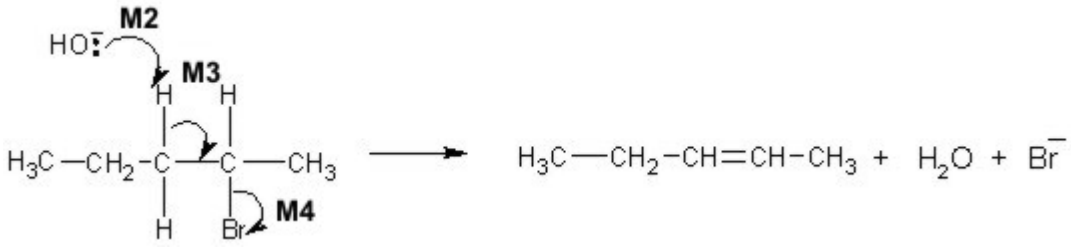
Mark schemes

1 (a) (i) **M1** Elimination



M2 must show an arrow from the lone pair on the oxygen
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.

*Max any 2 of 3 marks **for the mechanism** for wrong reactant (or wrong product if shown).*

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

4

(ii) **Structure for pent-1-ene**

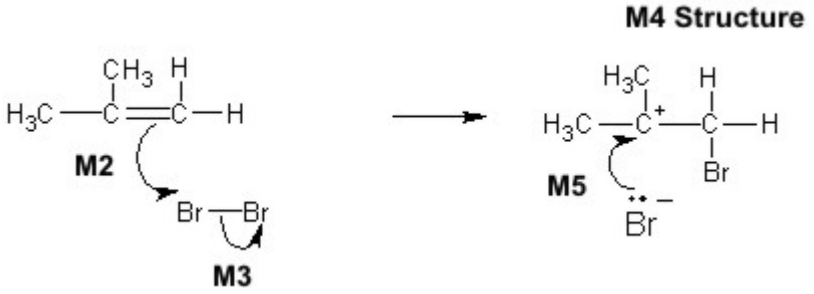
$CH_3CH_2CH_2CH=CH_2$

Penalise C_3H_7

Accept correct "sticks"

1

(b) **M1 Electrophilic addition**



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*

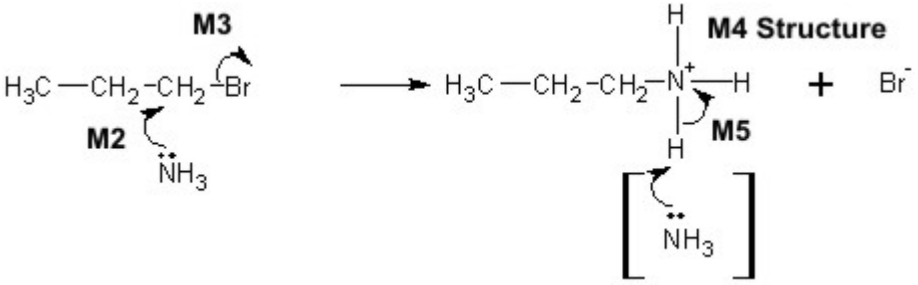
wrong organic reactant or wrong organic product (if shown) or primary carbocation.

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 original molecule

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 NH_3 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 **for the mechanism** for wrong organic reactant (or wrong organic product if shown)*

Accept the correct use of "sticks"

5

[15]

2 (a) (i) chlorotrifluoromethane

Spelling must be correct but do not penalise "flouro"

Ignore use of 1–

1

(ii) CF_3•

May be drawn out with dot on C

OR if as shown dot may be anywhere

1

(iii) An unpaired/non-bonded/unbonded/free/a single/one/lone electron

NOT "bonded electron" and NOT "paired electron"

NOT "pair of electrons"

NOT "electron s"

Ignore "(free) radical"

1

(b) **M1** $Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$

M2 $ClO\bullet + O_3 \rightarrow \mathbf{2}O_2 + Cl\bullet$

Mark independently

Equations could gain credit in either position

The dot can be anywhere on either radical

Penalise the absence of a dot on the first occasion that it is seen and then mark on. Do not make the same penalty in the next equation, but penalise the absence of a dot on the other radical.

Apply the list principle for additional equations

2

(c) (i) (If any factor is changed which affects an equilibrium), the (position of) equilibrium will shift/move so as to oppose the change.

OR

(When a system/reaction in equilibrium is disturbed), the equilibrium shifts/moves in a direction which tends to reduce the disturbance

Must refer to equilibrium

Ignore reference to "system" alone

A variety of wording will be seen here and the key part is the last phrase.

