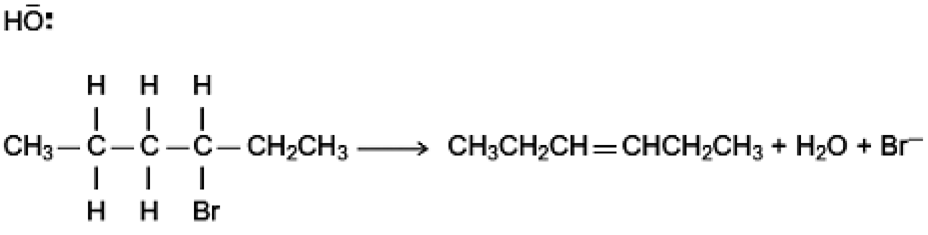
Q17.

Alkenes are useful intermediates in the synthesis of organic compounds.

(a) (i) Complete the elimination mechanism by drawing appropriate curly arrows.



$$\overset{-}{HO}: \quad CH_3-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{Br}{C}}-CH_2CH_3 \longrightarrow CH_3CH_2CH{=}CHCH_2CH_3 + H_2O + Br^-$$

(3)

(ii) Draw structures for the E and Z stereoisomers of hex-3-ene.

E isomer of hex-3-ene

Z isomer of hex-3-ene

(2)

(iii) State the meaning of the term *stereoisomers*.

(2)

(b) The equation for the first reaction in the conversion of hex-3-ene into hexan-3-ol is shown below.

$$CH_3CH_2CH{=}CHCH_2CH_3 + H_2SO_4 \longrightarrow CH_3CH_2CH_2CH(OSO_2OH)CH_2CH_3$$

Outline a mechanism for this reaction.

(4)

(Total 11 marks)

Q18.

Organic reaction mechanisms help chemists to understand how the reactions of organic compounds occur.
The following conversions illustrate a number of different types of reaction mechanism.

(a) When 2-bromopentane reacts with ethanolic KOH, two structurally isomeric alkenes are formed.

(i) Name and outline a mechanism for the conversion of 2-bromopentane into pent-2-ene as shown below.

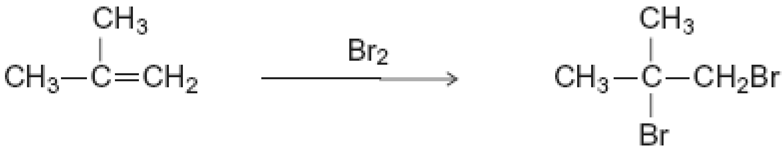
$$CH_3CH_2CH_2CHBrCH_3 \xrightarrow{\text{ethanolic KOH}} CH_3CH_2CH{=}CHCH_3$$

(4)

(ii) Draw the structure of the other structurally isomeric alkene produced when 2-bromopentane reacts with ethanolic KOH.

(1)

(b) Name and outline a mechanism for the following conversion.



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2 \xrightarrow{Br_2} CH_3-\underset{\underset{\displaystyle Br}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2Br$$

(5)

(c) Name and outline a mechanism for the following conversion.

$$CH_3CH_2CH_2Br \xrightarrow{NH_3} CH_3CH_2CH_2NH_2$$

(5)

(Total 15 marks)

Q19.

A student read the following passage on the Internet.

> Haloalkanes contain a polar covalent bond. The carbon atom of the polar covalent bond can be attacked by nucleophiles. Nucleophilic attack enables haloalkanes to undergo substitution reactions.
> A nucleophilic substitution reaction occurs when a haloalkane undergoes hydrolysis; the rate of hydrolysis of the haloalkane is influenced by the carbon–halogen bond enthalpy.

(a) Explain the meaning of each of the following terms in the information given above.

(i) *nucleophile*

(1)

(ii) *substitution,* as applied to nucleophilic substitution in a haloalkane

(1)

(iii) *hydrolysis*

(1)

(iv) *bond enthalpy,* as applied to a carbon–halogen bond.

(1)

(b) Outline a mechanism for the nucleophilic substitution reaction in which 2-bromopropane ($CH_3CHBrCH_3$) reacts with potassium hydroxide to form propan-2-ol.

