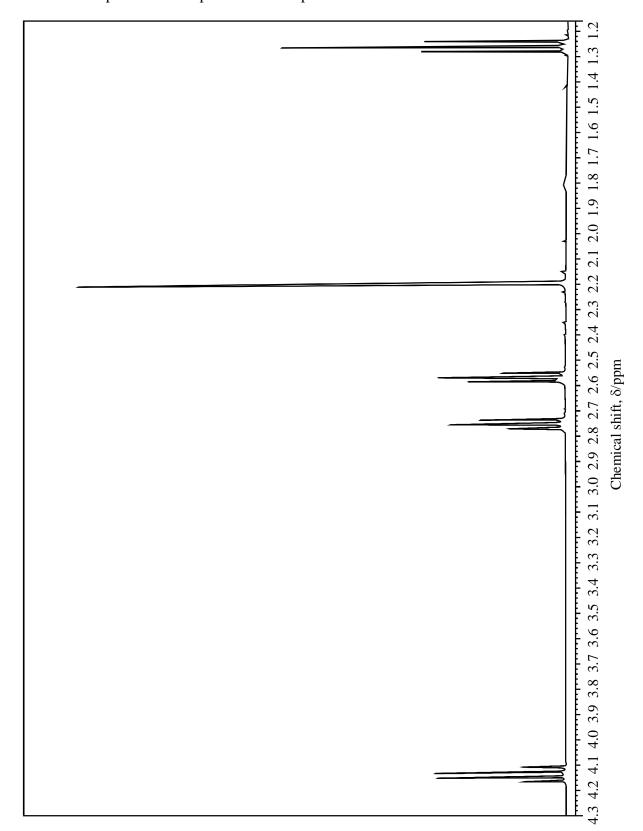
Chromatography and Spectroscopy 1

1. The proton n.m.r. spectrum of compound **X** is shown below.



Compound \mathbf{X} , $C_7H_{12}O_3$, contains both a ketone and an ester functional group. The measured integration trace for the peaks in the n.m.r. spectrum of \mathbf{X} gives the ratio shown in the table below.

Chemical shift, δ/ppm	4.13	2.76	2.57	2.20	1.26
Integration ratio	0.8	0.8	0.8	1.2	1.2

Refer to the spectrum, the information given above and the data below the Periodic Table provided to answer the following questions.

How many different types of proton are present in compound \mathbf{X} ?	
What is the whole-number ratio of each type of proton in compound \mathbf{X} ?	
Draw the part of the structure of \mathbf{X} which can be deduced from the presence of the peak at $\delta 2.20$.	•
The peaks at $\delta 4.13$ and $\delta 1.26$ arise from the presence of an alkyl group. Identify the group and explain the splitting pattern.	
Alkyl group	
Explanation	
Draw the part of the structure of X which can be deduced from the splitting of the peaks at $\delta 2.76$ and $\delta 2.57$.	
Deduce the structure of compound \mathbf{X} .	
(Total 9 m	(irk

a)		infra-red spectrum of Q contains on sible for this absorption.	ains a major absorp	ption at 1724 cm ⁻	¹ . Identify the bond
b)		mass spectrum of Q contains so has a major peak at $m/z = 4$		n peaks at $m/z = 10$	06 and $m/z = 108$.
	(i)	Suggest why there are two	molecular ion peal	ks.	
	(ii)	A fragment ion produced frelements. Identify this fragfrom the molecular ion of	ment ion and write		
		Fragment ion			
		Equation			
:)	The	proton n.m.r. spectrum of Q	was recorded.		
	(i)	Suggest a suitable solvent f	for use in recording	g this spectrum of	Q.
	(ii)	Give the formula of the stan spectra.	dard reference con	npound used in red	cording proton n.m.
i)		proton n.m.r. spectrum of \mathbf{Q} sber of adjacent, non-equivale	shows three peaks.	Complete the tab	le below to show th
			Peak 1	Peak 2	Peak 3
Ir	itegrat	ion value	3	3	1
	plitting	g pattern	doublet	singlet	Quartet
S				i	

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

2.

