3.2.8 Haloalkanes

Elimination

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148 minutes

145 marks

M1. (a) Alcohol: Reaction = Substitution (/ hydrolysis) **(1)**

Ignore reference to nucleophilic, but electrophilic give zero

Alcohol: Role = nucleophile (/ lone pair donor) **(1)**

Alkene: reaction = elimination **(1)**

Ignore ref to nucleophilic or electrophilic

Alkene: base (/ proton acceptor) **(1)**

If no indication of order in (a) assume as in question.
If order is wrong can still score 'role' mark.

4

(b) Alcohol: Role = butan-2-ol **(1)**

Not 2-hydroxybutane or but-2-ol

Appropriate structure for $CH_3CH(OH)\ CH_2CH_3$ **(1)**

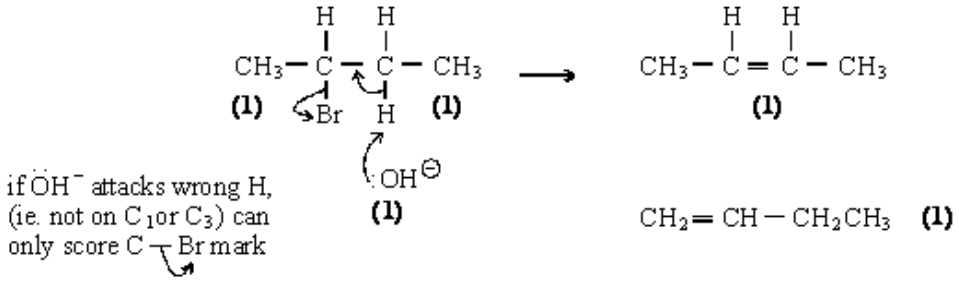
Brackets not essential

S_N2 version	S_N1 version
$\overset{\delta+}{C}-\overset{\delta-}{Br}$ bond is polar	C–Br bond is polar **(1)**
Lone pair of OH^-	C–Br bond breaks **(1)**
Attacks the $C^{\delta+}$	forming carbocation / carbonium ion **(1)**

M1 can be scored from a diagram, M2 and M3 from written explanation only

5

(c)



If but-2-ene not given here it may be obtained from cis / trans isomer

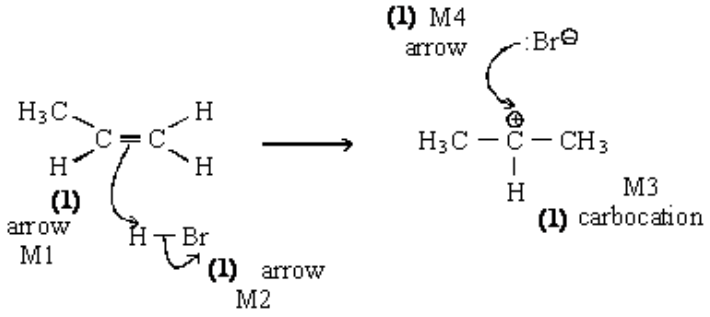
H lost from different carbon atoms (1)
H removes from C^1 and C^3 to give two isomers (1)
Draws clear Cis and trans isomers for but-2-ene

Can score these marks from a diagram

8

[17]

M2. (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* ·

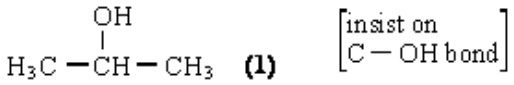
(ii) $CH_3CH_2\overset{\oplus}{C}H_2$ **(1)**

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

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

5

(b) (i) *Structure*:



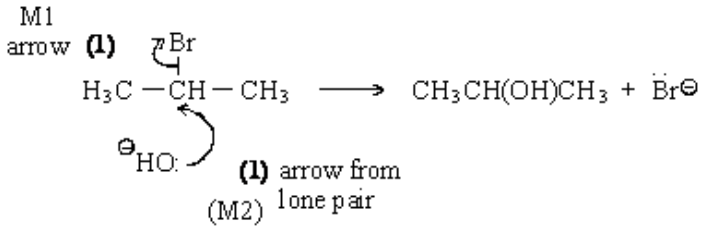
No credit for propan-1-ol even when named correctly
Credit propane-2-ol

Name: propan-2-ol **(1)**

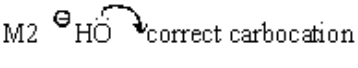
Not 2-hydroxypropane

(ii) *Name of mechanism*: nucleophilic substitution **(1) (both words)**
(NOT S_N1 or S_N2)

