Aromatic Substitution, Addition, and Elimination Reactions

1. Aromatic Substitution Reactions

a. Electrophilic Aromatic Substitution (EAS)

- Electrophile replaces hydrogen on aromatic ring.
- Examples: Nitration, Halogenation, Sulfonation, Friedel-Crafts.
- Steps: Electrophile formation, attack on ring, deprotonation.

b. Nucleophilic Aromatic Substitution (NAS)

- Nucleophile replaces leaving group (halide) on ring.
- Needs electron-withdrawing groups (EWGs) ortho/para.
- Mechanisms: Addition-Elimination (Meisenheimer), Elimination-Addition (Benzyne).

c. Benzyne Mechanism

- Strong base forms benzyne intermediate -> nucleophile attacks.
- Example: Aniline from chlorobenzene + NaNH.

d. Radical Substitution of Arenes

- Involves free radicals (light/heat).
- Example: Benzene -> Chlorobenzene (Cl, hv).

2. Nucleophilic Substitution at Saturated Carbon

a. SN1 (Unimolecular)

- 2-step, carbocation intermediate, tertiary carbon preferred.
- Polar protic solvents, weak nucleophiles.

b. SN2 (Bimolecular)

- One-step, backside attack, inversion of configuration.

- Favored by methyl/primary halides, strong nucleophiles.

c. SNi (Substitution Nucleophilic Internal)

- Retention of configuration, e.g., alcohols with HCl.

Factors:

- Structure: More branched -> SN1.

- Nucleophile: Strong -> SN2.

- Leaving group: Better LG favors reaction.

- Solvent: Protic = SN1, Aprotic = SN2.

3. Addition Reactions

a. Electrophilic Addition (Alkenes/Alkynes)

- Markovnikov's rule: H adds to C with more H.

- Example: HBr to alkene.

b. Nucleophilic Addition (Carbonyls)

- Example: Aldehyde + NaBH -> alcohol.

c. Free Radical Addition

- Anti-Markovnikov HBr in presence of peroxides.

4. Elimination Reactions

a. E1 (Unimolecular)

- Carbocation intermediate, tertiary carbon, heat.

- Competes with SN1.

b. E2 (Bimolecular)

- One-step, strong base, antiperiplanar transition.

- Follows Zaitsevs Rule.

c. E1CB (Conjugate Base)

- Carbanion intermediate, stabilized by EWG.

5. Elimination vs Substitution

Condition	Substitution (SN1/SN2)	Elimination (E1/E2)
Strong base	Favors E2	
Weak nucleophile/base	Favors SN1/E1	
High temperature	Favors elimination	
Steric hindrance	Favors E1/E2 over SN2	
Solvent type	Polar protic = SN1/E1	Aprotic = SN2