M1. (a) (i) M1 Elimination

$$H_3C - CH_2 - C - CH_3 \longrightarrow H_3C - CH_2 - CH = CH - CH_3 + H_2O + Br$$

M2 must show an arrow from the <u>lone pair on the oxygen</u> of a negatively charged hydroxide ion to a correct H atom

M3 must show an arrow from a C-H bond adjacent to the C-Br bond towards the appropriate C-C bond. Only award if a reasonable attempt has been made at the attack on the H atom of the appropriate adjacent C-H

M4 is independent provided it is from their original molecule

Award full marks for an E1 mechanism in which **M3** is on the correct carbocation.

N.B. These are double-headed arrows

For M1, accept "Base elimination" but no other prefix.

Penalise M2 if covalent KOH

Penalise **M4** for formal charge on C of C-Br or incorrect partial charges on C-Br

Ignore other partial charges

Penalise once only in any part of the mechanism for a line and two dots to show a bond.

<u>Max any 2 of 3 marks for the mechanism</u> for wrong reactant (or wrong product if shown).

Accept the correct use of "sticks" for the molecule except for the C-H being attacked

(ii) Structure for pent-1-ene

CH₃CH₂CH₂CH=CH₂

1

(b) M1 Electrophilic addition

M4 Structure H₃C — C → H₃C → H M2 → H₃C → C → H M5 ∴ Br Br M3

M2 must show an arrow from the double bond towards the Br atom of the Br-Br molecule

M3 must show the breaking of the Br-Br bond.

M4 is for the structure of the tertiary carbocation with Br on the correct carbon atom.

M5 must show an arrow from the lone pair of electrons on the negatively charged bromide ion towards the positively charged carbon atom.

N.B. These are double-headed arrows

For M1, both words required.

For the mechanism

M2 Ignore partial negative charge on the double bond.

M3 Penalise partial charges on Br-Br bond if wrong way and penalise formal charges

Penalise once only in any part of the mechanism for a line and two dots to show a bond

Max any 3 of 4 marks for the mechanism for

wrong organic reactant or wrong organic product (if shown) or primary carbocation.

If HBr is used, max 2 marks for their mechanism Accept the correct use of "sticks"

5

(c) M1 Nucleophilic substitution

M2 must show an arrow from the lone pair of electrons on the nitrogen atom of an ammonia molecule to the C atom.

M3 must show the movement of a pair of electrons from the C-Br bond to the Br atom. **M3** is independent provided it is from their <u>original molecule</u>

M4 is for the structure of the alkylammonium ion, which could be a condensed formula. A positive charge must be shown on/or close to, the N atom.

M5 is for an arrow from the N-H bond to the N atom.

Award full marks for an S_N1 mechanism in which M2 is the attack of the ammonia on the intermediate carbocation.

N.B. These are double-headed arrows

For M1, both words required.

Penalise M2 if NH3 is negatively charged.

Penalise **M3** for formal charge on C or incorrect partial charges

The second mole of ammonia is not essential for M5; therefore ignore any species here.

Penalise once only for a line and two dots to show a bond.

Max any 3 of 4 marks <u>for the mechanism</u> for wrong organic reactant (or wrong organic product if shown)

Accept the correct use of "sticks"

5

[15]

M2. (a) Electron pair donor

OR

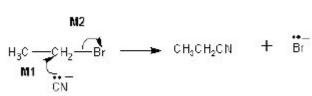
Species which uses a pair of electrons to form a co-ordinate / covalent bond.

QoL

Credit "lone pair" as alternative wording

1

(b)



- M1 Must show an arrow from the lone pair of electrons on the carbon atom of the negatively charged cyanide ion to the central C atom.
- M2 Must show the movement of a pair of electrons from the C-Br bond to the Br atom. Mark M2 independently.

Award full marks for an $S_{\scriptscriptstyle N}1$ mechanism in which M1 is the attack of the cyanide ion on the intermediate carbocation.

Penalise M1 if covalent KCN is used

Penalise M2 for formal charge on C or incorrect partial charges

Penalise once only for a line and two dots to show a bond.

