NEET Haloalkanes Mechanism MCQs (1–60)

Content

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MCQs 1–60 with Detailed Explanations

1. Order of mechanism for alcohol → alkyl chloride using $SOCl_2$ / pyridine

For the conversion of ethanol to chloroethane using $SOCl_2$ in the presence of pyridine, the reaction mainly proceeds by:

a. (S_N1) via carbocation
b. (S_N2) on chlorosulfite intermediate
c. Free radical chain mechanism
d. E1 elimination followed by addition

Answer: b
Explanation: $SOCl_2$ first forms an alkyl chlorosulfite (RO–SOCl) ester. Pyridine removes HCl and acts as a base, making a good leaving group. The chloride ion then attacks the carbon bearing –O–SOCl in a **backside (S_N2)** step. No carbocation is formed; rearrangements are absent.

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2. Why is $SOCl_2$ preferred over PCl_5 for preparing alkyl chlorides?

The use of $SOCl_2$ (with pyridine) is preferred over PCl_5 for converting alcohols to alkyl chlorides mainly because:

a. $SOCl_2$ is cheaper
b. Reaction with $SOCl_2$ is reversible
c. Gaseous by-products are formed and escape
d. Formation of carbocation is easier with $SOCl_2$

Answer: c
Explanation: With $SOCl_2$, by-products are SO_2 and HCl, both gases, which leave the reaction mixture. This **shifts equilibrium to products** and simplifies separation. With PCl_5, solid $POCl_3$ is formed that must be separated.

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3. Mechanism type for reaction of 3° alcohol with conc. HCl

Tertiary alcohols react rapidly with conc. HCl to give alkyl chlorides. The mechanism is:

a. (S_N1)
b. (S_N2)
c. Free radical
d. Electrophilic addition

Answer: a
Explanation: 3° alcohol is protonated to give an oxonium ion and then loses water, forming a stable **3° carbocation**. Chloride ion then attacks this carbocation. This two-step process is typical of **(S_N1)**.

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4. Finkelstein reaction is best explained as:

a. (S_N1) in protic solvent
b. (S_N2) in polar aprotic solvent
c. Free radical substitution
d. Aromatic electrophilic substitution

Answer: b
Explanation: Finkelstein reaction: (R–Cl) or (R–Br) + NaI in **dry acetone** → (R–I) + NaCl/NaBr (ppt). Acetone is **polar aprotic**; iodide is a strong nucleophile and attacks by backside displacement on the primary alkyl halide → **(S_N2)**. The precipitation of NaCl/NaBr drives the reaction.

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5. Why is dry acetone used in Finkelstein reaction?

a. To generate free radicals
b. Because NaI is insoluble in acetone
c. Because NaCl/NaBr precipitate in acetone
d. To stabilize carbocation

Answer: c
Explanation: NaI is soluble in acetone but NaCl/NaBr are not. As soon as halide exchange occurs, NaCl/NaBr **precipitate**, pulling equilibrium toward product. Also, aprotic acetone increases nucleophilicity of I^-.

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6. Swarts reaction mechanism type

In Swarts reaction, alkyl chloride/bromide is heated with AgF, Hg_2F_2, CoF_2 or SbF_3 to form alkyl fluoride. The reaction mainly proceeds via:

a. (S_N1)
b. (S_N2)
c. Electrophilic aromatic substitution
d. Elimination–addition

Answer: b
Explanation: Metal fluorides provide nucleophilic F^-, which replaces Cl^-/Br^- through **bimolecular substitution**. Carbocation

formation is disfavoured; hence (S_N2).

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7. Hunsdiecker reaction step that generates radicals

In Hunsdiecker reaction, silver carboxylate is treated with Br_2 in CCl_4 and heated. The decarboxylative formation of alkyl bromide occurs via:

a. Carbocation rearrangement
b. Radical chain mechanism
c. (S_N2) on carboxylate
d. Electrophilic aromatic substitution

Answer: b
Explanation: Silver carboxylate and Br_2 form an acyl hypobromite which on homolysis produces **alkyl radicals and CO_2**. These radicals then combine with Br• to give R–Br.

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8. Feature explaining order: 1° > 2° > 3° in (S_N2)

Which factor mainly governs the order of reactivity of alkyl halides toward (S_N2): 1° > 2° > 3°?

a. Stability of carbocation
b. Strength of C–X bond
c. Steric hindrance around reaction centre
d. Hyperconjugation

Answer: c
Explanation: (S_N2) requires backside attack on the carbon bearing the leaving group. Increasing alkyl substitution blocks approach of nucleophile (steric hindrance). So primary > secondary > tertiary.