Mechanism:



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

i.e. M1  M2 

5

(c) (i) elimination **(1)**
Ignore nucleophylic elimination
Penalise electrophilic elimination

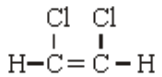
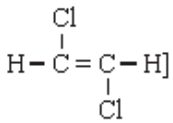
(ii) base **(1)**
OR proton acceptor
NOT nucleophile (base)

2

[12]

M3. (a) (i)

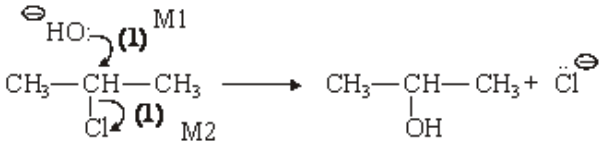
Isomer 1 either order *Isomer 2*

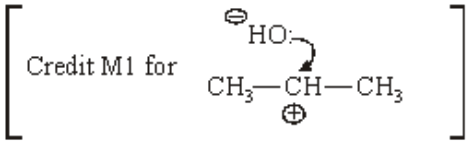
[credit  and ]

(ii) restricted rotation OR no rotation OR cannot rotate **(1)**

3

(b) (i) *Mechanism*:





M1 and M2 independent

Curly arrows must be from a bond or a lone pair

Do not penalise sticks

Penalise M1 if Na—OH *precedes (penalise this once)*

Penalise incorrect $\delta+$ $\delta-$ *for M2*

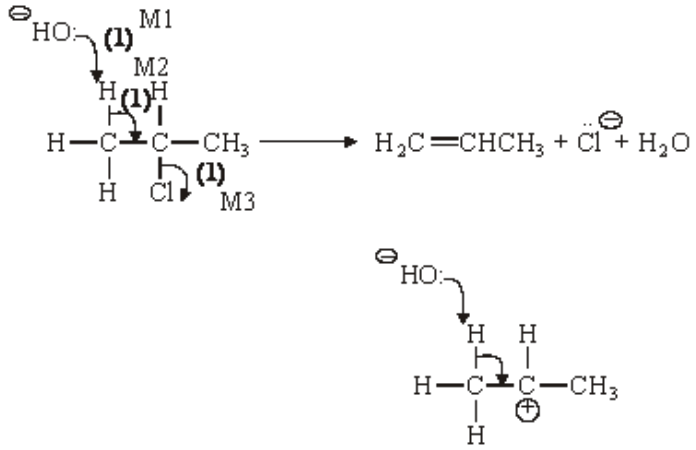
Penalise + on C atom for M2

Only allow M1 for incorrect haloalkane

Role of the hydroxide ion: nucleophile **(1)**
electron pair donor
lone pair donor

NOT nucleophilic substitution

(ii) *Mechanism*:



Only allow M1 and M2 for incorrect haloalkane unless RE on (i)

+ charge on H on molecule, penalise M1

M3 independent

M2 must be to correct C–C

M1 must be correct H atom

Credit M1 and M2 via carbocation mechanism

No marks after any attack of C ⊕ *by* OH^-

Role of the hydroxide ion: base **(1)**

proton acceptor

accepts H^+

7

[10]

M4. (a) M1 curly arrow <u>from lone pair</u> on oxygen of hydroxide ion to H atom on C-H adjacent to C-Br

1

M2 curly arrow <u>from single bond</u> of adjacent C-H <u>to adjacent single bond</u> C-C

(only credit M2 if M1 is being attempted to correct H atom)

1

M3 curly arrow <u>from C-Br bond</u> to side of Br atom

(credit M3 independently)

1

(b) Ml credit a correct structure for either geometrical isomer and its designation as either *cis* or *trans.*
OR credit two correct geometrical isomer structures (ignore the names)
OR credit two correct names for *cis* pent-2-ene and *trans* pent-2-ene (ignore the structures)

1

M2 credit a second mark if all four parts of the required structures and names are correct.

(credit "linear" structures)
(insist on the alkyl groups being attached clearly by C-C bonds)

1

(c) (i) Ml curly arrow from middle of C = C bond to H atom on H-Br

(penalise M1 if partial negative charge or formal positive charge on H)
(penalise Ml if pent-2-ene is used)

1

M2 curly arrow from H-Br bond to side of Br atom

1

M3 correct structure for correct secondary carbocation

1

M4 curly arrow from lone pair on bromide ion to the positive carbon of carbocation, ensuring that bromide ion has a negative charge.

