Organic Chemistry

Functional Groups and Reaction Mechanisms Quiz – Answer Key

1. **(C) Carboxylic acid.** Carboxylic acids contain the –COOH group (carbonyl + hydroxyl). Aldehydes have C=O bonded to H, ketones have C=O between two carbons, and esters have C=O bonded to –OR.

2. **(C) Concentration of both substrate and nucleophile.** S_N2 is bimolecular with rate = k[substrate][nucleophile]. Both species participate in the rate-determining step.

3. **(D) Tertiary carbocation.** Carbocation stability increases with substitution due to hyperconjugation and inductive electron donation: tertiary ¿ secondary ¿ primary ¿ methyl.

4. **(B) The middle carbon (C2).** Markovnikov's rule states that H adds to the carbon with more hydrogens, and Br adds to the more substituted carbon, forming the more stable carbocation intermediate.

5. **(B) $NaBH_4$.** Sodium borohydride is a mild reducing agent that reduces ketones and aldehydes to alcohols. $KMnO_4$ is an oxidizing agent, PCC oxidizes alcohols, and H_2SO_4 is an acid catalyst.

6. **True.** Enantiomers are non-superimposable mirror images with identical melting points, boiling points, and solubilities. They differ only in optical rotation direction (+/).

7. **False.** S_N1 proceeds through a planar carbocation intermediate, allowing nucleophilic attack from either face, resulting in racemization (mixture of retention and inversion). S_N2 proceeds with complete inversion (Walden inversion).

8. **False.** Aromatic compounds are less reactive than alkenes toward electrophilic addition because addition would destroy the aromatic stabilization. Instead, they undergo electrophilic aromatic substitution to preserve aromaticity.

9. **S_N1 Mechanism:**

   - Two-step process: (1) slow ionization to form carbocation, (2) fast nucleophilic attack
   - Rate = k[substrate] (unimolecular)
   - Favored by: tertiary substrates, weak nucleophiles, polar protic solvents (stabilize carbocation), good leaving groups
   - Stereochemistry: racemization (planar carbocation)

   S_N2 Mechanism:

   - One-step concerted process: nucleophile attacks as leaving group departs
   - Rate = k[substrate][nucleophile] (bimolecular)
   - Favored by: primary substrates (less steric hindrance), strong nucleophiles, polar aprotic solvents (don't solvate nucleophile), good leaving groups
   - Stereochemistry: complete inversion (backside attack)

Substrate effects: Methyl/primary → S_N2; tertiary → S_N1; secondary → depends on other factors.

10. Aromaticity criteria (Hückel's rule):

- Cyclic structure
- Planar (allows orbital overlap)
- Fully conjugated (p orbital on every atom in ring)
- Contains (4n + 2) electrons (n = 0, 1, 2...)

Benzene stability: Benzene has 6 electrons (n=1), satisfying Hückel's rule. The delocalized electrons create a continuous ring of electron density above and below the plane. Resonance energy (36 kcal/mol) makes benzene 36 kcal/mol more stable than hypothetical cyclohexatriene with localized double bonds.

Electrophilic aromatic substitution (EAS):

- Mechanism: electrophile attacks system → forms resonance-stabilized carbocation (arenium ion) → base removes H^+ to restore aromaticity
- Substitution rather than addition preserves the aromatic ring
- Examples: halogenation, nitration, sulfonation, Friedel-Crafts reactions

Conclusion: Aromatic stability drives reactivity patterns—substitution preserves the (4n+2) electron system while addition would destroy it.