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9. Feature explaining order: 3° > 2° > 1° in (S_N1)

For (S_N1) mechanisms, the order 3° > 2° > 1° is due to:

a. Stronger C–X bond in 3°
b. Better steric accessibility
c. Greater stability of carbocation by hyperconjugation and +I
d. Lower nucleophilicity near 3° carbon

Answer: c
Explanation: Rate-determining step in (S_N1) is **formation of carbocation**. Tertiary carbocations are most stable due to hyperconjugation and inductive effects from three alkyl groups.

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10. Solvent choice favouring (S_N1) mechanism

Which solvent will most strongly favour an (S_N1) reaction for tert-butyl bromide?

a. Dry acetone
b. DMSO
c. Water
d. Hexane

Answer: c
Explanation: (S_N1) requires ionization to carbocation and halide ion. Highly polar **protic** solvents (water, alcohol) solvate ions strongly and favour carbocation formation.

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11. Nucleophilicity vs basicity trend down a group in polar protic solvent

For halide ions in water, the nucleophilicity order is:

a. $F^- > Cl^- > Br^- > I^-$
b. $Cl^- > F^- > Br^- > I^-$
c. $I^- > Br^- > Cl^- > F^-$
d. $Br^- > I^- > Cl^- > F^-$

Answer: c
Explanation: In polar protic solvents, anions are strongly solvated by H-bonding. Small F^- is most strongly solvated, so nucleophilicity is lowest. Large I^- is least solvated and most polarizable → **$I^- > Br^- > Cl^- > F^-$**.

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12. Nucleophilicity order in polar aprotic solvents

In DMSO, the nucleophilicity order of halide ions becomes closer to their basicity. The order is:

a. $I^- > Br^- > Cl^- > F^-$
b. $F^- > Cl^- > Br^- > I^-$
c. $Br^- > I^- > Cl^- > F^-$
d. $Cl^- > F^- > Br^- > I^-$

Answer: b
Explanation: Polar aprotic solvents do not H-bond strongly to anions. Nucleophilicity parallels basicity: **F^- is strongest base → best nucleophile**.

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13. Leaving group ability vs basicity

Which of the following is the **best leaving group** in nucleophilic substitution?

a. HO^-

b. RO^-
c. I^-
d. NH_2^-

Answer: c
Explanation: Good leaving groups are weak bases. Among given, I^- is weakest base (conjugate base of strong acid HI). Strong bases like HO^-, RO^-, NH_2^- are poor leaving groups.

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14. Effect of resonance on leaving group ability

Which anion will be the **best leaving group**?

a. CH_3O^-
b. $C_6H_5O^-$ (phenoxide)
c. CF_3COO^-
d. NH_2^-

Answer: c
Explanation: CF_3COO^- is highly stabilized by resonance in carboxylate plus strong –I of CF_3, so it is an excellent leaving group. Phenoxide is also resonance-stabilized but less so. CH_3O^- and NH_2^- are strong bases, poor LGs.

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15. Competition between substitution and elimination for 3° alkyl halide with strong base

When 3° alkyl bromide is heated with alcoholic KOH, the major mechanism is:

a. (S_N1)
b. (S_N2)
c. E1
d. E2

Answer: d
Explanation: Alcoholic KOH supplies strong base (RO^-). Steric hindrance at 3° carbon makes (S_N2) impossible; (S_N1) would compete but at higher temperature and strong base, **E2 elimination** dominates.

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16. Preference for nitrile vs isonitrile formation from alkyl halides and KCN/AgCN

Reaction of alkyl halide with KCN in aqueous ethanol mainly gives R–CN, while with AgCN mainly yields R–NC. This is because:

a. CN^- is ambident nucleophile, and in KCN C-attack is favoured
b. CN^- is ambident nucleophile, and in KCN N-attack is favoured
c. AgCN is covalent and provides free C^- only
d. KCN is covalent and provides free N^- only

Answer: a
Explanation: CN^- is ambident. In ionic KCN, free CN^- attacks through carbon → nitrile via (S_N2). In covalent AgCN, bonding situation favours N-attack → isonitrile.

