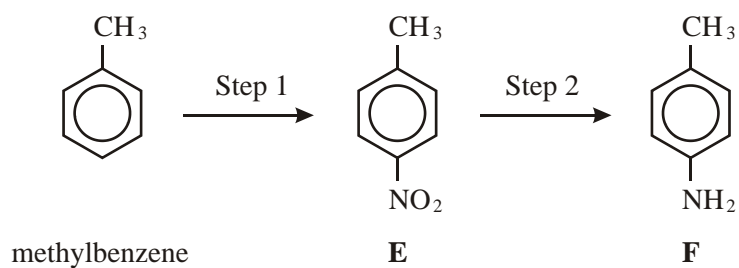# AQA A2 CHEMISTRY

TOPIC 4.10

ORGANIC SYNTHESIS AND ANALYSIS

TOPIC 4.11

STRUCTURE DETERMINATION

BOOKLET OF PAST EXAMINATION QUESTIONS

1. Consider the following reaction sequence.

methylbenzene   **E**   **F**

(a) For Step 1, name the mechanism and give the reagents involved.

Name of mechanism ....

Reagents ....

....

(3)

(b) For Step 2, give a reagent or combination of reagents. Write an equation for this reaction using [H] to represent the reductant.

Reagent(s) ....

Equation ....

(2)

(c) Give the *m/z* value of a major peak which could appear in the mass spectrum of methylbenzene, but not in the spectrum of either **E** or **F**.

....

(1)

(d) Draw the structure of the species formed by **F** in an excess of hydrochloric acid.

(1)

(e)   Compounds **G** and **H** are both monosubstituted benzenes and both are isomers of **F**. **G** is a primary amine and **H** is a secondary amine. Draw the structures of **G** and **H** below.

G

H

(2)
(Total 9 marks)

2.   (a)   Write an equation for the formation of methyl propanoate, $CH_3CH_2COOCH_3$, from methanol and propanoic acid.

....

(1)

(b)   Name and outline a mechanism for the reaction between methanol and propanoyl chloride to form methyl propanoate.

Name of mechanism ....

Mechanism

(5)

(c)   Propanoic anhydride could be used instead of propanoyl chloride in the preparation of methyl propanoate from methanol. Draw the structure of propanoic anhydride.

(1)

(d)   (i)   Give **one** advantage of the use of propanoyl chloride instead of propanoic acid in the laboratory preparation of methyl propanoate from methanol.

....

....

        (ii)   Give **one** advantage of the use of propanoic anhydride instead of propanoyl chloride in the industrial manufacture of methyl propanoate from methanol.

....

....

(2)

(e)   An ester contains a benzene ring. The mass spectrum of this ester shows a molecular ion peak at $m/z = 136$.

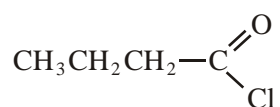   (i)   Deduce the molecular formula of this ester.

....

....

....

        (ii)   Draw **two** possible structures for this ester.

(3)
(Total 12 marks)

3. Compound **U** is shown below.

$$CH_3CH_2CH_2-C\overset{\displaystyle O}{\underset{\displaystyle Cl}{}}$$

(a) Name compound **U**.

....

(1)

(b) (i) State why the mass spectrum of **U** contains two molecular ion peaks.

....

(ii) Give the *m/z* values of these two peaks.

....

....

(2)

(c) Name and outline a mechanism for the reaction of **U** with CH_3OH

Name of mechanism ....

Mechanism

(5)
(Total 8 marks)

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

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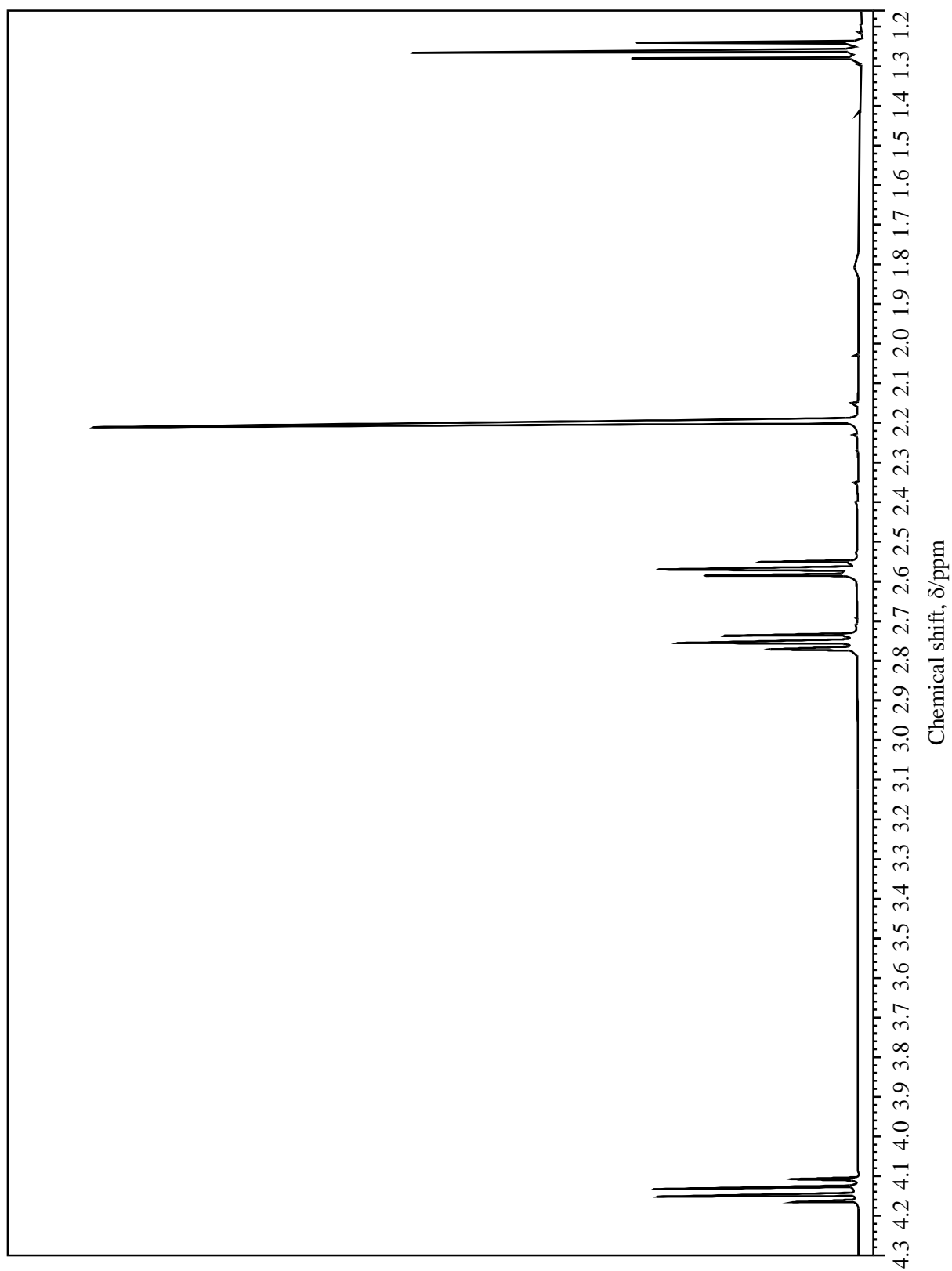
Compound **X**, $C_7H_{12}O_3$, contains both a ketone and an ester functional group. The measured integration trace for the peaks in the n.m.r. spectrum of **X** gives the ratio shown in the table below.

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.

(a)   How many different types of proton are present in compound **X**?

        ....
(1)

(b)   What is the whole-number ratio of each type of proton in compound **X**?

        ....
(1)

(c)   Draw the part of the structure of **X** which can be deduced from the presence of the peak at $\delta2.20$.

