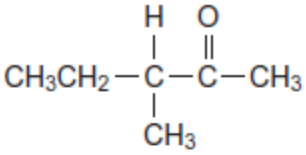
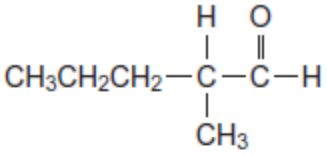
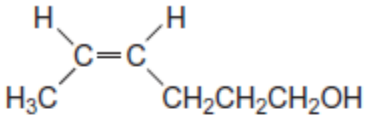
1 The following five isomers, **P**, **Q**, **R**, **S** and **T**, were investigated using test-tube reactions and also using n.m.r. spectroscopy.



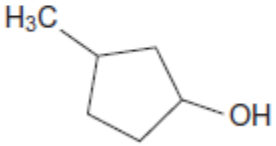
P



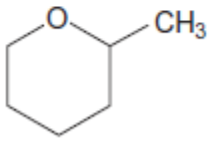
Q



R



S



T

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

Identify a reagent (or combination of reagents) you could use.
State what you would observe when both isomers are tested separately with this reagent or combination of reagents.

.....

.....

.....

.....

.....

(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.

.....

.....

.....

(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

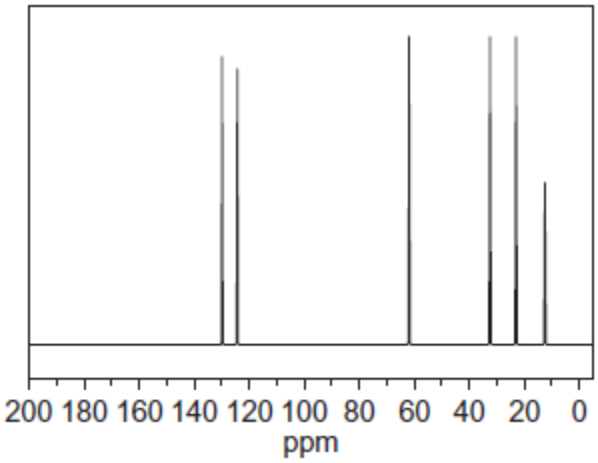
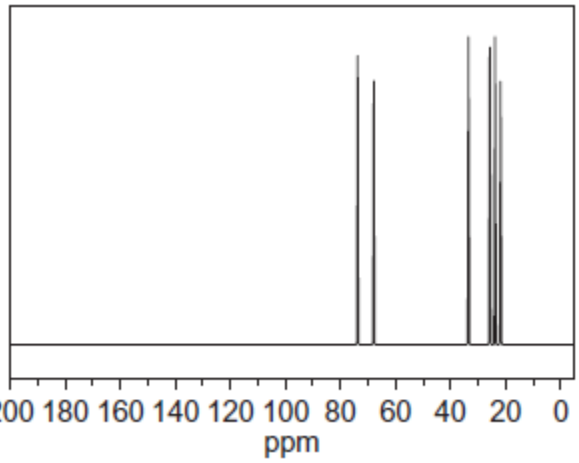
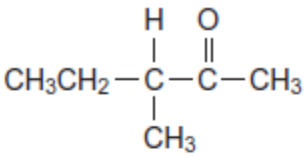


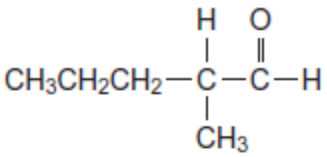
Figure 2



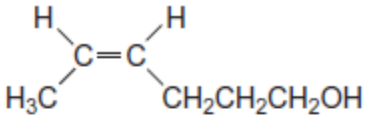
The structures of the five isomers are repeated to help you answer this question.



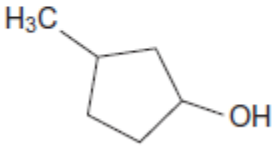
P



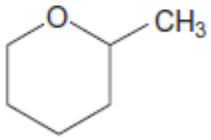
Q



R



S



T

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)

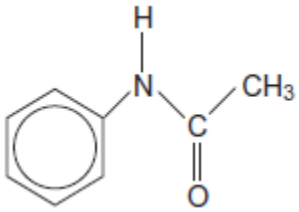
(f) **U** and **V** are other isomers of **P**, **Q**, **R**, **S** and **T**.
The ^{1}H n.m.r. spectrum of **U** consists of two singlets.
V is a cyclic alcohol that exists as optical isomers.

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

U **V**

(2)
(Total 17 marks)

2 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.

.....

.....

.....

(Total 1 mark)

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

Figure 1

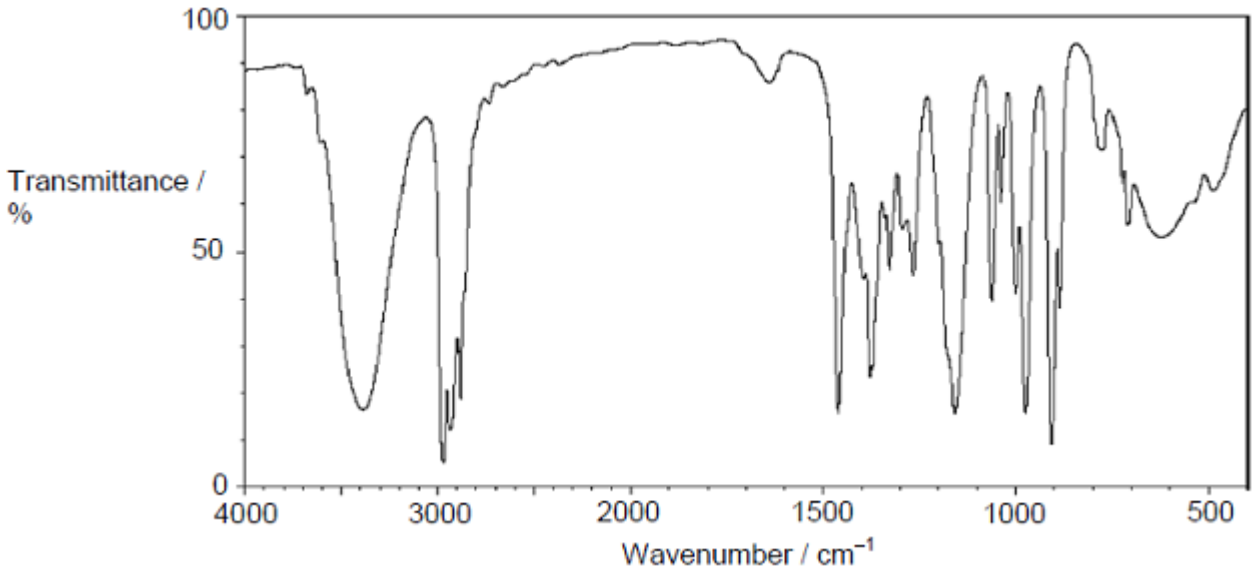
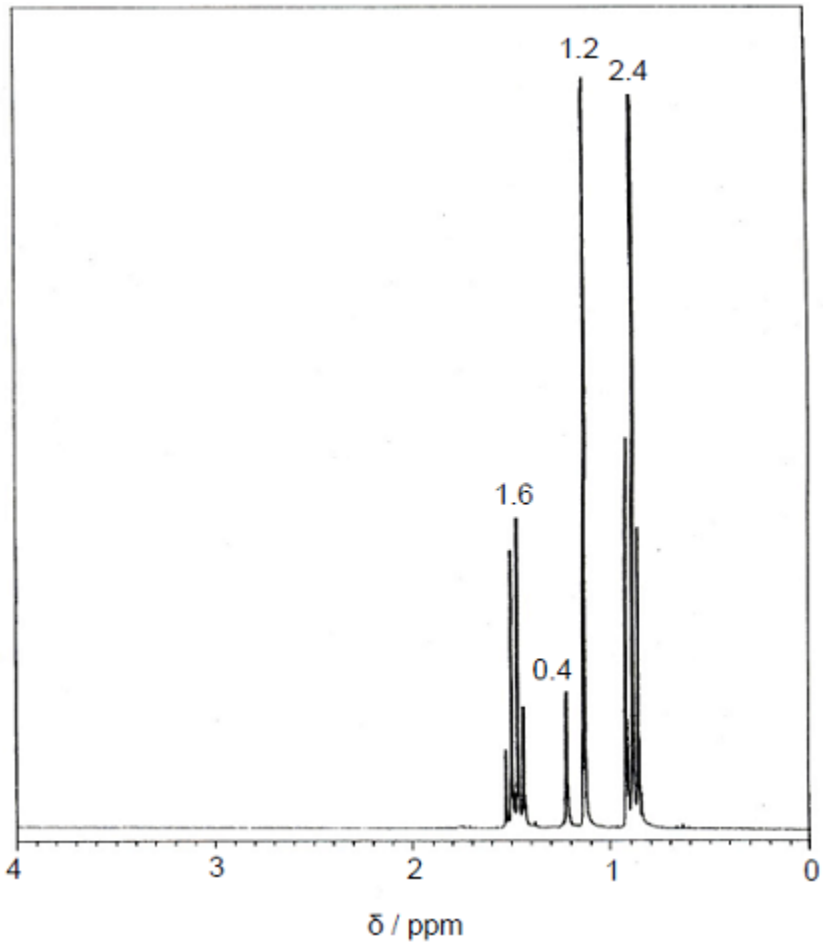


Figure 2



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

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

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

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

(Total 8 marks)

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

A Methylamine ⬭

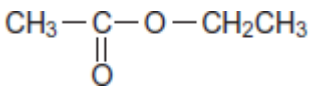
B Trimethylamine ⬭

C Diethylamine ⬭

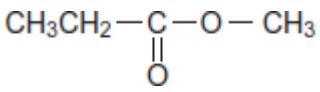
D Propylamine ⬭

(Total 1 mark)

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

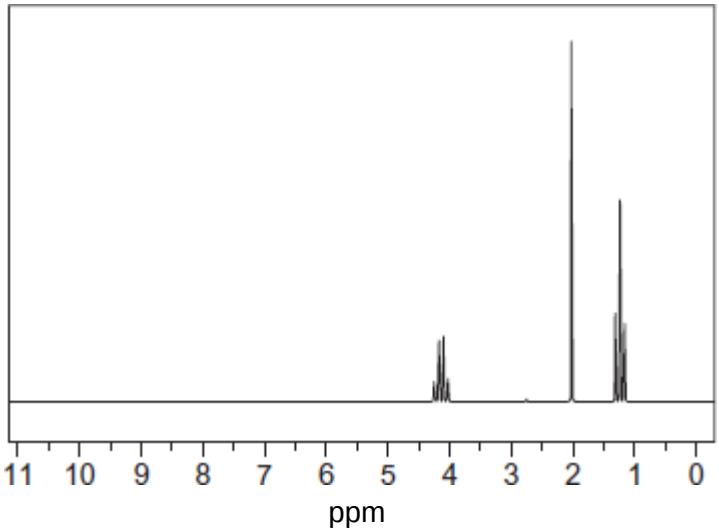


Ester 1



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.

.....

.....

.....

.....

.....

.....

.....

.....

(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.

.....

.....

.....

.....

.....

.....

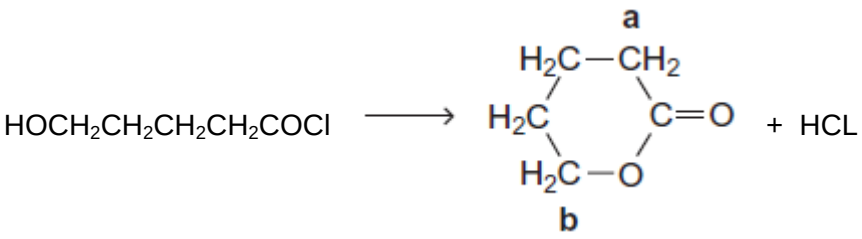
.....

(3)
(Total 11 marks)

6 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**.

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

(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.

.....

.....

.....

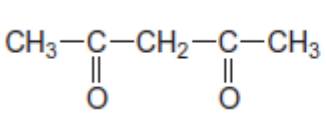
.....

.....

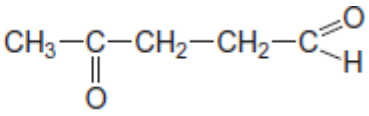
(2)

(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.

M is an ester that shows E-Z stereoisomerism.

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

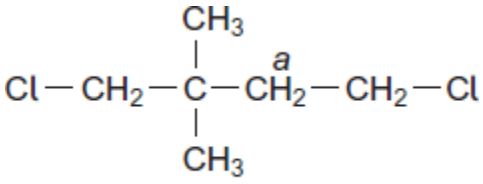
P is an optically active carboxylic acid.

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)

7 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*.

.....

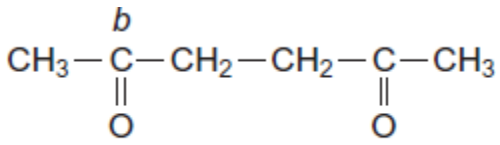
(1)

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

.....

(1)

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



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)

8 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 ^{1}H 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 .....

.....

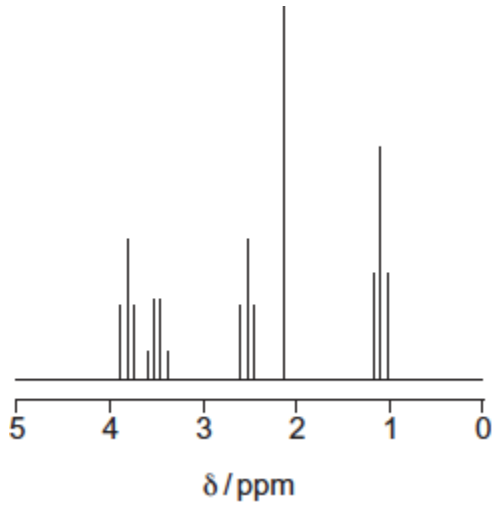
(2)

(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



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**.

(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)

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

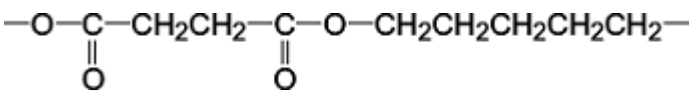
(a) Outline a mechanism for the reaction of CH_3CH_2COCl with CH_3OH and name the organic product formed.