(e)

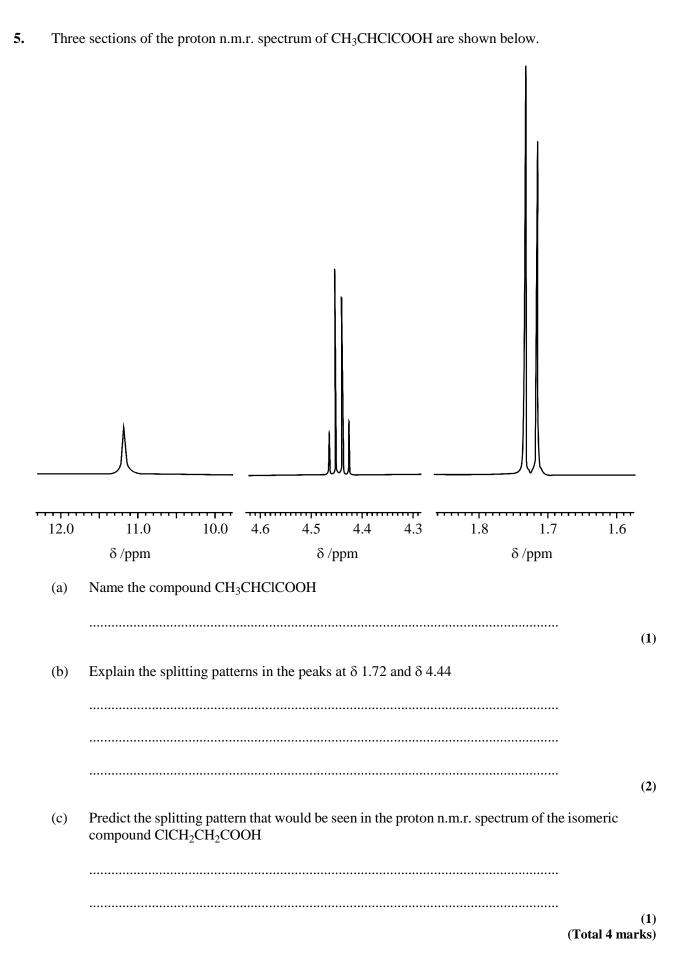
(1) (Total 8 marks)

				(1)
	(b)	equat	mass spectrum of ethyl propanoate contains a major peak at $m/z = 57$. Write an ion showing the fragmentation of the molecular ion to form the species responsible e peak at $m/z = 57$. Show the structure of this species in your answer.	
		•••••		(2)
	(c)		the structure of another ester which is an isomer of ethyl propanoate and which gives or peak at $m/z = 71$ in its mass spectrum.	
			(Total 4 ma	(1)
			(10tai 4 ma	1 N3)
4.	(a)	Fragn	mentation of the molecular ion of methylbutanone, $(CH_3)_2CHCOCH_3$, gives rise to dominant peaks at $m/z = 71$ and $m/z 43$.	
		(i)	Construct a balanced equation to show how fragmentation of the molecular ion gives rise to the peak at $m/z = 71$.	
		(ii)	In the fragmentation of $(CH_3)_2CHCOCH_3$, two fragments with m/z 43 are formed. Give the structural formula of each of these fragments.	
			Structure 1 Structure 2	
				(5)
	(b)	and m	molecular ion peaks appear in the mass spectrum of 2-chloropropane at m/z 78 $n/z = 80$. Explain why two molecular ion peaks are found and why the relative sities of the peaks are approximately 3 to 1, respectively.	
		•••••	(Total 8 ma	(3) rks)

3.

(a)

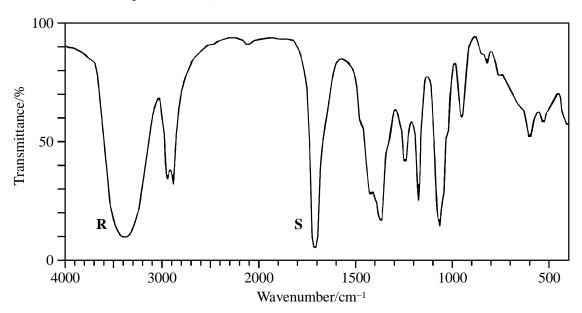
Draw the structure of ethyl propanoate.



6. Spectral data for use in this question are provided below the Periodic Table (first item on the database).

Compound \mathbf{Q} has the molecular formula $C_4H_8O_2$

(a) The infra-red spectrum of \mathbf{Q} is shown below.



Identify the type of bond causing the absorption labelled \mathbf{R} and that causing the absorption labelled \mathbf{S} .

R	
_	
S	
	(2)
	(=)

(b) ${f Q}$ does not react with Tollens' reagent. Identify a functional group which would react with these reagents and therefore cannot be present in ${f Q}$.

(1)

- (c) Proton n.m.r. spectra are recorded using a solution of a substance to which tetramethylsilane (TMS) has been added.
 - (i) Give two reasons why TMS is a suitable standard.

Reason 2

(ii) Give an example of a solvent which is suitable for use in recording an n.m.r. spectrum. Give a reason for your choice.

