3.2.8 Haloalkanes

Nucleophilic Substitution

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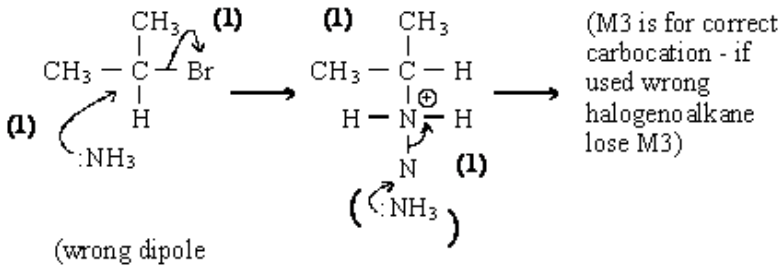
267 minutes

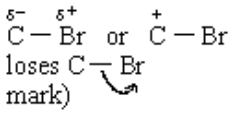
264 marks

M1. (a) *Name of mechanism*: nucleophilic substitution **(1)**

Mechanism:



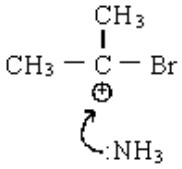
(wrong dipole



loses C — Br mark)

Marks S_N1 using same points

∴ *M2 requires*



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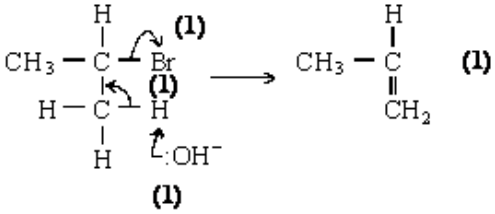
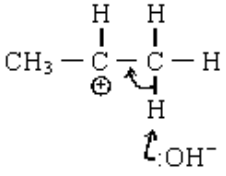
(b) *Role of potassium hydroxide*: Base **(1)**

Mechanism:



Mark E1 using same points

∴ M2/M3



5

[10]

M2. (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)**

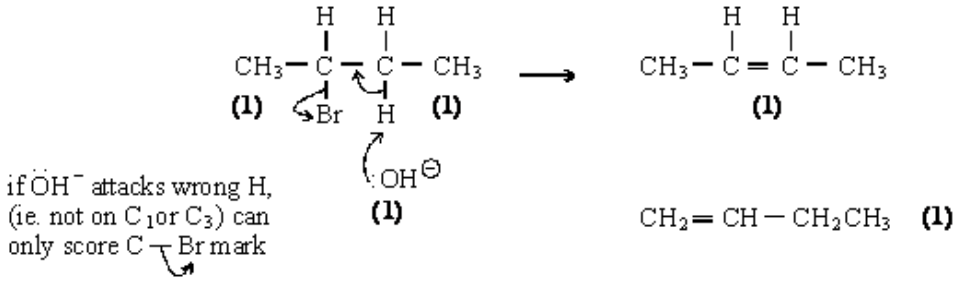
Brackets not essential

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]

M3. **Penalise missing • once only**

(i) $Cl_2 \rightarrow 2\ Cl\bullet$ **(1)**

(ii) $CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$ **(1)**

(iii) $CH_2Cl_2 + Cl\bullet \rightarrow CHCl_2\bullet + HCl$ **(1)**

$CHCl_2\bullet + Cl_2 \rightarrow CHCl_3 + Cl\bullet$ **(1)**

Can reverse order

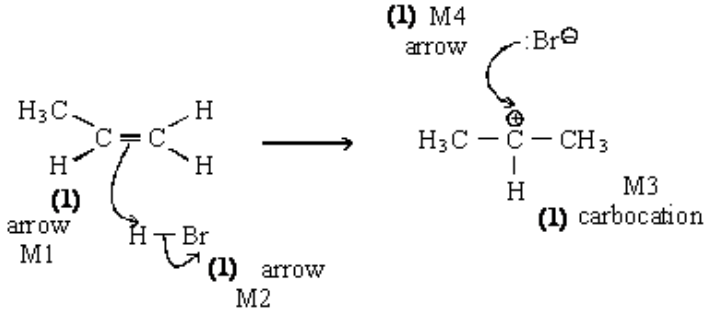
(iv) Effect on rate: increases **(1)** **If decrease given C.E zero marks**

Explanation: more Cl• radicals formed **(1)**

More Cl atoms, more Cl—Cl or Cl_2 bonds broken, more Cl_2 have E_A, increased rate of Cl• production

[6]

M4. (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* ·

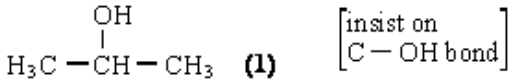
(ii) $CH_3CH_2\overset{\oplus}{C}H_2$ **(1)**

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*:



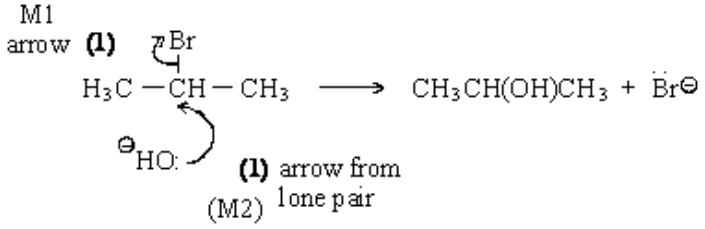
(1)

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 C — Br M2 ⊖HO correct carbocation

5

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

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

2

[12]

M5. (a) (i) $CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$ **(1)**

(ii) UV light / sunlight OR high T OR T ≥ 500°C **(1)**
maxT = 1000°C
NOT heat / light
Ignore pressure

2

(b) *Initial step*: $Cl_2 \rightarrow 2Cl\cdot$ **(1)**

Condition could be on first equation arrow

First propagation step: $CHCl_3 + Cl\cdot \rightarrow \dot{C}Cl_3 + HCl$ **(1)**

Second propagation step: $\dot{C}Cl_3 + Cl_2 \rightarrow CCl_4 + Cl\cdot$ **(1)**

A termination step: $\dot{C}Cl_3 + Cl\cdot \rightarrow CCl_4$ **(1)**

OR $2\dot{C}Cl_3 \rightarrow C_2Cl_6$

Not $2Cl\cdot \rightarrow Cl_2$

Ignore additional termination steps

4

[6]

M6. (a) Reaction 2: NaOH OR KOH **(1)** M1 alcohol (ic) OR ethanol (ic)**(1)** M2

ignore heat

Condition mark linked to correct reagent but award M2 if OH^- or base or alkali mentioned

Reaction 3: concentrated H_2SO_4 OR H_3PO_4 M1 **(1)** heat **(1)** M2

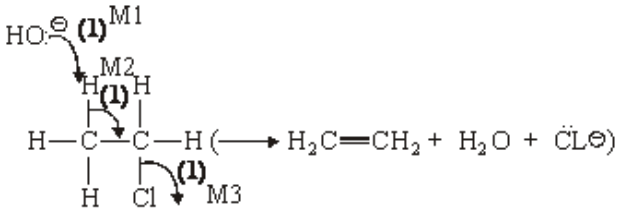
OR 150°C - 200°C

Condition mark linked to correct reagent but award M2 if H_2SO_4 or H_3PO_4, but not concentrated

Penalise reagent and condition if dilute H_2SO_4 / H_3PO_4

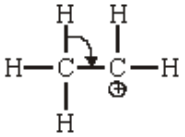
4

(b) Mechanism:



Award M3  *independently*
M1 and M2 must be to / from correct places

E1 mechanism possible in which M2



Name: of mechanism = elimination **(1)**

NOT dehydrohalogenation

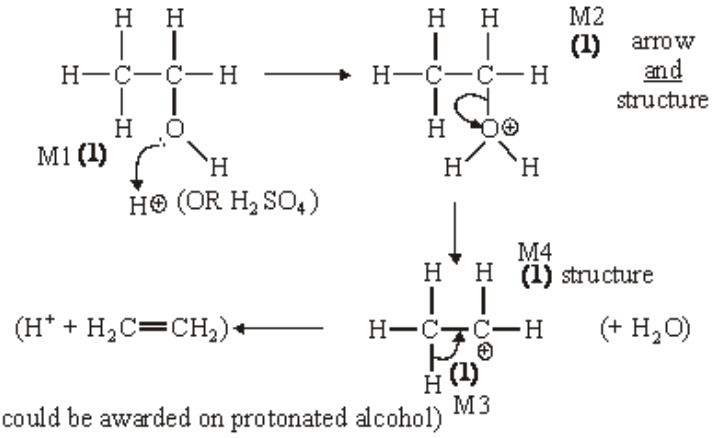
Ignore "base" OR "nucleophilic" before elimination

Reason: Reaction 2 has (very) low yield **(1)**

QoL OR chloroethane has to be made (from ethane)
OR chloroethane is expensive
OR chloroethane is not redily available

5

(c) Mechanism:



Name of mechanism = elimination **(1)**

NOT dehydration alone

Reason: Ethanol could come from (fermentation of) renewable

*QoL sugars / glucose / carbohydrates / sources **(1)***

6

[15]

M7. (a) (i) UV light OR sunlight OR T ≥ 450°C **(1)**
NOT high T

(ii) (free) radical substitution **(1)**

(iii) CCl_4 **(1)** OR named

3

(b) (i) $CH_3Cl + KCN \rightarrow CH_3CN + KCl$ **(1)**

CN^- Cl^-

(ii) nucleophilic substitution **(1)**

(iii) C–Br bond is weaker (than C–Cl bond)
OR C–Br bond enthalpy is less than C–Cl **(1)**
Ignore electronegativity

