

# Reaction Mechanism: Electrophilic Substitution In Benzene Nucleus

For  
B.Sc Chemistry(Part-II)  
Inorganic chemistry  
Paper-III  
Lecture-06



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# Electrophilic Substitution In Benzene Nucleus

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# Electrophilic Substitution In Benzene Nucleus

## Electron donating groups

Generally ortho/para directors for electrophilic aromatic substitutions

They increases the rate

## Electron withdrawing groups

Generally meta directors with the exception of the halogens which are also ortho/para directors

They have lone pairs of electrons that are shared with the aromatic ring

They decreases the rate

# Electrophilic Substitution In Benzene Nucleus

## Importance Electrophilic aromatic substitution :

- Important reactions in synthetic organic chemistry.
- Such reactions are used for the synthesis of important intermediates
- Used as precursors for the production of pharmaceutical , agrochemical and industrial products.

**Ortho** nitrotoluene is **more** reactive than **para** nitrotoluene towards Electrophilic Substitution reaction

Reason :

Ortho are less stable

Ortho and para directing groups are activating groups

They increase reactivity of the compound towards the reaction

para position is less reactive

# Electrophilic Substitution In Benzene Nucleus

## Electrophilic substitutions Reaction

- It involves displacement of a atom or functional group by an **electrophile** (generally a hydrogen atom) or positively charged atom.
- Species that are attracted to electrons

## Nucleophilic substitutions Reaction

- It involves displacement of a atom or functional group by an **nucleophile**
- Species that are attracted to positively charged (or partially positively charged).

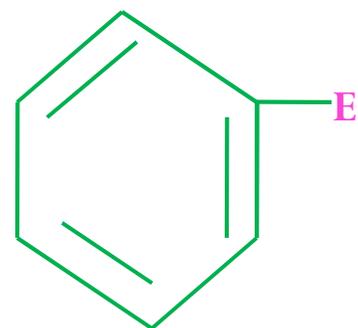
# Electrophilic Substitution In Benzene Nucleus



**Benzene**



Electrophilic substitution



**Substituted product**



# Electrophilic Substitution In Benzene Nucleus

## Electrophilic substitution of benzene

An **electrophile** substitutes the hydrogen atom of **benzene**.

Examples:

Nitration

Sulfonation

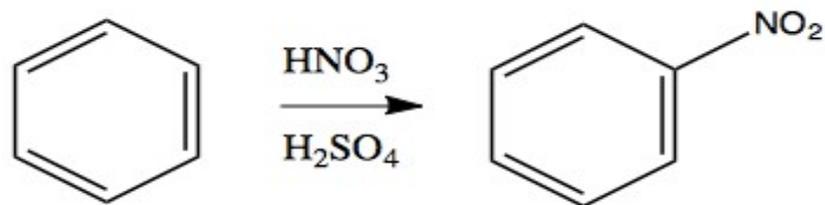
Halogenation

Friedel Craft's alkylation

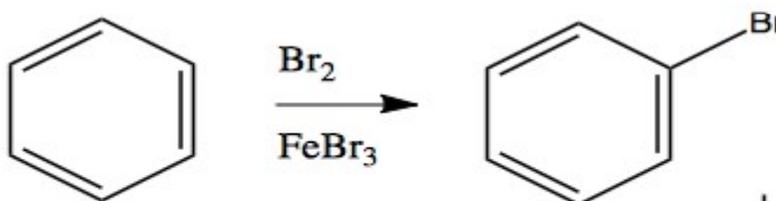
Acylation, etc.

# Electrophilic Substitution In Benzene Nucleus

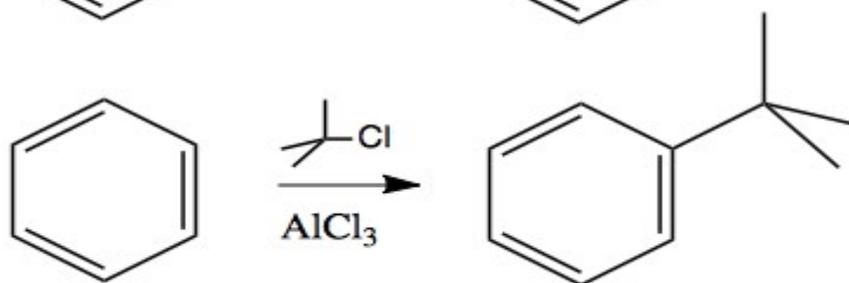
**Nitration**



**Halogenation**



**Alkylation and Acylation**



# Electrophilic Substitution In Benzene Nucleus

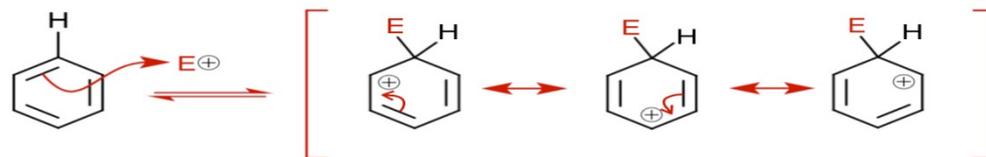
## Electrophilic Aromatic Substitution

- When a compound undergoes electrophilic aromatic substitution
- Aromaticity of the ring system is preserved.
- Proceed through carbocation intermediate.
- Many functional groups may be added to aromatic compounds

