Haloalkanes and Haloarenes

Class 12 Chemistry · 24 NEET MCQs with answers & explanations

Haloalkanes and Haloarenes covers nomenclature, preparation, properties and reactions of alkyl and aryl halides. NEET tests SN1 vs SN2 mechanisms, elimination reactions (E1/E2), nucleophilic substitution in aryl halides and the relative reactivity order. Reaction mechanism questions dominate.

Key Reactions & Mechanisms

Concept	Key Fact
SN2	Bimolecular; one step; backside attack; inversion; favoured by 1° halides + strong nucleophile
SN1	Unimolecular; two steps via carbocation; racemisation; favoured by 3° halides + polar protic solvent
E2 vs E1	E2: strong base, anti-periplanar; E1: via carbocation, weak base, 3° substrate
Wurtz reaction	2R−X + 2Na → R−R + 2NaX; gives higher alkane (even C only)
Grignard reagent	R−MgX + H_2O → R−H; reacts with CO_2, HCHO, RCHO, R_2CO
Aryl halide reactivity	Less reactive to nucleophilic substitution (resonance stabilisation of C−X bond)

Questions

Q1. The reactivity order of alkyl halides towards dehydrohalogenation is:

(A) R–F > R–Cl > R–Br > R–I
(B) R–I > R–Br > R–Cl > R–F
(C) R–I > R–Cl > R–Br > R–F
(D) R–F > R–I > R–Br > R–Cl

Q2. Which of the following halides contains a C(sp2)–X bond?

(A) Allyl chloride
(B) Benzyl chloride
(C) Vinyl chloride
(D) Ethyl chloride

Q3. Which reaction converts an alkyl bromide into an alkyl iodide using NaI in acetone?

(A) Fittig reaction
(B) Finkelstein reaction
(C) Swarts reaction
(D) Wurtz reaction

Q4. Which reagent converts a primary alcohol to alkyl chloride with SO_2 and HCl as by-products?

(A) $SOCl_2$
(B) PCl_3
(C) PCl_5
(D) $HCl/ZnCl_2$

Q5. Which of the following is a primary haloalkane?

(A) CH_3CH_2Cl
(B) $CH_3CHClCH_3$
(C) $(CH_3)_3CCl$
(D) C_6H_5Cl

Q6. Which of the following correctly describes the C–X bond in haloalkanes?

(A) Polar covalent bond
(B) Polar ionic bond
(C) Non-polar covalent bond
(D) Pure covalent bond

Q7. Which of the following has the highest boiling point?

(A) $CH_3CH_2CH_2Cl$
(B) $CH_3CH_2CH_2F$
(C) $CH_3CH_2CH_3$
(D) CH_3OCH_3

Q8. Which method is used to prepare chlorobenzene by direct ring halogenation?

(A) Cl_2 + $FeCl_3$ (Lewis acid catalyst)
(B) Friedel-Crafts alkylation with RCl
(C) Sulphonation with $ClSO_3H$
(D) Nitration then reduction

Q9. Which type of reaction involves replacement of halogen by an OH^- nucleophile?

(A) Nucleophilic substitution (SN)
(B) Electrophilic substitution (SE)
(C) Free radical substitution (SR)
(D) Nucleophilic elimination (E2)

Q10. Chloroform is prepared in the laboratory by the action of bleaching powder on which compound?

(A) Methanol
(B) Ethanol
(C) Methanal
(D) Ethane

Q11. Polar protic solvents (e.g., water, ethanol) favour SN1 over SN2. Which is the most accurate mechanistic explanation?

(A) They donate protons to the nucleophile, increasing its reactivity
(B) They increase substrate concentration by dissolving it
(C) They stabilize both the developing carbocation and the leaving group anion through hydrogen bonding and ion solvation, facilitating ionization
(D) They prevent elimination by hydrogen bonding with the beta hydrogen

Q12. Which of the following haloarenes undergoes SNAr fastest with NaOH, and why?

(A) Chlorobenzene — smallest halogen, least steric hindrance
(B) 2,4-Dinitrochlorobenzene — two nitro groups at ortho and para maximally stabilize the Meisenheimer complex
(C) p-Chlorotoluene — methyl group activates ring by hyperconjugation
(D) o-Chloroanisole — methoxy group donates electrons facilitating attack

Q13. Which type of reaction is most characteristic of haloarenes?