3

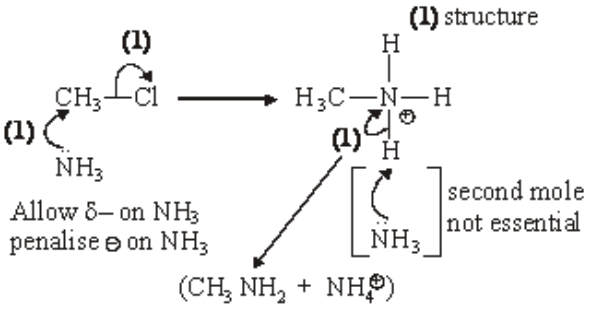
(c) CH_3COOH OR ethanoic acid **(1)**

1

(d) (i) $\overset{\delta+}{C}-\overset{\delta-}{Cl}$ OR C–Cl is polar **(1)** OR C atom is electron deficient / δ+

(ii) methylamine **(1)** only

(iii) S_N1 scores full marks



6

[13]

M8. (a) (i) (Free) radical substitution

(Both words needed)

1

(ii) M1 initiation ONLY

1

M2 ultra-violet light OR sunlight OR 1000°C ≥ T ≥ 450 °C

(Ignore reference to temperature if included with uv light)

(Penalise "high temperature" for M2)

1

(iii) $2\dot{C}H_3 \rightarrow C_2H_6$

(OR CH_3CH_3 as alternative to C_2H_6)

1

(iv) $CH_3Br + Br_2 \rightarrow CH_2Br_2 + HBr$

1

(b) (i) Electron pair donor

OR species with an electron pair able to form a covalent bond.

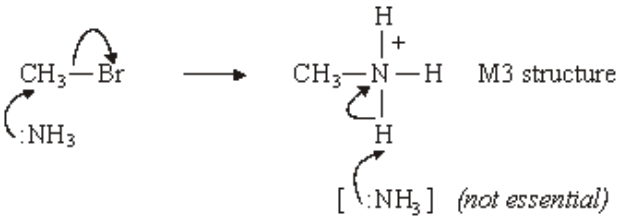
1

(ii) Methylamine

(Credit "aminomethane")

1

(iii)



1

M1 arrow to show breakage of C – Br bond

1

M2 arrow from lone pair on N of NH_3 to form bond with C

1

M4 arrow from bond of N – H to N atom of $CH_3\overset{+}{N}H_3$

(Ignore partial charges on haloalkane but penalise if incorrect)

(Accept $CH_3\overset{+}{N}H_3$ for M3)

(Full credit for carbocation mechanism; M1 for C – Br bond breakage and M2 for lone pair attack on carbocation)

(Second mole of ammonia not essential to mechanism for full credit)

1

[11]

M9. (a) (i) Electrophilic addition

(Both words required)

1

(ii) M1 the reaction to form 1-bromopropane goes *via* the primary carbocation OR 1° carbocation

OR *via* $CH_3CH_2\overset{+}{C}H_2$

M2 primary carbocations are less stable than secondary carbocations

(Credit converse arguments for M1 and M2 i.e. the reaction to form 2-bromopropane goes via the secondary carbocation , M1, and secondary carbocations are more stable than primary carbocations, M2)

(Accept the use of "carbonium ions" as an alternative to carbocation)

1

(b) M1 NaOH OR KOH OR correct name

1

M2 aqueous or solution in water *(ignore heat, reflux etc.)*

(Penalise M1 for hydroxide ion alone, but mark on and credit M2)
(Credit M2 ONLY for H_2O as reagent and heat / warm / T=50 to 100°C)
(NaOH(aq) scores M1 and M2 provided it is not contradicted)
(Penalise M2 if NaOH(aq) followed by concentrated or ethanol)
(Penalise M1 and M2 if followed by acid)

1

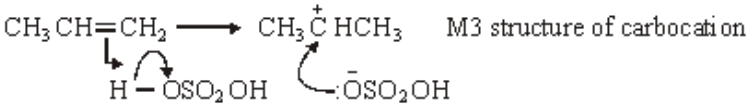
(c) Ethanolic OR alcoholic OR CH_3CH_2OH / CH_3OH solvent OR aqueous ethanol/alcohol
OR higher temperature *(must be comparative)*

(Ignore heat or heat under reflux)
(Credit part (c) independently from part (b))
(Penalise "ethanoic")

1

(d) (i) Secondary OR 2°

1

(ii) 

M1 arrow from double bond to H of H – O bond
M2 arrow from bond to oxygen atom to show H – O bond breakage
M4 arrow from lone pair of electrons to carbon atom of carbocation