        ....
(1)

(d)   The peaks at $\delta4.13$ and $\delta1.26$ arise from the presence of an alkyl group. Identify the group and explain the splitting pattern.

        Alkyl group ....

        Explanation ....

        ....

        ....
(3)

(e)   Draw the part of the structure of **X** which can be deduced from the splitting of the peaks at $\delta2.76$ and $\delta2.57$.

        ....
(1)

(f)   Deduce the structure of compound **X**.

        ....
(2)
(Total 9 marks)

5. Compound **Q** has the molecular formula C_4H_7ClO and does not produce misty fumes when added to water.

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

....

(1)

(b) 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)

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

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

....

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

....

(2)

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

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

(1)

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

(1)

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

(1)
(Total 9 marks)

6.   (a)   Draw the structure of ethyl propanoate.

(1)

(b)   Name and outline a mechanism for the formation of ethyl propanoate from propanoyl chloride and ethanol.

Name of mechanism ....

Mechanism

(5)

(c)   The mass spectrum of ethyl propanoate contains a major peak at $m/z = 57$. Write an equation showing the fragmentation of the molecular ion to form the species responsible for the peak at $m/z = 57$. Show the structure of this species in your answer.

....

(2)

(d)   Draw the structure of another ester which is an isomer of ethyl propanoate and which gives a major peak at $m/z = 71$ in its mass spectrum.

(1)
(Total 9 marks)

7.   (a)   (i)   Using mass spectrometry, what information in addition to M_r can be obtained from the precise value of the mass of the molecular ion of an organic compound?

....

(ii)   Suggest why, for most organic compounds, it is possible to detect a peak at one mass unit higher than that of the molecular ion.

....

(2)

(b)   Fragmentation 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)

(c)   Two molecular ion peaks appear in the mass spectrum of 2-chloropropane at m/z 78 and $m/z = 80$. Explain why two molecular ion peaks are found and why the relative intensities of the peaks are approximately 3 to 1, respectively.

....

....

....

....

(3)
(Total 10 marks)

8. Three sections of the proton n.m.r. spectrum of $CH_3CHClCOOH$ are shown below.
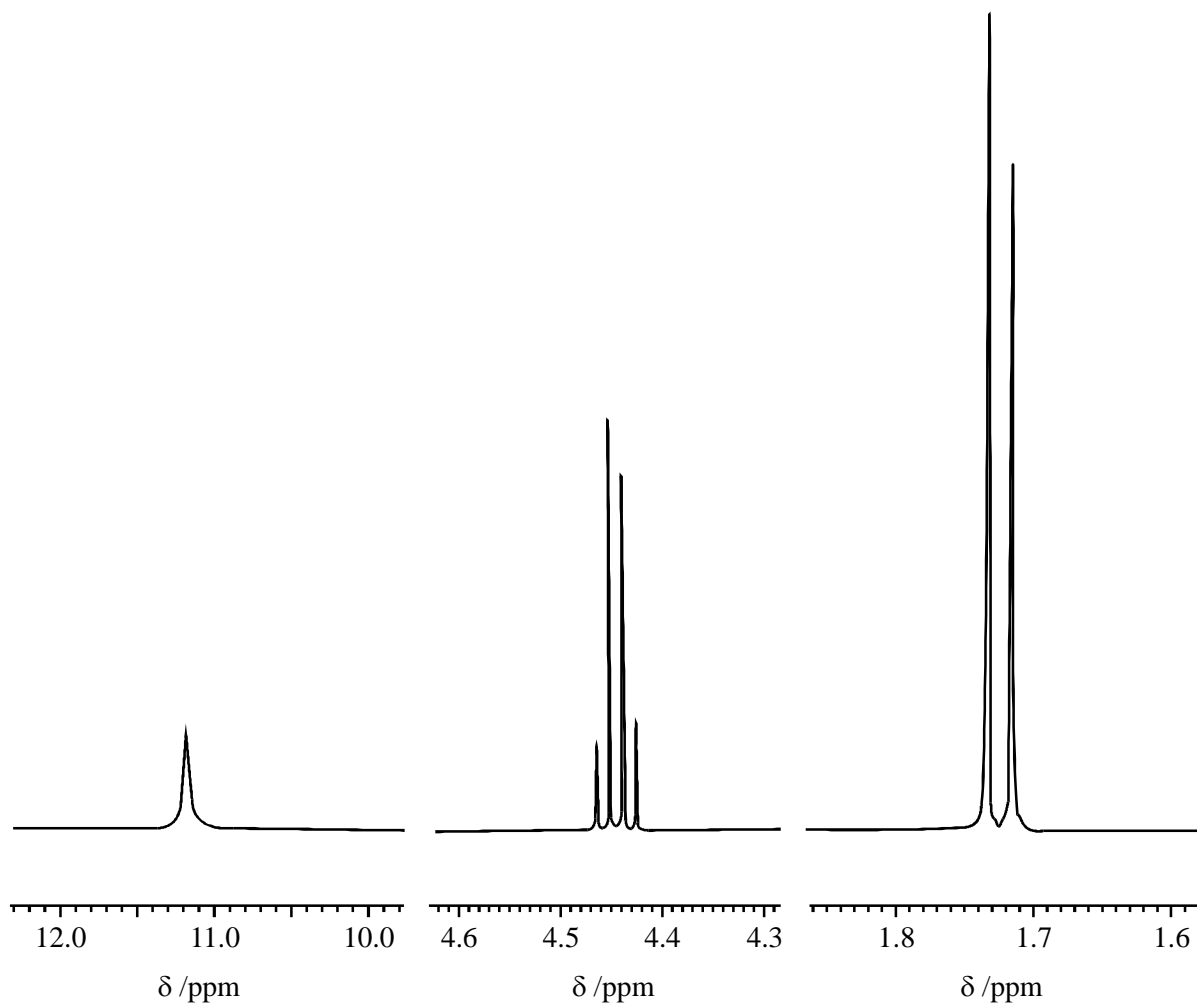
(a) Name the compound $CH_3CHClCOOH$

....

(1)

(b) Explain the splitting patterns in the peaks at δ 1.72 and δ 4.44

....

....

....

(2)

(c) Predict the splitting pattern that would be seen in the proton n.m.r. spectrum of the isomeric compound $ClCH_2CH_2COOH$

....

....

(1)

(d) The amino acid *alanine* is formed by the reaction of CH₃CHClCOOH with an excess of ammonia. The mechanism is nucleophilic substitution. Outline this mechanism, showing clearly the structure of *alanine*.

(5)

(e) The amino acid *lysine* has the structure

$$H_2N-(CH_2)_4 -\overset{\displaystyle H}{\underset{\displaystyle NH_2}{\overset{|}{\underset{|}{C}}}}- COOH$$
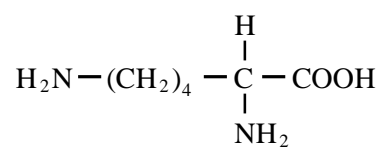
Draw structures to show the product formed in each case when lysine reacts with

(i)   an excess of aqueous HCl,

(ii)   an excess of aqueous NaOH,

(iii)   another molecule of lysine.

(3)
(Total 12 marks)

9. (a) (i) Write an equation for the reduction of pentan-2-one by aqueous $NaBH_4$ to form pentan-2-ol.

Use [H] to represent the reductant.

....

(ii) Name and outline a mechanism for this reduction.

Name of mechanism ....

Mechanism

(iii) State why the pentan-2-ol produced in this reaction is not optically active.

....

(7)

(b) Predict the *m/z* values of the two most abundant fragments in the mass spectrum of pentan-2-one.

Fragment 1 ....

Fragment 2 ....

