1 Pentanenitrile can be made by reaction of 1-bromobutane with potassium cyanide.

Which of these is the correct name for the mechanism of this reaction?

A Electrophilic addition ⬭

B Electrophilic substitution ⬭

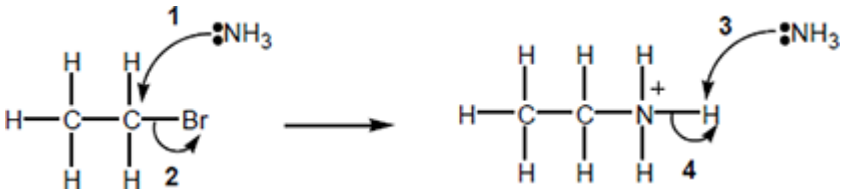
C Nucleophilic addition ⬭

D Nucleophilic substitution ⬭

(Total 1 mark)

2 This question is about a method that can be used to prepare ethylamine.

$$CH_3CH_2Br + 2NH_3 \longrightarrow CH_3CH_2NH_2 + NH_4Br$$



Which of the curly arrows in the mechanism is **not** correct?

A 1 ⬭

B 2 ⬭

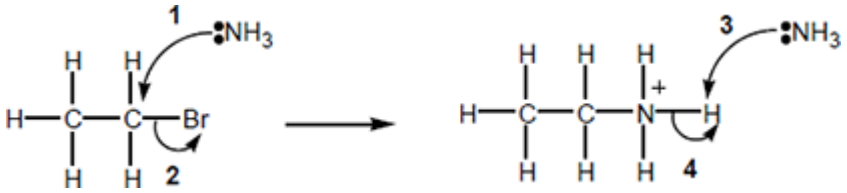
C 3 ⬭

D 4 ⬭

(Total 1 mark)

3 This question is about a method that can be used to prepare ethylamine.

$$CH_3CH_2Br + 2NH_3 \longrightarrow CH_3CH_2NH_2 + NH_4Br$$



Which statement about the reaction is **not** correct?

A Ethylamine is a primary amine. ⬭

B The mechanism is a nucleophilic substitution. ⬭

C Using an excess of bromoethane will prevent further reaction to form a mixture of amine products. ⬭

D Ammonium bromide is an ionic compound. ⬭

(Total 1 mark)

4 Why are fluoroalkanes unreactive?

A Fluorine is highly electronegative. ⬭

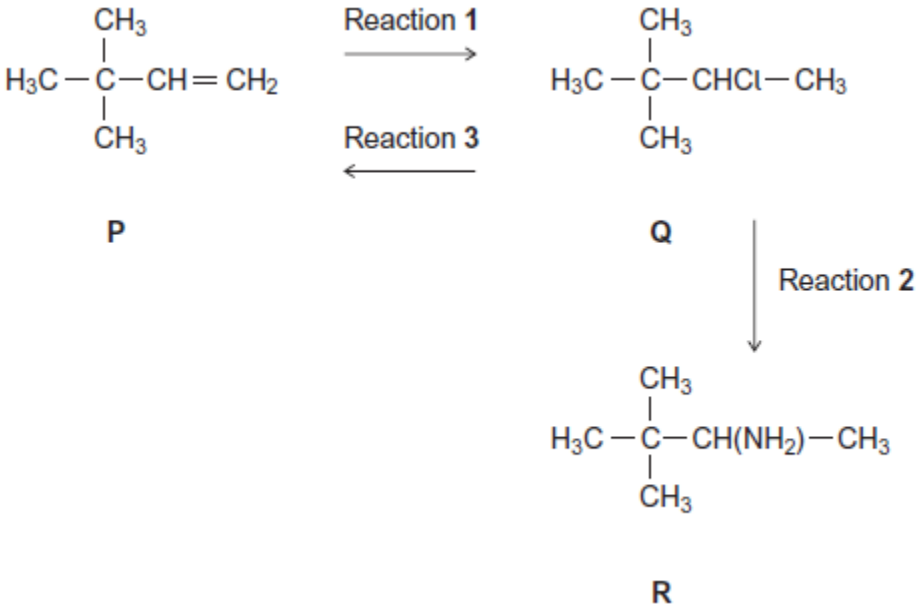
B The F^- ion is very stable. ⬭

C They are polar molecules. ⬭

D The C–F bond is very strong. ⬭

(Total 1 mark)

5 Consider the following scheme of reactions.



(a) Give the IUPAC name for compound **P** and that for compound **Q**.

P .....

Q .....

(2)

(b) The conversion of **P** into **Q** in Reaction **1** uses HCl

Name and outline a mechanism for this reaction.

.....

(5)

(c) The conversion of **Q** into **R** in Reaction **2** uses NH_3

Name and outline a mechanism for this reaction.

.....

(5)

(d) State the type of reaction shown by Reaction **3**.

Identify a reagent for this reaction.

Give **one** condition necessary for a high yield of product when **Q** is converted into **P**.

.....

.....

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.....

(3)

(e) Hydrogen bromide (HBr) could be used in the overall conversion of **P** into **R**, instead of using HCl
Hydrogen bromide is made by the reaction of NaBr with concentrated phosphoric acid.
Concentrated sulfuric acid is **not** used to make HBr from NaBr

Write an equation for the reaction of NaBr with H_3PO_4 to produce HBr and Na_3PO_4 only.

Identify **two** toxic gases that are formed, together with HBr, when NaBr reacts with concentrated H_2SO_4

State the role of H_2SO_4 in the formation of these two toxic gases.

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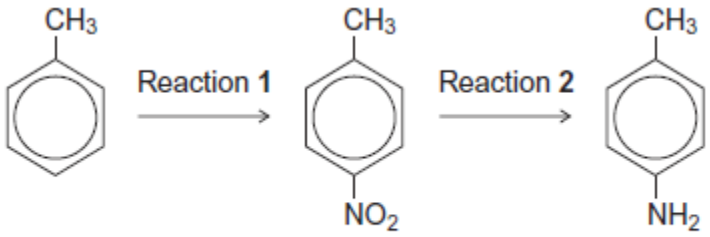
(4)
(Total 19 marks)

6 Consider the following reaction sequence starting from methylbenzene.



J

(a) Name the type of mechanism for reaction **1**.

.....

(1)

(b) Compound **J** is formed by reduction in reaction **2**.

(i) Give a reducing agent for this reaction.

.....

(1)

(ii) Write an equation for this reaction. Use [H] to represent the reducing agent.

.....

(1)

(iii) Give a use for **J**.

.....

(1)

(c) Outline a mechanism for the reaction of bromomethane with an excess of compound **J**.
You should represent **J** as RNH_2 in the mechanism.

(4)

(d) Compound **K** ($C_6H_5CH_2NH_2$) is a structural isomer of **J**.

Explain why **J** is a weaker base than **K**.

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(3)
(Total 11 marks)

7 Haloalkanes are used in the synthesis of other organic compounds.

(a) Hot concentrated ethanolic potassium hydroxide reacts with 2-bromo-3-methylbutane to form two alkenes that are structural isomers of each other. The major product is 2-methylbut-2-ene.

(i) Name and outline a mechanism for the conversion of 2-bromo-3-methylbutane into 2-methylbut-2-ene according to the equation.

$(CH_3)_2CHCHBrCH_3 + KOH \longrightarrow (CH_3)_2C{=}CHCH_3 + KBr + H_2O$

Name of mechanism .....

Mechanism

(4)

(ii) Draw the **displayed formula** for the other isomer that is formed.

(1)

(iii) State the type of structural isomerism shown by these two alkenes.

.....

(1)

(b) A small amount of another organic compound, **X**, can be detected in the reaction mixture formed when hot concentrated ethanolic potassium hydroxide reacts with 2-bromo-3-methylbutane.
Compound **X** has the molecular formula $C_5H_{12}O$ and is a secondary alcohol.

(i) Draw the **displayed formula** for **X**.

(1)

(ii) Suggest **one** change to the reaction conditions that would increase the yield of **X**.

.....

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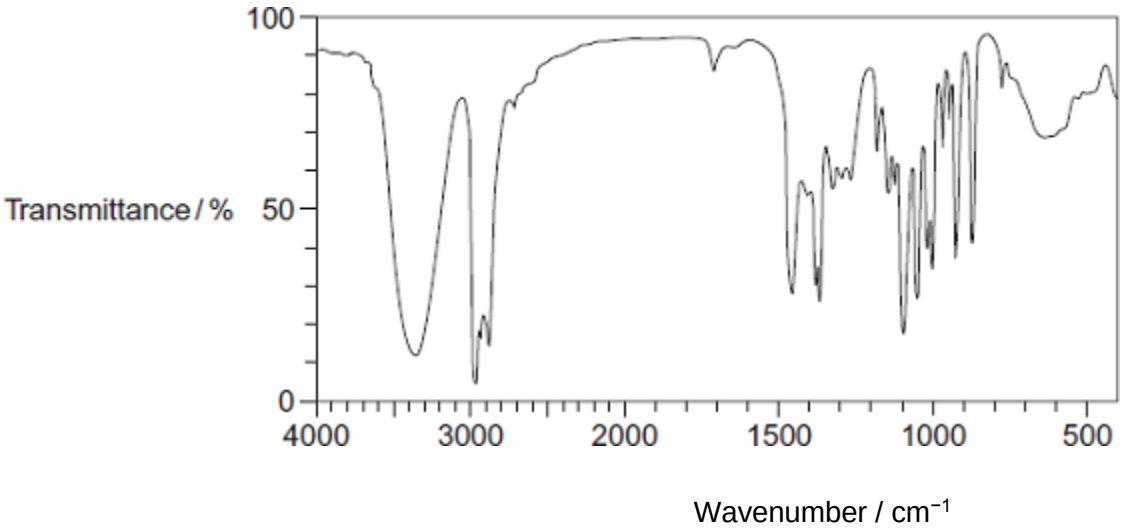
(1)

(iii) State the type of mechanism for the conversion of 2-bromo-3-methylbutane into **X**.

.....

(1)

(iv) Identify **one** feature of this infrared spectrum of a pure sample of **X** that may be used to confirm that **X** is an alcohol.
You may find it helpful to refer to **Table 1** on the Data Sheet.



Feature .....

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(1)
(Total 10 marks)

8 In each of the following questions, you should draw the structure of the compound in the space provided.

(a) Draw the structure of the alkene that would form 1,2-dibromo-3-methylbutane when reacted with bromine.

(1)

(b) Draw the structure of the alcohol with molecular formula $C_4H_{10}O$ that is resistant to oxidation by acidified potassium dichromate(VI).