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 .....

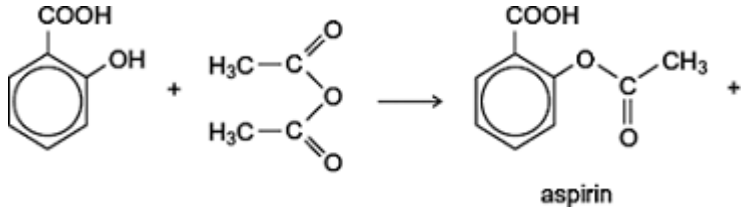
.....

.....

.....

(3)

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



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 .....

.....

.....

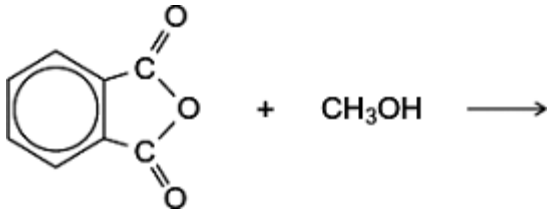
Advantage 2 .....

.....

.....

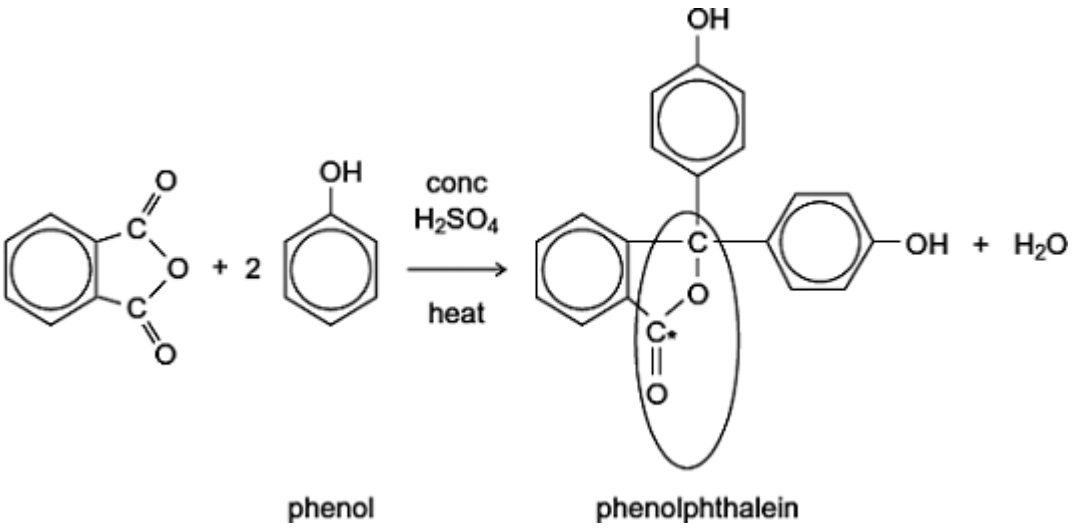
(2)

(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.



(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)

(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)

10 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 ^1H 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**

(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.

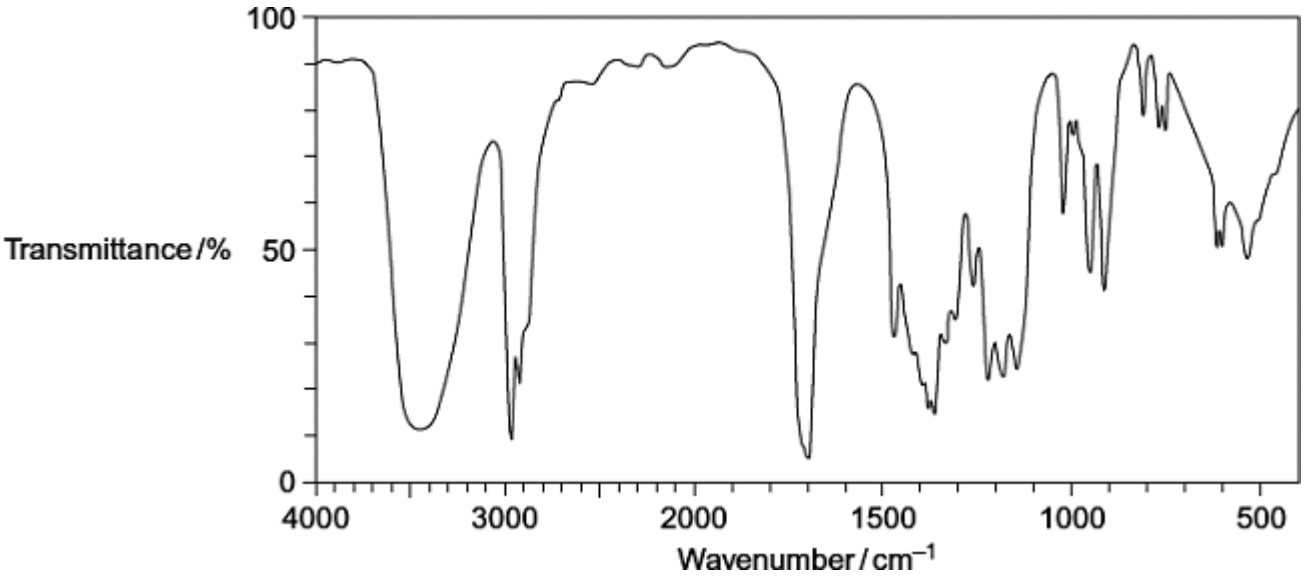
M **N**

(2)

(Total 8 marks)

11 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.

.....

(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** ($C_6H_{12}O_2$)

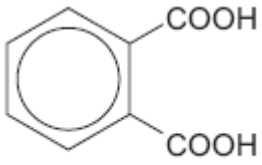
(1)

(Total 5 marks)

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

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.

.....

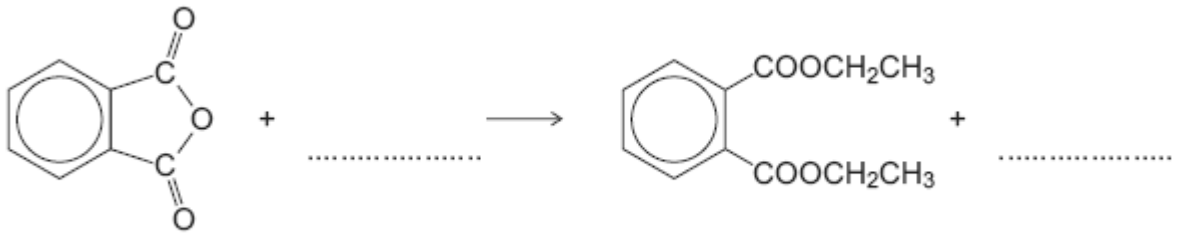
(1)

(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.

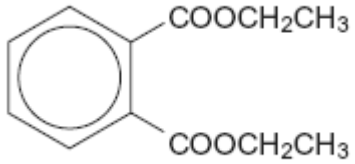
.....

(1)

(iii) One of the peaks in the ^{13}C n.m.r. spectrum of DEP is at δ = 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.



(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.

.....

.....

.....

.....

.....

(Extra space) .....

.....

.....

(2)
(Total 11 marks)

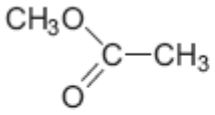
13 Organic chemists use a variety of methods to distinguish between compounds. These methods include analytical and spectroscopic techniques.

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

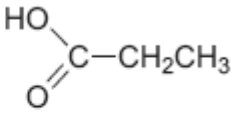
For each pair, suggest a suitable reagent or reagents that could be added separately to each compound in order to distinguish them.

Describe what you would observe with each compound.

(i)



E



F

.....

.....

.....

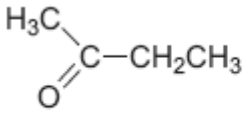
.....

.....

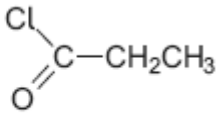
.....

(3)

(ii)



G



H

.....

.....

.....

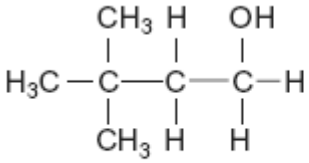
.....

.....

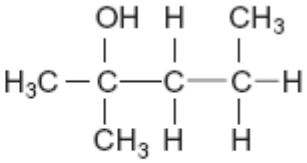
.....

(3)

(iii)



J



K

.....

.....

.....

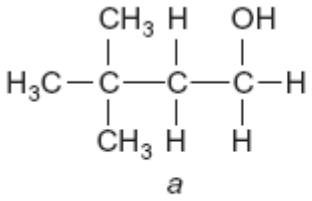
.....

.....

.....

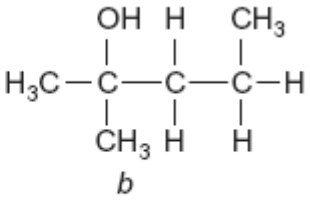
(3)

(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)

(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*.

.....

.....

.....

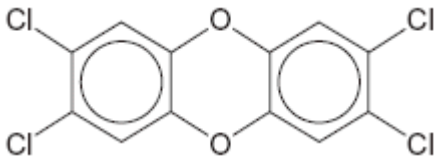
.....

.....

.....

(3)
(Total 15 marks)

14 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 .....

.....

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)

15 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**

(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 δ = 2.3 ppm and **F** has a quartet at δ = 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**

(2)
(Total 10 marks)

16 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**.

.....

(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)

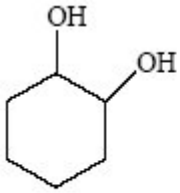
(f) Using the information in parts (a), (b) and (d) deduce the structure of compound **Q.**

(1)

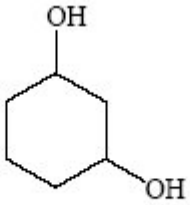
(g) A structural isomer of **Q** reacts with cold water to produce misty fumes. Suggest a structure for this isomer.

(1)
(Total 10 marks)

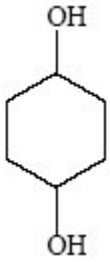
17 Three cyclic alcohols, cyclohexan–1,2-diol, cyclohexan–1,3-diol and cyclohexan–1,4-diol were compared using ^{13}C n.m.r. spectroscopy.



cyclohexan-1,2-diol

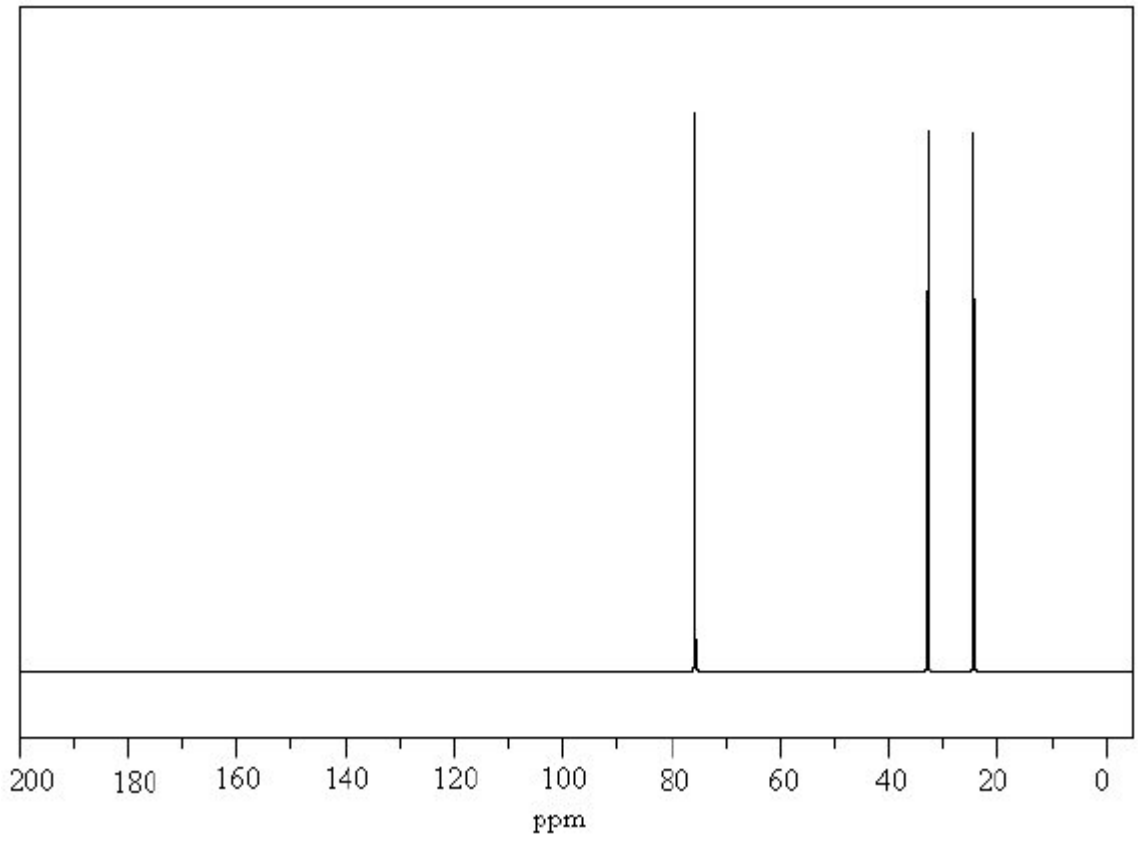


cyclohexan-1,3-diol



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.