(2)
(Total 9 marks)

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

Compound **Q** has the molecular formula $C_4H_8O_2$

(a) The infra-red spectrum of **Q** is shown below.
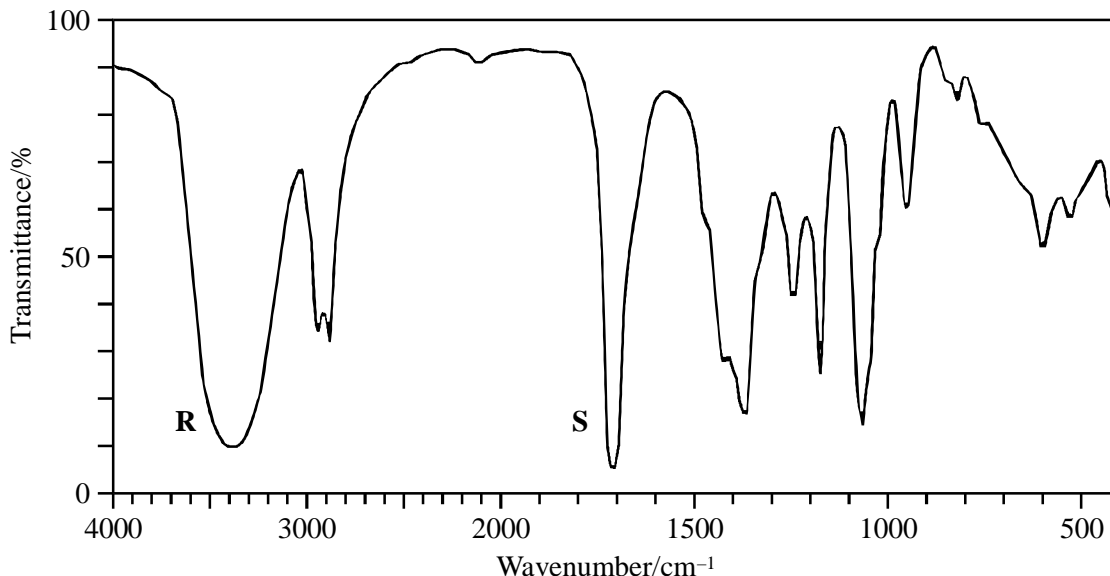
Identify the type of bond causing the absorption labelled **R** and that causing the absorption labelled **S**.

R ....

S ....

(2)

(b) **Q** does not react with Tollens' reagent or Fehling's solution. Identify a functional group which would react with these reagents and therefore cannot be present in **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 1 ....

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.

Solvent ....

Reason ....

(4)

(d)   The proton n.m.r. spectrum of **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 **Q** from the presence of the following in its n.m.r. spectrum?

(i)   The singlet peak at δ = 2.20

....

(ii)   The singlet peak at δ = 3.40

....

(iii)   Two triplet peaks

....

(3)

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

(1)
(Total 11 marks)

11. Consider the reaction scheme below which starts from butanone.

$$H_3C - \overset{\overset{\displaystyle O}{\|}}{C} - CH_2CH_3 \xrightarrow{\text{Reaction 1}} H_3C - \overset{\overset{\displaystyle CN}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}} - CH_2CH_3$$

A

Reaction 2 (downward arrow from butanone)

$$H_3C - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}} - CH_2CH_3 \xrightarrow[\text{180°C}]{\substack{\text{excess} \\ \text{conc, } H_2SO_4}} \text{but–1–ene and but–2–ene}$$

B
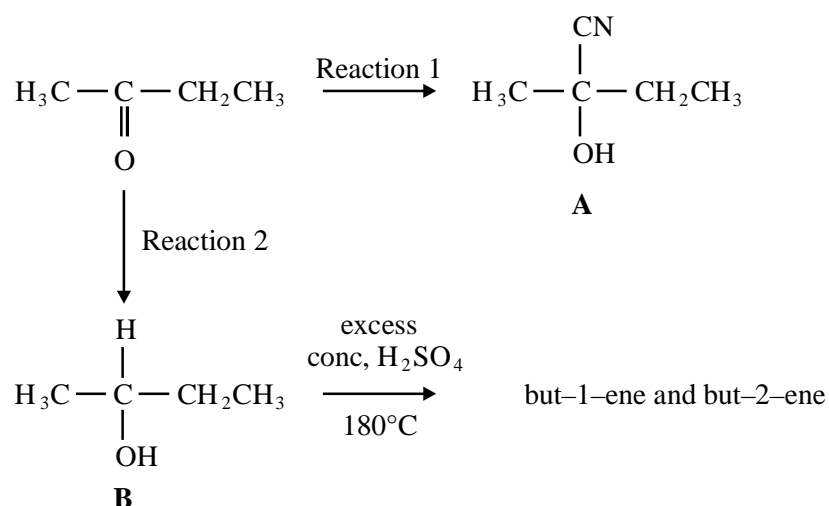
(a) (i)   Give a suitable reagent for Reaction I and state the type of mechanism involved.

Reagent. ....

Type of mechanism. ....

(ii) When 5.0 g of butanone were used to carry out Reaction 1, the yield was 64% of the theoretical maximum. Calculate the mass of compound **A** formed.

....

....

....

....

....

(6)

(b) (i) Give a suitable reagent for Reaction 2.

....

(ii) Product **B** is found to be optically inactive. Suggest why this is so.

....

....

(iii) Given the table of infra-red absorption data below, describe the two major differences between the infra-red spectra of butanone and of **B**.

(4)

(c) Outline a mechanism for the formation of but-1-ene by the dehydration of **B**.

(4)

(d) Draw the structure of the repeating unit in the polymer which can be formed from but-1-ene.

(1)
(Total 15 marks)

12. The proton n.m.r. spectrum of an ester, **A**, is shown below.
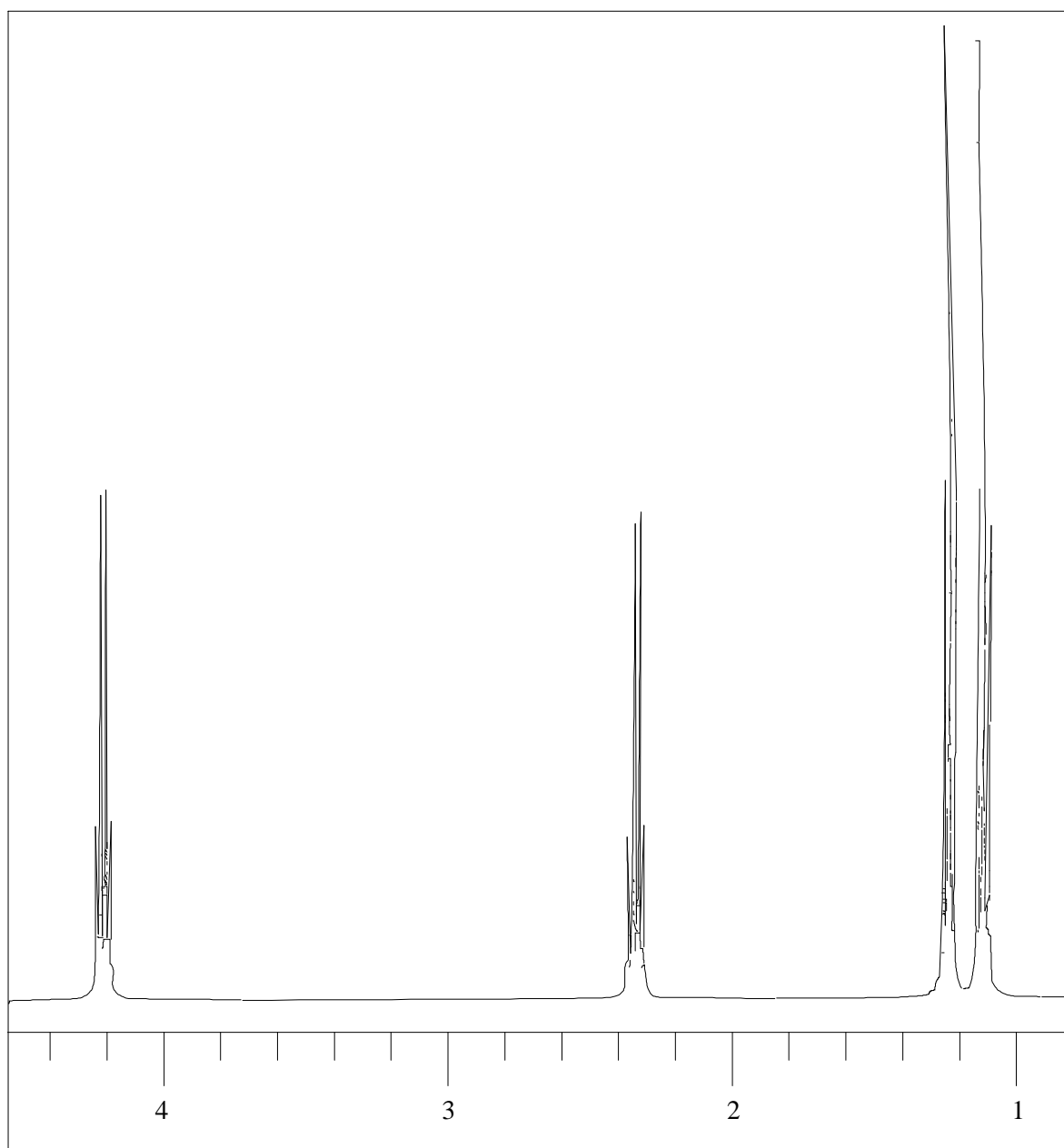
Chemical shift, δ/ppm

