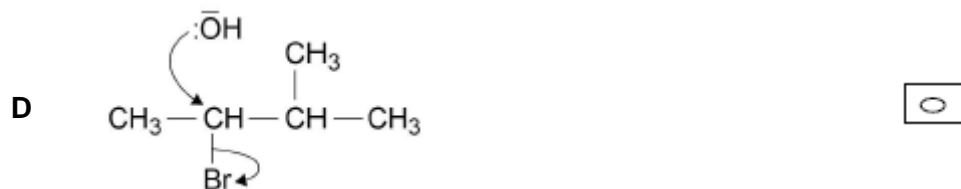
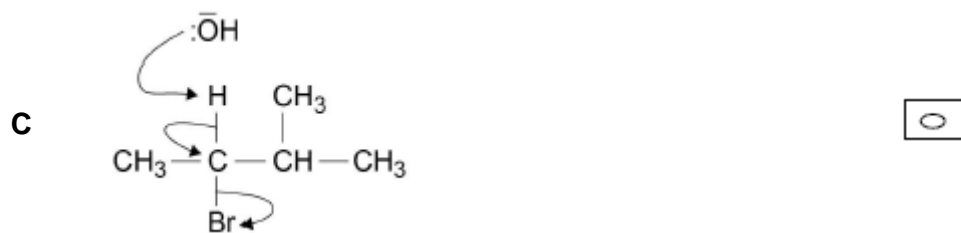
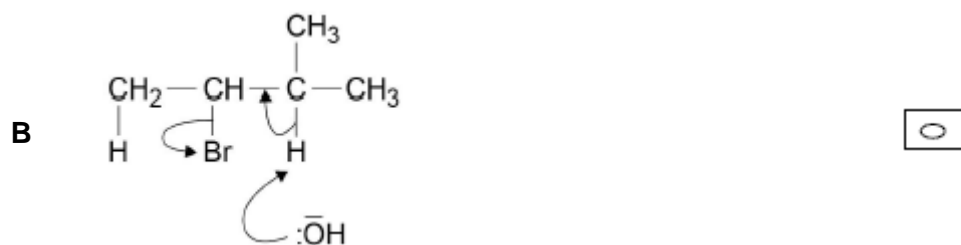
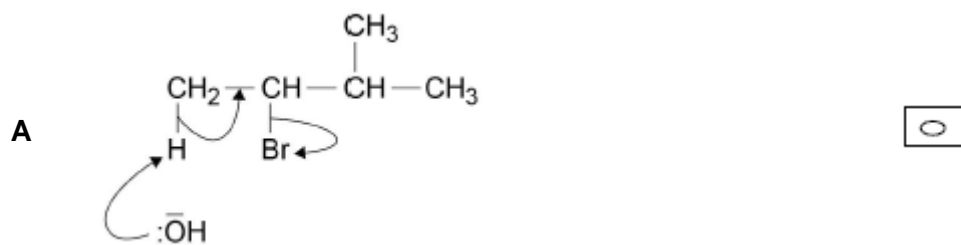


1

Which of the following is a correct mechanism for the formation of 2-methylbut-2-ene from 2-bromo-3-methylbutane?



(Total 1 mark)

2

There are many uses of halogenated organic compounds despite environmental concerns.

- (a) Bromotrifluoromethane is used in fire extinguishers in aircraft. Bromotrifluoromethane is formed when trifluoromethane reacts with bromine.



The reaction is a free-radical substitution reaction similar to the reaction of methane with chlorine.

- (i) Write an equation for each of the following steps in the mechanism for the reaction of  $\text{CHF}_3$  with  $\text{Br}_2$

Initiation step

.....

First propagation step

.....

Second propagation step

.....

A termination step

.....

(4)

- (ii) State **one** condition necessary for the initiation of this reaction.

.....

(1)

- (b) Bromine-containing and chlorine-containing organic compounds may have a role in the decomposition of ozone in the upper atmosphere.

- (i) Draw an appropriate **displayed formula** in the space provided to complete the following equation to show how  $\text{CBrF}_3$  may produce bromine atoms in the upper atmosphere.



.....

(1)

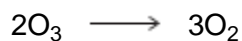
- (ii) In the upper atmosphere, it is more likely for  $\text{CBrF}_3$  to produce bromine atoms than it is for  $\text{CClF}_3$  to produce chlorine atoms.

Suggest **one** reason for this.

.....  
.....  
.....

(1)

- (iii) Bromine atoms have a similar role to chlorine atoms in the decomposition of ozone. The overall equation for the decomposition of ozone is



Write **two** equations to show how bromine atoms ( $\text{Br}\bullet$ ) act as a catalyst in the decomposition of ozone.

Explain how these two decomposition equations show that bromine atoms behave as a catalyst.

Equation 1

.....

Equation 2

.....

Explanation .....

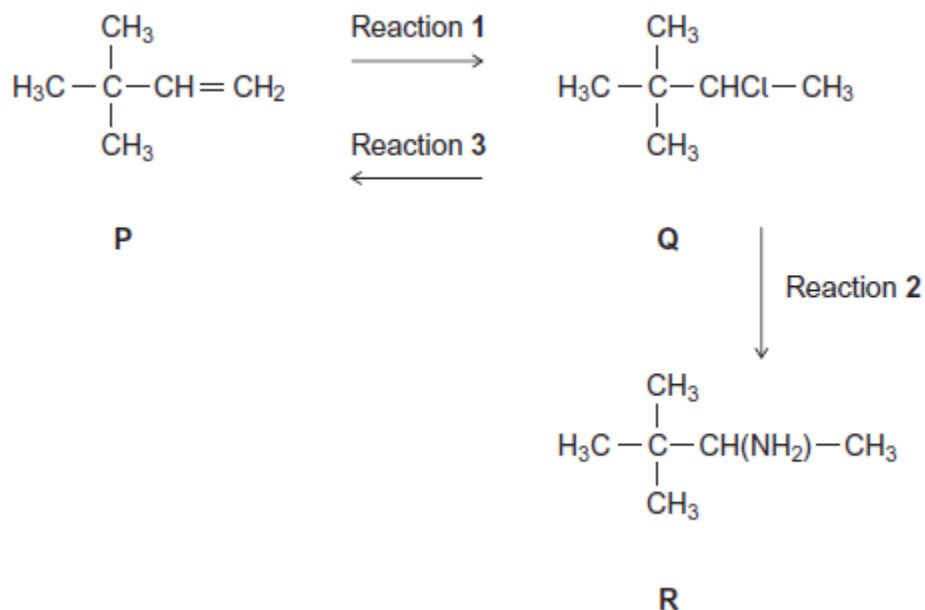
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(3)  
(Total 10 marks)

3

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<sub>3</sub>

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**.

.....  
.....  
.....  
.....  
.....

(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.

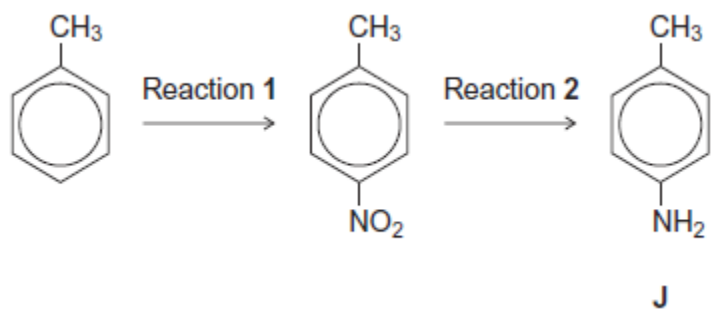
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(4)

(Total 19 marks)

4

Consider the following reaction sequence starting from methylbenzene.



(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  $\text{RNH}_2$  in the mechanism.

(4)

- (d) Compound **K** ( $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ ) is a structural isomer of **J**.

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

.....

.....

.....

.....


.....

.....

(3)  
(Total 11 marks)

5

The following table gives the names and structures of some structural isomers with the molecular formula  $C_5H_{10}$ .

	Name of isomer	Structure
Isomer 1	pent-2-ene	$CH_3CH = CHCH_2CH_3$
Isomer 2	cyclopentane	
Isomer 3	3-methylbut-1-ene	$(CH_3)_2CHCH = CH_2$
Isomer 4	2-methylbut-2-ene	$(CH_3)_2C = CHCH_3$
Isomer 5	2-methylbut-1-ene	$H_2C = C(CH_3)CH_2CH_3$

(a) Isomer 1 exists as E and Z stereoisomers.

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

.....  
.....  
.....  
.....  
.....

(2)

(ii) Draw the structure of the E stereoisomer of Isomer 1.

(1)



- (b) A chemical test can be used to distinguish between separate samples of Isomer **1** and Isomer **2**.

Identify a suitable reagent for the test.

State what you would observe with Isomer **1** and with Isomer **2**.

Reagent.....

Observation with Isomer **1**.....

.....

Observation with Isomer **2**.....

.....

(3)

- (c) Use **Table A** on the Data Sheet when answering this question.  
Isomer **3** and Isomer **4** have similar structures.

- (i) State the infrared absorption range that shows that Isomer **3** and Isomer **4** contain the same functional group.

.....

.....

(1)

- (ii) State **one** way that the infrared spectrum of Isomer **3** is different from the infrared spectrum of Isomer **4**.

.....

.....

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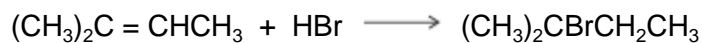
(1)

- (d) Two alcohols are formed by the hydration of Isomer **4**.

Draw the **displayed formula** for the alcohol formed that is oxidised readily by acidified potassium dichromate(VI).

(1)

- (e) Isomer **4** reacts with hydrogen bromide to give two structurally isomeric bromoalkanes.
- (i) Name and outline a mechanism for the reaction of Isomer **4** with hydrogen bromide to give 2-bromo-2-methylbutane as the major product.



Name of mechanism.....

Mechanism

(5)

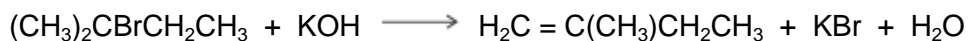
- (ii) The minor product in this reaction mixture is 2-bromo-3-methylbutane.

Explain why this bromoalkane is formed as a minor product.

.....  
 .....  
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(2)

- (f) Name and outline a mechanism for the following reaction to form Isomer **5**. State the role of the hydroxide ion in this reaction.



Name of mechanism .....

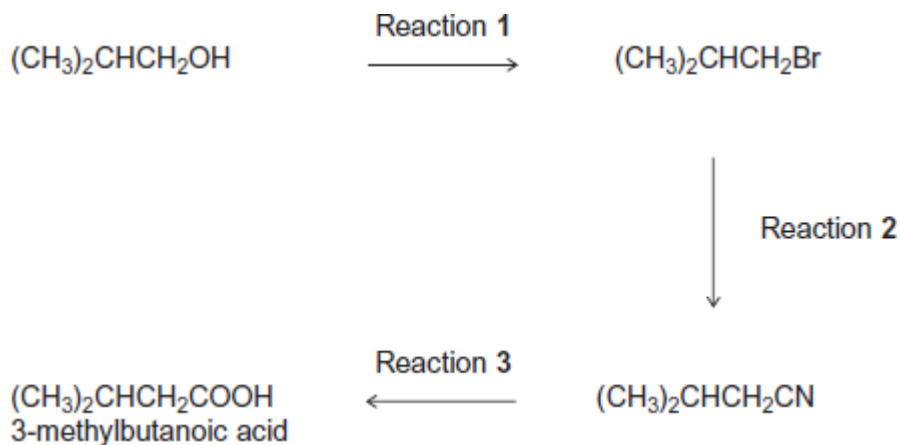
Mechanism

Role of hydroxide ion .....

