AQA A-LEVEL CHEMISTRY · 7405

CHEMISTRY



EXAM QUESTION PACK

3.3.15 NMR SPECTROSCOPY

SCORE	PERCENTAGE
/327	%

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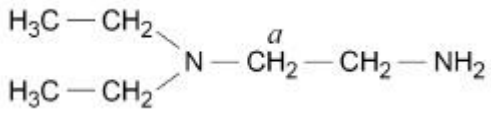
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Q1.

There are several isomers with the molecular formula $C_6H_{16}N_2$

(a) One isomer is shown.



Give the number of peaks in the ^{13}C NMR spectrum of this isomer.

State and explain the splitting pattern of the peak for the hydrogens labelled *a* in its ^{1}H NMR spectrum.

Number of ^{13}C peaks _____

Splitting pattern _____

Explanation _____

_____

_____

_____

(3)

(b) Draw the structure of the isomer of $C_6H_{16}N_2$ used to make nylon 6,6

(1)

(c) Draw the structure of the isomer of $C_6H_{16}N_2$ that contains two **primary** amine groups and has only two peaks in its ^{13}C NMR spectrum.

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(1)

(d) Draw the structure of the isomer of $C_6H_{16}N_2$ that contains two **tertiary** amine groups and has only two peaks in its ^{13}C NMR spectrum.

(1)

(Total 6 marks)

Q2.

How many peaks are there in the ^{13}C NMR spectrum of 1,4-dimethylbenzene?

A 8 ⬭

B 4 ⬭

C 3 ⬭

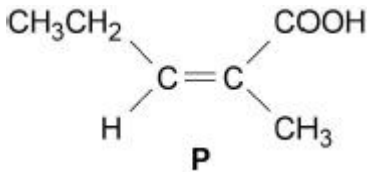
D 2 ⬭

(Total 1 mark)

Q3.

This question is about six isomers of $C_6H_{10}O_2$

(a) Give the full IUPAC name of isomer **P**.



P

_____

(1)

(b) A sample of P was mixed with an excess of oxygen and the mixture ignited. After cooling to the original temperature, the total volume of gas remaining was 335 cm^3

When this gas mixture was passed through aqueous sodium hydroxide, the carbon dioxide reacted and the volume of gas decreased to 155 cm^3

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Both gas volumes were measured at 25 °C and 105 kPa

Write an equation for the combustion of **P** in an excess of oxygen and calculate the mass, in mg, of **P** used.

The gas constant $R = 8.31\ J\ K^{-1}\ mol^{-1}$

Mass of **P** used _____ mg

(5)

(c) Isomer Q ($C_6H_{10}O_2$) is a cyclic compound. The infrared spectrum of **Q** is shown in **Figure 1** and the ^{13}C NMR spectrum of **Q** is shown in **Figure 2**.

Figure 1

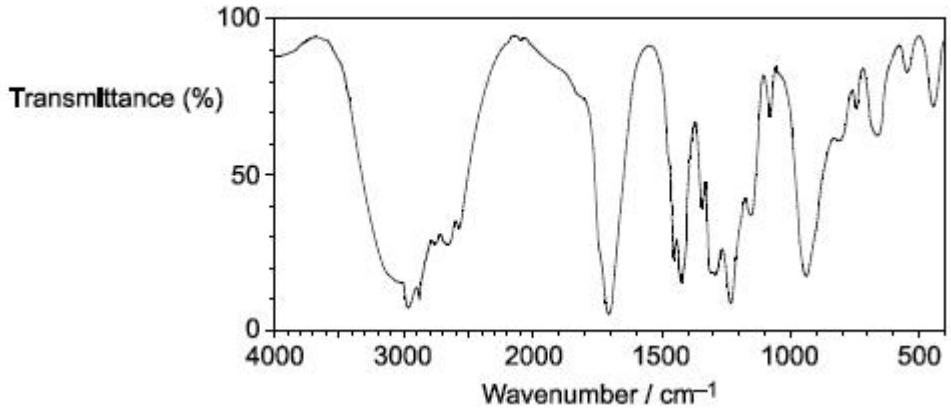
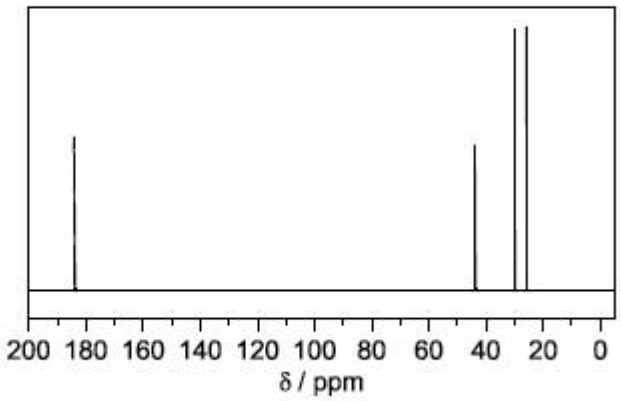


Figure 2



Use these spectra and Tables **A** and **C** in the Data Booklet to deduce the structure of **Q**.

In your answer, state one piece of evidence you have used from each spectrum.

Structure of **Q**.

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Evidence from **Figure 1**

_____

_____

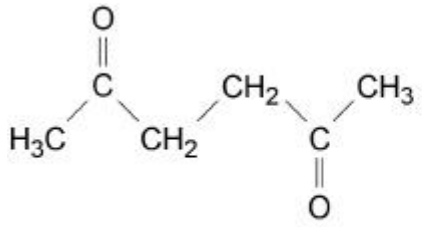
Evidence from **Figure 2**

_____

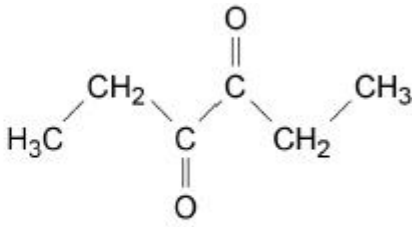
_____

(3)

(d) Isomers **R** and **S** are shown.



R



S

Although the ^{13}C spectra of **R** and **S** both show the same number of peaks, the spectra can be used to distinguish between the isomers.

Justify this statement using Table **C** from the Data Booklet.

Give the number of peaks for each isomer.

Justification

_____

_____

_____

_____

Number of peaks _____

(3)

(e) Although the ^{1}H spectra of **R** and **S** both show the same number of peaks, the spectra can be used to distinguish between the isomers.

Justify this statement using the splitting patterns of the peaks.

Give the number of peaks for each isomer.

Justification

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_____

_____

_____

_____

Number of peaks _____

(3)

(f) The action of heat on 5-hydroxyhexanoic acid can lead to two different products.

On gentle heating, 5-hydroxyhexanoic acid loses water to form a cyclic compound, **T** ($C_6H_{10}O_2$).

Under different conditions, 5-hydroxyhexanoic acid forms a polyester.

Draw the structure of **T**.

Draw the repeating unit of the polyester and name the type of polymerisation.

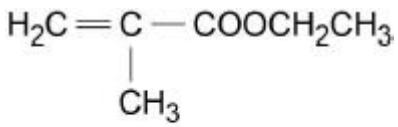
Structure of **T**

Repeating unit of polyester

Type of polymerisation _____

(3)

(g) Isomer **U** is shown.



U

The polymer formed by **U** and the polymer formed by 5-hydroxyhexanoic acid in part (f) both contain ester groups that can be hydrolysed.

Draw the repeating unit of the polymer formed by **U**.

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Justify the statement that, although both polymer structures contain ester groups, the polymer formed by **U** is not biodegradable.

Repeating unit of polymer formed by **U**.

Justification

_____

_____

_____

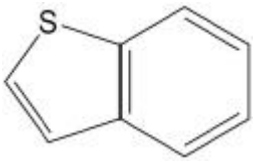
_____

(3)

(Total 21 marks)

Q4.

How many peaks does this compound have in its ^{13}C spectrum?



A 5 ○

B 6 ○

C 7 ○

D 8 ○

(Total 1 mark)

Q5.

^{1}H NMR, ^{13}C NMR and infrared spectroscopy are used in organic chemistry to distinguish between compounds and to identify them.

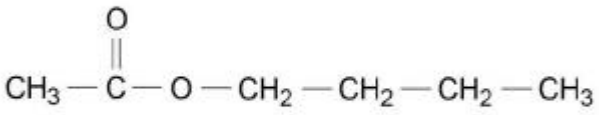
(a) Give the skeletal formula of the compound that is used as the standard when recording a ^{13}C NMR spectrum.

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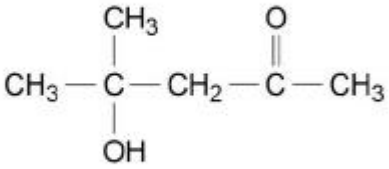
(1)

(b) Four isomers of $C_6H_{12}O_2$, **P**, **Q**, **R** and **S**, shown in **Figure 1**, were analysed by ^{13}C NMR spectrometry.

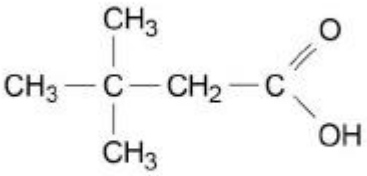
Figure 1



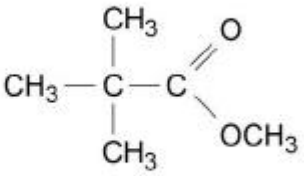
P



Q



R



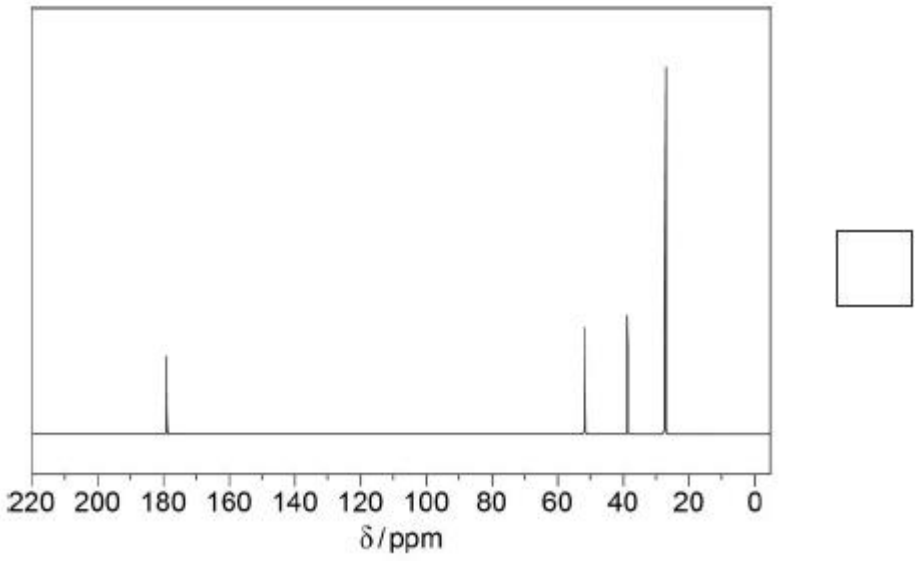
S

The ^{13}C NMR spectra of three of these isomers are shown in **Figure 2**.

