substituents

1. Definition

- Substituents that decrease the reactivity of benzene toward electrophilic substitution are called ring-deactivating substituents.
- They withdraw electrons from the ring (by strong **–I effect** or **–M effect**), making the ring **electron deficient** and less reactive toward electrophiles.
- These substituents usually carry a partial or complete positive charge on the atom directly attached to the ring.



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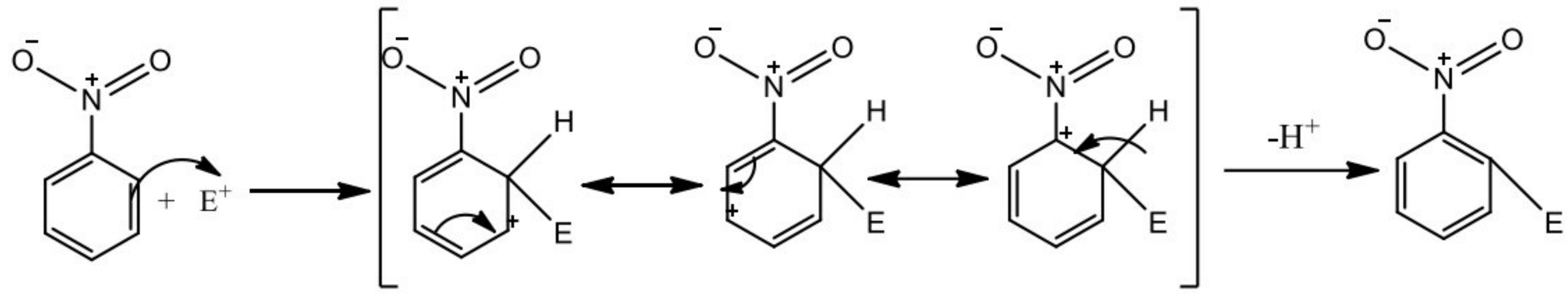
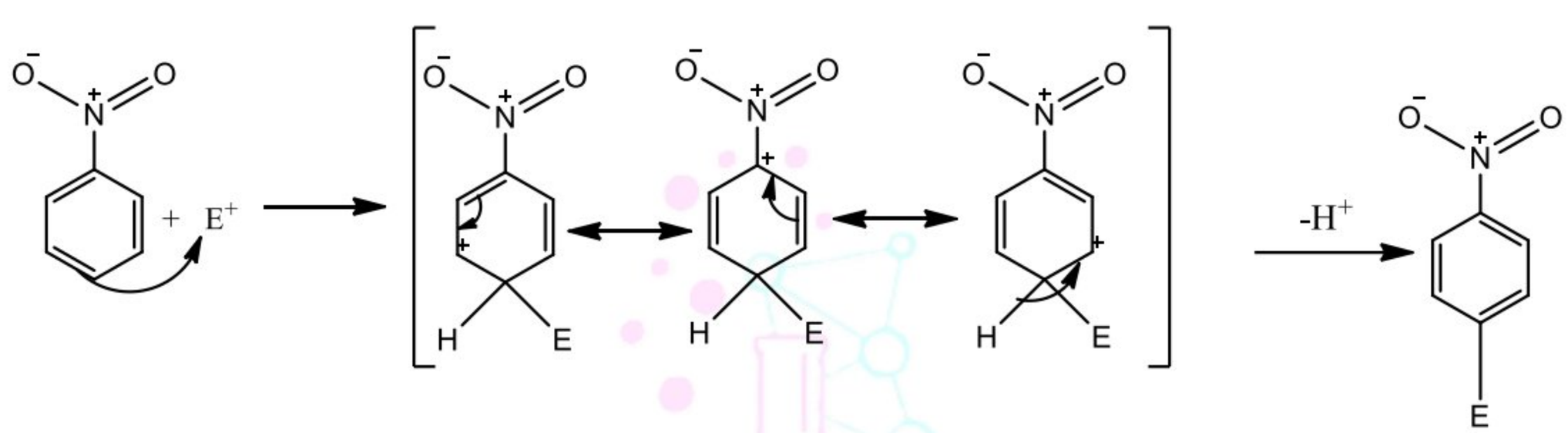
2. Why Are They Meta-Directing?

- During electrophilic attack, the benzene ring forms an arenium ion (σ-complex).
- If substitution occurs at the ortho or para positions, resonance structures place the **positive** charge directly next to the substituent atom (which is already electron-deficient). This causes **very strong destabilization**.
- In contrast, if substitution occurs at the **meta position**, none of the resonance structures place the positive charge directly on the carbon attached to the substituent → **less destabilization**.
- Therefore, electron-withdrawing groups stabilize the arenium ion **better at meta** than at ortho/para.

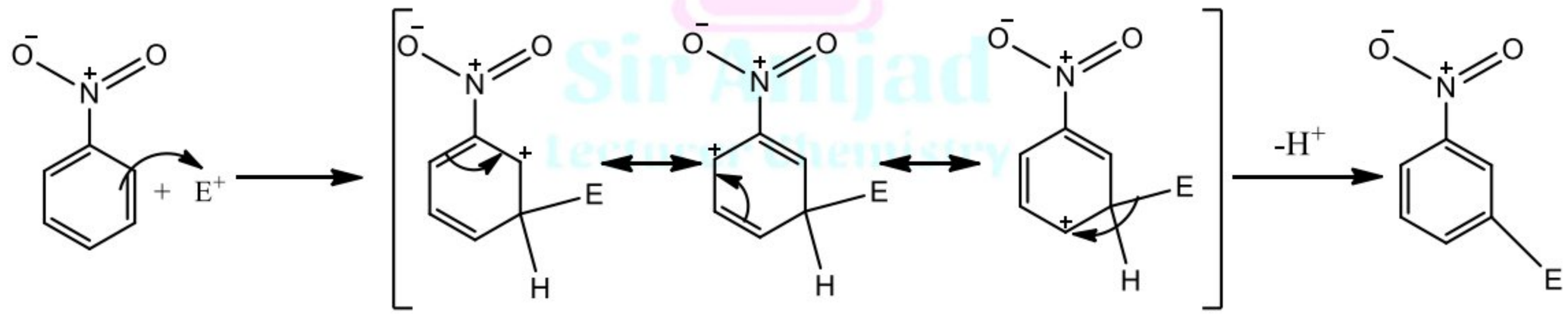
Ortho attack:



Para attack:



Meta attack:



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3. Examples of Meta-Directing Substituents

- **Strong deactivators** (very powerful electron-withdrawing groups):
  - –NO_2 (nitro)
  - –SO_3H (sulfonic acid group)
  - –CN (cyano)
  - –CHO (formyl)
  - –COOH (carboxyl)
  - –COOR (ester group)
  - –COR (acyl group)

All of these groups pull electron density away through **–I (inductive)** and/or **–M (resonance withdrawal)** effects.

Summary Table

Substituent	Effect on Ring Reactivity	Directing Effect	Reason
$–NO_2$, –CN, $–SO_3H$, –CHO, –COOH, –COR, –COOR	Strongly deactivating	Meta-directing	Withdraw electrons (–I and/or –M) → destabilize ortho/para carbocations

For More Information:

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HSSC-I: https://chat.whatsapp.com/DMYmTNYItL98P7IC5cwSoj

HSSC-II: https://chat.whatsapp.com/DMYmTNYItL98P7IC5cwSoj

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