(Penalise M1 if arrow goes to H_2SO_4 or to formal positive charge on H, but ignore partial charges on sulphuric acid unless wrong)

(Credit M2 for H^+ ion)

(For M4, accept negative charge anywhere on the ion)

4

(iii) Catalyst ONLY

(Ignore homogeneous, heterogeneous)

1

[12]

M10. (a) M1 X is 1,2-dibromoethane only

1

M2 electrophilic addition

(both words needed)

1

M3 the double bond is a centre of electron density
OR electron-rich
OR nucleophilic
OR a source of an electron pair
OR a pi cloud/bond of electrons

1

M4 a dipole or polarity is induced/created/formed in the Br-Br bond/molecule -
award this mark only if the quality of language justifies the award.

1

(b) nucleophilic substitution

(both words needed)

1

Mechanism M1 curly arrow <u>from lone pair</u> on oxygen of hydroxide ion to C atom of C-Br

1

Mechanism M2 curly arrow <u>from C-Br bond</u> to side of Br atom

(a possible repeat error here from Question 4a)
(award a maximum of one mark for the wrong haloalkane)
(credit an SNl mechanism in which Ml will be a curly arrow <u>from the lone pair</u> on oxygen of the hydroxide ion to the correct positive <u>carbon</u> atom)

1

Y is susceptible to attack by hydroxide ions for one of the following reasons

- the C-Br bond is polar
- the carbon atom is partially positive (or shown as such)
- the carbon atom is electron deficient

1

(c) M1 oxygen

(ignore "air")

1

M2 silver or silver-based

(penalise silver nitrate)

1

M3 Z is epoxyethane

1

M4 epoxyethane

- has a strained ring structure
- has a bond angle of 60°
- has a bond angle significantly less than tetrahedral

(ignore "unstable", "has strained bonds", "is stressed")

1

(d) Ethane-1,2-diol is used in antifreeze
OR in the manufacture of PET/Terylene/polyester
(penalise "solvent" or "plasticiser")

1

Hazard in Route *via* X/Y

- o bromine is toxic or corrosive
- o sodium hydroxide is corrosive or caustic

1

Hazard in Route *via* epoxyethane

- o risk of explosion in reaction 4
- o epoxyethane is toxic
- o epoxyethane is a respiratory irritant
- o epoxyethane causes neurological damage

1

[15]

M11. (a) (i) Electron pair/ lone pair acceptor OR seeking/bonds with an electron pair
(insist on reference to a pair of electrons)

1

(ii) M1 curly arrow from middle of C=C bond of the alkene towards/ alongside the H atom of the H-Br;
(penalise arrows which go towards one of the carbon atoms)
(ignore a partial negative charge on the C=C)

1

M2 curly arrow from H-Br bond to side of Br atom;
(penalise M2 if there are formal charges on HBr or if there are partial charges which are the wrong)
(penalise M2 if the single bond has two dots in addition to the line)

1

M3 correct structure for carbocation;
(penalise M3 if the positive charge is placed on the end of a bond)
(penalise M3 if any alkene other than ethene is used - all other marks can score)

1

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

(b) (i) M1 Oxygen *OR* O_2*;*

(do not credit "air" alone, but otherwise ignore)

M2 silver *OR* Ag OR silver-based

(penalise silver nitrate)

1

(ii) correct structure for epoxyethane;

(penalise poorly presented C-O bonds)

1

(iii) water

OR

H_2O;

(credit steam OR H_2SO_4 (aqueous OR dilute) OR NaOH(aq) OR HCl(aq),
OR H_3PO_4(aq), but insist that (aq) is included)
(do not credit HCl or H_2SO_4 (concentrated or without water present))

1

(c) (i) M1: potassium cyanide OR KCN OR sodium Cyanide OR NaCN;

(ignore conditions - dissolved in (aq) or (alc) or KOH(aq) all work)
(penalise HCN)

1

M2: propanenitrile;

(credit propan-1-nitrile OR propan nitrile, but not propanitrile)

1

(ii) M1: ammonia OR NH_3;

(If formula is written, insist that it is correct)
(ignore conditions, but penalise acidic)

1

M2: ethylamine;

(credit aminoethane)

1

(iii) M1: curly arrow <u>from lone pair</u> on nitrogen of (correct formula for) ammonia towards/alongside C atom of C-Br;

(penalise M1 if formula of ammonia is wrong or has a negative charge or has no lone pair or arrow is from negative charge)

1

M2: curly arrow <u>from C-Br bond</u> towards/alongside side Br atom;

(credit M2 independently)
(penalise M2 if formal positive charge on C atom of C-Br)

1

M3: correct structure of the ethylammonium ion;