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17. Mechanistic reason for lower yield of isonitrile from tertiary halides with AgCN

When a tertiary alkyl halide reacts with AgCN, yield of isonitrile is low because:

a. (S_N1) is not possible at tertiary carbon
b. CN^- is too weak nucleophile
c. CN^- is strong base promoting elimination (E1/E2)
d. Formation of nitrene competes

Answer: c
Explanation: Tertiary halides in presence of basic CN^- tend to form carbocation and then undergo **elimination to alkene**, since CN^- is a strong base. Substitution to give R–NC competes poorly.

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18. Ambident nucleophile: CN^-

In the reaction of alkyl halide with CN^-, which statement best describes why CN^- is called an ambident nucleophile?

a. It can act as both electrophile and nucleophile
b. It has two nucleophilic sites, C and N
c. It can undergo (S_N1) and (S_N2)
d. It can both substitute and eliminate

Answer: b
Explanation: Ambident nucleophiles possess two different atoms each capable of donating lone pair. In CN^-, both C and N can attack electrophilic carbon.

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19. Identification of mechanism: allylic bromination by NBS

When propene is treated with N-bromosuccinimide (NBS) and light, allylic bromide is formed primarily via:

a. (S_N1)
b. (S_N2)
c. Radical substitution at allylic position
d. Electrophilic addition to double bond

Answer: c
Explanation: NBS under light generates Br• radicals. Abstraction of allylic H forms an allylic radical, resonance stabilized, which then combines with Br• to give allylic bromide.

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20. Allylic vs vinylic halides: ease of (S_N1)

Which will undergo (S_N1) most readily?

a. Allyl chloride
b. Vinyl chloride
c. Ethyl chloride
d. Chlorobenzene

Answer: a
Explanation: Allyl carbocation is resonance-stabilized; vinylic cation is very unstable. Ethyl cation is less stable than allyl. Chlorobenzene cannot form aryl cation easily.

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21. Benzylic vs ordinary alkyl halide in (S_N1)

Which statement is true about benzyl chloride?

a. Undergoes (S_N2) only
b. Does not undergo substitution at all
c. Undergoes (S_N1) very easily due to resonance-stabilized benzyl carbocation
d. Its reaction rate is same as that of ethyl chloride in (S_N1)

Answer: c
Explanation: Benzyl carbocation is stabilized by resonance with aromatic ring, so benzyl chloride ionizes easily in polar protic solvent.

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22. Best reagent to prepare pure CH_3CH_2Cl from ethanol

The most suitable reagent for converting ethanol to pure chloroethane with minimal by-products is:

a. Conc. HCl / $ZnCl_2$ (Lucas reagent)
b. PCl_5
c. $SOCl_2$ in presence of pyridine
d. NaCl / conc. H_2SO_4

Answer: c
Explanation: $SOCl_2$ + pyridine converts alcohol to alkyl chloride with gaseous by-products (SO_2, HCl) that escape, giving pure product.

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23. Boiling point of haloalkanes vs alkanes

Boiling point of haloalkanes is higher than that of corresponding alkanes primarily because:

a. They undergo (S_N1) reactions
b. They undergo (S_N2) reactions
c. They have stronger dipole–dipole and van der Waals interactions
d. They contain heavier isotopes

Answer: c
Explanation: Presence of polar C–X bond and larger size of halogen increases intermolecular attractions, raising boiling point.

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24. Density order of haloalkanes

Which trend in density is generally correct for simple alkyl halides with same alkyl group?

a. RI < RBr < RCl

b. RI > RBr > RCl
c. RCl > RBr > RI
d. RI = RBr = RCl

Answer: b
Explanation: As atomic mass of halogen increases from Cl → Br → I, density increases: **RI > RBr > RCl**.

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25. Carbocation rearrangement possibility in $SOCl_2$ vs HX

Which statement is correct?

a. Reaction of alcohols with $SOCl_2$ can show hydride shift rearrangements.
b. Reaction of alcohols with HX can show carbocation rearrangements.
c. Both can show rearrangements.
d. Neither show rearrangements.

Answer: b
Explanation: $SOCl_2$ proceeds via concerted (S_N2) on chlorosulfite ester; no carbocation, so no rearrangement. With HX, protonated alcohol can lose water to form carbocation; rearrangements may occur.

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26. Relative rate in Lucas test

The Lucas test is based on:

a. Different (S_N2) rates for 1°, 2°, 3° alcohols
b. Different (S_N1) rates due to carbocation stability
c. Different radical substitution rates
d. Different oxidation states of carbon

Answer: b
Explanation: Lucas reagent leads to (S_N1) substitution. 3° alcohol (fastest carbocation formation) turns cloudy immediately; 2° slower; 1° very slow.