(with the exception of pent-2-ene, if the wrong alkene is used, only penalise the structure M3)
(penalise the use of two dots in addition to a covalent bond, once only)

1

(ii) 1-bromopentane

1

(iii) Ml 2-bromopentane is formed *via* the secondary (or 2°) carbocation

1

OR 1-bromopentane is formed *via* the primary (or 1°) carbocation
M2 a secondary carbocation is more stable than a primary carbocation -
award this mark only if the quality of language justifies the award.

(the argument must involve clear statements about carbocations)

1

[12]

M5. (a) 2-bromobutane;

1

(b) Elimination;

(penalise "nucleophilic" OR "electrophilic" before the word "elimination")

1

M1: curly arrow from lone pair on oxygen of hydroxide ion to H atom on correct C-H adjacent to C-Br;

(penalise M1 if KOH shown as covalent with an arrow breaking the bond)

1

M2: curly arrow from single bond of adjacent C-H to adjacent single bond C-C;

(only credit M2 if M1 is being attempted to correct H atom)

1

M3: curly arrow from C-Br bond to side of Br atom;

(credit M3 independently unless arrows contradict)
(Credit possible repeat error from 2(c)(iii) for M3)
(If the wrong haloalkane is used OR but-1-ene is produced, award MAX. 2 marks for the mechanism)
(If E1 mechanism is used, give full credit in which M1 and M2 are for correct curly arrows on the correct carbocation)

(c) (i) (structural) isomers/hydrocarbons/compounds/they have the same molecular formula, but different structural formulas/different structures; 1

(penalise statements which are not expressed in good English and which do not refer clearly to structural isomers i.e. plural)
(penalise statements which refer to "different (spatial) arrangements")
(credit" different displayed formulas")
(Q of L mark)

(ii) Correct structure for but-1-ene;

1

[7]

M6. (a) (base) elimination

(penalise other words before 'elimination' e.g. nucleophilic)

1

M1: curly arrow from lone pair of electrons on oxygen of hydroxide ion

(insist on a lone pair of electrons on the oxygen atom and a negative charge, but only credit this mark if the attack is to a correct H atom)

1

M2: curly arrow from the middle of the C-H bond to the middle of the C–C bond

1

(only credit this mark if the arrow originates from the correct C–H bond and if an attempt has been made at M1)

M3: curly arrow from the middle of the C–Br bond towards/alongside the Br atom

(credit M3 independently unless the bond breaking is contradicted by an additional arrow)

(penalise curly arrow if the C–Br has a formal positive charge)

(credit full marks for an E1 mechanism, with M2 awarded for a correct curly arrow on the correct carbocation)

(award a maximum of two marks for either an incorrect haloalkane or an incorrect organic product)

(maximum 2 marks for use of 'sticks' for the haloalkane, unless RE from 2(b), when credit can be given)

(b) (i) **M1**: compounds with the same structural formula

1

M2: but the bonds/groups/atoms have different spatial arrangements or orientation or configuration/are arranged differently in space/3D

(ignore reference to the same molecular formula for M1)

1

(ii) **M1**: correct structural representation for cis-but-2-ene and its name or its identification as the cis isomer

1

M2: correct structural representation for trans-but-2-ene and its name or its identification as the trans isomer

(accept representations which are 90° to linear)

(award one mark for two correct structures but either wrong/no names)

(maximum 1 mark for an incorrect alkene)

1

(iii) geometric(al) or cis-trans

1

(c) nucleophile or electron pair donor

(penalise 'base')

1

(d) $CH_3CH_2CH_2CH_2Br + 2NH_3 \rightarrow CH_3CH_2CH_2CH_2NH_2 + NH_4Br$

(M1 correct product)

(M2 balanced equation using $2NH_3$ and leading to NH_4Br)

(penalise M1 for use of $C_4H_9NH_2$ or for incorrect haloalkane, but allow consequent correct balancing of equation with 2 moles of ammonia)

2

(1–)butylamine

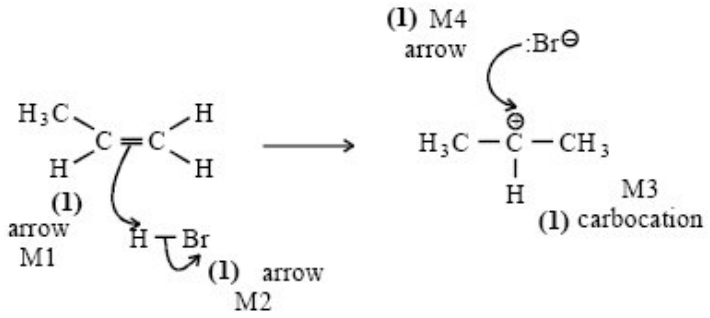
(credit 1–aminobutane and butyl–1–amine)

