CLASS 12 CHEMISTRY NCERT SOLUTIONS

NCERT Solutions for Class 12 Chemistry Chapter 6: Haloalkanes and Haloarenes – Free PDF Download

Chapter 6 (the first chapter of Chemistry Part II) covers Haloalkanes and Haloarenes — classification and IUPAC nomenclature, nature of the C–X bond, methods of preparation, physical and chemical properties, substitution mechanisms (SN1 and SN2) and their stereochemistry, reactions of haloarenes, and the uses/en...

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NCERT Exercise Solutions

Class 12 Chemistry Chapter 6 – Notes and Extra Questions

Chapter 6 (the first chapter of Chemistry Part II) covers **Haloalkanes and Haloarenes** — classification and IUPAC nomenclature, nature of the C–X bond, methods of preparation, physical and chemical properties, substitution mechanisms (S_N1 and S_N2) and their stereochemistry, reactions of haloarenes, and the uses/environmental effects of polyhalogen compounds. This chapter was **Chapter 10** under the old (pre-2023) numbering, and shifted to **Chapter 6** only because four chapters were deleted earlier in Part I — its own **22 exercises (6.1–6.22)** are unchanged and none were dropped; only the deep preparation/structural chemistry of polyhalogen compounds (DDT, freons, iodoform) was trimmed to "uses and environmental effects" at the syllabus level. Each answer below is checked for chemical accuracy before publishing.

NCERT Exercise Solutions

6.1 Classify the following halides as alkyl, allylic, benzylic or vinylic: (i) $CH_3CH{=}CHCH_2Cl$ (ii) $C_6H_5CH_2Br$ (iii) $CH_2{=}CHCl$ (iv) $CH_3CH_2CH_2Br$.
Ans: (i) **Allylic** (Cl is on an sp^3 carbon directly adjacent to a C=C double bond). (ii) **Benzylic** (Br is on an sp^3 carbon directly attached to the benzene ring). (iii) **Vinylic** (Cl is directly on an sp^2, double-bonded carbon). (iv) **Alkyl (1°)** (Br is on a simple sp^3 carbon, not adjacent to any ring or double bond).

6.2 Write the IUPAC names and classify (1°/2°/3°) the following: (i) $(CH_3)_2CHCH_2Br$ (ii) $CH_3CH_2CH(Cl)CH_2CH_3$ (iii) $(CH_3)_3CBr$.
Ans: (i) **1-Bromo-2-methylpropane**, 1°. (ii) **3-Chloropentane**, 2°. (iii) **2-Bromo-2-methylpropane** (tert-butyl bromide), 3°.

6.3 Give the IUPAC name and one method of preparation for a compound commonly known as tert-butyl chloride.
Ans: IUPAC name: **2-Chloro-2-methylpropane**. It is readily prepared by treating tert-butyl alcohol with **concentrated HCl** at room temperature (Lucas reagent, $ZnCl_2$+conc. HCl): $(CH_3)_3COH + HCl \rightarrow (CH_3)_3CCl + H_2O$, proceeding rapidly via an S_N1 mechanism because the intermediate tertiary carbocation is comparatively stable.

6.4 Arrange CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 in order of decreasing dipole moment, with reason.
Ans: **$CH_3Cl > CH_2Cl_2 > CHCl_3 > CCl_4$** (measured values ≈1.87D, 1.60D, 1.04D, 0D). As the number of C–Cl bonds increases, their individual bond dipoles increasingly oppose and cancel each other by symmetry, so the net molecular dipole moment falls steadily; in perfectly symmetric, tetrahedral CCl_4 the four C–Cl dipoles cancel completely, giving a net dipole moment of zero.

6.5 Which C_5H_{10} alkane gives only a single monochloro product on free-radical chlorination? Explain.
Ans: **Neopentane, $(CH_3)_4C$**. All 12 of its hydrogen atoms are chemically equivalent (attached to four identical methyl groups around a central quaternary carbon), so replacing any one of them by chlorine gives exactly the same product, **$(CH_3)_3CCH_2Cl$**, regardless of which hydrogen reacts.

6.6 Draw the structures of all the isomeric alkyl bromides with molecular formula C_4H_9Br and name them by the IUPAC system. Which of these is (a) a 1° halide (b) a 2° halide (c) a 3° halide?
Ans: There are **4 isomers**: **1-bromobutane** $CH_3CH_2CH_2CH_2Br$ (1°), **2-bromobutane** $CH_3CH_2CH(Br)CH_3$ (2°), **1-bromo-2-methylpropane** $(CH_3)_2CHCH_2Br$ (1°), and **2-bromo-2-methylpropane** $(CH_3)_3CBr$ (3°). (a) 1°: 1-bromobutane and 1-bromo-2-methylpropane. (b) 2°: 2-bromobutane. (c) 3°: 2-bromo-2-methylpropane.