(5)  
 (Total 21 marks)

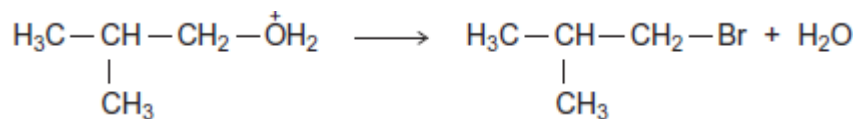
6

The carboxylic acid 3-methylbutanoic acid is used to make esters for perfumes. The following scheme shows some of the reactions in the manufacture of this carboxylic acid.



- (a) One of the steps in the mechanism for Reaction 1 involves the replacement of the functional group by bromine.
- (i) Use your knowledge of organic reaction mechanisms to complete the mechanism for this step by drawing **two** curly arrows on the following equation.

$\text{BF}_3$ :



(2)

- (ii) Deduce the name of the mechanism in part (i).

Give the IUPAC name of  $(\text{CH}_3)_2\text{CHCH}_2\text{Br}$

.....  
.....  
.....

(2)

- (b) Reaction **3** is an acid-catalysed reaction in which water is used to break chemical bonds when the CN functional group is converted into the COOH functional group. Infrared spectroscopy can be used to distinguish between the compounds in this reaction.

Deduce the name of the type of reaction that occurs in Reaction **3**.

Identify **one** bond in  $(\text{CH}_3)_2\text{CHCH}_2\text{CN}$  and a **different** bond in  $(\text{CH}_3)_2\text{CHCH}_2\text{COOH}$  that can be used with infrared spectroscopy to distinguish between each compound.

For each of these bonds, give the range of wavenumbers at which the bond absorbs.

Use **Table A** on the Data Sheet when answering this question.

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**(3)**

- (c) When 3-methylbutanoic acid reacts with ethanol in the presence of an acid catalyst, an equilibrium is established. The organic product is a pleasant-smelling ester.



The carboxylic acid is very expensive and ethanol is inexpensive. In the manufacture of this ester, the mole ratio of carboxylic acid to ethanol used is 1 to 10 rather than 1 to 1.

- (i) Use Le Chatelier's principle to explain why a 1 to 10 mole ratio is used. In your explanation, you should **not** refer to cost.

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(Extra space) .....  
.....

**(3)**

- (ii) Explain how a catalyst increases the rate of a reaction.

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.....  
.....  
.....

(Extra space) .....  
.....

**(2)**

**(Total 12 marks)**

**7**

The carbonyl compound  $\text{CH}_3\text{CH}_2\text{CHO}$  reacts very slowly with HCN

(a) Name and outline a mechanism for the reaction of  $\text{CH}_3\text{CH}_2\text{CHO}$  with HCN

Name of mechanism .....

Mechanism

**(5)**

(b) The reaction in part (a) produces a pair of enantiomers.

(i) Draw the structure of each enantiomer to show how they are related to each other.

**(2)**

(ii) State and explain how you could distinguish between the two enantiomers.

.....  
.....  
.....  
.....

**(2)**

(c) Give the IUPAC name of the product of the reaction in part (a).

.....

**(1)**

(d) In practice, KCN rather than HCN is added to the carbonyl compound.

Given that  $K_a$  for HCN =  $4.0 \times 10^{-10} \text{ mol dm}^{-3}$ , suggest why the reaction with HCN is very slow.

.....  
.....  
.....  
.....

**(2)**

(e) Acrylic fibres are used as a substitute for wool. Acrylics are copolymers of acrylonitrile with other compounds.

Acrylonitrile is the common name for the following compound.



(i) Acrylonitrile can be formed from propene.

Write an equation for the reaction of propene with ammonia and oxygen to form acrylonitrile and one other product.

.....

**(1)**

(ii) The term copolymer is used to describe the product obtained when two or more different monomers form a polymer.

Draw the repeating unit of the acrylic copolymer that contains 75% acrylonitrile monomer and 25% chloroethene monomer.

**(1)**

(iii) Name the type of polymerisation involved in part (ii)

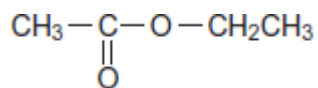
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**(1)**

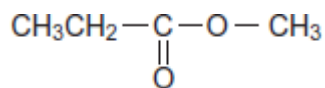
**(Total 15 marks)**

8

(a) **Ester 1** and **Ester 2** were studied by  $^1\text{H}$  n.m.r. spectroscopy.

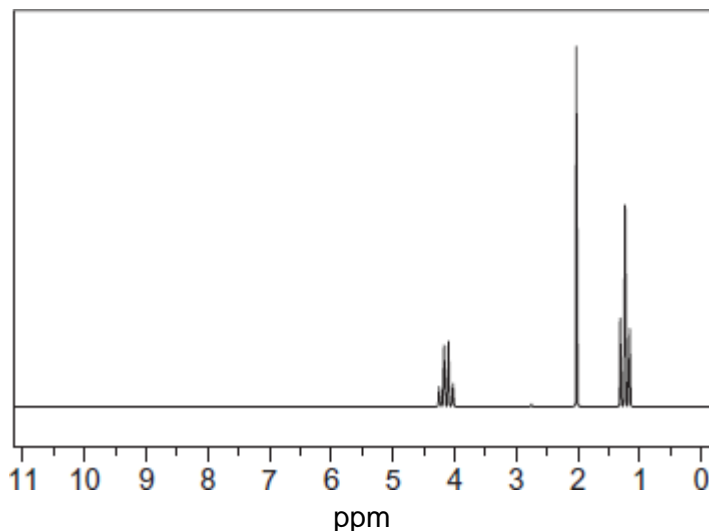


**Ester 1**



**Ester 2**

One of the two esters produced this spectrum.



Deduce which of the two esters produced the spectrum shown. In your answer, explain the position and splitting of the quartet peak at  $\delta = 4.1$  ppm in the spectrum.

Predict the  $\delta$  value of the quartet peak in the spectrum of the other ester.

Use **Table B** on the Data Sheet.

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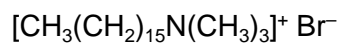
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(4)



(b) Cetrimide is used as an antiseptic.



cetrimide

Name this type of compound.

Give the reagent that must be added to  $\text{CH}_3(\text{CH}_2)_{15}\text{NH}_2$  to make cetrimide and state the reaction conditions.

Name the type of mechanism involved in this reaction.

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.....

**(4)**

(c) Give a reagent that could be used in a test-tube reaction to distinguish between benzene and cyclohexene.

Describe what you would see when the reagent is added to each compound and the test tube is shaken.

.....  
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**(3)**

**(Total 11 marks)**

9

Chlorine can be used to make chlorinated alkanes such as dichloromethane.

- (a) Write an equation for each of the following steps in the mechanism for the reaction of chloromethane (CH<sub>3</sub>Cl) with chlorine to form dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>).

Initiation step

.....

First propagation step

.....

Second propagation step

.....

The termination step that forms a compound with empirical formula CH<sub>2</sub>Cl.

.....

(4)

- (b) When chlorinated alkanes enter the upper atmosphere, carbon-chlorine bonds are broken. This process produces a reactive intermediate that catalyses the decomposition of ozone. The overall equation for this decomposition is



- (i) Name the type of reactive intermediate that acts as a catalyst in this reaction.

.....

(1)

- (ii) Write **two** equations to show how this intermediate is involved as a catalyst in the decomposition of ozone.

Equation 1.....

Equation 2.....

(2)

(Total 7 marks)

**10**

- (a) Name and outline a mechanism for the reaction of 2-bromo-2-methylpropane with ethanolic potassium hydroxide to form the alkene 2-methylpropene,  $(\text{CH}_3)_2\text{C}=\text{CH}_2$

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*

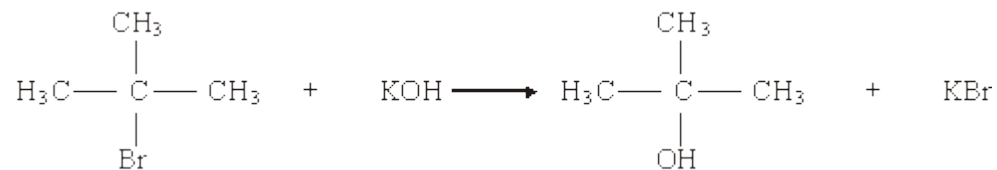
Name ..... Name .....

- (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  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$  reacts with an excess of ammonia. Name the organic product of this reaction.

Equation .....

Name of product .....

(3)  
(Total 13 marks)

11

Chlorination of ethane follows a free-radical substitution mechanism. This mechanism is similar to that which occurs when methane is chlorinated. The overall equation for the reaction of ethane to form chloroethane is given below.



State the conditions and outline a mechanism for this reaction. Show how butane can be formed in this reaction.

(Total 5 marks)

12

The mechanism for the reaction of methane with fluorine is a free-radical substitution similar to the chlorination of methane.

- (a) Outline the following steps in the mechanism for the reaction of methane with fluorine to form fluoromethane,  $\text{CH}_3\text{F}$

*Initiation step*

.....

*First propagation step*

.....

*Second propagation step*

.....

*A termination step*

.....

(4)

- (b) Write an overall equation for the reaction of fluorine with fluoromethane to form tetrafluoromethane.

.....

(1)

(Total 5 marks)

13

- (a) Addition reactions to both alkenes and carbonyl compounds can result in the formation of isomeric compounds.

- (i) Choose an alkene with molecular formula  $C_4H_8$  which reacts with HBr to form two structural isomers. Give the structures of these two isomers and name the type of structural isomerism shown.

Outline a mechanism for the formation of the major product.

- (ii) Using HCN and a suitable carbonyl compound with molecular formula  $C_3H_6O$ , outline a mechanism for an addition reaction in which two isomers are produced. Give the structures of the two isomers formed and state the type of isomerism shown.

(14)

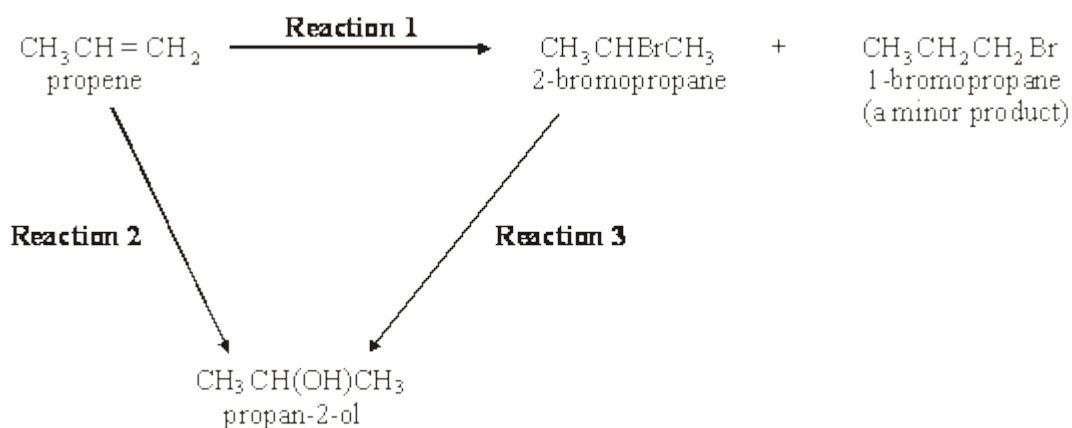
- (b) Explain why ethanoyl chloride reacts readily with nucleophiles.  
Write an equation for one nucleophilic addition–elimination reaction of ethanoyl chloride.  
(A mechanism is not required.)