(award QoL mark for correct spelling)

1

[13]

M7. (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) $\oplus$
$CH_3CH_2CH_2$
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*: $H_3C-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$ **(1)** [insist on C — OH bond]

1

Name: propan-2-ol

Not 2-hydroxypropane

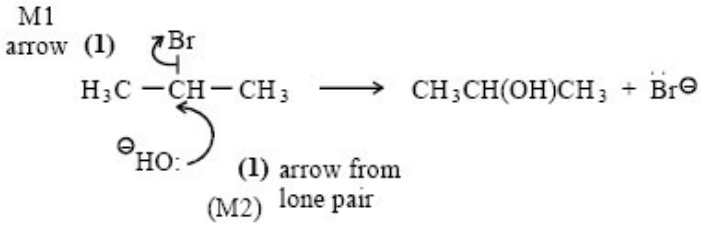
1

(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]

M8. (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

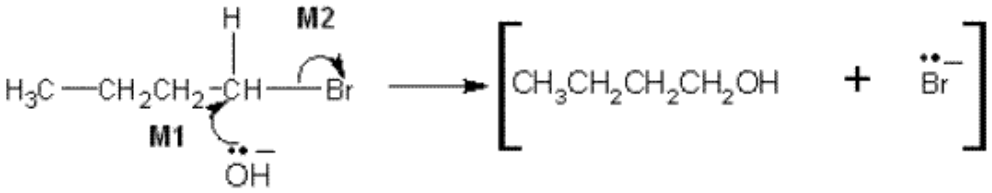
1

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]

M9. (a) (i) Electron pair donor

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) Replacement of the halogen (atom) (by the nucleophile)

OR

The carbon-halogen bond/C-X 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) Splitting molecules using/by water

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

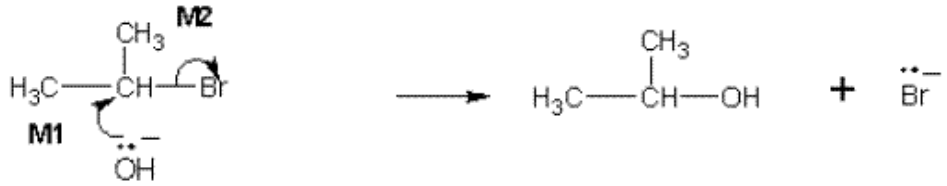
(Heat) energy/enthalpy required/needed/absorbed (at constant pressure) for homolysis of the (C–X/the carbon-halogen) bond

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

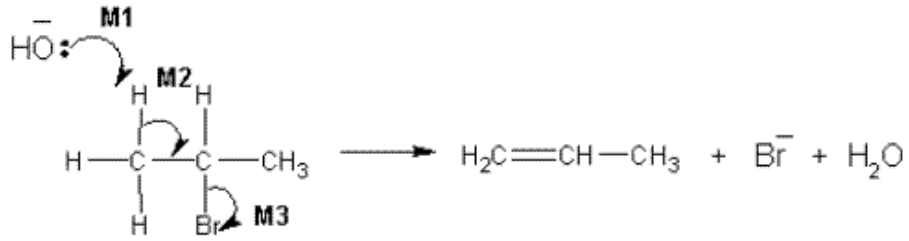
Penalise once only for a line and two dots to show a bond.

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 <u>to the correct</u> 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 <u>original molecule</u>

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

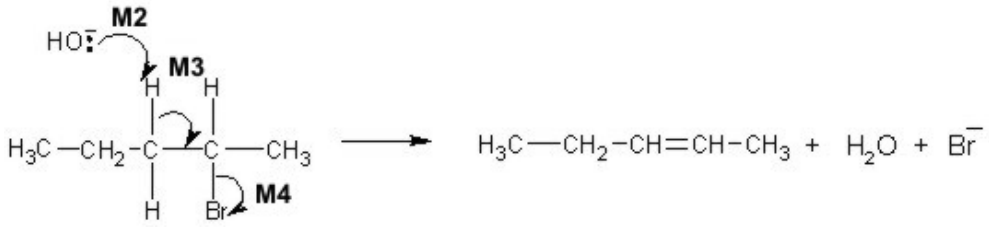
M2 could be on the spectrum

Ignore reference to other absorptions

2

[11]