Reason

(4)

(d) The proton n.m.r. spectrum of \mathbf{Q} shows 4 peaks.

The table below gives δ values for each of these peaks together with their splitting patterns and integration values.

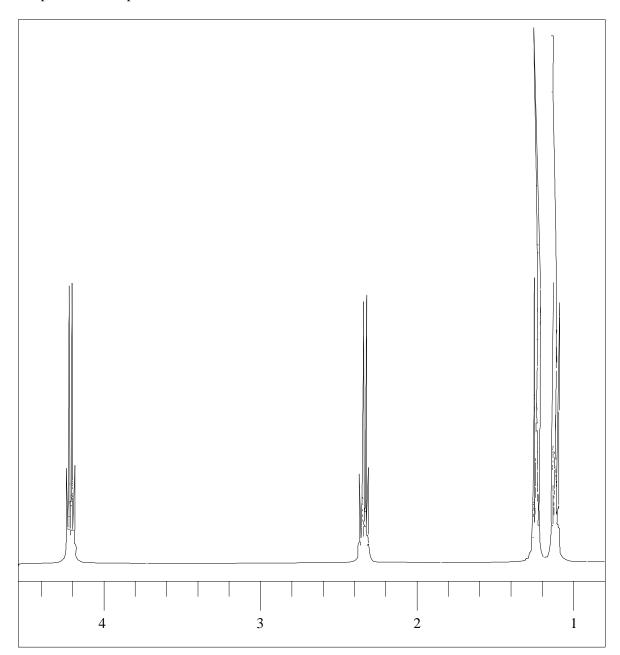
δ/ppm	2.20	2.69	3.40	3.84
Splitting pattern	singlet	triplet	singlet	triplet
Integration value	3	2	1	2

What can be deduced about the structure of \mathbf{Q} from the presence of the following in its n.m.r. spectrum?

(i)	The singlet peak at $\delta = 2.20$	
(ii)	The singlet peak at $\delta = 3.40$	
(iii)	Two triplet peaks	
		(3)

(e) Using your answers to parts (a), (b) and (d), deduce the structure of compound \mathbf{Q} .

(1) (Total 11 marks) 7. The proton n.m.r. spectrum of an ester, \mathbf{A} , is shown below.



Chemical shift, δ/ppm

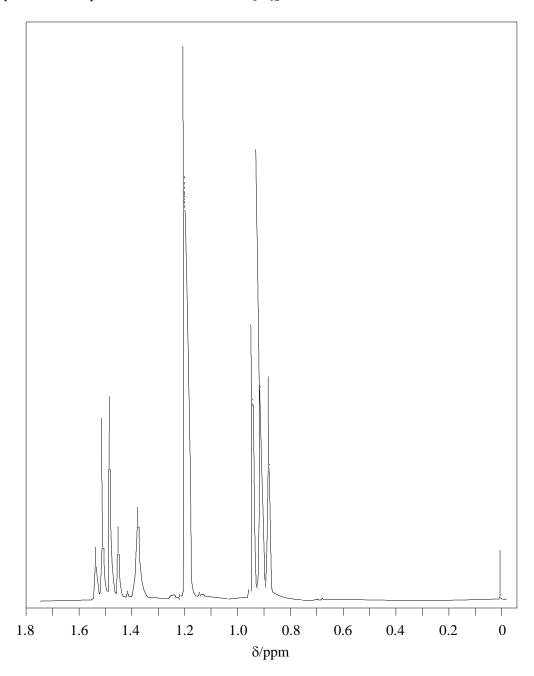
The measured integration trace gives the ratio 0.50 to 0.50 to 0.75 to 0.75 for the peaks at δ 4.13, 2.32, 1.33 and 1.09, respectively.

(a)	The mass spectrum of compound A has a molecular ion peak at $m/z = 102$. Deduce the molecular formula of compound A .
	•

(3)

(b)	What is the ratio of the n	umbers of eac	ch type of prot	ton?		
						(1)
(c)	What can be deduced aboun.m.r. spectrum?	out the arrang	ement of prote	ons from the sp	olitting patteri	ns in the
		••••••				(1)
(d)	Deduce the structure of c of equivalent protons.	ompound A a	nd label with	the letters a, b,	c and d the fo	our groups
						(1)
(e)	Assign the various signal previously labelled a, b, o		below to the g	groups of proto	ons in compou	and A
	Chemical shift, δ/ppm	1.09	1.33	2.32	4.13	
	Label of group					
					1	(4) (Total 10 marks)

8. The proton n.m.r. spectrum of an alcohol, \mathbf{A} , $C_5H_{12}O$, is shown below



The measured integration trace gives the ratio 0.90 to 0.45 to 2.70 to 1.35 for the peaks at δ 1.52, 1.39, 1.21 and 0.93, respectively.