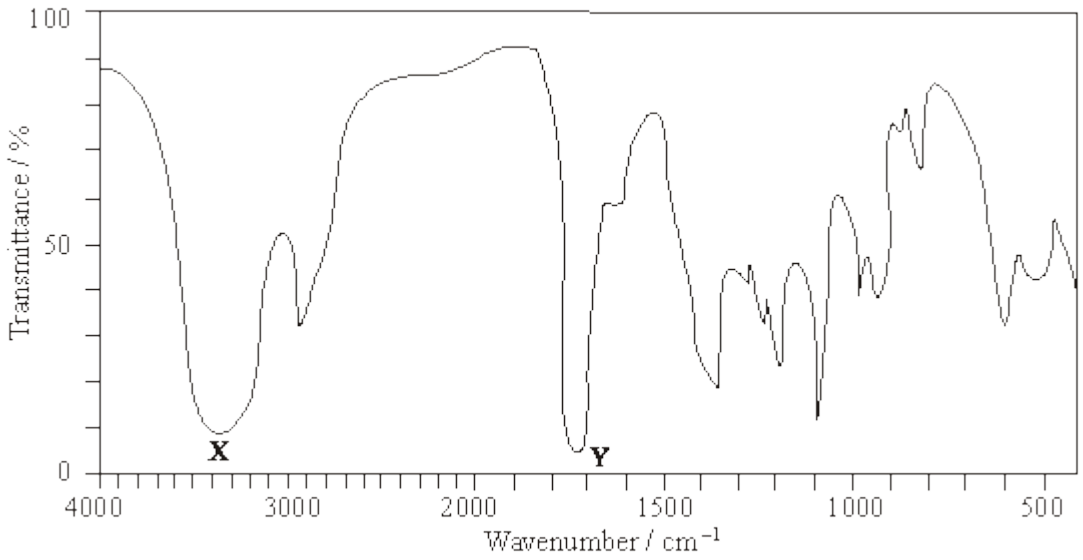
.....

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

.....

(Total 5 marks)

18 (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)

19 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)

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)

20 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

.....

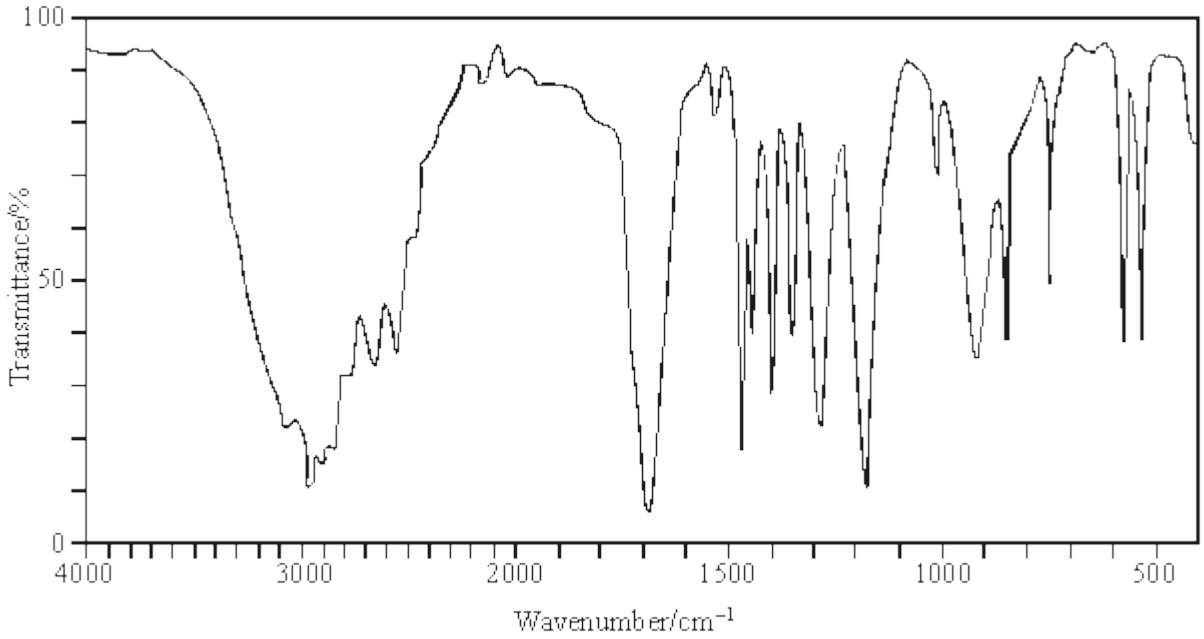
(iii) Two triplet peaks.

.....

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

(4)

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



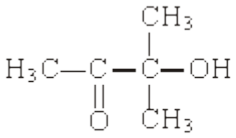
(i) What can be deduced from the broad absorption centred on 3000 cm^{-1} in the infra-red spectrum of **X**?

.....

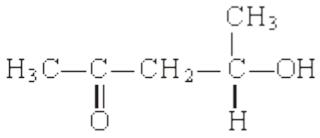
(ii) Given that the proton n.m.r. spectrum of **X** contains only two peaks with the integration ratio 9:1, deduce the structure of **X**.

(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)

(Total 9 marks)

21 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)

22 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 $C_5H_{10}O_2$

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 $C_3H_6C_{l2}$ **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)

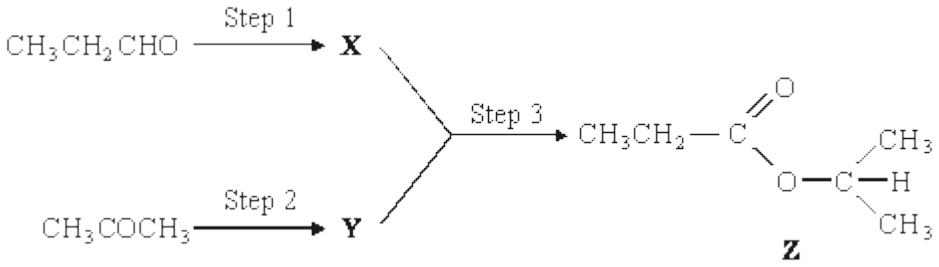
23 (a) Describe how propanal, CH_3CH_2CHO, and propanone, CH_3COCH_3, can be distinguished using

(i) a chemical test and

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

(5)

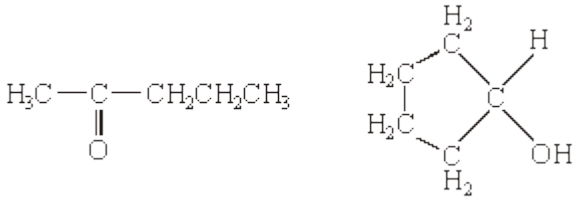
(b) Compound **Z** can be produced by the reaction of compound **X** with compound **Y** as shown in the synthesis outlined below.



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.

(10)
(Total 15 marks)

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



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 .....

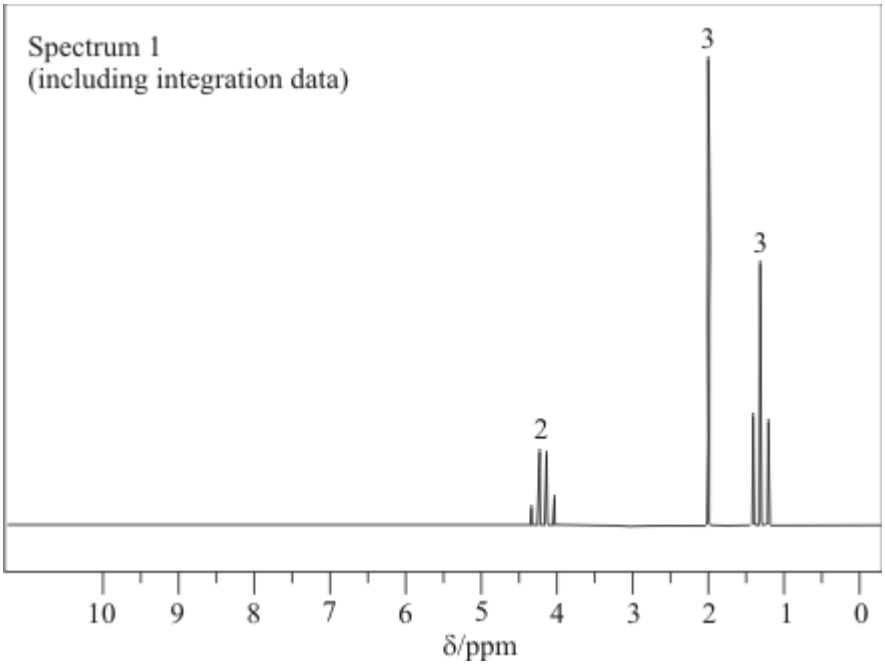
Observation with **E** .....

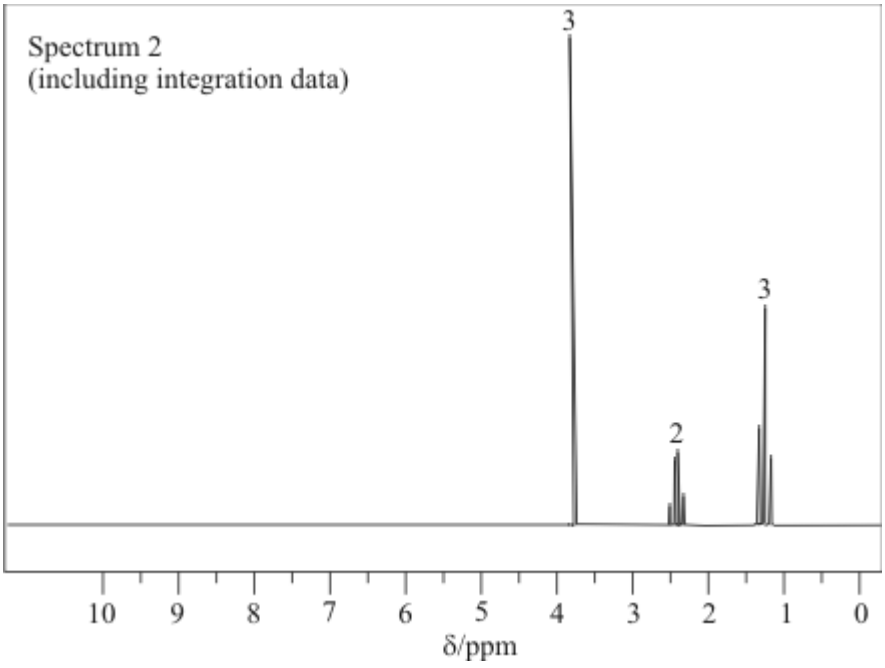
(2)
(Total 9 marks)

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





(4)
(Total 10 marks)

26 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)

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

A butyl methanoate

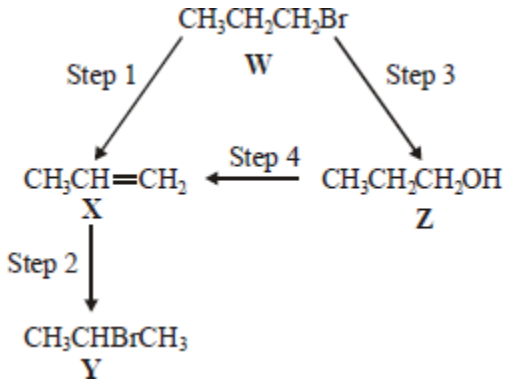
B propyl ethanoate

C ethyl propanoate

C methyl butanoate

(Total 1 mark)

28 For this question refer to the reaction scheme below.



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.

C **X** has geometrical isomers.

(Total 1 mark)

29 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)

30 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 $C_6H_{12}O_2$

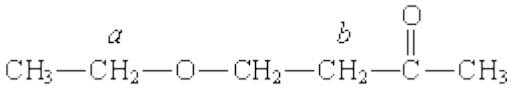
(a) Isomer **A**, $C_6H_{12}O_2$, is a neutral compound and is formed by the reaction between compounds **X** and **Y** in the presence of a small amount of concentrated sulphuric acid.
X and **Y** can both be formed from propanal by different redox reactions.
X has an absorption in its infra-red spectrum 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.



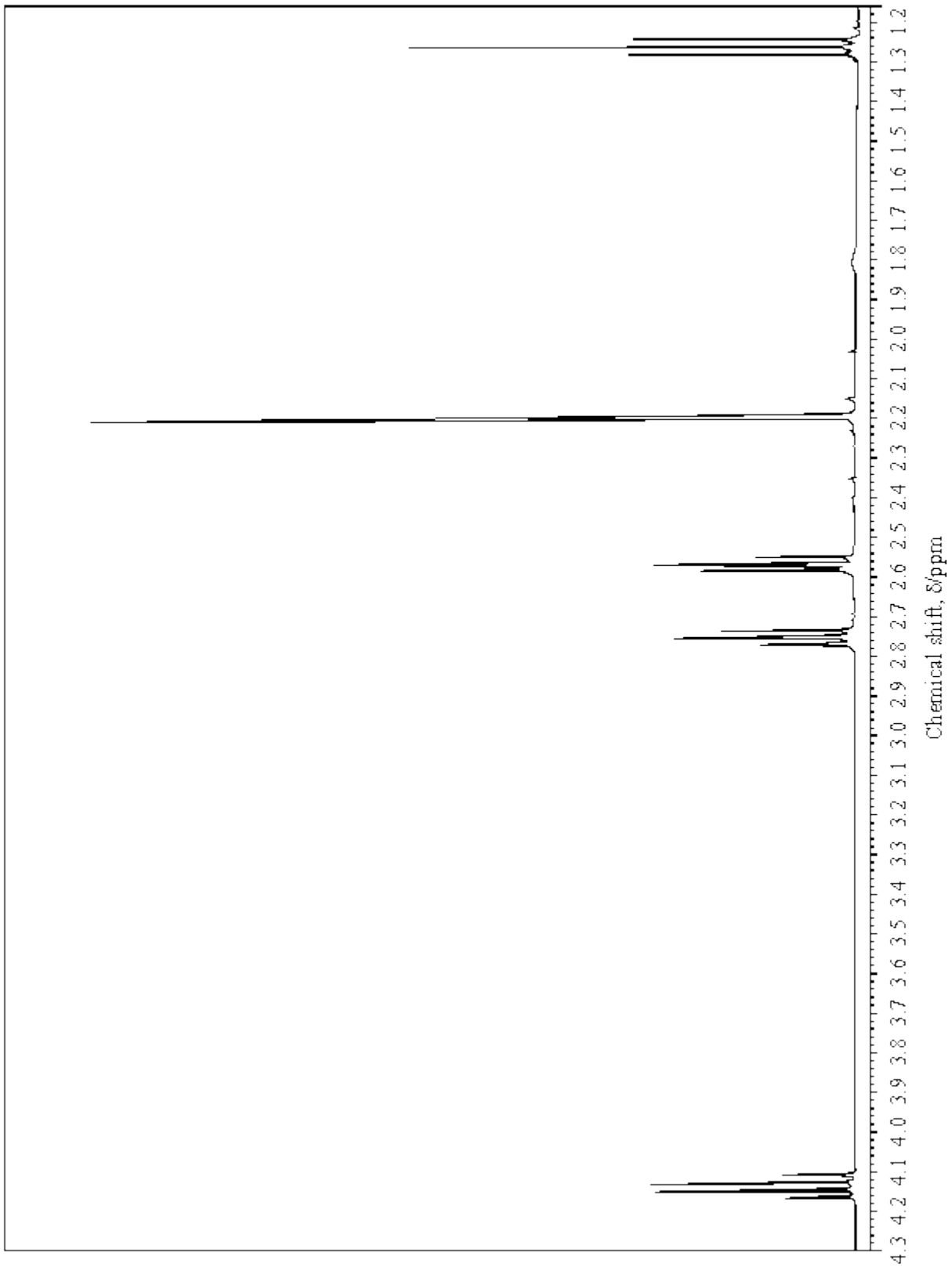
A proton n.m.r. spectrum is obtained for **F**. Using Table 1 at the back of the Periodic Table (PT), predict a value of δ for the protons labelled *a* and also for those labelled *b*. State and account for the splitting patterns of the peaks assigned to the protons *a* and *b*.