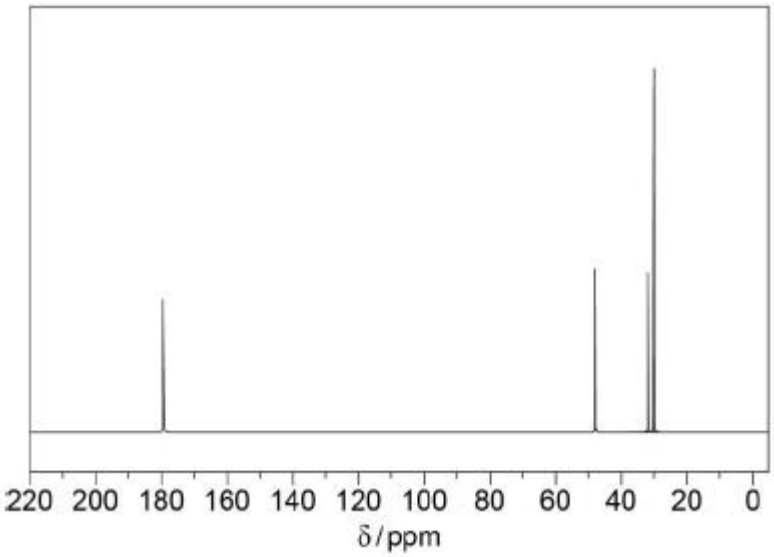
Use **Table C** in the Data Booklet to help you to identify which isomer produces each spectrum.

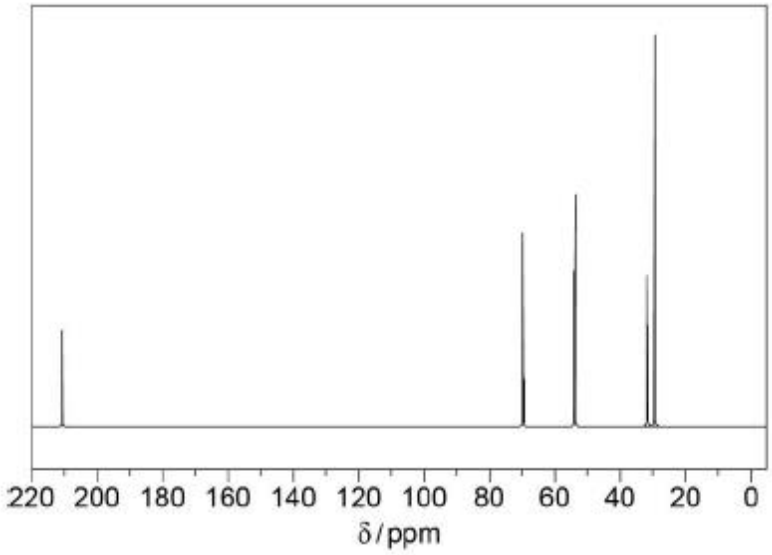
Write the letter of each isomer opposite its spectrum in **Figure 2**.

Figure 2



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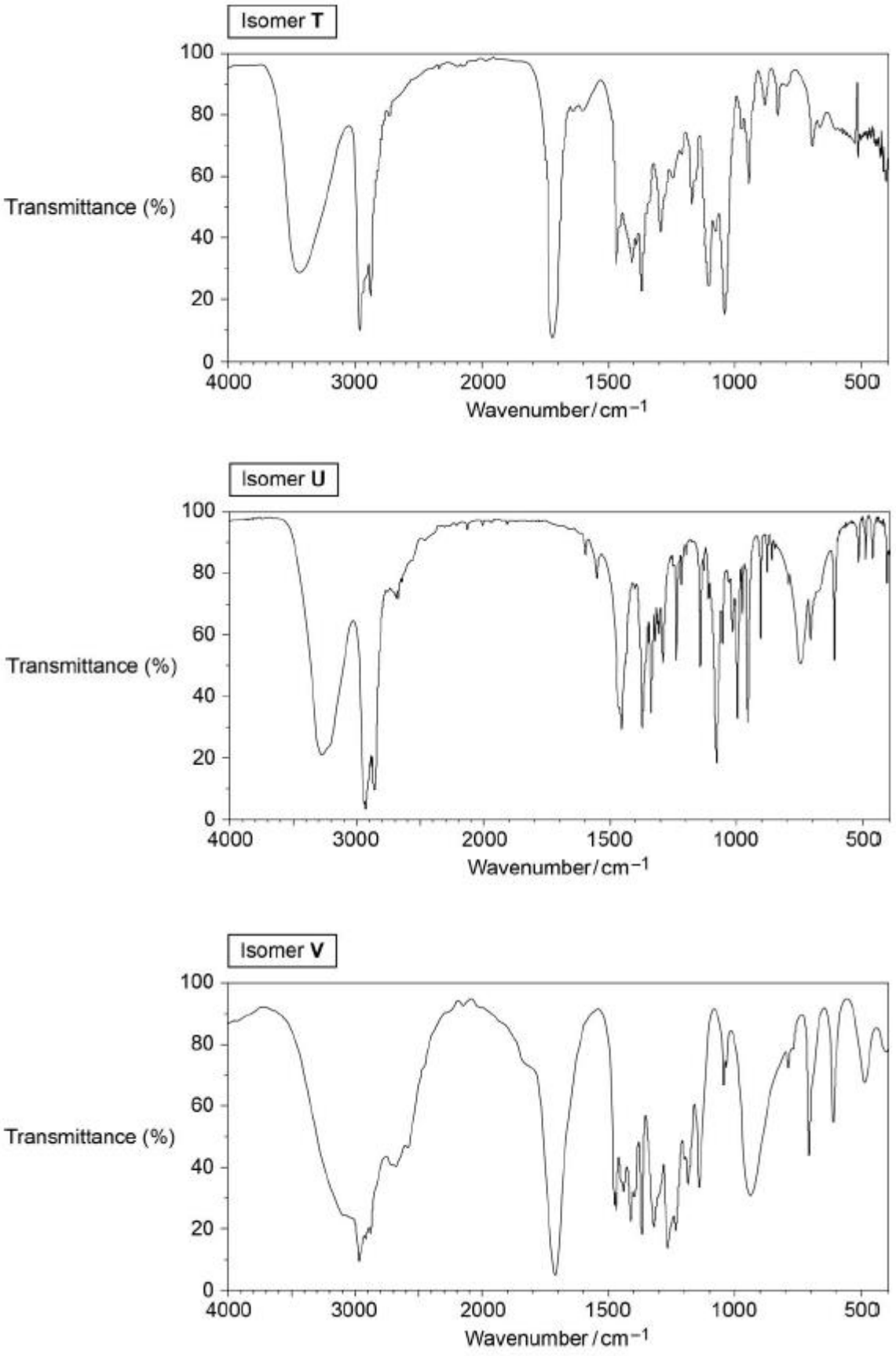


(3)

(c) The infrared spectra shown in **Figure 3** are those of three different isomers of $C_6H_{12}O_2$, isomers **T**, **U** and **V**.

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Figure 3



Identify the functional group(s) present in each isomer **T**, **U** and **V** of $C_6H_{12}O_2$ using **Table A** in the Data Booklet.

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Explain your answer.

(6)

(d) The integration values for the peaks in the ^{1}H NMR spectrum of **X**, a different isomer of $C_6H_{12}O_2$, are given in the table below.

Chemical shift, δ/ppm	3.7	3.5	2.6	2.2	1.1
Integration value	0.6	0.6	0.6	0.9	0.9
Splitting pattern	triplet	quartet	triplet	singlet	triplet

Deduce the simplest ratio of the relative numbers of protons in each environment in compound **X**.

(1)

(e) Use the data in the table above and **Table B** in the Data Booklet to help you answer this question.

Deduce the part of the structure of **X** that causes the signal at δ= 3.5 and the part of the structure at **X** that causes the signal at δ=2.2.

Explain the splitting patterns of these peaks.

Signal at δ= 3.5

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Signal at δ= 2.2 _____

(4)

(f) Deduce the structure of compound **X**, $C_6H_{12}O_2$

Use your answer from part **(e)** to help you.

You are **not** required to explain how you deduced the structure.

(2)

(Total 17 marks)

Q6.

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

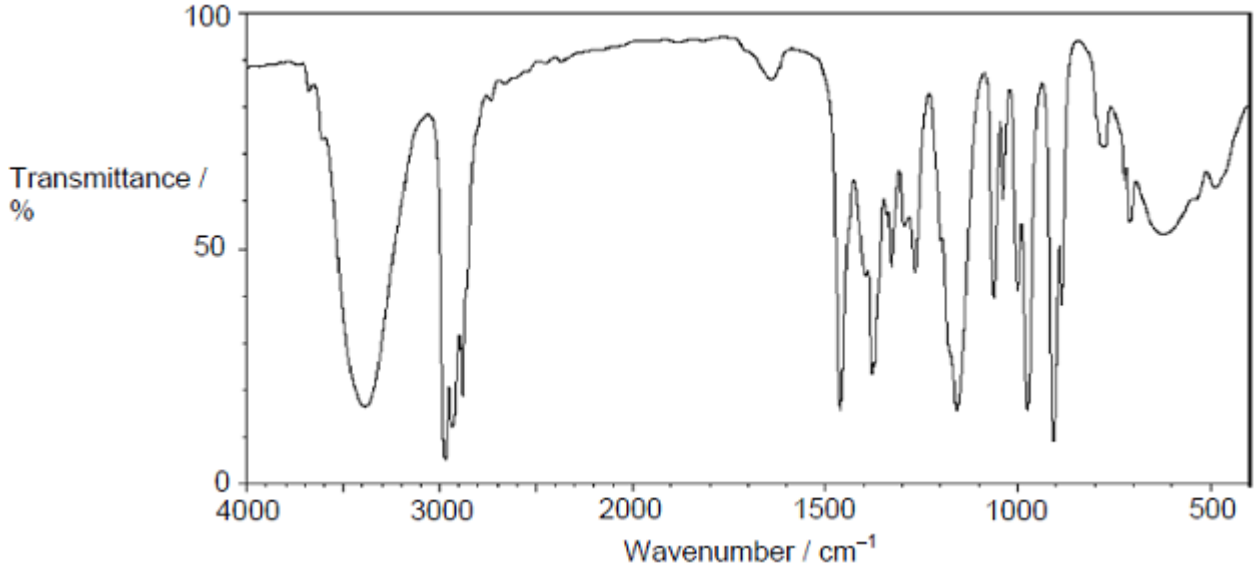
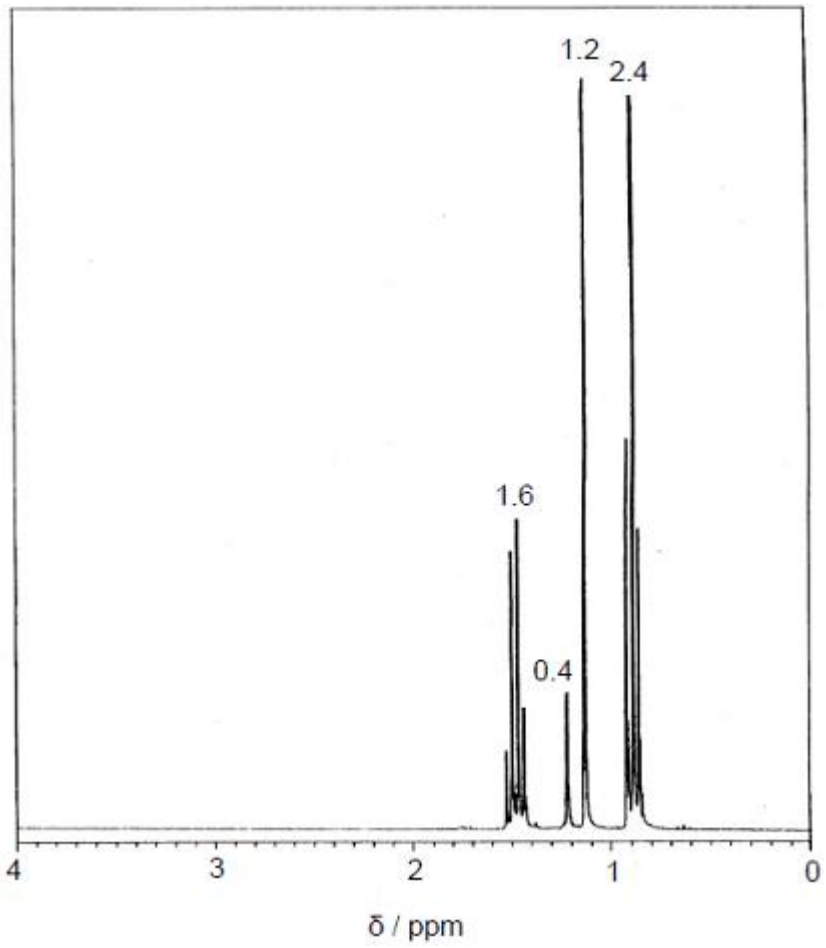