(a)	What compound is responsible for the signal at δ 0?	
		(1)
(b)	How many different types of proton are present in compound A?	
		(1)

(c)	What	is the ratio of the numbers of each type of proton?	
	•••••		(1)
(d)			is
	Group	p	
	Expla	ination	
	•••••		(3)
(e)	What	can be deduced from the single peak at δ 1.21 and its integration value?	
			(1)
(f)	Give	the structure of compound A.	
		(Total 8	(1) 8 marks)
	(i)	Give the structural formula of the ester.	
	(ii)	How many different types of proton are present in this ester?	
	(iii)	Describe the splitting pattern of the ethyl group in the n.m.r. spectrum of the ester-	
		(Total 3	(3) 3 marks)
	(d) (e)	(d) The p group Group Exploit (ii)	(d) The peaks at δ 1.52 and δ 0.93 arise from the presence of a single alkyl group. Identify the group and explain the splitting pattern. Group

o)	The gr	graph below shows part of the mass spectrum of an organic compound, A	which has
	the mo	nolecular formula C_4H_{10} .	
	relat abund		
			-
		0 10 20 30 40 50 60 m/e	;
	(i)	Draw graphical formulae for the structural isomers of C_4H_{10} .	
		Isomer 1 Isomer 2	
		Suggest the formula of the fragment that corresponds to each of the followalues shown in the mass spectrum of compound A .	owing m/e
		43	
		29	
		15	•••••

(c)	(i)	Suggest graphical formulae for two structural isomers with the molecular f $C_3H_6O_2$. Each isomer contains a single functional group. The functional gr different in the two isomers.	
		Isomer 3 Isomer 4	
			(2)
	(")		(2)
	(ii)	Give the name of the type of compound that each isomer represents.	
		Isomer 3	
		Isomer 4	(2)
			Total 13 marks)
		e parts (a) to (f) below concerns a different pair of isomers. Deduce one possi ormula for each of the species A to L .	ble
(a)		d B have the molecular formula $C_2H_4O_2$. An aqueous solution of A reacts where \mathbf{B} does not.	ith
	A	В	
			(2)
(b)		d D have the molecular formula C_3H_8O . C has a broad absorption band at 0 cm^{-1} in its infra-red spectrum, but D does not.	
	C	D	

11.

(c)	E and F have the molecular formula proton n.m.r. spectrum but F has two	$C_3H_6C1_2$. E has only one peak in its low resolution o.	
	E	F	
			(2)
(d)		a C_3H_6O and both have strong absorption bands at sectra. G turns acidified potassium dichromate(VI)	
	G	Н	
			(2)
(e)		C_4H_9Br . I shows optical activity, but J does not.	
	I	J	
			(2)
		(Total 10 r	(2) marks)

Carb	onyl compounds can be reduced	d to alcohols.
(i)		action of propanone to the corresponding alcohol and gent. In the equation you may use the symbol [H] for
	Equation	
	Reducing agent	
(ii)	Two isomeric carbonyl components have 3 peaks in their low-resonants.	bunds, A and B , with molecular formula C_4H_8O both blution proton n.m.r. spectra.
		C which has 5 peaks in its low-resolution proton n.m.r. f B forms alcohol D which has 4 peaks in its pectrum.
	Draw one possible structure for	or each of these 4 compounds.
	Carbonyl compound A	Alcohol ${f C}$
	Carbonyl compound B	Alcohol D

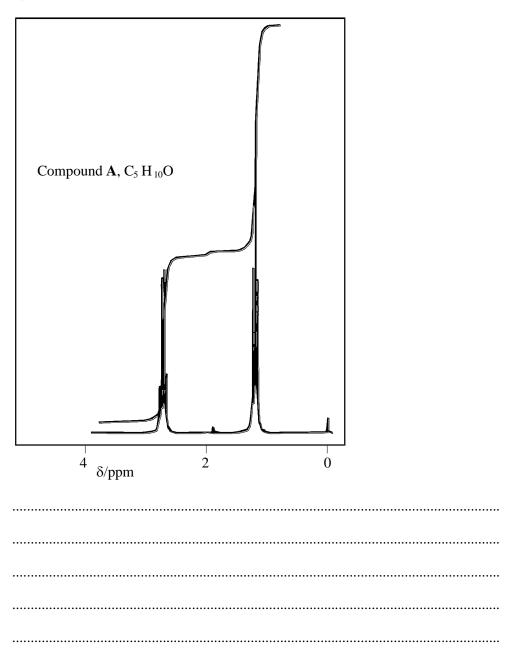
12.