(credit the structure drawn out with all four bonds around the nitrogen atom OR written as $C_2H_5NH_3^+$ OR $CH_3CH_2NH_3^+$)

1

M4: curly arrow <u>from the middle of one of the H-N bonds</u> towards the positive *N atom*;

(possible to credit M4 on an incorrect ethylammonium ion with no positive charge)
(ignore use of ammonia or bromide ion etc. to remove proton from ethylammonium ion)
(If the wrong haloalkane is used, award MAX. 3 marks for the mechanism) (If S_N1 mechanism is used, give full credit in which M1 is for a curly arrow from the lone pair of the N atom of (correct formula for) ammonia towards/alongside the positive carbon atom of $CH_3CH_2^+$)

[17]

M12. (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 <u>middle of the C–Br bond</u> 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]

M13. (a) (i) 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.

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

1

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 M3 curly arrow if the C–Br has a formal positive charge)

(ignore partial charges on the C–Br bond, but penalise if incorrect)

(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 an incorrect haloalkane)

(ignore products)

1

(ii) Haloalkane/C_2H_5Br is made from ethane

OR haloalkane is not (readily) available
OR haloalkane is expensive
OR it is (too) expensive/costly
OR (reaction) yield is too low/poor
OR it is too slow
OR a valid reference to nucleophilic substitution/alcohol formation occurring as an alternative reaction.

(ignore references to temperature or to energy consumption)

(do not credit statements which refer to the idea that this route is not chosen, because industry chooses another route e.g. cracking)

1

(b) (i) Strained ring/ bonds/ structure/molecule
OR three–membered ring
OR 60^{o} bond angle
OR bond angle much less than tetrahedral

(penalise "stressed ring")

(ignore "weak bonds", ignore "unstable")

1

(ii) ethane–1,2–diol OR correct structure

(penalise ethylene glycol OR 1,2–dihydroxyethane if these appear alone)

(credit ethan–1,2–diol)

(If both a structure and a formula are given, credit either correct one of these provided the other is a good, if imperfect, attempt)

1

(used in) antifreeze
OR
for OR in the manufacture/making/formation of terylene, polyester, PET only

(ignore reference to terylene etc. if they accompany "antifreeze"

(penalise "de–icer", "solvent", "surfactant", "plasticizer")

(If the candidate indicates that the product is antifreeze ,then this can gain credit, but not if contradicted in its use e.g. as de–icer)

1

[7]

M14. (a) Electron pair donor

OR

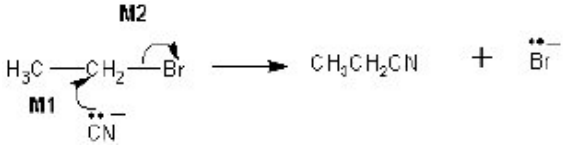
Species which uses a pair of electrons
to form a co-ordinate / covalent bond.

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

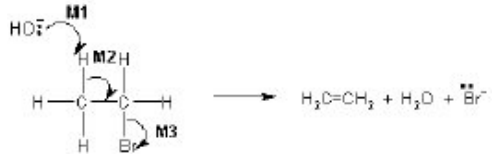
The idea that ammonia acts both initially as a nucleophile and then as a base

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.

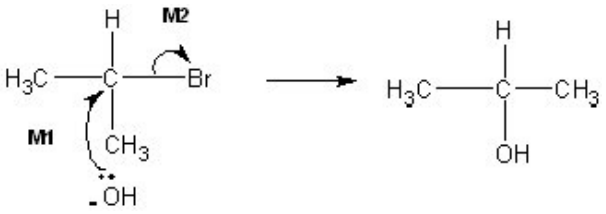
<u>Mechanism</u>
Penalise M1 if covalent KOH
Penalise M3 for formal charge on C or incorrect partial charges
Penalise once only for a line and two dots to show a bond.
*Max 2 marks **for the mechanism** for wrong reactant or "sticks"*

3

[8]

M15. (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)

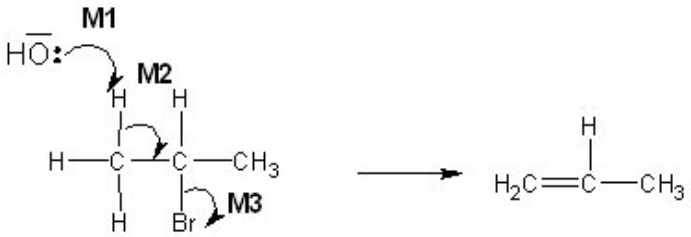
It must be clear that the discussion is about the carbon atom of the C–Br bond. NOT just reference to a polar molecule.
Ignore X for halogen

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]