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 numbers of each type of proton?

        ....

        (1)

(c)   What can be deduced about the arrangement of protons from the splitting patterns in the
        n.m.r. spectrum?

        ....

        (1)

(d)   Deduce the structure of compound **A** and label with the letters a, b, c and d the four groups
        of equivalent protons.

        (1)

(e)   Assign the various signals in the table below to the groups of protons in compound **A**
        previously labelled a, b, c and d.

Chemical shift, δ/ppm	1.09	1.33	2.32	4.13
Label of group				

        (4)
        (Total 10 marks)

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

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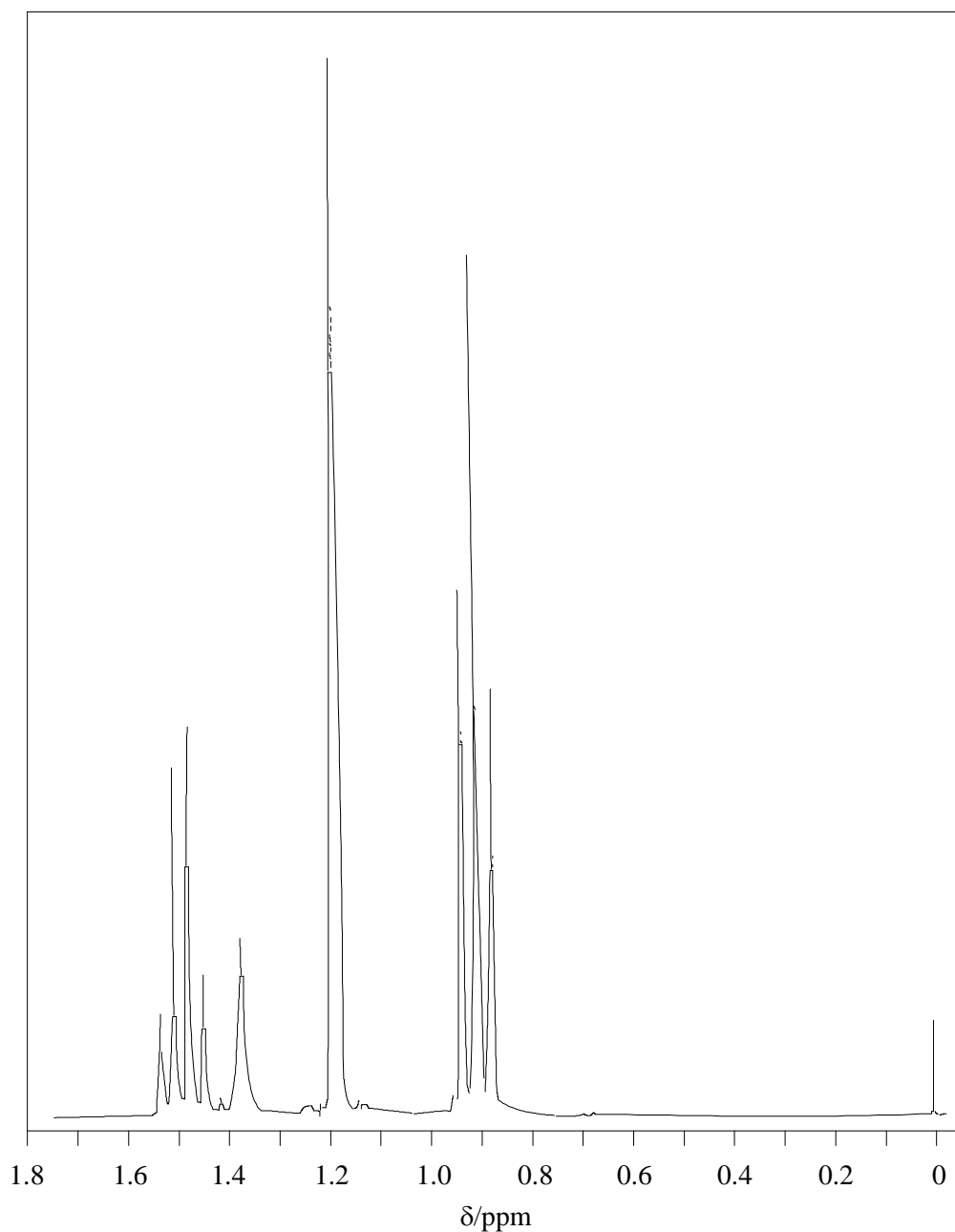
The measured integration trace gives the ratio 0.90 to 0.45 to 2.70 to 1.35 for the peaks at δ 1.52, 1.39, 1.21 and 0.93, respectively.

(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)   The peaks at δ 1.52 and δ 0.93 arise from the presence of a single alkyl group. Identify this group and explain the splitting pattern.

Group...

Explanation...

....

(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.

(1)
(Total 8 marks)

14.   The ester formed when ethanol reacts with ethanoic anhydride was analysed by high-resolution proton n.m.r. spectroscopy.

(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.

....

(3)
(Total 3 marks)

15. (a) Define the term *structural isomerism*.

....

....

....

(2)

(b) The graph below shows part of the mass spectrum of an organic compound, **A**, which has the molecular formula C_4H_{10}.
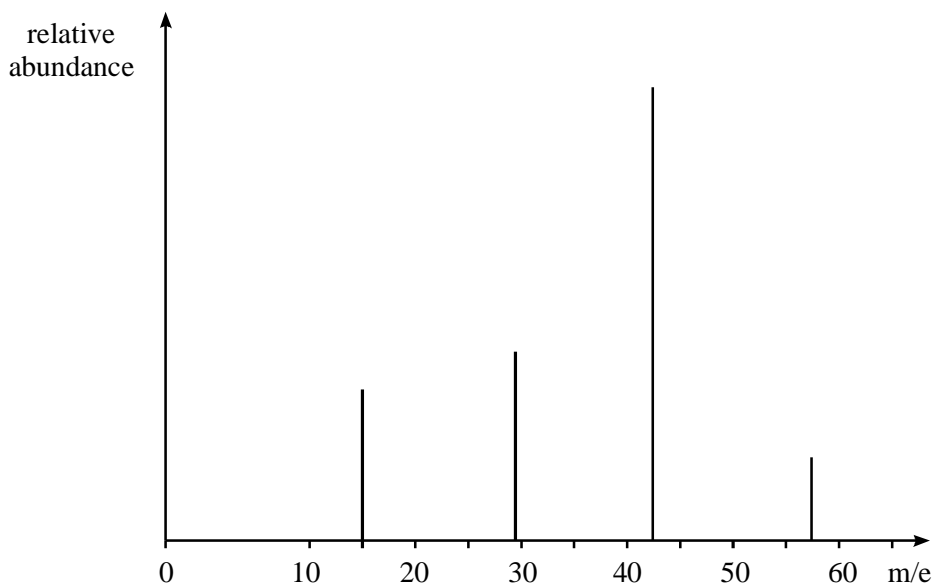
(i) Draw graphical formulae for the structural isomers of C_4H_{10}.

