Q1. The following pairs of compounds can be distinguished by simple test−tube reactions.

For each pair of compounds, give a reagent (or combination of reagents) that, when added separately to each compound, could be used to distinguish between them. State what is observed in each case.

(a) Butan−2−ol and 2−methylpropan−2−ol

Reagent .....

Observation with butan−2−ol

.....

.....

Observation with 2−methylpropan−2−ol

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(3)

(b) Propane and propene

Reagent .....

Observation with propane

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Observation with propene

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(3)

(c) Aqueous silver nitrate and aqueous sodium nitrate

Reagent .....

Observation with aqueous silver nitrate

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Observation with aqueous sodium nitrate

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(3)

(d) Aqueous magnesium chloride and aqueous barium chloride

Reagent .....

Observation with aqueous magnesium chloride

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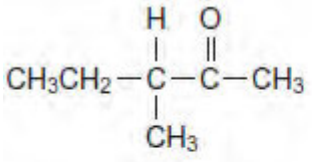
Observation with aqueous barium chloride

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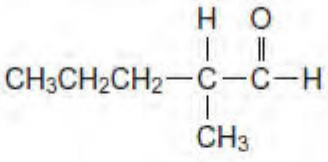
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(3)
(Total 12 marks)

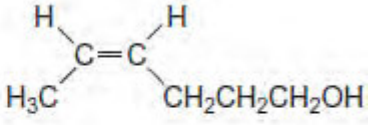
Q2. The following five isomers, **P**, **Q**, **R**, **S** and **T**, were investigated using test-tube reactions and also using n.m.r. spectroscopy.



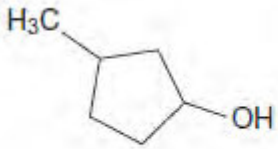
P



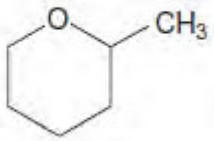
Q



R



S



T

(a) A simple test-tube reaction can be used to distinguish between isomers **P** and **S**.

Identify a reagent (or combination of reagents) you could use.

State what you would observe when both isomers are tested separately with this reagent or combination of reagents.

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(3)

(b) A simple test-tube reaction can be used to distinguish between isomer **Q** and all the other isomers.

Identify a reagent (or combination of reagents) you could use.
State what you would observe when **Q** is tested with this reagent or combination of reagents.

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(2)

(c) State which **one** of the isomers, **P**, **Q**, **R**, **S** and **T**, has the least number of peaks in its ^{1}H n.m.r. spectrum.
Give the number of peaks for this isomer.

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(2)

(d) Write the **molecular** formula of the standard used in ^{13}C n.m.r. spectroscopy.
Give **two** reasons why this compound is used.

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(3)

(e) **Figure 1** and **Figure 2** show the ^{13}C n.m.r. spectra of two of the five isomers.