Figure 2

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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.

(Total 8 marks)

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Q7.

Which amine has only **three** peaks in its proton NMR spectrum?

A Methylamine ⬭

B Trimethylamine ⬭

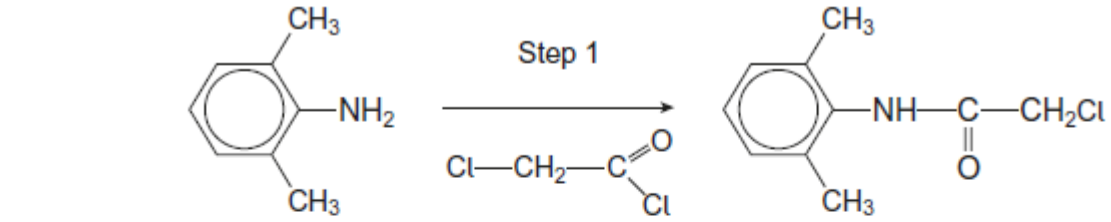
C Diethylamine ⬭

D Propylamine ⬭

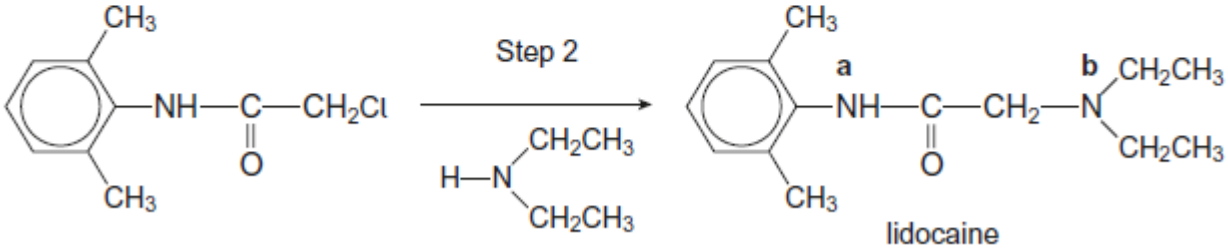
(Total 1 mark)

Q8.

Lidocaine is a local anaesthetic used in dentistry and in minor surgical operations.
The synthesis of lidocaine in 2 steps from 2,6-dimethylphenylamine is shown.



X



Y

(a) (i) Give the IUPAC name of reagent **X** in Step 1.

_____

(1)

(ii) Outline a mechanism for Step 1.
In your answer, use RNH_2 to represent 2,6-dimethylphenylamine.

(4)

(b) Name the mechanism for Step 2.

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_____

(1)

(c) Which of these is the total number of peaks in the ^{13}C n.m.r spectrum of lidocaine?

Tick (✓) one box.

8 ☐ 9 ☐ 11 ☐ 12 ☐

(1)

(d) Calculate the percentage by mass of hydrogen in a molecule of lidocaine.

_____

_____

_____

(2)

(e) Give the name, including the classification, of the functional group that contains the nitrogen atom labelled **b**.

_____

(1)

(f) Lidocaine is used medically as the salt lidocaine hydrochloride.

(i) Suggest which one of the nitrogen atoms labelled **a** or **b** is protonated in lidocaine hydrochloride. Explain your answer.

Nitrogen atom protonated _____

Explanation _____

_____

_____

_____

(3)

(ii) Suggest why lidocaine hydrochloride is used medically in preference to lidocaine.
Explain your answer.

_____

_____

_____

_____

(2)

(Total 15 marks)

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Q9.

Compound **R** contains 61.0% carbon and 11.9% hydrogen by mass. The remainder is oxygen.
The mass spectrum of **R** contains a molecular ion peak at m/z = 118.

(a) Use these data to show that the molecular formula of **R** is $C_6H_{14}O_2$.

_____

_____

_____

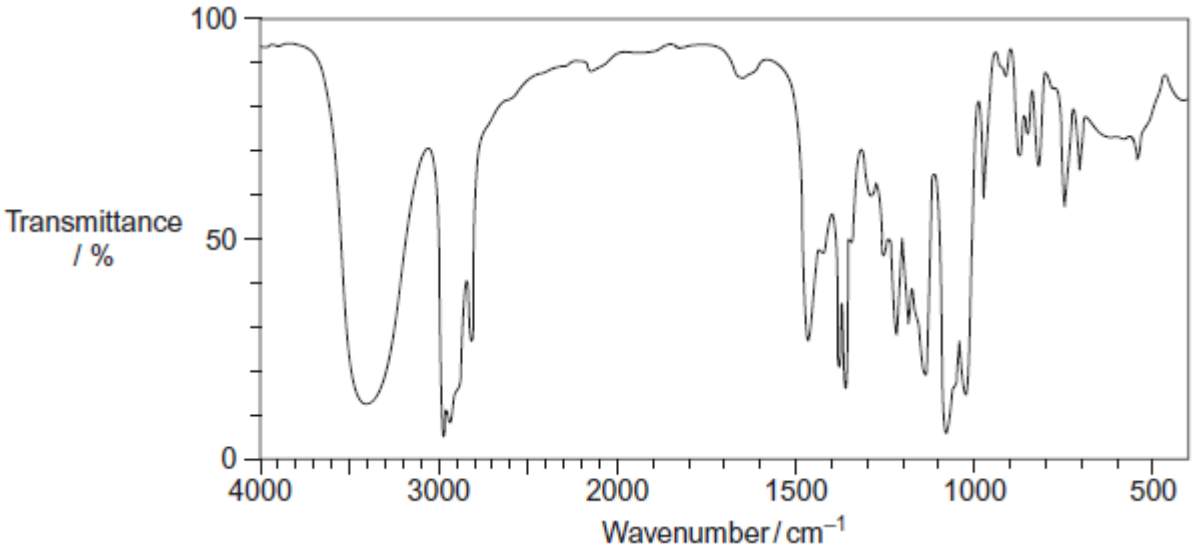
_____

_____

_____

(3)

(b) The infrared spectrum of **R** ($C_6H_{14}O_2$) is shown below.



The proton n.m.r. spectrum of **R** contains five peaks. The chemical shift values, integration ratios and splitting patterns of these peaks are given in the table.

Chemical shift/ppm	3.8	3.2	3.1	1.4	1.1
Integration ratio	2	3	1	2	6
Splitting patterns	triplet	singlet	singlet	triplet	singlet

When **R** is warmed with acidified potassium dichromate(VI) a green solution is formed.

Use **Table A** and **Table B** on the data sheet and all of the data provided in the question to deduce the structure of **R**.

In your answer, explain how you have used the data provided in the question.

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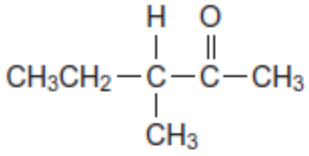
(9)

(Total 12 marks)

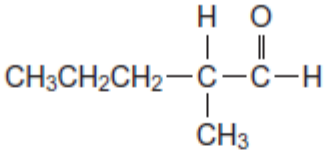
Q10.

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

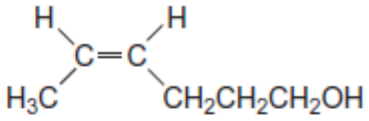
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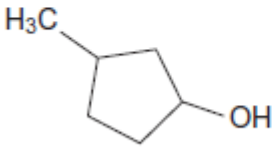
P



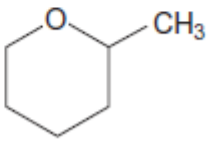
Q



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.

_____

_____

_____

_____

_____

(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.

_____

_____

_____

_____

(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.

_____

_____

_____

_____

_____

(3)

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

Figure 1

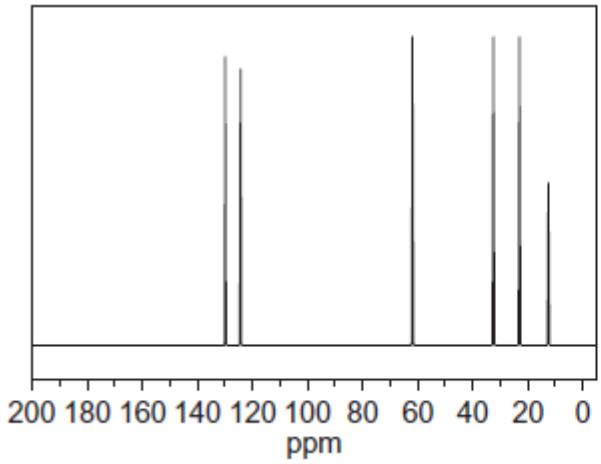
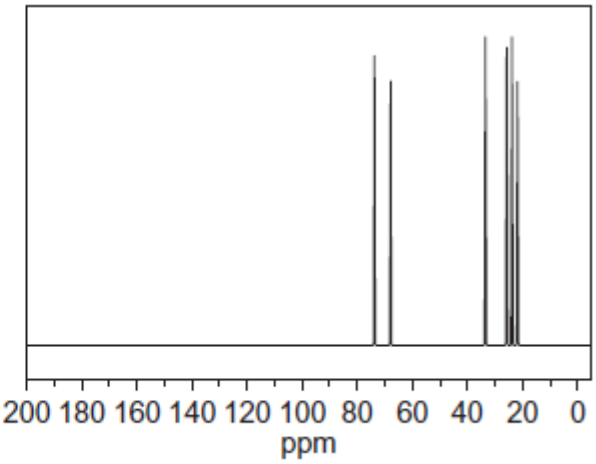
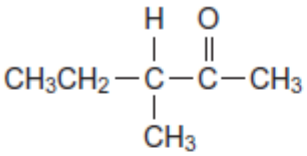


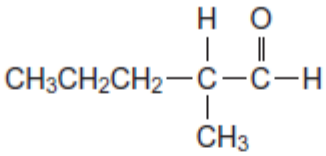
Figure 2



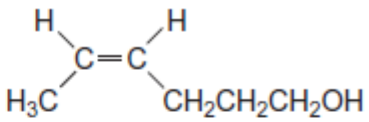
The structures of the five isomers are repeated to help you answer this question.