(1)

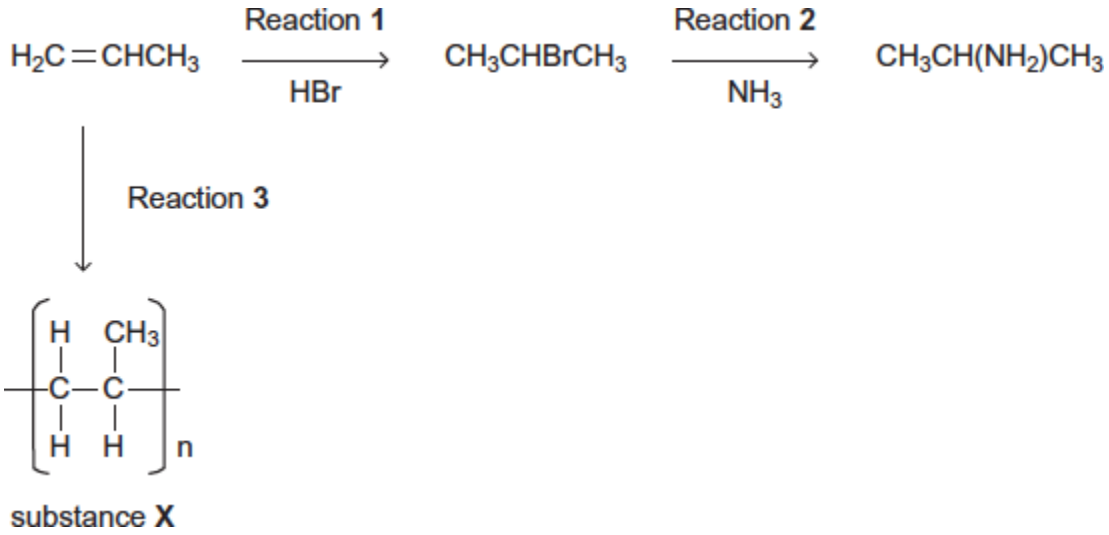
(c) Draw the structure of the alkene that has a peak, due to its molecular ion, at $m/z = 42$ in its mass spectrum.

(1)

(d) Draw the structure of the organic product with $M_r = 73$, made from the reaction between 2-bromobutane and ammonia.

(1)
(Total 4 marks)

9 Consider the following reactions.



substance **X**

(a) Name and outline a mechanism for Reaction **1**.

Name of mechanism .....

Mechanism

(5)

(b) Name and outline a mechanism for Reaction **2**.

Name of mechanism .....

Mechanism

(5)

(c) State the type of reaction in Reaction **3**.
Give the name of substance **X**.

.....

.....

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(2)

(d) The haloalkane produced in Reaction **1** can be converted back into propene in an elimination reaction using ethanolic potassium hydroxide.

$$CH_3CHBrCH_3 \xrightarrow{KOH} H_2C{=}CHCH_3$$

Outline a mechanism for this conversion.

(3)
(Total 15 marks)

10 The reaction of butane-1,4-diol with butanedioic acid produces the polymer PBS used in biodegradable packaging and disposable cutlery.
Butanedioic acid is produced by two different processes.

Process 1

- Aqueous sodium hydroxide reacts with 1,4-dibromobutane to make butane-1,4-diol.
- Butane-1,4-diol is oxidised to butanedioic acid.

Process 2

- Glucose reacts with carbon dioxide in the presence of microorganisms to produce butanedioic acid directly.
- The carbon dioxide used in this process is obtained from a local factory that produces bioethanol.

(a) Deduce **one** safety reason and one environmental reason why **Process 2** is preferred to **Process 1**.

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(Extra space) .....

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(2)

(b) (i) Name and outline a mechanism for the following reaction that occurs in **Process 1**.

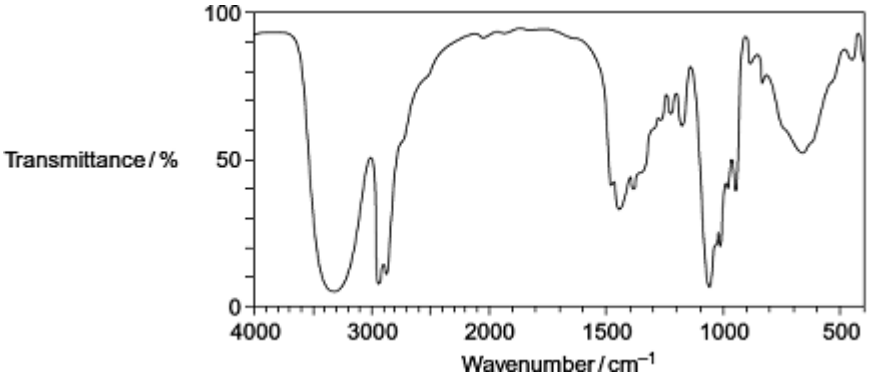
.....

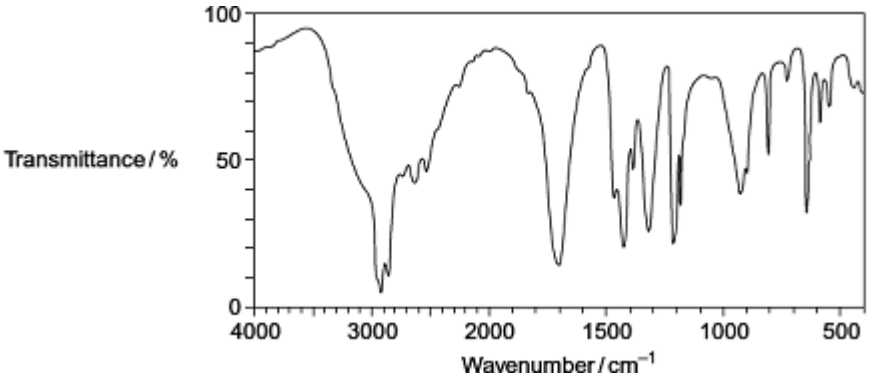
(3)

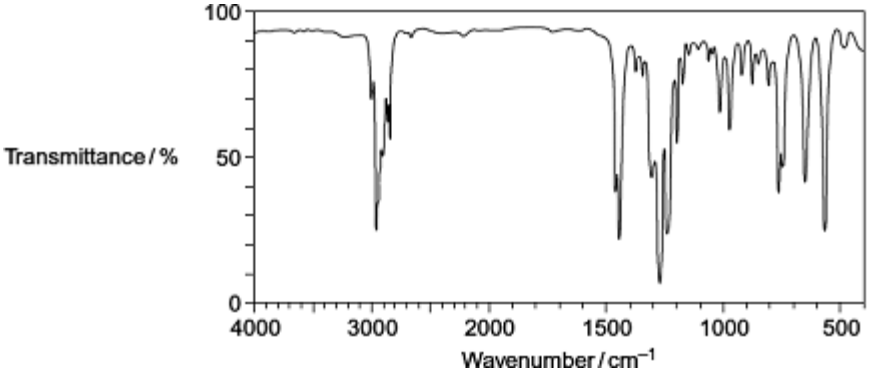
(ii) The infrared spectra shown are those of three compounds.

Compound **A** 1,4-dibromobutane
Compound **B** butane-1,4-diol
Compound **C** butanedioic acid

Identify the compound responsible for each spectrum by writing the correct letter, **A**, **B** or **C**, in the box next to each spectrum.
You may find it helpful to refer to **Table 1** on the Data Sheet.







(3)

(c) In the production of bioethanol, glucose ($C_6H_{12}O_6$) is converted into a dilute aqueous solution of ethanol and carbon dioxide.

Give the name of this process and state **three** essential conditions necessary to produce a good yield of ethanol.

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(Extra space) .....

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(4)

(d) State the class of alcohols to which the diol butane-1,4-diol belongs.

Identify a suitable reagent or combination of reagents for the conversion of butane-1,4-diol into butanedioic acid ($HOOCCH_2CH_2COOH$).

Write an equation for this oxidation reaction using [O] to represent the oxidising agent.

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(Extra space) .....

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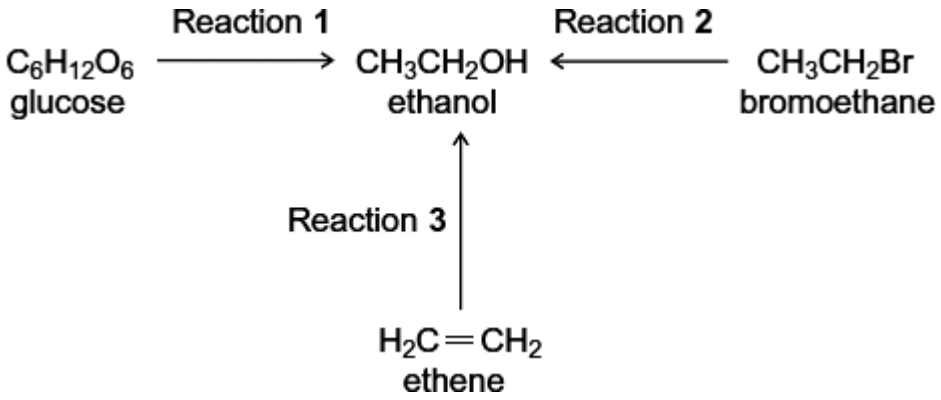
(3)
(Total 15 marks)

11 Three different ways of producing ethanol are shown below.



(a) Reaction **1** produces a 15% aqueous solution of ethanol.
It is claimed that the ethanol produced in this way is a carbon-neutral biofuel.

Write an equation for Reaction **1** and name the process.

Write an equation for the complete combustion of ethanol.

Explain why the ethanol produced by this process may **not** be a *carbon-neutral* biofuel.

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(Extra space) .....

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(5)

(b) Give a reagent and conditions for Reaction **2**.

$CH_3CH_2Br \xrightarrow{\text{Reaction 2}} CH_3CH_2OH$

Name and outline a mechanism for Reaction **2**.

Suggest **one** reason, other than safety, why this method is **not** used in industry to make ethanol.

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(Extra space) .....

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(6)

(c) Reaction **3** is used in industry.

Identify a suitable catalyst for Reaction **3**.

Identify the type of reaction.

Give **two** conditions, in addition to the presence of a catalyst, necessary for Reaction **3** to produce a high yield of ethanol.

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(Extra space) .....

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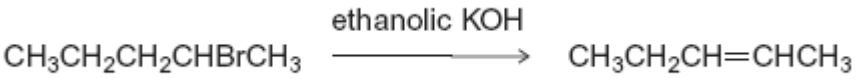
(4)
(Total 15 marks)

12 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.