Figure 1

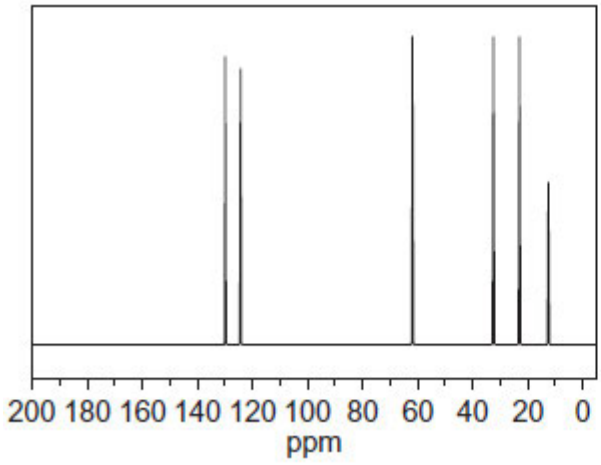
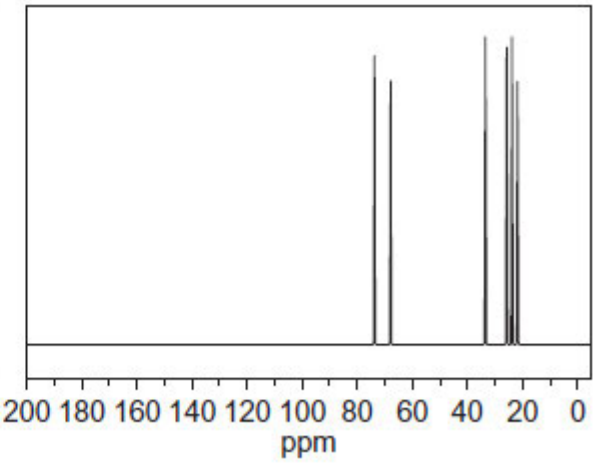
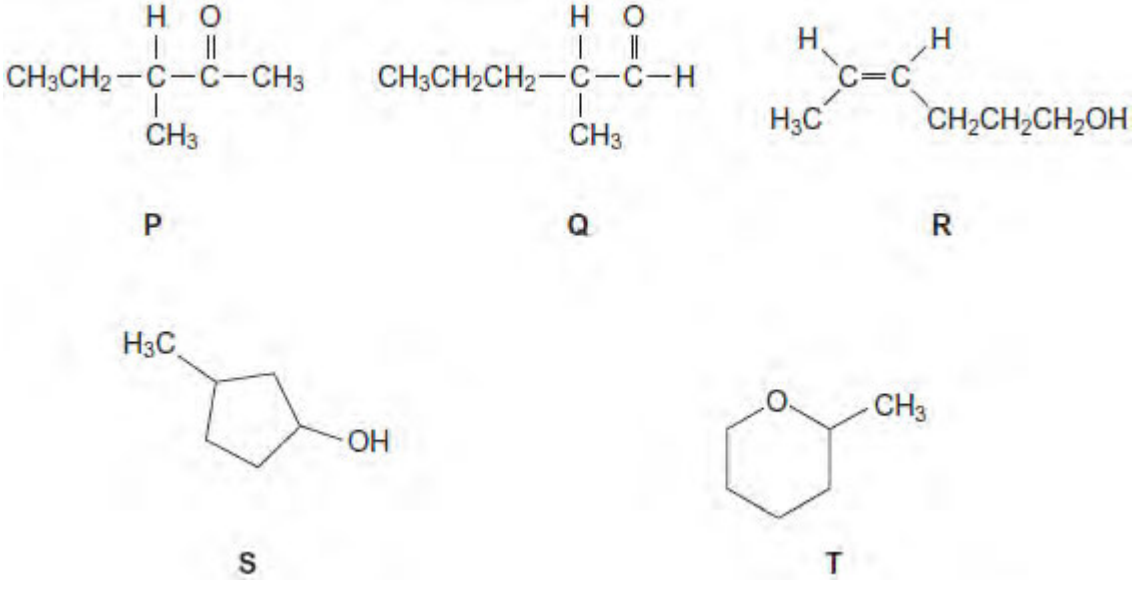


Figure 2



The structures of the five isomers are repeated to help you answer this question.



State which isomer produces the spectrum in **Figure 1** and which isomer produces

the spectrum in **Figure 2**.

Explain your answer.

You do not need to identify every peak in each spectrum.
Use **Table C** on the Data Sheet to answer the question.

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(5)

(f) **U** and **V** are other isomers of **P**, **Q**, **R**, **S** and **T**.
The ^{1}H n.m.r. spectrum of **U** consists of two singlets.
V is a cyclic alcohol that exists as optical isomers.

Draw the structure of **U** and the structure of **V**.

U **V**

(2)
(Total 17 marks)

Q3. 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**.

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(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.

$$(CH_3)_2C = CHCH_3 + HBr \longrightarrow (CH_3)_2CBrCH_2CH_3$$

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.

$$(CH_3)_2CBrCH_2CH_3 + KOH \longrightarrow H_2C = C(CH_3)CH_2CH_3 + KBr + H_2O$$

Name of mechanism .....