(4)

(Total 18 marks)

**14**

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**.

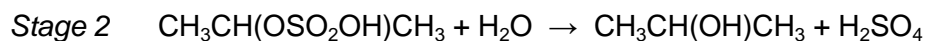
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**(3)**(b) Give a suitable reagent and state the essential conditions required for **Reaction 3**.*Reagent* .....*Conditions* .....**(2)**(c) The reagent used for **Reaction 3** can also be used to convert 2-bromopropane into propene. State the different conditions needed for this reaction.

.....

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

(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)

15

(a) Bromomethane,  $\text{CH}_3\text{Br}$ , 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.

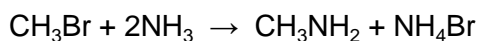
.....

- (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.



- (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)

16

(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.

.....

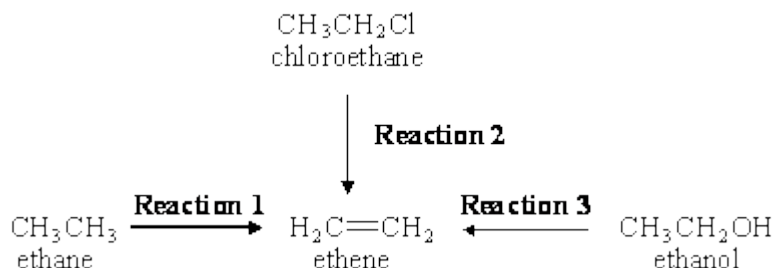
(iii) Outline a mechanism for this reaction.

**(6)**

**(Total 13 marks)**

**17**

Ethene is an important starting point for the manufacture of plastics and pharmaceutical chemicals. Most of the ethene used by industry is produced by the thermal cracking of ethane obtained from North Sea gas (**Reaction 1**). It is also possible to make ethene either from chloroethane (**Reaction 2**) or from ethanol (**Reaction 3**).



- (a) Give essential conditions and reagents for each of **Reactions 2** and **3**. (4)
- (b) Name and outline a mechanism for **Reaction 2**. Suggest a reason why chloroethane is **not** chosen by industry as a starting material to make ethene commercially. (5)
- (c) Name and outline a mechanism for **Reaction 3**. Suggest why this route to ethene may become used more commonly in the future as supplies of North Sea gas begin to run out. (6)

(6)  
(Total 15 marks)

**18**

When chlorine reacts with trichloromethane, tetrachloromethane,  $\text{CCl}_4$ , is formed.

- (a) (i) Write the overall equation for this reaction.

.....

- (ii) State **one** essential condition for this reaction.

.....

(2)

- (b) The mechanism for the chlorination of trichloromethane is free-radical substitution, which proceeds by a series of steps. Write equations for the steps named below in this chlorination.

*Initiation step*

.....

*First propagation step*

.....

*Second propagation step*

.....

*A termination step*

.....

(4)  
(Total 6 marks)

19

- (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*

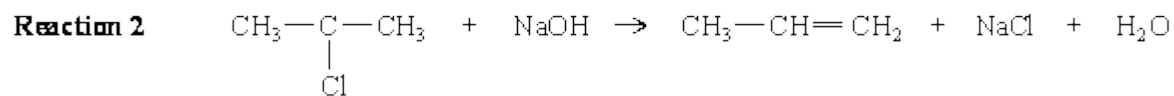
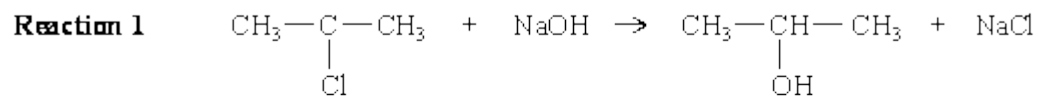
*Isomer 2*

- (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.



- (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*

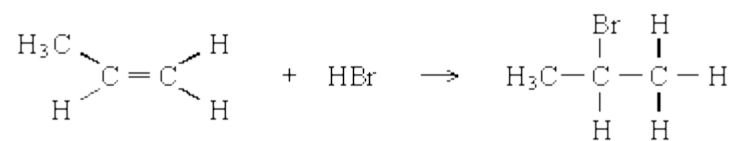
*Role of the hydroxide ion* .....

(7)  
(Total 10 marks)

**20**

- (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.

.....

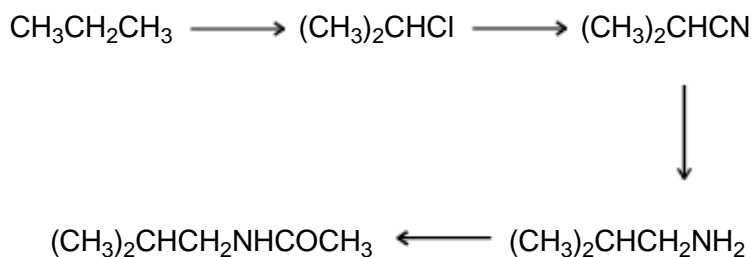
(ii) State the role of sodium hydroxide in this reaction.

.....

(2)  
(Total 12 marks)

21

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)

22

In the presence of ultraviolet light, methane and chlorine react to form a number of chlorine-containing products, including  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$

(i) Write an equation for the initiation step in the mechanism for this reaction.

.....

(ii) Write the overall equation for the formation of  $\text{CHCl}_3$  from  $\text{CH}_2\text{Cl}_2$  and  $\text{Cl}_2$

.....

(iii) Write equations for the two propagation steps by which  $\text{CH}_2\text{Cl}_2$  is converted into  $\text{CHCl}_3$

Equation 1 .....

Equation 2 .....



- (iv) Suggest what effect increasing the intensity of the ultraviolet light would have on the rate of the reaction between methane and chlorine. Explain your answer.

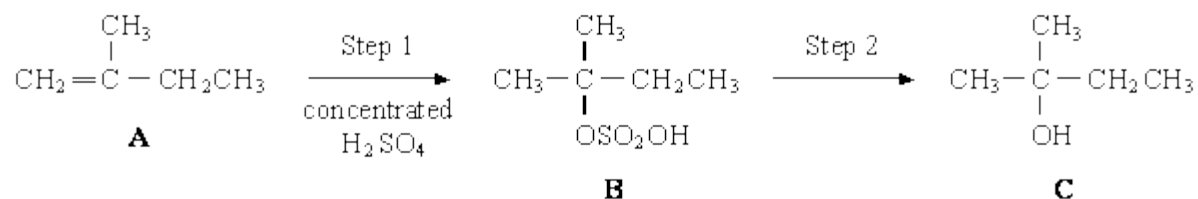
Effect on rate .....

Explanation .....

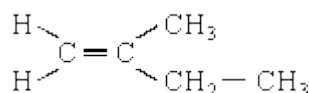
(Total 6 marks)

23

The reaction scheme below shows the conversion of compound **A**, 2-methylbut-1-ene, into compound **B** and then into compound **C**.



- (a) The structure of **A** is shown below. Circle those carbon atoms which must lie in the same plane.



(1)

- (b) Outline a mechanism for the reaction in Step 1.

(4)

- (c) State the reagent and condition used in Step 2. Name compound **C**.

Reagent .....

Condition .....

Name of compound **C** .....

(3)

- (d) When compound **A** is converted into compound **C**, a second alcohol, **D**, is also formed. Alcohol **D** is isomeric with **C** but is formed as a minor product. Identify alcohol **D** and explain why it is formed as the minor product.

Identity of alcohol **D** .....

Explanation .....

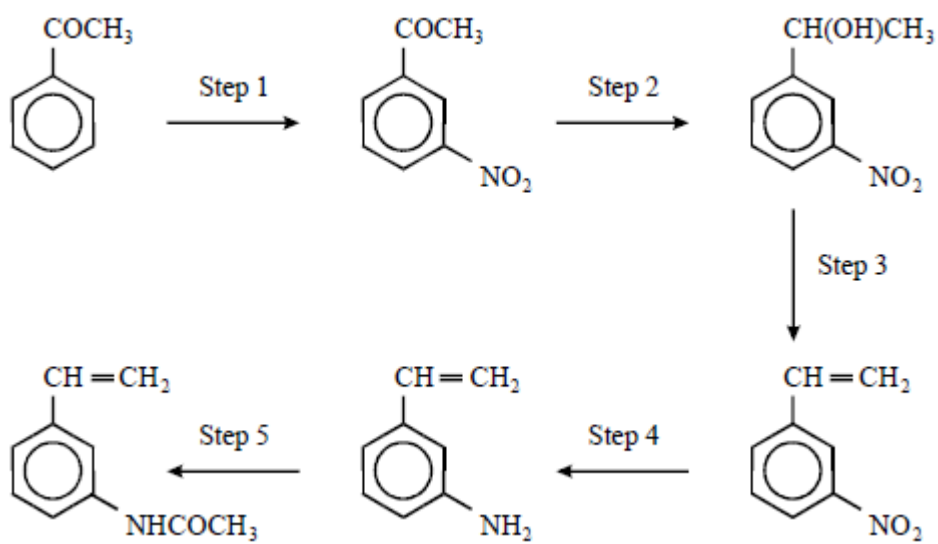
.....

.....

(3)  
(Total 11 marks)

24

Refer to the following reaction sequence:



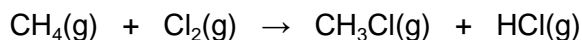
Which one of the following types of reaction mechanism is **not** involved in the above sequence?

- A electrophilic addition
- B electrophilic substitution
- C addition-elimination
- D elimination

(Total 1 mark)

25

The equation below represents a reaction between methane and chlorine.



- (a) State an essential condition required for this reaction to occur. Explain why this condition is essential.

*Condition* .....

*Explanation* .....

(2)

- (b) (i) State the type of mechanism involved in the above reaction.

.....

- (ii) Name the three types of step involved in this mechanism.

*Step 1* .....

*Step 2* .....

*Step 3* .....

(4)

- (c) In addition to  $\text{CH}_3\text{Cl}$ , compounds such as  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CH}_2\text{Cl}$  may also be formed when chlorine reacts with methane.

- (i) Write equations for the two steps in the mechanism by which  $\text{CH}_2\text{Cl}_2$  is formed from  $\text{CH}_3\text{Cl}$

*Equation 1* .....

*Equation 2* .....

- (ii) Write an equation to represent a step in the mechanism in which  $\text{CH}_3\text{CH}_2\text{Cl}$  is formed.

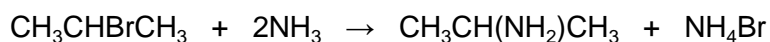
.....