(4)

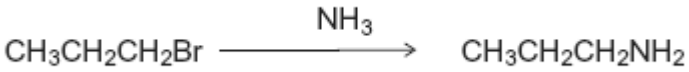
(ii) Draw the structure of the other structurally isomeric alkene produced when 2-bromopentane reacts with ethanolic KOH.

(1)

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

(5)

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



(5)
(Total 15 marks)

13 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.

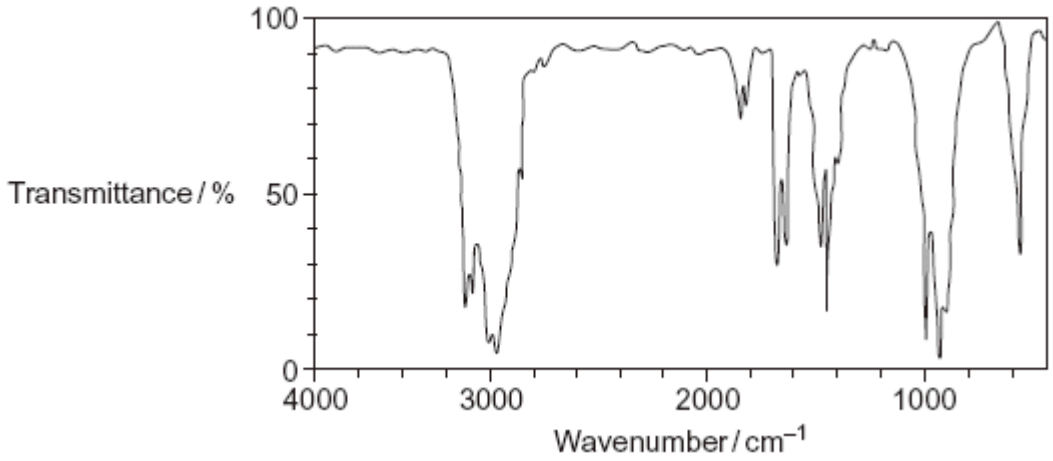
(2)

(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.

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(2)
(Total 11 marks)

14 A student carried out an experiment to study the rates of hydrolysis of some haloalkanes.

(a) In the experiment, two different haloalkanes were placed in separate test tubes containing silver nitrate solution. The haloalkanes reacted with the water in the silver nitrate solution. The student timed how long it took for the first appearance of the silver halide precipitate in each tube at a constant temperature. This time was used to provide a measure of the initial rate of reaction.
The student obtained the following results.

	1-bromobutane	1-iodobutane
Time to form a precipitate / s	480	15

(i) State the meaning of the term *hydrolysis*.

.....

.....

(1)

(ii) State the colour of the precipitate formed when iodide ions react with silver nitrate and write the **simplest** ionic equation for this reaction.

Colour of precipitate .....

Simplest ionic equation

.....

(2)

(iii) Use your knowledge of the reactions of halide ions with silver nitrate to suggest why the student did **not** include 1-fluorobutane in this experiment.

.....

.....

(2)

(b) The student used the following enthalpy data to try to account for the different initial rates of hydrolysis of the haloalkanes used in part (a). The student deduced that the rate of hydrolysis of a haloalkane is influenced by the strength of the carbon–halogen bond in the haloalkane.

	C–Br	C–I
Bond enthalpy / kJ mol^{-1}	276	238

State how the experimental evidence enabled the student to make this deduction.

.....

.....

(1)

(c) The student had read that the reaction of water with haloalkanes was similar to the reaction of aqueous sodium hydroxide with haloalkanes and was an example of a nucleophilic substitution reaction.

(i) State the meaning of the term *nucleophile*.

.....

(1)

(ii) When a hydroxide ion collides with a molecule of 1-bromobutane, the following reaction occurs.

$$CH_3CH_2CH_2CH_2Br + OH^- \rightarrow CH_3CH_2CH_2CH_2OH + Br^-$$

Outline the nucleophilic substitution mechanism for this reaction.

(2)

(d) The reaction of hydroxide ions with 2-bromo-2-methylpropane may occur by a different mechanism from the one in part (c). This different mechanism involves the formation of a carbocation.

(i) Complete the following equation by drawing the structure of the carbocation formed when the C–Br bond in 2-bromo-2-methylpropane is broken.

.....

(1)

(ii) Suggest **one** reason why this reaction occurs by a mechanism involving a carbocation, but the reaction in part (c) (ii) does not.

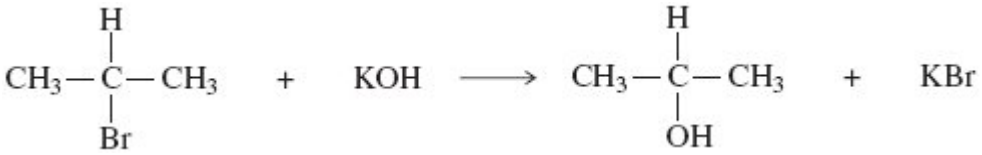
.....

.....

(1)

(Total 11 marks)

15 (a) Consider the following reaction.



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

Name of mechanism .....

Mechanism

(3)

(ii) Name the haloalkane in this reaction.

.....

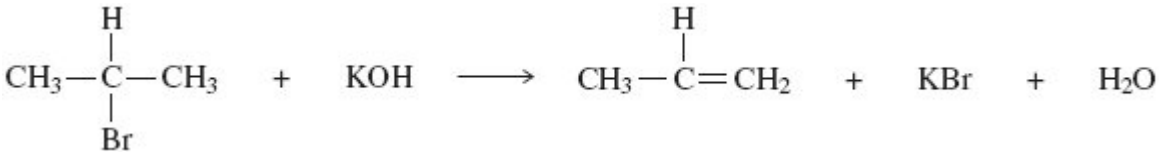
(1)

(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.



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)

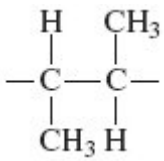
(d) Alkenes can be polymerised to produce poly(alkenes).

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

.....

(1)

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

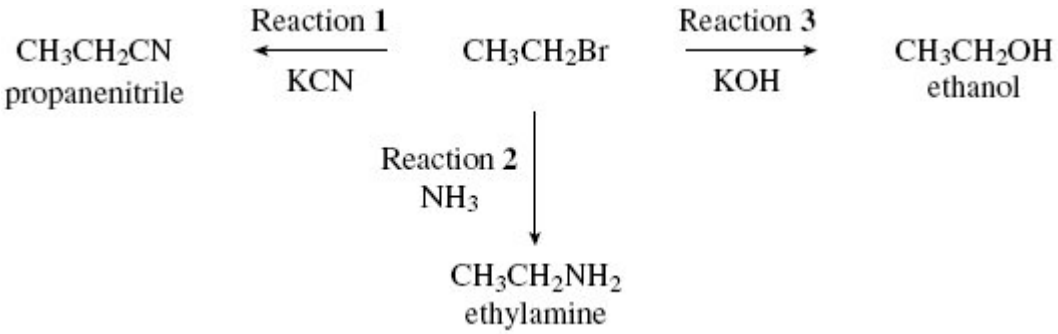


Name of alkene .....

(1)

(Total 12 marks)

16 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 .....

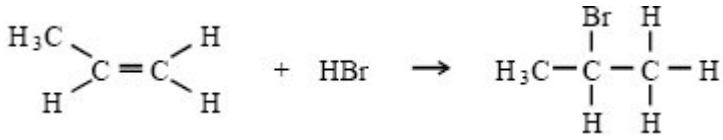
Mechanism

(4)
(Total 8 marks)

17 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)

18 Which one of the following statements explains best why fluoroalkanes are the least reactive haloalkanes?

A Fluorine is much more electronegative than carbon.

B The F^- ion is the most stable halide ion.

C The C–F bond is the most polar carbon–halogen bond.

D The C–F bond is the strongest carbon–halogen bond.

(Total 1 mark)

19 (a) Name and outline a mechanism for the reaction of 2-bromo-2-methylpropane with ethanolic potassium hydroxide to form the alkene 2-methylpropene, $(CH_3)_2C=CH_2$

Name of mechanism .....

Mechanism

(4)

(b) Two stereoisomers of but-2-ene are formed when 2-bromobutane reacts with ethanolic potassium hydroxide.

(i) Explain what is meant by the term *stereoisomers*.

.....

.....

(ii) Draw the structures and give the names of the **two** stereoisomers of but-2-ene.

Stereoisomer 1 *Stereoisomer 2*

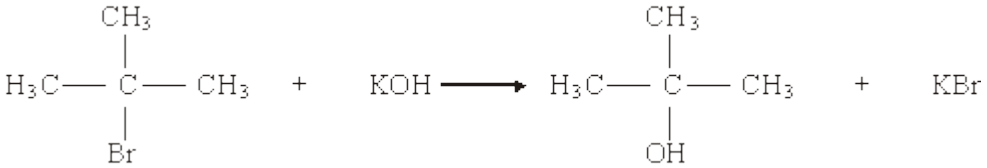
Name ..... *Name* .....

(iii) Name this type of stereoisomerism.

.....

(5)

(c) When 2-bromo-2-methylpropane reacts with aqueous potassium hydroxide, 2-methylpropan-2-ol is formed as shown by the following equation.



State the role of the hydroxide ions in this reaction.

.....

(1)

(d) Write an equation for the reaction that occurs when $CH_3CH_2CH_2CH_2Br$ reacts with an excess of ammonia. Name the organic product of this reaction.

Equation .....

Name of product .....

(3)
(Total 13 marks)

20 Which one of the following reactions does **not** involve donation of an electron pair?

A $H^+ + CH_3NH_2 \rightarrow CH_3NH_3^+$

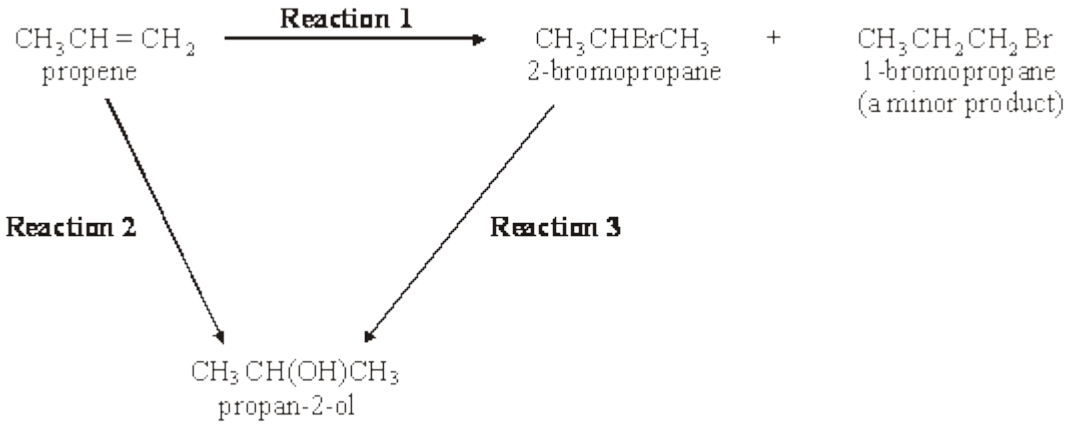
B $AlCl_3 + Cl^- \rightarrow A1C1_4^-$

C $CH_3Cl + CN^- \rightarrow CH_3CN + Cl^-$

D $\frac{1}{2}Cl_2 + I^- \rightarrow Cl^- + \frac{1}{2}I_2$

(Total 1 mark)

21 Consider the following reaction scheme.



(a) (i) Name the mechanism for **Reaction 1**.