Isomer 1   Isomer 2

(2)

(ii) Suggest the formula of the fragment that corresponds to each of the following m/e values shown in the mass spectrum of compound **A**.

43 ....

29 ....

15 ....

(3)

(iii) Deduce which of the isomers drawn in (i) corresponds to compound **A**. Give a reason for your answer.

....

....

(2)

(c) (i) Suggest graphical formulae for **two** structural isomers with the molecular formula $C_3H_6O_2$. Each isomer contains a single functional group. The functional groups are different in the two isomers.

Isomer 3   **Isomer 4**

(2)

(ii) Give the name of the type of compound that each isomer represents.

Isomer 3 ....

Isomer 4 ....

(2)
(Total 13 marks)

16.   Each of the parts (a) to (f) below concerns a different pair of isomers. Deduce one possible structural formula for each of the species **A** to **L**.

(a)   **A** and **B** have the molecular formula $C_2H_4O_2$. An aqueous solution of **A** reacts with calcium carbonate to liberate carbon dioxide, but **B** does not.

A   **B**

(2)

(b)   **C** and **D** have the molecular formula C_3H_8O. **C** has a broad absorption band at 3300 cm^{-1} in its infra-red spectrum, but **D** does not.

C   **D**

(2)

(c)   **E** and **F** have the molecular formula $C_3H_6Cl_2$. **E** has only one peak in its low resolution proton n.m.r. spectrum but **F** has two.

E   **F**

(2)

(d)   **G** and **H** have the molecular formula C_3H_6O and both have strong absorption bands at about 1700 cm^{-1} in their infra-red spectra. **G** turns acidified potassium dichromate(VI) solution green but **H** does not.

G   **H**

(2)

(e)   **I** and **J** have the molecular formula C_4H_9Br. **I** shows optical activity, but **J** does not.

   I   **J**

(2)

(f)   **K** and **L** have the molecular formula C_5H_{10}. **K** has a weak absorption band at $1650 \ cm^{-1}$ in its infra-red spectrum, but **L** does not.

   K   **L**

(2)
(Total 12 marks)

17.   (a)   Name and outline a mechanism for the reaction between propanone and hydrogen cyanide.

   Name ....

   Mechanism

(5)

(b)   Carbonyl compounds can be reduced to alcohols.

(i)   Write an equation for the reduction of propanone to the corresponding alcohol and identify a suitable reducing agent. In the equation you may use the symbol [H] for the reducing agent.

Equation ....

Reducing agent ....

(ii)   Two isomeric carbonyl compounds, **A** and **B**, with molecular formula C_4H_8O both have 3 peaks in their low-resolution proton n.m.r. spectra.

Reduction of **A** forms alcohol **C** which has 5 peaks in its low-resolution proton n.m.r. spectrum whereas reduction of **B** forms alcohol **D** which has 4 peaks in its low-resolution proton n.m.r. spectrum.

Draw one possible structure for each of these 4 compounds.

Carbonyl compound **A**   *Alcohol* **C**

Carbonyl compound **B**   *Alcohol* **D**

(6)
(Total 11 marks)

18. Compound **A**, $C_5H_{10}O$, reacts with $NaBH_4$ to give **B**, $C_5H_{12}O$. Treatment of **B** with concentrated sulphuric acid yields compound **C**, C_5H_{10}. 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

Compound **A**, $C_5 H_{10}O$

4   δ/ppm   2   0
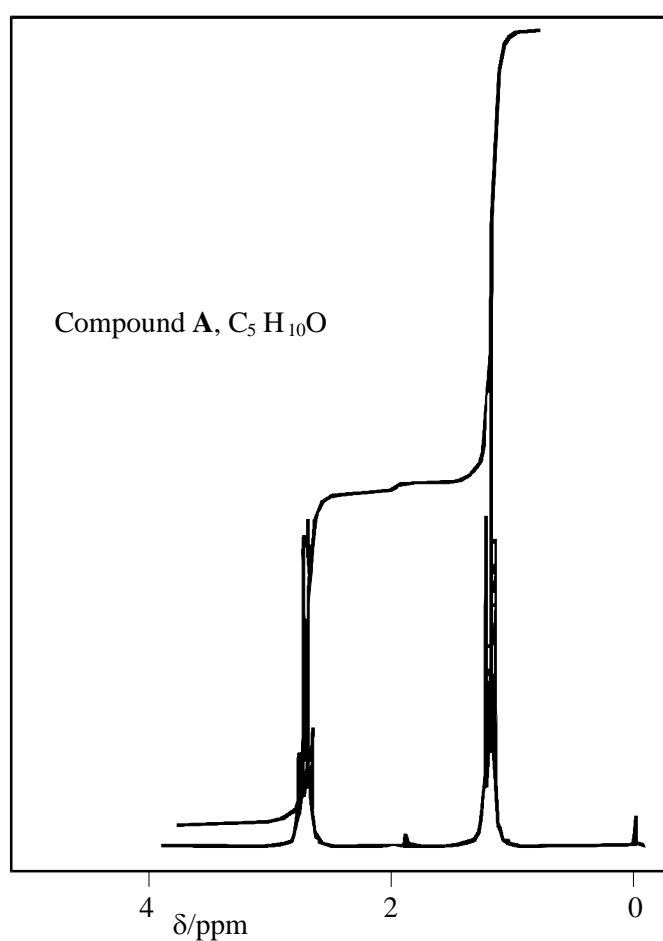
(Total 20 marks)

19. (a) The infra-red spectrum of compound **A**, $C_3H_6O_2$, is shown below.
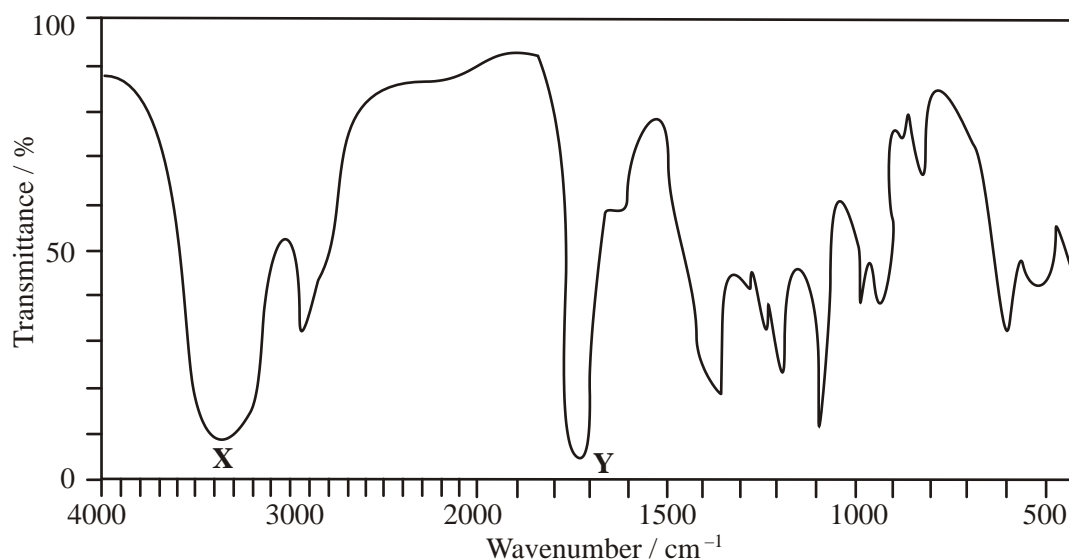
Identify the functional groups which cause the absorptions labelled **X** and **Y**.