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27. Choosing between (S_N1) and (S_N2) for 2° alkyl halide

Which set of conditions will favour (S_N2) for a secondary alkyl bromide?

a. Polar protic solvent + weak nucleophile
b. Polar aprotic solvent + strong nucleophile
c. Non-polar solvent + no nucleophile
d. High temperature + weak base

Answer: b
Explanation: (S_N2) is favoured by strong nucleophile (CN^-, N_3^- etc.) and polar aprotic solvents (DMSO, DMF) which increase nucleophilicity and disfavor carbocation formation.

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28. Effect of bulky base on substitution vs elimination

t-BuO^- (tert-butoxide) reacting with 2-bromobutane in t-BuOH primarily gives:

a. 1-butene via E2
b. 2-butene via E2
c. 2-butanol via (S_N2)
d. Butane via reduction

Answer: b
Explanation: Bulky but strong base t-BuO^- works via **E2 elimination**. Saytzeff rule: more substituted alkene (2-butene) predominates. (S_N2) is sterically hindered.

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29. Identification of best nucleophile among given bases in protic solvent

In water, which of the following is the best nucleophile?

a. OH^-
b. NH_3
c. H_2O
d. ROH

Answer: a
Explanation: Negatively charged species are better nucleophiles than their neutral counterparts. OH^- is strongly basic and nucleophilic.

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30. Order of nucleophilicity among RO^-, $RCOO^-$, HO^-, ArO^- in protic solvent

What is the decreasing order of nucleophilicity in water?

a. $RO^- > HO^- > RCOO^- > ArO^-$
b. $ArO^- > RO^- > HO^- > RCOO^-$
c. $RCOO^- > ArO^- > RO^- > HO^-$
d. $HO^- > RO^- > RCOO^- > ArO^-$

Answer: a
Explanation: Stronger base → better nucleophile if charge and size similar. RO^- and HO^- are strong bases; $RCOO^-$ and ArO^- are resonance-stabilized weaker bases. Among RO^- and HO^-, alkoxide is more basic.

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31. Effect of polar protic solvent on nucleophilicity of basic anions

Why do strongly basic anions like F^- and OH^- often show lower nucleophilicity than expected in polar protic solvents?

a. They are too small to approach carbon
b. They are strongly solvated by H-bonding which forms a solvation shell
c. They convert to radicals
d. They oxidize the substrate

Answer: b
Explanation: Polar protic solvents can hydrogen-bond strongly to small anions, surrounding them with solvent molecules. This reduces effective nucleophilicity.

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32. Identification of substrate showing no (S_N2) reaction

Which of the following substrates will **not** undergo (S_N2) with a strong nucleophile?

a. CH_3Br
b. CH_3CH_2Br
c. $(CH_3)_3CBr$
d. $CH_2=CH–CH_2Br$

Answer: c
Explanation: Tertiary carbon in $(CH_3)_3CBr$ is completely blocked. (S_N2) requires backside approach; steric hindrance prevents it.

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33. Reaction type for vinyl/aryl halides with nucleophiles

Chlorobenzene does not undergo ordinary (S_N1) or (S_N2)

because:

a. C–Cl bond has pure single bond character
b. C–Cl bond has partial double bond character due to resonance
c. Benzene ring repels nucleophiles mechanically
d. Chloride is not a leaving group here

Answer: b
Explanation: In chlorobenzene, lone pair on Cl participates in resonance with benzene ring, giving partial double bond character to C–Cl, shortening and strengthening the bond. Formation of unstable aryl cation and back-side attack are both disfavoured.

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34. Effect of β-hydrogen on elimination

Which halide will **not** undergo β-elimination (dehydrohalogenation) to form an alkene with alcoholic KOH?

a. CH_3CH_2Cl
b. CH_3Cl
c. $CH_3CH_2CH_2Br$
d. $CH_3CH_2CH_2CH_2Cl$

Answer: b
Explanation: β-elimination requires a β-hydrogen on carbon adjacent to C–X. In CH_3Cl there is no β-carbon, so no β-H available.

