Level: CIE AS and A Level (9701)
Subject: Chemistry
Topic: CIE Chemistry
Type: Mark Scheme

2002

XVIII

1583

Chemistry CIE AS & A Level
To be used for all exam preparation for 2025+
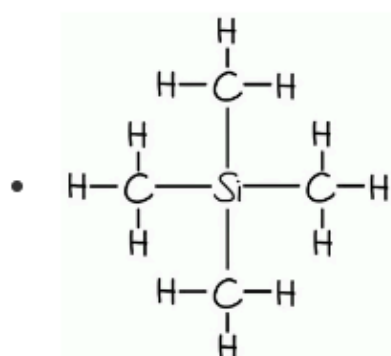
CHEMISTRY

AS and A

This to be used by all students studying CIE AS and A level Chemistry (9701) But students of other boards may find it useful
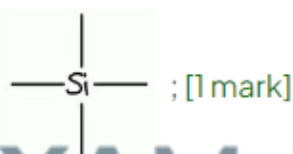
Mark Scheme

Answer 1.

a) The name and structure of the chemical that is commonly used as a standard in NMR spectroscopy are:

- Tetramethylsilane; [1 mark]

OR

; [1 mark]

- Whilst the abbreviation TMS is commonly used, it is not sufficient for the mark
- When drawing the structure, a partially displayed structure with CH_3 groups not displayed would be accepted
- You should be aware of TMS as the common reference standard for both ^{13}C NMR and ^{1}H NMR spectroscopy
- You should be able to name it, draw it and explain why it is used

b) The number of expected peaks in the ^{1}H-NMR of each compound is:

- **A** = 3; [1 mark]
- **B** = 4; [1 mark]
- **C** = 1; [1 mark]

[Total: 3 marks]

- **Tip:** Draw out and annotate the compounds as this can help you see the environments
  - You can sometimes make spotting different hydrogen environments easier by using symmetry – always double check your thinking though!
- The diagrams below show the different hydrogen environments
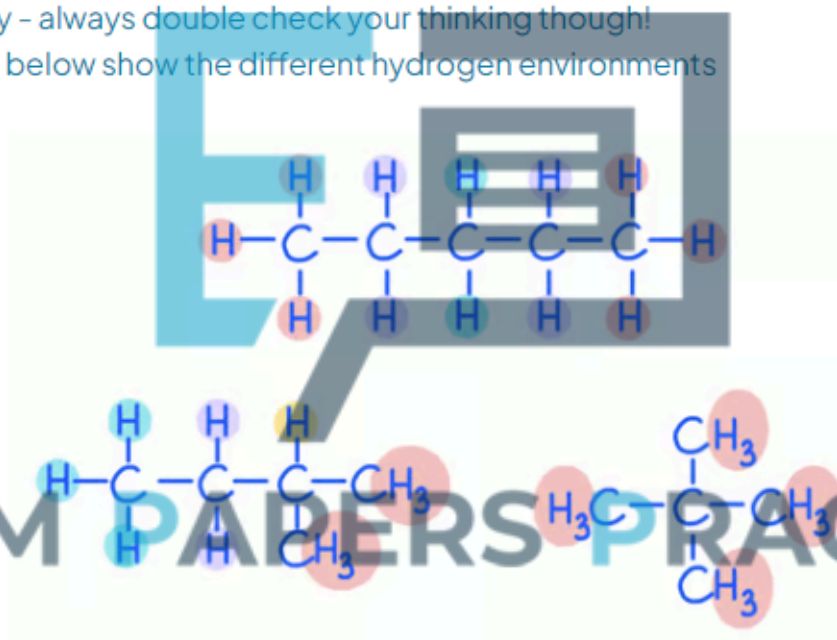
- Each peak on the NMR spectrum relates to hydrogens in the same environments, i.e. 3 different hydrogen environments would have 3 peaks

c) The methyl groups in compounds **B** and **C** give a doublet and singlet respectively because:

- The splitting pattern depends on the neighbouring hydrogens/protons; [1 mark]
- Isomer **B** gives a doublet as the methyl groups have 1 neighbouring proton
  AND
  $n + 1 = 1 + 1 = 2$; [1 mark]
- Isomer **C** gives a singlet as the methyl groups have no neighbouring protons
  AND
  $n + 1 = 0 + 1 = 1$; [1 mark]

[Total: 3 marks]

- The splitting pattern of any hydrogen is dependent on its environment / the neighbours
- **Remember**: The number of peaks a signal splits into = $n + 1$
  - Where n = the number of hydrogens on the adjacent carbon
  - So if the methyl group has 1 neighbouring hydrogen, this will show as a doublet as $1 + 1 = 2$
- The same functional / alkyl groups may not have the same splitting patterns and chemical shifts

d) The number of different carbon environments in each of the compounds is:

- **A** = 3; [1 mark]
- **B** = 4; [1 mark]
- **C** = 2; [1 mark]

[Total: 3 marks]

- **Tip:** You can sometimes make spotting different carbon environments easier by not drawing in all of the hydrogens as well as using symmetry – always double-check your answer
- In the diagram below the different highlights represent the different carbon environments
  - Make sure you **do** include hydrogens within functional groups, e.g. CHO, to make sure you aren't missing carbon environments that are actually different

C—C—C—C—C

C—C—C—CH$_3$
       CH$_3$

C—C—C
   C
   C
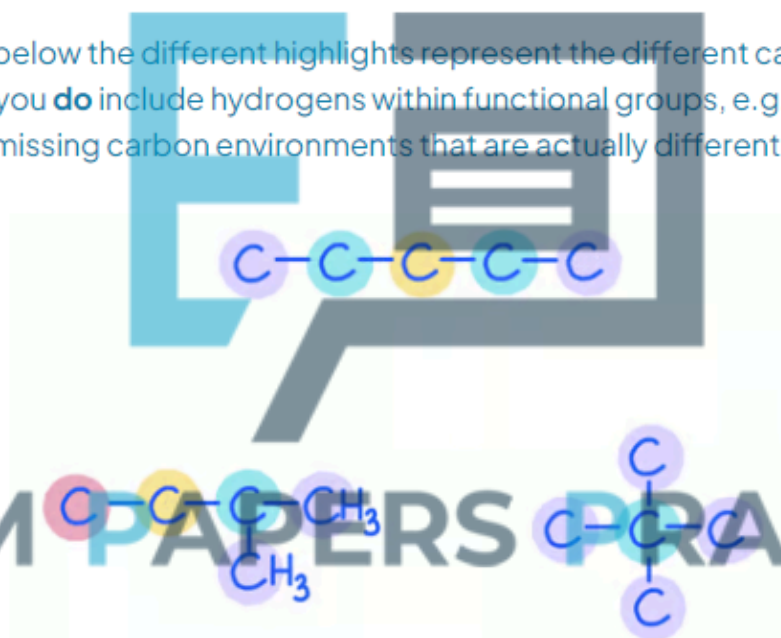
Answer 2.

a)

i) To show that the empirical formula of compound **X** is C_3H_6O:

- Dividing the % of each element by the A_r:

  Carbon = $\dfrac{62.1}{12.0}$ **AND** hydrogen = $\dfrac{10.3}{1.0}$ **AND** oxygen = $\dfrac{27.6}{16.0}$

  OR

  Carbon = 5.175 **AND** hydrogen = 10.3 **AND** oxygen = 1.725; [1 mark]

- Dividing by the smallest answer / calculating the ratio:

  Carbon = $\dfrac{5.175}{1.725}$ **AND** hydrogen = $\dfrac{10.3}{1.725}$ **AND** oxygen = $\dfrac{1.725}{1.725}$

  OR

  Carbon = 3 **AND** hydrogen = 5.97 **AND** oxygen = 1; [1 mark]

ii) The molecular formula of compound **X** is:

- C_3H_6O

  AND

  (Because,) the empirical formula mass equals the molecular formula mass; [1 mark]

[Total: 3 marks]