.....

(ii) Explain why 1-bromopropane is only a minor product in **Reaction 1**.

.....

.....

.....

(3)

(b) Give a suitable reagent and state the essential conditions required for **Reaction 3**.

Reagent .....

Conditions .....

(2)

(c) The reagent used for **Reaction 3** can also be used to convert 2-bromopropane into propene. State the different conditions needed for this reaction.

.....

(1)

(d) **Reaction 2** proceeds in two stages.

Stage 1 $CH_3CH{=}CH_2 + H_2SO_4 \rightarrow CH_3CH(OSO_2OH)CH_3$

Stage 2 $CH_3CH(OSO_2OH)CH_3 + H_2O \rightarrow CH_3CH(OH)CH_3 + H_2SO_4$

(i) Name the class of alcohols to which propan-2-ol belongs.

.....

(ii) Outline a mechanism for Stage 1 of **Reaction 2**, using concentrated sulphuric acid.

(iii) State the overall role of the sulphuric acid in **Reaction 2**.

.....

(6)
(Total 12 marks)

22 (a) Bromomethane, CH_3Br, can be formed by a reaction between bromine and methane.

The mechanism for this reaction is similar to the mechanism for the chlorination of methane.

(i) Name the mechanism for this reaction.

.....

(ii) Give the name of, and state an essential condition for, the first step in the mechanism for this reaction.

Name .....

Essential condition .....

(iii) Write an equation for a termination step in the mechanism for this reaction which gives ethane as a product.

.....

(iv) Bromomethane can undergo further substitution. Write an overall equation for the reaction between bromomethane and bromine in which dibromomethane is formed.

.....

(5)

(b) Bromomethane reacts with the nucleophile ammonia according to the following equation.

$CH_3Br + 2NH_3 \rightarrow CH_3NH_2 + NH_4Br$

(i) Explain what is meant by the term *nucleophile*.

.....

.....

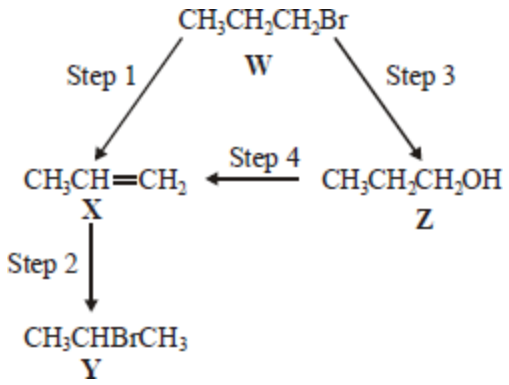
(ii) Name the organic product of this reaction.

.....

(iii) Outline a mechanism for this reaction.

(6)
(Total 11 marks)

23 For this question refer to the reaction scheme below.



Which one of the following statements is **not** correct?

A Reaction of **W** with sodium cyanide followed by hydrolysis of the resulting product gives propanoic acid.

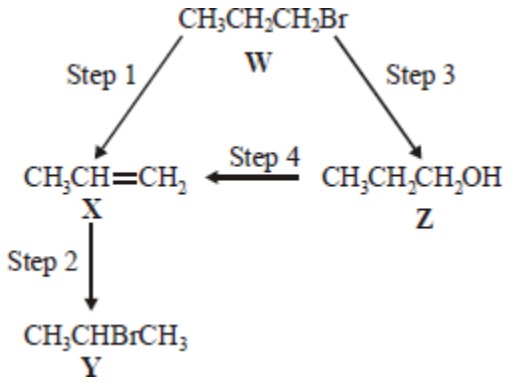
B Mild oxidation of **Z** produces a compound that reacts with Tollens' reagent, forming a silver mirror.

C **Z** reacts with ethanoic acid to produce the ester propyl ethanoate.

C **W** undergoes addition polymerisation to form poly(propene).

(Total 1 mark)

24 For this question refer to the reaction scheme below.



Which one of the following reagents would **not** bring about the reaction indicated?

A Step 1 : alcoholic KOH

B Step 2 : aqueous Br_2

C Step 3 : aqueous NaOH

C Step 4 : concentrated H_2SO_4

(Total 1 mark)

25 (a) Chloromethane can be made by the reaction of chlorine with methane.

(i) Give **one** essential condition for this reaction.

.....

(ii) Name the mechanism for this reaction.

.....

(iii) Further substitution can occur during this reaction. Identify the main organic product when a large excess of chlorine is used in this reaction.

.....

(3)

(b) Ethanenitrile can be made by reacting chloromethane with potassium cyanide.

(i) Write an equation for this reaction.

.....

(ii) Name the mechanism for this reaction.

.....

(iii) Explain, in terms of bond enthalpies, why bromomethane reacts faster than chloromethane with potassium cyanide.

.....

.....

.....

(3)

(c) Ethanenitrile can be hydrolysed to a carboxylic acid by heating it under reflux with a dilute acid. Identify the carboxylic acid formed in this reaction.

.....

(1)

(d) Chloromethane can react with ammonia to produce a primary amine.

(i) What feature of the chloromethane molecule makes it susceptible to attack by an ammonia molecule?

.....

(ii) Name the amine produced in this reaction.

.....

(iii) Outline a mechanism for this reaction.

(6)
(Total 13 marks)

26 (a) Compounds with double bonds between carbon atoms can exhibit geometrical isomerism.

(i) Draw structures for the two geometrical isomers of 1,2-dichloroethene.

Isomer 1 *Isomer 2*

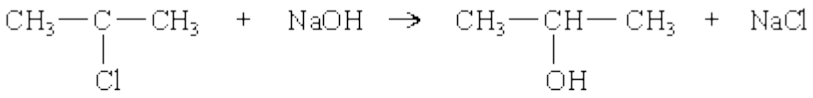
(ii) What feature of the double bond prevents isomer 1 from changing into isomer 2?

.....

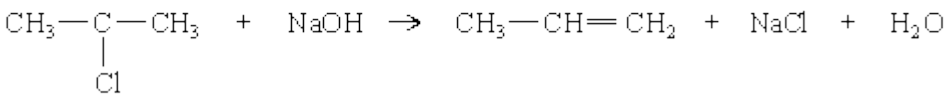
(3)

(b) When 2-chloropropane reacts with sodium hydroxide, two different reactions occur. Each reaction produces a different organic product.

Reaction 1



Reaction 2



(i) Outline a mechanism for **Reaction 1** and state the role of the hydroxide ion in this reaction.

Mechanism

Role of the hydroxide ion .....

(ii) Outline a mechanism for **Reaction 2** and state the role of the hydroxide ion in this reaction.

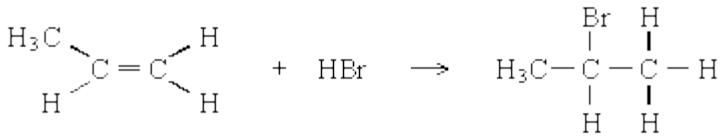
Mechanism

Role of the hydroxide ion .....

(7)
(Total 10 marks)

27 (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.

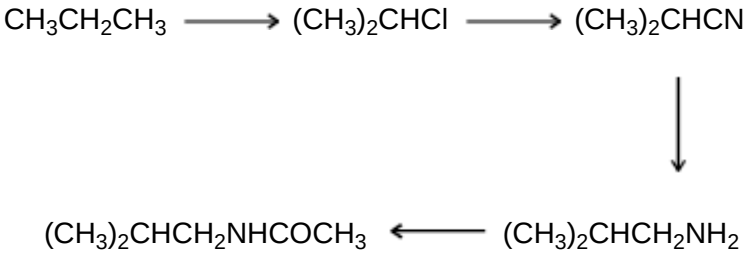
.....

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

.....

(2)
(Total 12 marks)

28 Which one of the following types of reaction mechanism is **not** involved in the above sequence?



A free-radical substitution

B nucleophilic substitution

C elimination

D nucleophilic addition-elimination

(Total 1 mark)

29 Reaction of 2-bromobutane with potassium hydroxide can produce two types of product depending on the solvent used. In aqueous solution, the formation of an alcohol, **E**, is more likely but in ethanolic solution the formation of alkenes is more likely.

(a) For each type of product, name the type of reaction occurring and state the role of the potassium hydroxide.

(4)

(b) Name alcohol **E** and draw its structural formula. By reference to the structure of the halogenoalkane, explain why the initial step in the mechanism of the reaction producing the alcohol occurs.

(5)

(c) When 2-bromobutane reacts with ethanolic potassium hydroxide, two structurally isomeric alkenes are produced, one of which shows stereoisomerism.

Outline the mechanism for the formation of one of the structurally isomeric alkenes. Explain why two structurally isomeric alkenes are formed and draw the structure of the second structural isomer. Draw the structural formulae of the two stereoisomers.

(8)

(Total 17 marks)

30 (a) The equation below shows the reaction of 2-bromopropane with an excess of ammonia.

$$CH_3CHBrCH_3 + 2NH_3 \rightarrow CH_3CH(NH_2)CH_3 + NH_4Br$$

Name and outline the mechanism involved.

Name of mechanism ……

Mechanism

(5)

(b) When 2-bromopropane is heated with ethanolic potassium hydroxide, an elimination reaction occurs. State the role of potassium hydroxide and outline a mechanism for this reaction.

Role of potassium hydroxide .....