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35. Orientation of elimination (Saytzeff rule)

On heating 2-bromobutane with alcoholic KOH, the major product is:

a. 1-butene

b. cis-2-butene
c. trans-2-butene
d. Mixture of cis- and trans-2-butene with minor 1-butene

Answer: d
Explanation: Dehydrohalogenation of 2-bromobutane gives mainly 2-butene (both cis and trans), with trans slightly more stable, and minor 1-butene. This follows Saytzeff rule.

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36. Nucleophilicity vs leaving group ability of same species

Cl^- is a **better leaving group** than F^- but a **poorer nucleophile** than F^- in polar aprotic solvent because:

a. Cl^- is heavier
b. Cl^- is more basic
c. Cl^- is less basic but larger and more polarizable
d. F^- has no electrons for nucleophilic attack

Answer: c
Explanation: Leaving group ability increases as basicity decreases; Cl^- is weaker base than F^-, so better LG. In polar aprotic solvent, nucleophilicity parallels basicity, so F^- is better nucleophile.

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37. Solvent identification

Which of the following is **polar aprotic**?

a. CH_3OH
b. H_2O
c. CH_3COOH
d. Dimethyl sulfoxide (DMSO)

Answer: d
Explanation: DMSO has high dielectric constant but cannot donate H-bond (no O–H or N–H). It is polar aprotic.

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38. Mechanism favored by DMSO

For a primary alkyl bromide reacting with sodium ethoxide in DMSO, the major pathway is:

a. (S_N1)
b. (S_N2)
c. E1
d. Radical substitution

Answer: b
Explanation: Primary substrate + strong nucleophile/base + polar aprotic solvent strongly favour (S_N2).

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39. Competition of ambident nucleophile CN^- sites in protic vs aprotic solvent

For a primary alkyl bromide with CN^- as nucleophile, which combination primarily increases formation of nitrile (R–CN) over isonitrile (R–NC)?

a. Polar protic solvent + AgCN
b. Polar aprotic solvent + KCN
c. Non-polar solvent + AgCN
d. Any solvent + KCN

Answer: b
Explanation: We want free CN^- with C-end attack and (S_N2). KCN is ionic; polar aprotic solvent (DMSO, DMF) enhances nucleophilicity of C-end, so nitrile predominates.

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40. Identification of rate-determining step in (S_N1)

For hydrolysis of tert-butyl chloride in water, which step is rate determining?

a. Attack of water on carbocation
b. Proton transfer from oxonium ion to water
c. Ionization of C–Cl bond to give carbocation and Cl^-
d. Formation of hydrogen bond with solvent

Answer: c
Explanation: (S_N1) involves: (1) slow ionization of R–Cl → R^+ + Cl^- (rate-determining) and (2) fast nucleophilic attack by water followed by deprotonation. Rate depends only on substrate concentration.

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41. Nature of intermediate in Finkelstein reaction of 1-bromopropane with NaI/acetone

The key high-energy species in the transition state/intermediate of this reaction is:

a. Carbocation ($CH_3CH_2CH_2$^+)
b. Carbanion ($CH_3CH_2CH_2$^-)
c. Pentacoordinate carbon with partial bonds to Br and I
d. Free radical ($CH_3CH_2CH_2$cdot)

Answer: c
Explanation: Finkelstein proceeds via (S_N2). In the transition state, carbon is simultaneously partially bonded to Br (leaving) and I (entering), giving a **pentacoordinate, trigonal-bipyramidal-like**

arrangement.

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42. Stereochemical outcome of (S_N2) on chiral alkyl halide

When (R)-2-bromobutane undergoes (S_N2) with OH^- in acetone, the configuration of the product 2-butanol will be:

a. Retained (R) only
b. Inverted (S) only
c. Racemic mixture
d. Impossible to predict

Answer: b
Explanation: (S_N2) is a **single-step backside attack** leading to inversion of configuration (Walden inversion). Thus (R)-2-bromobutane → (S)-2-butanol.

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43. Stereochemical outcome of (S_N1) on chiral alkyl halide

The hydrolysis of optically active tert-butyl chloride in water gives tert-butyl alcohol that is:

a. Completely retained configuration
b. Completely inverted configuration
c. Racemic (optically inactive)
d. More of inverted than retained

Answer: c
Explanation: In (S_N1), planar carbocation is formed. Nucleophile can attack from either side with almost equal probability, giving **racemic mixture** (optically inactive) if no neighbouring group participation.