- To calculate an empirical formula:
  1. Divide the number for each element (either in g or as a percentage) by its relative atomic mass
  2. Divide those values by the smallest one to get a ratio of elements
  3. Multiply the values if necessary to get a ration with values that are close to whole numbers
  4. Write the empirical formula as your answer
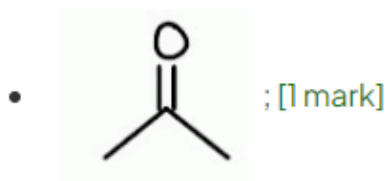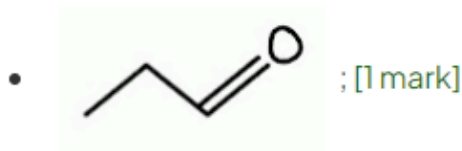- To determine the molecular formula
  - Calculate the mass of the empirical formula
  - Work out how many empirical formulas are required to make the M_r
  - Write the molecular formula
- **Careful:** In this question, the mass of the empirical formula is the same as the M_r
  - This means that the empirical formula is the molecular formula

b) The structures of **two** isomers of compound **X** that contain a carbonyl group are:

- ; [1 mark]

- ; [1 mark]

[Total: 2 marks]

- Displayed and structural formulae would be accepted for the marks
  - This is because the question does not specify how the answers should be presented
- **Remember:** The molecular formula of compound **X** from part (a) is C_3H_6O
- The two possible isomers compounds contain a carbonyl group / C=O
  - This means that there are two carbons left to place
  - They can be placed consecutively, as a chain to form propanal
  - They can be placed on either side of the carbonyl group to form propanone

c)

i) The number of peaks in the carbon-13 NMR spectrum of cyclopropanol is:

- Two / 2: [1 mark]

ii) **One** change that can be made to the solvent used for the proton NMR is:

- Change / swap the $CDCl_3$ for D_2O; [1 mark]

How this will affect the spectrum produced:

- The OH peak / peak at around 3.5 ppm will disappear; [1 mark]

[Total: 3 marks]

- For part (i)
  - There is a line of symmetry through the molecule which means that:
    - The two CH_2 carbons have the same environment
    - The CHOH has a different environment
- For part (ii)
  - One common change that can easily be applied to NMR spectroscopy is to change the solvent
  - The peak at 3.5 ppm is the proton of the OH group because it is the only singlet group
    - You should be aware that the deuterium from the D_2O solvent will exchange with the proton from the OH group
    - This means that the peak at 3.5 ppm will disappear

Answer 3.

a)

i) $CDCl_3$ is used as a solvent instead of $CHCl_3$ because:

- It / $CDCl_3$ does not give a peak (on the spectrum)
  OR
  $CHCl_3$ does give a peak (on the spectrum); [1 mark]

ii) TMS is added to give the small peak at chemical shift $\delta = 0$ because:

- Its chemical shifts can be compared /
  OR
  It is the reference / standard; [1 mark]
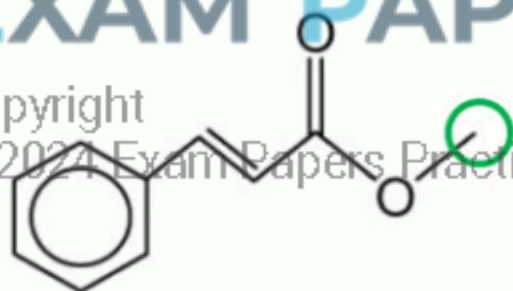
[Total: 2 marks]

- The use of TMS as a reference standard for calibration is a relatively common one-mark question

b) The proton environment which causes the peak at chemical shift 3.8 ppm is:

- The $-CH_3$ group (in $-OCH_3$); [1 mark]
- It is a singlet caused by no adjacent / neighbouring hydrogen atoms; [1 mark]
- A peak area of 3 means there are 3 hydrogen atoms in this environment; [1 mark]

[Total: 3 marks]