M16. (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

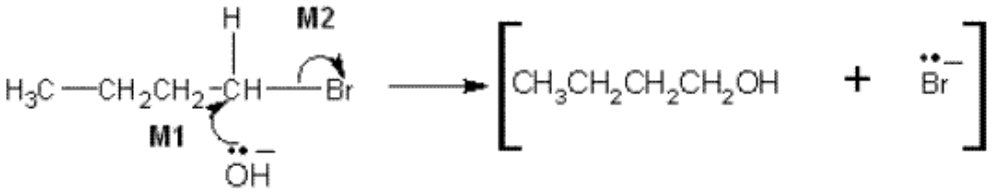
OR

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]

M17. (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

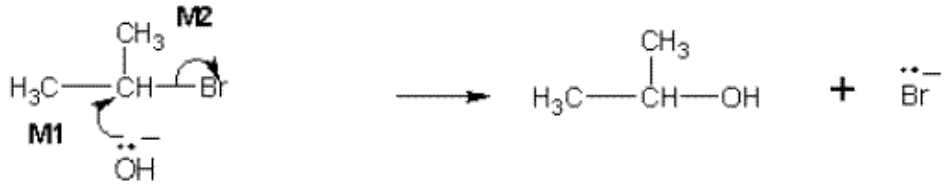
(Heat) energy/enthalpy required/needed/absorbed (at constant pressure) for homolysis of the (C–X/the carbon-halogen) bond

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

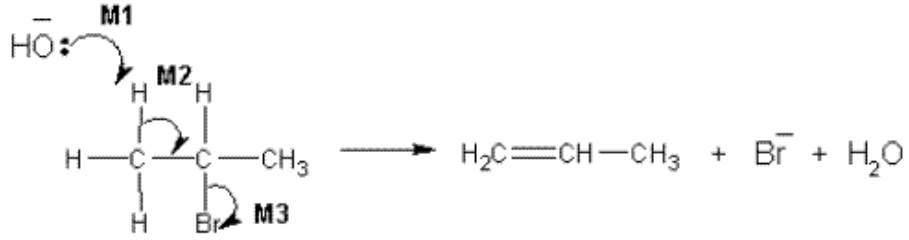
Penalise once only for a line and two dots to show a bond.

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

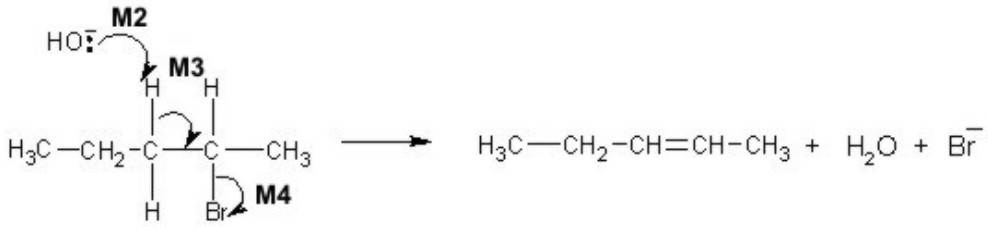
M2 could be on the spectrum

Ignore reference to other absorptions

2

[11]

M18. (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**

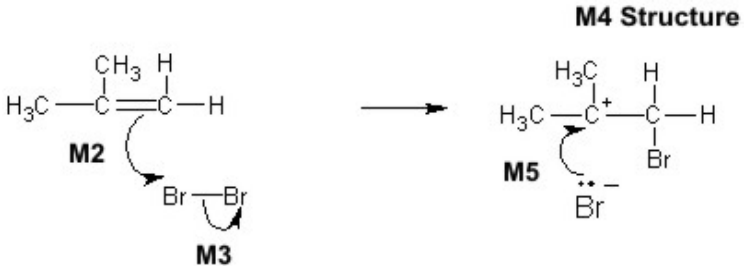
$CH_3CH_2CH_2CH{=}CH_2$

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*

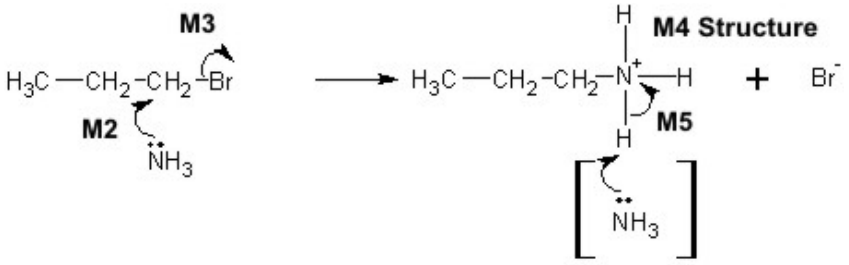
wrong organic reactant or wrong organic product (if shown) or primary carbocation.