Mechanism

Role of hydroxide ion .....

(5)
(Total 21 marks)

Q1. Butane and propanal are compounds with M_r = 58.0, calculated using data from your Periodic Table.

(a) A mass spectrometer can be used to distinguish between samples of butane and propanal.

The table shows some precise relative atomic mass values.

Atom	Precise relative atomic mass
^{1}H	1.00794
^{12}C	12.00000

(i) Use data from the table to show that, to 3 significant figures, a more accurate value for the M_r of butane is 58.1

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(1)

(ii) State why the precise relative atomic mass quoted in the table for the ^{12}C isotope is exactly 12.00000

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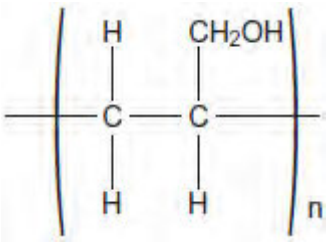
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(1)

(b) Draw a **displayed formula** for the organic product that is formed when propanal is oxidised by warm Tollens' reagent.

(1)

(c) Prop−2−en−1−ol is an isomer of propanal and can be polymerised to form a polymer represented by the following structure.



(i) Draw the structure of prop−2−en−1−ol.

(1)

(ii) Deduce the type of polymerisation that results in the formation of this polymer from prop−2−en−1−ol.

.....

(1)

(iii) There are two functional groups in prop−2−en−1−ol. Each of these functional groups contains a bond with a characteristic absorption range in the infrared spectrum.

Use **Table A** on the Data Sheet to suggest a bond and its absorption range for each of the two functional groups.

Bond 1 ..... Absorption range .....

Bond 2 ..... Absorption range .....

(2)

(d) Compound **X** is another isomer of propanal. The infrared spectrum of **X** shows an absorption in the range 1680−1750 cm^{-1}.

(i) Draw the structure of **X**.

(ii) Which of the following, **A**, **B**, **C** or **D**, represents the type of isomerism shown by **X** and propanal?

Write the correct letter, **A**, **B**, **C** or **D**, in the box.

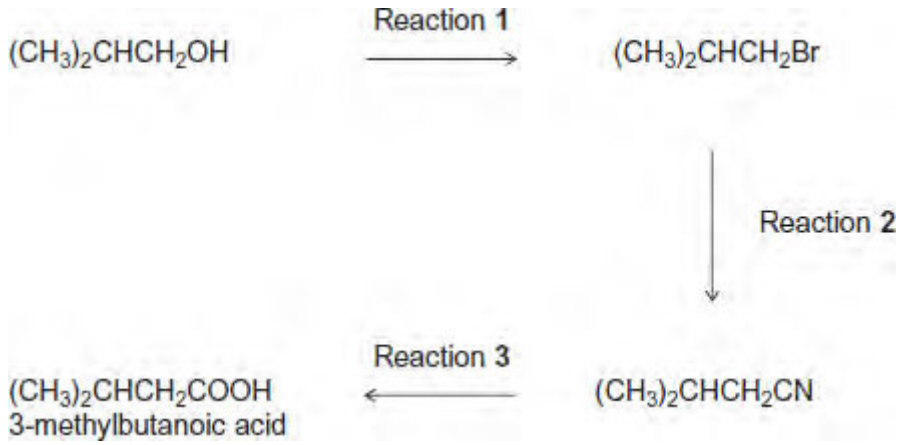
A chain isomerism
B E−Z isomerism
C functional group isomerism

D position isomerism

☐

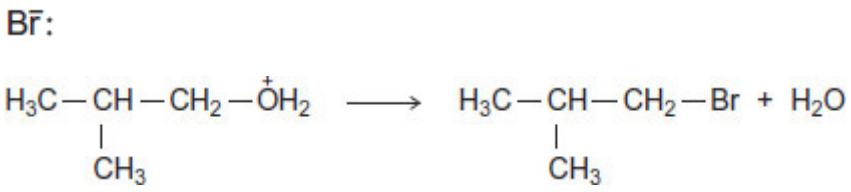
(1)
(Total 9 marks)

Q2. 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.