(3)

(Total 9 marks)

26

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



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.

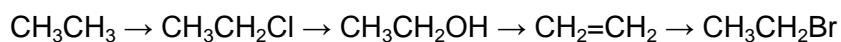
*Role of potassium hydroxide* .....

*Mechanism*

(5)  
(Total 10 marks)

27

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

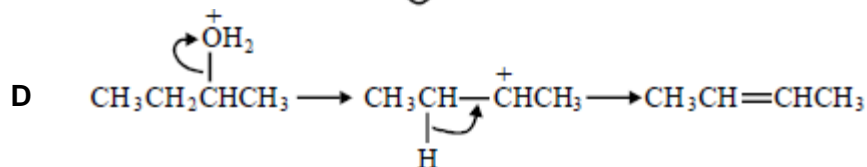
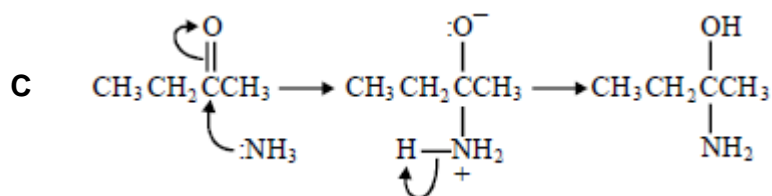
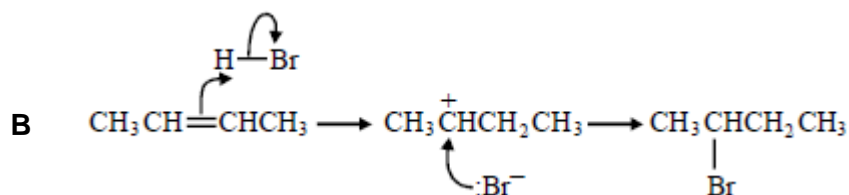
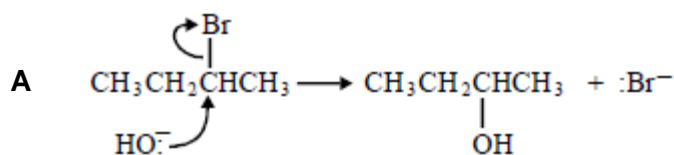


- A electrophilic addition
- B electrophilic substitution
- C nucleophilic substitution
- D free-radical substitution

(Total 1 mark)

28

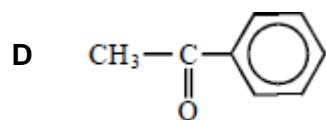
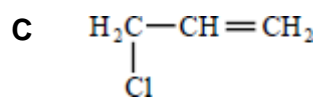
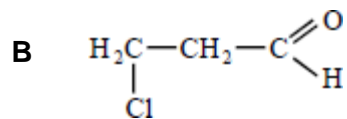
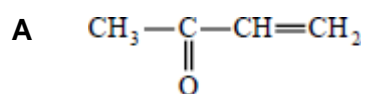
In which of the following is a curly arrow used incorrectly?



(Total 1 mark)

29

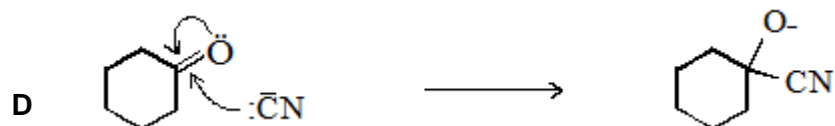
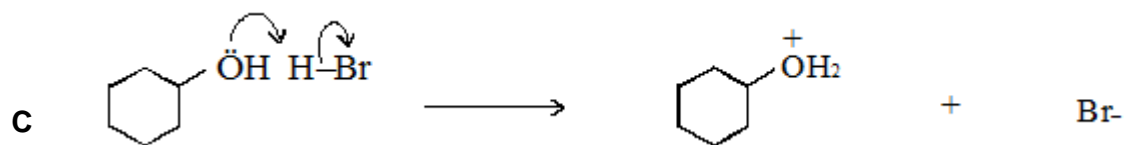
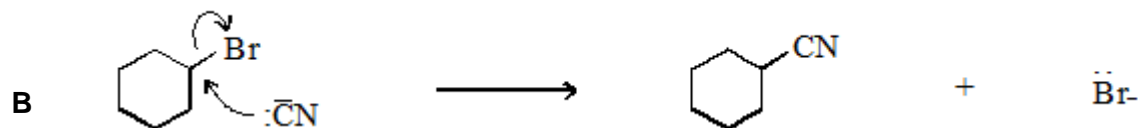
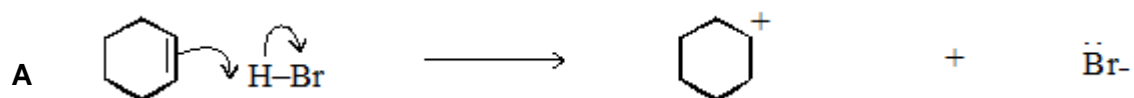
Which one of the following can react both by nucleophilic addition and by nucleophilic substitution?



(Total 1 mark)

30

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



(Total 1 mark)

## Mark schemes

1

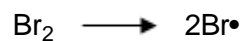
B

[1]

2

(a) (i)

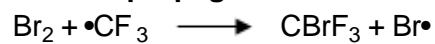
**Initiation**



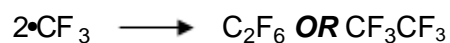
**First propagation**



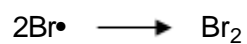
**Second propagation**



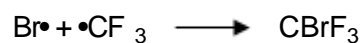
**Termination**



**OR**



**OR**



*Penalise absence of dot once only*

*Credit the dot anywhere on the radical*

4

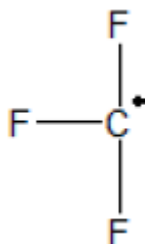
(ii) Ultra-violet / uv / sunlight

**OR**

T > 100°C OR high temperature

1

(b) (i)



*Displayed formula required with the radical dot on carbon*

1

- (ii) (The) C–Br (bond) breaks more readily / is weaker than (the) C–Cl (bond) (or converse)

**OR**

The C–Br bond enthalpy / bond strength is less than that for C–Cl (or converse)

*Requires a comparison between the two bonds*

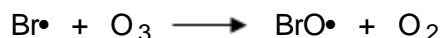
*Give credit for an answer that suggests that the UV frequency / energy may favour C–Br bond breakage rather than C–Cl bond breakage*

*Ignore correct references either to size, polarity or electronegativity*

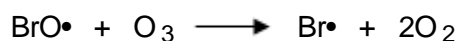
*Credit correct answers that refer to, for example “the bond between carbon and bromine requires less energy to break than the bond between carbon and chlorine”*

1

- (iii) **M1**



**M2**



*M1 and M2 could be in either order*

*Credit the dot anywhere on the radical*

*Penalise absence of dot once only*

*Penalise the use of multiples once only*

**M3 One of the following**

They / it / the bromine (atom)

- does not appear in the overall equation
- is regenerated
- is unchanged at the end
- has not been used up
- provides an alternative route / mechanism

3

[10]

3

- (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**

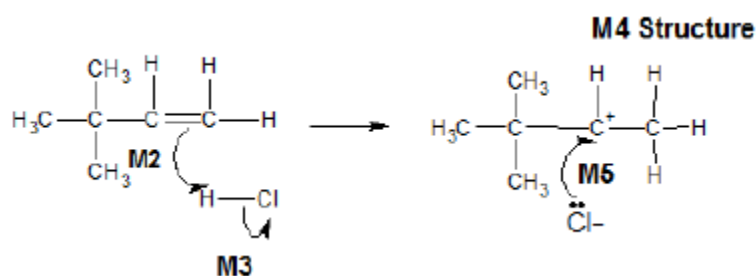
accept 2-chloro-3,3-dimethylbutane

*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*

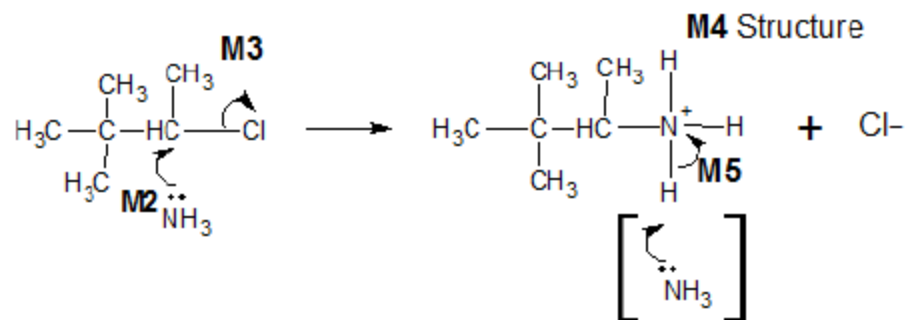
*Credit the correct use of "sticks"*

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

(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"

(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**



*M1 Credit correct ionic species in the equation*

**M2 and M3**

SO<sub>2</sub> **and** Br<sub>2</sub> identified

**M4**

Concentrated sulfuric acid

- is an oxidising agent
- oxidises the bromide (ion) or Br<sup>-</sup> 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<sub>2</sub> and Br<sub>2</sub>*

- *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]

4

(a) Electrophilic substitution

*Both words needed*

*Ignore minor misspellings*

1

(b) (i) Sn / HCl

**OR** H<sub>2</sub> / Ni **OR** H<sub>2</sub> / Pt **OR** Fe / HCl **OR** Zn / HCl **OR** SnCl<sub>2</sub> / HCl

*Ignore conc or dil with HCl,*

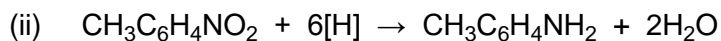
*Allow (dil) H<sub>2</sub>SO<sub>4</sub> but not conc H<sub>2</sub>SO<sub>4</sub>*

*Not allow HNO<sub>3</sub> or H<sup>+</sup>*

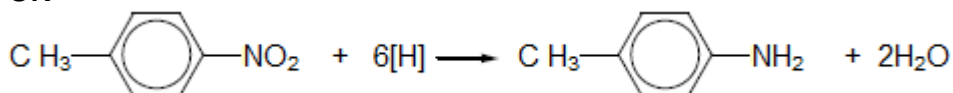
*Ignore NaOH after Sn / HCl*

*Ignore catalyst*

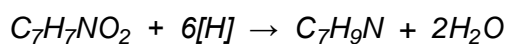
1



OR



Allow molecular formulae as structures given



Qu states use  $[\text{H}]$ , so penalised  $3\text{H}_2$

1

(iii) making dyes

OR making quaternary ammonium salts

OR making (cationic) surfactants

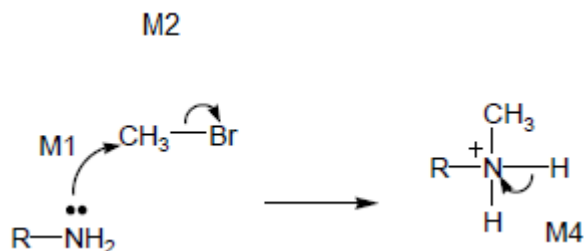
OR making hair conditioner

OR making fabric softener

OR making detergents

1

(c)