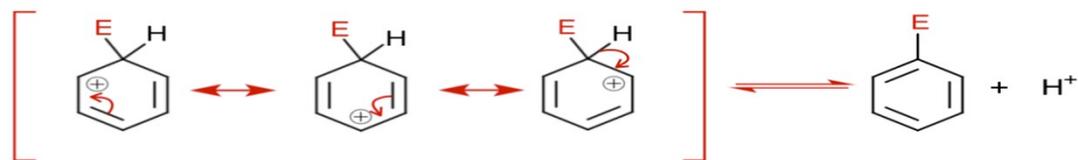
For example:

Benzene reacts with bromine to form bromobenzene.

### Step 1: Electrophilic Attack



### Step 2: Proton Loss

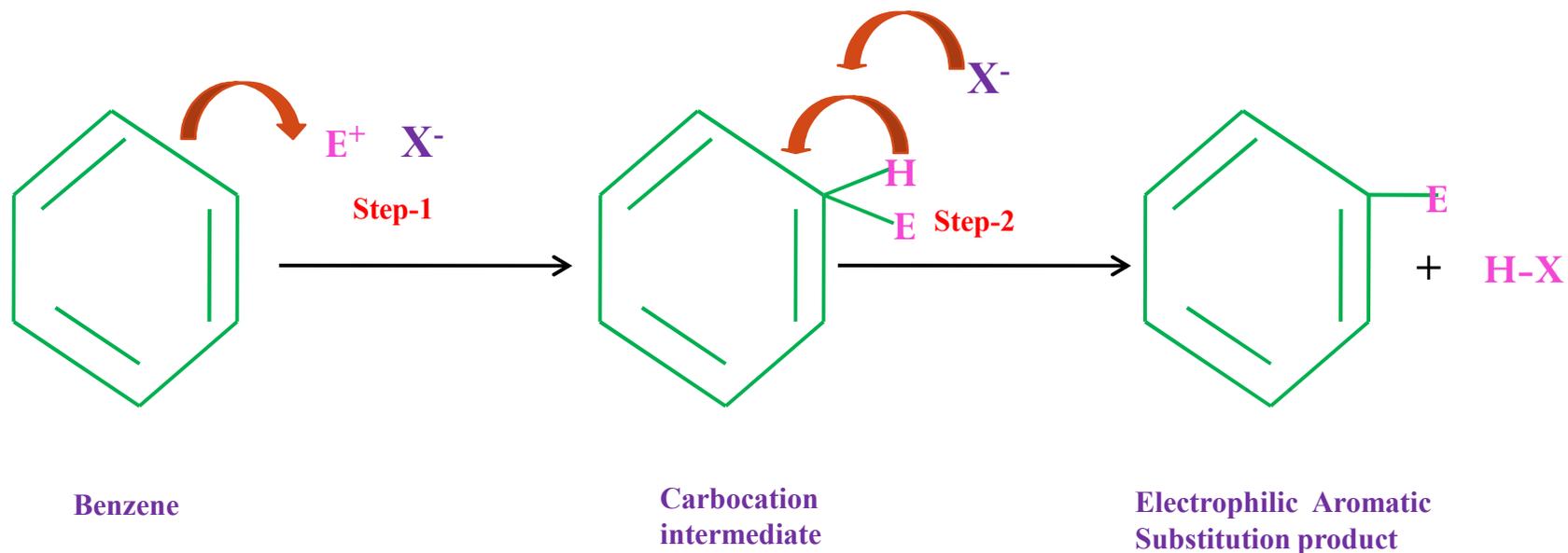


Resonating structure

# Electrophilic Substitution In Benzene Nucleus

## Mechanism of nucleophilic substitution at saturated carbon

Electrophilic Aromatic Substitution Mechanism, Step 1: Attack of the Electrophile (E) by a Pi-bond Of the Aromatic Ring.



Electrophilic substitution of benzene

# Electrophilic Substitution In Benzene Nucleus

**Step-1: Attack of electrophile by aromatic pi bond**

**Formation of C-E**

**Breaking of C-C(pi or = bond)**

**Step-2: Deprotonation adjacent to carbocation restores aromaticity**

**Breaking of C=C(pi or = bond)**

**Formation of C-C & H-X bond**

# Electrophilic Substitution In Benzene Nucleus

## Problem for practice:

**Q1.** Is ortho or para more stable?

**Q2.** Why does electrophilic aromatic substitution occur?