(2)

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

Give the IUPAC name of $(CH_3)_2CHCH_2Br$

.....

.....

.....

(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 $(CH_3)_2CHCH_2CN$ and a **different** bond in $(CH_3)_2CHCH_2COOH$ 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.

$$(CH_3)_2CHCH_2COOH + CH_3CH_2OH \rightleftharpoons \underset{\text{an ester}}{(CH_3)_2CHCH_2COOCH_2CH_3} + H_2O$$

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) .....

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(3)

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

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(Extra space) .....

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(2)

(Total 12 marks)

Q3. Glucose can decompose in the presence of microorganisms to form a range of products. One of these is a carboxylic acid (M_r = 88.0) containing 40.9% carbon and 4.5% hydrogen by mass.

(a) Deduce the empirical and molecular formulas of the carboxylic acid formed.

Empirical formula = ... Molecular formula = ...

(4)

(b) Ethanol is formed by the fermentation of glucose.

A student carried out this fermentation reaction in a beaker using an aqueous solution of glucose at a temperature of 25 °C in the presence of yeast.

Write an equation for the reaction occurring during fermentation.

.....

(1)

(c) In industry, this fermentation reaction is carried out at 35 °C rather than 25 °C.

Suggest **one** advantage and **one** disadvantage for industry of carrying out the fermentation at this higher temperature.

Advantage .....

.....

Disadvantage .....

.....

(2)

(d) The method used by the student in part (b) would result in the ethanol being contaminated by ethanoic acid.

How does this contamination occur?

.....

.....

(1)

(e) Give **two** differences between the infrared spectrum of a carboxylic acid and that of an alcohol other than in their fingerprint regions.
Use **Table A** on the Data Sheet.

Difference 1 .....

.....

Difference 2 .....

.....

(2)
(Total 10 marks)

Q4. 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**.

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(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.

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(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.

$$(CH_3)_2C = CHCH_3 + HBr \longrightarrow (CH_3)_2CBrCH_2CH_3$$

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.

$$(CH_3)_2CBrCH_2CH_3 + KOH \longrightarrow H_2C = C(CH_3)CH_2CH_3 + KBr + H_2O$$

Name of mechanism .....

Mechanism

Role of hydroxide ion .....

(5)
(Total 21 marks)

Q5. The infrared spectrum (**Figure 1**) and the ^{1}H NMR spectrum (**Figure 2**) of compound **R** with molecular formula $C_6H_{14}O$ are shown.