An alternative to shift/move would be the idea of changing/altering the position of equilibrium

1

(ii) **M1** The (forward) reaction/to the right is endothermic or takes in heat

OR The reverse reaction/to the left is exothermic or gives out heat

M2 The equilibrium moves/shifts to oppose the increase in temperature

M2 depends on a correct statement for M1

For M2 accept

The equilibrium moves/shifts

- *to take in heat/lower the temperature*
- *to promote the endothermic reaction and take in heat/ lower the temperature*
- *to oppose the change and take in heat/lower the temperature*

(leading to the formation of more ozone)

2

(d) Any one of

- Pentane <u>does not contain chlorine</u> OR <u>C–Cl</u> (bond)
- Pentane is <u>chlorine-free</u>
- Pentane <u>does not release chlorine</u> (atoms/radicals)

Ignore reference to F OR C–F OR halogen

Ignore "Pentane is not a CFC"

Ignore "Pentane is a hydrocarbon"

Ignore "Pentane only contains C and H"

Ignore "Pentane is C_5H_{12}"

1

[9]

3

(a) (i) <u>Electron pair donor</u>

OR

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

Credit "lone pair" as alternative wording

Credit "electron pair donator"

1

(ii) <u>Replacement of the halogen</u> (atom) (by the nucleophile)

OR

The <u>carbon-halogen bond/C-X</u> breaks and a bond forms with the nucleophile or between the carbon and the nucleophile

They must describe the idea of substitution in a haloalkane.

Accept the idea that a nucleophile replaces the halogen which becomes a halide ion

Penalise reference to "halogen molecule" and penalise the idea that the haloalkane contains a halide

1

(iii) <u>Splitting molecules using/by water</u>

OR

breaking/splitting/dissociating (C¡VX) bond(s)/using/by water

NOT simply the reaction with water or simply the addition of water.

Ignore "compound"

1

(iv) (Heat) energy/enthalpy required/needed/absorbed (at constant pressure) to break/split it/the (carbon-halogen) bond

OR

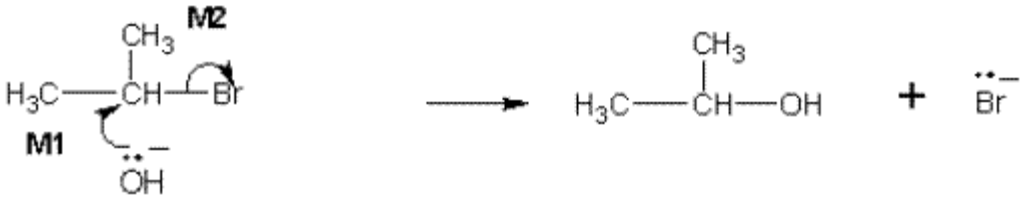
(Heat) energy/enthalpy required/needed/absorbed (at constant pressure) for homolysis of the (C–X/the carbon-halogen) bond

Ignore bond formation

Ignore "average"

1

(b)



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.

Award full marks for an S_N1 mechanism in which M1 is the attack of the hydroxide ion on the intermediate carbocation.

Penalise M1 if covalent KOH is used

Penalise M2 for formal charge on C or incorrect partial charges

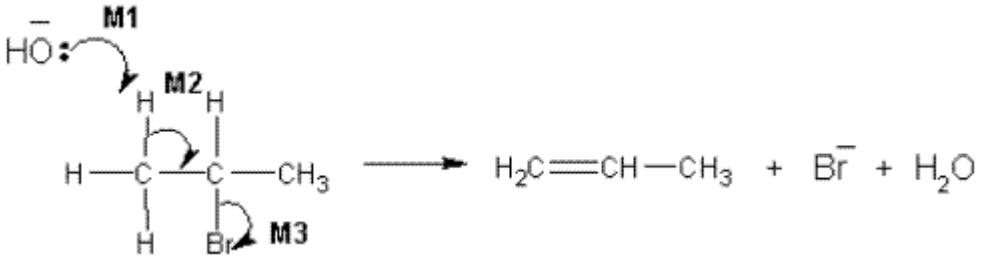
Penalise once only for a line and two dots to show a bond.

Max 1 mark for the wrong reactant

Accept the correct use of "sticks"

2

(c) (i)



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 provided it is from the original molecule

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

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 wrong reactant

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

3

(ii) **M1** Stated that the spectrum has an absorption/absorbance/ peak in the range 1620 cm^{-1} to 1680 (cm^{-1}) or specified correctly in this range from the spectrum

M2 depends on correct range or wavenumber being specified

M2 (Infrared absorption) due to C=C OR carbon-carbon double bond

QoL for correct M1 statement which includes both the word absorption (or alternative) and the correct range or wavenumber

Allow "peak" OR "dip" OR "spike" OR "trough"
OR "low transmittance" as alternatives for absorption.