(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)

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



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 δ2.20.

.....

(1)

(d) The peaks at δ4.13 and δ1.26 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 δ2.76 and δ2.57.

.....

(1)

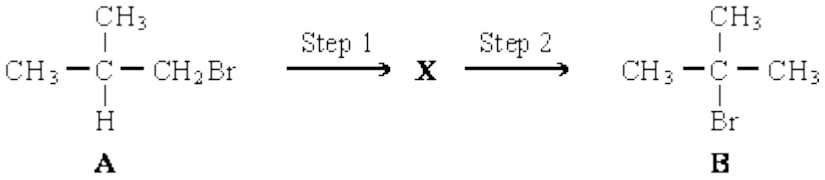
(f) Deduce the structure of compound **X**.

.....

(2)

(Total 9 marks)

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



A **B**

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)

33 Which one of the following has a singlet peak in its proton n.m.r. spectrum?

A ethyl propanoate

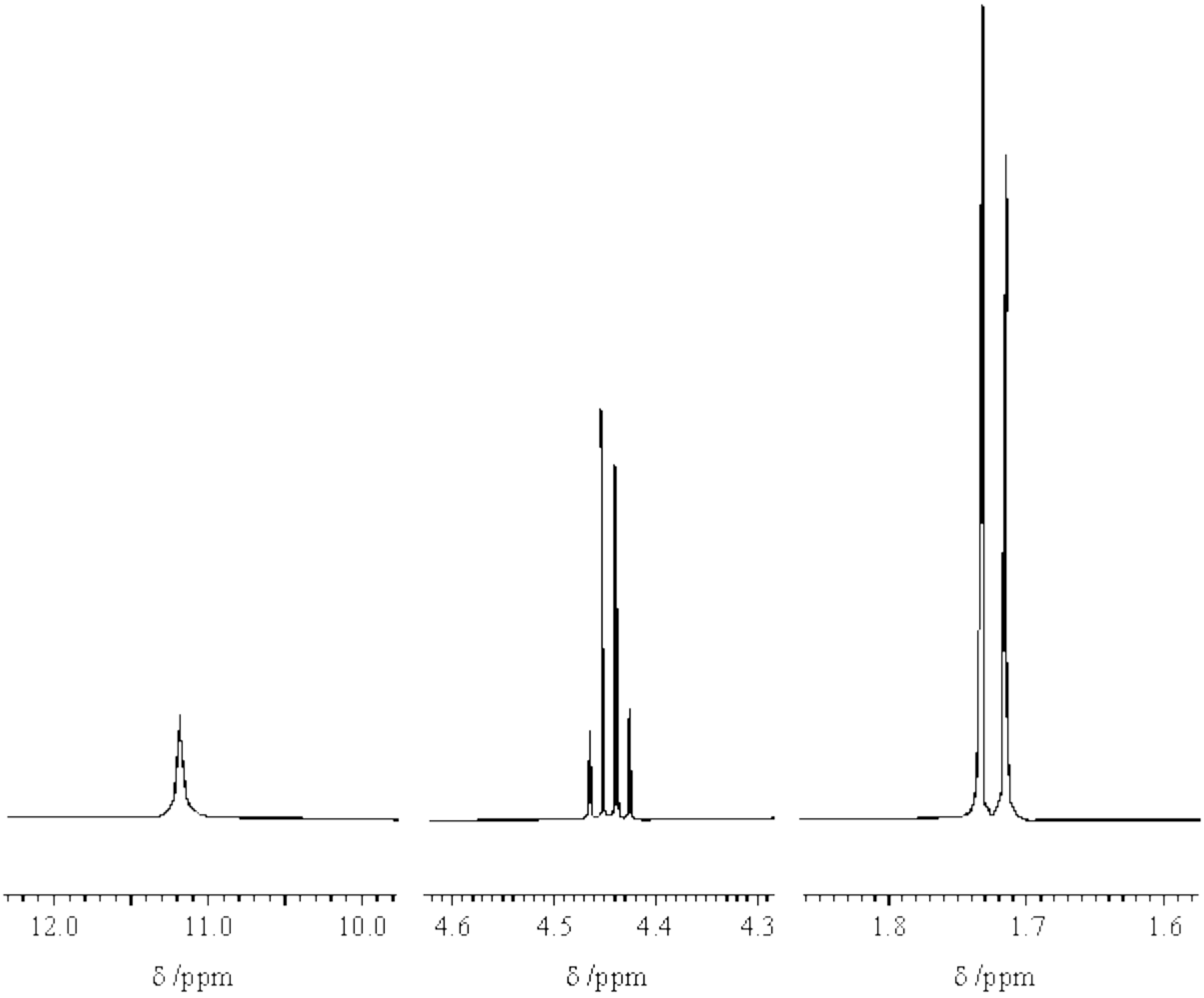
B propyl methanoate

C hexan-3-one

D 2-chlorobutane

(Total 1 mark)

34 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 $ClCH_2CH_2COOH$

.....

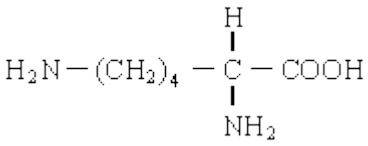
.....

(1)

(d) The amino acid *alanine* is formed by the reaction of $CH_3CHClCOOH$ 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



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)

35 Propene reacts with hydrogen bromide to form a mixture of saturated organic products. The proton n.m.r. spectrum of the major organic product has

A 3 peaks with relative intensities 3 : 2 : 2

B 2 peaks with relative intensities 3 : 4

C 3 peaks with relative intensities 3 : 1 : 3

D 2 peaks with relative intensities 6 : 1

(Total 1 mark)

36 Hydrogen and carbon monoxide were mixed in a 2:1 mole ratio. The mixture was allowed to reach equilibrium according to the following equation at a fixed temperature and a total pressure of 1.75×10^4 kPa.

$$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$$

(a) The equilibrium mixture contained 0.430 mol of carbon monoxide and 0.0850 mol of methanol.

(i) Calculate the number of moles of hydrogen present in the equilibrium mixture.

.....

(ii) Hence calculate the mole fraction of hydrogen in the equilibrium mixture.

.....

.....

.....

(iii) Calculate the partial pressure of hydrogen in the equilibrium mixture.

.....

.....

.....

(5)

(b) In a different mixture of the three gases at equilibrium, the partial pressure of carbon monoxide was 7550 kPa, the partial pressure of hydrogen was 12300 kPa and the partial pressure of methanol was 2710 kPa.

(i) Write an expression for the equilibrium constant, K_p, for this reaction.

.....

(ii) Calculate the value of the equilibrium constant, K_p, for the reaction under these conditions and state its units.

K_p .....

.....

Units .....

(3)

(c) Two isomeric esters **E** and **F** formed from methanol have the molecular formula $C_6H_{12}O_2$

Isomer **E** has only 2 singlet peaks in its proton n.m.r. spectrum.

Isomer **F** is optically active.

Draw the structures of these two isomers.

*Isomer **E***

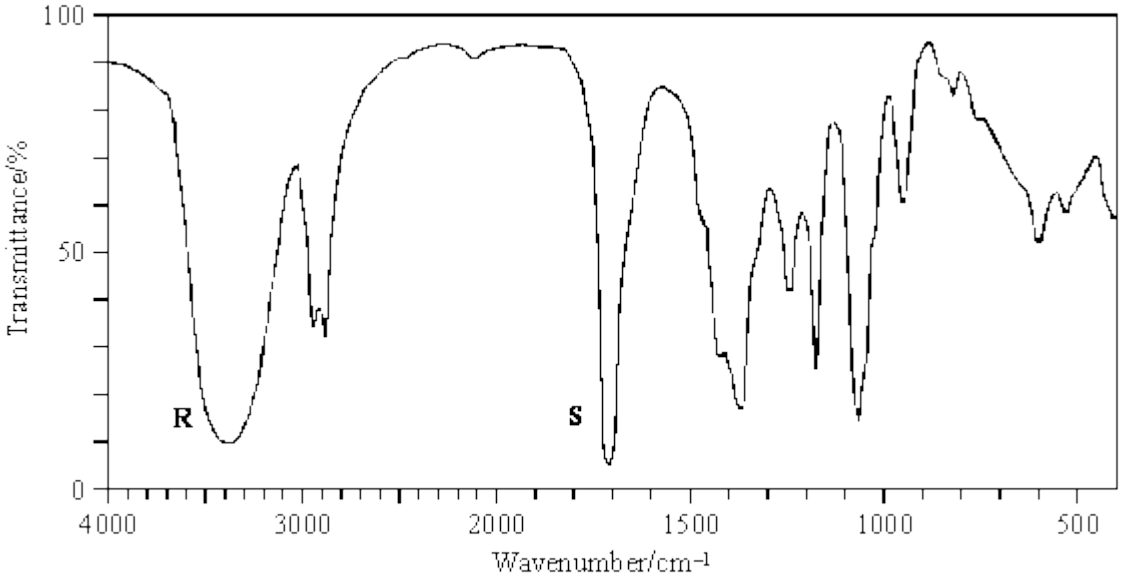
*Isomer **F***

(2)
(Total 10 marks)

37 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)

38 How many peaks will be observed in the low-resolution proton n.m.r. spectrum of $(CH_3)_2CHCOO(CH_2)_3CH_3$?

A 4

B 5

C 6

D 7

(Total 1 mark)

1

(a) Reagent

Acidified
$K_2Cr_2O_7$

Acidified
$KMnO_4$

I_2 / NaOH

Named
RCOOH with HCl or H_2SO_4

Named
RCOCl

Allow names including potassium permanganate

Wrong or no reagent CE = 0

1

P (ketone)
no reaction
no reaction
Yellow ppt
no reaction
no reaction

Penalise incorrect formulae or incomplete reagent, such as $K_2Cr_2O_7$ or acidified dichromate, but mark on.

1

S (2° alcohol)
(orange to) green
(purple to) colourless
no reaction
fruity or sweet smell
Misty fumes

Allow no change or nvc but penalise <u>nothing or no observation</u>

If 2 reagents added sequentially or 2 different reagents used for P and S then CE = 0

1

(b) Tollens'
silver mirror / solid

1

Fehling's / Benedicts
red ppt

1

(c) **G**

P

If not P then no marks for clip

1

5 OR five

1

(d) $C_4H_{12}Si$

Must be molecular formula

Wrong substance CE = 0 for clip

1

Any **two** from

- <u>One or single</u> peak OR all (four) carbon atoms are equivalent or one environment

1

- upfield from others or far away from others or far to right
- non toxic OR inert
- low boiling point or volatile or easy removed from sample

Ignore and don't credit single peak linked to 12 equivalent H or has a peak at δ = 0

but use list principle for wrong statements

1
1

(e) Figure 1 is **R**

*If not **R** cannot score M2*

M1

1

90−150 (ppm) or value in range is (two peaks for) C = C / alkene

M2

1

Figure 2 is **T**

*If not **T** cannot score M4 or M5*

M3

1

50-90 (ppm) or value in range is C—O or alcohol or ether

M4

1

two peaks (so not S which would have only one)

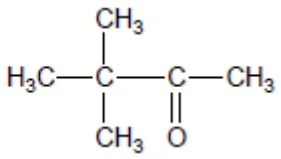
M5

1

(f)

U

$C_6H_{12}O_6$

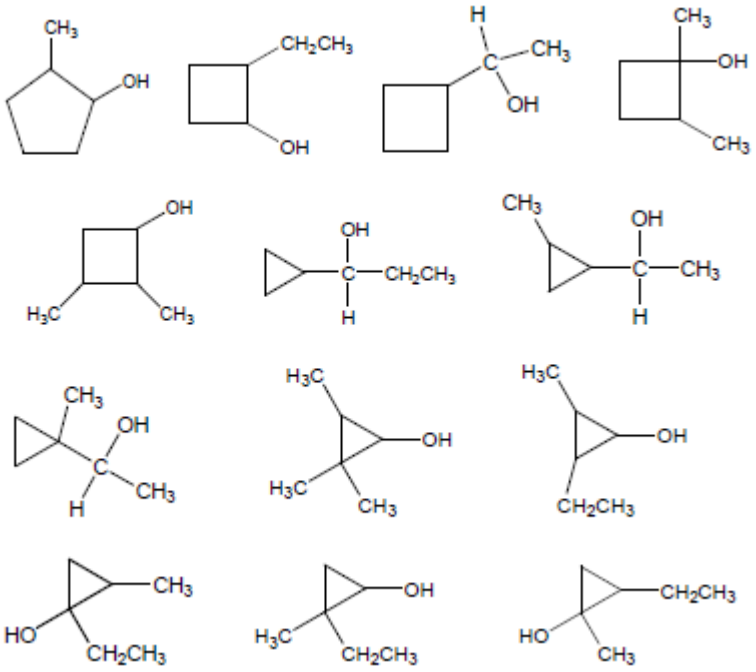


1

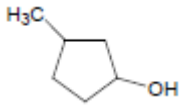
Answers include

V

$C_6H_{12}O_6$



*Not allow **S***



*because **V** must be an isomer of **S***

[17]

2 6 / six

[1]

3 **IR**

Extended response

Absorption at 3360 cm^{-1} shows OH alcohol present

Deduction of correct structure without explanation scores maximum of 4 marks as this does not show a clear, coherent line of reasoning.