Figure 1

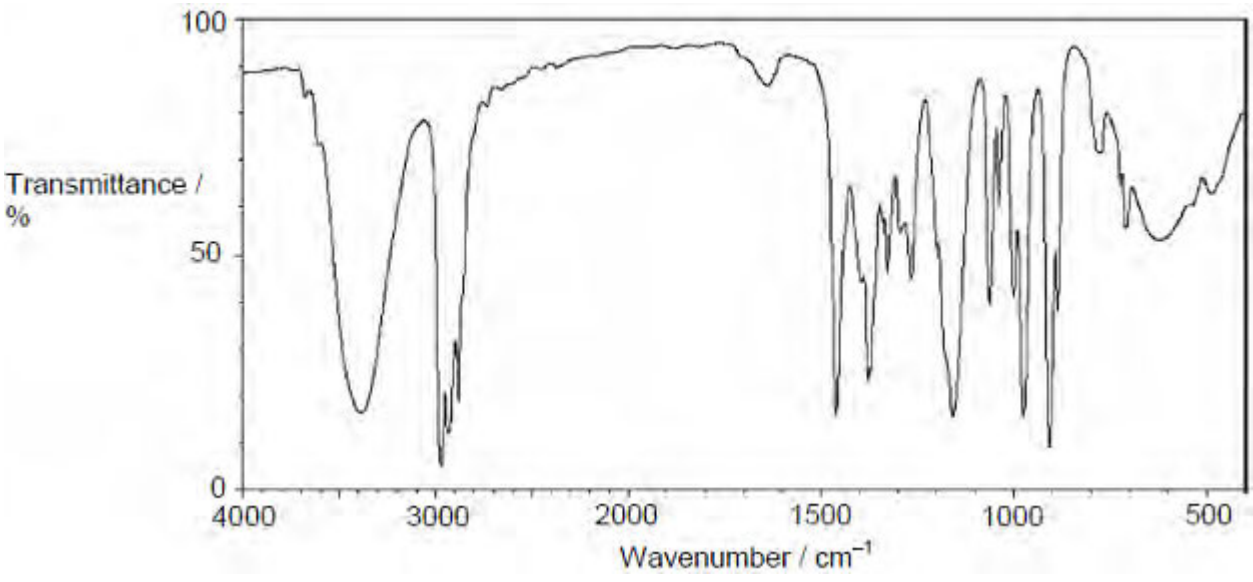
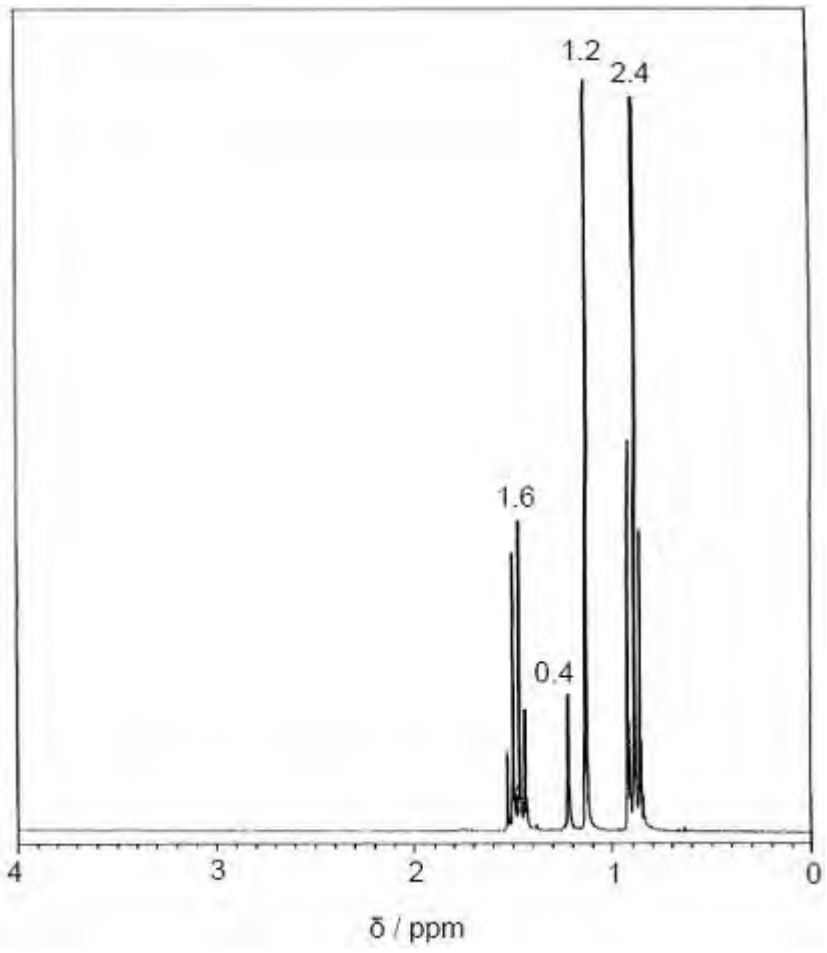


Figure 2



The relative integration values for the NMR peaks are shown on **Figure 2**.

Deduce the structure of compound **R** by analysing **Figure 1** and **Figure 2**.
Explain each stage in your deductions.

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

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(Total 8 marks)

Q1. Butane and propanal are compounds with M_r = 58.0, calculated using data from your Periodic Table.