For M2 it is not sufficient simply to state that an alkene has C=C

M2 could be on the spectrum

Ignore reference to other absorptions

2

[11]

4 (a) (i) Splitting/breaking C─ X/bond(s) using/by (adding)/with water

OR

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

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 less energy to break/the lower bond enthalpy (energy)/weaker bond means the precipitate/reaction/hydrolysis occurs faster/quicker/takes less time

OR

The bond that takes more energy/the higher bond enthalpy (energy)/stronger bond means the precipitate/reaction/hydrolysis occurs slower/takes longer/takes more time

Insist on comparative on both bond strength and rate of reaction

1

(c) (i) An electron pair donor

OR

Forms a covalent or co-ordinate or dative bond by donating a pair of electrons

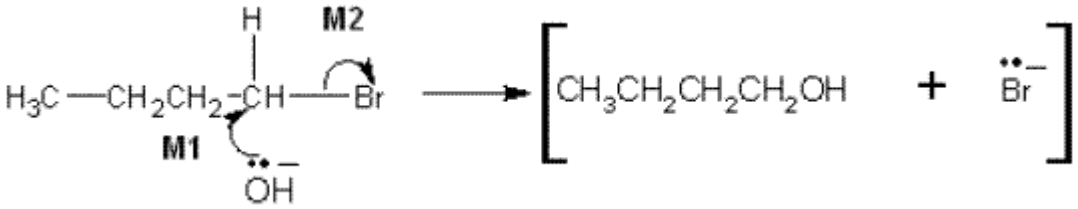
1

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_N1 mechanism*** *is used.*

Do not penalise the use of "sticks"

2

(d) (i) Structure of tertiary carbocation $(CH_3)_3C^+$ 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) Tertiary carbocation/carbonium ion (from 2-bromo-2-methylpropane) is more stable (than the primary carbocation/carbonium ion)

OR

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

QoL

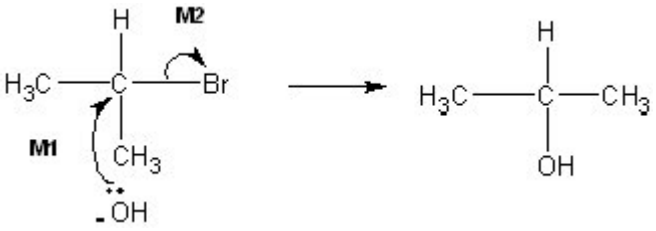
Ignore reference to the alleged relative stability of haloalkanes

1

[11]

5 (a) (i) Nucleophilic substitution

1



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_N1 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)

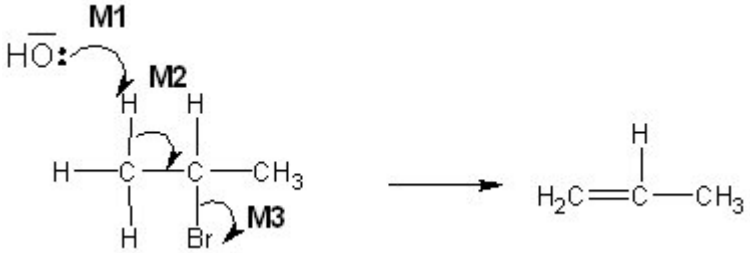
It must be clear that the discussion is about the carbon atom of the C–Br bond. NOT just reference to a polar molecule.
Ignore X for halogen

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 **for the mechanism** 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

- alcohol(ic)/ethanol(ic) (solvent)
- high concentration of KOH/alkali/hydroxide ***OR*** concentrated 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

(ii) But-2-ene ONLY (hyphens not essential)

Ignore references to cis and trans or E/Z

Ignore butane

1

[12]

6

(a) Electron pair donor

OR

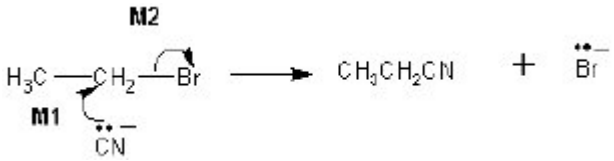
Species which uses a pair of electrons to form a co-ordinate / covalent bond.

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_N1 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 / $CH_3CH_2NH_2$ 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

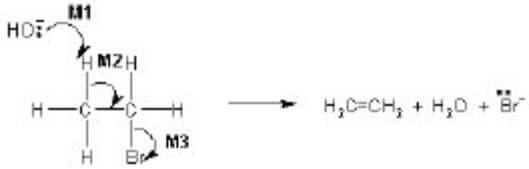
The idea that ammonia acts <u>both</u> initially as a nucleophile and then as a base

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.