(6) (Total 6 marks) 13. Compound **A**, C₅H₁₀O, reacts with NaBH₄ to give **B**, C₅H₁₂O. Treatment of **B** with concentrated sulphuric acid yields compound **C**, C₅H₁₀. Acid-catalysed hydration of **C** gives a mixture of isomers, **B** and **D**.

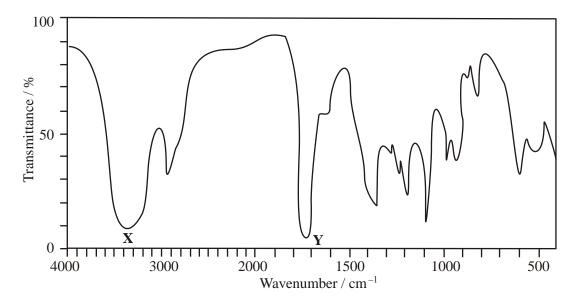
Fragmentation of the molecular ion of **A**, $[C_5H_{10}O]^{+\bullet}$, leads to a mass spectrum with a major peak at m/z 57. The infra-red spectrum of compound **A** has a strong band at 1715 cm⁻¹ and the infra-red spectrum of compound **B** has a broad absorption at 3350 cm⁻¹ (Table). The proton n.m.r. spectrum of **A** has two signals at δ 1.06 (triplet) and 2.42 (quartet), respectively (Spectrum).

Use the analytical and chemical information provided to deduce structures for compounds A, B, C and D, respectively. Include in your answer an equation for the fragmentation of the molecular ion of A and account for the appearance of the proton n.m.r. spectrum of A. Explain why isomers B and D are formed from compound C.

Spectrum



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



Identify the functional groups which cause the absorptions labelled ${\bf X}$ and ${\bf Y}$.

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

Label as ${\bf A}$ the structure which represents a pair of optical isomers.

(6)

)	Draw the structures of the three $\textbf{branched-chain}$ 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.
	aikelies leact with brothine.
	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)

15.	(a)	The reaction of but-1-ene with chlorine produces 1,2-dichlorobutane, C ₄ H ₈ Cl ₂	
		(i) Given that chlorine exists as a mixture of two isotopes, 35 Cl and 37 Cl, predict the number of molecular ion peaks and their m/z values in the mass spectrum of $C_4H_8Cl_2$	
		(ii) The mass spectrum of 1,2-dichlorobutane contains peaks at $m/z = 77$ and 79. Draw the structure of the fragment ion which produces the peak at $m/z = 77$ and write an equation showing its formation from the molecular ion.	
			(6)
	(b)	The reaction of but-2-ene with hydrogen chloride forms a racemic mixture of the stereoisomers of 2-chlorobutane.	
		Name the type of stereoisomerism shown by 2-chlorobutane and give the meaning of the term <i>racemic mixture</i> . State how separate samples of the stereoisomers could be distinguished.	
			(4)

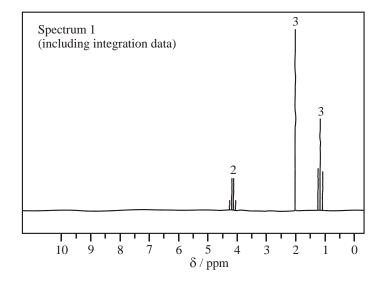
	(c)	The 1	reaction of but-2-ene with chlorine produces 2,3-dichlorobutane, C ₄ H ₈ Cl ₂
		(i)	State the number of peaks, their integration ratio and any splitting of peaks in the proton n.m.r. spectrum of 2,3-dichlorobutane.
		(ii)	Compound S , an isomer of $C_4H_8Cl_2$, produces a proton n.m.r. spectrum which consists only of a singlet, a triplet and a quartet with an integration ratio of 3:3:2 respectively.
			Compound T , also an isomer of C ₄ H ₈ Cl ₂ , produces a proton n.m.r. spectrum which consists only of two singlets with an integration ratio of 3:1
			Draw the structures of S and of T .
			(6) (Total 16 marks)
16.			c acid, HOOCCH=CHCOOH, occurs as two stereoisomers. One of the isomers ms the acid anhydride $C_4H_2O_3$ when warmed.
	(a)	Draw show	when the two isomers of butenedioic acid and name the type of isomerism vn.
			the structures of the two isomeric acids to suggest why only one of them readily forms and anhydride when warmed. Draw the structure of the acid anhydride formed.