(A) Electrophilic aromatic substitution
(B) Nucleophilic substitution (SN2)
(C) Nucleophilic addition to ring
(D) Elimination to give benzyne

Q14. Which of the following is correctly identified as an allylic halide?

(A) $CH_2=CHCl$
(B) $CH_2=CHCH_2Cl$
(C) $C_6H_5CH_2Cl$
(D) $CH_3CH_2CH_2Cl$

Q15. Which of the following best explains why benzyl chloride undergoes SN1 reactions more readily than ethyl chloride?

(A) Benzyl carbocation is stabilised by resonance with the ring
(B) Benzyl C–Cl bond is weaker due to induction
(C) Benzyl chloride has lower molecular mass
(D) Ethyl carbocation is a primary carbocation

Q16. Which of the following is a vinylic halide?

(A) CH_3CH_2Cl
(B) C_6H_5Cl
(C) $CH_2=CHCH_2Cl$
(D) $CH_2=CHCl$

Q17. Which of the following pairs is correctly matched?

(A) Allylic halide — halogen on sp^2 carbon of C=C
(B) Vinylic halide — halogen on carbon next to C=C
(C) Benzylic halide — halogen on carbon next to benzene ring
(D) Aryl halide — halogen on sp^3 carbon of ring

Q18. The correct IUPAC name of $CH_3CHClCH_3$ is:

(A) 1-chloropropane
(B) 2-chloropropane
(C) 3-chloropropane
(D) Propyl chloride

Q19. Which of the following correctly describes aryl halides?

(A) Halogen is on sp^3 carbon of benzene ring
(B) Halogen is directly bonded to sp^2 carbon of benzene ring
(C) Halogen is on carbon adjacent to benzene ring
(D) Halogen is bonded to the π system, not carbon

Q20. Which of the following is a tertiary haloalkane?

(A) CH_3CH_2Cl
(B) $CH_3CHClCH_3$
(C) $CH_2ClCH_2CH_3$
(D) $(CH_3)_3CCl$

Q21. Which of the following is a benzyl halide?

(A) $C_6H_5CH_2Cl$
(B) C_6H_5Cl
(C) $CH_2=CHCl$
(D) CH_3CH_2Cl

Q22. Which of the following is correctly classified as an aralkyl halide?

(A) C_6H_5Cl
(B) $C_6H_5CH_2Cl$
(C) CH_3Cl
(D) $C_6H_5CH=CHCl$

Q23. Which of the following correctly explains why primary haloalkanes are least sterically hindered among 1°, 2°, and 3° haloalkanes?

(A) They have the highest C–X bond polarity
(B) They form the most stable carbocation
(C) Only one alkyl group is bonded to the carbon bearing the halogen
(D) They have lower molecular mass than 2° and 3° alkyl halides

Q24. The correct common name of CH_3Cl is:

(A) Methane chloride
(B) Monochloro methane
(C) Carbon monochloride
(D) Methyl chloride

Answer key

1-B	**2-C**	**3-B**	**4-A**	**5-A**	**6-A**	**7-A**	**8-A**
9-A	**10-B**	**11-C**	**12-B**	**13-A**	**14-B**	**15-A**	**16-D**
17-C	**18-B**	**19-B**	**20-D**	**21-A**	**22-B**	**23-C**	**24-D**

Answers with explanations

Q1 — Answer: (B) R–I > R–Br > R–Cl > R–F
The key factor is the leaving-group ability during C–X bond cleavage. C–I is the weakest bond and I^- is the best leaving group, whereas C–F is the strongest bond. Therefore dehydrohalogenation reactivity follows R–I > R–Br > R–Cl > R–F.

Q2 — Answer: (C) Vinyl chloride
In vinyl chloride, chlorine is directly attached to an sp2-hybridised carbon of the C=C double bond. Allyl and benzyl chlorides have halogen on an sp3 carbon; ethyl chloride is a simple primary haloalkane with sp3 carbon.