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44. Mechanism for reaction of allyl bromide with aqueous KOH at room temperature

Allyl bromide (CH_2=CH–CH_2Br) reacts with aqueous KOH mainly by:

a. (S_N1) because allyl carbocation is very stable
b. (S_N2) due to primary carbon and resonance-stabilized transition state
c. E2 elimination to give conjugated diene
d. Radical substitution

Answer: b
Explanation: Though allyl carbocation is stable, the substrate is primary and aqueous KOH provides strong nucleophile OH^-. Reaction proceeds fast by **(S_N2)** with additional stabilization of transition state by resonance.

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45. Comparative rate: benzyl bromide vs n-propyl bromide in (S_N2)

In reaction with CN^- in DMSO, which alkyl bromide reacts faster?

a. Benzyl bromide
b. n-Propyl bromide
c. Both equal
d. None reacts by (S_N2)

Answer: a
Explanation: Both are primary, but benzyl substrate's transition state is stabilized by **resonance with benzene ring** even in (S_N2) (partial positive character at benzylic carbon). So benzyl bromide is more reactive.

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46. Role of pyridine in reaction of alcohol with $SOCl_2$

Pyridine is used because it:

a. Acts only as nucleophile
b. Acts only as oxidizing agent
c. Absorbs HCl formed and drives reaction forward
d. Forms radicals

Answer: c
Explanation: Pyridine is a **base**. It reacts with HCl to form pyridinium chloride, removing HCl from medium, preventing reverse reaction and promoting SN2 substitution.

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47. Order of reactivity for (S_N1): benzylic, allylic, tertiary

Arrange the following chlorides in decreasing order of (S_N1) reactivity: benzyl chloride (I), tert-butyl chloride (II), allyl chloride (III).

a. I > II > III
b. II > I > III
c. II > III > I
d. I > III > II

Answer: a
Explanation: Stability of carbocation: **benzylic (resonance over aromatic ring) > tertiary (hyperconjugation) > allylic**. More stable carbocation → faster (S_N1).

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48. Solvent effect on Hunsdiecker reaction

Why is CCl_4 often used as solvent in Hunsdiecker reaction?

a. It is polar protic and stabilizes carbocation
b. It dissolves ionic silver salt strongly
c. It is non-polar and supports radical chain without participating
d. It donates hydrogen to radicals

Answer: c
Explanation: Hunsdiecker is a **radical** process. CCl_4 is inert, non-polar, and does not quench radicals or provide competing side reactions; it simply acts as a medium for homolysis of acyl hypobromite.

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49. Identification of best substrate for E1 elimination

Which substrate will favour E1 mechanism with weak base in ethanol?

a. 1-bromopropane
b. 2-bromopropane
c. tert-Butyl bromide
d. Benzyl bromide

Answer: c
Explanation: E1 requires stable carbocation and polar protic solvent with weak base. tert-Butyl bromide forms highly stable tertiary carbocation → E1 (and SN1) possible. Benzyl also stabilizes carbocation, but typical textbook emphasis for E1 is tertiary.

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50. Mechanism when 2-bromobutane is treated with aqueous KOH (moderate temp)

Major product and mechanism are:

a. 2-butanol via (S_N1)
b. 2-butanol via (S_N2)
c. 1-butene via E2
d. 2-butene via E2

Answer: a
Explanation: Secondary alkyl halide + aqueous (protic) solvent with weak base tends toward **(S_N1) substitution**. Some E1 occurs, but major product is 2-butanol.

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51. Effect of strong base and heat on 2-bromobutane in alcoholic KOH

Changing conditions to alcoholic KOH and high temperature gives mainly:

a. 2-butanol via (S_N1)
b. 2-butanol via (S_N2)
c. 2-butene via E2
d. 1-butene via E1

Answer: c
Explanation: Strong base (alkoxide) and heat shift competition toward **E2 elimination** giving more substituted 2-butene.

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52. Relative leaving group ability among sulfonate esters and halides

Which is the best leaving group?

a. Cl^-
b. Br^-
c. Tosylate (TsO^-, p-$CH_3C_6H_4SO_3^-$)
d. OH^-

Answer: c
Explanation: Tosylate anion is highly resonance-stabilized over aromatic ring and sulfonyl group, making it an excellent leaving group, even better than halides.

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53. Why are silver salts ($AgNO_3$) often used to test for (S_N1) reactivity of alkyl halides?