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]

M19. (a) (i) $CH_4 + \mathbf{3}F_2 \longrightarrow CHF_3 + \mathbf{3}HF$

1

(ii) **M1 Initiation**

$F_2 \longrightarrow 2F\bullet$

M2 First propagation

$F\bullet + CHF_3 \longrightarrow \bullet CF_3 + HF$

M3 Second propagation

$F_2 + \bullet CF_3 \longrightarrow CF_4 + F\bullet$

M4 Termination (must make C_2F_6)

$\mathbf{2}\bullet CF_3 \longrightarrow C_2F_6$ or CF_3CF_3

Penalise absence of dot once only.

Radical dot on $\bullet CF_3$ can be anywhere but if the structure is drawn out, the dot must be on the carbon atom. Penalise this error once only.

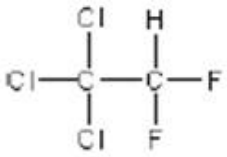
Penalise once only for a line and two dots to show a bond.

Penalise each of "Fl" and lower case F, once only in this clip

4

(b) (i) Displayed formula

e.g.



<u>All bonds</u> must be drawn out.
Ignore bond angles. Penalise "sticks"

1

(ii) **M1** <u>C–Cl</u> bond OR <u>carbon-chlorine</u> bond

M2 <u>chlorine atom</u> OR <u>chlorine (free) radical</u>

M3 $\mathbf{2}O_3 \longrightarrow \mathbf{3}O_2$

M1 NOT carbon-halogen
Penalise incorrect spelling of chlorine <u>once only</u> in this clip
M2 ignore formulae
Ignore Cl_2 or Cl• or ClO• balanced on <u>both</u> sides of the equation
Ignore other equations leading to the overall equation

3

[9]

M20. (a) **M1 Safety (in Process 1)**

Sodium hydroxide / alkali is corrosive / harmful / caustic or sodium hydroxide is alkali(ne)

Ignore references to chromium compounds

OR

Bromine compounds are toxic / poisonous

*"Carbon-neutral" alone is insufficient for **M2***

M2 Environmental

Ignore references to greenhouse gases

Process 2 could be used as a carbon sink / for carbon capture

OR

uses waste / recycled CO_2 / CO_2 from the factory / CO_2 from the bioethanol (or biofuel) production

OR

reduces or limits the amount of CO_2 released / given out (into the atmosphere)

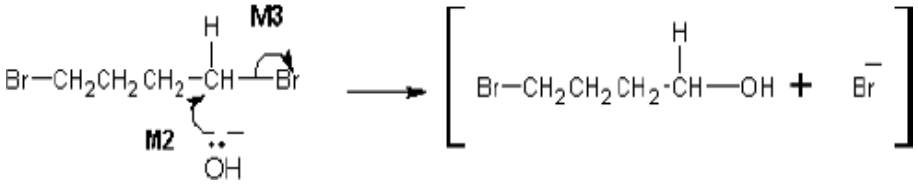
OR

Process 2 uses renewable glucose / renewable resource(s)

2

(b) (i) M1 nucleophilic substitution

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



M2 must show an arrow from the lone pair of electrons on the oxygen atom of the negatively charged hydroxide ion to the C atom.

*Penalise **M2** if covalent NaOH / KOH is used*

*Penalise one mark from **M2** or **M3** if half-headed arrows are used*

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 the original molecule

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

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

For **M2** and **M3** award full marks for an S_N1 mechanism

*For **M2** and **M3**, maximum 1 of 2 marks for the mechanism if wrong reactant is used.*

*Penalise **M3** if an extra arrow is drawn from the Br of the C–Br bond to, for example, K^+*

Accept the correct use of "sticks

NB The arrows here are double-headed

3

(ii) **M1** B

M2 C

M3 A

3

(c) **M1** fermentation

*Mark **M2** to **M4** independently*

Three conditions in any order for M2 to M4

Penalise "bacteria" and "phosphoric acid" using the list principle

M2 (enzymes from) yeast or zymase

M3 25°C ≤ T ≤ 42°C OR 298 K ≤ T ≤ 315 K

Ignore reference to "aqueous" or "water", "closed container", "pressure, "lack of oxygen",

"concentration of ethanol" and "batch process" (i.e. not part of the list principle)

M4 anaerobic / no oxygen / no air OR neutral pH

4

(d) **M1** primary OR 1° (alcohol)

Mark independently

M2 <u>acidified potassium or sodium dichromate</u>

*For **M2**, it must be a whole reagent and/or correct formulae*

OR H_2SO_4 / $K_2Cr_2O_7$ OR H^+ / $K_2Cr_2O_7$

Do not penalise incorrect attempt at formula if name is correct or vice versa

Accept phonetic spelling

If oxidation state given in name, it must be correct.