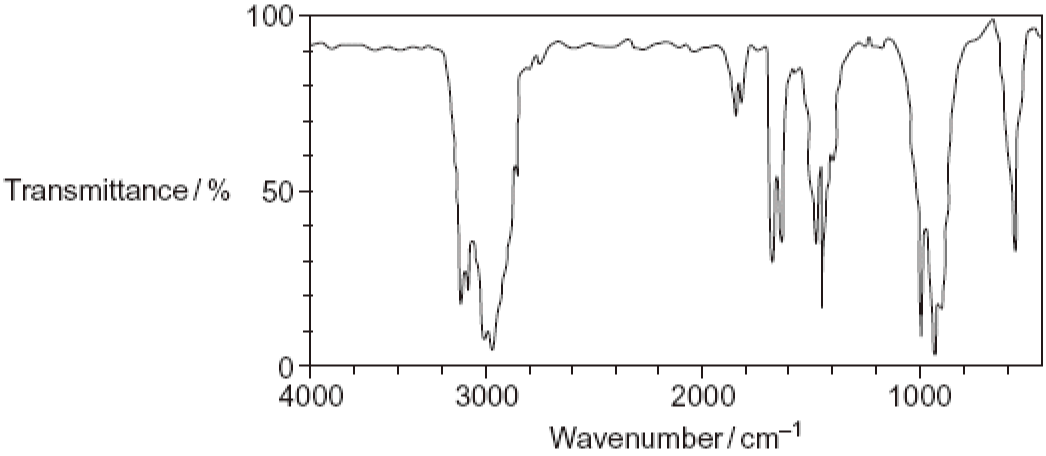
(2)

(c) Haloalkanes also undergo elimination reactions to produce alkenes.

(i) Outline a mechanism for the elimination reaction in which 2-bromopropane reacts with potassium hydroxide to form propene.

(3)

(ii) A student obtained the following infrared spectrum for the product from this elimination reaction.



Use information from the infrared spectrum to state and explain how the student deduced that the product was an alkene.
You may find it helpful to refer to **Table 1** on the Data Sheet.

____

____

____

____

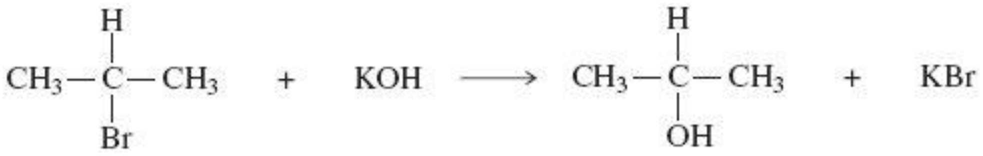
____

(2)

(Total 11 marks)

Q20.

(a) Consider the following reaction.



$CH_3CH(Br)CH_3 + KOH \rightarrow CH_3CH(OH)CH_3 + KBr$

(i) Name and outline a mechanism for this reaction.

Name of mechanism ____

Mechanism

(3)

(ii) Name the haloalkane in this reaction.

____

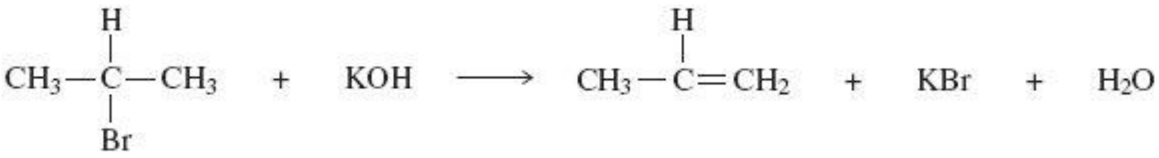
(1)

(iii) Identify the characteristic of the haloalkane molecule that enables it to undergo this type of reaction.

____

(1)

(b) An alternative reaction can occur between this haloalkane and potassium hydroxide as shown by the following equation.



$$CH_3-CH(Br)-CH_3 + KOH \longrightarrow CH_3-CH=CH_2 + KBr + H_2O$$

Name and outline a mechanism for this reaction.

Name of mechanism ____

Mechanism

(4)

(c) Give **one** condition needed to favour the reaction shown in part (b) rather than that shown in part (a).

____

(1)

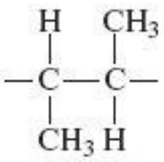
(d) Alkenes can be polymerised to produce poly(alkenes).

