

2.5.3 Primary substitution and structural evidence

Name: _____ Class: _____ Date: _____

Total: 29 marks

KEY WORDS nucleophile

Objective

Construct complete formulae and substitution mechanisms, then interpret matched isomer evidence. All questions and marking guidance are original.

1 Key knowledge and worked examples

A displayed formula shows every atom and bond. A skeletal formula omits carbon labels and carbon-bound hydrogen; every line end or corner is a carbon. Heteroatoms and hydrogen attached to them remain explicit. Number the longest suitable chain to give the functional group its required lowest locant.

■ Worked classification

2-Methylpropan-1-ol, $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$, is primary: its OH-bearing carbon is attached to only one other carbon. Branching elsewhere does not make an alcohol tertiary. Count neighbours of the functional-group carbon, not all carbons in the molecule.

In primary substitution, the nucleophile's lone pair goes to the carbon bearing halogen, and the C–halogen pair goes to the halogen. OH^- gives a neutral alcohol directly. NH_3 first gives a positively charged alkylammonium ion; a second NH_3 removes a proton and receives it as NH_4^+ . Include the arrow from the breaking N–H bond back to the nitrogen.

For hydrolysis comparisons, keep solvent mixture, temperature, concentrations and detection conditions fixed. Using isomeric bromides also keeps the leaving halide the same. A precipitate endpoint still measures an indirect comparative rate; it does not by itself establish the detailed mechanism.

2 Practice

2.1 Classify each conversion: ethene + Br₂ → 1,2-dibromoethane; ethanol → ethene + water; bromoethane + OH⁻ → ethanol + Br⁻; ethanol + [O] → ethanal + water; ethanal + 2[H] → ethanol; bromoethane + water → ethanol + HBr; many ethene molecules → poly(ethene). Use addition, elimination, substitution, oxidation, reduction, hydrolysis and polymerisation; identify the hydrolysis case as substitution too. [4]

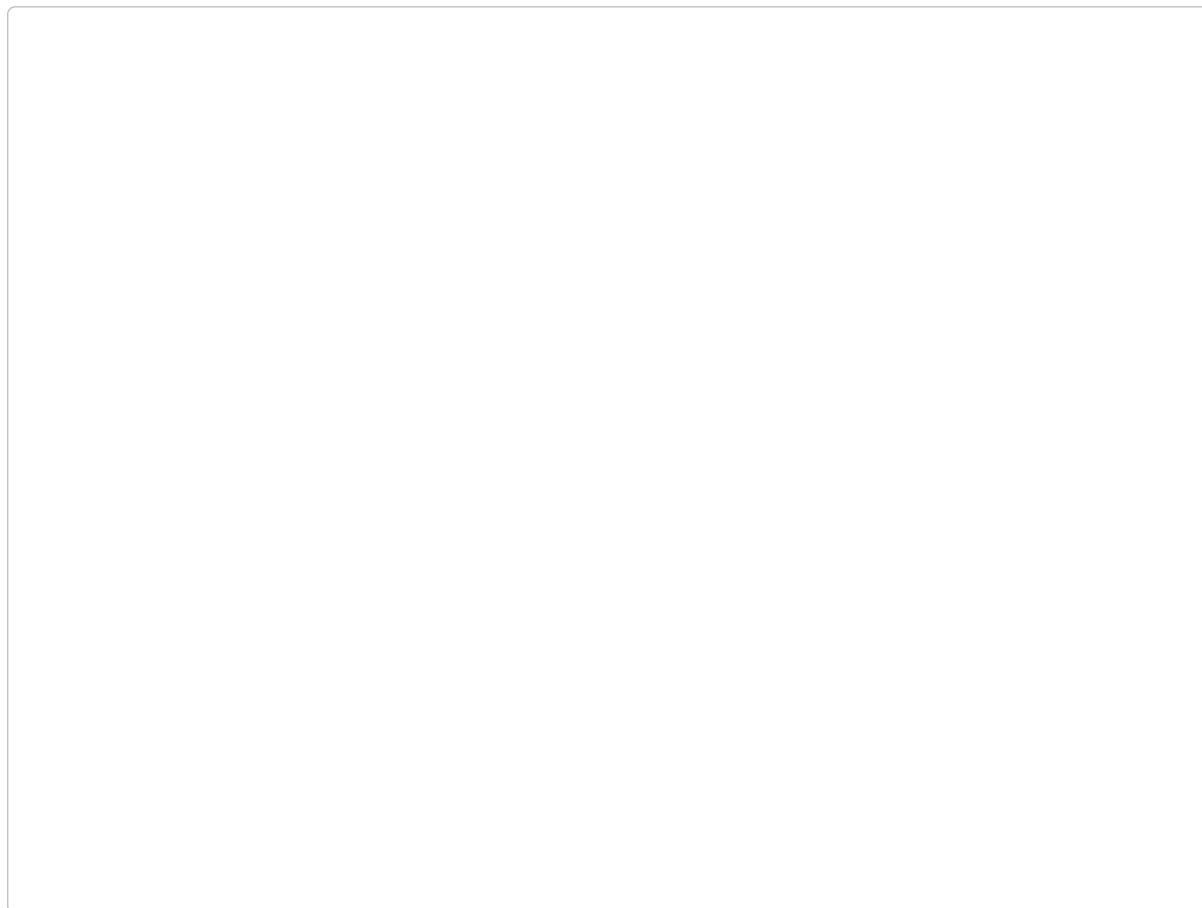
2.2 Under matched aqueous/ethanolic AgNO₃ conditions, 1-bromobutane, 2-bromobutane and 2-bromo-2-methylpropane reach the same visible AgBr endpoint after 180, 70 and 5.0 s respectively. Classify each, rank hydrolysis rates and calculate the tertiary/primary comparative rate ratio using 1/t. State one limitation of treating this endpoint as an exact kinetic measurement. [5]

2.3 Name $\text{CH}_3\text{CHBrCH}_3$ and $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$. For each, draw its complete displayed formula and a skeletal formula. Include the O–H bond in the displayed alcohol.[6]

3 Exam-style questions

3.1 Draw the full electron-pair mechanism for warm aqueous OH^- reacting with primary 1-bromopropane. Show the donating lone pair, both curly arrows, C–Br polarity and the charged products. Name the organic product. [4]

3.2 Draw both stages of the reaction of 1-bromopropane with excess alcoholic ammonia under pressure. Show donating lone pairs, all curly arrows, the alkylammonium intermediate, proton transfer and final ions. Explain why the amine product can react further with halogenoalkane. [6]



3.3 Classify $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ and $(\text{CH}_3)_3\text{COH}$ as primary, secondary or tertiary alcohols. Explain why the first and last classifications differ despite both molecules having four carbons. [4]
