Unit 8 · Haloalkanes

HARDER PRACTICE QUESTIONS

Full marks 46

Write your answers on separate paper. Show your working.

1 Reading a rate law: two bromides [11]

a. Two isomers of C_4H_9Br, P and Q, are each hydrolyzed by sodium hydroxide in the same solvent (aqueous ethanol) at the same temperature. One of them is 1-bromobutane and the other is 2-bromo-2-methylpropane. Kushal measures the initial rates: [8]

Run	Bromide	[bromide] (mol/L)	$[OH^-]$ (mol/L)	Initial rate (mol L^{-1} s^{-1})
1	P	0.010	0.10	1.2×10^{-6}
2	P	0.020	0.10	2.4×10^{-6}
3	P	0.010	0.20	2.4×10^{-6}
4	Q	0.010	0.10	2.0×10^{-5}
5	Q	0.020	0.10	4.0×10^{-5}
6	Q	0.010	0.20	2.0×10^{-5}

i. Find the order of each reaction with respect to the bromide and to OH^-, and write the rate law of each. (2)

ii. Which bromide is P and which is Q? Give the reasoning that links the rate law to the structure. (2)

iii. Find the rate constant of Q's reaction and the time for 75% of Q to react in run 4. How long would it take in run 6? (3)

iv. Kushal doubles both the bromide and the hydroxide concentrations of run 1, and of run 4. By what factor does each initial rate change? (1)

b. Sandesh reasons: "OH^- isn't in Q's rate law, so in the same solvent with **no** NaOH at all Q would not react." Explain what really happens to Q in the aqueous ethanol with no NaOH: how fast it reacts compared with run 4, and what products form. [3]

2 What the polarimeter shows [5]

Abhishek starts from a sample of one enantiomer of 2-bromobutane, call it A. A rotates plane-polarized light to the left. Under his conditions, pure butan-2-ol with **the same arrangement in space** as A would rotate light by −13.5°, and its mirror image by +13.5°.

- Run 1: A with concentrated NaOH in aqueous acetone. The butan-2-ol formed rotates light by **+13.5**°.
- Run 2: A warmed with silver nitrate in aqueous ethanol. The butan-2-ol formed rotates light by **+1.6**°.

i. What does each run tell you about the mechanism? (2)

ii. Work out the percentage of each enantiomer of butan-2-ol formed in run 2, and explain why it is not exactly 50 : 50 and why the excess is the form it is. (2)

iii. Abhishek writes: "A turns light to the left and the alcohol of run 1 turns it to the right, so the sign changed: that proves inversion." Is his reasoning sound? (1)

3 The four bromides C_4H_9Br [8]

a. W, X, Y and Z are the four structural isomers of C_4H_9Br. Barsha finds: [5]

- With silver nitrate in ethanol at room temperature, Z gives a cream precipitate at once and X after a few minutes; W and Y give one only on warming.
- Her sample of X is optically active.
- With hot alcoholic KOH, Y and Z give the **same** single alkene; W gives a single, different alkene; X gives two alkenes (counting the cis and trans forms of one alkene as one), one of them the major product.
- The alcohol made from X with aqueous NaOH gives a yellow precipitate when warmed with iodine and NaOH.

Name W, X, Y and Z, and name the alkene or alkenes each gives (the major one for X).

b. i. Two of the four findings above are not needed to name the compounds. Which two, and why are the other two enough? (1) [3]

ii. Riya predicts that the alcohol made from Z will give the yellow precipitate too, "since it has a CH_3 group on the carbon that carries the OH". Is she right? Explain. (2)

4 One alkene, not two [6]

a. Pratiksha needs **pure but-1-ene**, $CH_2{=}CHCH_2CH_3$. She can have either 1-bromobutane or 2-bromobutane, and hot alcoholic KOH. Her friend says: "Use 2-bromobutane: secondary halides eliminate more easily." Which should she use? Give the reasoning, and say what she gives up by choosing it. [3]

b. Nischal wants **2-methylpropan-2-ol**. He plans to boil 2-bromo-2-methylpropane with concentrated alcoholic KOH "so the reaction is fast". What will he mostly get instead, and why? Suggest a better way to make the alcohol, naming the reagents. [3]

5 Building a longer chain [8]

a. Your only organic starting materials are bromoethane, methanal (HCHO) and ethanal (CH_3CHO); you may use any inorganic reagent or solvent. Plan a route, with the reagent and condition on each arrow, to each of these: [6]

i. propanoic acid, CH_3CH_2COOH (2)

ii. butan-1-amine, $CH_3CH_2CH_2CH_2NH_2$ (3)

iii. butan-2-ol, $CH_3CH_2CH(OH)CH_3$ (1)

b. Is the butan-2-ol made in part iii above optically active? Explain, comparing it with what happens to the carbocation in an SN1 reaction. [2]

6 A clean chloride out of the flask [5]

Sadikshya is to make 1-chlorobutane (boiling point 78 °C) from butan-1-ol in the school laboratory. There is no thionyl chloride: she has Lucas reagent and phosphorus pentachloride.

i. She is to do the reaction in the cold. Which reagent should she use? Explain why not the other, and how she can then get the 1-chlorobutane free of the by-products. (2)

ii. Next week she is to make 2-chloro-2-methylpropane from 2-methylpropan-2-ol. Would you change the reagent? Explain. (1)

iii. Densities (g/mL): water 1.00, 1-chlorobutane 0.89, 1-bromobutane 1.27, bromoethane 1.46. Last week she made bromoethane and kept the lower layer from the separating funnel. Which layer should she keep today, and which when she makes 1-bromobutane? (2)

7 One order or two? [3]

For the halogen, the order of reactivity is R–I > R–Br > R–Cl in **both** SN1 and SN2. For the carbon, the orders are **opposite**: 3° > 2° > 1° in SN1, but 1° > 2° > 3° in SN2. Explain why one change gives the same order in both mechanisms and the other gives opposite orders.