Mechanism

(5)
(Total 10 marks)

31 Which one of the following mechanisms is **not** involved in the reaction sequence below?

$CH_3CH_3 \rightarrow CH_3CH_2Cl \rightarrow CH_3CH_2OH \rightarrow CH_2{=}CH_2 \rightarrow CH_3CH_2Br$

A electrophilic addition

B electrophilic substitution

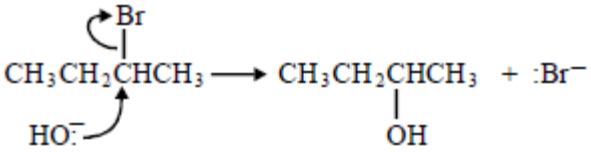
C nucleophilic substitution

D free-radical substitution

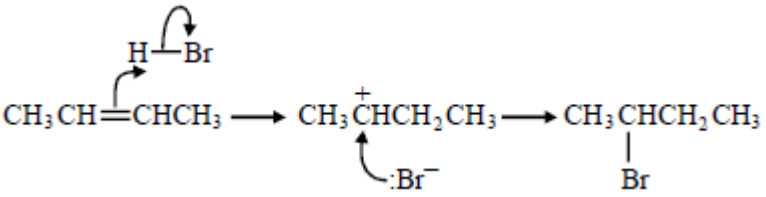
(Total 1 mark)

32 In which of the following is a curly arrow used incorrectly?

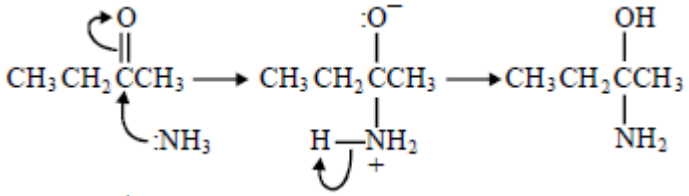
A



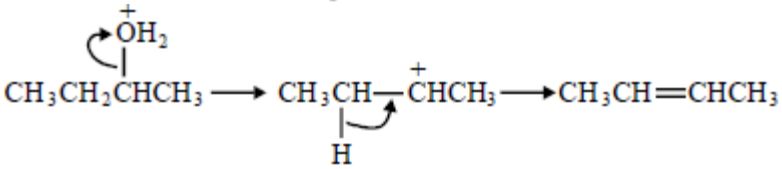
B



C



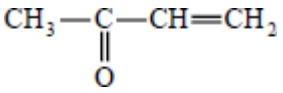
D



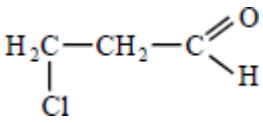
(Total 1 mark)

33 Which one of the following can react both by nucleophilic addition and by nucleophilic substitution?

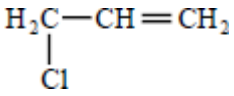
A



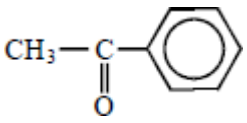
B



C



D

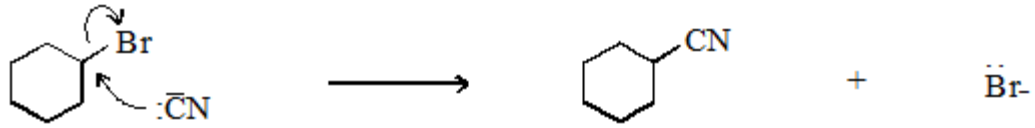


(Total 1 mark)

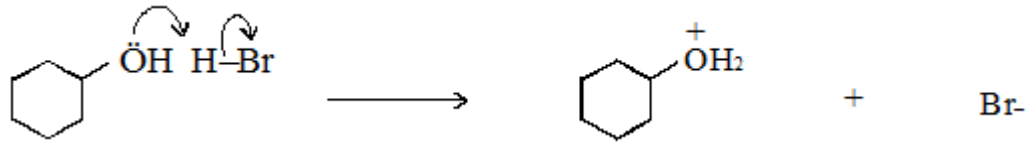
34 In which one of the following are the curly arrows **not** used correctly?

A

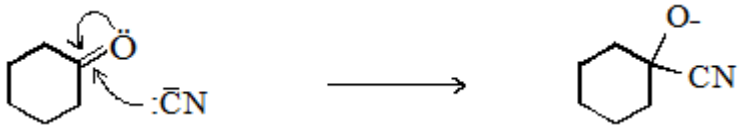
B



C



D



(Total 1 mark)

35 Which one of the following is **not** a suitable method for the preparation of ethanol?

A oxidation of ethane

B hydration of ethene

C reduction of ethanal

D hydrolysis of bromoethane

(Total 1 mark)

36 Which one of the following reactions involves nucleophilic addition?

A $CH_3CH = CH_2 + HBr \rightarrow CH_3CHBrCH_3$

B $CH_3CH_2CH_3 + Cl_2 \rightarrow CH_3CHClCH_3 + HCl$

C $CH_3CH_2CH_2Br + NaOH \rightarrow CH_3CH_2CH_2OH + NaBr$

D $CH_3CH_2CHO + HCN \rightarrow CH_3CH_2CH(OH)CN$

(Total 1 mark)

Mark schemes

1 D

[1]

2 D

[1]

3 C

[1]

4 D

[1]

5 (a) **P** 3,3−dimethylbut−1−ene

OR

accept 3,3−dimethylbutene

Ignore absence of commas, hyphens and gaps

Require correct spelling

Q 3−chloro−2,2−dimethylbutane

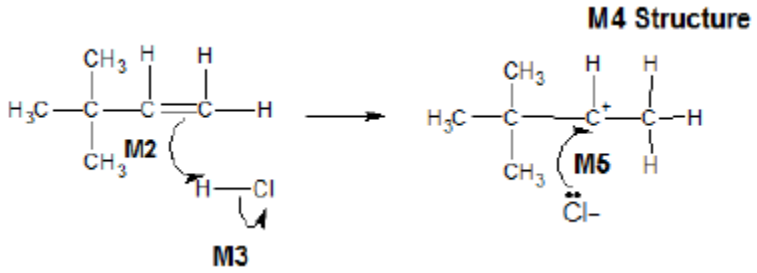
OR

accept 2−chloro−3,3−dimethylbutane

In Q, "chloro" must come before "dimethyl"

2

(b) **M1 Electrophilic addition**



M2 must show an arrow from the double bond towards the H atom of HCl
M3 must show the breaking of the H−Cl bond
M4 is for the structure of the carbocation
M5 must show an arrow from the lone pair of electrons on the negatively charged chloride ion towards the positively charged carbon atom on their carbocation.

NB The arrows here are double−headed

M1 *both words required*

For the mechanism

M3 *Penalise incorrect partial charge on H−Cl bond and penalise formal charges*

Ignore partial negative charge on the double bond.

Maximum 3 of 4 marks for a correct mechanism *using HBr or the wrong organic reactant or wrong organic product (if shown) or a primary carbocation*

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

Credit the correct use of "sticks"

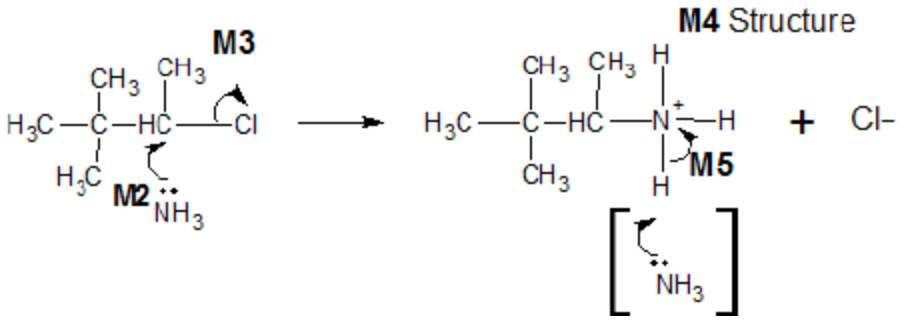
For ***M5****, credit attack on a partially positively charged carbocation structure, but penalise* ***M4***

5

(c) **M1** **Nucleophilic substitution**

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

Accept phonetic spelling



M2 must show an arrow from the lone pair of electrons **on the nitrogen atom** of an ammonia molecule to the correct C atom
M3 must show the movement of a pair of electrons from the C− Cl bond to the Cl atom. Mark **M3** independently 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

NB These are double-headed arrows

For the mechanism

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

*Penalise **M3** for formal charge on C of the C−Cl or incorrect partial charges on C−Cl*

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

*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

***Maximum 3 of 4 marks for the mechanism** for wrong organic reactant OR wrong organic product if shown*

Accept the correct use of "sticks"

5

(d) **M1** (base) elimination

***M1** Dehydrohalogenation*

M2 KOH **OR** NaOH

M3 Must be consequential on a correct reagent in **M2**, but if incomplete or inaccurate attempt at reagent (e.g. hydroxide ion), **penalise M2 only and mark on**

Any **one** from

- high temperature OR hot OR heat / boil under reflux
- concentrated
- alcohol / ethanol (as a solvent) / (ethanolic conditions)

***M3** not "reflux" alone*

***M3** if a temperature is stated it must be in the range 78°C to 200 °C*

Ignore "pressure"

3

(e) **M1**

$3NaBr + H_3PO_4 \longrightarrow 3HBr + Na_3PO_4$

***M1** Credit correct ionic species in the equation*

M2 and M3

SO_2 **and** Br_2 identified

M4

Concentrated sulfuric acid

- is an oxidising agent
- oxidises the bromide (ion) or Br^- or NaBr or HBr
- is an electron acceptor

*In **M2** and **M3** the two gases need to be identified. If equations are used using sulfuric acid and the toxic gases are not identified clearly, allow one mark for the formulas of SO_2 and Br_2*

- *apply the list principle as appropriate but ignore any reference to HBr*
- *the marks are for identifying the two gases either by name or formula*

4

[19]

6

(a) Electrophilic substitution

Both words needed

Ignore minor misspellings

1

(b) (i) Sn / HCl

OR H_2 / Ni **OR** H_2 / Pt **OR** Fe / HCl **OR** Zn / HCl **OR** $SnCl_2$ / HCl

Ignore conc or dil with HCl,

Allow (dil) H_2SO_4 but not conc H_2SO_4

Not allow HNO_3 or H^+

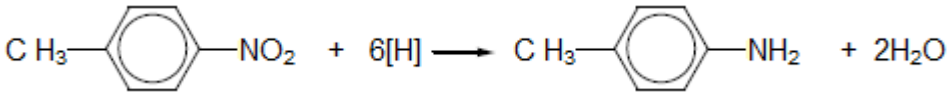
Ignore NaOH after Sn / HCl

Ignore catalyst

1

(ii) $CH_3C_6H_4NO_2 + 6[H] \rightarrow CH_3C_6H_4NH_2 + 2H_2O$

OR



Allow molecular formulae as structures given

$C_7H_7NO_2 + 6[H] \rightarrow C_7H_9N + 2H_2O$

Qu states use [H], so penalised $3H_2$

1

(iii) making dyes

OR making quaternary ammonium salts

OR making (cationic) surfactants

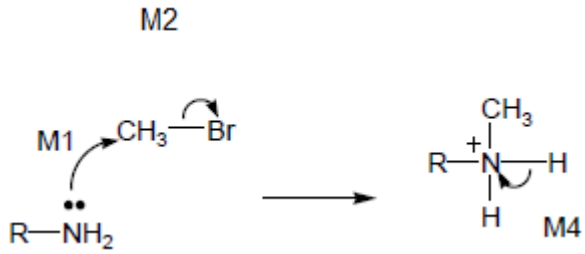
OR making hair conditioner

OR making fabric softener

OR making detergents

1

(c)



