Class 12 Chemistry · Chapter 6: Haloalkanes and Haloarenes

Answer key and marking scheme · 20 marks · about 40 minutes · based on NCERT

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1. Butan-1-ol is converted to 1-chlorobutane by thionyl chloride. The method is preferred because the by-products are [1]

(a) H_3PO_3 and HCl
(b) $POCl_3$ and HCl
(c) SO_2 and HCl, both gases
(d) H_2O alone

Answer: (c) $R{-}OH + SOCl_2 \rightarrow R{-}Cl + SO_2 + HCl$. Both by-products are gases that escape, leaving the alkyl chloride pure. H_3PO_3 comes from PCl_3, $POCl_3$ from PCl_5.

2. How many structurally different monochloro products can form when 2,3-dimethylbutane, $(CH_3)_2CH{-}CH(CH_3)_2$, undergoes free radical chlorination? [1]

(a) 1
(b) 2
(c) 3
(d) 4

Answer: (b) The molecule is symmetrical: all twelve CH_3 hydrogens are equivalent and the two CH hydrogens are equivalent. Two types of hydrogen give two monochlorides: $ClCH_2CH(CH_3)CH(CH_3)_2$ and $(CH_3)_2CClCH(CH_3)_2$.

3. 1-Methylcyclohexene reacts with HCl. The main product is [1]

(a) 1-chloro-1-methylcyclohexane
(b) 1-chloro-2-methylcyclohexane
(c) chloromethylcyclohexane
(d) 1,2-dichloro-1-methylcyclohexane

Answer: (a) By Markovnikov's rule H adds to the ring CH of the double bond (the carbon with more hydrogens) and Cl to the carbon carrying the methyl group, giving the tertiary chloride 1-chloro-1-methylcyclohexane. (d) would need Cl_2, not HCl.

4. $CH_3CH_2CH_2CHCl_2$ is best described as [1]

(a) a vic-dihalide, 1,2-dichlorobutane
(b) a gem-dihalide, 1,1-dichlorobutane
(c) a gem-dihalide, 2,2-dichlorobutane
(d) a vic-dihalide, 1,1-dichlorobutane

Answer: (b) Both chlorine atoms sit on the same (terminal) carbon, so the compound is geminal (an alkylidene halide, butylidene chloride); its IUPAC name is 1,1-dichlorobutane. Vicinal would need the two halogens on adjacent carbons.

5. The halide $(CH_3CH_2)_3C{-}Cl$ is classified as [1]

(a) a primary alkyl halide
(b) a secondary alkyl halide
(c) a tertiary alkyl halide
(d) a vinylic halide

Answer: (c) The carbon carrying chlorine is bonded to three ethyl groups, i.e. to three other carbon atoms, so the halide is tertiary (3°). The carbon is sp^3, so it is not vinylic.

6. How would you convert 4-chloroaniline into 1-bromo-4-chlorobenzene? Write the reagents and conditions for each step. [2]

Step 1: diazotise 4-chloroaniline with $NaNO_2$ and HBr at 273–278 K, giving 4-chlorobenzene diazonium bromide, $ClC_6H_4N_2^+Br^-$. Step 2: warm the diazonium salt with cuprous bromide, Cu_2Br_2; $-N_2^+$ is replaced by $-Br$ with loss of N_2 (Sandmeyer), giving 1-bromo-4-chlorobenzene.

- $NaNO_2$ + HBr, 273–278 K, diazonium salt (1)
- Cu_2Br_2, Sandmeyer, product named (1)

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7. Write the structures of the alkenes formed when 2-bromo-2,3-dimethylbutane, $(CH_3)_2CBr–CH(CH_3)_2$, is heated with alcoholic KOH, and say which is the major product. [2]

β-hydrogens are on the two methyl groups of C-2 and on C-3. Removing H from a C-2 methyl gives $CH_2=C(CH_3)CH(CH_3)_2$, 2,3-dimethylbut-1-ene. Removing the C-3 hydrogen gives $(CH_3)_2C=C(CH_3)_2$, 2,3-dimethylbut-2-ene. By Zaitsev's rule the major product is 2,3-dimethylbut-2-ene, with four alkyl groups on the double-bond carbons.

