

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 + $\text{Br}_2 \rightarrow$ 1,2-dibromoethane; ethanol $\rightarrow$ ethene + water; bromoethane + $\text{OH}^- \rightarrow$ ethanol + Br^- ; ethanol + $[\text{O}] \rightarrow$ ethanal + water; ethanal + $2[\text{H}] \rightarrow$ ethanol; bromoethane + water $\rightarrow$ ethanol + HBr; many ethene molecules $\rightarrow$ 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 AgNO_3 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]

Solutions

Original marking guidance: M1 method, A1 accuracy, B1 reasoning. Completed drawings are original answers; only the reactive lone pairs need be shown.

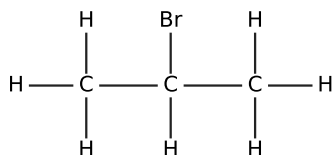
2.1 In order: addition; elimination; substitution; oxidation; reduction; hydrolysis (also substitution); polymerisation. B1 per two correctly classified conversions, up to three marks for the first six; B1 for polymerisation and recognising hydrolysis as substitution. In hydrolysis, water replaces the halogen and supplies the OH group; the categories can overlap.

2.2 Primary, secondary, tertiary respectively; tertiary > secondary > primary under these conditions. Comparative rate ratio = $(1/5.0)/(1/180) = 36$. Precipitate visibility depends on mixing/detection threshold; $1/t$ assumes the same extent is reached and is not a complete rate law. All three have formula C_4H_9Br and release the same halide.

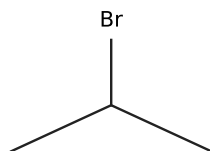
2.3

2-Bromopropane: $CH_3CHBrCH_3$

Displayed formula

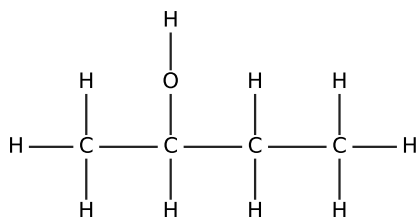


Skeletal formula

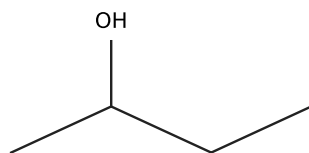


Butan-2-ol: $CH_3CH(OH)CH_2CH_3$

Displayed formula



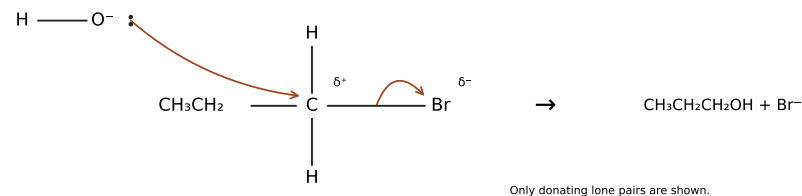
Skeletal formula



B1 for each correct name, displayed formula and skeletal formula (six marks). The middle carbon has one H and one Br in 2-bromopropane; the OH-bearing carbon has one H in butan-2-ol. An omitted O–H hydrogen makes the displayed alcohol incomplete.

3.1

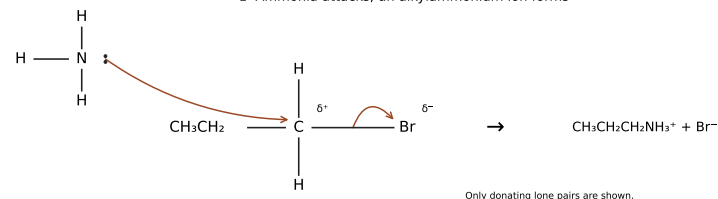
Hydroxide substitutes for bromide



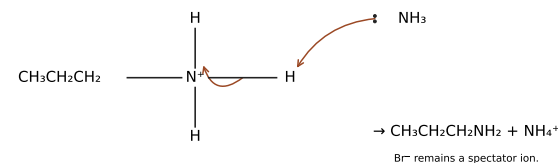
B1 for the O lone-pair arrow to the carbon bearing Br; B1 for the C–Br bond-pair arrow to Br; B1 for correct $C\delta^+/Br\delta^-$ and neutral alcohol plus Br^- ; B1 for propan-1-ol. Total charge is -1 on each side.

3.2

1. Ammonia attacks; an alkylammonium ion forms



2. A second ammonia removes a proton



B1 for NH_3 lone-pair attack on carbon; B1 for C–Br pair to Br; B1 for $CH_3CH_2CH_2NH_3^+$ and Br^- ; B1 for the second NH_3 lone-pair arrow to an N-bound H; B1 for the N–H pair returning to N and propan-1-amine plus NH_4^+ . The amine's nitrogen retains a lone pair and can attack another halogenoalkane, causing further substitution. Excess ammonia favours the primary amine; it does not make further substitution impossible.

3.3 Primary, secondary, tertiary respectively. The OH-bearing carbon is attached to one carbon in the first and three carbons in the last; total carbon count is irrelevant.