(i) State the type of polymerisation that alkenes undergo.

____

(1)

(ii) Name the alkene that gives a polymer with the repeating unit shown below.



$$-CH(CH_3)-CH(CH_3)-$$

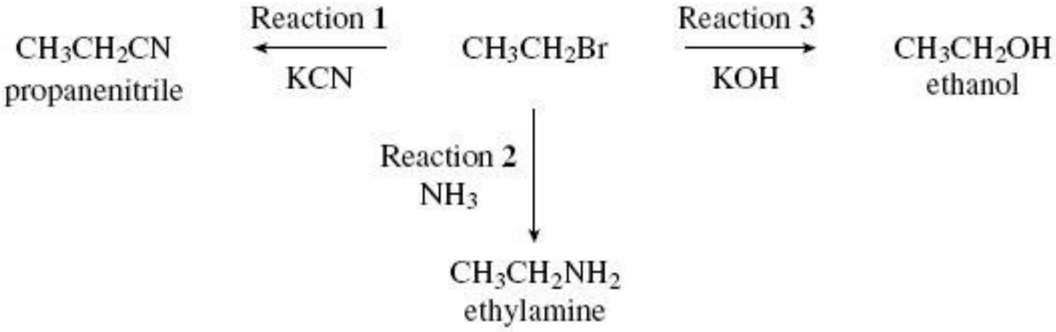
Name of alkene ____

(1)

(Total 12 marks)

Q21.

Nucleophiles react with bromoethane in substitution reactions. This type of reaction is illustrated in the following scheme.



(a) State what is meant by the term *nucleophile*.

____

(1)

(b) Outline a mechanism for the reaction of potassium cyanide with bromoethane (Reaction **1**).

(2)

(c) Explain why an excess of ammonia is needed in Reaction **2** to produce a high yield of ethylamine.

____

____

(1)

(d) When potassium hydroxide reacts with bromoethane, ethene can also be formed. Name and outline a mechanism for this reaction.

Name of mechanism ____

Mechanism

(4)

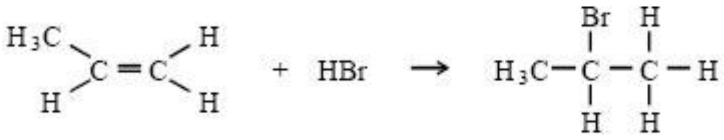
(Total 8 marks)

Q22.

Organic reaction mechanisms help to develop an understanding of how and why reactions occur.

(a) Propene reacts with hydrogen bromide by an electrophilic addition mechanism forming 2-bromopropane as the major product.

The equation for this reaction is shown below.



(i) Outline the mechanism for this reaction, showing the structure of the intermediate carbocation formed.

(ii) Give the structure of the alternative carbocation which could be formed in the reaction between propene and hydrogen bromide.

(5)

(b) A substitution reaction occurs when 2-bromopropane reacts with aqueous sodium hydroxide.

(i) Draw the structure of the organic product of this reaction and give its name.

Structure

Name ____

(ii) Name and outline the mechanism for this reaction.

Name of mechanism ______________________________

Mechanism

(5)

(c) Under different conditions, 2-bromopropane reacts with sodium hydroxide to produce propene.

(i) Name the mechanism for this reaction

____

(ii) State the role of sodium hydroxide in this reaction

____

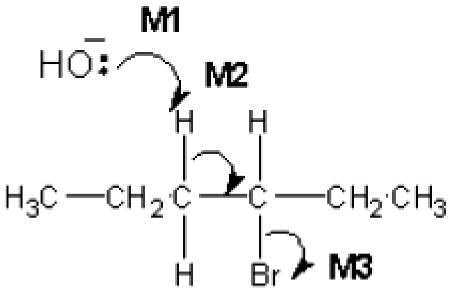
(2)

(Total 12 marks)

Mark Scheme

Q17.