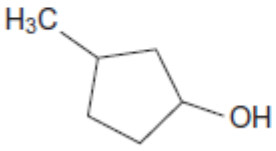
P



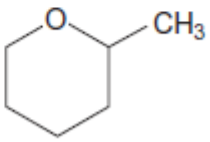
Q



R



S



T

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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.

(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**.

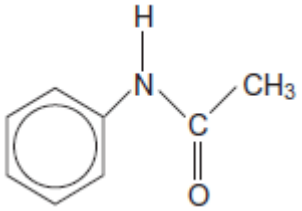
U **V**

(2)
(Total 17 marks)

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Q11.

The structure of N-phenylethanamide is



Use this structure to determine the number of peaks in the ^{13}C n.m.r. spectrum of N−phenylethanamide.

_____

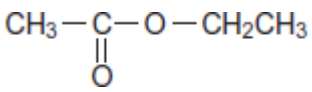
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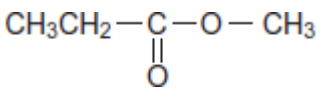
(Total 1 mark)

Q12.

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

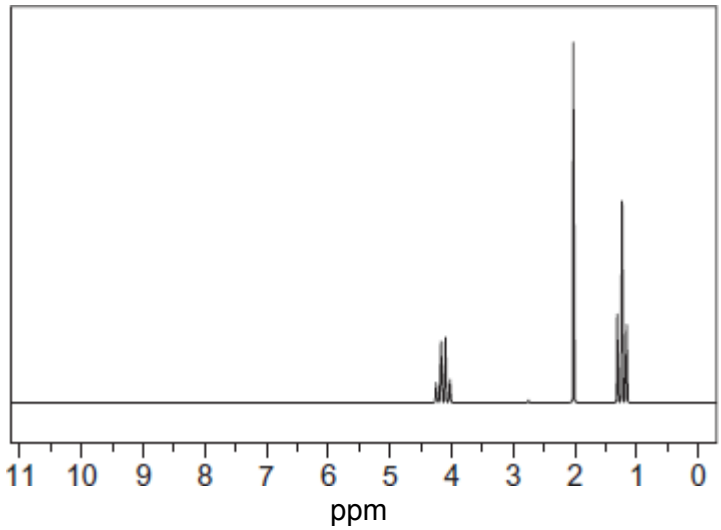


Ester 1



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 δ = 4.1 ppm in the spectrum.

Predict the δ value of the quartet peak in the spectrum of the other ester.

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

_____

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(4)

(b) Cetrimide is used as an antiseptic.

$[CH_3(CH_2)_{15}N(CH_3)_3]^+ Br^-$

cetrimide

Name this type of compound.

Give the reagent that must be added to $CH_3(CH_2)15NH_2$ to make cetrimide and state the reaction conditions.

Name the type of mechanism involved in this reaction.

(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)

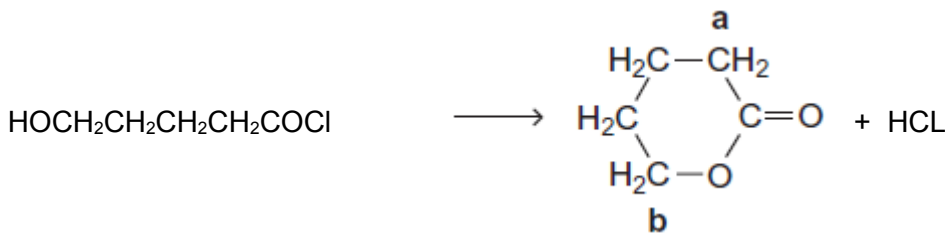
(Total 11 marks)

Q13.

This question is about some isomers of $C_5H_8O_2$

(a) Compound **H** is a cyclic ester that can be prepared as shown.

On the structure of **H**, two of the carbon atoms are labelled.



H

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

Use **Table C** on the Data Sheet to give the ^{13}C n.m.r. δ value for the carbon atom labelled **a** and the δ value for the carbon atom labelled **b**.

_____

_____

_____

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_____

_____

(7)

(ii) $HOCH_2CH_2CH_2CH_2COCl$ can also react to form a polyester in a mechanism similar to that in part (i).

Draw the repeating unit of the polyester and name the type of polymerisation involved.

_____

_____

_____

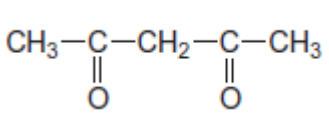
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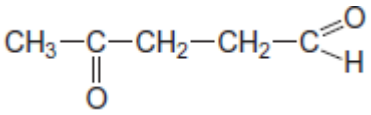
(2)

(b) State how you could distinguish between compounds **J** and **K** by a simple test-tube reaction.

State how you could distinguish between **J** and **K** by giving the number of peaks in the ^1H n.m.r. spectrum of each compound.



J



K

_____

_____

_____

_____

_____

_____

_____

_____

(5)

(c) Draw the structure of each of the following isomers of $C_5H_8O_2$
Label each structure you draw with the correct letter **L**, **M**, **N**, **P** or **Q**.

L is methyl 2-methylpropenoate.

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M is an ester that shows E-Z stereoisomerism.

N is a carboxylic acid with a branched carbon chain and does **not** show stereoisomerism.

P is an optically active carboxylic acid.

Q is a cyclic compound that contains a ketone group and has only two peaks in its ^{1}H n.m.r. spectrum.

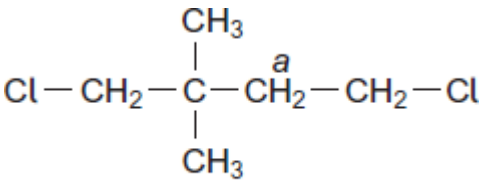
(5)

(Total 19 marks)

Q14.

N.m.r. spectroscopy can be used to study the structures of organic compounds.

(a) Compound **J** was studied using ^{1}H n.m.r. spectroscopy.



J

(i) Identify a solvent in which **J** can be dissolved before obtaining its ^{1}H n.m.r. spectrum.

_____

(1)

(ii) Give the number of peaks in the ^{1}H n.m.r. spectrum of **J**.

_____

(1)

(iii) Give the splitting pattern of the protons labelled *a*.

_____

(1)

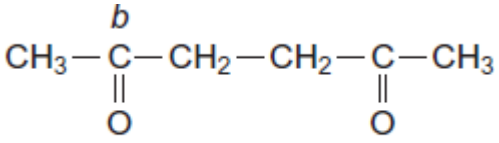
(iv) Give the IUPAC name of **J**.

_____

(1)

(b) Compound **K** was studied using ^{13}C n.m.r. spectroscopy.

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K

(i) Give the number of peaks in the ^{13}C n.m.r. spectrum of **K**.

_____

(1)

(ii) Use **Table 3** on the Data Sheet to suggest a δ value of the peak for the carbon labelled *b*.

_____

(1)

(iii) Give the IUPAC name of **K**.

_____

(1)

(Total 7 marks)

Q15.

This question concerns isomers of $C_6H_{12}O_2$ and how they can be distinguished using n.m.r. spectroscopy.

(a) The non-toxic, inert substance TMS is used as a standard in recording both ^1H and ^{13}C n.m.r. spectra.

(i) Give **two** other reasons why TMS is used as a standard in recording n.m.r. spectra.

Reason 1 _____

_____

Reason 2 _____

_____

(2)

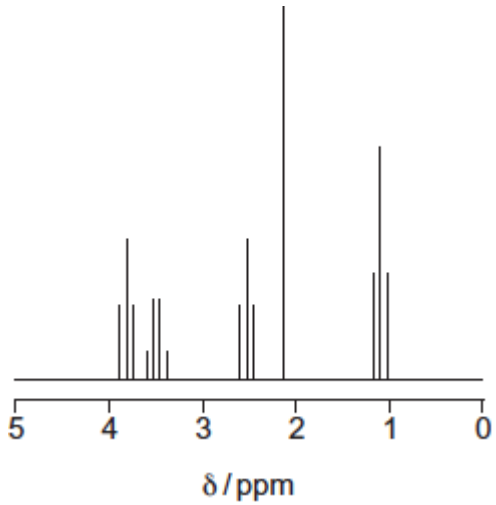
(ii) Give the structural formula of TMS.

(1)

(b) The proton n.m.r. spectrum of compound **P** ($C_6H_{12}O_2$) is represented in **Figure 1**.

Figure 1

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The integration trace gave information about the five peaks as shown in **Figure 2**.

Figure 2

δ / ppm	3.8	3.5	2.6	2.2	1.2
Integration ratio	2	2	2	3	3

(i) Use **Table 2** on the Data Sheet, **Figure 1** and **Figure 2** to deduce the structural fragment that leads to the peak at δ 2.2.

(1)

(ii) Use **Table 2** on the Data Sheet, **Figure 1** and **Figure 2** to deduce the structural fragment that leads to the peaks at δ 3.5 and 1.2.

(1)

(iii) Use **Table 2** on the Data Sheet, **Figure 1** and **Figure 2** to deduce the structural fragment that leads to the peaks at δ 3.8 and 2.6.

(1)

(iv) Deduce the structure of **P**.

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(1)

(c) These questions are about different isomers of **P** ($C_6H_{12}O_2$).

(i) Draw the structures of the two esters that both have only two peaks in their proton n.m.r. spectra. These peaks both have an integration ratio of 3:1.

Ester 1

Ester 2

(2)

(ii) Draw the structure of an optically active carboxylic acid with five peaks in its ^{13}C n.m.r. spectrum.

(1)

(iii) Draw the structure of a cyclic compound that has only two peaks in its ^{13}C n.m.r. spectrum and has no absorption for C = O in its infrared spectrum.

(1)
(Total 11 marks)

Q16.

Acyl chlorides and acid anhydrides are important compounds in organic synthesis.

(a) Outline a mechanism for the reaction of CH_3CH_2COCl with CH_3OH and name the organic product formed.

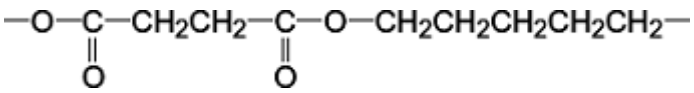
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Mechanism

Name of organic product _____

(5)

(b) A polyester was produced by reacting a diol with a diacyl chloride. The repeating unit of the polymer is shown below.



(i) Name the diol used.

_____

(1)

(ii) Draw the displayed formula of the diacyl chloride used.