- both alkenes drawn (1)
- 2,3-dimethylbut-2-ene major, by Zaitsev (1)

8. Identify the asymmetric carbon in 3-bromohexane, $CH_3CH_2CHBrCH_2CH_2CH_3$. Name two physical properties its two enantiomers share and the one property in which they differ. [2]

C-3 is asymmetric: it carries H, Br, an ethyl group and a propyl group, four different groups. The two enantiomers have the same melting point, boiling point and refractive index; they differ only in rotating plane-polarised light, by equal amounts in opposite directions.

- C-3, with H, Br, C_2H_5 and C_3H_7 (1)
- two shared properties and opposite rotation (1)

9. Show how you would carry out: (i) propan-2-ol to 2-bromopropane, (ii) 2-bromopropane to 2-iodopropane, (iii) 2-iodopropane to propene. Give reagents and conditions. [3]

(i) Heat propan-2-ol with red phosphorus and bromine (PBr_3 formed in situ): $3(CH_3)_2CHOH + PBr_3 \rightarrow 3(CH_3)_2CHBr + H_3PO_3$. (ii) Heat with NaI in dry acetone (Finkelstein): $(CH_3)_2CHBr + NaI \rightarrow (CH_3)_2CHI + NaBr\downarrow$. (iii) Heat with alcoholic KOH (β-elimination): $(CH_3)_2CHI + KOH \rightarrow CH_3CH=CH_2 + KI + H_2O$.

- red P/Br_2 (PBr_3) or constant-boiling HBr (1)
- NaI, dry acetone (1)
- alcoholic KOH, heat, propene (1)

10. 2-Bromo-2-methylbutane is hydrolysed in water. Write the mechanism in two numbered steps with equations, the rate expression, and one reason why the reaction is fast. [3]

Step 1 (slow, reversible): $(CH_3)_2CBrCH_2CH_3 \rightleftharpoons (CH_3)_2C^+CH_2CH_3 + Br^-$; the energy to break C–Br comes from solvation of the ions by water. Step 2 (fast): $(CH_3)_2C^+CH_2CH_3 + H_2O \rightarrow (CH_3)_2C(OH)CH_2CH_3 + H^+$, giving 2-methylbutan-2-ol. Rate = $k[(CH_3)_2CBrCH_2CH_3]$, first order: only the halide is in the slow step. The reaction is fast because the carbocation is tertiary and stabilised by three alkyl groups.

- slow ionisation to the tertiary carbocation (1)
- fast attack, 2-methylbutan-2-ol (1)
- first-order rate law, tertiary cation stability (1)

11. An optically active compound X, C_4H_9Cl, gives mainly Y, C_4H_8, when heated with alcoholic KOH. X with magnesium in dry ether, followed by water, gives butane. Identify X and Y, give the minor alkene, and explain why X is optically active. [3]

X is 2-chlorobutane, $CH_3CHClCH_2CH_3$, the only C_4H_9Cl with an asymmetric carbon: C-2 carries H, Cl, CH_3 and C_2H_5. With alcoholic KOH it can lose a β-H from C-3 or C-1; by Zaitsev's rule Y is but-2-ene, $CH_3CH=CHCH_3$, and but-1-ene is the minor product. X + Mg → $CH_3CH(MgCl)CH_2CH_3$; this with water gives $CH_3CH_2CH_2CH_3$, butane, which confirms the unbranched four-carbon chain.

- X = 2-chlorobutane, asymmetric C-2 (1)
- Y = but-2-ene major, but-1-ene minor (1)
- Grignard then water gives butane (1)