M1

1

NMR

There are 4 peaks which indicates 4 different environments of hydrogen

Maximum of 6 marks if no structure given OR if coherent logic not displayed in the explanations of how two of OH, CH_3 and CH_2CH_3 are identified.

M2 **1**

The integration ratio = 1.6 : 0.4 : 1.2 : 2.4

The simplest whole number ratio is 4 : 1 : 3 : 6

M3 **1**

The singlet (integ 1) must be caused by H in OH alcohol

M4 **1**

The singlet (integ 3) must be due to a CH_3 group with no adjacent H

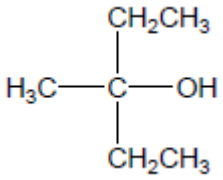
M5 **1**

Quartet + triplet suggest CH_2CH_3 group

M6 **1**

Integration 4 and integration 6 indicates two equivalent CH_2CH_3 groups

M7 **1**



M8 **1**

[8]

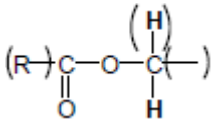
4 C

[1]

5 (a) M1 Ester **1**

If Ester 2, can score M3 only.

1

M2 peak at δ = 4.1 due to 

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

1

M3 (δ = 4.1 peak is) quartet as adjacent / next to / attached to CH_3

1

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

1

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

1

M2 CH_3Br or bromomethane

Penalise contradictory formula and name.

1

M3 Excess (CH_3Br or bromomethane)

Mention of acid eg H_2SO_4 OR alkali eg NaOH loses both M2 and M3.

1

M4 Nucleophilic substitution

Can only score M3 if reagent correct.

Ignore alcohol or ethanol (conditions) or Temp.

1

(c)

	Bromine (penalise Br but mark on)	Acidified $KMnO_4$ (Penalise missing acid but mark on)

Wrong reagent = no marks.

If bromine colour stated it must be red, yellow, orange, brown or any combination, penalise wrong starting colour.

1

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

Ignore 'clear', 'nothing'.

Allow colour fades slowly.

Allow 'nvc' for no visible change.

1

cyclohexene	(Bromine) decolourised	(Acidified $KMnO_4$) decolourised

1

[11]

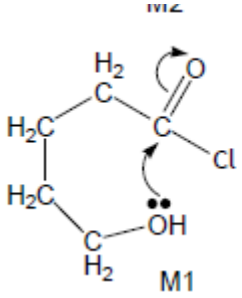
6

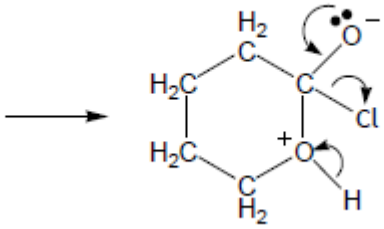
(a) (i) (nucleophilic) addition-elimination

Not electrophilic addition-elimination

Ignore esterification

1





M4 for 3 arrows and lp

M3 for structure

- *If wrong nucleophile used or O–H broken in first step, can only score M2.*
- *M2 not allowed independent of M1, but allow M1 for correct attack on C+*
- *+ rather than δ+ on C=O loses M2.*
- *If Cl lost with C=O breaking lose M2.*
- *M3 for correct structure <u>with charges</u> but lone pair on O is part of M4.*
- *Only allow M4 after correct / very close M3.*
- *Ignore HCl shown as a product.*

4

a 20-50 (ppm) or single value or range entirely within this range

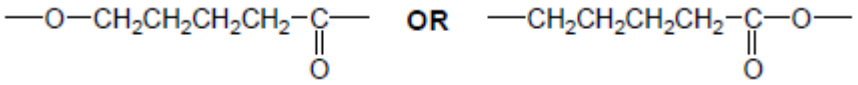
If values not specified as a or b then assume first is a.

1

b 50-90 (ppm) or single value or range entirely within this range

1

(ii)

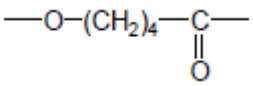


Must have trailing bonds, but ignore n.

1

OR –$OCH_2CH_2CH_2CH_2CO$– **OR** –$CH_2CH_2CH_2CH_2COO$–

Allow



but not - C_4H_8–

one unit only

Condensation

1

(b)

	Tollens'	Fehling's / Benedicts	Acidified potassium dichromate

Penalise wrong formula for Tollens or missing acid with potassium dichromate but mark on.

1

J	No reaction / no (visible) change / no silver mirror	No reaction / no (visible) change / stays blue / no red ppt	No reaction / no (visible) change / stays orange / does not turn green

Ignore 'clear', 'nothing'.

Penalise wrong starting colour for dichromate.

1

K	Silver <u>mirror</u> / grey <u>ppt</u>	Red <u>ppt</u> (allow brick red or red-orange)	(orange) turns green

1

J Two (peaks)

Allow trough, peak, spike.

1

K Four (peaks)

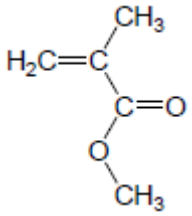
Ignore details of splitting.

If values not specified as J or K then assume first is J.

1

(c) If all the structures are unlabelled, assume that the first drawn ester is L, the second ester is M; the first drawn acid is N, the second P. The cyclic compound should be obvious.

L
ester



OR $H_2C=C(CH_3)COOCH_3$

All $C_5H_8O_2$ L to P must have C=C.

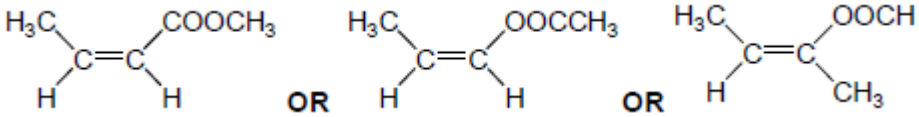
Allow CH_3–.

Allow $-CO_2CH_3$ etc.

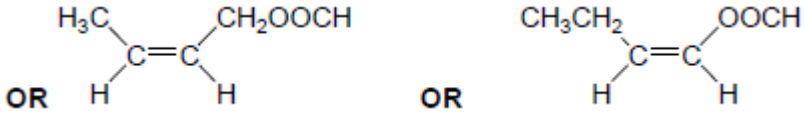
Allow $CH_2C(CH_3)COOCH_3$.

1

M

ester 

$CH_3CH=CHCOOCH_3$ $CH_3CH=CHOOCCH_3$ $CH_3CH=C(CH_3)OOCH$



$CH_3CH=CHCH_2OOCH$ $CH_3CH_2CH=CHOOCH$

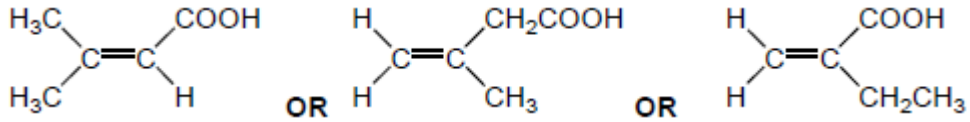
Allow either E–Z isomer.

Allow CH_3- or C_2H_5- but not CH_2CH_3-.

Allow $CH_3CHCHCOOCH_3$ etc.

1

N

acid 

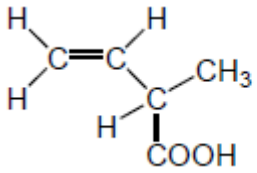
$(CH_3)_2C=CHCOOH$ $H_2C=C(CH_3)CH_2COOH$ $H_2C=C(COOH)CH_2CH_3$

Allow CH_3- or C_2H_5- but not CH_2CH_3-.

Allow $-CO_2H$.

Not cyclic isomers.

Not the optically active isomer.

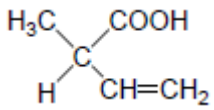


which is P anyway

Allow $(CH_3)_2CCHCOOH$ etc.

1

P

acid 

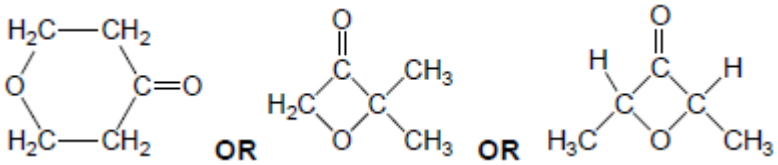
Allow $-CO_2H$.

$CH_3CH(COOH)CH=CH_2$

Allow $CH_3CH(CO_2H)CHCH_2$ or $CH_3CH(CO_2H)C_2H_3$.

1

Q



Not cyclic esters.

1

[19]

7 (a) (i) $CDCl_3$ or CD_2Cl_2 or C_6D_6 or CCl_4

Not D_2O Allow CD_3Cl

1

(ii) 4 **or four**

1

(iii) Triplet or 3 or three

1

(iv) 1,4-dichloro-2,2-dimethylbutane

Do not penalise different or missing punctuation or extra spaces.

Spelling must be exact and order of letters and numbers as here.

1

(b) (i) 3 or three

1

(ii) 190-220 (cm^{-1})

Allow a single number within the range.

***OR** a smaller range entirely within this range.*

1

(iii) hexan**e**-2,5-dione

Do not penalise different or missing punctuation or extra spaces.

Spelling must be exact and order of letters and numbers as here.

NB so must have middle e

1

[7]

8 (a) (i) Single / one (intense) peak / signal ***OR*** all H or all C in same environment ***OR*** 12 equiv H or 4 equiv C

Do not allow non-toxic or inert (both given in Q)

Any 2 from three

Ignore peak at zero

OR

Upfield / to the right of (all) other peaks ***OR*** well away from others ***OR*** doesn't interfere with other peaks

Ignore cheap

Ignore non-polar

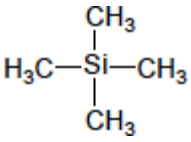
OR

Low bp ***OR*** volatile ***OR*** can easily be removed

Ignore mention of solubility

2

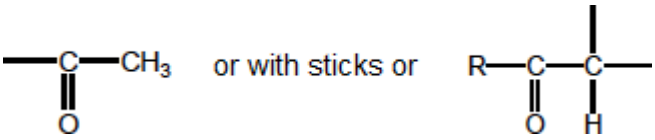
(ii)



Allow $Si(CH_3)_4$

1

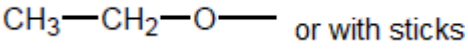
(b) (i)



Ignore any group joined on other side of CO
Ignore missing trailing bond
Ignore charges

1

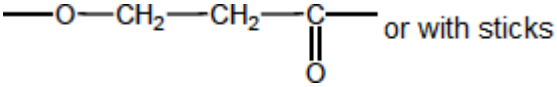
(ii)



Ignore any group joined on other side of −O−
Ignore missing trailing bond
Ignore charges as if MS fragment

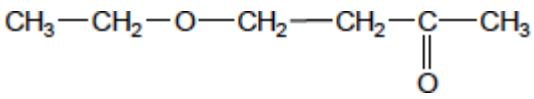
1

(iii)



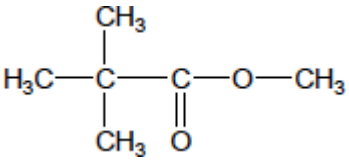
Ignore missing trailing bonds
Ignore charges as if MS fragment

1

(iv) 

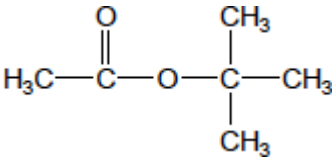
1

(c) (i) Check structure has 6 carbons



Allow $(CH_3)_3CCOOCH_3$ or $(CH_3)_3CCO_2CH_3$

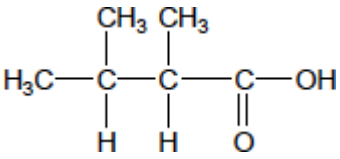
1



Allow $CH_3COOC(CH_3)_3$ or $CH_3CO_2C(CH_3)_3$

1

(ii) Check structure has 6 carbons

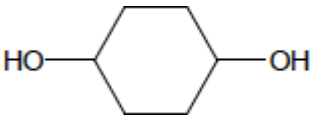


Allow $(CH_3)_2CHCH(CH_3)COOH$ or $(CH_3)_2CHCH(CH_3)CO_2H$

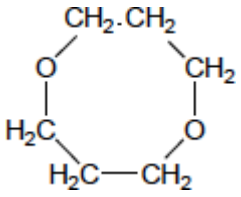
Penalise C_3H_7

1

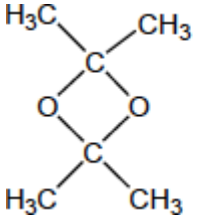
(iii) Check structure has 6 carbons

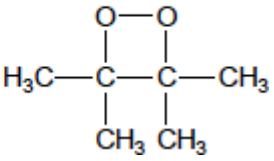


OR



Allow



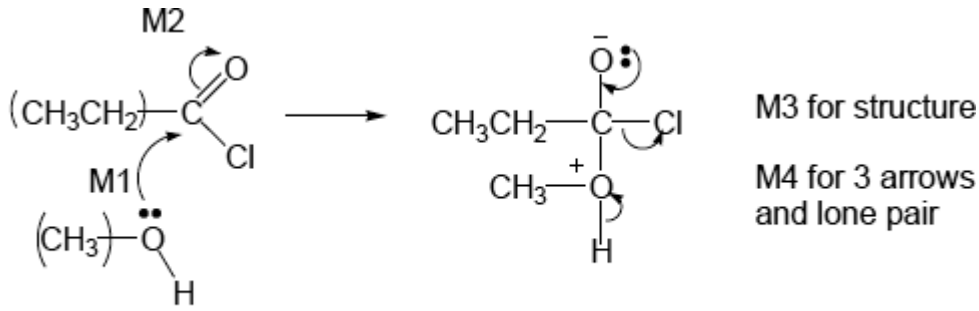
OR 

1

[11]