(1)

(iii) A shirt was made from this polyester. A student wearing the shirt accidentally splashed aqueous sodium hydroxide on a sleeve. Holes later appeared in the sleeve where the sodium hydroxide had been.

Name the type of reaction that occurred between the polyester and the aqueous sodium hydroxide. Explain why the aqueous sodium hydroxide reacted with the polyester.

Type of reaction _____

Explanation _____

_____

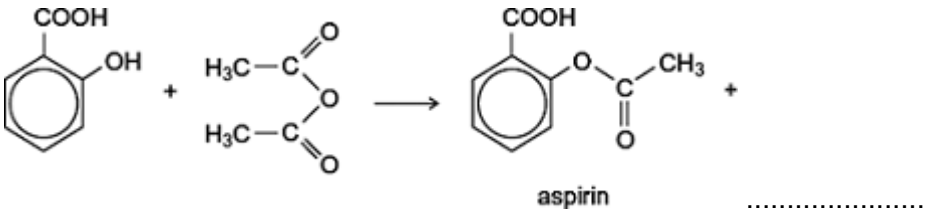
_____

_____

(3)

(c) (i) Complete the following equation for the preparation of aspirin using ethanoic anhydride by writing the structural formula of the missing product.

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aspirin .....

(1)

(ii) Suggest a name for the mechanism for the reaction in part (c)(i).

_____

(1)

(iii) Give **two** industrial advantages, other than cost, of using ethanoic anhydride rather than ethanoyl chloride in the production of aspirin.

Advantage 1 _____

_____

_____

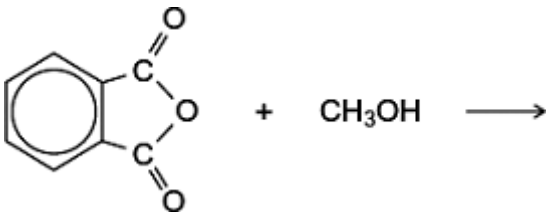
Advantage 2 _____

_____

_____

(2)

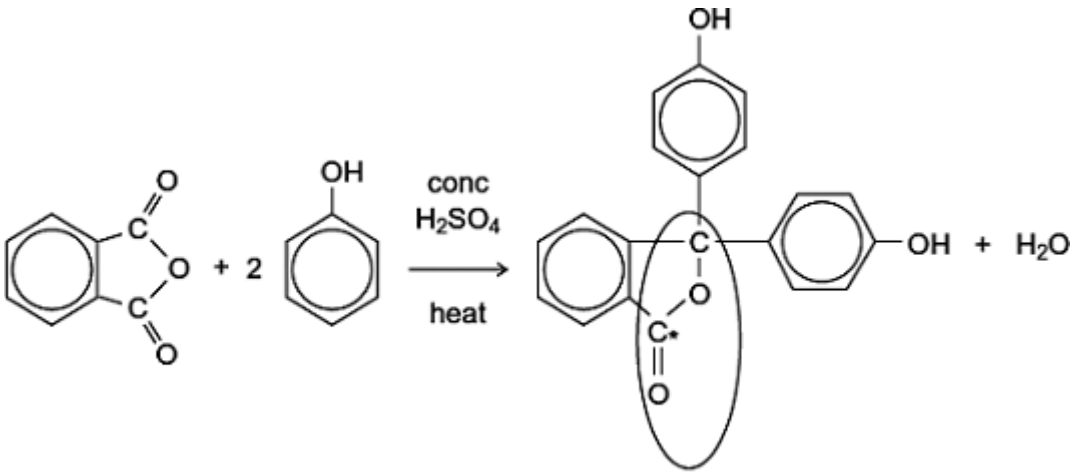
(d) Complete the following equation for the reaction of one molecule of benzene-1,2-dicarboxylic anhydride (phthalic anhydride) with one molecule of methanol by drawing the structural formula of the single product



(1)

(e) The indicator phenolphthalein is synthesised by reacting phthalic anhydride with phenol as shown in the following equation.

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phenol phenolphthalein

(i) Name the functional group ringed in the structure of phenolphthalein.

_____

(1)

(ii) Deduce the number of peaks in the ^{13}C n.m.r. spectrum of phenolphthalein.

_____

(1)

(iii) One of the carbon atoms in the structure of phenolphthalein shown above is labelled with an asterisk (*).
Use **Table 3** on the Data Sheet to suggest a range of δ values for the peak due to this carbon atom in the ^{13}C n.m.r. spectrum of phenolphthalein.

_____

(1)

(f) Phenolphthalein can be used as an indicator in some acid–alkali titrations.
The pH range for phenolphthalein is 8.3 – 10.0

(i) For **each** acid.alkali combination in the table below, put a tick (✓) in the box if phenolphthalein could be used as an indicator.

Acid	**Alkali**	**Tick box (✓)**
sulfuric acid	sodium hydroxide	
hydrochloric acid	ammonia	
ethanoic acid	potassium hydroxide	
nitric acid	methylamine	

(2)

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(ii) In a titration, nitric acid is added from a burette to a solution of sodium hydroxide containing a few drops of phenolphthalein indicator.
Give the colour **change** at the end-point.

_____

(1)

(Total 21 marks)

Q17.

When the molecular formula of a compound is known, spectroscopic and other analytical techniques can be used to distinguish between possible structural isomers.

Draw **one** possible structure for each of the compounds described in parts (a) to (d).

(a) Compounds **F** and **G** have the molecular formula $C_6H_4N_2O_4$ and both are dinitrobenzenes.
F has two peaks in its ^{13}C n.m.r. spectrum.
G has three peaks in its ^{13}C n.m.r. spectrum.

F **G**

(2)

(b) Compounds **H** and **J** have the molecular formula C_6H_{12}.
Both have only one peak in their ^{1}H n.m.r. spectra.
H reacts with aqueous bromine but **J** does not.

H **J**

(2)

(c) **K** and **L** are cyclic compounds with the molecular formula $C_6H_{10}O$.
Both have four peaks in their ^{13}C n.m.r. spectra.
K is a ketone and **L** is an aldehyde.

K **L**

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(2)

(d) Compounds **M** and **N** have the molecular formula $C_6H_{15}N$.
M is a tertiary amine with only two peaks in its ^1H n.m.r. spectrum.
N is a secondary amine with only three peaks in its ^1H n.m.r. spectrum.

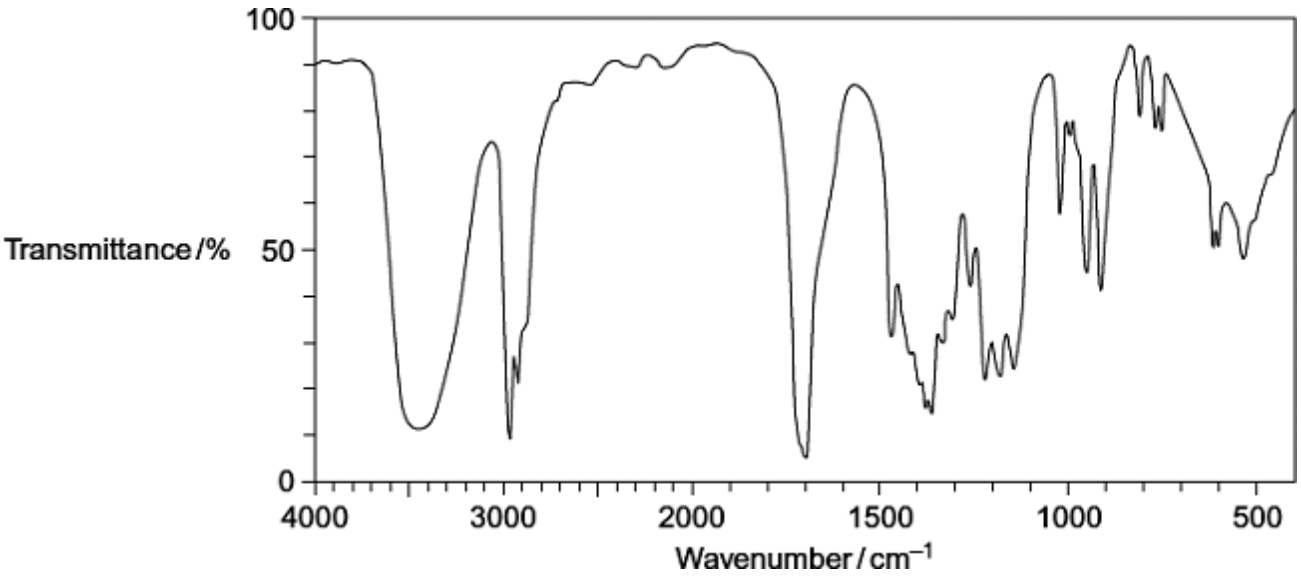
M **N**

(2)
(Total 8 marks)

Q18.

Compound **X** ($C_6H_{12}O_2$) was analysed by infrared spectroscopy and by proton nuclear magnetic resonance spectroscopy.

(a) The infrared spectrum of **X** is shown below.
Use **Table 1** on the Data Sheet to help you answer the question.



Identify the functional group that causes the absorption at 3450cm^{-1} in the spectrum.

_____

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(1)

(b) The proton n.m.r. spectrum of **X** consists of 4 singlet peaks.

The table below gives the chemical shift for each of these peaks, together with their integration values.

δ /ppm	1.2	2.2	2.6	3.8
Integration value	6	3	2	1

Use **Table 2** on the Data Sheet to help you answer the following questions.

Use the chemical shift and the integration data to show what can be deduced about the structure of **X** from the presence of the following in its proton n.m.r. spectrum.

(i) The peak at δ = 2.6

_____

(1)

(ii) The peak at δ = 2.2

_____

(1)

(iii) The peak at δ = 1.2

_____

(1)

(iv) Deduce the structure of **X** ($C_6H_{12}O_2$)

(1)

(Total 5 marks)

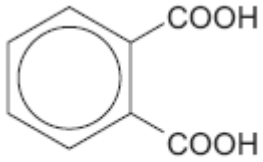
Q19.

Items softened with plasticisers have become an essential part of our modern society.

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Compound **S**, shown below, is commonly known as phthalic acid.

Esters of phthalic acid are called phthalates and are used as plasticisers to soften polymers such as PVC, poly(chloroethene).



S

(a) Give the IUPAC name for phthalic acid.

_____

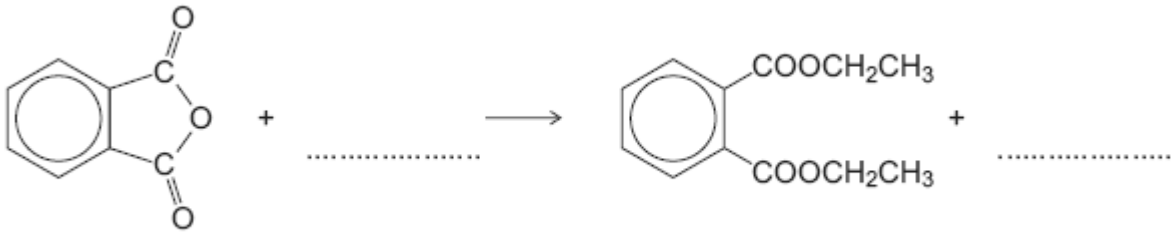
(1)

(b) Draw the displayed formula of the repeating unit of poly(chloroethene).