M3

NO Mark for name of mechanism

Allow  $\text{SN}1$

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  $\text{RNH}_2$  or  $\text{NH}_3$  removing  $\text{H}^+$  but penalise  $\text{Br}^-$

4

(d) lone or electron pair on N

If no mention of lone pair  $\text{CE} = 0$

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  $\pi$  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]

5

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

*Penalise **M1** if 'same structure' or 'different structural / displayed formula'.*

**M2** with atoms / bonds / groups arranged differently in space

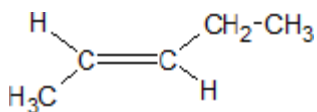
**OR** atoms / bonds / groups with different spatial arrangements / different orientation

*Ignore references to 'same molecular formula' or 'same empirical formula'.*

*Mark independently.*

2

(ii)



*Credit C-H<sub>3</sub>C*

*Credit C<sub>2</sub>H<sub>5</sub>*

*Penalise C-CH<sub>3</sub>CH<sub>2</sub>*

1

(b) **M1** Br<sub>2</sub> OR bromine (water) OR bromine (in CCl<sub>4</sub> / organic solvent)

*If **M1**, has no reagent or an incorrect reagent, **CE=0**.*

*Ignore 'acidified'.*

**M2** Isomer 1: decolourised / goes colourless / loses its colour

*For **M1** penalise Br (or incorrect formula of other correct reagent), but mark on.*

**M3** Isomer 2: remains orange / red / yellow / brown / the same **OR** no reaction / no (observable) change **OR** reference to colour going to the cyclopentane layer

*For **M1**, it must be a whole reagent and / or correct formula.*

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

*OR 'manganate(IV)' or incorrect formula, penalise **M1**, but mark on.*

**Alternatives : potassium manganate(VII)**

**M1** KMnO<sub>4</sub> in acid **M2** colourless **M3** purple

**M1** KMnO<sub>4</sub> in alkali / neutral **M2** brown solid **M3** purple

Credit for the use of **iodine**

**M1** iodine (solution / in KI) **M2** colourless **M3** (brown) to purple (credit no change)

Credit for the use of **concentrated H<sub>2</sub>SO<sub>4</sub>**

**M1** concentrated H<sub>2</sub>SO<sub>4</sub> **M2** brown **M3** no change / colourless

*Ignore 'goes clear'.*

*Ignore 'nothing (happens)'.*

*Ignore 'no observation'.*

*No credit for combustion observations.*

3

(c) (i) (Both infrared spectra show an absorption in range) **1620 to 1680** (cm<sup>-1</sup>)

*Ignore reference to other ranges (eg for C–H or C–C).*

1

(ii) The fingerprint (region) / below 1500 cm<sup>-1</sup> will be different **or** its fingerprinting will be different

**OR**

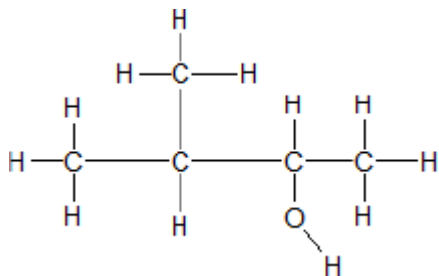
different absorptions / peaks are seen (in the region) below 1500 cm<sup>-1</sup> (or a specified region within the fingerprint range)

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

**QoL**

1

(d)



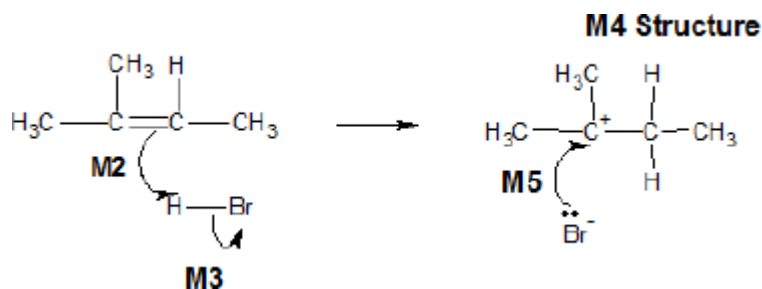
All bonds must be drawn.

Ignore bond angles.

1

(e) (i) **M1 Electrophilic addition**

**M1** both words needed.



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

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

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

**M3** must show the breaking of the H–Br bond

**M3** Penalise incorrect partial charges on H–Br bond and penalise formal charges.

**M4** is for the structure of the tertiary carbocation

Penalise **M4** if there is a bond drawn to the positive charge.

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 positively charged carbon atom of either a secondary or a tertiary carbocation

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

**Max 3 of any 4 marks in the mechanism** for wrong organic reactant or wrong organic product (if shown) or secondary carbocation.

**Max 2 of any 4 marks in the mechanism** for use of bromine.

Do not penalise the correct use of 'sticks'.

**NB** The arrows here are double-headed

5

- (ii) **M1** Reaction goes via intermediate carbocations / carbonium ions  
*M1 is a lower demand mark for knowledge that carbocations are involved.*

**M2 (scores both marks and depends on M1)**

Tertiary carbocation / carbonium ion is more stable (than the secondary carbocation / carbonium ion)

**OR**

Secondary carbocation / carbonium ion is less stable (than the tertiary carbocation / carbonium ion)

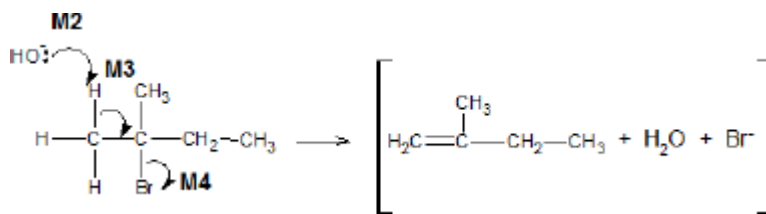
*M2 is of higher demand and requires the idea that the secondary carbocation is less stable or the tertiary carbocation is more stable. Reference to incorrect chemistry is penalised.*

*A carbocation may be defined in terms of alkyl groups / number of carbon atoms, rather than formally stated.*



(f) **M1 Elimination**

*M1 credit 'base elimination' but no other qualifying prefix.*



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

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

*Penalise **M2** if covalent KOH*

**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**)

**M4** is independent provided it is from their original molecule **BUT penalise **M2, M3** and **M4** if nucleophilic substitution** shown

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

**NB The arrows here are double-headed**

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

*Penalise **M4** if an additional arrow is drawn from the Br of the C-Br bond to, for example, K<sup>+</sup>.*

*Ignore other partial charges.*

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

***Max 2 of any 3 marks in the mechanism** for wrong reactant or wrong organic product (if shown) or a correct mechanism that leads to the alkene 2-methylbut-2-ene.*

*Credit the correct use of "sticks" for the molecule except for the C-H being attacked.*

**M5** hydroxide ion behaves as a base / proton acceptor / electron pair donor / lone pair donor

*Penalise **M5** if 'nucleophile'.*

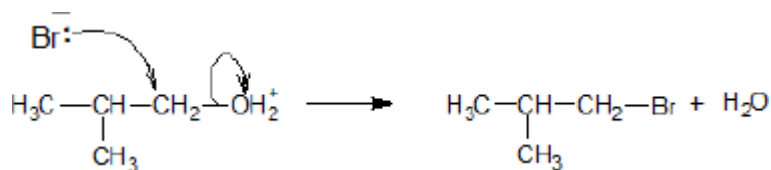
**6**

- (a) (i) **M1** double-headed curly arrow from the lone pair of the bromide ion to the C atom of the CH<sub>2</sub>

*Penalise additional arrows.*

- M2** double-headed arrow from the bond to the O atom

As follows



2

- (ii) **M1** nucleophilic substitution

*M1 both words needed (allow phonetic spelling).*

- M2** 1-bromo(-2-)methylpropane

*M2 Require correct spelling in the name but ignore any hyphens or commas.*

2

- (b) **M1** hydrolysis

*For M1 give credit for 'hydration' on this occasion only.*

- M2** C≡N with absorption range 2220–2260 (cm<sup>-1</sup>)

*Credit 1 mark from M2 and M3 for identifying C≡N and either O–H(acids) or C=O or C–O without reference to wavenumbers or with incorrect wavenumbers.*

- M3** O–H(acids) with absorption range 2500–3000 (cm<sup>-1</sup>)

**OR**

- C=O with absorption range 1680–1750 (cm<sup>-1</sup>)

**OR**

- C–O with absorption range 1000–1300 (cm<sup>-1</sup>)

*Apply the list principle to M3*

3

(c) (i) **M1** Yield / product **OR** ester increases / goes up / gets more

**M2** (By Le Chatelier's principle) the position of equilibrium is driven / shifts / moves to the right / L to R / in the forward direction / to the product(s)

**M3 – requires a correct statement in M2**

(The position of equilibrium moves)

to oppose the increased concentration of ethanol

to oppose the increased moles of ethanol

to lower the concentration of ethanol

to oppose the change and decrease the ethanol

*If no reference to **M1**, marks **M2** and **M3** can still score BUT if **M1** is incorrect CE=0*

*If there is reference to 'pressure' award **M1** ONLY.*

3

(ii) **M1**

Catalysts provide an alternative route / pathway / mechanism

**OR**

surface adsorption / surface reaction occurs

*For **M1**, not simply 'provides a surface' as the only statement.*

***M1** may be scored by reference to a specific example.*

**M2**

that has a lower / reduced activation energy

**OR**

lowers / reduces the activation energy

*Penalise **M2** for reference to an increase in the energy of the molecules.*

*For **M2**, the student may use a definition of activation energy without referring to the term.*

*Reference to an increase in successful collisions in unit time alone is not sufficient for **M2** since it does not explain why this has occurred.*

2

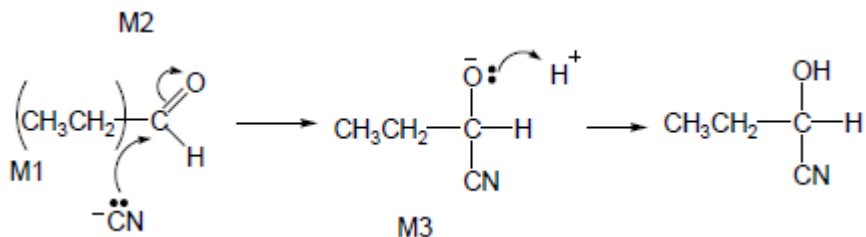
[12]

7

(a) Nucleophilic addition

1

M4 for lp, arrow and H<sup>+</sup>

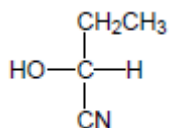


Allow C<sub>2</sub>H<sub>5</sub>- for CH<sub>3</sub>CH<sub>2</sub>-

- M1 and M4 include lone pair and curly arrow.
- Allow: CN<sup>-</sup> but arrow must start at lone pair on C.
- M2 not allowed independent of M1, but allow M1 for correct attack on C<sup>+</sup>.
- + rather than δ<sup>+</sup> on C=O loses M2.
- Penalise incorrect partial charges.
- M3 is for correct structure including minus sign but lone pair is part of M4.
- Penalise extra curly arrows in M4.