Max 1 mark for the wrong reactant or "sticks"

2

(c) Ethylamine / CH₃CH₂NH₂ is a nucleophile

OR

Ethylamine could react further

OR

Ethylamine could make secondary / tertiary amines

OR

To make reaction with ammonia more likely

OR

To minimise further substitution

OR

The idea of releasing free amine from the salt

OR

The idea of removing a proton from the intermediate alkylammonium ion

OR

The idea that ammonia acts both initially as a nucleophile and

then as a base

Do not credit a simple reference to the equation or the mechanism requiring two moles of ammonia.

1

(d) Elimination

Credit "base elimination" but NOT "nucleophilic elimination" No other prefix.

1

- M1 Must show an arrow from the lone pair on oxygen of a negatively charged hydroxide ion to the correct H atom
- M2 Must show an arrow from the correct C-H bond to the C-C bond and should only be awarded if an attempt has been made at M1
- M3 Is independent.

Award full marks for an E1 mechanism in which M2 is on the correct carbocation.

Mechanism

Penalise M1 if covalent KOH

Penalise M3 for formal charge on C or incorrect partial charges

Penalise once only for a line and two dots to show a bond.

Max 2 marks for the mechanism for wrong reactant or "sticks"

3

[8]

M3.(a) (i)

If wrong carbocation, lose structure mark
If wrong alkene, lose structure mark
Can still score ¾ i.e. penalise M3
Penalise M2 if polarity included incorrectly
no bond between H and Br
bond is shown as or

(ii) ⊕
CH₃CH₂CH₂
credit secondary carbocation here if primary carbocation has been used in (i)

4

1

1

1

1

Ignore attack on this carbocation by $\ddot{B}r$ Θ

(b) (i) Structure:
$$H_3C - CH - CH_3$$
 (1) $\begin{bmatrix} insist on \\ C - OH bond \end{bmatrix}$

Name: propan-2-ol Not 2-hydroxypropane

(ii) Name of mechanism: nucleophilic substitution (both words) (NOT $S_N 1$ or $S_N 2$)

Mechanism:

M1
arrow (1)
$$CBr$$
 $H_3C - CH - CH_3 \longrightarrow CH_3CH(OH)CH_3 + B_1\Theta$
 Θ_{HO}
(1) arrow from
 $(M2)$ lone pair

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2

(c) (i) elimination

1

1

1

(ii) base

OR proton acceptor NOT nucleophile

[12]

M4. (a) (i) <u>Nucleophilic substitution</u>

2

M1 must show an arrow from the lone pair of electrons on the oxygen atom of the negatively charged hydroxide ion to the central C atom.

M2 must show the movement of a pair of electrons from the C-Br bond to the Br atom. Mark M2 independently.

Penalise M1 if covalent KOH is used

Penalise M2 for formal charge on C or incorrect partial charges

Penalise once only for a line and two dots to show a bond.

Max 1 mark for the mechanism for the wrong reactant and/or "sticks"

Ignore product

Award full marks for an $S_{N}1$ mechanism in which M1 is the attack of the hydroxide ion on the intermediate carbocation.

(ii) 2-bromopropane ONLY

1

(iii) Polar C-Br OR polar carbon-bromine bond OR dipole on C-Br

OR δ + (δ –)

C atom of carbon–bromine bond is δ+/electron deficient **OR** C—Br

(Credit carbon–halogen bond as an alternative to carbon–bromine bond)

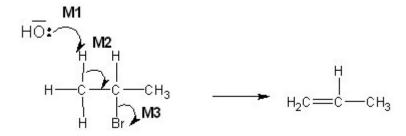
It must be clear that the discussion is about the carbon atom of the C–Br bond. NOT just reference to a polar molecule. Ignore X for halogen

1

(b) Elimination

Credit "base elimination" but NOT "nucleophilic elimination" No other prefix.

1



3

M1 must show an arrow from the lone pair on oxygen of a negatively charged hydroxide ion to the correct H atom

M2 must show an arrow from the correct C-H bond to the C-C bond and should only be awarded if an attempt has been made at M1 **M3** is independent.