(1)

(c) The ester diethyl phthalate (DEP) is used in food packaging and in cosmetics.

(i) Complete the following equation showing the formation of DEP from phthalic anhydride.



DEP

(2)

(ii) Deduce the number of peaks in the ^{13}C n.m.r. spectrum of DEP.

_____

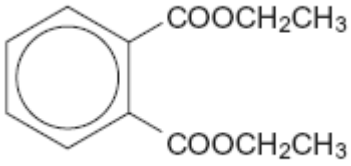
(1)

(iii) One of the peaks in the ^{13}C n.m.r. spectrum of DEP is at $\delta = 62$ ppm.

Table 3 on the Data Sheet can be used to identify a type of carbon atom responsible for this peak.

Draw a circle around **one** carbon atom of this type in the structure below.

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(1)

(d) The mass spectrum of DEP includes major peaks at *m/z* = 222 (the molecular ion) and at *m/z* = 177

Write an equation to show the fragmentation of the molecular ion to form the fragment that causes the peak at *m/z* = 177

_____

(2)

(e) Because of their many uses, phthalates have been tested for possible adverse effects to humans and to the environment.

An organisation that represents the manufacturers of plasticisers asserts that experimental evidence and research findings show that phthalates do not pose a risk to human health because they biodegrade in a short time scale.

According to the organization's research, phthalates do not represent a risk for humans or for the environment and they are biodegradable.

(i) Hydrolysis of DEP in an excess of water was found to follow first order kinetics.

Write a rate equation for this hydrolysis reaction using DEP to represent the ester.

_____

(1)

(ii) Suggest what needs to be done so that the public could feel confident that the research discussed above is reliable.

_____

_____

_____

_____

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_____

(2)

(Total 11 marks)

Q20.

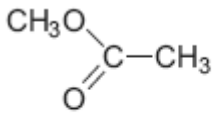
Organic chemists use a variety of methods to distinguish between compounds. These methods include analytical and spectroscopic techniques.

(a) The following compounds can be distinguished by observing what happens in test-tube reactions.

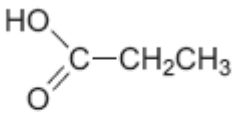
For each pair, suggest a suitable reagent or reagents that could be added separately to each compound in order to distinguish them.

Describe what you would observe with each compound.

(i)



E



F

_____

_____

_____

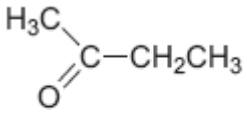
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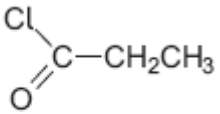
_____

(3)

(ii)



G



H

_____

_____

_____

_____

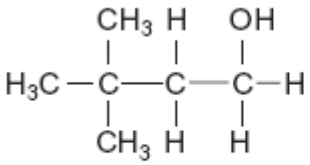
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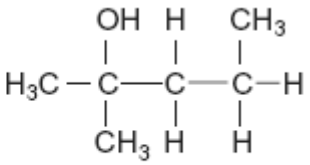
_____

(3)

(iii)



J



K

_____

_____

_____

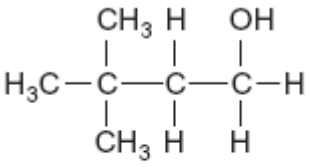
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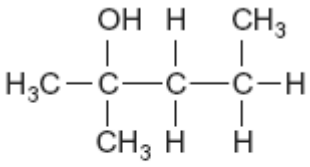
(3)

(b) Compounds **J** and **K** can also be distinguished using spectroscopic techniques such as ^{1}H n.m.r.



a

J



b

K

(i) Name compound **J**.

Give the total number of peaks in the ^{1}H n.m.r. spectrum of **J**.

State the splitting pattern, if any, of the peak for the protons labelled *a*.

_____

_____

_____

_____

_____

_____

(3)

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(ii) Name compound **K**.

Give the total number of peaks in the ^{1}H n.m.r. spectrum of **K**.

State the splitting pattern, if any, of the peak for the protons labelled *b*.

_____

_____

_____

_____

_____

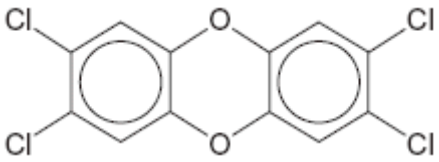
_____

(3)

(Total 15 marks)

Q21.

In 2008, some food products containing pork were withdrawn from sale because tests showed that they contained amounts of compounds called dioxins many times greater than the recommended safe levels.
Dioxins can be formed during the combustion of chlorine-containing compounds in waste incinerators. Dioxins are very unreactive compounds and can therefore remain in the environment and enter the food chain.
Many dioxins are polychlorinated compounds such as tetrachlorodibenzodioxin (TCDD) shown below.



In a study of the properties of dioxins, TCDD and other similar compounds were synthesised. The mixture of chlorinated compounds was then separated before each compound was identified by mass spectrometry.

(a) Fractional distillation is **not** a suitable method to separate the mixture of chlorinated compounds before identification by mass spectrometry.
Suggest how the mixture could be separated.

_____

(1)

(b) The molecular formula of TCDD is $C_{12}H_4O_2Cl_4$

Chlorine exists as two isotopes ^{35}Cl (75%) and ^{37}Cl (25%).
Deduce the number of molecular ion peaks in the mass spectrum of TCDD and calculate the *m/z* value of the most abundant molecular ion peak.

Number of molecular ion peaks _____

_____

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m/z value of the most abundant molecular ion peak _____

_____

(2)

(c) Suggest **one** operating condition in an incinerator that would minimise the formation of dioxins.

_____

_____

(1)

(d) TCDD can also be analysed using ^{13}C n.m.r.

(i) Give the formula of the compound used as the standard when recording a ^{13}C spectrum.

_____

(1)

(ii) Deduce the number of peaks in the ^{13}C n.m.r. spectrum of TCDD.

_____

(1)

(Total 6 marks)

Q22.

Organic chemists use a variety of methods to identify unknown compounds. When the molecular formula of a compound is known, spectroscopic and other analytical techniques are used to distinguish between possible structural isomers. Use your knowledge of such techniques to identify the compounds described below.

Use the three tables of spectral data on the Data Sheet where appropriate.

Each part below concerns a different pair of structural isomers.
Draw **one** possible structure for each of the compounds **A** to **J**, described below.

(a) Compounds **A** and **B** have the molecular formula C_3H_6O
A has an absorption at 1715 cm^{-1} in its infrared spectrum and has only one peak in its ^1H n.m.r. spectrum.
B has absorptions at 3300 cm^{-1} and at 1645 cm^{-1} in its infrared spectrum and does **not** show *E*–*Z* isomerism.

A **B**

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(2)

(b) Compounds **C** and **D** have the molecular formula C_5H_{12}
In their ^1H n.m.r. spectra, **C** has three peaks and **D** has only one.

C **D**

(2)

(c) Compounds **E** and **F** are both esters with the molecular formula $C_4H_8O_2$
In their ^1H n.m.r. spectra, **E** has a quartet at $\delta = 2.3$ ppm and **F** has a quartet at $\delta = 4.1$ ppm.

E **F**

(2)

(d) Compounds **G** and **H** have the molecular formula $C_6H_{12}O$
Each exists as a pair of optical isomers and each has an absorption at about 1700 cm^{-1} in its infrared spectrum. **G** forms a silver mirror with Tollens' reagent but **H** does not.

G **H**

(2)

(e) Compounds **I** and **J** have the molecular formula $C_4H_{11}N$ and both are secondary amines. In their ^{13}C n.m.r. spectra, **I** has two peaks and **J** has three.

I **J**

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(2)
(Total 10 marks)

Q23.

It is necessary to use several analytical techniques to determine the structure of an unknown compound.

An analytical chemist was asked to determine the structure of compound **Q** which was found in a waste tank in a mixture of volatile liquids.

Compound **Q** has the molecular formula C_4H_7ClO. It is a volatile liquid which does not produce misty fumes when added to water.

(a) Suggest how the chemist could obtain a sample of **Q** for analysis from the mixture of volatile liquids.

_____

(1)

(b) The infra-red spectrum of Q contains a major absorption at 1724 cm^{-1}. Identify the bond which causes this absorption.

_____

(1)

(c) The mass spectrum of Q contains two molecular ion peaks at *m/z* = 106 and *m/z* = 108.
It also has a major peak at *m/z* = 43.

(i) Suggest why there are two molecular ion peaks.

_____

(ii) A fragment ion produced from **Q** has *m/z* = 43 and contains atoms of **three** different elements. Identify this fragment ion and write an equation showing its formation from the molecular ion of **Q**.

Fragment ion _____

Equation _____

(3)

(d) The proton n.m.r. spectrum of **Q** was recorded.

(i) Suggest a suitable solvent for use in recording this spectrum of **Q**.

_____

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(ii) Give the formula of the standard reference compound used in recording proton n.m.r. spectra.

_____

(2)

(e) The proton n.m.r. spectrum of Q shows 3 peaks. Complete the table below to show the number of adjacent, non-equivalent protons responsible for the splitting patterns.

	Peak 1	Peak 2	Peak 3
Integration value	3	3	1
Splitting pattern	doublet	singlet	quartet
Number of adjacent, non-equivalent protons	1		

(1)

(f) Using the information in parts (a), (b) and (d) deduce the structure of compound **Q**.

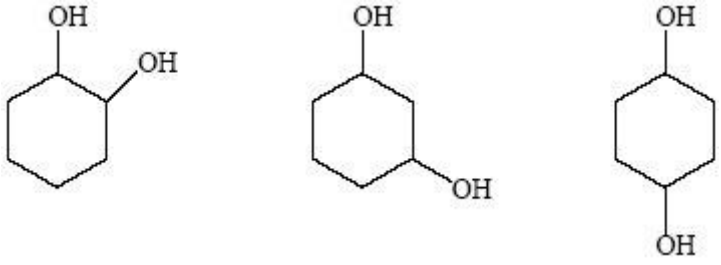
(1)

(g) A structural isomer of **Q** reacts with cold water to produce misty fumes. Suggest a structure for this isomer.

(1)
(Total 10 marks)

Q24.