4

(b) (i) M1



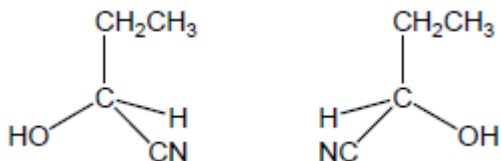
M1 for correct structure of product of part (a).

Allow C<sub>2</sub>H<sub>5</sub>- for CH<sub>3</sub>CH<sub>2</sub>-.

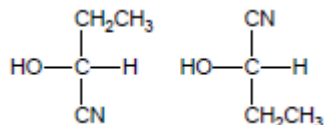
Penalise wrongly bonded, OH or CN or CH<sub>2</sub>CH<sub>3</sub> once only in clip.

1

M2

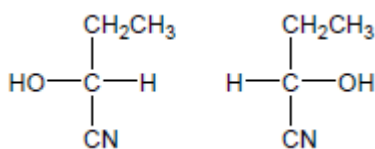


M2 cannot be gained by simply swapping two or more groups with no attempt to show a mirror image., e.g. do not allow M2 for



because these do not show the enantiomers as mirror images.

Students must show an attempt at mirror images, eg allow

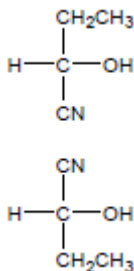


ie vertical groups same and horizontal swapped as if there was a mirror between them

No mirror need be shown

Do not penalize wedge bond when wedge comes into contact with both C & N

However these two could score M2 if placed as below as if with a "mirror" horizontally between them.



1

- (ii) M1 (Plane) polarized light  
M2 only scores following correct M1

1

M2 Rotated in opposite directions (equally) (only allow if M1 correct or close)

Not just in different directions but allow one rotates light to the left and one to the right.

Not molecules rotate.

1

- (c) 2-hydroxybutane(-1-)nitrile

1

- (d) Weak acid / (acid) only slightly / partially dissociated / ionised  
*Ignore rate of dissociation.*

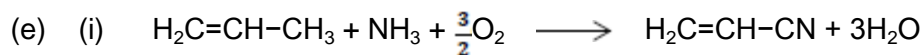
1

[CN<sup>-</sup>] very low

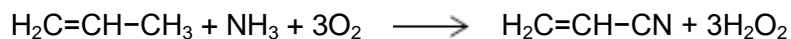
*Allow (very) few cyanide ions.*

*Mark independently.*

1



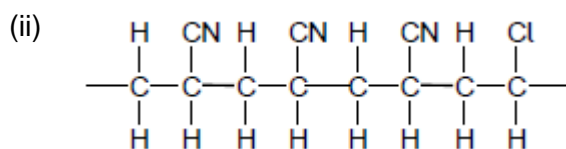
**OR**



*OR doubled.*

*Allow C<sub>3</sub>H<sub>6</sub> and CH<sub>2</sub>CHCN or C<sub>3</sub>H<sub>3</sub>N on this occasion only.*

1

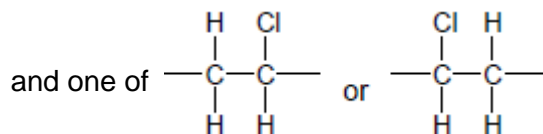
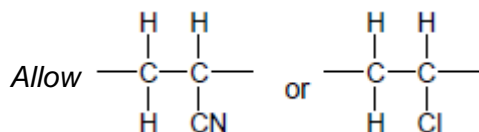
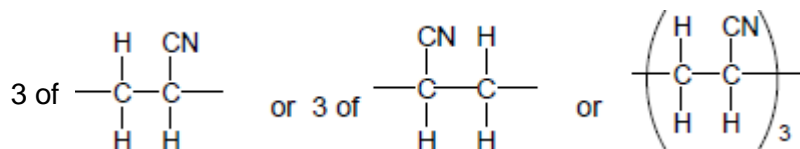


*Ignore n.*

*Must show trailing bonds.*

*Do not penalise C–NC bond here on this occasion.*

Must contain, in any order,



*Allow –CH<sub>2</sub>CH(CN)CH<sub>2</sub>CHCl– etc.*

1

- (iii) Addition (polymerization)

*Allow self-addition.*

*Do not allow additional.*

1

[15]

**8**

(a) M1 Ester 1

*If Ester 2, can score M3 only.*

1

M2 peak at  $\delta = 4.1$  due to  $(R)-C(=O)-O-\overset{\overset{(H)}{\uparrow}}{\underset{\underset{H}{\downarrow}}{\text{C}}}-$

*When marking M2 and M3, check any annotation of structures in the stem at the top of the page.*

1

M3 ( $\delta = 4.1$  peak is) quartet as adjacent / next to / attached to CH<sub>3</sub>

1

M4 Other spectrum quartet at  $\delta = 2.1-2.6$  (or value in this range)

1

(b) M1 Quaternary (alkyl) ammonium salt / bromide

1

M2 CH<sub>3</sub>Br or bromomethane*Penalise contradictory formula and name.*

1

M3 Excess ( CH<sub>3</sub>Br or bromomethane)*Mention of acid eg H<sub>2</sub>SO<sub>4</sub> OR alkali eg NaOH loses both M2 and M3.*

1

M4 Nucleophilic substitution

*Can only score M3 if reagent correct.**Ignore alcohol or ethanol (conditions) or Temp.*

1

(c)

	Bromine	Acidified KMnO <sub>4</sub>
	(penalise Br but mark on)	(Penalise missing acid but mark on)

*Wrong reagent = no marks.**If bromine colour stated it must be red, yellow, orange, brown or any combination, penalise wrong starting colour.*

1

Benzene	no reaction / colour remains / no (visible) change	no reaction / colour remains / no (visible) change
---------	--	--

*Ignore 'clear', 'nothing'.*

*Allow colour fades slowly.*

*Allow 'nvc' for no visible change.*

1

cyclohexene	(Bromine) decolourised	(Acidified KMnO <sub>4</sub> ) decolourised
-------------	------------------------	---

1

[11]

9

(a) **Initiation**



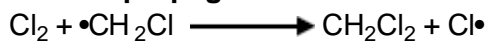
*Penalise absence of dot once only.*

**First propagation**



*Credit the dot anywhere on the radical.*

**Second propagation**



**Termination (must make 1,2-dichloroethane)**



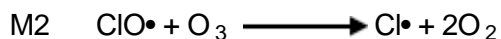
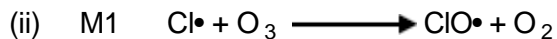
*Penalise C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>*

4

(b) (i) (chlorine free) radical

*Ignore formula.*

1



***M1** and **M2** could be in either order.*

*Credit the dot anywhere on the radical.*

*Penalise absence of dot once only.*

*Individual multiples acceptable but both need to be doubled if two marks are to be awarded.*

2

[7]



(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

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

1

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

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

*(penalise 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)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} + 2\text{NH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 + \text{NH}_4\text{Br}$   
(M1 correct product)  
(M2 balanced equation using  $2\text{NH}_3$  and leading to  $\text{NH}_4\text{Br}$ )  
(penalise M1 for use of  $\text{C}_4\text{H}_9\text{NH}_2$  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]

11

M1: uv light/sunlight

OR

T = 450 °C to 1000 °C;

(do not credit "high temperature")  
(ignore references to pressure or catalyst)  
(penalise M1 if aqueous chlorine OR chlorine water)  
(credit M1 if the condition appears over the arrow of the initiation step)

M2:  $\text{Cl}_2 \rightarrow 2\text{Cl}\cdot$ ;

(credit correct half arrows, but penalise (once in the question) the use of double headed arrows)

M3:  $\text{C}_2\text{H}_6 + \text{Cl}\cdot \rightarrow \text{CH}_3\text{CH}_2\cdot + \text{HCl}$ ;

(credit  $\text{CH}_3\text{CH}_3$  for ethane and  $\text{C}_2\text{H}_5\cdot$  for the ethyl radical)

M4:  $\text{CH}_3\text{CH}_2\cdot + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_5\text{Cl} + \text{Cl}\cdot$ ;



*(penalise the absence of dots once only in this question)*

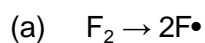
*(penalise subsequent ionic reactions as contradictions for each reaction contradicted)*

*(if neither M3 nor M4 scored, allow  $\text{CH}_3\text{CH}_2\cdot + \text{Cl}\cdot \rightarrow \text{C}_2\text{H}_5\text{Cl}$  for one mark)*

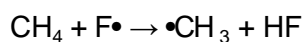
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[5]

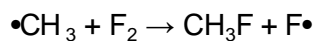
12



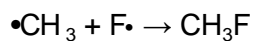
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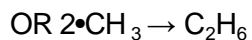
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1



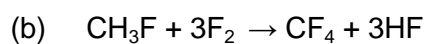
1



*(allow credit on this occasion for  $2\text{F}\cdot \rightarrow \text{F}_2$ )*

*(penalise incorrect symbol F1, once only)*

*(penalise absence of radical dot once only)*



1

[5]

13

- (a) (i) An appropriate alkene;  $\text{CH}_3\text{CH}_2\text{CHCH}_2$  or  $(\text{CH}_3)_2\text{CCH}_2$  1
- Isomer 1 1
- Isomer 2 1
- Position isomerism 1
- Mechanism
- electrophilic attack and electron shift to Br (Unless  $\text{H}^+$  used) 1
- carbocation 1
- reaction with carbocation  
*[Allow mechanism marks for the alkene  $\text{CH}_3\text{CHCHCH}_3$ ]  
[Allow one mark if mechanism for minor product given]* 1
- (ii) An appropriate carbonyl;  $\text{CH}_3\text{CH}_2\text{CHO}$  1
- Mechanism nucleophilic attack and electron shift to O 1
- anion intermediate 1
- reaction with anion  
*[Allow mechanism marks for the carbonyl  $(\text{CH}_3)_2\text{CO}$ ]* 1
- Isomer 1 1
- Isomer 2 1
- Optical isomerism  
*NB Isomer structures must be tetrahedral  
NB Penalise "stick" structures once in part (a)* 1

- (b) QoL  
 Large charge on carbonyl carbon atom due to bonding to O and Cl 1
- Nucleophiles have electron pairs which can be donated 1
- Equation Species 1
- Balanced 1

[18]

14

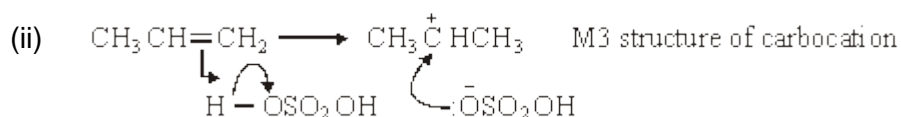
- (a) (i) Electrophilic addition  
*(Both words required)* 1
- (ii) M1 the reaction to form 1-bromopropane goes via the primary carbocation OR 1° carbocation
- OR via  $\text{CH}_3\text{CH}_2\overset{+}{\text{C}}\text{H}_2$
- M2 primary carbocations are less stable than secondary carbocations  
*(Credit converse arguments for M1 and M2 i.e. the reaction to form 2-bromopropane goes via the secondary carbocation, M1, and secondary carbocations are more stable than primary carbocations. M2)*  
*(Accept the use of "carbonium ions" as an alternative to carbocation)* 1
- (b) M1 NaOH OR KOH OR correct name 1
- M2 aqueous or solution in water *(ignore heat, reflux etc.)*  
*(Penalise M1 for hydroxide ion alone, but mark on and credit M2)*  
*(Credit M2 ONLY for H<sub>2</sub>O as reagent and heat / warm / T=50 to 100°C)*  
*(NaOH(aq) scores M1 and M2 provided it is not contradicted)*  
*(Penalise M2 if NaOH(aq) followed by concentrated or ethanol)*  
*(Penalise M1 and M2 if followed by acid)* 1