Q3 — Answer: (B) Finkelstein reaction
Finkelstein reaction is a halide-exchange reaction using NaI in dry acetone. NaBr (or NaCl) precipitates out of acetone, driving the equilibrium forward to give the alkyl iodide.

Q4 — Answer: (A) $SOCl_2$
Thionyl chloride ($SOCl_2$) reacts with alcohols to give alkyl chlorides; by-products SO_2 and HCl are gases that escape, driving the reaction to completion. PCl_5 also gives alkyl chloride but produces $POCl_3$ (liquid) as by-product, making purification harder. $SOCl_2$ is the preferred reagent precisely because of its gaseous by-products.

Q5 — Answer: (A) CH_3CH_2Cl
In CH_3CH_2Cl, the carbon bearing Cl is bonded to only one other carbon, making it primary. $CH_3CHClCH_3$ is secondary (two C neighbours) and $(CH_3)_3CCl$ is tertiary (three C neighbours). C_6H_5Cl is an aryl halide, not a haloalkane at all.

Q6 — Answer: (A) Polar covalent bond
The C–X bond involves unequal sharing of electrons due to the higher electronegativity of halogen compared to carbon, making it polar covalent — not ionic (no complete electron transfer). A pure or non-polar covalent bond would require equal electronegativities, which is never the case for C–X.

Q7 — Answer: (A) $CH_3CH_2CH_2Cl$
$CH_3CH_2CH_2Cl$ has a higher molecular mass and stronger van der Waals + dipole–dipole forces than the corresponding alkane (propane) or ether (dimethyl ether). $CH_3CH_2CH_2F$ is the key trap — same carbon chain but fluorine's weaker polarisability gives it lower dispersion forces than the chloro compound despite higher C–X polarity.

Q8 — Answer: (A) Cl_2 + $FeCl_3$ (Lewis acid catalyst)
Benzene reacts with Cl_2 in the presence of $FeCl_3$ (Lewis acid) via electrophilic aromatic substitution — $FeCl_3$ activates Cl_2 by forming Cl^+ (electrophile). Friedel-Crafts alkylation introduces alkyl groups, not halogen. Sulphonation introduces $–SO_3H$, not –Cl.

Q9 — Answer: (A) Nucleophilic substitution (SN)
OH^- is a nucleophile — it attacks the electrophilic carbon bearing the halogen, displacing X^- via nucleophilic substitution. Electrophilic substitution involves attack by an electrophile on an electron-rich centre (e.g., benzene ring). Free radical substitution involves radical intermediates, not ionic nucleophiles.

Q10 — Answer: (B) Ethanol
In the laboratory, chloroform is made by warming ethanol with bleaching powder. Bleaching powder supplies chlorine, which oxidises ethanol to acetaldehyde, chlorinates it to chloral (CCl_3CHO), and the $Ca(OH)_2$ present then hydrolyses chloral to $CHCl_3$ (haloform reaction). Methanol, methanal and ethane cannot give a $CH_3CO–$ unit, so they do not form chloroform this way.

Q11 — Answer: (C) They stabilize both the developing carbocation and the leaving group anion through hydrogen bonding and ion solvation, facilitating ionization
Polar protic solvents stabilize the transition state of ionization via solvation of both ionic fragments — cation (by lone pairs) and anion (by H-bonding). Option D is a trap — H-bonding with β-H would actually reduce E2, not explain SN1 preference.

Q12 — Answer: (B) 2,4-Dinitrochlorobenzene — two nitro groups at ortho and para maximally stabilize the Meisenheimer complex
2,4-Dinitrochlorobenzene is the classic benchmark SNAr substrate: two EWGs at ortho and para positions both stabilize the Meisenheimer complex by resonance. Option C is the trap — methyl (EDG) actually deactivates the ring for SNAr. Option D (methoxy) is an EDG, also deactivating.

Q13 — Answer: (A) Electrophilic aromatic substitution
The benzene ring is electron-rich and readily attacked by electrophiles; EAS is the dominant reaction class for haloarenes. Nucleophilic substitution at the aryl carbon is extremely difficult unless strongly activating groups (e.g., $–NO_2$ at ortho/para) are present. Addition to the aromatic ring is disfavoured as it would destroy the delocalisation energy.