9

(a)



methyl propanoate (**NO** mark for name of mechanism)

- *M2 not allowed independent of M1, but allow M1 for correct attack on C+*
- *+ rather than δ+ on C=O loses M2*
- *If Cl lost with C=O breaking, max1 for M1*
- *M3 for correct structure <u>with charges</u> but lp on O is part of M4*
- *only allow M4 after correct/very close M3*
- *ignore Cl^- removing H^+*

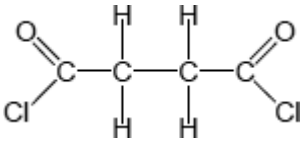
4

(b) (i) pentan<u>e</u>-<u>1,5</u>-diol

Second 'e' and numbers needed

Allow <u>1,5</u>-pentan<u>e</u>diol but this is not IUPAC name

(ii)



Must show ALL bonds

1

(iii) All three marks are independent

M1 (base or alkaline) Hydrolysis (allow close spelling)

1

Allow (nucleophilic) addition-elimination or saponification

M2 <u>δ+ C</u> in polyester

1

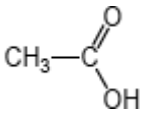
M3 reacts with OH^- or hydroxide ion

1

Not reacts with NaOH

1

(c) (i)



Allow CH_3COOH or CH_3CO_2H

1

(ii) (nucleophilic) addition-elimination

Both addition and elimination needed and in that order

OR

(nucleophilic) addition followed by elimination

*Do **not** allow electrophilic addition-elimination / esterification*

Ignore acylation

1

(iii) any **two** from: ethanoic anhydride is

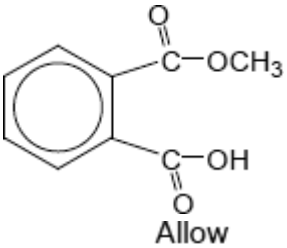
- less corrosive
- less vulnerable to hydrolysis
- less dangerous to use,
- less violent/exothermic/vigorous reaction OR more controllable rxn
- does not produce toxic/corrosive/harmful fumes (of HCl) OR does not produce HCl
- less volatile

***NOT** COST*

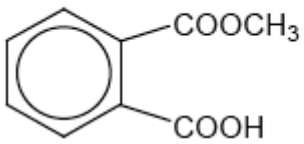
List principle beyond two answers

2

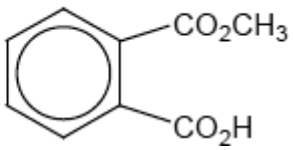
(d)



Allow



or



1

(e) (i) ester

*Do **not** allow ether*

Ignore functional group/linkage/bond

1

(ii) 12 or twelve (peaks)

1

(iii) 160 – 185

Allow a number or range within these limits

Penalize extra ranges given

Ignore units

1

(f) (i)

sulfuric acid	sodium hydroxide	✓
hydrochloric acid	ammonia	X or blank
ethanoic acid	potassium hydroxide	✓
nitric acid	methylamine	X or blank

4 correct scores 2

3 correct scores 1

2 or 1 correct scores 0

2

(ii) Pink to colourless

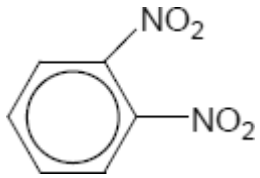
Allow 'red' OR 'purple' OR 'magenta' instead of 'pink'

*Do **not** allow 'clear' instead of 'colourless'*

1

[21]

10 (a)

F	G
	

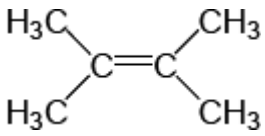
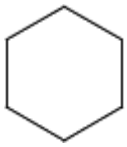
Penalize $-O_2N$ once

Penalise missing circle once

Don't penalise attempt at bonding in NO_2

1

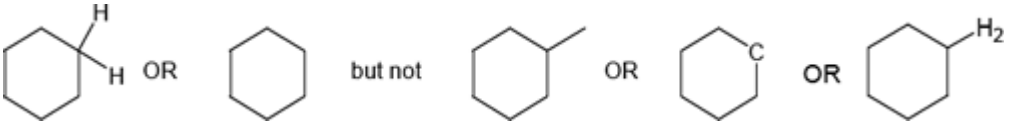
(b)

H	J
	

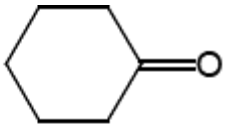
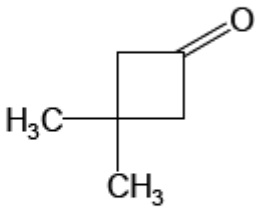
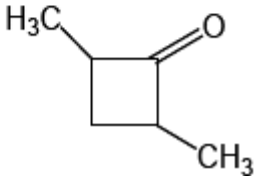
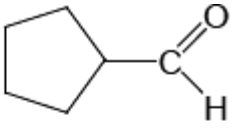
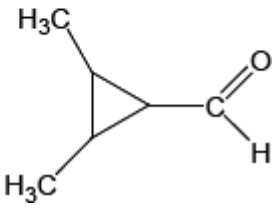
*If **both H** and **J** correct but reversed, award one mark*

1

A carbon in saturated ring structures should be shown as

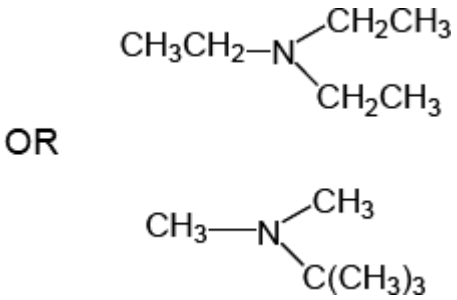
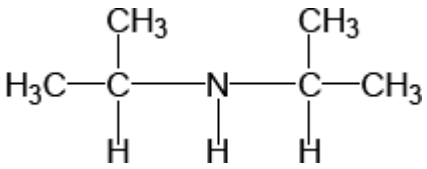


(c)

K	L
 OR  OR 	 OR 

1

(d)

M	N
 OR	

Allow C_2H_5 but

NOT allow C_4H_9 or C_3H_7

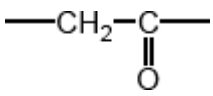
1
1

[8]

11 (a) OH alcohols

1

(b) (i) 2.6



Ignore any group on RHS

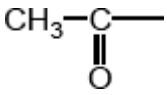
*Must clearly indicate relevant **two** H on a C next to C=O*

On LHS, penalise H or CH or CH_2 or CH_3

Ignore missing trailing bonds or attached R groups

1

(ii) 2.2



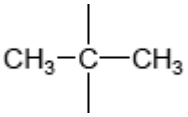
Ignore all groups on RHS

*Must clearly indicate relevant **three** H on C next to C=O*

Ignore missing trailing bonds or attached R group

1

(iii) 1.2



Or in words: two <u>equivalent</u> CH_3 groups

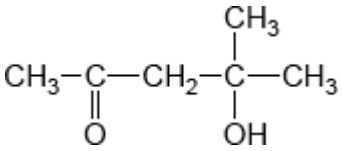
Must clearly indicate two <u>equivalent</u> methyl groups.

Penalise attached H

Ignore missing trailing bonds or attached R groups

1

(iv)



1

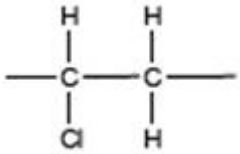
[5]

12 (a) <u>Benzene-1,2-dicarboxylic acid</u>

Allow 1,2-benzenedicarboxylic acid

1

(b)



Must show all bonds including trailing bonds

Ignore n

1

(c) (i) 2 C_2H_5OH

NB Two ethanols

1

H_2O

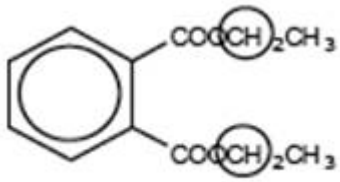
but only one water

1

(ii) 6 or six

1

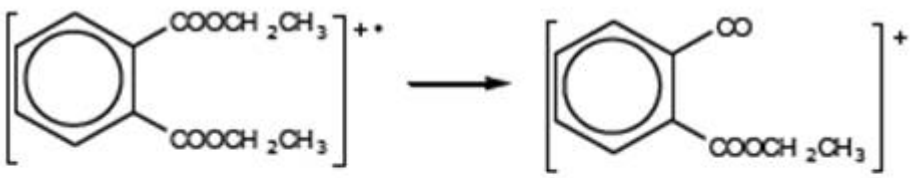
(iii)

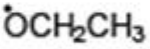


Ignore overlap with O to the left or H to the right, but must only include this one carbon. either or allow both (as they are identical)

1

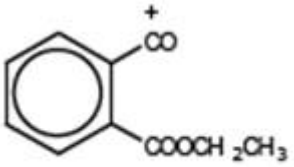
(d)





$[DEP]^{+\cdot}$

OR $[C_{12}H_{14}O_4]^{+\cdot} \rightarrow [C_{10}H_9O_3]^{+} + [C_2H_5O]^{\cdot}$



Allow + on C or O in

1

Dot must be on O in radical

1

(e) (i) Rate = k[DEP]

Must have brackets but can be ( )

1

(ii) Any **two** of

- experiment repeated/continued over a long period
- repeated by independent body/other scientists/avoiding bias
- investigate breakdown products
- results made public

Not just repetition

Ignore animal testing

2 max

[11]

13 (a) (i) Single reagent

If wrong single reagent, CE = zero

Incomplete single reagent (e.g. carbonate) or wrong formula (e.g.$NaCO_3$) loses reagent mark, but mark on

For “no reaction” allow “nothing”

Different reagents

If different tests on E and F; both reagents and any follow on chemistry must be correct for first (reagent) mark.
Reagent must react: i.e. not allow Tollens on G (ketone) – no reaction.
Second and third marks are for correct observations.
i.e. for different tests on E and F, if one reagent is correct and one wrong, can score max 1 for correct observation with correct reagent.

PCl_5 PCl_3

$SOCl_2$

1

E ester

Na_2CO_3/$NaHCO_3$ named carbonate

metal e.g.Mg

no reaction

no reaction

named indicator

no effect

No reaction

1

F acid

Na_2CO_3/$NaHCO_3$ named carbonate

Effervescence or CO_2

metal e.g.Mg

Effervescence or H_2

named indicator

acid colour

fumes

1

(ii) Single reagent

If wrong single reagent, CE = zero
Incomplete single reagent (e.g. carbonate) or wrong formula (e.g.$NaCO_3$) loses reagent mark, but mark on
For "no reaction" allow "nothing"

Different reagents

If different tests on E and F; **both** reagents and any follow on chemistry must be correct for first (reagent) mark.
Reagent must react: i.e. not allow Tollens on G (ketone) – no reaction.
Second and third marks are for correct observations.

1

i.e. for different tests on E and F, if one reagent is correct and one wrong, can score max 1 for correct observation with correct reagent.

G ketone

$AgNO_3$

no reaction

Na_2CO_3/$NaHCO_3$ named carbonate

water

no reaction

named indicator

no effect

Named alcohol

no reaction

Named amine or ammonia

no reaction

1

H Acyl chloride

$AgNO_3$

(white) ppt

Na_2CO_3/$NaHCO_3$ named carbonate

Effervescence or CO_2 or fumes or exothermic

water

fumes

named indicator

acid colour

Named alcohol

Smell or fumes

Named amine or ammonia

fumes

1

Allow iodoform test or Brady's reagent (2,4,dnph) test (both positive for G)

(iii) Single reagent

If wrong single reagent, CE = zero
Incomplete single reagent (e.g. carbonate) or wrong formula (e.g.$NaCO_3$) loses reagent mark, but mark on

For "no reaction" allow "nothing"

Different reagents

If different tests on E and F; **both** reagents and any follow on chemistry must be correct for first (reagent) mark.

Reagent must react: i.e. not allow Tollens on G (ketone) – no reaction.

Second and third marks are for correct observations.

i.e. for different tests on E and F, if one reagent is correct and one wrong, can score max 1 for correct observation with correct reagent.