(a) (i)



Penalise one mark from their total if half-headed arrows are used

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

Ignore other partial charges

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

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

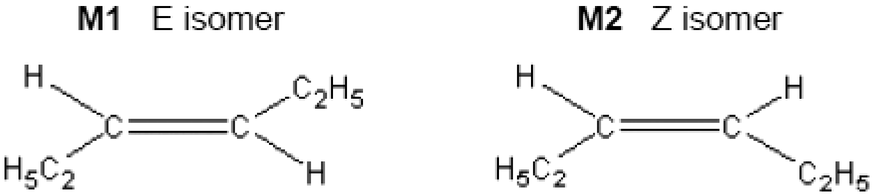
M2 must show an arrow from the correct C–H bond to the correct C–C bond. Only award if an arrow is shown attacking the H atom of the correct C–H bond in **M1**

M3 is independent but **CE=0 if nucleophilic substitution**

N.B these are double-headed arrows

3

(ii)



Award 1 mark if both correct stereoisomers but in the wrong places

Accept no other alkenes.

Be reasonably lenient on the bonds to ethyl (or to CH_2CH_3) since the question is about E and Z positions but penalise once only if connection is clearly to the CH_3 of CH_2CH_3

Accept linear structures

2

(iii) **M1** (Compounds / molecules with) the same structural formula

*Penalise **M1** if "same structure"*

M2 with atoms/bonds/groups arranged differently in space

Ignore references to "same molecular formula" or "same empirical *formula" or any reference to "displayed formula"*

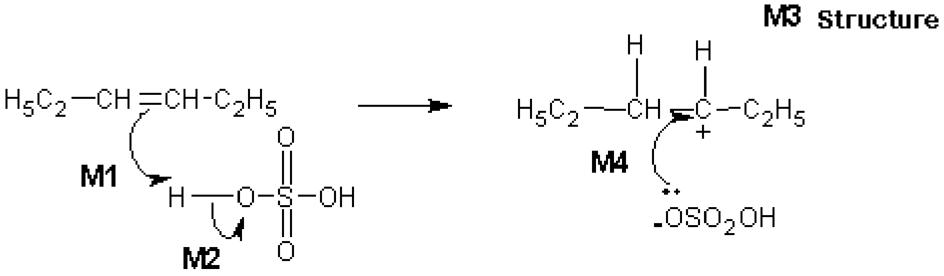
OR

atoms/bonds/groups that have different spatial arrangements / different orientation.

Mark independently

2

(b)



M1must show an arrow from the double bond towards the H atom of the H – O bond OR HO on a compound with molecular formula for H_2SO_4

M1 could be to an H+ ion and M2 an independent O – H bond break on a compound with molecular formula for H_2SO_4

***M1** Ignore partial negative charge on the double bond.*

M2 must show the breaking of the O – H bond.

***M2** Penalise partial charges on O – H bond if wrong way and penalise formal charges*

In M2 do not penalise incorrect structures for H_2SO_4

M3 is for the structure of the carbocation.

M4 must show an arrow from the lone pair of electrons on the correct oxygen of the negatively charged ion towards a correct (positively charged) carbon atom.

***M4** NOT HSO_4^-*

*For **M4**, credit as shown or $^{-:}OSO_3H$ ONLY with the negative charge anywhere on this ion*

OR correctly drawn out with the negative charge placed correctly on oxygen

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

NB The arrows here are double-headed

Max 3 of any 4 marks for wrong organic reactant or wrong organic product (if shown)

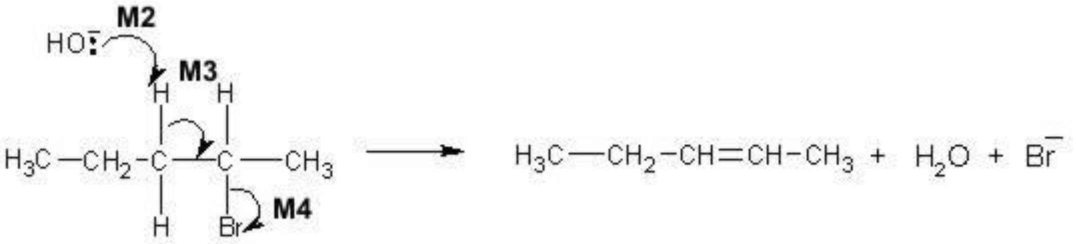
Accept the correct use of "sticks"

4

[11]

Q18.

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



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

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 <u>no other prefix</u>.