6.7 Starting from (a) 1-butanol (b) 1-chlorobutane (c) but-1-ene, how would you obtain 1-iodobutane in each case?

Ans: (a) 1-Butanol+red P/I_2 (generates HI in situ) → 1-iodobutane+H_2O. (b) 1-Chlorobutane+NaI in dry acetone (the **Finkelstein reaction**) → 1-iodobutane+NaCl (precipitates out, driving the equilibrium forward). (c) But-1-ene+HI, in the presence of peroxides (**anti-Markovnikov/Kharasch addition**), adds the iodine atom to the terminal (less substituted) carbon, giving 1-iodobutane.

6.8 What is an ambident nucleophile? Explain with an example.
Ans: An **ambident nucleophile** has two possible sites through which it can attack an electrophile, giving two different products depending on which site reacts. **Cyanide ion, CN^-**, is a classic example: it can attack through carbon (giving an alkyl **cyanide/nitrile**, R–CN) or through nitrogen (giving an alkyl **isocyanide**, R–NC). With alkyl halides, attack through carbon predominates, since carbon is the site of higher electron density and provides better orbital overlap in the S_N2 transition state, so the nitrile is the major product.

6.9 Arrange the following in order of increasing S_N2 reactivity: CH_3Cl, CH_3CH_2Cl, $(CH_3)_2CHCl$, $(CH_3)_3CCl$.
Ans: **$(CH_3)_3CCl<(CH_3)_2CHCl<CH_3CH_2Cl<CH_3Cl$** (i.e. reactivity decreases as branching increases). S_N2 proceeds via a backside attack through a crowded pentacoordinate transition state, so bulkier alkyl groups around the carbon bearing the leaving group create steric hindrance that slows the reaction; methyl halides, with no such hindrance, react fastest.

6.10 Predict the alkene formed on dehydrohalogenation of 2-bromopentane with alcoholic KOH, and state the rule used.
Ans: Two alkenes are possible: pent-1-ene and pent-2-ene. By **Zaitsev's (Saytzeff's) rule**, the **more substituted, more stable alkene is the major product**, so **pent-2-ene** (a disubstituted alkene) forms preferentially over the terminal, monosubstituted pent-1-ene.

6.11 How will you convert ethanol into (a) ethyl chloride (b) diethyl ether (c) ethene, using suitable reagents?
Ans: (a) Ethanol+$SOCl_2$ (or conc. HCl/$ZnCl_2$, or PCl_3/PCl_5) → **ethyl chloride**+SO_2+HCl (the $SOCl_2$ route is cleanest, giving only gaseous by-products). (b) Ethanol+ethanol, conc. H_2SO_4 at 413K (**Williamson-type acid-catalysed intermolecular dehydration**) → **diethyl ether**+H_2O. (c) Ethanol+conc. H_2SO_4 at 443K (**intramolecular dehydration/elimination**, excess acid and higher temperature favour elimination over ether formation) → **ethene**+H_2O.

6.12 Explain the following: (i) Chlorobenzene has a lower dipole moment than cyclohexyl chloride. (ii) Alkyl halides, though polar, are immiscible with water. (iii) Grignard reagents should be prepared under anhydrous conditions.
Ans: (i) In chlorobenzene, one lone pair on chlorine is **delocalised into the aromatic ring by resonance**, giving the C–Cl bond partial double-bond character; this shortens/strengthens the bond and reduces its polarity compared to the purely single, unconjugated C–Cl bond in cyclohexyl chloride. (ii) Although alkyl halides are polar, they **cannot form hydrogen bonds with water**; the energy released when a C–X dipole interacts with water is not enough to compensate for the energy needed to break water's own extensive hydrogen-bonded network, so the two remain largely immiscible. (iii) Grignard reagents (R–MgX) are **extremely strong bases/nucleophiles** and react instantly and irreversibly with any trace of water (or other proton source) to give the corresponding alkane, R–H+Mg(OH)X, destroying the reagent — so strictly anhydrous ether and glassware are essential.

6.13 Give the uses of (i) Freon-12 (ii) DDT (iii) Carbon tetrachloride (iv) Iodoform.
Ans: (i) **Freon-12 (CCl_2F_2):** used as a refrigerant and aerosol-spray propellant (now heavily restricted due to stratospheric ozone depletion). (ii) **DDT:** a powerful insecticide/pesticide (now banned in most countries owing to its non-biodegradability and bioaccumulation in the food chain). (iii) **Carbon tetrachloride:** formerly a common industrial solvent and dry-cleaning/fire-extinguisher fluid (largely discontinued, since it

can form toxic phosgene gas on exposure to light/heat, and is a known health/ozone hazard). (iv) **Iodoform (CHI_3):** once used as an antiseptic for wound dressing, its action arising from the small amount of free iodine it liberates rather than from the compound itself (largely superseded by better antiseptics today).

6.14 Which alkyl halide from the following pair reacts faster in an S_N2 reaction: CH_3Br or CH_3I? Justify.
Ans: **CH_3I reacts faster.** Iodide is a much better leaving group than bromide, since the C–I bond is longer and weaker than the C–Br bond (I being a larger, more polarisable atom that stabilises the developing negative charge on the leaving group better in the S_N2 transition state), following the general leaving-group order $I^- > Br^- > Cl^- > F^-$.