- (c) Ethanolic OR alcoholic OR  $\text{CH}_3\text{CH}_2\text{OH}$  /  $\text{CH}_3\text{OH}$  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  $2^\circ$

1



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  $\text{H}_2\text{SO}_4$  or to formal positive charge on H, but ignore partial charges on sulphuric acid unless wrong)

(Credit M2 for  $\text{H}^+$  ion)

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

4

- (iii) Catalyst ONLY

(Ignore homogeneous, heterogeneous)

1

[12]

15

- (a) (i) (Free) radical substitution  
(Both words needed)

1

- (ii) M1 initiation ONLY

1

M2 ultra-violet light OR sunlight OR  $1000^\circ\text{C} \geq T \geq 450^\circ\text{C}$

(Ignore reference to temperature if included with uv light)

(Penalise "high temperature" for M2)

1

- (iii)  $2\dot{\text{C}}\text{H}_3 \rightarrow \text{C}_2\text{H}_6$

(OR  $\text{CH}_3\text{CH}_3$  as alternative to  $\text{C}_2\text{H}_6$ )

1

- (iv)  $\text{CH}_3\text{Br} + \text{Br}_2 \rightarrow \text{CH}_2\text{Br}_2 + \text{HBr}$

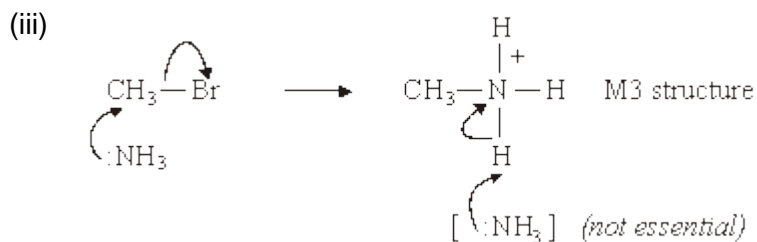
1

- (b) (i) Electron pair donor  
OR species with an electron pair able to form a covalent bond.

1

- (ii) Methylamine  
(Credit "aminomethane")

1



1

M1 arrow to show breakage of C – Br bond

1

M2 arrow from lone pair on N of NH<sub>3</sub> to form bond with C

1

M4 arrow from bond of N – H to N atom of CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>

(Ignore partial charges on haloalkane but penalise if incorrect)

(Accept CH<sub>3</sub>N<sup>+</sup>H<sub>3</sub> 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]

16

- (a) (i) UV light OR sunlight OR  $T \geq 450^\circ\text{C}$  (1)  
NOT high T

- (ii) (free) radical substitution (1)

- (iii) CCl<sub>4</sub> (1) OR named

3

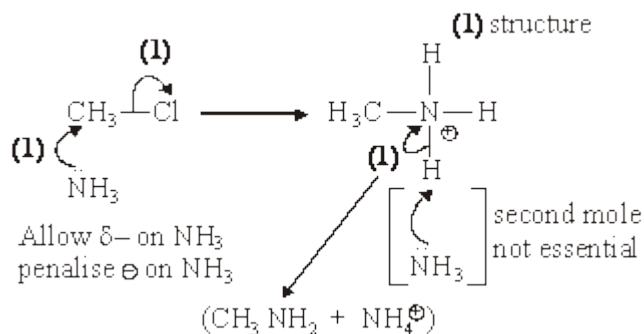
- (b) (i)  $\text{CH}_3\text{Cl} + \text{KCN} \rightarrow \text{CH}_3\text{CN} + \text{KCl}$  (1)  
                      $\text{CN}^-$                      $\text{Cl}^-$
- (ii) nucleophilic substitution (1)
- (iii) C-Br bond is weaker (than C-Cl bond)  
 OR C-Br bond enthalpy is less than C-Cl (1)  
*Ignore electronegativity*

3

- (c)  $\text{CH}_3\text{COOH}$  OR ethanoic acid (1)

1

- (d) (i)  $\overset{\delta+}{\text{C}}-\overset{\delta-}{\text{Cl}}$  OR C-Cl is polar (1) OR C atom is electron deficient /  $\delta+$
- (ii) methylamine (1) only
- (iii)  $\text{S}_{\text{N}}1$  scores full marks



6

[13]

17

- (a) Reaction 2: NaOH OR KOH (1) M1 alcohol (ic) OR ethanol (ic)(1) M2  
*ignore heat*

Condition mark linked to correct reagent but award M2 if  $\text{OH}^-$  or base or alkali mentioned

Reaction 3: concentrated  $\text{H}_2\text{SO}_4$  OR  $\text{H}_3\text{PO}_4$  M1 (1) heat (1) M2  
 OR  $150^\circ\text{C} - 200^\circ\text{C}$

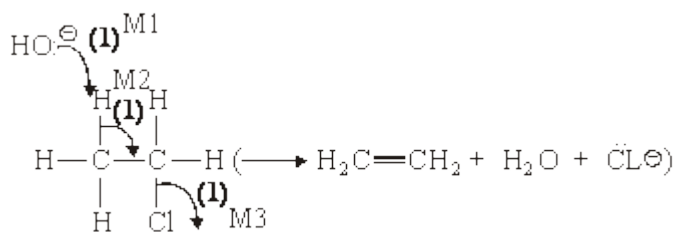
Condition mark linked to correct reagent but award M2 if  $\text{H}_2\text{SO}_4$  or  $\text{H}_3\text{PO}_4$ , but not concentrated

Penalise reagent and condition if dilute  $\text{H}_2\text{SO}_4 / \text{H}_3\text{PO}_4$

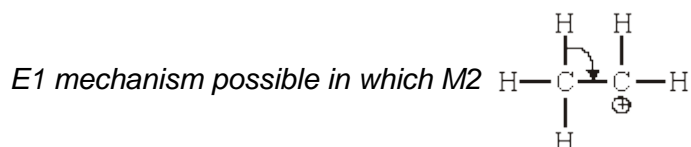
4



(b) Mechanism:



Award M3 ( $\text{C}-\text{Cl}$ ) independently  
M1 and M2 must be to / from correct places



Name: of mechanism = elimination (1)

NOT dehydrohalogenation

Ignore "base" OR "nucleophilic" before elimination

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

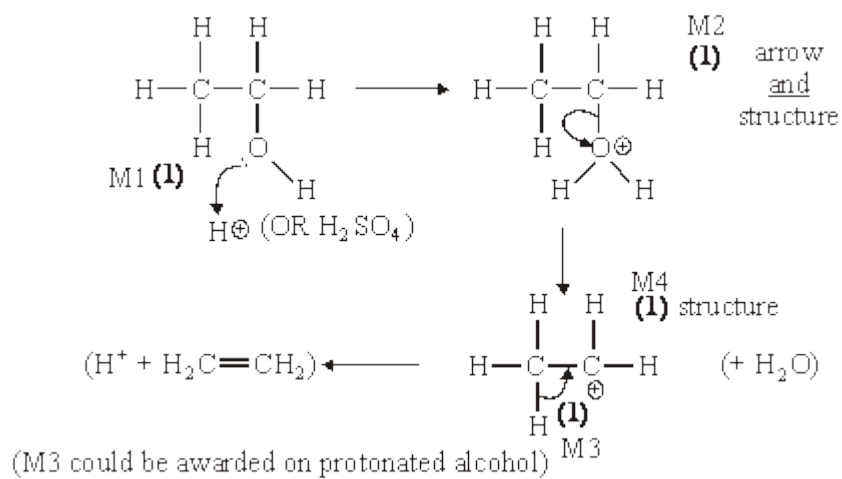
QoL OR chloroethane has to be made (from ethane)

OR chloroethane is expensive

OR chloroethane is not readily available

5

(c) Mechanism:



Name of mechanism = elimination (1)

*NOT dehydration alone*

Reason: Ethanol could come from (fermentation of) renewable

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

6

[15]

18

(a) (i)  $\text{CHCl}_3 + \text{Cl}_2 \rightarrow \text{CCl}_4 + \text{HCl}$  (1)

(ii) UV light / sunlight OR high T OR  $T \geq 500^\circ\text{C}$  (1)

*max T = 1000°C*

*NOT heat / light*

*Ignore pressure*

2

(b) *Initial step:*  $\text{Cl}_2 \rightarrow 2\text{Cl}\cdot$  (1)

*Condition could be on first equation arrow*

*First propagation step:*  $\text{CHCl}_3 + \text{Cl}\cdot \rightarrow \dot{\text{C}}\text{Cl}_3 + \text{HCl}$  (1)

*Second propagation step:*  $\dot{\text{C}}\text{Cl}_3 + \text{Cl}_2 \rightarrow \text{CCl}_4 + \text{Cl}\cdot$  (1)

*A termination step:*  $\dot{\text{C}}\text{Cl}_3 + \text{Cl}\cdot \rightarrow \text{CCl}_4$  (1)

OR  $2\dot{\text{C}}\text{Cl}_3 \rightarrow \text{C}_2\text{Cl}_6$

*Not*  $2\text{Cl}\cdot \rightarrow \text{Cl}_2$

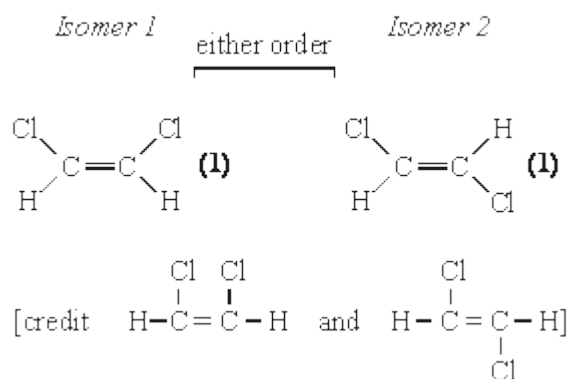
*Ignore additional termination steps*

4

[6]

19

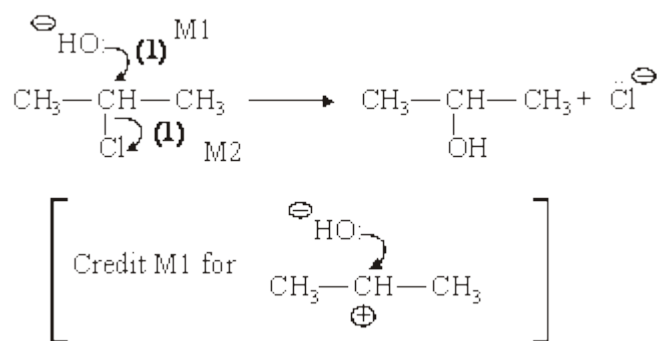
(a) (i)