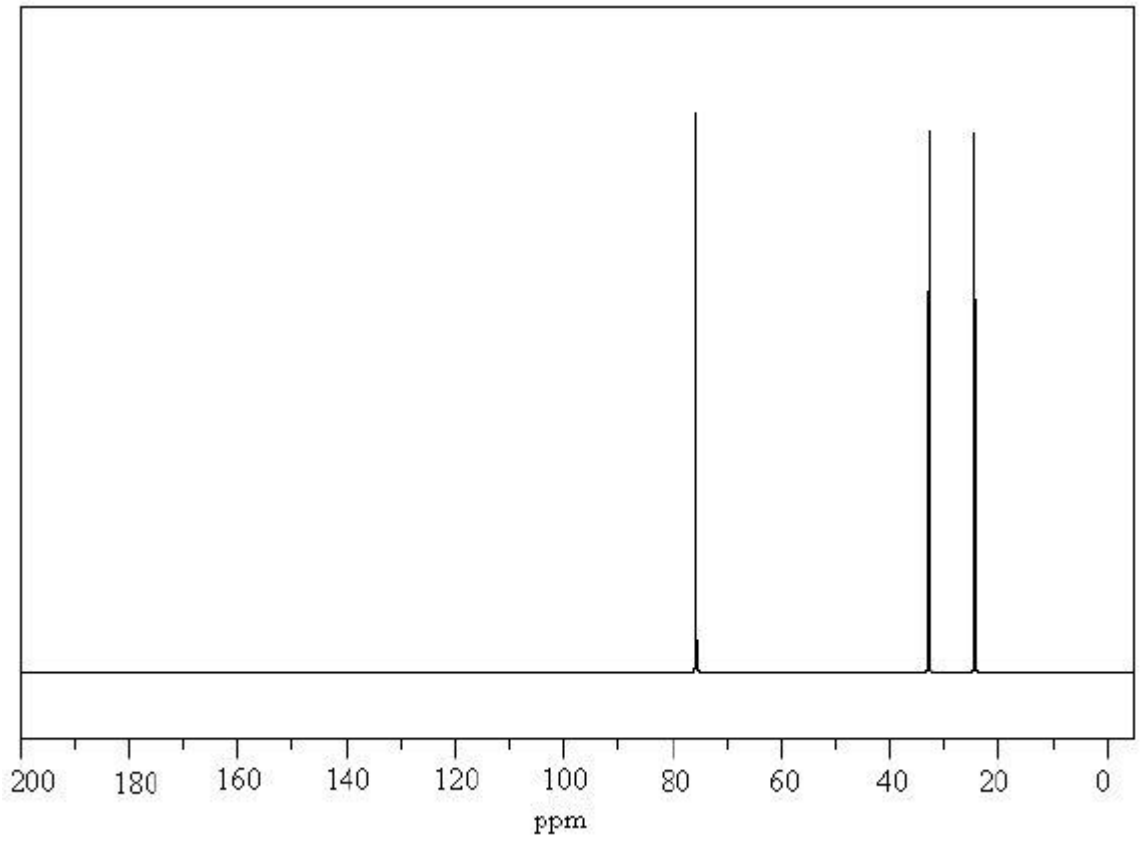
Three cyclic alcohols, cyclohexan–1,2-diol, cyclohexan–1,3-diol and cyclohexan–1,4-diol were compared using ^{13}C n.m.r. spectroscopy.



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cyclohexan-1,2-diol cyclohexan-1,3-diol cyclohexan-1,4-diol

The ^{13}C n.m.r. spectrum of cyclohexan-1,2-diol is shown below.



(a) (i) Explain why there are three peaks.

_____

_____

_____

(ii) Proton n.m.r. chemical shift data is shown in Table 1 on the reverse of the Periodic Table. Chemical shift values for ^{13}C vary similarly with chemical environment.

Suggest the δ value of the peak in the spectrum above which corresponds to the absorption for carbon atom 1 in cyclohexan-1,2-diol.

_____

(b) (i) Predict the number of peaks in the ^{13}C n.m.r. spectrum of cyclohexan-1,3-diol.

_____

(ii) Predict the number of peaks in the ^{13}C n.m.r. spectrum of cyclohexan-1,4-diol.

_____

(c) Suggest why the structures drawn above represents several stereoisomers.

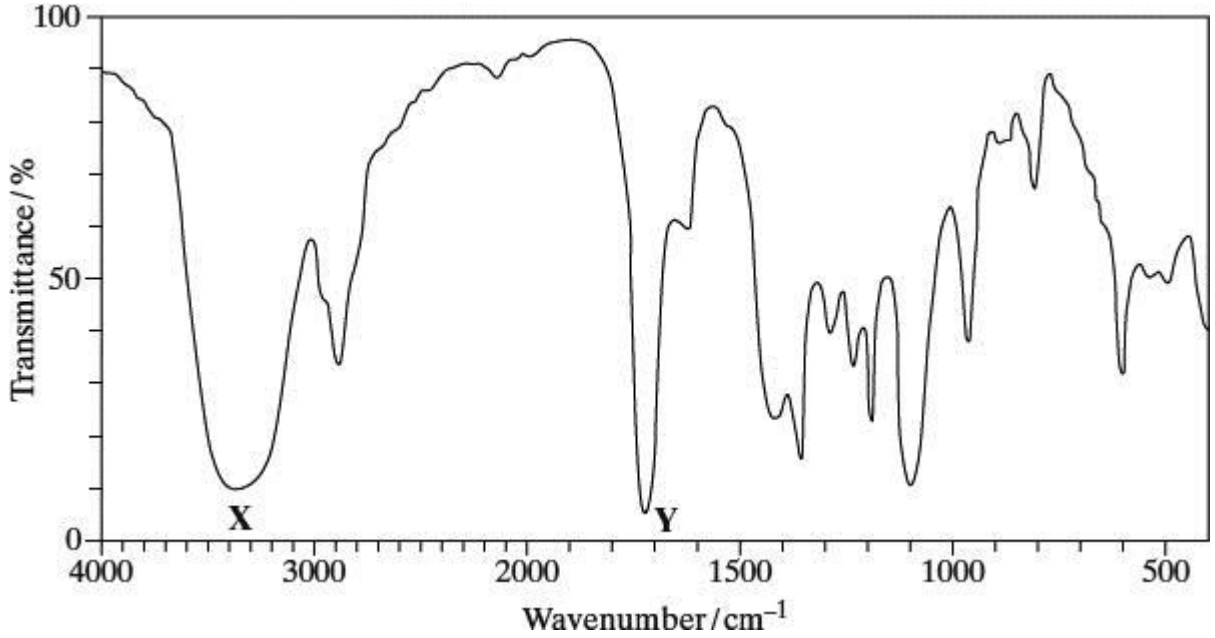
_____

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(Total 5 marks)

Q25.

(a) The infra-red spectrum of compound **A**, $C_3H_6O_2$, is shown below.



Identify the functional groups which cause the absorptions labelled **X** and **Y**.

Using this information draw the structures of the three possible structural isomers for **A**.

Label as **A** the structure which represents a pair of optical isomers.

(6)

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(b) Draw the structures of the three **branched-chain** alkenes with molecular formula C_5H_{10}

Draw the structures of the three dibromoalkanes, $C_5H_{10}Br_2$, formed when these three alkenes react with bromine.

One of these dibromoalkanes has only three peaks in its proton n.m.r. spectrum. Deduce the integration ratio and the splitting patterns of these three peaks.

(10)

(Total 16 marks)

Q26.

Which one of the following pairs of reagents reacts to form an organic product that shows only 2 peaks in its proton n.m.r. spectrum?

A butan-2-ol and acidified potassium dichromate(VI)

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B ethanoyl chloride and methanol

C propanoic acid and ethanol in the presence of concentrated sulphuric acid

D ethene and hydrogen in the presence of nickel

(Total 1 mark)

Q27.

This question concerns four isomers, **W**, **X**, **Y** and **Z**, with the molecular formula $C_5H_{10}O_2$

(a) The proton n.m.r. spectrum of **W** shows 4 peaks.
The table below gives the chemical shifts, δ values, for each of these peaks, together with their splitting patterns and integration values.

δ/ppm	2.18	2.59	3.33	3.64
Splitting pattern	singlet	triplet	singlet	triplet
Integration value	3	2	3	2

State what can be deduced about the structure of **W** from the presence of the following in its n.m.r. spectrum.

(i) The singlet peak at δ = 2.18

_____

(ii) The singlet peak at δ = 3.33

_____

(iii) Two triplet peaks.

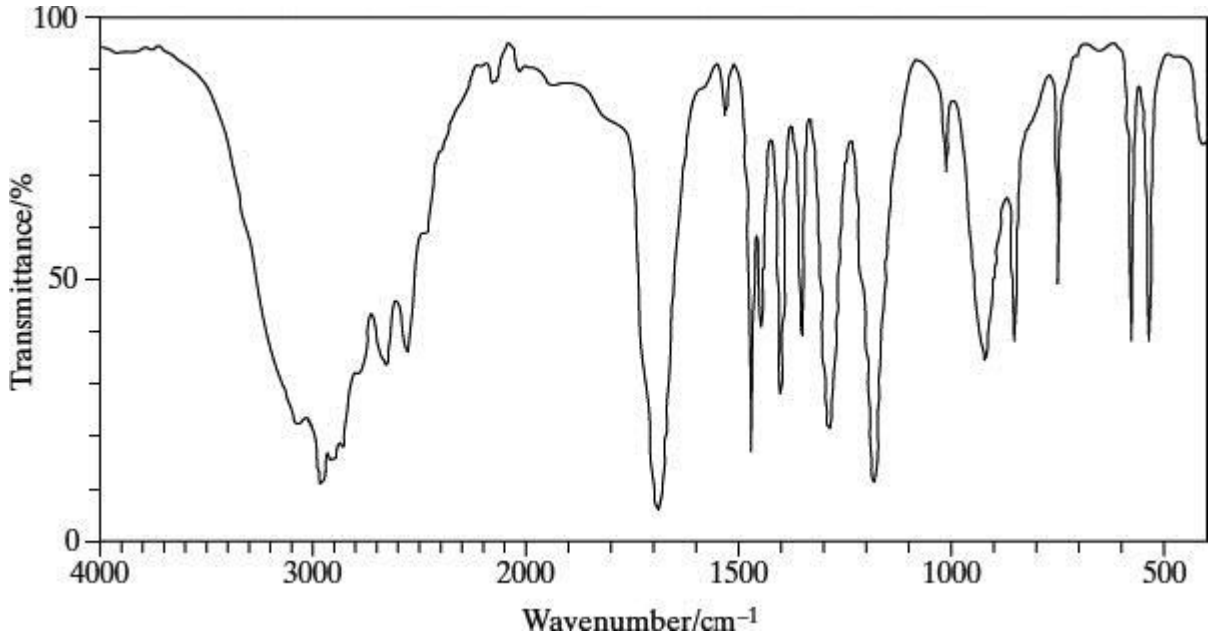
_____

(iv) Hence, deduce the structure of **W**.

(4)

(b) The infra-red spectrum of **X** is shown below.

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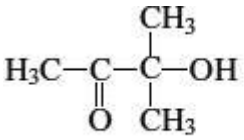
(i) What can be deduced from the broad absorption centred on 3000 cm^{-1} in the infra-red spectrum of **X**?

_____

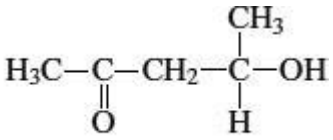
(ii) Given that the proton n.m.r. spectrum of **X** contains only two peaks with the integration ratio 9:1, deduce the structure of **X**.

(2)

(c) Isomers **Y** and **Z** have the structures shown below.



Y



Z

Identify the two reagents you could use in a simple chemical test to distinguish between **Y** and **Z**. State what you would observe when each of **Y** and **Z** is tested with a mixture of these two reagents.

Reagents _____

*Observation with **Y*** _____

*Observation with **Z*** _____

(3)

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(Total 9 marks)

Q28.

Which one of the following pairs reacts to form an organic product with only 2 singlets in its proton n.m.r. spectrum?

