

Exercise walk-through

2.5.3

Primary substitution and structural evidence

Pearson Edexcel · International A-Level · Chemistry

Opposite solubility trends explain the evidence

- 1 **Set up** $\text{Ba}(\text{OH})_2$ is more soluble: its equal saturated volume contains more OH^- and needs more acid.
- 2 **Reason** BaSO_4 is less soluble: equal initial cation amounts give more solid with excess sulfate.
- 3 **Conclude** Solubility controls dissolved amount; it is different from dissociation strength.

Controls distinguish chemical evidence from contamination

- 1 Set up** Match measured amounts, particle size, apparatus and heating rate; compare sample temperature at a consistent decomposition criterion.
- 2 Reason** CO_2 : milky limewater; O_2 : glowing splint relights; NO_2 : brown and acidic.
- 3 Conclude** Clean flame-test wire and keep the flame region/loading consistent. Na yellow, K lilac, Ca brick-red, Sr crimson-red; sodium carry-over can mask another colour.

Independent identification

Your turn

$\text{C}_3\text{H}_6\text{O}$ has a carbonyl IR absorption and gives a positive Fehling's test. Which structure fits all evidence?

- A. CH_3COCH_3
- B. $\text{CH}_3\text{CH}_2\text{CHO}$
- C. $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
- D. CH_3COOH

Exercises 2.1·2.2

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]

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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.

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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 C₄H₉Br and release the same halide.

Exercise 2.3

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]

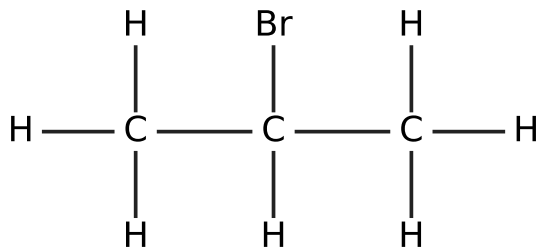
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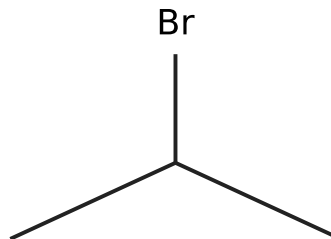
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2-Bromopropane: $\text{CH}_3\text{CHBrCH}_3$

Displayed formula



Skeletal formula

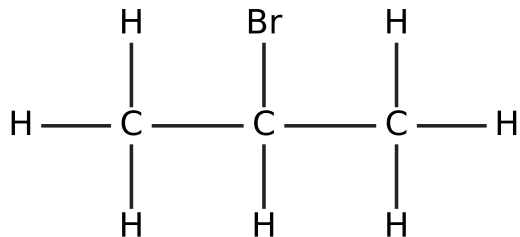


Full solution 2.3 (1/2)

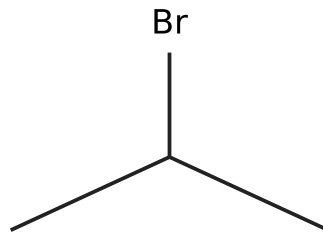
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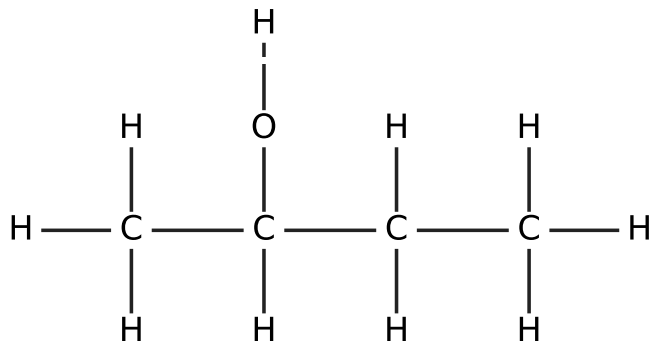
Skeletal formula



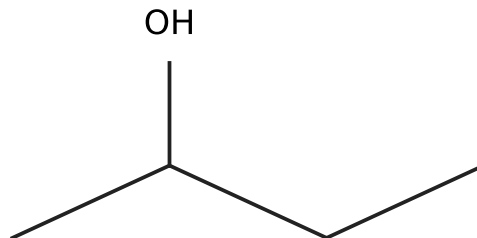
Full solution 2.3 (2/2)

Butan-2-ol: $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$

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.

