Aliphatic Electrophilic Substitution (AES)

Definition: Aliphatic electrophilic substitution is a reaction in which an electrophile (E■) replaces an atom or a group (usually hydrogen or another substituent) from an aliphatic compound.
Reaction: R–H + E■ → R–E + H■

Key Features:

• Occurs in aliphatic (open-chain) compounds.
• Involves electrophiles, not nucleophiles.
• Mechanism proceeds via formation of a carbocation intermediate.
• The leaving group and solvent polarity play major roles in reactivity.

General Mechanism:

Step 1: Formation of Carbocation – Electrophile attacks the aliphatic molecule generating a carbocation intermediate.
R–H + E■ → [R■] + HE
Step 2: Departure of Leaving Group – The leaving group (often H■) departs forming the substituted product.
[R■] → R–E + H■

Examples:

• Halogenation: CH■CH■OH + Cl■ → CH■CHClOH + HCl
• Nitration: CH■ + NO■■ → CH■NO■ + H■
• Sulfonation: CH■CH■OH + SO■ → CH■CH■OSO■H

Factors Affecting Reactivity:

1. Nature of Leaving Group: Better leaving group → faster reaction (I■ > Br■ > Cl■ > F■).
2. Solvent Polarity: Polar solvents stabilize carbocations, increasing rate (e.g., water, ethanol).
3. Nature of Substrate: Reactivity depends on carbocation stability (3° > 2° > 1° > CH■).
4. Strength of Electrophile: Stronger electrophiles attack more easily (NO■■ > SO■ > Cl■).

Comparison: Aliphatic vs Aromatic Electrophilic Substitution

Feature	Aliphatic	Aromatic
Intermediate	Carbocation (sp^3)	Arenium ion (resonance stabilized)
Reactivity	Depends on carbocation stability	Depends on ring activation/deactivation
Typical Substrates	Alkanes, alcohols	Benzene and derivatives
Example	Nitration of methane	Nitration of benzene

Electrophilic Substitution Accompanied by Double Bond Shift

Definition: In some aliphatic electrophilic substitution reactions, when an electrophile attacks an unsaturated compound (like an alkene), the substitution is accompanied by a shift of the double bond. This occurs through carbocation rearrangement to form a more stable intermediate.

Mechanism:

Step 1: Electrophilic attack on π-bond forming carbocation.
RCH=CH■ + E■ → RCH(E)–CH■■
Step 2: Double bond shifts to stabilize the carbocation.
RCH(E)–CH■■ → RCH■–CH(E)
Step 3: Deprotonation gives substituted product with shifted double bond.
RCH■–CH(E) → RCH=CHE + H■

Example: Allylic Chlorination

CH■=CH–CH■ + Cl■ → CH■=CH–CH■Cl + HCl
This involves electrophilic attack, formation of an allylic carbocation, and double bond rearrangement.

Key Concepts:

Concept	Description
Type of Reaction	Electrophilic substitution with double bond rearrangement
Intermediate	Carbocation stabilized by resonance or rearrangement
Common System	Allylic or conjugated alkenes
Result	Substitution product with shifted double bond

Summary:

• Electrophile attacks a π-bond forming a carbocation.
• Double bond shifts to stabilize the carbocation intermediate.
• Deprotonation gives the substituted product with shifted double bond.
• Common in allylic, benzylic, or conjugated alkenes.