



Electrophilic Substitution Reactions - Lecture Notes

Electrophilic substitution reactions are typical of aromatic compounds like benzene due to their electron-rich structure. These reactions involve the substitution of an atom, typically hydrogen, by an electrophile. Benzene and other aromatic compounds undergo these reactions because of their stable π -electron cloud, which makes them susceptible to attack by electrophiles.

Mechanism of Electrophilic Substitution Reactions

The general mechanism involves the following steps:

1. Generation of the Electrophile:

- The electrophile (E^+) is generated by reacting the reagent with a catalyst. For example, in nitration, nitric acid (HNO_3) reacts with sulfuric acid (H_2SO_4) to form the nitronium ion (NO_2^+), which acts as the electrophile.

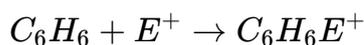
Example:



2. Attack of the Electrophile:

- The π -electrons of the aromatic ring attack the electrophile, forming a carbocation intermediate (arenium ion), which is resonance-stabilized.

Example (for benzene):



The aromatic ring loses its aromaticity temporarily in this step.

3. Deprotonation:

- The proton (H^+) attached to the carbon that formed the bond with the electrophile is removed by a base, restoring the aromaticity of the ring.

Example:

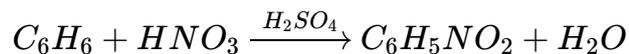


Common Electrophilic Substitution Reactions

1. Nitration:

- **Reagents:** Concentrated nitric acid and concentrated sulfuric acid.

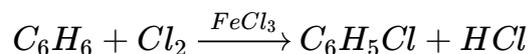
- **Electrophile:** Nitronium ion (NO_2^+).
- **Reaction:**



- Product: Nitrobenzene.

2. Halogenation:

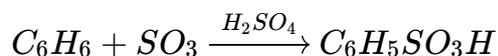
- **Reagents:** Halogen (Cl_2 or Br_2) and a Lewis acid catalyst (FeCl_3 or FeBr_3).
- **Electrophile:** Halonium ion (Cl^+ or Br^+).
- **Reaction:**



- Product: Chlorobenzene.

3. Sulfonation:

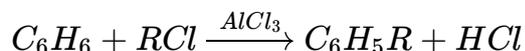
- **Reagents:** Fuming sulfuric acid (SO_3 in H_2SO_4).
- **Electrophile:** Sulfur trioxide (SO_3).
- **Reaction:**



- Product: Benzene sulfonic acid.

4. Friedel-Crafts Alkylation:

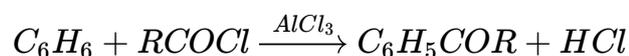
- **Reagents:** Alkyl halide (RCl) and a Lewis acid catalyst (AlCl_3).
- **Electrophile:** Carbocation (R^+).
- **Reaction:**



- Product: Alkyl benzene (e.g., toluene from methyl chloride).

5. Friedel-Crafts Acylation:

- **Reagents:** Acyl chloride (RCOCl) and a Lewis acid catalyst (AlCl_3).
- **Electrophile:** Acylium ion (RCO^+).
- **Reaction:**



- Product: Aryl ketone (e.g., acetophenone).

Directing Effects of Substituents

- **Ortho/Para Directors:** Substituents like $-\text{OH}$, $-\text{NH}_2$, $-\text{CH}_3$ increase the electron density on the ring via resonance or hyperconjugation, activating the ring and directing electrophiles to the ortho and para positions.

Example: Bromination of anisole ($\text{C}_6\text{H}_5\text{OCH}_3$) gives para-bromoanisole as the major product.

- **Meta Directors:** Substituents like $-\text{NO}_2$, $-\text{COOH}$ are electron-withdrawing groups. They deactivate the ring and direct electrophiles to the meta position.

Example: Nitration of nitrobenzene yields meta-dinitrobenzene.

This summary provides a comprehensive overview of electrophilic substitution reactions along with their mechanisms and examples .