1

J Primary alcohol

$K_2Cr_2O_7$/ H^+

goes green

$KMnO_4$/ H^+

decolourised / goes brown

Lucas test ($ZnCl_2$/HCl)

Penalise missing H^+ but mark on

1

K Tertiary alcohol

$K_2Cr_2O_7$/ H^+

No reaction

$KMnO_4$/ H^+

no reaction

Lucas test ($ZnCl_2$/HCl)

Rapid cloudiness

1

If uses subsequent tests e.g. Tollens/Fehlings, test must be on product of oxidation

(b) (i) 3,3-dimethylbutan-1-ol

Allow 3,3-dimethyl-1-butanol

1

4

1

Triplet on three

1

(ii) 2-methylpentan-2-ol

Allow 2-methyl-2-pentanol

1

5

1

Singlet or one or no splitting

1

[15]

14 (a) chromatography (allow GLC TLC GC HPLC)

allow any qualification

1

(b) 5

1

Allow 320(.0) or 322(.0)

1

(c) Use of excess air/oxygen or high temperature (over 800 °C)
or remove chlorine-containing compounds before incineration

1

(d) (i) $Si(CH_3)_4$ allow SiC_4H_{12}

allow displayed formula and do not penalise sticks

Not TMS

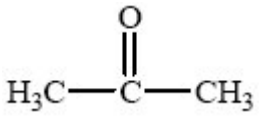
1

(ii) 3

1

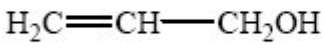
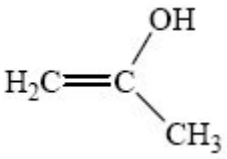
[6]

15 (a) A



allow CH_3COCH_3

1

B  or 

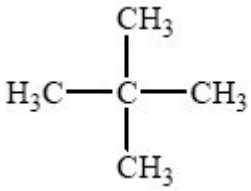
must show C=C

Penalise sticks once per pair

1

(b) C $CH_3CH_2CH_2CH_2CH_3$

1

D 

NOT cyclopentane which is only C_5H_{10}

Penalise sticks once per pair

1

(c) E $CH_3CH_2COOCH_3$

Allow $C_2H_5CO_2CH_3$

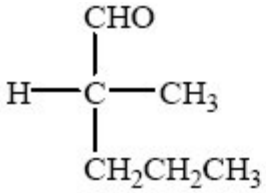
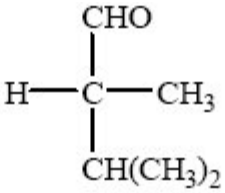
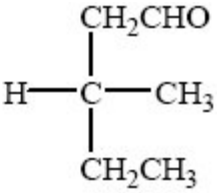
1

F $CH_3COOCH_2CH_3$

Allow $CH_3CO_2CH_2CH_3$ or $CH_3CO_2C_2H_5$

Penalise sticks once per pair

1

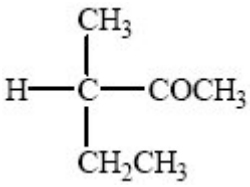
(d) G  **OR**  **OR** 

allow C_3H_7 allow C_3H_7 allow C_2H_5

not C_5H_{11} nor C_4H_9

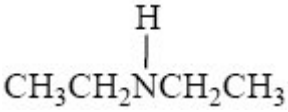
Penalise sticks once per pair

1

H 

allow C_2H_5

1

(e) I 

allow C_2H_5

1

J 

NOT C_3H_7

Penalise sticks once per pair

1

[10]

16 (a) GLC or distillation

1

(b) C=O

1

(c) (i) Cl has two isotopes

1

(ii) $CH_3\overset{+}{C}=O$

1

$C_4H_7ClO^{+\bullet} \rightarrow CH_3\overset{+}{C}=O + C_2H_4Cl^{\bullet}$

1

(d) (i) e.g. $CDCl_3$ or CCl_4

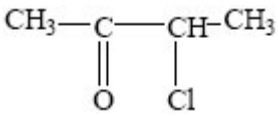
1

(ii) $Si(CH_3)_4$

1

(e) 0 and 3

1

(f) 

1

(g) $CH_3CH_2CH_2COCl$ or $(CH_3)_2CHCOCl$

1

[10]

17 (a) (i) There are three pairs of equivalent carbon atoms

1

(ii) 75ppm

1

(b) (i) 4

1

(ii) 2

1

(c) Each structure can represent a pair of cis/Z and trans/E isomers
OR
Optical isomers

1

[5]

18 (a) **X** (O–H) <u>(alcohols)</u>

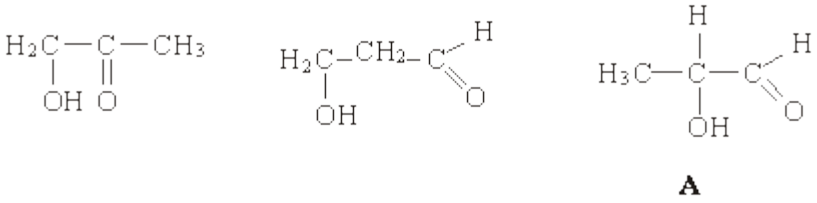
penalise acid or missing "alcohol"

1

Y C=O

allow carbonyl

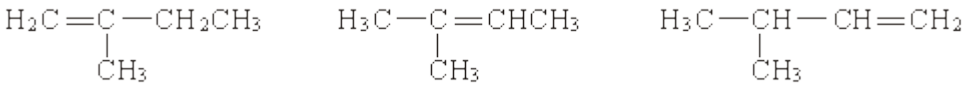
1



A

NOT acid

4

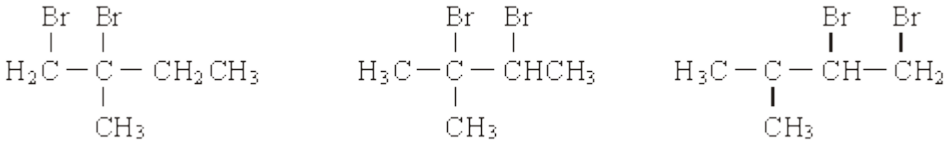
(b) 

Allow conseq dibromocompounds following incorrect unbranched alkenes

NOT allow dibromocompound consequent on a duplicate alkene

NOT allow monobromocompounds if HBr added

3



3

6:3:1 either next to correct structure or to none

1

Allow a mark for identifying correct dibromocompound with three peaks even if integration ratio is wrong

1

if 6:3:1 missing or wrong, no marks for splitting

Only award a mark for splitting if it is clear which integration number it refers to

6 singlet or drawn

1

3 doublet or drawn

1

1 quartet/quadruplet or drawn

1

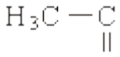
(max 10 marks)

[16]

19 B

[1]

20 (a) (i)


or $RCOCH_3$;

(or description in words)
(ignore trailing bonds)

1

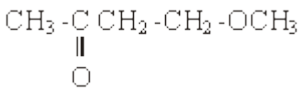
(ii) 
or $ROCH_3$;

(allow 1 if both (i) and (ii) give CH_3- or H_3C– only)

1

(iii) CH_2CH_2 or two <u>adjacent</u> methylene groups;

1

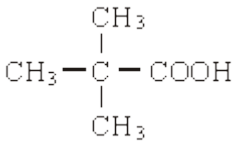
(iv) 

OR

$CH_3COCH_2CH_2OCH_3$;

1

(b) (i) OH <u>in acids</u> or (carboxylic) acid present

(ii) 

(c)

reagent	$K_2Cr_2O_7$ /H^+	$KMnO_4$ /H^+
Y	no reaction	no reaction
Z	orange to green or turns green	purple to colourless or turns colourless

5

[9]

21 D

[1]

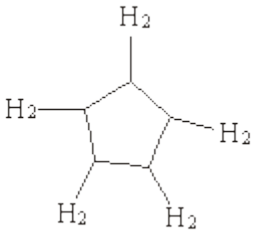
22 (a) **A** any C_5 alkene

1

B

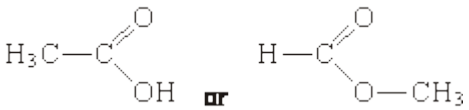
etc

penalise



1

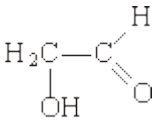
(b) **C**



or CH_3COOH or $HCOOCH_3$

1

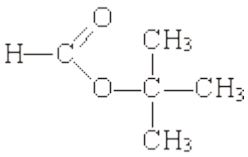
D



or $HOCH_2CHO$

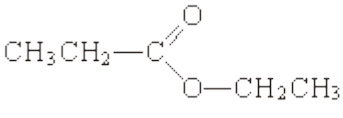
1

(c) **E**



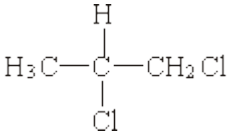
1

F



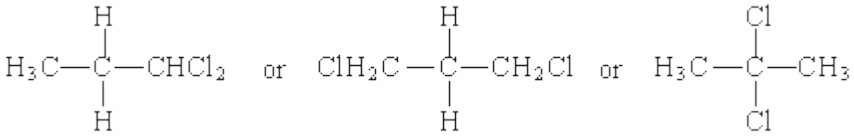
1

(d) **G**



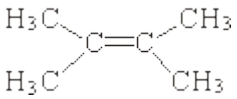
1

H



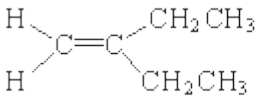
1

(e) **I**



1

J



(allow C_2H_5) **NOT** hex-3-ene

1

[10]

23 (a) (i)

Reagent	Tollens	Fehlings or Benedicts	$K_2Cr_2O_7/H^+$ or acidified	$KMnO_4/H^+$	I_2/NaOH
Propanal	silver (mirror)	red ppt or goes red *(not red solution)*	goes green	goes colourless	No reaction
Propanone	no reaction	no reaction	no reaction	no reaction	Yellow (ppt)

(penalise incomplete reagent e.g. $K_2Cr_2O_7$ or $Cr_2O_7^{2-}/H^+$ then mark on)

3

(ii) propanal 3 peaks

ignore splitting even if wrong

1

propanone 1 peak

1

(b) **X** is CH_3CH_2COOH or propanoic acid if both name and formula given, both must be correct, but

1

Y is $CH_3CH(OH)CH_3$ or propan-2-ol allow propanol with correct formula

1

Mark the type of reaction and reagent/condition independently.
The reagent must be correct or close to score condition

Step 1 Oxidation

$K_2Cr_2O_7/H^+$ or other oxidation methods as above
allow $Cr_2O_7^{2-}H^+$ if penalised above (ecf)
reflux (not Tollens/Fehlings) or heat

1

Step 2	reduction or nucleophilic addition	reduction or nucleophilic addition	reduction or hydrogenation
	$NaBH_4$	$LiAlH_4$	H_2
	in (m)ethanol or water or ether or dry	ether or dry	Ni / Pt etc

1

1

1

Step 3 esterification or (nucleophilic) addition-elimination or condensation

1

(conc) H_2SO_4 or HCl

1

warm (allow without acid reagent if **X** and **Y** given as reagents)

1

or reflux or heat

1

[15]

24 (a) Pentan-2-one

1

(b) (i) 1680 – 1750 (cm^{-1})

1

(ii) 3230 – 3550 or 1000 – 1300 (cm^{-1})

1

(iii) 4

1

(c)

Reagent	$K_2Cr_2O_7/H^+$	$KMnO_4/H^+$	Na	CH_3COOH/H_2SO_4	1
with **C**	no reaction	no reaction	no reaction	no reaction	1
with **D**	goes green	goes colourless	effervescence	smell	1

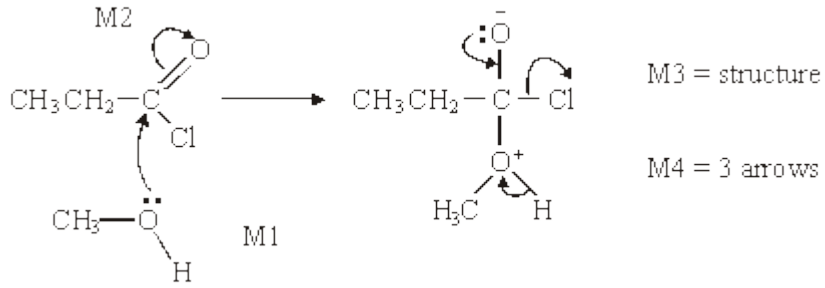
(penalise incomplete reagent e.g. $K_2Cr_2O_7$ or $Cr_2O_7^{2-}/H^+$ then mark on)

(d)

Reagent	Tollens	Fehlings or Benedicts	1
with **E**	silver (mirror)	red ppt or goes red *(not red solution)*	1

[9]

25 **X** is methyl propanoate



1

M1 for arrow and lone pair,

4

M2 for arrow
addition-elimination

1

Spectrum 2

if thinks Spectrum 1 = X can only score for structure of Y

1

Y is $CH_3COOCH_2CH_3$

1

The two marks for explanation are awarded for discussing one or more of the four peaks (not those for the CH_3 of the ethyl groups)
for <u>stated δ values</u> the integration or the splitting should be related to the structure: e.g. structure of **X** shows that
at δ 3.7 – 4.1 **(1)** spectrum of **X** should have integration 3 / singlet **(1)**

or

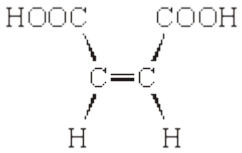
at δ 2.1 – 2.6 **(1)** spectrum of **X** should have integration 2 / quartet **(1)**

Spectrum 2 has these
[OR Spectrum 1 has
at 3.7 – 4.1 **(1)** quartet / integration 2 **(1)** so not **X**
at 2.1 – 2.6 **(1)** singlet / integration 3 **(1)** so not **X**]

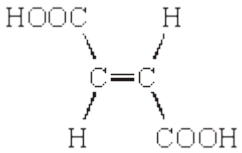
2

[10]

26 (a)



1



1

NB The bonds shown in the structure must be correct

Isomerism: E-Z isomerism

If written answer is correct, ignore incorrect labelling of structures.
If no written answer, allow correctly labelled structures.

1

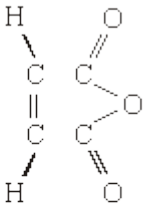
Both COOH groups must be on the same side/ close together/ cis

1

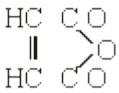
No rotation about C=C axis

1

Structure

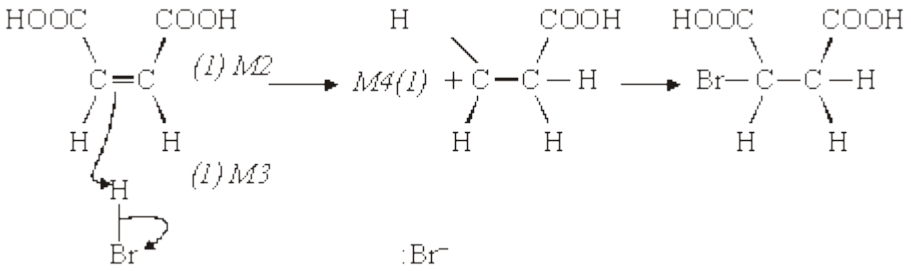


Allow



1

(b) Br_2 / HBr / H_2SO_4 / H^+ / Br^+ / NO_2^+ (*Mark M1*)



NB If electrophile H^+ / Br^+ / NO_2^+ allow M1, M2 and M4
If the acid is incorrect, M2 and M3 can still be scored
Allow M4 consequentially if repeat error from part (a)

4

(c) e.g. $2NaOH + HO_2CCHCHCO_2H \rightarrow NaO_2CCHCHCO_2Na + 2H_2O$

Both H replaced

1

Balanced for atoms and charges

1

NB Allow ionic equations and
$2NaOH + C_4H_4O_4 \rightarrow C_4H_2O_4Na_2 + 2H_2O$
Allow one if structure incorrect but molecular formula correct
Allow one for a correct equation showing one H replaced

(d) *M1* Two peaks

1

M2 No splitting or singlets

1

M3 (Two) non-equivalent protons or two proton environments

1

M4 No adjacent protons

1

M5 Same area under the two peaks or same relative intensity

1

NB Doublet could score M1 and M3 or M5 (Max 2)
More than two peaks CE = 0
Apply the "list principle" to incorrect answers if more than 3 given

Max 3

[15]

27 C **[1]**

28 D **[1]**

29 (a) $K_2Cr_2O_7/H_2SO_4$ reuced by

$CH_3CH_2CH_2CH_2OH$ **(1)**

oxidised to $CH_3(CH_2)_2CHO$ **(1)**
and $CH_3(CH_2)_2COOH$ **(1)**

$CH_3CH_2CH_2CHO$ **(1)**

oxidised to $CH_3(CH_2)_2COOH$ **(1)**

Equation: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ **(1)**

Note: Deduct one if all three compounds given as reducing agents.