*Penalise **M2** if covalent KOH*

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

Ignore other partial charges

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

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

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

4

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

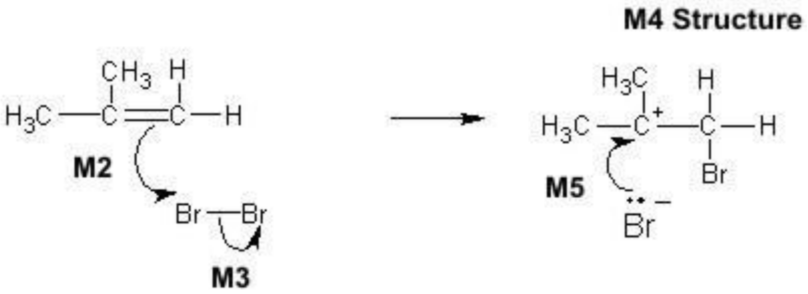
$CH_3CH_2CH_2CH=CH_2$

Penalise C_3H_7

Accept correct "sticks"

1

(b) **M1 <u>Electrophilic addition</u>**



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

*<u>Max any 3 of 4 marks **for the mechanism**</u> for*

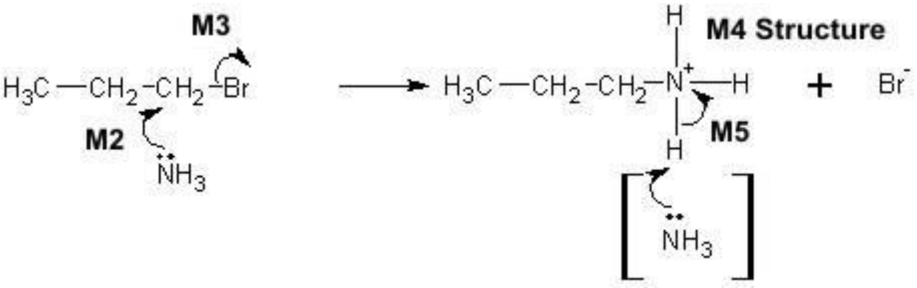
wrong organic reactant or wrong organic product (if shown) or primary carbocation.

*If HBr is used, max 2 marks **for their mechanism***

Accept the correct use of "sticks"

5

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



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

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

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

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

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

N.B. These are double-headed arrows

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

*Penalise **M2** if 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]

Q19.

(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

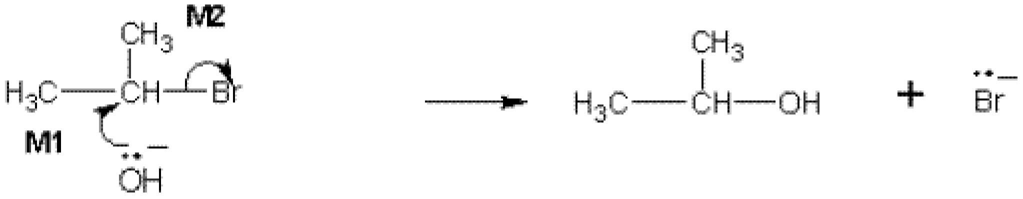
(Heat) energy/enthalpy required/needed/absorbed (at constant pressure) for homolysis of the (C–X/the carbon-halogen) bond

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

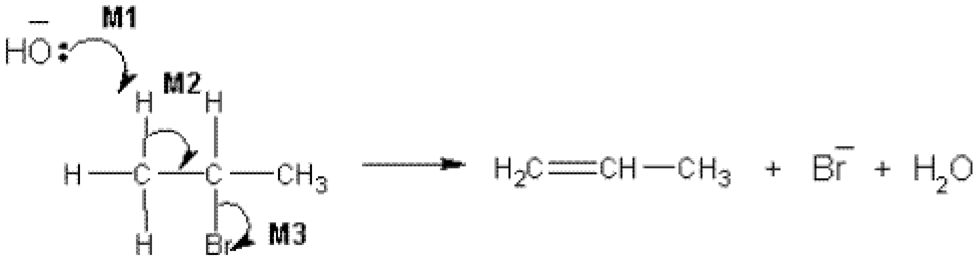
Penalise once only for a line and two dots to show a bond.