*For **M2** accept acidified potassium manganate(VII)*

OR correct combination of formula and name

M3

$HOCH_2CH_2CH_2CH_2OH + \mathbf{4}[O] \longrightarrow HOOCCH_2CH_2COOH + \mathbf{2}H_2O$

*For **M3** structures must be correct and not molecular formula*

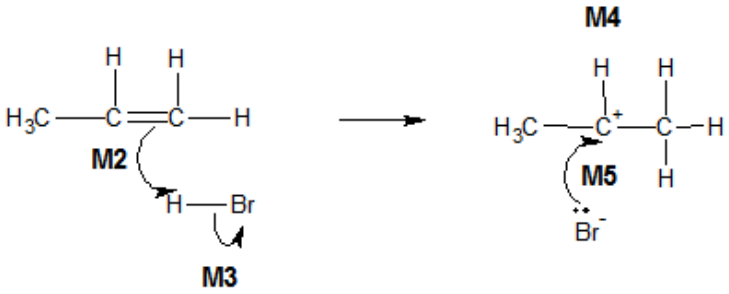
3

[15]

M21. (a) **M1 <u>electrophilic addition</u>**

*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

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

Accept the correct use of sticks

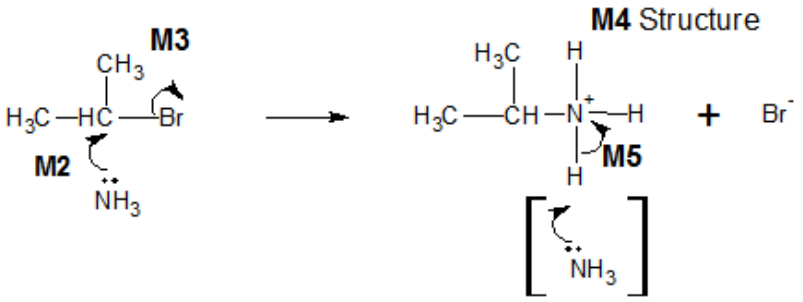
NB These are double-headed arrows

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"

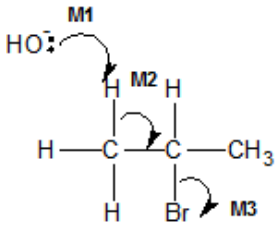
Credit polyprop-1-ene and polypropylene

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]

M22. (a) Structure for 3-methylbut-1-ene

$H_2C=CHCH(CH_3)_2$

Any correct structural representation.

Credit "sticks" and require the double bond.

1

(b) Structure for 2-methylpropan-2-ol

$(CH_3)_3COH$

Any correct structural representation.

Credit "sticks".

1

(c) Structure for propene

$H_2C=CHCH_3$

Any correct structural representation.
Credit "sticks" and require the double bond.

1

(d) Structure for 2-aminobutane

$CH_3CH_2CH(NH_2)CH_3$

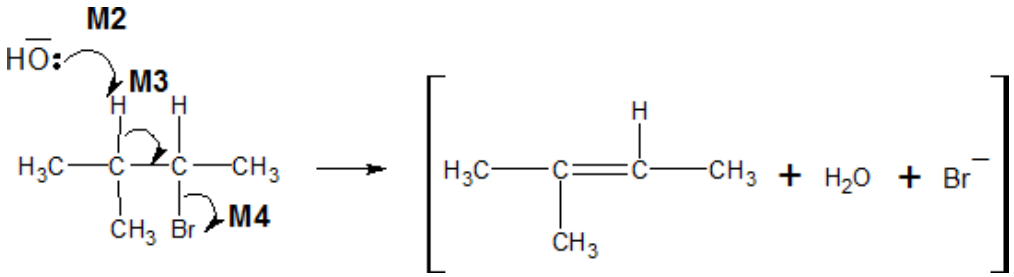
Any correct structural representation.
Credit "sticks".

1

[4]

M23. (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

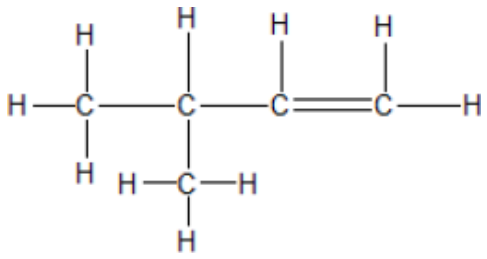
Award full marks for an E1 mechanism in which **M4** is on the correct carbocation

*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

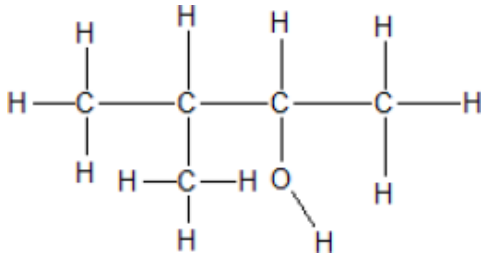
1

(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]