

Organic Reactions and Mechanisms



Here are some key terms commonly used in organic reaction mechanisms:

1. Nucleophile

- **Definition:** A nucleophile is a species that donates an electron pair to form a chemical bond in reaction. It is often negatively charged or neutral with lone pairs (e.g., OH^- , NH_3).
- **Example:** In the reaction of OH^- with CH_3Br (methyl bromide), OH^- is the nucleophile that attacks the carbon in a nucleophilic substitution reaction ($\text{S}_\text{N}2$).

2. Electrophile

- **Definition:** An electrophile is a species that accepts an electron pair. It is electron-deficient and often positively charged or neutral with an empty orbital (e.g., H^+ , NO_2^+).
- **Example:** In the nitration of benzene, the nitronium ion (NO_2^+) acts as the electrophile that attacks the electron-rich benzene ring.

3. Leaving Group

- **Definition:** A leaving group is an atom or group that is displaced as a stable species (often an anion) during a reaction. A good leaving group is stable once it has left (e.g., halides like Cl^- , Br^-).
- **Example:** In the reaction of CH_3Br with OH^- , Br^- is the leaving group that is displaced.

4. Reaction Intermediate

- **Definition:** A short-lived, reactive species formed during the conversion of reactants to products. Common intermediates include carbocations, carbanions, radicals, and carbene.
- **Example:** In an $\text{S}_\text{N}1$ reaction, a carbocation intermediate forms after the leaving group departs.

5. Carbocation

- **Definition:** A carbocation is a positively charged carbon species (C^+) that results from the departure of a leaving group, especially in an $\text{S}_\text{N}1$ or electrophilic addition reaction.
- **Example:** In the $\text{S}_\text{N}1$ reaction of tert-butyl chloride, the formation of the tert-butyl carbocation ($\text{C}(\text{CH}_3)_3^+$) is the rate-determining step.

6. Radical

- **Definition:** A radical is a species with an unpaired electron. Radicals are highly reactive and typically form through homolytic bond cleavage.
- **Example:** The chlorine radical (Cl^\cdot) generated in the chlorination of methane is a key species in free radical substitution reactions.

7. Transition State

- **Definition:** The high-energy state through which reactants pass during the conversion to products. It represents the point of maximum energy along the reaction pathway.
- **Example:** In an SN2 reaction, the transition state involves partial bonds between the nucleophile and the carbon, and the leaving group still partially attached.

8. Activation Energy (Ea)

- **Definition:** The minimum energy required for a reaction to occur, representing the energy difference between the reactants and the transition state.
- **Example:** A higher activation energy means that the reaction proceeds more slowly.

9. Regioselectivity

- **Definition:** A reaction is regioselective if it favors the formation of one constitutional isomer over another.
- **Example:** In Markovnikov's rule, the electrophilic addition of HX to an alkene places the hydrogen on the carbon with more hydrogens, leading to regioselective product formation.

10. Stereoselectivity

- **Definition:** Stereoselectivity refers to the preference of a reaction to form one stereoisomer over another.
- **Example:** In an E2 elimination, the reaction is stereoselective, favoring the formation of the trans alkene over the cis alkene.

11. Stereospecificity

- **Definition:** A reaction is stereospecific if the stereochemistry of the reactant determines the stereochemistry of the product.
- **Example:** In the SN2 reaction, inversion of configuration occurs at the carbon center being attacked by the nucleophile.

12. Markovnikov's Rule

- **Definition:** In the addition of HX to an unsymmetrical alkene, the hydrogen attaches to the carbon with more hydrogen atoms, and the halide attaches to the carbon with fewer hydrogen atoms.
- **Example:** The addition of HBr to propene follows Markovnikov's rule, forming 2-bromopropane.

13. Anti-Markovnikov Addition

- **Definition:** In the presence of peroxides, the addition of HX to alkenes proceeds with the hydrogen attaching to the less substituted carbon (opposite of Markovnikov's rule).
- **Example:** The addition of HBr to propene in the presence of peroxides forms 1-bromopropane.

14. Heterolytic and Homolytic Bond Cleavage

- **Definition:**
 - **Heterolytic Cleavage:** Both bonding electrons are transferred to one atom, forming ions.
 - **Homolytic Cleavage:** One electron from the bond goes to each atom, forming radicals.
- **Example:**
 - Heterolytic: $\text{CH}_3\text{Cl} \rightarrow \text{CH}_3^+ + \text{Cl}^-$

- Homolytic: $\text{Cl}_2 \xrightarrow{h\nu} 2\text{Cl}^\cdot$

15. Inductive Effect

- **Definition:** The electron-withdrawing or electron-donating effect transmitted through sigma bonds due to the electronegativity of atoms or groups.
- **Example:** The presence of an electronegative group (like Cl) in a molecule withdraws electron density, stabilizing a nearby carbocation.

16. Resonance

- **Definition:** The delocalization of electrons in a molecule where the electron density can be represented by multiple contributing structures (resonance structures).
- **Example:** The resonance in benzene, where the π -electrons are delocalized over all six carbon atoms, gives benzene extra stability.

17. Hyperconjugation

- **Definition:** The interaction of sigma bonds (usually C-H) with an adjacent empty or partially filled p-orbital, stabilizing carbocations.
- **Example:** The stability of the tertiary carbocation in an SN1 reaction is enhanced by hyperconjugation from adjacent alkyl groups.

18. Electrophilic and Nucleophilic Addition

- **Definition:**
 - **Electrophilic Addition:** An electrophile adds to an electron-rich unsaturated bond (e.g., alkenes).
 - **Nucleophilic Addition:** A nucleophile adds to an electron-deficient site (e.g., carbonyl group).

Example:

- Electrophilic: Addition of Br_2 to ethene.
- Nucleophilic: Addition of HCN to aldehydes and ketones.

These key terms are essential for understanding the mechanisms and pathways of various organic reactions.