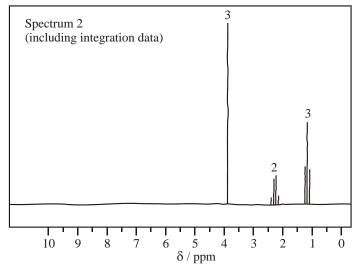
(b)	Identify one electrophile which will react with butenedioic acid and outline a mechanism for this reaction.
(c)	Write an equation for a reaction which occurs when butenedioic acid is treated with an excess of aqueous sodium hydroxide.
(d)	Describe and explain the appearance of the proton n.m.r. spectrum of butenedioic acid.
	(3) (Total 15 marks)

17. (a) Name ester X, $CH_3CH_2COOCH_3$.

(1)

(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 Sheetand the integration data on the spectra to help you to explain your deduction. Suggest a structure for **Y**.





(4) (Total 5 marks)

	three compounds CH ₃ CH ₂ CH ₂ CH ₂ OH, (CH ₃) ₃ COH and CH ₃ CH ₂ CH ₂ CHO can be nguished by use of the following three reagents
	 potassium dichromate(VI) acidified with dilute sulphuric acid Tollens' reagent ethanoic acid, together with a small amount of concentrated sulphuric acid.
(a)	Identify which of these three organic compounds would reduce acidified potassium dichromate(VI). Give the structures of the organic products formed. Write a half-equation for the reduction of dichromate(VI) ions in acidic solution.
	(6)
(b)	Identify which one of these three organic compounds would reduce Tollens' reagent. Give the structure of the organic product formed. Write a half-equation for the reduction of Tollens' reagent.
	(3)
(c)	Identify which of these three organic compounds would react with ethanoic acid in the presence of concentrated sulphuric acid. In each case, give the structure of the organic product formed.
	(4)
(d)	State the number of peaks in the proton n.m.r. spectra of CH ₃ CH ₂ CH ₂ CH ₂ OH and of (CH ₃) ₃ COH. (Analysis of peak splitting is not required.)
	(2)
	(Total 15 marks)

18.

19.	(a)	Draw the structure of each of the three ketones which have the molecular formula $C_5H_{10}O$. For each compound give the ratio of the areas under each peak in its low-resolution proton n.m.r. spectrum.	
			(6)
	(b)	Draw the structure of each of the four aldehydes which also have the molecular formula $C_5H_{10}O$. Label with the letter \mathbf{X} the compound which has only two peaks in its low-resolution proton n.m.r. spectrum. Label with the letter \mathbf{Y} the compound which has five peaks with the ratios of the areas under each peak 3:3:2:1:1 in its low-resolution proton n.m.r. spectrum. Label with the letter \mathbf{Z} the compound which shows optical isomerism.	
	(c)	Explain why aldehydes react with Tollen's (or Fehling's) reagent but ketones do not.	(7)
		(Total 16 ma	(3) arks)

•••••		
(ii)	and $H_3C C = C CH_3$ CH_3	
	C D	
 (iii)	CH ₃ COOCH ₃ and CH ₃ CH ₂ COOH	
	E F	
•••••		
•••••		
infra-	how compounds E and F in part (a)(iii) above could be distinguished by their red spectra, without using the fingerprint region. Explain how <i>fingerprinting</i> is entify a compound.	s used
•••••		

Describe, by giving reagents and stating observations, how you could distinguish between the compounds in the following pairs using a simple test-tube reaction for each pair.

20.

(a)

- 21. Compounds **A** to **G** are all isomers with the molecular formula $C_6H_{12}O_2$
 - Isomer A, C₆H₁₂O₂, is a neutral compound and is formed by the reaction between compounds X and Y in the presence of a small amount of concentrated sulphuric acid. X and Y can both be formed from propanal by different redox reactions.
 X has an absorption in its infra-red spectrum at 1750 cm⁻¹.

Deduce the structural formulae of **A**, **X** and **Y**. Give suitable reagents, in each case, for the formation of **X** and **Y** from propanal and state the role of concentrated sulphuric acid in the formation of **A**.

(7)

(b) Isomers **B**, **C**, **D** and **E** all react with aqueous sodium carbonate to produce carbon dioxide. Deduce the structural formulae of the three isomers that contain an asymmetric carbon atom.

The fourth isomer has only three singlet peaks in its proton n.m.r. spectrum. Deduce the structural formula of this isomer and label it **E**.

(4)

(c) Isomer **F**, C₆H₁₂O₂, has the structural formula shown below, on which some of the protons have been labelled.

$$a$$
 CH_3
 CH_2
 CH_2
 CH_2
 CH_3
 CH_3

A proton n.m.r. spectrum is obtained for **F**. Predict a value of δ for the protons labelled a and also for those labelled b. State and account for the splitting patterns of the peaks assigned to the protons a and b.

