

CLASS 12

CHEMISTRY

EXTRA QUESTIONS

Class 12 Chemistry Chapter 6 Haloalkanes and Haloarenes – Extra Questions with Answers

These extra practice questions for Class 12 Chemistry Chapter 6 – Haloalkanes and Haloarenes go beyond the NCERT textbook exercises to reinforce nomenclature, substitution mechanisms, and the reactivity of haloalkanes versus haloarenes. Useful for board exam revision and quick concept checks.

Contents

Very Short Answer Type Questions (1 Mark)

Short Answer Type Questions (2–3 Marks)

Higher Order Thinking Skills (HOTS)

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Very Short Answer Type Questions (1 Mark)

Q1. Why is the C–Cl bond in chlorobenzene shorter than the C–Cl bond in an alkyl chloride?

Ans: In chlorobenzene, resonance delocalises a chlorine lone pair into the ring, giving the C–Cl bond partial double-bond character, which shortens and strengthens it compared to the pure single bond in an alkyl chloride.

Q2. Name the reaction used to convert an alkyl chloride into the corresponding alkyl iodide using sodium iodide in dry acetone.

Ans: The **Finkelstein reaction**.

Q3. Which is a better nucleophile in the S_N2 reaction: I^- or F^- , and why?

Ans: I^- — being large and highly polarisable, it is a better nucleophile (and also a much better leaving group) than the small, poorly polarisable F^- .

Q4. What is Walden inversion?

Ans: The inversion of spatial configuration at a stereocentre that occurs during an S_N2 reaction, as the incoming nucleophile attacks from the side directly opposite the leaving group.

Short Answer Type Questions (2–3 Marks)

Q5. Explain why $(CH_3)_3CBr$ reacts with aqueous NaOH mainly by the S_N1 mechanism, while CH_3Br reacts mainly by S_N2 .

Ans: $(CH_3)_3CBr$ is a **tertiary** halide, so ionisation gives a relatively **stable tertiary carbocation** (stabilised by hyperconjugation/inductive donation from three methyl groups), favouring the two-step S_N1 pathway; it is also too sterically hindered for backside S_N2 attack. CH_3Br has **no alkyl substituents to stabilise a carbocation** and no steric hindrance to backside attack, so it reacts by the concerted, single-step S_N2 mechanism instead.

Q6. Why does S_N1 hydrolysis of an optically active alkyl halide generally give a racemic (or largely racemised) product?

Ans: The rate-determining step forms a **planar, sp^2 -hybridised carbocation intermediate**, which has lost the original tetrahedral stereocentre. The incoming nucleophile can then attack this planar cation from either face with roughly equal probability, so the product is obtained as a nearly 1:1 mixture of both configurations, i.e. a racemic mixture (in practice, slightly more inversion than retention is often seen due to ion-pairing/shielding effects on one face by the departing group).

Q7. Arrange in decreasing order of boiling point and explain: n-butyl chloride, n-butyl bromide, n-butyl iodide, n-butyl fluoride.

Ans: **n-Butyl iodide > n-butyl bromide > n-butyl chloride > n-butyl fluoride**. Boiling point increases with the mass and polarisability of the halogen atom, since heavier, more polarisable halogens strengthen the van der Waals (London dispersion) forces between molecules.

Higher Order Thinking Skills (HOTS)

Q8. Two secondary alkyl halides, 2-bromobutane and 2-bromo-1,1,1-trifluorobutane (with a $-CF_3$ group replacing the terminal $-CH_3$), are compared for S_N1 reactivity. Predict which reacts faster,

and explain in terms of the intermediate formed.

Ans: **2-Bromobutane reacts faster** by the S_N1 pathway. Ionisation of either substrate forms a secondary carbocation at C2, but in the trifluoro compound the strongly **electron-withdrawing $-CF_3$ group inductively pulls electron density away** from the developing positive charge on the adjacent carbon, destabilising the carbocation intermediate significantly. Since S_N1 rate depends directly on carbocation stability, the electron-withdrawing fluorines make ionisation much less favourable, so 2-bromobutane (with only electron-donating alkyl/hyperconjugative stabilisation and no such destabilising group) ionises, and reacts, considerably faster.

Q9. Chlorobenzene undergoes electrophilic substitution to give predominantly ortho and para products, even though chlorine is deactivating overall. Reconcile these two facts using resonance and inductive effects.

Ans: Chlorine exerts two opposing effects on the ring: a strong **$-I$ (inductive) effect**, which withdraws electron density through the sigma-bond framework and deactivates the ring overall (making chlorobenzene less reactive than benzene towards electrophiles); and a **$+M$ (resonance/mesomeric) effect**, in which one of chlorine's lone pairs is donated into the ring's π -system, which specifically increases electron density at the **ortho and para positions** (via the resonance structures placing negative charge there). Because the $+M$ effect governs the directing behaviour (where substitution occurs) while the $-I$ effect governs the overall rate (how reactive the ring is), the two effects are not contradictory: chlorine slows the reaction down overall (net deactivator) while still directing whatever substitution does occur to the ortho/para positions.

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