M3

NO Mark for name of mechanism

Allow SN1

M1 for lone pair on N and arrow to C or mid point of space between N and C

M2 for arrow from bond to Br

M3 for structure of protonated secondary amine

M4 for arrow from bond to N or + on N

For M4: ignore RNH_2 or NH_3 removing H^+ but penalise Br^-

4

(d) lone or electron pair on N

If no mention of lone pair CE = 0

If lone pair mentioned but not on N then lose M1 and mark on

M1

1

in **J** spread / delocalised into ring (or not delocalised in K)

Ignore negative inductive effect of benzene

*Allow interacts with **Π** cloud for M2*

M2

1

less available (for protonation or donation in **J**)

M3

OR

in **K** there is a positive inductive effect / electron releasing)

M2

more available (for protonation or donation in **K**)

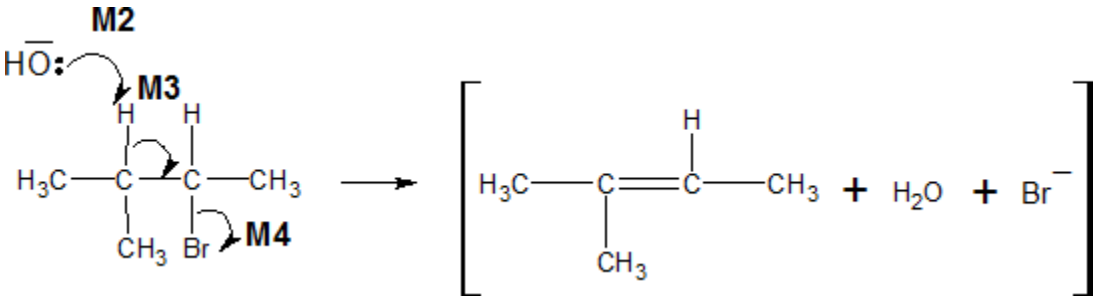
M3

1

[11]

7 (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

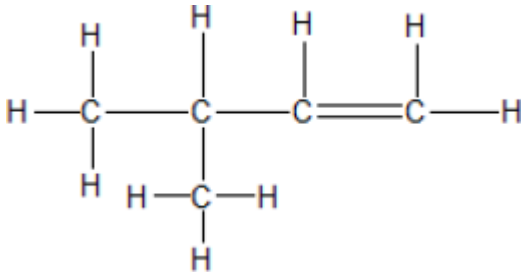
Award full marks for an E1 mechanism in which **M4** is on the correct carbocation

*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

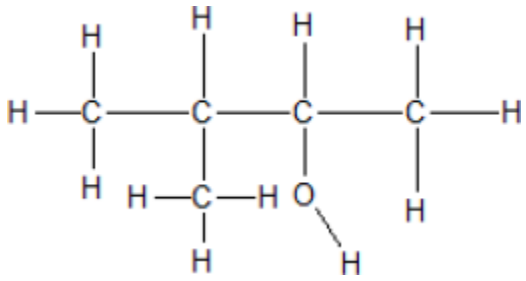
1

(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]

8 (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

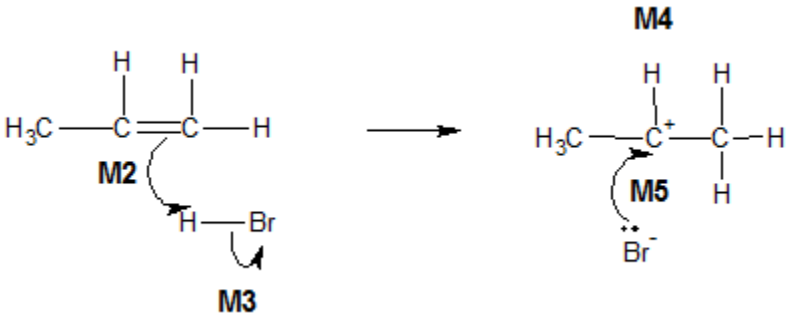
[4]

9

(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

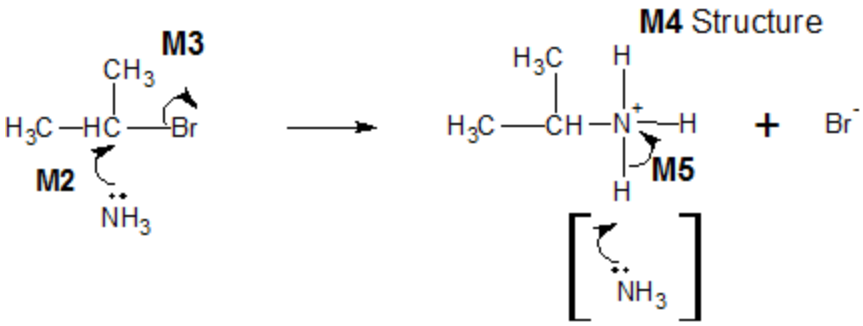
NB These are double-headed arrows

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"

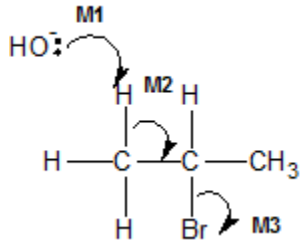
Credit polyprop-1-ene and polypropylene

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]

10 (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)

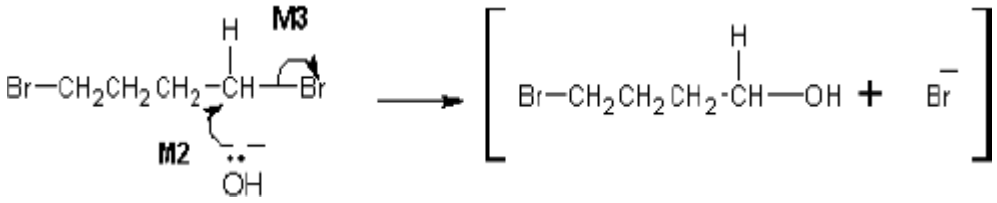
OR

Process 2 uses renewable glucose / renewable resource(s)

2

(b) (i) M1 <u>nucleophilic substitution</u>

*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 <u>original molecule</u>

*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** <u>fermentation</u>

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

Three conditions <u>in any order</u> 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]

11 (a) **M1** $C_6H_{12}O_6 \longrightarrow \mathbf{2}CH_3CH_2OH + \mathbf{2}CO_2$
($2C_2H_5OH$)

Mark independently

For M1 and M3 ignore state symbols and credit multiples

For M1 and M3 penalise C_2H_6O once only

M2 fermentation

M3 $CH_3CH_2OH + \mathbf{3}O_2 \longrightarrow \mathbf{2}CO_2 + \mathbf{3}H_2O$
(C_2H_5OH)

M4 A specified process e.g. planting / harvesting / transport / extracting sugar / distilling ethanol solution / fertiliser production etc.

M5 The specified process uses / burns (fossil) fuel that releases CO_2

For M5, "releases / increases carbon emissions" is insufficient as an alternative to releases CO_2

5

(b) **M1** sodium or potassium hydroxide / NaOH / KOH

Mark on to M2 from hydroxide ion

M2 depends on correct M1

Ignore OH^- if KOH/ OH^-

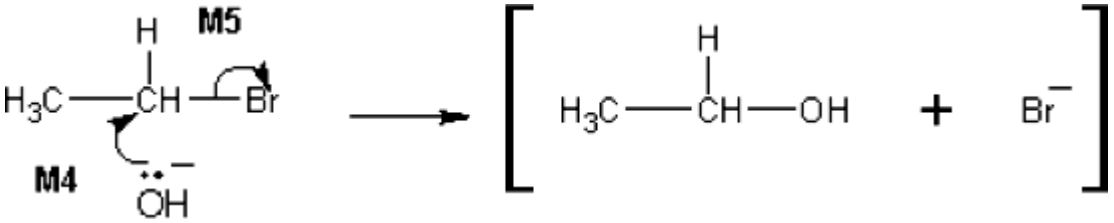
warm / heat / reflux <u>and</u> aqueous or (aq) or water

For M2 ignore "dilute"

For M2 penalise T > 100 °C

M3 <u>nucleophilic substitution</u>

Acidified KOH/NaOH or H_2SO_4 with KOH/NaOH loses M1 and M2



For M3, both words required

NB The arrows here are double-headed

M4 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 M4 if covalent NaOH / KOH is used

Penalise one mark from M4 or M5 if half-headed arrows are used

M5 must show the movement of a pair of electrons from the

C— Br bond to the Br atom. Mark M5 independently provided it is from their <u>original molecule.</u>

Penalise M5 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 M4 and M5, award full marks for an S_N1 mechanism

For M4 and M5, maximum 1 of 2 marks if wrong reactant is used.