<u>Mechanism</u>
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]

7

(a) **M1** (Free-) **radical substitution**

Both words needed

1

M2 $Cl_2 \rightarrow 2Cl\bullet$

1

M3 $Cl\bullet + CH_4 \rightarrow \bullet CH_3 + HCl$

1

M4 $Cl_2 + \bullet CH_3 \rightarrow CH_3Cl + Cl\bullet$

1

M5 $CH_4 + 3Cl_2 \rightarrow CHCl_3 + 3HCl$

Penalise the absence of a radical dot once only

***Ignore termination steps except, if and only if <u>both</u>** M3 and M4 do not score, then accept for one mark*
$Cl\bullet + \bullet CH_3 \rightarrow CH_3Cl$

1

(b) **M1** UV (light)/ sunlight / light / UV radiation

M2 C–Cl or carbon-chlorine bond breakage
OR
homolysis of C–Cl
OR
equation to show a chlorine-containing organic compound forming two radicals

For M1 and M2, ignore use of Cl_2, but credit UV and C–Cl bond breakage if seen

1

M3 $Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$

1

M4 $ClO\bullet + O_3 \rightarrow Cl\bullet + 2O_2$

Ignore other equations
Penalise the absence of a radical dot once only
Accept radical dot anywhere on either radical.

1

M5 Any **one** from

- Combination $2O_3 \rightarrow 3O_2$
- Stated that Cl• / chlorine atom is regenerated / not used up
- Stated that the Cl• / chlorine atom is unaffected by the process.

1

For M5 accept Cl• on both sides of the equation

M6 Stated that the role of the Cl• / chlorine atom is to find an alternative route ***OR*** lower E_a / activation energy

1

(c) **M1** Halothane contains C–Cl / Cl

OR

Desflurane does not contain C–Cl bonds / Cl

OR

Desflurane contains C–F / F as the only halogen

Mark independently.
For M1, credit the idea that desflurane contains C–F bonds that are difficult to break OR that halothane contains C–Cl bonds which are easy to break.

1

M2 Desflurane / molecules that have fluorine as the only halogen, cause no damage / do not deplete / do not react with the ozone (layer)

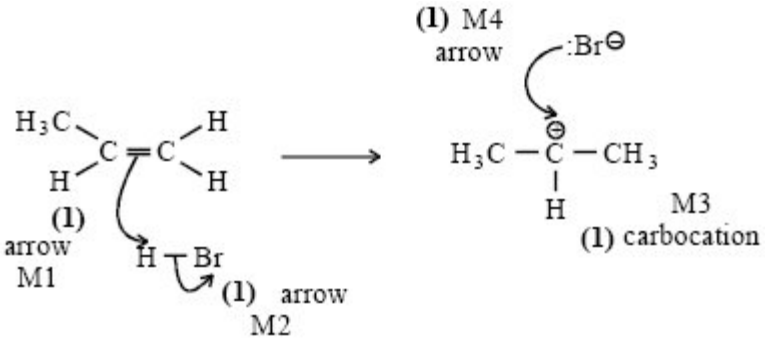
OR

Halothane / chlorine-containing molecules, damage / deplete / react with the ozone (layer)

1

[13]

8 (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 •

4

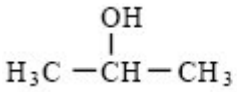
(ii) ⊕

$CH_3CH_2CH_2$

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

Ignore attack on this carbocation by $\ddot{Br}^{\ominus}$

1

(b) (i) *Structure*:  **(1)** [insist on C — OH bond]

1

Name: propan-2-ol

Not 2-hydroxypropane

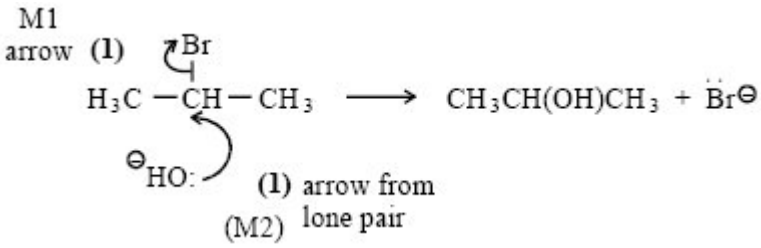
1

(ii) *Name of mechanism*: nucleophilic substitution **(both words)**

(NOT S_N1 or S_N2)

1

Mechanism:



penalise incorrect polarity on C-Br (M1)
Credit the arrows even if incorrect haloalkane
If S_N1, both marks possible

2

(c) (i) elimination

1

(ii) base

OR proton acceptor

NOT nucleophile

1

[12]

9 A

[1]

10 D

[1]