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

3

(b) (i) *Mechanism:*



*M1 and M2 independent*

*Curly arrows must be from a bond or a lone pair*

*Do not penalise sticks*

*Penalise M1 if  $\text{Na-OH}$  precedes (penalise this once)*

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

*Penalise + on C atom for M2*

*Only allow M1 for incorrect haloalkane*

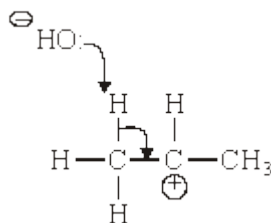
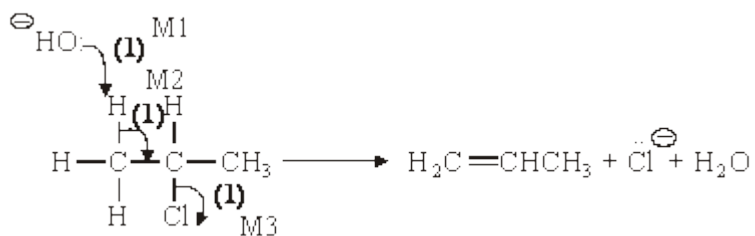
*Role of the hydroxide ion: nucleophile (1)*

*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<sup>⊕</sup> by OH<sup>-</sup>

Role of the hydroxide ion: base (1)

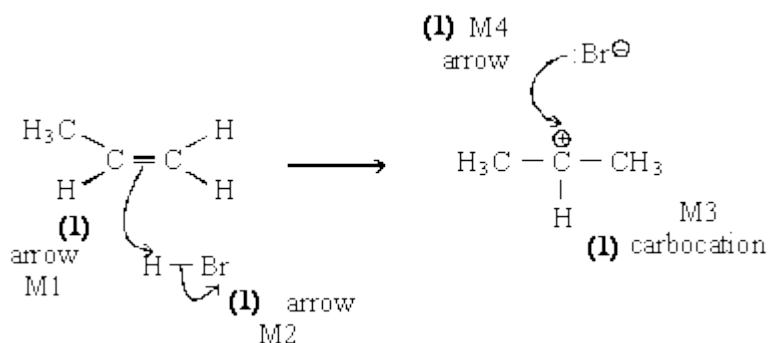
proton acceptor

accepts H<sup>+</sup>

7

[10]

(a) (i)



*If wrong carbocation, lose structure mark*

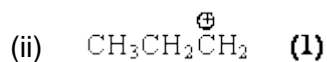
*If wrong alkene, lose structure mark*

*Can still score  $\frac{3}{4}$  i.e. penalise M3*

*Penalise M2 if polarity included incorrectly*

*no bond between H and Br*

*bond is shown as  $\overset{\ominus}{\text{H}}-\text{Br}$  or  $\text{H}-\overset{\oplus}{\text{Br}}$*

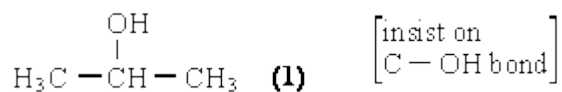


*credit secondary carbocation here if primary carbocation has been used in (i)*

*Ignore attack on this carbocation by  $\text{Br}^-$*

5

(b) (i) Structure:



*No credit for propan-1-ol even when named correctly*

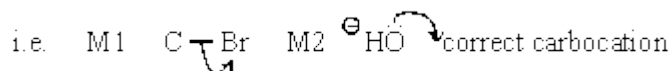
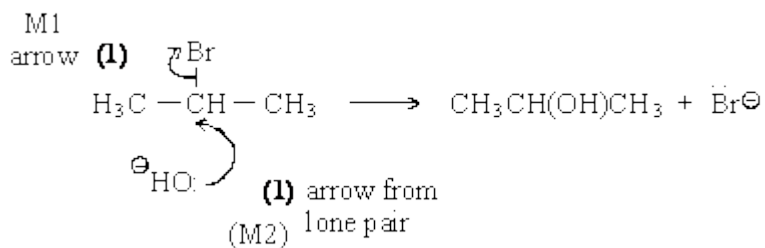
*Credit propane-2-ol*

Name: propan-2-ol (1)

*Not 2-hydroxypropane*

- (ii) *Name of mechanism: nucleophilic substitution (1) (both words)*  
**(NOT S<sub>N</sub>1 or S<sub>N</sub>2)**

*Mechanism:*



5

- (c) (i) **elimination (1)**  
*Ignore nucleophilic elimination*  
*Penalise electrophilic elimination*

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

2

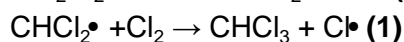
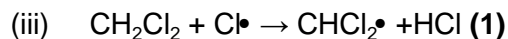
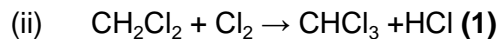
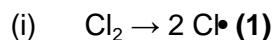
[12]

21

[1]

22

Penalise missing • once only

*Can reverse order*

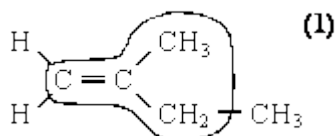
(iv) Effect on rate: increases (1) If decrease given C.E zero marks

Explanation: more Cl• radicals formed (1)*More Cl atoms, more Cl—Cl or Cl—Cl bonds broken, more Cl<sub>2</sub> have**E<sub>A</sub>, increased rate of Cl• production*

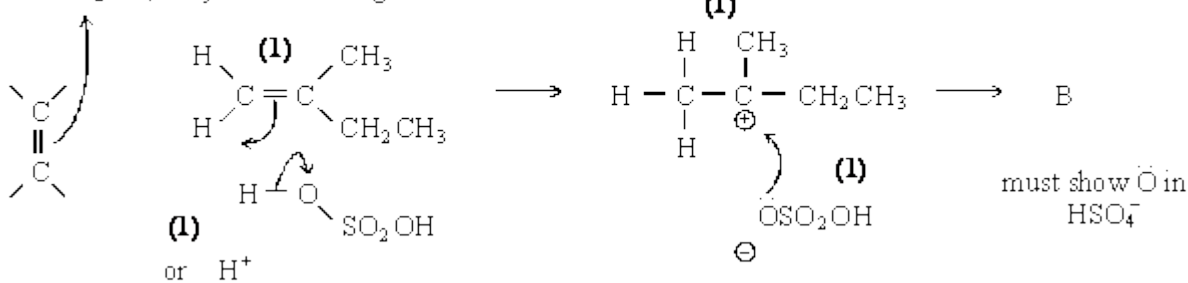
[6]

23

(a)

*May circle 4 C's separately*

1

(b) H<sup>+</sup> can score M1 + M2H<sub>2</sub>SO<sub>4</sub> only M1 - see diagram not M2*Ignore δ+ and δ- unless wrong*

4

(c) Reagent: H<sub>2</sub>O or water **OR steam, Or dilute sulphuric acid** (1)

Condition: heat, or warm, or boil or reflux [50-100°C] (1)

Name of compound **C**: 2-methylbutan-2-ol (1)*Allow 2-methylbutane-2-ol**Penalise hydroxy-2-methylbutane and 2-methylbut-2-ol once only in the paper*

3



- (d) *Identity of alcohol D: 2-methylbutan-1-ol (1),  
OR its structure, could describe  
structure*

*Explanation: C formed via t-carbocation; D via p-carbocation, (1)  
tertiary more stable than primary (1)*

*If have wrong carbocation can still score stability mark*

3

[11]

**24**

[1]

**25**

- (a) *Condition: U.V. light or sunlight or 450°C or high temp (1)*

*Explanation: U.V. light etc. provides energy to break(Cl-Cl) bond (1)*

*Do not accept reference to  $E_a$  or wrong bond or 'to make Cl radicals'*

2

- (b) (i) (Free) radical substitution (1)

(ii) *Step 1: initiation (1)*

*Step 2: propagation (1)*

*Step 3: termination (1)*

*Any order*

*Don't be too harsh on spelling*

4

- (c) (i) *Equation 1:  $\text{CH}_3 + \text{Cl}\cdot \rightarrow \text{CH}_2\text{Cl}\cdot + \text{HCl}$  (1)*

*Equation 2:  $\text{CH}_2\text{Cl}\cdot + \text{Cl}_2 \rightarrow \text{CH}_2\text{Cl}_2 + \text{Cl}\cdot$  (1)*

*or  $\text{CH}_2\text{Cl}\cdot + \text{Cl}\cdot \rightarrow \text{CH}_2\text{Cl}_2$*

*Mark equ independently*

*any order*

(ii)  *$\text{CH}_2\text{Cl}\cdot + \text{CH}_3\cdot \rightarrow \text{CH}_3\text{CH}_2\text{Cl}$  (1)*

*or  $\text{CH}_3\text{CH}_2\cdot + \text{Cl}_2 \rightarrow \text{CH}_3\text{CH}_2\text{Cl} + \text{Cl}\cdot$*

*or  $\text{CH}_3\text{CH}_2\cdot + \text{Cl}\cdot \rightarrow \text{CH}_3\text{CH}_2\text{Cl}$*

*Equ must have  $\text{CH}_3\text{CH}_2\text{Cl}$  as product*

*Accept  $\text{C}_2\text{H}_5\text{Cl}$*

*Penalise absence of  $\cdot$  once only*

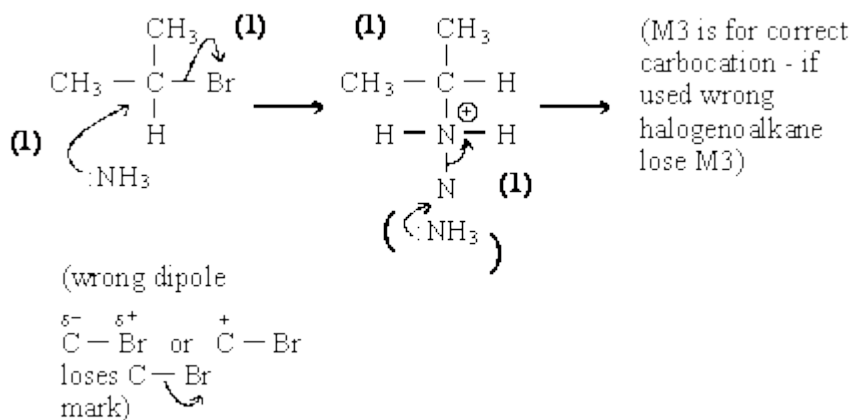
3

[9]

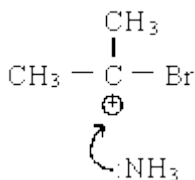
26

(a) Name of mechanism: nucleophilic substitution (1)

Mechanism:

Marks  $S_N1$  using same points

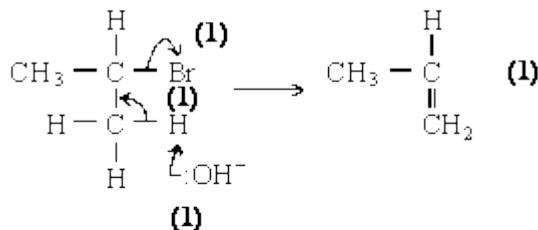
∴ M2 requires



5

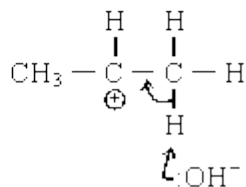
(b) Role of potassium hydroxide: Base (1)

Mechanism:



Mark E1 using same points

∴ M2/M3



5

[10]

B  
27

[1]

C  
28

[1]

**B**  
**29**

[1]

**D**  
**30**

[1]