(a) A mass spectrometer can be used to distinguish between samples of butane and propanal.

The table shows some precise relative atomic mass values.

Atom	Precise relative atomic mass
^{1}H	1.00794
^{12}C	12.00000

(i) Use data from the table to show that, to 3 significant figures, a more accurate value for the M_r of butane is 58.1

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(1)

(ii) State why the precise relative atomic mass quoted in the table for the ^{12}C isotope is exactly 12.00000

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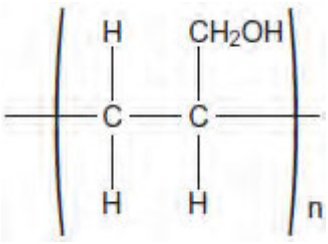
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(1)

(b) Draw a **displayed formula** for the organic product that is formed when propanal is oxidised by warm Tollens' reagent.

(1)

(c) Prop−2−en−1−ol is an isomer of propanal and can be polymerised to form a polymer represented by the following structure.



(i) Draw the structure of prop−2−en−1−ol.

(1)

(ii) Deduce the type of polymerisation that results in the formation of this polymer from prop−2−en−1−ol.

.....

(1)

(iii) There are two functional groups in prop−2−en−1−ol. Each of these functional groups contains a bond with a characteristic absorption range in the infrared spectrum.

Use **Table A** on the Data Sheet to suggest a bond and its absorption range for each of the two functional groups.

Bond 1 ..... Absorption range .....

Bond 2 ..... Absorption range .....

(2)

(d) Compound **X** is another isomer of propanal. The infrared spectrum of **X** shows an absorption in the range 1680−1750 cm^{-1}.

(i) Draw the structure of **X**.

(ii) Which of the following, **A**, **B**, **C** or **D**, represents the type of isomerism shown by **X** and propanal?

Write the correct letter, **A**, **B**, **C** or **D**, in the box.

A chain isomerism
B E−Z isomerism
C functional group isomerism

D position isomerism

☐

(1)
(Total 9 marks)

Q2. The manufacture of food grade phosphoric acid for use in cola drinks begins with the production of pure white phosphorus from the mineral fluoroapatite, $Ca_5F(PO_4)_3$

(a) Complete the following equation for the manufacture of phosphorus.

$$....Ca_5F(PO_4)_3 + 9SiO_2 + ...C \longrightarrow 9CaSiO_3 + CaF_2 + ...CO + ...P$$

(1)

(b) As the phosphorus cools, it forms white phosphorus, P_4

Give the oxidation state of phosphorus in each of the following.

P_4 .....

H_3PO_4 .....

(2)

(c) Fertiliser grade phosphoric acid is manufactured from sulfuric acid and calcium phosphate.
Use the following precise relative atomic mass data to show how mass spectrometry can be used to distinguish between pure sulfuric acid (H_2SO_4) and pure phosphoric acid (H_3PO_4) which both have M_r = 98 to two significant figures.

Atom	Precise relative atomic mass
^{1}H	1.00794
^{16}O	15.99491
^{31}P	30.97376
^{32}S	32.06550

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(1)

(d) Concentrated phosphoric acid is used as a catalyst in the hydration of propene to form the alcohol $CH_3CH(OH)CH_3$ as the main organic product.
The industrial name for this alcohol is isopropyl alcohol.

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

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(Extra space) .....

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(1)

(ii) State the meaning of the term *hydration*.

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(Extra space) .....

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(1)

(iii) Write an equation for the hydration of propene to form isopropyl alcohol.
Give the IUPAC name for isopropyl alcohol.