A ethene and bromine

B propan-2-ol and acidified potassium dichromate(VI)

C ethanol and concentrated sulphuric acid

D epoxyethane and water in the presence of dilute sulphuric acid

(Total 1 mark)

Q29.

Each of the parts (a) to (e) below concerns a different pair of isomers.

Draw one possible structure for each of the species **A** to **J**, using Table 2 on the Data Sheet where appropriate.

(a) Compounds **A** and **B** have the molecular formula C_5H_{10}
A decolourises bromine water but **B** does not.

A **B**

(2)

(b) Compounds **C** and **D** have the molecular formula $C_2H_4O_2$

Each has an absorption in its infra-red spectrum at about 1700 cm^{-1} but only **D** has a broad absorption at 3350 cm^{-1}

C **D**

(2)

(c) Compounds **E** and **F** are esters with the molecular formula $C_5H_{10}O_2$

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The proton n.m.r. spectrum of **E** consists of two singlets only whereas that of **F** consists of two quartets and two triplets.

E **F**

(2)

(d) Compounds **G** and **H** have the molecular formula $C_3H_6Cl_2$ **G** shows optical activity but **H** does not.

G **H**

(2)

(e) Compounds **I** and **J** have the molecular formula C_6H_{12}

Each has an absorption in its infra-red spectrum at about 1650 cm^{-1} and neither shows geometrical isomerism. The proton n.m.r. spectrum of **I** consists of a singlet only whereas that of **J** consists of a singlet, a triplet and a quartet.

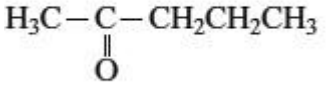
I **J**

(2)
(Total 10 marks)

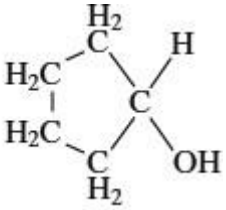
Q30.

Compounds **C** and **D**, shown below, are isomers of $C_5H_{10}O$

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C



D

(a) Name compound **C**.

_____

(1)

(b) Use **Table 2** on the Data Sheet to help you to answer this question.

(i) Suggest the wavenumber of an absorption which is present in the infra-red spectrum of **C** but not in that of **D**.

_____

(ii) Suggest the wavenumber of an absorption which is present in the infra-red spectrum of **D** but not in that of **C**.

_____

(2)

(c) Deduce the number of peaks in the proton n.m.r. spectrum of **C**.

_____

(1)

(d) Identify a reagent that you could use to distinguish between **C** and **D**. For each of **C** and **D**, state what you would observe when the compound is treated with this reagent.

Reagent _____

Observation with **C** _____

Observation with **D** _____

(3)

(e) Compound **E**, $CH_3CH_2CH_2CH_2CHO$, is also an isomer of $C_5H_{10}O$

Identify a reagent which will react with **E** but not with **C** or **D**. State what you would observe when **E** is treated with this reagent.

Reagent _____

Observation with **E** _____

(2)

(Total 9 marks)

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Q31.

(a) Describe how propanal, CH_3CH_2CHO, and propanone, CH_3COCH_3, can be distinguished using

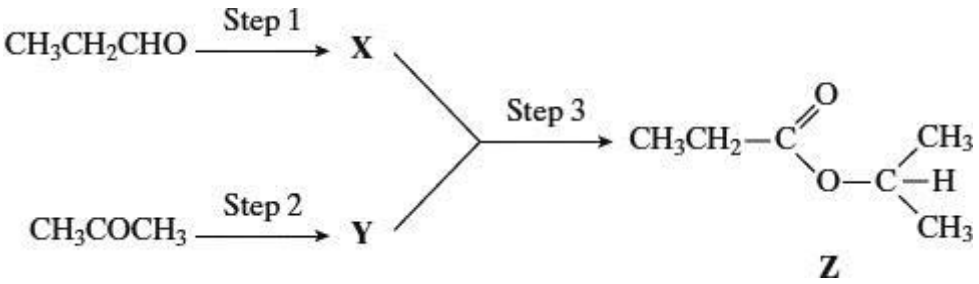
(i) a chemical test and

(3)

(ii) the number of peaks in their proton n.m.r. spectra.

(2)

(b) Compound **Z** can be produced by the reaction of compound **X** with compound **Y** as shown in the synthesis outlined below.



Identify compounds **X** and **Y**.
For each of the three steps in the synthesis, name the type of reaction involved and give reagents and conditions. Equations are **not** required.

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(10)

(Total 15 marks)

Q32.

(a) Ester **X**, $CH_3CH_2COOCH_3$, can be produced by the reaction between propanoyl chloride and methanol. Name **X** and outline a mechanism for this reaction. Name the mechanism involved.

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_____

_____

_____

_____

_____

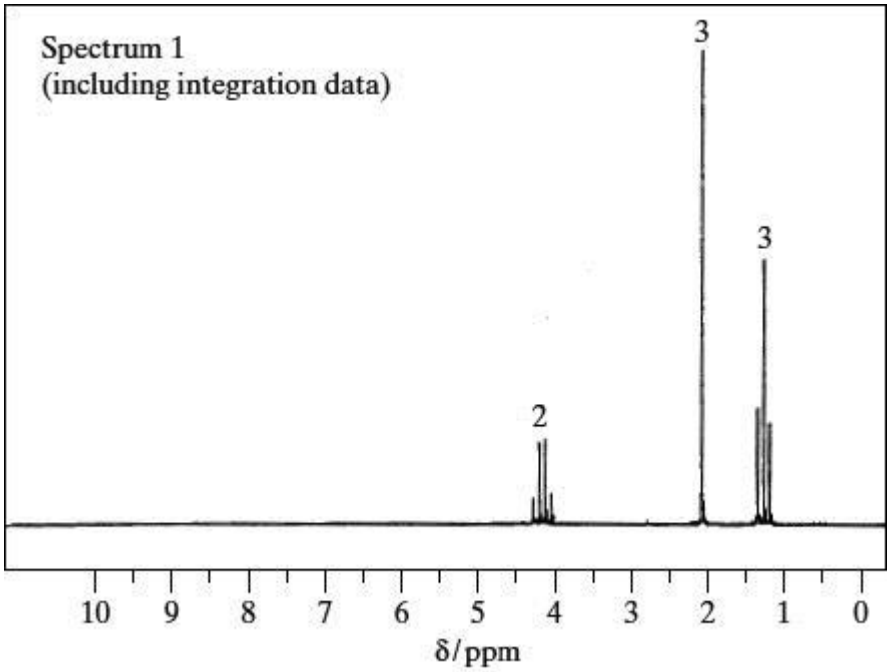
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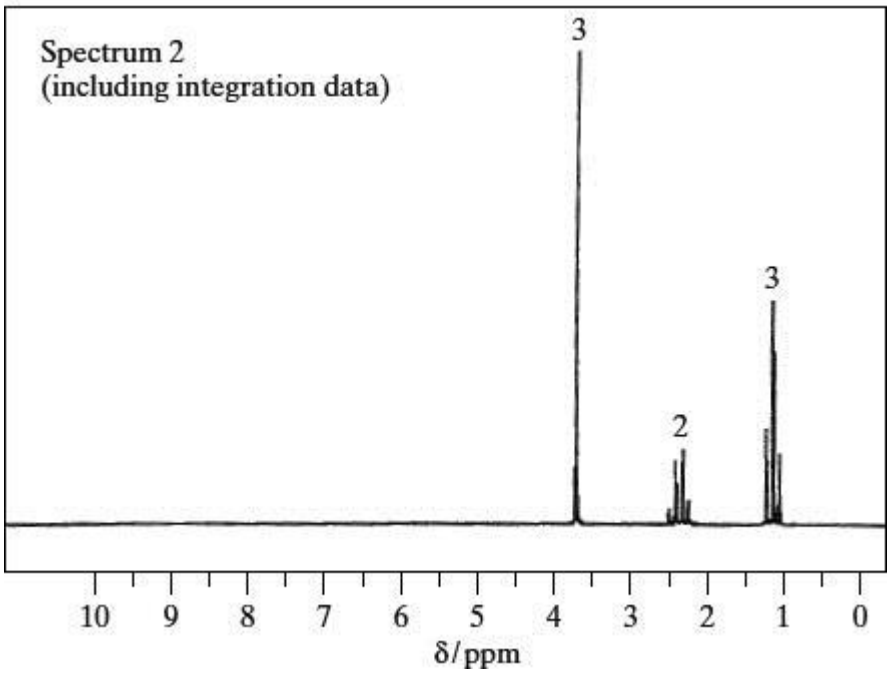
_____

(6)

(b) The proton n.m.r. spectrum of **X** is shown below together with that of an isomeric ester, **Y**. Deduce which of Spectrum 1 and Spectrum 2 is that obtained from **X**. Use **Table 1** on the Data Sheet and the integration data on the spectra to help you to explain your deduction. Suggest a structure for **Y**.

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(4)

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(Total 10 marks)

Q33.

Butenedioic acid, HOOCCH=CHCOOH, occurs as two stereoisomers. One of the isomers readily forms the acid anhydride $C_4H_2O_3$ when warmed.

(a) Draw the structures of the two isomers of butenedioic acid and name the type of isomerism shown.
Use the structures of the two isomeric acids to suggest why only one of them readily forms an acid anhydride when warmed. Draw the structure of the acid anhydride formed.

(6)

(b) Identify one electrophile which will react with butenedioic acid and outline a mechanism for this reaction.

(4)

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(c) Write an equation for a reaction which occurs when butenedioic acid is treated with an excess of aqueous sodium hydroxide.

_____

_____

_____

_____

(2)

(d) Describe and explain the appearance of the proton n.m.r. spectrum of butenedioic acid.

_____

_____

_____

_____

_____

_____

(3)

(Total 15 marks)

Q34.

Which one of the following does **not** have a singlet peak in its proton n.m.r. spectrum?

A butyl methanoate

B propyl ethanoate

C ethyl propanoate

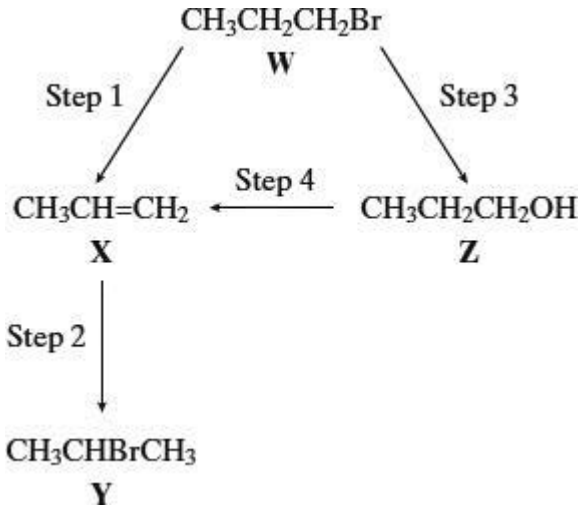
D methyl butanoate

(Total 1 mark)

Q35.

For this question refer to the reaction scheme below.

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

A **W** and **Y** are structural isomers.

B **Z** is a primary alcohol.

C **Y** gives two peaks in its proton n.m.r. spectrum.

D **X** has geometrical isomers.

(Total 1 mark)

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