M10. (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**

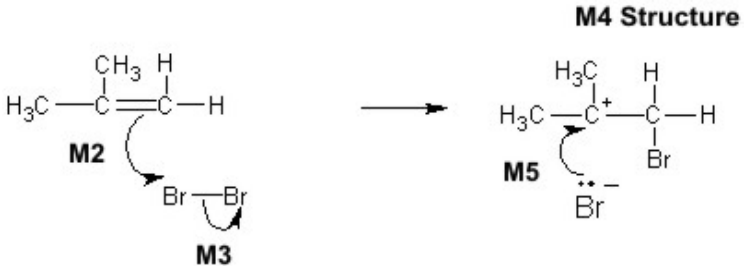
$CH_3CH_2CH_2CH=CH_2$

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*

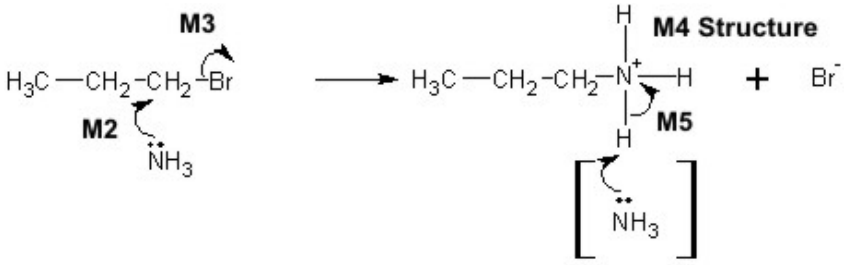
wrong organic reactant or wrong organic product (if shown) or primary carbocation.

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"

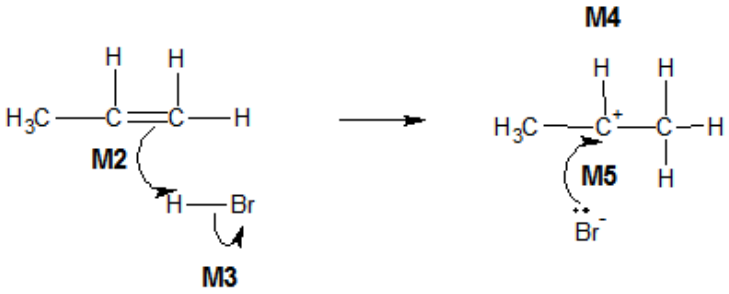
5

[15]

M11. (a) **M1 electrophilic addition**

*For **M1**, both words required*

Accept phonetic spelling



For the mechanism

***M2** Ignore partial negative charge on the double bond*

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

***M3** Penalise partial charges on H–Br bond if wrong way and penalise formal charges*

M3 must show the breaking of the H–Br bond

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

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

***Maximum any 3 of 4 marks for the mechanism** for wrong (organic) reactant **OR** wrong organic product (if shown) **OR** primary carbocation*

Accept the correct use of sticks

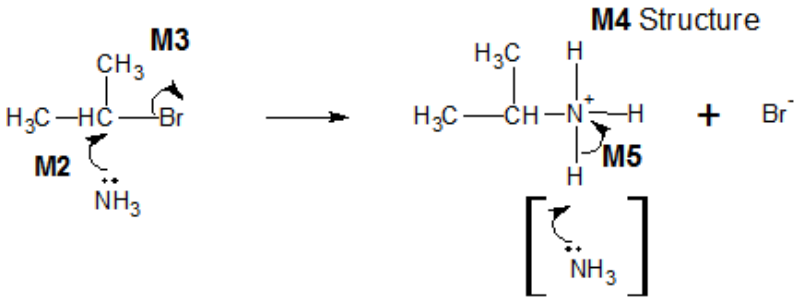
NB These are double-headed arrows

5

(b) **M1 <u>Nucleophilic substitution</u>**

*For **M1**, both words required*

Accept phonetic spelling



For the mechanism

*Penalise **M2** if NH_3 is negatively charged*

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

*Penalise **M3** for formal charge on C of the C–Br or incorrect partial charges on C–Br*

*Penalise **M3** for an additional arrow from the Br to something else*

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

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

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

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

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

***<u>Maximum any 3 of 4 marks for the mechanism</u>** for wrong organic reactant **OR** wrong organic product if shown*

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

Accept the correct use of "sticks"

NB These are double-headed arrows

5

(c) M1 (addition) polymerisation OR poly-addition

Ignore "additional"