Mechanism

Penalise M1 if covalent KOH

Penalise M3 for formal charge on C or incorrect partial charges

Penalise once only for a line and two dots to show a bond.

Max 2 marks <u>for the mechanism</u> for wrong reactant and/or "sticks"

Ignore product

Award full marks for an E1 mechanism in which M2 is on the correct carbocation.

- (c) Any one condition from this list to favour elimination;
 Apply the list principle
 - <u>alcohol(ic)/ethanol(ic)</u> (solvent)
 - <u>high concentration</u> of KOH/alkali/hydroxide *OR* <u>concentrated</u> KOH/hydroxide

Ignore "aqueous"

high temperature or hot or heat under reflux or T = 78 to 100°C
 Ignore "excess"

1

(d) (i) Addition (polymerisation) ONLY Penalise "additional"

1

1

(ii) <u>But-2-ene</u> ONLY (hyphens not essential)

Ignore references to cis and trans or

E/Z

Ignore butane

[12]

M5. (a) (i) <u>Splitting/breaking C— X/bond(s) using/by (adding)/with water</u>

OR

<u>Splitting/breaking the molecule/substance/compound using/by</u> (adding)/<u>with water</u>

NOT simply the reaction of/with water

NOT simply the addition or adding of water.

NOT the "splitting of water"

Accept any halogen bond, but penalise other specified bonds

1

- (ii) M1 yellow ONLY
 - **M2** Ag $^+$ + $I^ \rightarrow$ AgI (Ag $^+$ I^-)

For M1, penalise cream(y) OR white Ignore pale or light or dark (yellow)

For M2, ignore state symbols

2

(iii) M1 AgF OR silver fluoride is soluble/dissolves (in water)

M2 No result

OR no precipitate

OR no (visible) change would occur

OR colourless solution

Accept "silver flouride"

Mark independently

Ignore reference to C – F bond breakage in M1

Ignore "no reaction" and "nothing"

2

(b) The bond that takes <u>less</u> energy to break/the low<u>er</u> bond enthalpy (energy)/weak<u>er</u> bond means the precipitate/reaction/hydrolysis occurs fast<u>er/</u>quicker/takes <u>less time</u>

OR

The bond that takes <u>more</u> energy/the high<u>er</u> bond enthalpy (energy)/strong<u>er</u> bond means the precipitate/reaction/hydrolysis occurs slow<u>er</u>/takes longer/takes <u>more time</u>

Insist on comparative on <u>both</u> bond strength and rate of reaction

1

(c) (i) An electron pair donor

OR

Forms a covalent or co-ordinate or dative bond by <u>donating</u> <u>a pair of electrons</u>

1

Answer must refer to an electron pair.

Credit "lone pair"

"Attracted" does not equal "donated"

(ii)

M1 must show an arrow from the lone pair of electrons on the

oxygen atom of the negatively charged hydroxide ion to the central C atom.

M2 must show the movement of a pair of electrons from the C—Br bond to the Br atom. Mark M2 independently.

NB The arrows here are double-headed

Penalise M1 if covalent NaOH is used

Penalise M2 for formal charge on C or incorrect partial charges

Penalise once only for a line and two dots to show a bond.

Max 1 mark for the wrong reactant

Award 1 mark only for C-Br bond breakage if **an S**_N**1 mechanism** is used.

Do not penalise the use of "sticks"

2

(d) (i) Structure of tertiary carbocation (CH₃)₃C+ or drawn out

Insist on a full positive charge on the central C atom.

Penalise a bond to the positive charge.

Be lenient on vertical C-C bonds

1

(ii) <u>Tertiary carbocation/carbonium ion</u> (from 2-bromo-2-methylpropane) is <u>more stable</u> (than the primary carbocation/carbonium ion)

OR

<u>Primary carbocation/carbonium ion</u> (from 2-bromo-2-methylpropane) is <u>less stable</u> (than the tertiary carbocation/carbonium ion)

QoL

Ignore reference to the alleged relative stability of haloalkanes

1

[11]