Penalise M5 if an extra arrow is drawn from the Br of the C–Br bond to, for example, K^+span>

Do not penalise the use of "sticks"

M6 One statement from

- The yield is (very) low / not a high yield OR elimination occurs / ethene formed
- The rate of reaction slow
- <u>Bromoethane</u> has to be manufactured / made first
- <u>Bromoethane</u> is expensive

For M6 ignore references to other costs and expenses

6

(c) **M1** <u>concentrated</u> phosphoric acid / <u>conc</u>. H_3PO_4 ***OR*** <u>concentrated</u> sulfuric acid / conc. H_2SO_4

Answers in any order

Ignore reference to support medium in M1

M2 hydration or (electrophilic) addition

For M3 and M4 <u>any two</u> from

Do not apply the list principle to these three chosen criteria in M3 and M4

- <u>Excess</u> ethene

  OR <u>Excess</u> steam / water / H_2O

  OR remove the ethanol as it forms

  OR recycle the ethene

- <u>Specified</u> Pressure

  50 atm ≤ P ≤ 100 atm

  OR 5000 kPa ≤ P ≤ 10000 kPa

  OR 5 MPa ≤ P ≤ 10 MPa

- <u>High</u>Temperature unless they give a value that is not in the ranges given here;

  OR 300 °C ≤ T ≤ 600 °C

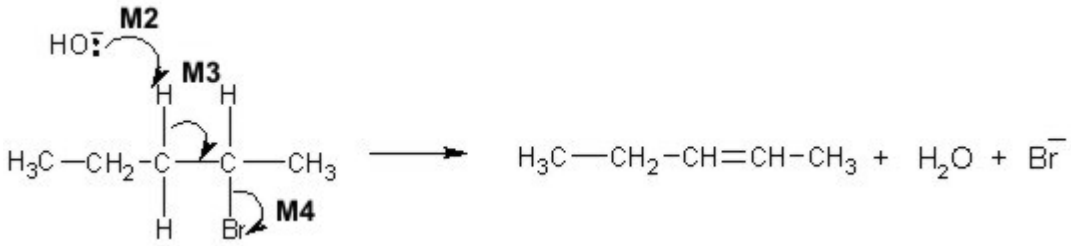
  OR 570 K ≤ T ≤ 870 K

  Accept a reference to "low temperature" if they specify a correct temperature range or a correct temperature in the range

4

[15]

12 (a) (i) **M1** <u>Elimination</u>



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**

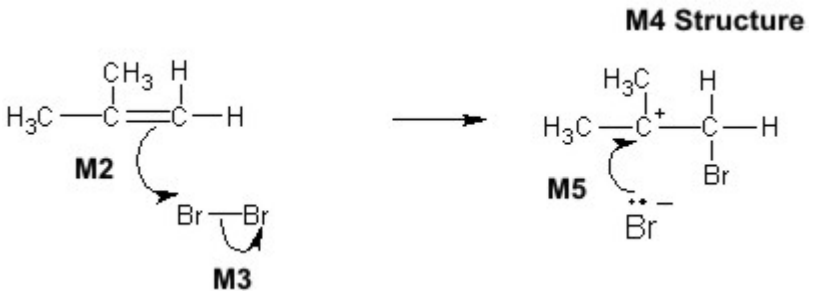
$CH_3CH_2CH_2CH=CH_2$

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

Max any 3 of 4 marks ***for the mechanism*** *for*

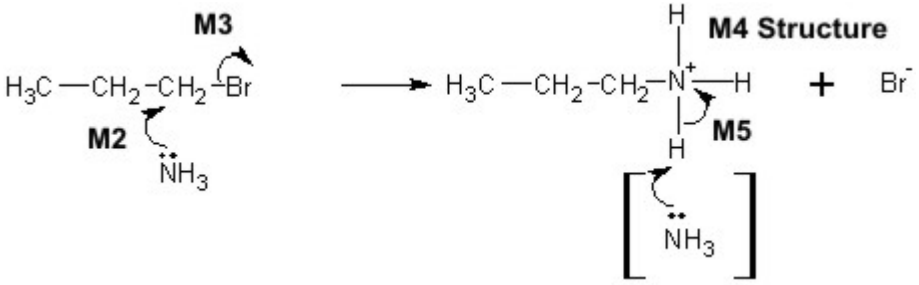
wrong organic reactant or wrong organic product (if shown) or primary carbocation.

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]

13 (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

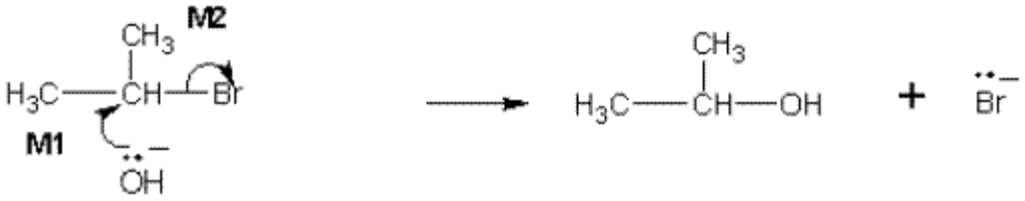
(Heat) energy/enthalpy required/needed/absorbed (at constant pressure) for homolysis of the (C–X/the carbon-halogen) bond

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

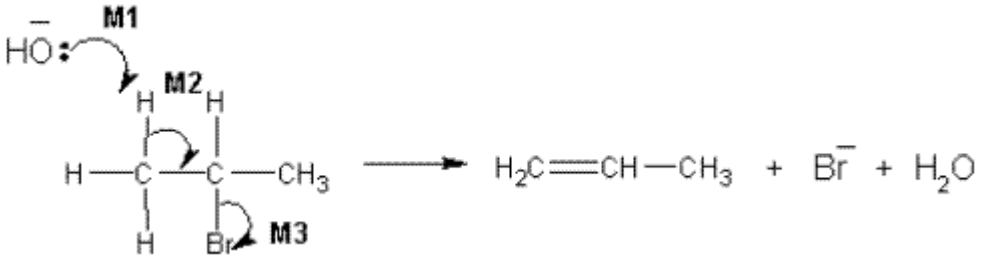
Penalise once only for a line and two dots to show a bond.

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]

14 (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

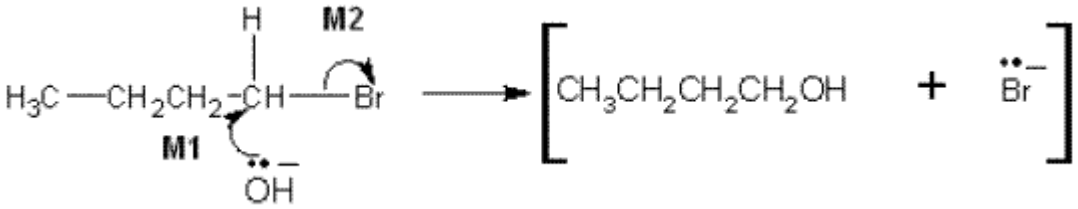
1

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

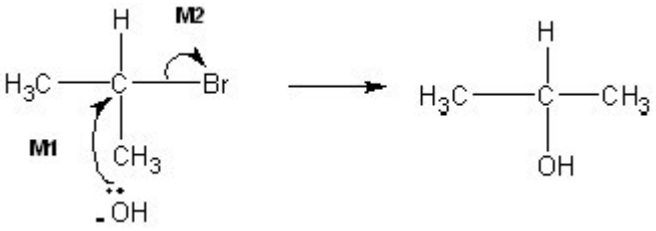
Ignore reference to the alleged relative stability of haloalkanes

1

[11]

15 (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)

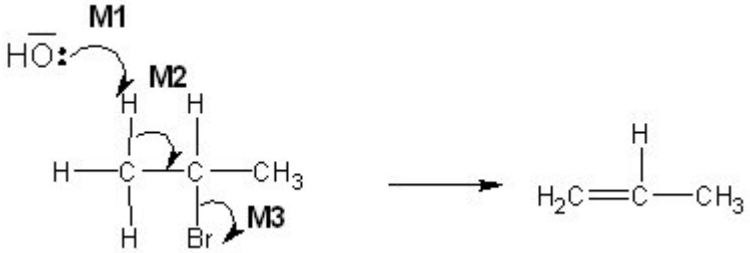
It must be clear that the discussion is about the carbon atom of the C–Br bond. NOT just reference to a polar molecule.
Ignore X for halogen

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]

16 (a) Electron pair donor

OR

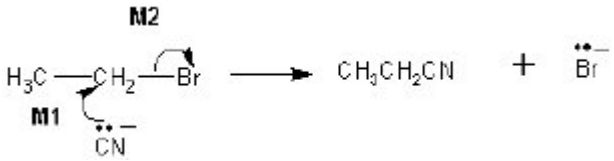
Species which uses a pair of electrons to form a co-ordinate / covalent bond.

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

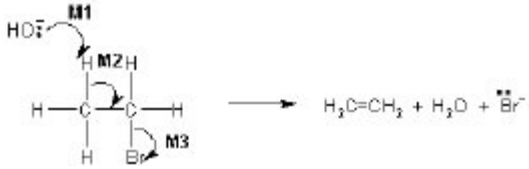
The idea that ammonia acts <u>both</u> initially as a nucleophile and then as a base

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.

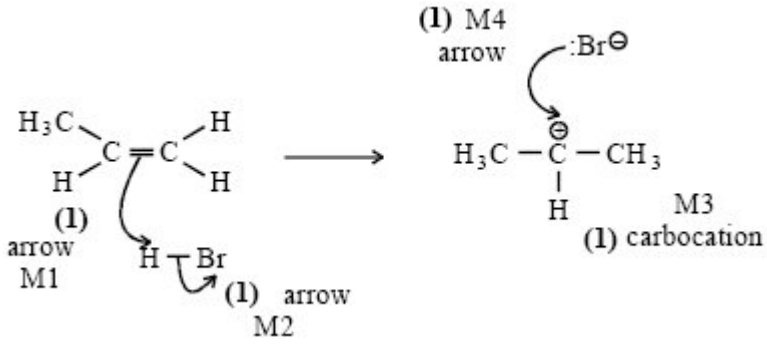
Award full marks for an E1 mechanism in which M2 is on the correct carbocation.

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

3

[8]

17 (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 •—•

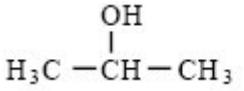
4

(ii) $\overset{\oplus}{CH_3CH_2CH_2}$

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*:  **(1)** [insist on C — OH bond]

1

Name: propan-2-ol

Not 2-hydroxypropane

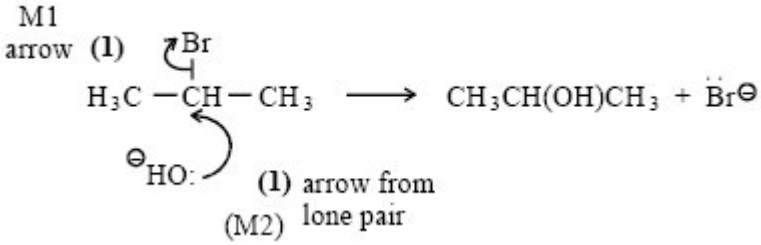
1

(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 <u>the arrows</u> even if incorrect haloalkane
If S_N1, <u>both marks</u> possible

2

(c) (i) elimination

1

(ii) base

OR proton acceptor

NOT nucleophile

1

[12]

18 D

[1]

19 (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]

20 D

[1]

21 (a) (i) Electrophilic addition

(Both words required)

1

(ii) M1 the reaction <u>to form 1-bromopropane</u> goes *via* the <u>primary carbocation</u> OR 1^o carbocation

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

M2 <u>primary carbocations are less stable than secondary carbocations</u>

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

(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^oC)
(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)

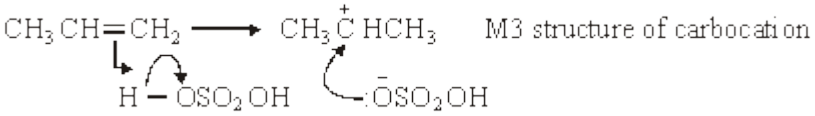
(Credit part (c) independently from part (b))

(Penalise "ethanoic")

1

(d) (i) Secondary OR 2^o

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]

22 (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.