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)

(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)

20. (a) The reaction of but-1-ene with chlorine produces 1,2-dichlorobutane, $C_4H_8Cl_2$

(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.

(i)   Name the type of stereoisomerism shown by 2-chlorobutane and give the meaning of the term *racemic mixture*. State how separate samples of the stereoisomers could be distinguished.

(ii)   By considering the shape of the reactive intermediate involved in the mechanism of this reaction, explain how a racemic mixture of the two stereoisomers of 2-chlorobutane is formed.

(7)

(c)   The reaction of but-2-ene with chlorine produces 2,3-dichlorobutane, $C_4H_8Cl_2$

(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 $C_4H_8Cl_2$, 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 19 marks)

21.   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)

(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)

22. Propanoyl chloride can be used, together with a catalyst, in Step 1 of the synthesis of 1-phenylpropene from benzene via compounds **P** and **Q** as shown below.
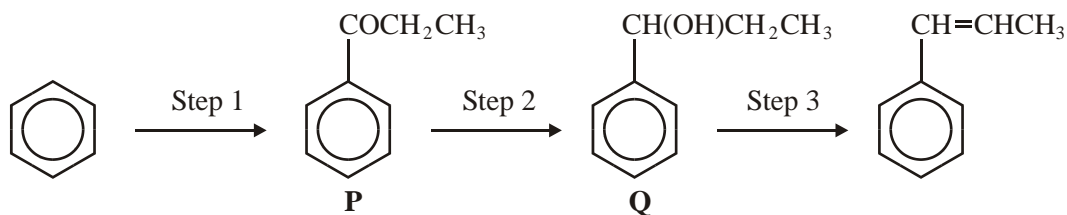
(a) The mechanism of Step 1 is an electrophilic substitution. Write an equation to show the formation of the electrophile from propanoyl chloride. Outline the mechanism of the reaction of this electrophile with benzene in Step 1.

(5)

(b) The mass spectrum of **P** contains a molecular ion peak at $m/z = 134$ and major fragmentation peaks at $m/z = 105$ and 77. Identify the species responsible for the peak at $m/z = 105$ and also that responsible for the peak at $m/z = 77$. Write an equation for the formation, from the molecular ion, of the species responsible for the peak at $m/z = 105$.

(4)

(c) $NaBH_4$ can be used in the reaction in Step 2. Name the mechanism involved in this reaction. Molecules of **Q** show optical isomerism but the sample of **Q** formed in Step 2 is optically inactive. State, in terms of their structure, why molecules of **Q** show optical isomerism. Explain, by reference to the mechanism, why the sample of **Q** obtained in Step 2 is not optically active.

(7)

(d) Identify a suitable reagent for the reaction in Step 3.
Name the type of stereoisomerism shown by the product of this reaction. State what is required in the structure of molecules to allow them to show this type of stereoisomerism.

(4)

(Total 20 marks)

23. (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.

(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 Sheetand the integration data on the spectra to help you to explain your deduction. Suggest a structure for **Y**.
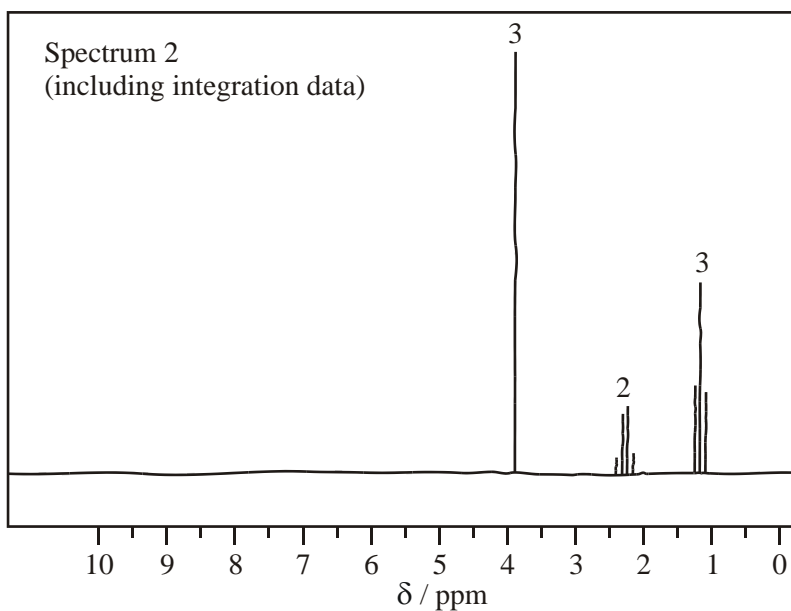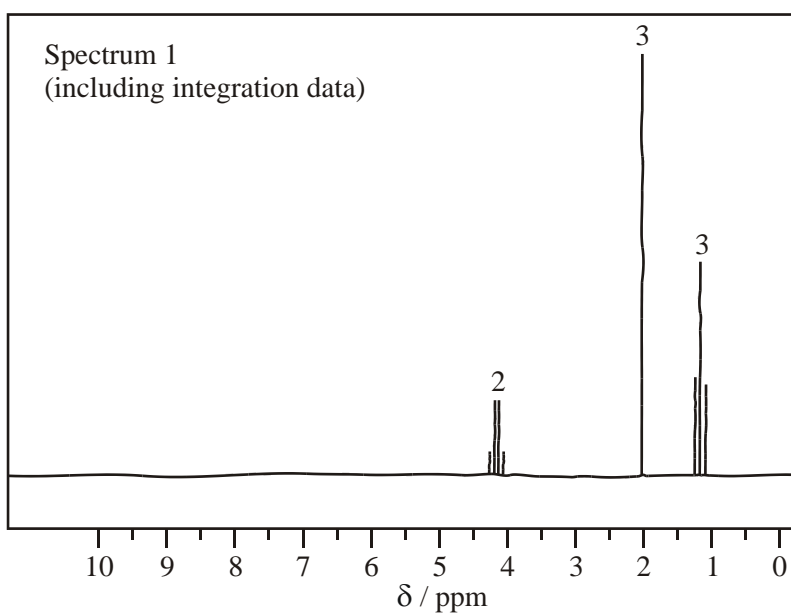
(4)
(Total 10 marks)

24. The three compounds $CH_3CH_2CH_2CH_2OH$, $(CH_3)_3COH$ and $CH_3CH_2CH_2CHO$ can be distinguished by use of the following three reagents

1.   potassium dichromate(VI) acidified with dilute sulphuric acid
2.   Tollens' reagent
3.   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 $CH_3CH_2CH_2CH_2OH$ and of $(CH_3)_3COH$. (Analysis of peak splitting is not required.)

(2)
(Total 15 marks)

25.   (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 **X** the compound which has only two peaks in its low-resolution proton n.m.r. spectrum. Label with the letter **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 **Z** the compound which shows optical isomerism.

(7)

(c)   When carbonyl compounds react with HCN, racemic mixtures are often produced. Name the type of mechanism involved and explain what is meant by the term *racemic mixture*. Choose any carbonyl compound which does **not** form a racemic mixture when it reacts with HCN and draw the structure of the product formed by the reaction of this carbonyl compound with HCN.