(6)

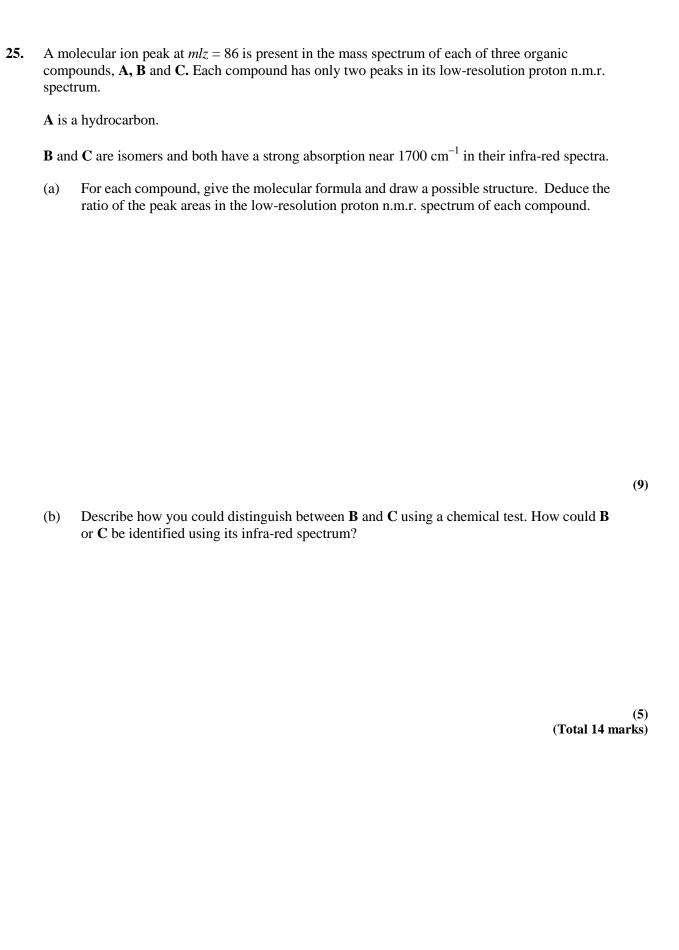
(d) Isomer **G**, C₆H₁₂O₂, contains six carbon atoms in a ring. It has an absorption in its infra-red spectrum at 3270 cm⁻¹ and shows only three different proton environments in its proton n.m.r. spectrum. Deduce a structural formula for **G**.

(2) (Total 19 marks)

22.	The conversion of compound A into compound	B can be achieved in two steps as shown below.
	CIT	CYY

	H •		Br B	
	A		В	
	w the number of peaks in compounds A and B .	their proton n.m.r. spectra v	would enable you to dis	tinguish
				(Total 2
Proton n.	m.r. spectroscopy can be	used to distinguish between	the following isomers:	
	HOCH ₂ CH ₂ OCH ₃ A	HOCH ₂ OCH ₂ CH ₃ B	CH ₃ OCH ₂ OCH ₃	
		e the appearance of the high		
and accor	unt for any splitting patter	e the appearance of the high rns. Assume that the OH pro	otons are not coupled to	any other
and accor	unt for any splitting patter	rns. Assume that the OH pro	otons are not coupled to	any other
and accor	unt for any splitting patter	rns. Assume that the OH pro	otons are not coupled to	any other
and accor	unt for any splitting patter	rns. Assume that the OH pro	otons are not coupled to	any other
and accor	unt for any splitting patter	rns. Assume that the OH pro	otons are not coupled to	any other
	unt for any splitting patter	rns. Assume that the OH pro	otons are not coupled to	any other
and accordence or a constant accordence or a c	unt for any splitting patter	rns. Assume that the OH pro	otons are not coupled to	any other
and according ac	unt for any splitting patter	rns. Assume that the OH pro	otons are not coupled to	any other
and according ac	unt for any splitting patter	rns. Assume that the OH pro	otons are not coupled to	any other
and accorprotons	unt for any splitting patter	rns. Assume that the OH pro	otons are not coupled to	any other

		ne of compounds \mathbf{A} , \mathbf{B} , \mathbf{C} $\mathbf{C}_4\mathbf{H}_9\mathbf{C}\mathbf{I}$, are given below			
CH_3	CH ₂ CH ₂ CH ₂ Cl	CH ₃ CH(Cl)CH ₂ CH ₃	(CH ₃) ₂ CHCH ₂ Cl	$(CH_3)_2C(Cl)CH_3$	
	A	В	C	D	
Low 4 pe	resolution ¹ H NN aks, one spectrum	MR analysis of compound with 3 peaks and one sp	ls A , B , C and D prodectrum with a single j	luces two spectra with peak.	
(i)	Give the name	of compound D .			
					(1)
(ii)	Identify the cor Explain your re	mpound (A , B , C or D) we asoning.	hose NMR spectrum	shows a single peak.	
					(2)
(iii)	deduce the ratio	mpound (A , B , C or D) we of the areas under these	peaks. Explain your	reasoning.	
					(3)
(v)		ical formula for the produ ve an outline of the mech			(3)
				(Total 10 m	(4) arks)