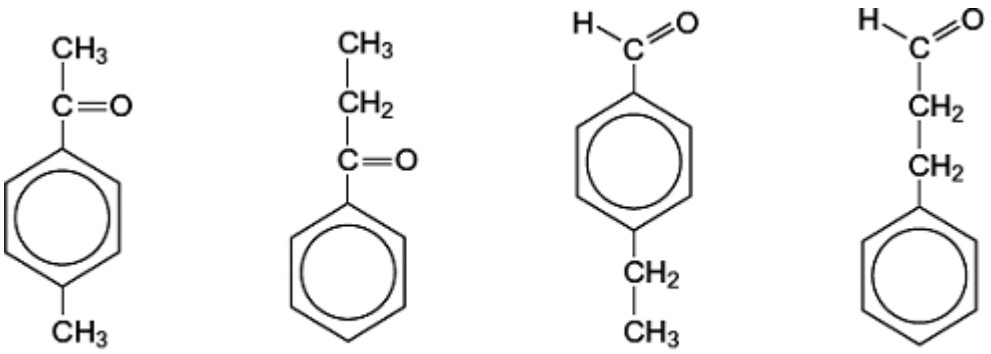
Equation .....

IUPAC name .....

(2)
(Total 8 marks)

Q3. Mass spectrometry is used by organic chemists to help distinguish between different compounds.

Four isomers of $C_9H_{10}O$, shown below, were analysed by mass spectrometry.



A **B** **C** **D**

The mass spectra obtained from these four isomers were labelled in random order as I, II, III and IV.

Each spectrum contained a molecular ion peak at *m/z* = 134

The data in the table below show the *m/z* values greater than 100 for the major peaks in each spectrum due to fragmentation of the molecular ion. The table also shows where no major peaks occurred.

Spectrum	*m/z* values for major peaks	No major peak at *m/z*
I	119	133, 105
II	133, 119 and 105	
III	133, 105	119
IV	105	133, 119

(a) Two of the molecular ions fragmented to form an ion with *m/z* = 133 by losing a radical.
Identify the radical that was lost.

.....

(1)

(b) Two of the molecular ions fragmented to form an ion with *m/z* = 119 by losing a

radical.
Identify the radical that was lost.

.....

(1)

(c) Three of the molecular ions fragmented to form ions with *m/z* = 105 by losing a radical with M_r = 29

Identify **two** different radicals with M_r = 29 that could have been lost.

Radical 1 .....

Radical 2 .....

(2)

(d) Consider the structures of the four isomers and the fragmentations indicated in parts (a) to (c).
Write the letter **A**, **B**, **C** or **D**, in the appropriate box below, to identify the compound that produces each spectrum.

Spectrum I ☐

Spectrum II ☐

Spectrum III ☐

Spectrum IV ☐

(4)
(Total 8 marks)

Q4. A scientist used mass spectrometry to analyse a sample of the air near a fertiliser factory. The sample of air included traces of a gas which was shown by its molecular ion to have a precise M_r = 44.00105

(a) State the meaning of the term *molecular ion*.

.....

.....

(1)

(b) (i) Use the following data to show that the trace gas was dinitrogen oxide (N_2O).

Show your working.

Atom	Precise relative atomic mass
^{12}C	12.00000
^{14}N	14.00307
^{16}O	15.99491

.....

.....

(1)

(ii) Propane is used as a fuel in the fertiliser factory. State why both propane and its combustion product, carbon dioxide, might have been identified as the trace gas if the scientist had used relative molecular masses calculated to one decimal place.

.....

.....

(1)

(iii) State why the precise relative atomic mass for the ^{12}C isotope is exactly 12.00000

.....

(1)

(c) Dinitrogen oxide is formed when ammonia is oxidised according to the following equation.

$$2NH_3(g) + 2O_2(g) \rightarrow N_2O(g) + 3H_2O(l)$$

(i) Use the standard enthalpies of formation in the table below to calculate a value for the standard enthalpy change of this reaction.

	$NH_3(g)$	$O_2(g)$	$N_2O(g)$	$H_2O(l)$
$\Delta H_f^{\ominus}$/ kJ mol^{-1}	–46	0	+82	–286

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.....

.....

(3)

(ii) State **one** condition necessary for enthalpies of formation to be quoted as standard values at a specified temperature of 298 K.

.....

(1)
(Total 8 marks)