(4)

(d)   Explain why aldehydes react with Tollen's (or Fehling's) reagent but ketones do not.

(3)
(Total 20 marks)

26. (a) 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.

(i)

$$CH_3$$
$$|$$
$$H_3C-C-OH$$
$$|$$
$$H$$
$$\textbf{A}$$

and

$$CH_3$$
$$|$$
$$H_3C-C-CHO$$
$$|$$
$$H$$
$$\textbf{B}$$

(ii)

⬡   and H_3C, H_3C $C=C$ CH_3, CH_3

C   **D**

(iii) CH_3COOCH_3 and CH_3CH_2COOH

E   **F**
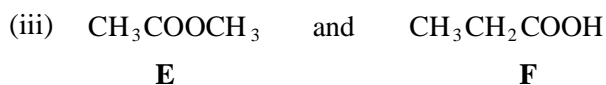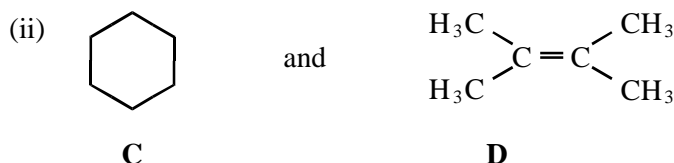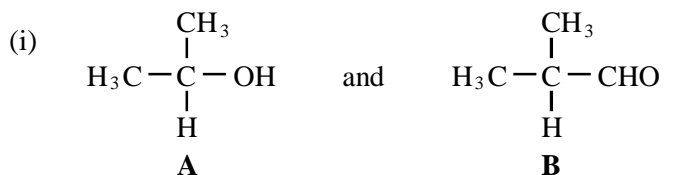
(8)

(b) State how compounds **E** and **F** in part (a)(iii) above could be distinguished by their infra-red spectra, without using the fingerprint region. Explain how *fingerprinting* is used to identify a compound.

(3)

(c) Suggest the structure of the fragment responsible for the major peak in the mass spectrum of compound **E** and state its *m/z* value. Write an equation showing the formation of this fragment from the molecular ion.

(4)

(Total 15 marks)

27. Use the data given on the back of the Periodic Table (PT) to help you answer this question.
Compounds **A** to **G** are all isomers with the molecular formula $C_6H_{12}O_2$

(a) Isomer **A**, $C_6H_{12}O_2$, 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**, $C_6H_{12}O_2$, has the structural formula shown below, on which some of the protons have been labelled.

$$\overset{a}{CH_3-CH_2}-O-CH_2-\overset{b}{CH_2}-\overset{\overset{O}{\|}}{C}-CH_3$$
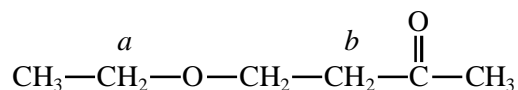
A proton n.m.r. spectrum is obtained for **F**. Using Table 1 at the back of the Periodic Table (PT), predict a value of δ for the protons labelled a and also for those labelled b. State and account for the splitting patterns of the peaks assigned to the protons a and b.

(6)

(d) Isomer **G**, $C_6H_{12}O_2$, 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)

28. The conversion of compound **A** into compound **B** can be achieved in two steps as shown below.

$$\underset{\textbf{A}}{\overset{\overset{\displaystyle CH_3}{\overset{|}{}}}{\underset{\overset{|}{H}}{CH_3-C-CH_2Br}}} \xrightarrow{\text{Step 1}} \textbf{X} \xrightarrow{\text{Step 2}} \underset{\textbf{B}}{\overset{\overset{\displaystyle CH_3}{\overset{|}{}}}{\underset{\overset{|}{Br}}{CH_3-C-CH_3}}}$$
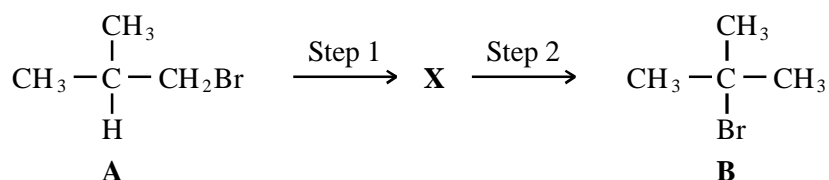
The intermediate compound, **X**, has an absorption at 1650 cm^{-1} in its infra-red spectrum.

(a) Identify compound **X**. Explain your answer.

(2)

(b) For each step in this conversion, give the reagents and essential conditions required and outline a mechanism.

(11)

(c) Show how the number of peaks in their proton n.m.r. spectra would enable you to distinguish between compounds **A** and **B**.

(2)
(Total 15 marks)

29. In the presence of $AlCl_3$, ethanoyl chloride reacts with the dialkylbenzene **A**, C_8H_{10}, to form a **single** compound **B**, $C_{10}H_{12}O$. Compound **B** is converted into **C**, $C_{10}H_{14}O$, on treatment with $NaBH_4$. Compound **D** is produced when compound **C** is warmed with concentrated H_2SO_4.

Compound **B** has a strong absorption band in the infra-red at 1685 cm^{-1}, compound **C** has a broad absorption at 3340 cm^{-1} and compound **D** has an absorption band close to 1630 cm^{-1}.

(a) Show how the information provided in the question and the data in the Table below can be used to deduce structures for compounds **A**, **B**, **C** and **D**.
Explain the significance of the fact that B is obtained as a single compound.

(9)

(b) Name the types of reaction taking place in each step and outline a mechanism for the formation of compound **D** from compound **C** and concentrated sulphuric acid.

(7)

(c) Explain briefly why compound **C** can exist in stereoisomeric forms.

(2)

(Total 18 marks)

30. Proton n.m.r. spectroscopy can be used to distinguish between the following isomers:

$$HOCH_2CH_2OCH_3 \qquad HOCH_2OCH_2CH_3 \qquad CH_3OCH_2OCH_3$$
$$\textbf{A} \qquad\qquad\qquad \textbf{B} \qquad\qquad\qquad \textbf{C}$$

For each of these isomers, describe the appearance of the high-resolution proton n.m.r. spectrum and account for any splitting patterns. Assume that the OH protons are not coupled to any other protons.

(Total 15 marks)

31. (a) The nitration of benzene is an example of electrophilic substitution. The reagents for this nitration are concentrated sulphuric acid and concentrated nitric acid in a 1:1 ratio and the reaction is performed at 60 °C.

(i) Explain what is meant by the term *electrophile* and the term *substitution.*

(2)

(ii) Give the name, or formula, of the electrophile involved in this reaction and write an equation or equations to show its formation from the reagents. Write a mechanism for the nitration of benzene.

(6)

(iii) Explain why the temperature of the reaction should not be allowed to rise above 60°C.

(1)

(b) Chlorobenzene is also prepared by electrophilic substitution. State the reagent(s) and condition(s) required for this reaction to occur.

(3)

(c) The structural formulae of compounds **A, B, C** and **D,** which are the four structural isomers of molecular formula C_4H_9Cl, are given below.

$CH_3CH_2CH_2CH_2Cl$ $CH_3CH(Cl)CH_2CH_3$ $(CH_3)_2CHCH_2Cl$ $(CH_3)_2C(Cl)CH_3$

   A   **B**   **C**   **D**
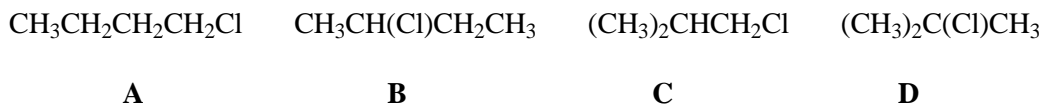
Low resolution ^{1}H NMR analysis of compounds **A, B, C** and **D** produces two spectra with 4 peaks, one spectrum with 3 peaks and one spectrum with a single peak.