Exercise 3.1

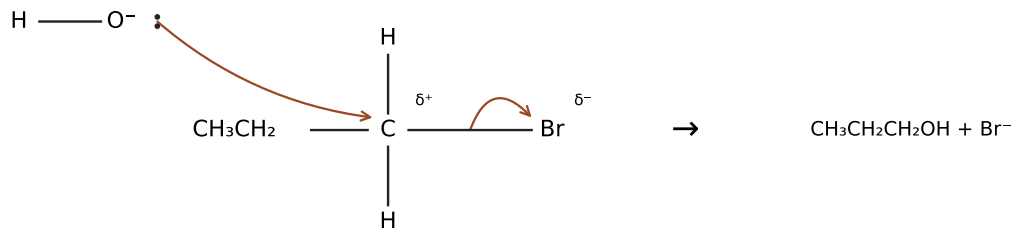
3.1 Draw the full electron-pair mechanism for warm aqueous OH^- reacting with primary 1-bromopropane. Show the donating lone pair, both curly arrows, C–Br polarity and the charged products. Name the organic product. [4]

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3.1

Hydroxide substitutes for bromide



Only donating lone pairs are shown.

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 $\text{C}\delta^+/\text{Br}\delta^-$ and neutral alcohol plus Br^- ; B1 for propan-1-ol. Total charge is -1 on each side.

Exercise 3.2

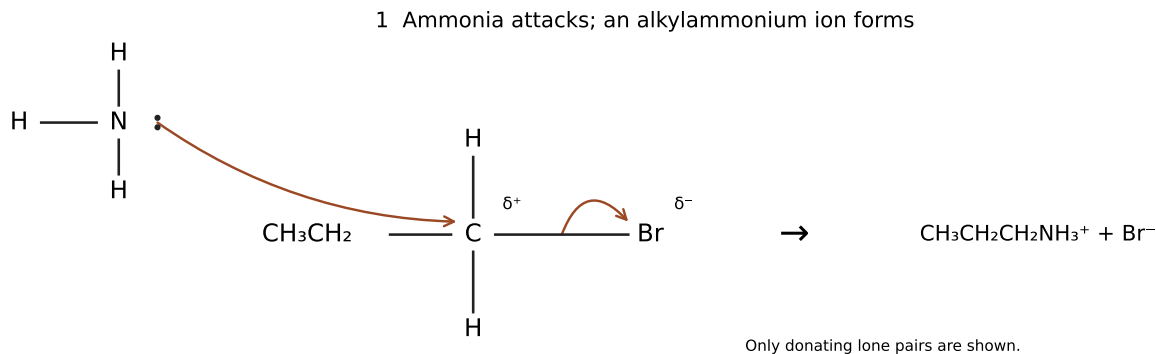
3.2 Draw both stages of the reaction of 1-bromopropane with excess alcoholic ammonia under pressure. Show donating lone pairs, all curly arrows, the alkylammonium intermediate, proton transfer and final ions. Explain why the amine product can react further with halogenoalkane.

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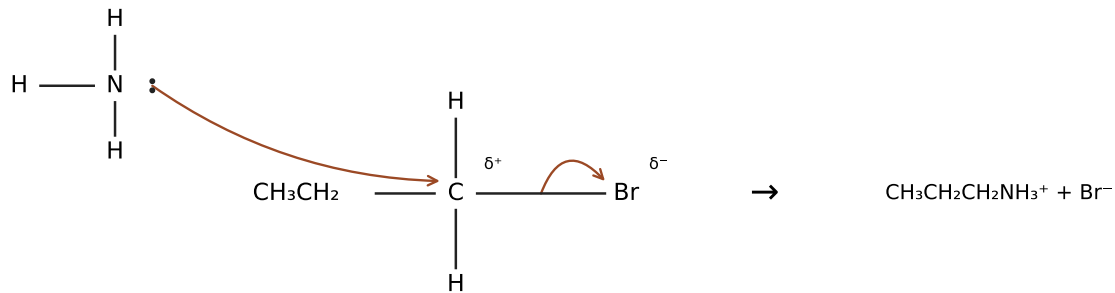


2 A second ammonia removes a proton

Full solution 3.2 (1/2)

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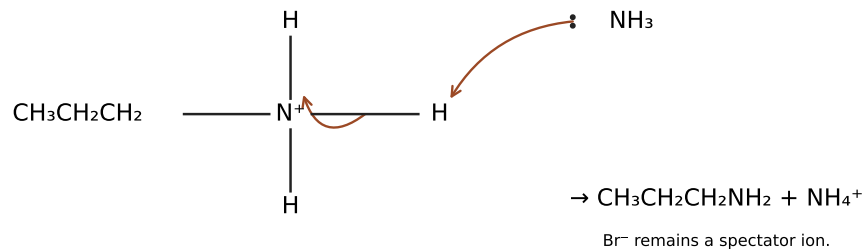
1 Ammonia attacks; an alkylammonium ion forms



Only donating lone pairs are shown.

2 A second ammonia removes a proton

Full solution 3.2 (2/2)



B1 for NH_3 lone-pair attack on carbon; B1 for $\text{C}-\text{Br}$ pair to Br ; B1 for $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3^+$ 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.

Exercise 3.3

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.

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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.