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 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

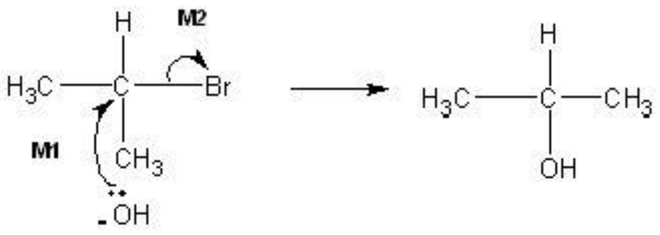
2

[11]

Q20.

(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)

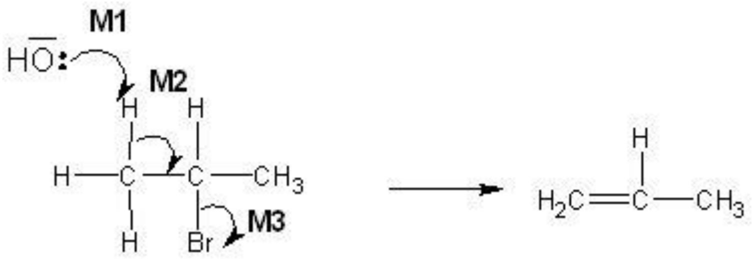
It must be clear that the discussion is about the carbon atom of the C–Br bond. NOT just reference to a polar molecule.
Ignore X for halogen

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]

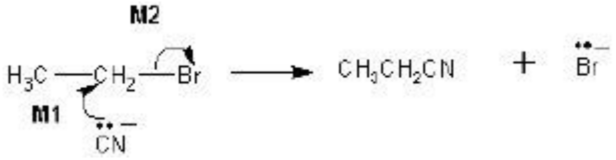
Q21.

(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

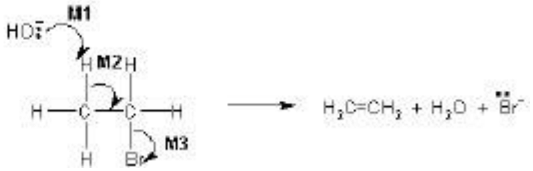
The idea that ammonia acts <u>both</u> initially as a nucleophile and then as a base

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.

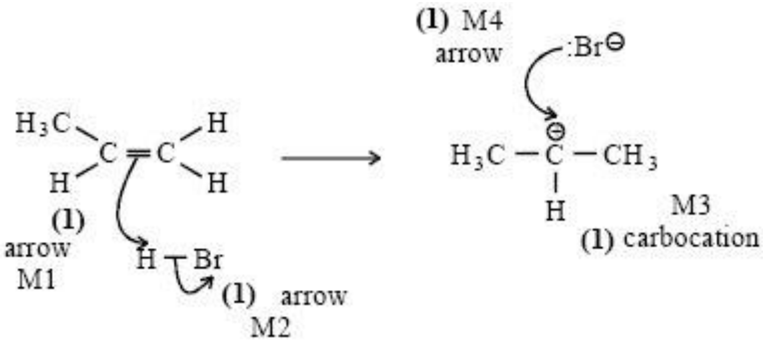
*Max 2 marks **for the mechanism** for wrong reactant or "sticks"*

3

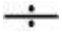
[8]

Q22.

(a) (i)



If wrong carbocation, lose structure mark
If wrong alkene, lose structure mark
Can still score ¾ i.e. penalise M3

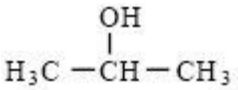
Penalise M2 if polarity included incorrectly
no bond between H and Br
bond is shown as  or 

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*: 

$H_3C-\overset{OH}{CH}-CH_3$

[insist on C — OH bond]

1

Name: propan-2-ol

Not 2-hydroxypropane

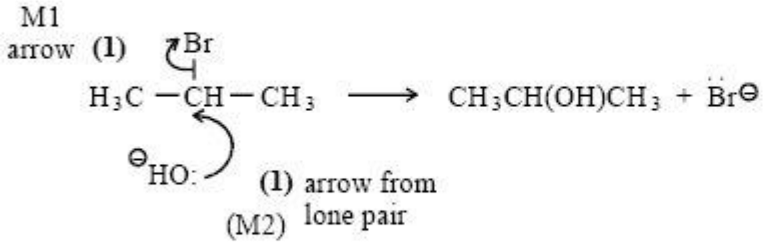
1

(ii) *Name of mechanism*: <u>nucleophilic substitution</u> **(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]