(i) Give the name of compound **D.**

(1)

(ii) Identify the compound **(A, B, C** or **D)** whose NMR spectrum shows a single peak. Explain your reasoning.

(2)

(iii) Identify the compound **(A, B, C** or **D)** whose NMR spectrum shows three peaks and deduce the ratio of the areas under these peaks. Explain your reasoning.

(3)

(iv) When refluxed with an alcoholic solution of KOH, compound **B** undergoes an elimination reaction. Two structurally isomeric products are formed. Draw the graphical formulae of these two structural isomers.

(2)

(v) Draw the graphical formula for the product of the reaction between compound **C** and NaOH(aq). Give an outline of the mechanism involved in this reaction.

(4)
(Total 24 marks)

32. (a) The fragmentation of a molecular ion $(M–R)^{+\bullet}$, formed in the ionisation chamber of a mass spectrometer, can be represented by the equation

$$(M–R)^{+\bullet} \rightarrow M^+ + R^\bullet$$
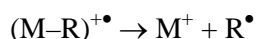
Identify the three types of species shown in the equation and explain what takes place in this conversion.

(4)

(b) The mass spectrum of chloroethane shows two molecular ion peaks at m/z values of 64 and 66. The peak at $m/z = 64$ is approximately three times as intense as that at $m/z = 66$. Explain this observation and show, by means of an equation, how the molecular ion of chloroethane fragments to give rise to a peak at an m/z value of 29.

(4)

(c) Suggest why the mass spectrum of 1,2-dichloroethane shows peaks at m/z values of 98, 100 and 102.

(4)
(Total 12 marks)

33. A molecular ion peak at $m/z = 86$ is present in the mass spectrum of each of three organic compounds, **A**, **B** and **C**. Each compound has only two peaks in its low-resolution proton n.m.r. spectrum.

A is a hydrocarbon.

B and **C** are isomers and both have a strong absorption near 1700 cm^{-1} in their infra-red spectra.

A table of infra-red absorption data is provided below.

(a) For each compound, give the molecular formula and draw a possible structure. Deduce the ratio of the peak areas in the low-resolution proton n.m.r. spectrum of each compound.

(9)

(b) Describe how you could distinguish between **B** and **C** using a chemical test. How could **B** or **C** be identified using its infra-red spectrum?

(5)

(c) **D** and **E** are isomers of **B** and **C.**

D has infra-red absorptions at 3300 cm^{-1} and also at 1650 cm^{-1}.

E has an infra-red absorption at 3300 cm^{-1} but none near 1650 cm^{-1}.

Draw and label one possible structure each for **D** and **E.** Explain your answer.

(4)
(Total 18 marks)

34. (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.

(4)

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

Q has only two peaks in its low resolution proton n.m.r. spectrum, but **R** and **S** each have three peaks.

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

Draw structures of the compounds **Q, R, S**, **T** and **U** and explain how the n.m.r. and i.r. data support your conclusions. A table of infra-red absorption data is provided below.
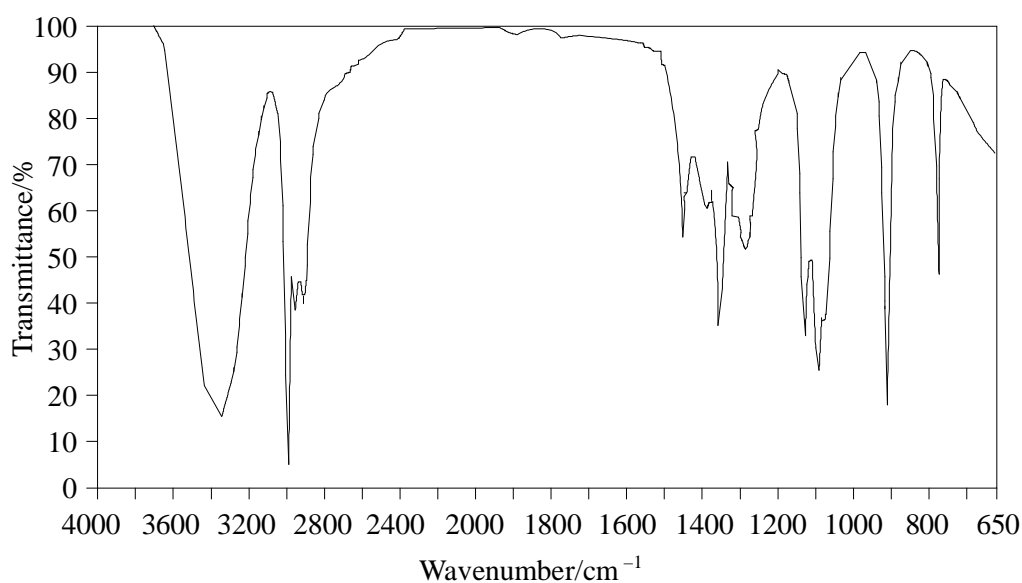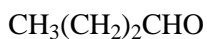

T
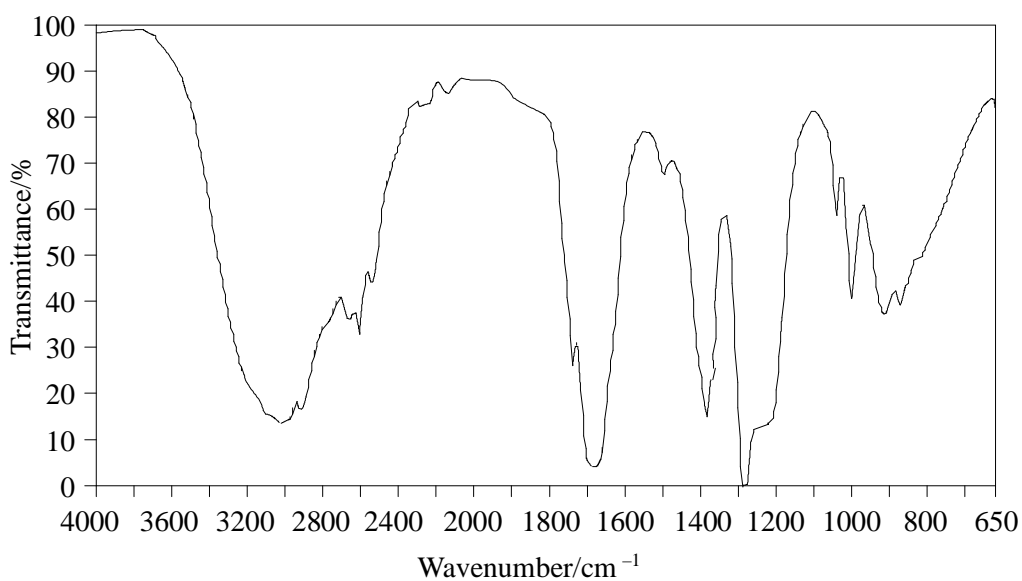
U

(11)
(Total 15 marks)

35. 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.

$CH_3(CH_2)_2CHO$ $(CH_3)_2CHCHO$ $CH_3COC_2H_5$ $CH_3COOC_2H_5$

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

(a) Draw graphical formulae for **A**, **B**, **C** and **D**, clearly indicating which is which. Give the names of **A**, **B**, **C** and **D**.

(8)

(b) Compound **D** can be made by a reaction called esterification. State the names of **two** compounds needed for the reaction and give a condition used in the reaction.

(3)

(c) Give the name and draw the graphical formula of an isomer of compound **D** that is **not** an ester.

(2)

(d) Describe **one** chemical test that would distinguish between **B** and **C**, and state what you would observe in each case.

(3)

(e) The ^{1}H 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 ^{1}H 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.

(2)

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

(2)

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

(1)

(f) Compound **C** reacts with HCN. Give the name of the type of mechanism, and an outline of the mechanism for this reaction.

(5)
(Total 26 marks)