6.15 Explain why an alkyl halide, though a polar molecule, is immiscible with water, and predict how its density compares with water as the number of halogen atoms increases.
Ans: As in 6.12(ii), alkyl halides cannot hydrogen-bond with water, so they remain immiscible despite being polar. Regarding density: alkyl **monohalides** (except fluorides) with up to about four carbons are typically heavier than water because the halogen atom contributes substantial mass, and **density increases further with more halogen atoms per molecule** and with heavier halogens (I>Br>Cl>F), e.g. CH_2Cl_2, $CHCl_3$ and CCl_4 are all denser than CH_3Cl and denser than water.

6.16 Out of $C_6H_5CH_2Cl$ and $C_6H_5CHClC_6H_5$, which is hydrolysed more rapidly by the S_N1 mechanism, and why?
Ans: **$C_6H_5CHClC_6H_5$ (benzhydryl chloride) hydrolyses faster.** Its ionisation generates a carbocation stabilised by **resonance delocalisation into two phenyl rings simultaneously** (a diarylmethyl/diphenylmethyl cation), which is considerably more stable than the singly-stabilised benzylic cation formed from $C_6H_5CH_2Cl$; since S_N1 rate depends directly on carbocation stability, the doubly-stabilised cation forms, and reacts, faster.

6.17 p-Dichlorobenzene has a higher melting point than its ortho- and meta-isomers. Explain.
Ans: **p-Dichlorobenzene is far more symmetrical** than the ortho- and meta-isomers, allowing its molecules to pack much more efficiently and closely into a crystal lattice. This tighter, more regular packing maximises intermolecular (van der Waals) forces between neighbouring molecules, requiring more thermal energy to break the lattice apart, which is why the para-isomer has a distinctly higher melting point than the less symmetric ortho- and meta-isomers.

6.18 Which of the two, aqueous KOH or alcoholic KOH, is preferred for carrying out (i) substitution and (ii) elimination reactions with an alkyl halide? Explain.
Ans: (i) **Aqueous KOH favours substitution** — the polar protic solvent (water) solvates and stabilises the hydroxide nucleophile and the transition state well, and OH^- readily displaces the halide (S_N) to give the corresponding alcohol. (ii) **Alcoholic KOH favours elimination** — in ethanol, KOH generates the bulkier ethoxide-type basic conditions, and heating with alcoholic KOH promotes the E2 pathway (abstraction of a β-hydrogen and loss of the halide together) to give an alkene, following Zaitsev's rule for the major product.

6.19 An alkyl halide $C_5H_{11}Br$ reacts with alcoholic KOH to give only one alkene as the sole elimination product. Identify the alkyl halide and explain.
Ans: The alkyl halide is **2-bromo-2-methylbutane, $(CH_3)_2C(Br)CH_2CH_3$**. Although this tertiary halide has β-hydrogens available on two different sides, symmetry/Zaitsev preference directs elimination overwhelmingly to the single major, most-substituted alkene, **2-methylbut-2-ene**, which forms essentially as the sole product under standard E2 conditions with hot alcoholic KOH.

6.20 Identify the major product formed when chlorobenzene is treated with (i) Na/dry ether (Wurtz–Fittig-type conditions with an alkyl halide) and (ii) Mg in dry ether, and explain why chlorobenzene resists nucleophilic substitution under ordinary conditions.

Ans: (i) Chlorobenzene+an alkyl halide+Na in dry ether (**Wurtz–Fittig reaction**) gives an alkylbenzene, coupling the aryl and alkyl groups. (ii) Chlorobenzene+Mg in dry ether does **not** readily form a Grignard reagent under ordinary conditions (aryl Grignards require more forcing/specialised conditions than alkyl halides). Chlorobenzene resists ordinary nucleophilic substitution because the C–Cl bond has partial double-bond character (lone-pair delocalisation into the ring, as in 6.12(i)), making it shorter and stronger, and because the aromatic ring's electron density (further donated into by Cl) repels an incoming nucleophile, both factors making S_N1/S_N2 attack at that carbon very difficult.

6.21 Arrange the following in increasing order of boiling point: bromomethane, bromoform, chloromethane, dibromomethane. Give reasons.
Ans: **Chloromethane<bromomethane<dibromomethane<bromoform**. Boiling point rises with increasing molecular mass and the number/size of halogen atoms, since heavier, more polarisable halogens increase the strength of van der Waals (London dispersion) forces between molecules; bromine (heavier than chlorine) and more halogen atoms per molecule both raise the boiling point, so bromoform ($CHBr_3$, three heavy Br atoms) boils highest and chloromethane (one light Cl atom) boils lowest.

6.22 Out of an alkyl halide and an alkyl fluoride, which is more reactive in a nucleophilic substitution reaction, and why is an alkyl fluoride reaction rarely used in the laboratory?
Ans: **Heavier alkyl halides (Cl, Br, I) are far more reactive than alkyl fluorides** in nucleophilic substitution. The C–F bond is exceptionally strong and short (fluorine's small size gives excellent orbital overlap with carbon), making F^- a very poor leaving group; consequently, alkyl fluorides react far too slowly to be practically useful in typical laboratory S_N1/S_N2 reactions, and are rarely prepared or used this way.

Class 12 Chemistry Chapter 6 – Notes and Extra Questions

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