6

(b) Tollens' reduced by

$CH_3CH_2CH_2CHO$ **(1)**

oxidised to $CH_3(CH_2)_2COOH$ **(1)**

Equation $[Ag(NH_3)_2]^+ + e^- \rightarrow Ag + 2NH_3$ **(1)**

3

(c) $CH_3CH_2CH_2CH_2OH$ **(1)**

Product $CH_3CH_2CH_2CH_2OOCCH_3$ **(1)**

$(CH_3)_3COH$

Product $(CH_3)_3COOCCH_3$ **(1)**

4

(d) $CH_3CH_2CH_2OH$ has five peaks **(1)**

$(CH_3)_3COH$ has two peaks **(1)**

2

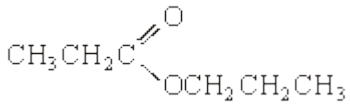
[15]

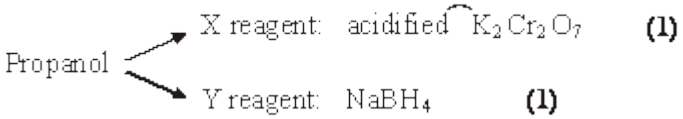
30 (a) X contains > C=O **(1)**

if X and Y reversed lose this mark but allow remaining max 6/7

∴ X is CH_3CH_2COOH **(1)**

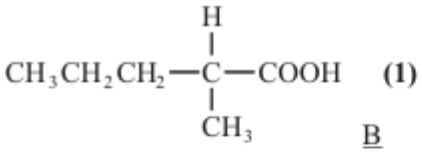
∴ Y is $CH_3CH_2CH_2OH$ **(1)**

∴ A is  **(1)**

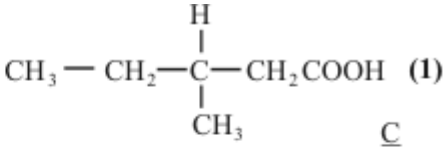


Conc H_2SO_4 : catalyst **(1)**

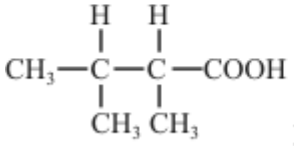
7

(b)  **(1)**

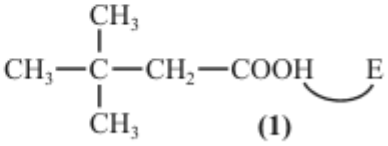
B

 **(1)**

C

 **(1)**

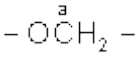
D

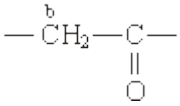
 **(1)**

E

in any order

4

(c)  3.1 – 3.9 **(1)**

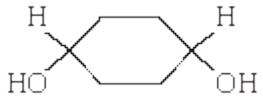
 2.1 – 2.6 **(1)**

a: quartet **(1)** 3 adjacent H **(1)**

b: triplet **(1)** 2 adjacent H **(1)**

6

(d) 3269 cm^{-1} ∴ OH alcohol **(1)**

∴ G is  (1)

2

Notes

(a) first mark for C=O stated or shown in **X**

Ignore wrong names

Y $\underline{CH_3CH_2}CH_2OH$

allow C_3H_7 in **A** if **Y** correct or vice versa

Allow **(1)** for **A** if correct conseq to wrong **X** and **Y**

other oxidising agents: acidified $KMnO_4$; Tollens; Fehlings

other reducing agents: $LiAlH_4$; Na/ethanol; Ni/H_2; Zn or Sn or Fe/HCl

(b) give **(1)** for carboxylic acid stated or COOH shown in <u>each</u> suggestion

(1) for correct **E**

any 2 out of 3 for **B**, **C** or **D**

allow C_3H_7 for either the **B** or **D** shown on the mark scheme

i.e. a correct structure labelled **B**, **C** or **D** or **E** will gain 2.

(c) protons a – *quartet* must be correct to score *3 adjacent H* mark. Same for b

(d) allow **(1)** for any OH (alcohol) shown correctly in any structure – ignore extra functional groups. Structure must be completely correct to gain second mark

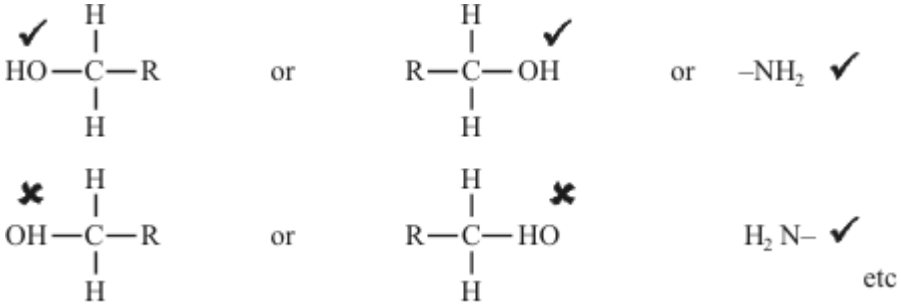
[19]

<u>Organic points</u>

(1) <u>Curly arrows:</u> must show movement of a pair of electrons,
i.e. from bond to atom or from lp to atom / space
e.g.

(2) Structures

penalise sticks (i.e. ) once per paper



Penalise once per paper

allow CH_3– or $–CH_3$ or  or CH_3
or H_3C–

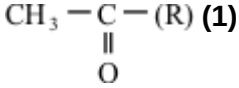
31 (a) 5 **(1)**

1

(b) 2:2:2:3:3 **(1)**

any order but not multiples

1

(c)  **(1)**

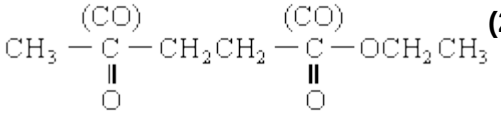
1

(d) CH_3CH_2 or C_2H_5 or ethyl **(1)**
δ4.13 (quartet) : CH_2 peak split by CH_3 / next to CH_3 **(1)**
δ1.26 (triplet) : CH_3 peak split by CH_2 / next to CH_2 **(1)**

3

(e) CH_2CH_2 **(1)**

1

(f)  **(2)**

*allow **(1)** for $CH_3COCH_2CH_2OCOCH_2CH_3$*

or $CH_3COOCH_2CH_2COCH_2CH_3$

Must be $C_7H_{12}O_3$

2

[9]

32 (a) Identity of **X**; 2-methylpropene **(1)**

Absorption at 1650 cm^{-1} indicates an alkene present **(1)**

OR a chemical answer e.g. Br_2 (aq) brown to colourless

2

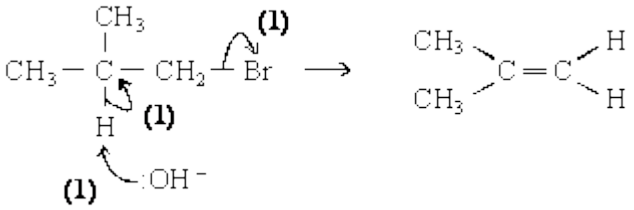
(b) Reagents

Step 1 KOH (allow NaOH) **(1)** alcoholic **(1)** warm **(1)**

Only allow solvent and warm if reagent correct

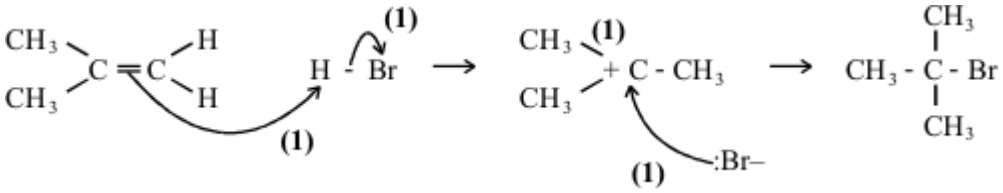
Step 2 HBr **(1)**

Mechanism: A → **X**



Or a carbocation mechanism

Mechanism **X** → B



11

(c) A gives three peaks **(1)**
B gives one peak **(1)**

Allow one for "A has more peaks than B" when no number of peaks is given

2

[15]

33 B

[1]

34 (a) 2-chloropropanoic acid **(1)**

1

(b) δ 1.72 Doublet :: next to CH **(1)**

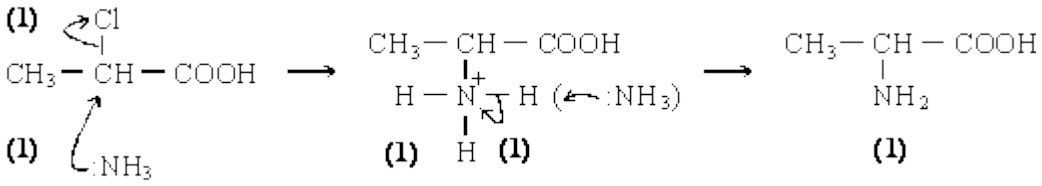
δ 4.44 Quartet :: next to CH_3 **(1)**

2

(c) Two triplets **(1)**

1

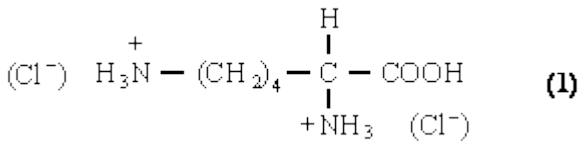
(d)



Allow S_N1

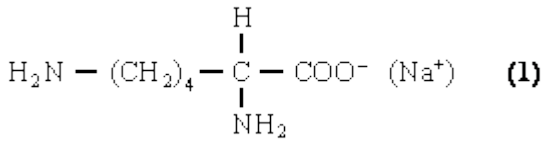
5

(e) (i)



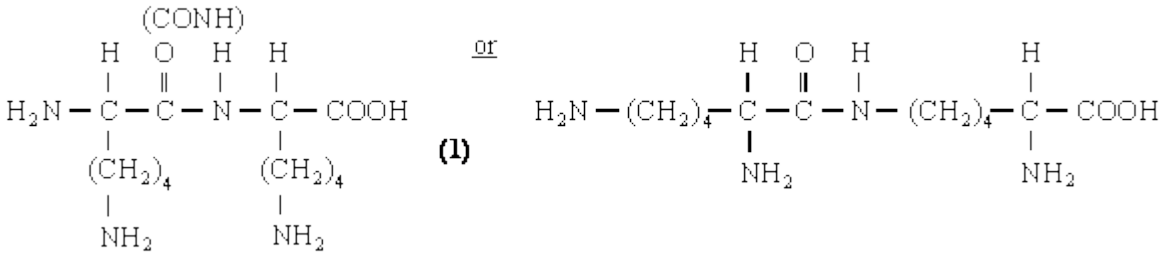
(1)

(ii)



(1)

(iii)



(1)

Or anhydride

3

[12]

35 D

[1]

36 (a) (i) 0.86 **(1)**

(ii) total moles = 0.86 + 0.43 +0.085 = 1.375 **(1)**

$\therefore$ mole fraction of H_2 = $\frac{0.86}{1.375}$ = 0.625 **(1)**

(0.62 - 0.63)

Conseq on (i)

(iii) pp = mole fract^n × total P **(1)**

= 0.625 × 1.75 × 10^4

= 1.09 × 10^4 (kPa) **(1)**

or 1.1(0)

Ignore units

Conseq on (ii)

5

(b) (i) $K_p = \frac{P_{CH3OH}}{P^2_{H_2} \times P_{co}}$ **(1)**

Penalise [ ]

(ii) $K_p = \frac{2710}{(12300)^2 \times (7550)}$ = 2.37 (2.4) × 10^{-9} **(1)**

OR 2.37 × 10^{-15}

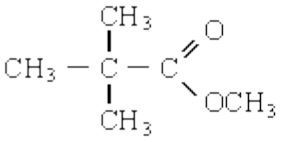
Units: kPa^{-2} **(1)**

or Pa^{-2}

not conseq to wrong K_p expression

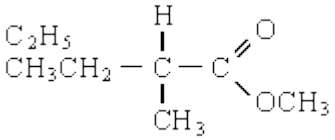
3

(c) *Isomer **E**:*



(1) allow $(CH_3)_3CCOOCH_3$ or $(CH_3)_3CCO_2CH_3$

*Isomer **F**:*



(1)

2

[10]

37 (a) ***R***: O-H (alcohols) **(1)**
S: C=O or carbonyl **(1)**

2

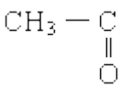
(b) aldehyde **(1)** -CHO or RCHO **(1)**

1

(c) (i) *Reason 1*: TMS inert or non-toxic or volatile / easily removed
Reason 2: single (intense) peak
peak of 12 protons
has 12 equivalent protons
all protons in same environment
OR
peak / signal upfield of others
highly shielded
more shielded
peak away from others or $\delta = 0$ or low
not solvent, not cheap
any 2 reasons × (1)

(ii) *Solvent*: $CDCl_3$ or CCl_4 **(NOT D_2O)**
Reason: proton free **(1)**
allow no hydrogens (atoms)
NOT H^+ / hydrogen ions

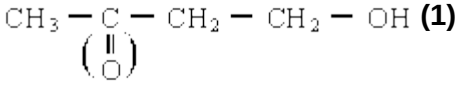
4

(d) (i)  **(1)**

(ii) –OH **(1)**

(iii) $-CH_2-CH_2-$ **(1)**

3

(e)  **(1)**

1

[11]

38 C

[1]