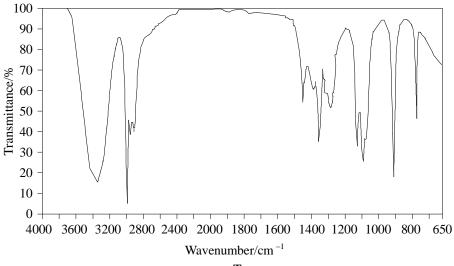


26. (a) Explain what is meant by the fingerprint region of an infra-red spectrum and describe how it is used to confirm the identity of organic molecules.

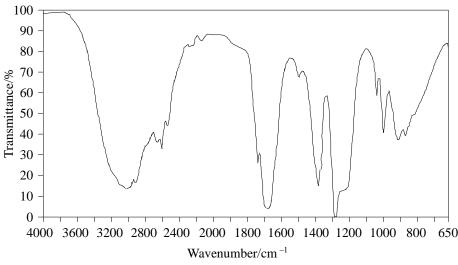
(b) Each of three isomeric esters, \mathbf{Q} , \mathbf{R} and \mathbf{S} , of molecular formula $C_5H_{10}O_2$ has a branched structure.

 ${\bf Q}$ has only two peaks in its low resolution proton n.m.r. spectrum, but ${\bf R}$ and ${\bf S}$ each have three peaks.

Hydrolysis of ${\bf R}$ in acid conditions forms compounds ${\bf T}$ and ${\bf U}$. The low-resolution proton n.m.r. spectrum of ${\bf T}$ has three peaks and that of ${\bf U}$ has two peaks. Infra-red spectra of ${\bf T}$ and ${\bf U}$ are shown below.

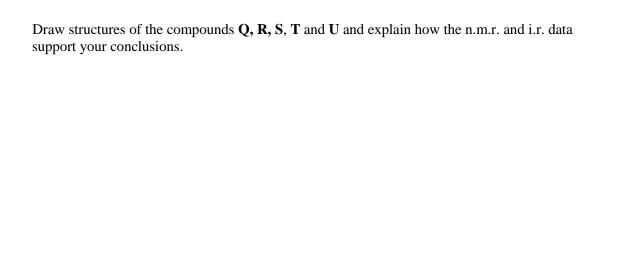


T



U

(4)



(11) (Total 15 marks)

27.	Simple organic compounds, including structural isomers, can be distinguished from each other by chemical tests, or by spectroscopic methods, or by a combination of both. This question concerns the four compounds whose structural formulae are shown below.					
	CH ₃ (CH ₂) ₂ CHO	(CH ₃) ₂ CHCHO	CH ₃ COC ₂ H ₅	CH ₃ COOC ₂ H ₅	
		A	В	C	D	
	(a)	Draw graphica names of A, B		C and D , clearly indicat	ing which is which. Give the	
	(b)			ction called esterificatio and give a condition use	on. State the names of two ed in the reaction.	(8)
	(c)	Give the name ester.	e and draw the graphi	cal formula of an isome	r of compound D that is not an	(3)
	(d)	Describe one would observe		uld distinguish between	B and C , and state what you	(2)
						(3)

(e) The ¹H NMR spectra of **A**, **B**, **C** and **D** can be used to distinguish between some of the structures by considering the numbers of peaks and the ratios of the areas under them. The following table shows some results of a ¹H NMR investigation into **A**, **B**, **C** and **D**. Each of the four spectra is referred to by a number.

Spectrum	Number of peaks	Ratio of areas under the peaks
1	3	6:1:1
2	4	3:2:2:1
3	3	3:2:3
4	3	3:2:3

(i) Which compound (**A**, **B**, **C** or **D**) corresponds to spectrum 1? Give a reason for your choice.

(ii) Which compound (**A**, **B**, **C** or **D**) corresponds to spectrum 2? Give a reason for your choice.

(iii) Explain why spectrum 3 and spectrum 4 have the same number of peaks and the same ratio of areas under them.

(1) (Total 21 marks)

(2)

(2)