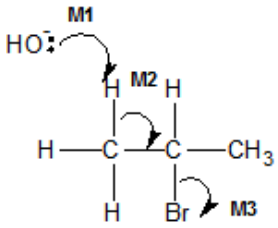
Credit polyprop-1-ene and polypropylene

M2 poly(propene) / polypropene

Penalise "condensation polymerisation"

2

(d)



*Penalise **M1** if covalent KOH*

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

*Penalise **M3** for formal charge on C of C–Br or incorrect partial charges on C−Br.*

M2 must show an arrow from a correct C–H bond adjacent to the C–Br bond to the appropriate C–C bond. Only award if an arrow is shown attacking the H atom of a correct C−H bond in **M1**

Ignore other partial charges

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

M3 is independent provided it is from their original molecule, but **CE=0 if nucleophilic substitution**

***Maximum any 2 of 3 marks** for wrong organic reactant*

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

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

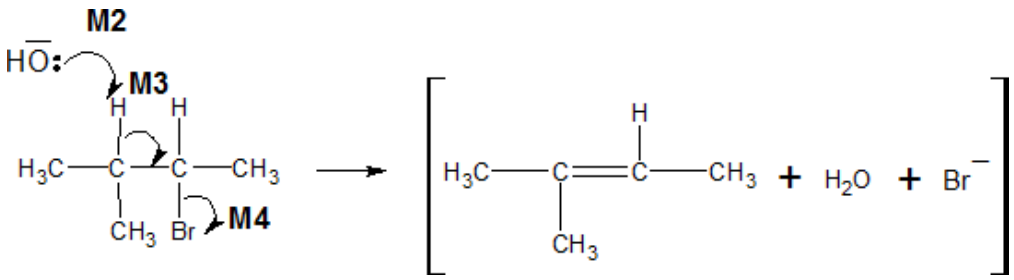
NB These are double-headed arrows

3

[15]

M12. (a) (i) M1 **Elimination**

M1 *Credit "base elimination" but no other prefix.*



*Penalise **M2** if covalent KOH*

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

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

Ignore other partial charges

M3 must show an arrow from a correct C−H bond adjacent to the C−Br bond to a correct C-C bond. Only award if an arrow is shown attacking the H atom of a correct adjacent C−H bond in **M2**

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

M4 is independent provided it is from their original molecule, **BUT CE=0 for the mechanism (penalise M2, M3 and M4 only) if nucleophilic substitution mechanism is shown**

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

Credit the correct use of "sticks" for the molecule except for the C−H being attacked

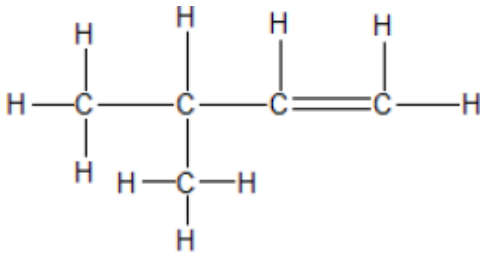
Award full marks for an E1 mechanism in which **M4** is on the correct carbocation

*Penalise **M4**, if an additional arrow is drawn from Br eg to K^+*

NB These are double-headed arrows

4

(ii) Displayed formula for 3-methylbut-1-ene



All bonds and atoms must be drawn out, but ignore bond angles

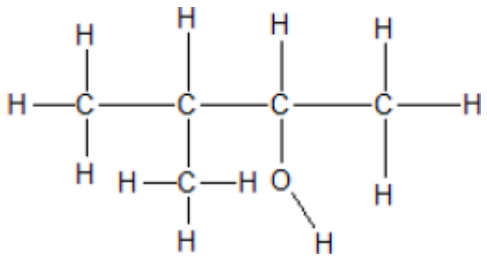
1

(iii) Position(al) (isomerism or isomer)

Penalise any other words that are written in addition to these.

1

(b) (i) Displayed formula for 3-methylbutan-2-ol



All bonds and atoms must be drawn out, but ignore bond angles.

1

(ii) Any **one** from

- Lower / decreased temperature **OR** cold
- Less concentrated (comparative) ***OR*** dilute KOH
- Water (as a solvent) / (aqueous conditions)

Ignore "pressure".

1

(iii) Nucleophilic substitution

Both words needed - credit phonetic spelling.

1

(iv) (Strong / broad) absorption / peak in the range **3230 to 3550** cm^{-1} or specified value in this range or marked correctly on spectrum

*Allow the words "dip" **OR** "spike" **OR** "trough" **OR** "low transmittance" as alternatives for absorption.*

1

[10]