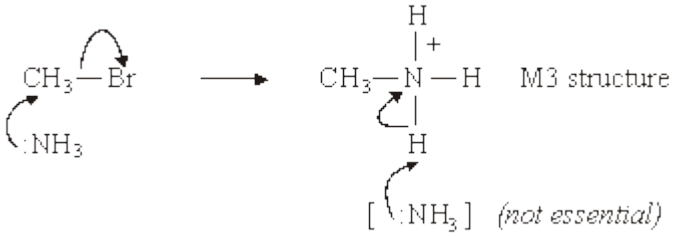
1

(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]

23 A

[1]

24 B

[1]

25 (a) (i) UV light OR sunlight OR T ≥ 450°C **(1)**

NOT high T

(ii) (free) <u>radical substitution</u> **(1)**

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

3

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

CN^- Cl^-

(ii) <u>nucleophilic substitution</u> **(1)**

(iii) <u>C–Br bond</u> is <u>weaker</u> (than C–Cl bond)
OR <u>C–Br bond</u> enthalpy is <u>less than</u> C–Cl **(1)**

Ignore electronegativity

3

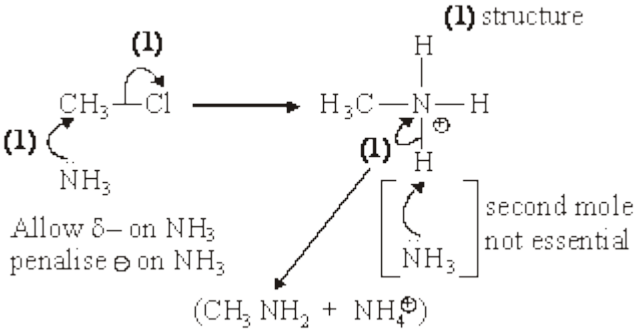
(c) CH_3COOH OR ethanoic acid **(1)**

1

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

(ii) methylamine **(1)** <u>only</u>

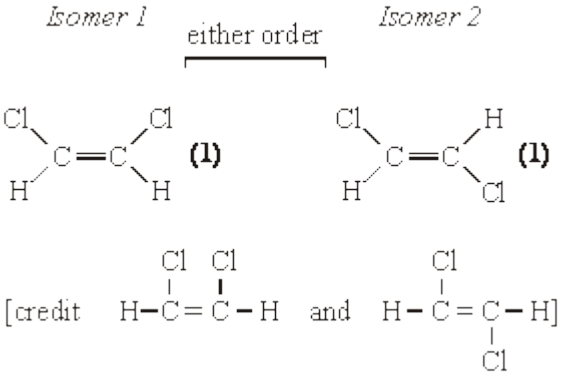
(iii) S_N1 scores full marks



6

[13]

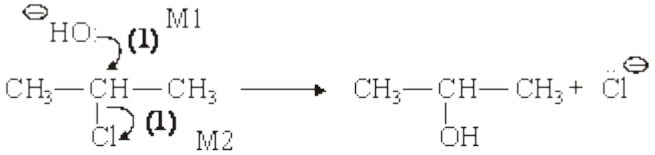
26 (a) (i)

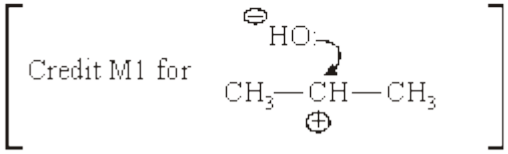


(ii) restricted <u>rotation</u> OR no <u>rotation</u> OR cannot <u>rotate</u> **(1)**

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*

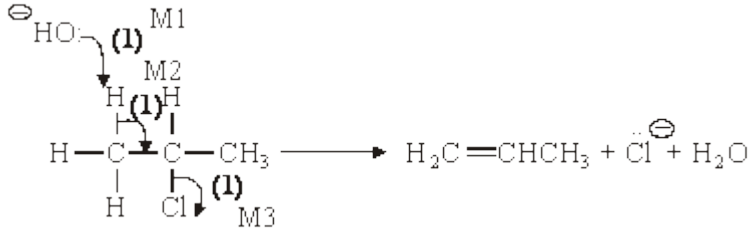
Penalise + on C atom for M2

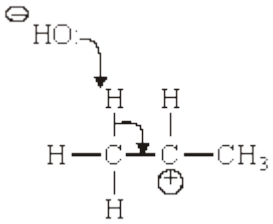
Only allow M1 for incorrect haloalkane

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)**

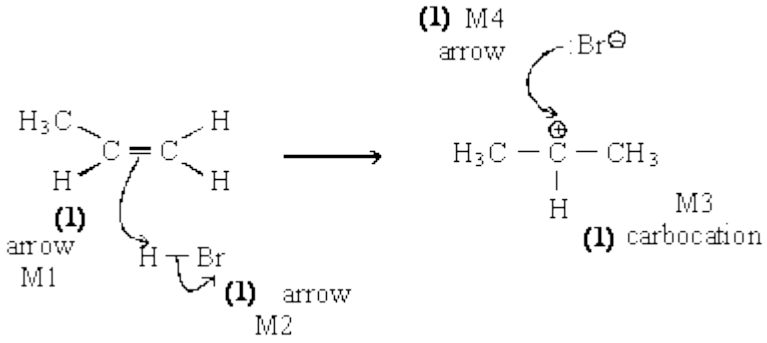
proton acceptor

accepts H^+

7

[10]

27 (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* ⟷

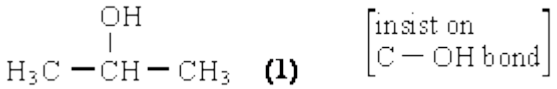
(ii) $CH_3CH_2\overset{\oplus}{C}H_2$ **(1)**

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*:



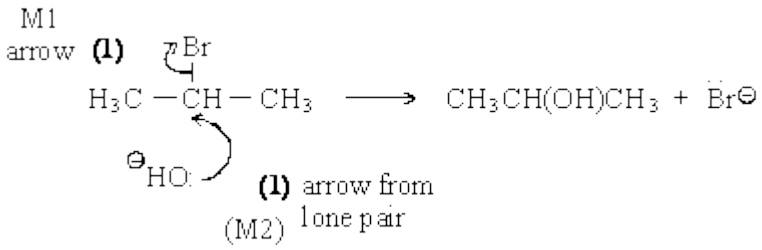
No credit for propan-1-ol even when named correctly
Credit propane-2-ol

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

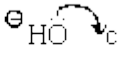
Not 2-hydroxypropane

(ii) *Name of mechanism*: nucleophilic substitution **(1) (both words)**
(NOT S_N1 orS_N2)

Mechanism:



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

i.e. M1 M2  correct carbocation

5

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

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

2

[12]

28 C

[1]

29 (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)**

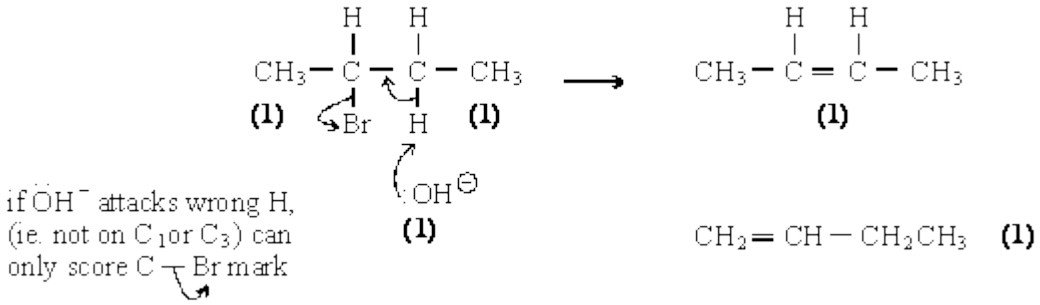
Brackets not essential

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)

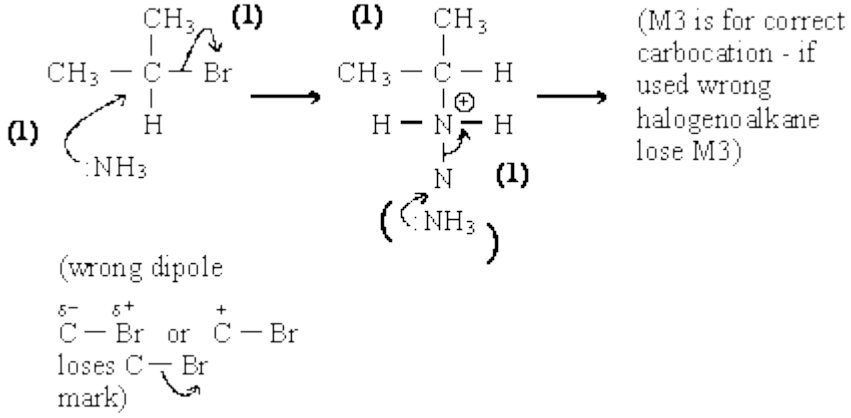
Draws clear Cis and trans isomers for but-2-ene

Can score these marks from a diagram

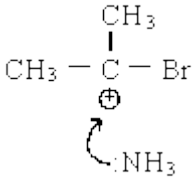
8

[17]

30 (a) *Name of mechanism*: nucleophilic substitution **(1)**
Mechanism:

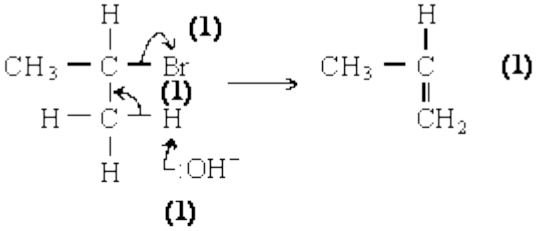


Marks S_N1 using same points
∴ *M2 requires*



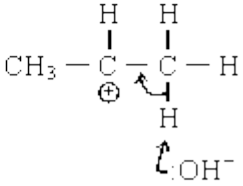
5

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



Mark E1 using same points

∴ M2/M3



5

[10]

31 B **[1]**

32 C **[1]**

33 B [1]

34 D [1]

35 A [1]

36 D [1]