In ethanol-$AgNO_3$ solution, fast formation of precipitate indicates:

a. Direct reaction of Ag^+ with carbon
b. Formation of free halide ion by ionization ((S_N1))
c. (S_N2) mechanism
d. Radical chain

Answer: b
Explanation: In polar protic ethanol, alkyl halide ionizes slowly to give carbocation and halide ion. **Ag^+ combines with X^- forming AgX precipitate**, shifting equilibrium and giving visual indication of (S_N1) reactivity.

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54. Order of nucleophilicity in protic solvent: SH^-, OH^-, Br^-, N_3^-

In water, which is the correct decreasing order of nucleophilicity?

a. $SH^- > Br^- > N_3^- > OH^-$
b. $OH^- > SH^- > N_3^- > Br^-$
c. $SH^- > OH^- > N_3^- > Br^-$
d. $Br^- > SH^- > OH^- > N_3^-$

Answer: c
Explanation: In protic solvents, **soft, larger and more polarizable**

anions are better nucleophiles even if slightly weaker bases. SH^- (large, polarizable) > OH^-; N_3^- is delocalized (weaker base) but still better than halide Br^- here. Many books give SH^- > OH^- > N_3^- > Br^-.

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55. Effect of ring position on physical properties (given in text: para isomer highest mp)

Which statement best explains why p-dichlorobenzene has higher melting point than its o- and m-isomers?

a. It has strongest C–Cl bond
b. It has highest molecular weight
c. It is more symmetrical and packs better in crystal lattice
d. It undergoes (S_N1) faster

Answer: c
Explanation: Para isomer is more **symmetrical**, allowing efficient crystal packing and stronger lattice forces → higher melting point. This is a structural, not mechanistic, effect but comes directly from your text.

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56. Relative reactivity of allylic vs saturated halide towards radical substitution

Under radical bromination conditions (Br_2/hv), which reacts faster?

a. Propyl bromide
b. Allyl bromide
c. Both equal
d. Neither reacts

Answer: b
Explanation: Allylic radicals are resonance-stabilized, so

abstraction of allylic H is easier. Thus **allylic positions are more reactive** towards radical substitution.

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57. Mechanism for formation of vicinal dihalides from alkenes with X_2

Addition of Br_2 to ethene in CCl_4 giving 1,2-dibromoethane occurs via:

a. Simultaneous two-step radical chain
b. Carbocation intermediate and anti/ syn mixture
c. Cyclic bromonium ion intermediate leading to anti addition
d. Syn addition by concerted mechanism

Answer: c
Explanation: Electrophilic addition: Br_2 polarizes; Br^+ attacks alkene forming **cyclic bromonium ion**. Then Br^- attacks anti to ring, giving **anti addition** vicinal dibromide.

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58. Mechanism of addition of HX to alkene in absence of peroxide

The addition of HBr to propene (no peroxide) gives major product 2-bromopropane via:

a. Radical anti-Markovnikov addition
b. Ionic Markovnikov addition via carbocation
c. Concerted (S_N2)
d. Rearrangement-free pericyclic reaction

Answer: b
Explanation: In absence of peroxide, reaction proceeds by **ionic mechanism**: protonation of alkene to more stable secondary carbocation followed by Br^- attack (Markovnikov rule).

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59. Mechanism of addition of HBr to alkene in presence of benzoyl peroxide

When propene is treated with HBr in presence of benzoyl peroxide, the major product is 1-bromopropane because reaction proceeds via:

a. (S_N1)
b. Radical chain involving Br• (anti-Markovnikov)
c. (S_N2)
d. E2

Answer: b
Explanation: Peroxides generate radicals (RO•) which abstract H from HBr forming Br•. Br• adds to double bond giving more stable radical at less substituted carbon, followed by H• transfer from HBr. This gives **anti-Markovnikov** product 1-bromopropane.

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60. Reason anti-Markovnikov addition is observed with HBr only, not HCl or HI

Peroxide effect (Kharasch effect) is seen with HBr but not with HCl or HI because:

a. HCl and HI do not form radicals
b. Chain propagation steps for HCl and HI are energetically unfavourable
c. HBr is least polar
d. HCl and HI always prefer ionic mechanism

Answer: b
Explanation: For HCl, the step R• + HCl → RH + Cl• is strongly endothermic; for HI, I• + H–I → HI + I• is exothermic but the first

	step (RO• + HI → ROH + I•) is too slow and competing side reactions dominate. Only for HBr are both propagation steps sufficiently **exothermic** to sustain radical chain → peroxide effect observed.
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