Q14 — Answer: (B) $CH_2=CHCH_2Cl$
An allylic halide has the halogen on a carbon adjacent to (not part of) a C=C double bond; $CH_2=CHCH_2Cl$ fits this exactly. $CH_2=CHCl$ is vinylic (halogen on the double bond carbon). $C_6H_5CH_2Cl$ is benzylic. $CH_3CH_2CH_2Cl$ is a simple primary alkyl halide.

Q15 — Answer: (A) Benzyl carbocation is stabilised by resonance with the ring
On ionisation, the benzyl carbocation delocalises positive charge over the ring via resonance, lowering activation energy for SN1. Ethyl chloride also gives a primary carbocation but without any resonance stabilisation. Bond polarity and molecular mass are irrelevant to SN1 rate here.

Q16 — Answer: (D) CH_2=CHCl
A vinylic halide has the halogen directly on a sp² carbon of a C=C double bond; CH_2=CHCl is the only such compound here. C_6H_5Cl is an aryl halide (halogen on aromatic sp² carbon, a common trap). CH_2=$CHCH_2Cl$ is allylic, not vinylic.

Q17 — Answer: (C) Benzylic halide — halogen on carbon next to benzene ring
A benzylic halide (e.g., $C_6H_5CH_2Cl$) has halogen on the –CH_2– carbon adjacent to the ring, not on the ring itself. Allylic halogen is adjacent to, not on, the double bond (eliminating A). Vinylic is on the C=C carbon, not adjacent (eliminating B). Aryl halide carbon is sp², not sp³ (eliminating D).

Q18 — Answer: (B) 2-chloropropane
The longest chain has 3 carbons (propane); halogen is on C2 giving the lowest possible locant, so the name is 2-chloropropane. 1-chloropropane would place the halogen on the terminal carbon (that is $CH_3CH_2CH_2Cl$, a different compound). Propyl chloride is the common name, not IUPAC.

Q19 — Answer: (B) Halogen is directly bonded to sp² carbon of benzene ring
In aryl halides like C_6H_5Cl, the halogen is directly bonded to a ring carbon that is sp² hybridised. Option A is wrong because ring carbons are sp², not sp³. Option C describes benzylic halides. The halogen is bonded to a specific carbon, not the π system.

Q20 — Answer: (D) $(CH_3)_3CCl$
In $(CH_3)_3CCl$, the carbon bearing Cl is bonded to three other carbons — the definition of tertiary. $CH_3CHClCH_3$ is secondary (two C neighbours). $CH_2ClCH_2CH_3$ is primary (one C neighbour, a strong trap due to the three-carbon chain). CH_3CH_2Cl is also primary.

Q21 — Answer: (A) $C_6H_5CH_2Cl$
A benzyl halide has the halogen on the –CH_2– group directly attached to a benzene ring. C_6H_5Cl is an aryl halide (halogen on the ring itself), which is the key trap. CH_2=CHCl is vinylic and CH_3CH_2Cl is a simple primary alkyl halide.

Q22 — Answer: (B) $C_6H_5CH_2Cl$
Aralkyl (arene + alkyl) halides have the halogen on an alkyl side chain attached to an aromatic ring; $C_6H_5CH_2Cl$ fits this exactly. C_6H_5Cl is an aryl halide (halogen on ring, not side chain). C_6H_5CH=CHCl is a vinylic-type halide on a side chain, not a saturated aralkyl halide.

Q23 — Answer: (C) Only one alkyl group is bonded to the carbon bearing the halogen
Steric hindrance around the reaction site increases with the number of alkyl groups on the carbon bearing the halogen. A primary carbon has only one such alkyl group, leaving the carbon most accessible to nucleophiles or bases. Bond polarity and carbocation stability are unrelated to steric bulk.

Q24 — Answer: (D) Methyl chloride
In common nomenclature, alkyl halides are named as alkyl group + halide; the methyl group (CH_3–) + chloride gives methyl chloride. "Methane chloride" mimics IUPAC logic incorrectly. "Monochloro methane" confuses substitutive nomenclature. "Carbon monochloride" is a completely incorrect trivial name.

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