- For splitting patterns remember the following;
  - Singlet ($n + 1 = 1$) - no H on adjacent atoms
  - Doublet ($n + 1 = 2$) - adjacent CH
  - Triplet ($n + 1 = 3$) - adjacent CH_2
  - Quartet ($n + 1 = 4$) - adjacent CH_3
- Table 1.1 shows that the chemical shift at δ 3.8 ppm can be an alkyl group next to an electronegative atom such as oxygen, CH_3–O, –CH_2–O
- From the spectrum, the peak at δ 3.8 ppm is a singlet
  - The only part of the compound that can produce a singlet is a –CH_3 group on the end of the molecule
  - This –CH_3 group is next to an electronegative oxygen atom which agrees with the proton NMR information in Table 6.1
- In your answer, you also have to reference that the peak area is 3, which tells you that there are three hydrogen atoms in this environment
- **Remember:** The ratio of the relative areas under each peak gives the ratio of the number of protons responsible for each peak
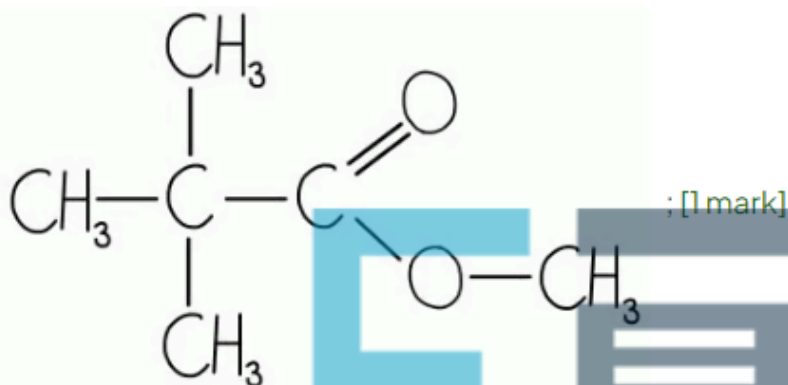
c) The two esters with formula $C_6H_{12}O_2$ that each have only two peaks, both singlets, in their ^{1}H NMR spectra are:

- $(CH_3)_3CCOOCH_3$
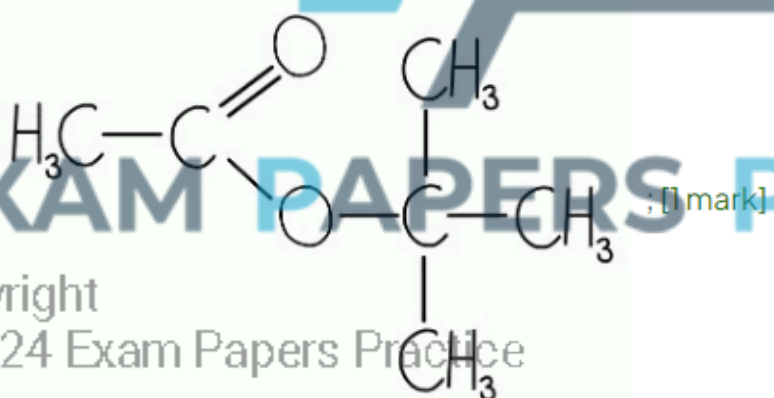 **OR**

; [1 mark]

- $CH_3COOC(CH_3)_3$
  OR

; [1 mark]

[Total: 2 marks]

- The first thing to notice in the question is that you are asked to draw two esters from the isomer $C_6H_{12}O_2$
- -COOC will feature in your drawings but make sure you try to focus on the fact that you need to draw the correct hydrogen environments as it says in the question the relative peak areas are 3:1 for both esters
  - This means that there are 3 CH_3 groups to 1 CH_3 group in the ester isomer and then in between them is the ester bond -COOC
- It is then a case of drawing one ester and then 'flipping' the three methyl groups to the other side of the ester bond
- **Remember:** Always double-check you have 4 bonds coming out of each carbon atom and not lose easy marks

d)

i) The simplest ratio of protons in each environment is:

- 2:2:2:3:3 [1 mark]

ii) To describe and explain the splitting patterns of the peaks at δ = 3.5 and δ = 1.2:

- δ 3.5 = is for a CH_2 group next to the -O-CH_2; [1 mark]
- δ 3.5 = is a quartet because of an adjacent CH_3 group; [1 mark]
- δ 1.2 = is for a CH_3-CH_2 ; [1 mark]
- δ 1.2 = is a triplet because of an adjacent CH_2 group; [1 mark]

[Total: 5 marks]

- **Remember:** The integration value tells you the ratio of the relative areas under each peak
- So an answer of 2:2:2:3:3 can be found as the **simplest whole number ratio from the integration value:**
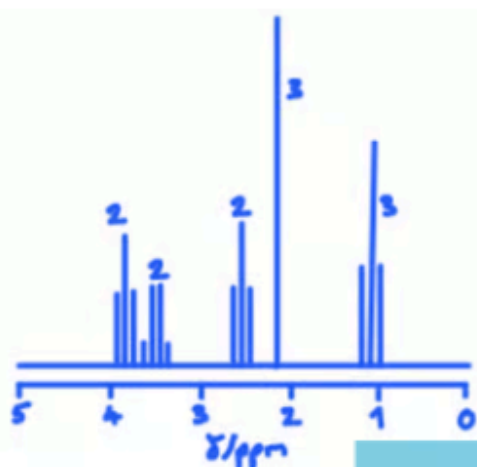
- Write the corresponding ratios onto the spectrum so you can clearly see how the split patterns apply to the peaks
- You need to reference the **type of proton** the chemical shift value is showing as well as **explain what these split patterns are telling you**
- The isomer is drawn below, showing the relationship between the proton environments and the integration values:
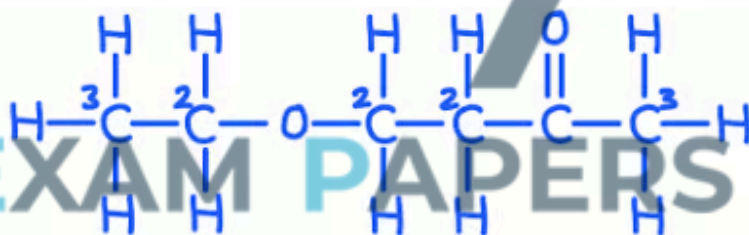
e) The isomer which produced the spectrum is:

- B; [1 mark]

[Total: 1 mark]

- There are four peaks on the spectra which correspond to four different carbon environments
    - 30 ppm; C–CH_3 and there are three equivalent CH_3 groups
    - Just above 30 ppm; for the carbon atom with three CH_3 groups attached
    - 50 ppm; C–C=O for the CH_2 group
    - 180 ppm; RC=O for the COOH group

For more help visit our website https://www.exampaperspractice.co.uk/

Answer 4.

a) The completed table assigning spectra **A** and **B** is:

Spectrum	Organic compound	Explanation
A	Ethane-1,2-diol	The highest m/e for spectrum **A** is 62 which matches the M_r of ethanediol, $C_2H_6O_2$
B	Ethanedioic acid	The highest m/e for spectrum **B** is 90 which matches the M_r of ethanedioic acid, $C_2H_2O_4$

- Spectrum **A**: Correct organic compound and explanation; [1 mark]
- Spectrum **B**: Correct organic compound and explanation; [1 mark]

[Total: 2 marks]

- Sometimes tiny peaks appear at M_r +1 which are due to isotopes, principally ^{13}C
- However, the amount of naturally occurring ^{13}C is around 1%, so it is unlikely to show up unless it is a very high-resolution mass spectrum

b) The completed table assigning spectra **C** and **D** is:

Spectrum	Organic compound	Explanation
C	Ethanedioic acid	Spectrum **C** contains a peak at 1700–1750 cm^{-1} which matches the C=O in ethanedioic acid
D	Ethane-1,2-diol	In spectrum D, there is a broad peak at 3200–3600 cm^{-1} which is characteristic of O–H in alcohols

- Spectrum **C**: Correct organic compound and explanation; [1 mark]
- Spectrum **D**: Correct organic compound and explanation; [1 mark]

[Total: 2 marks]

- Ethanedioic acid is a hydrated solid acid, so there are O–H bonds from the water molecules as well as the carboxylic acid groups, making it a little hard to interpret the IR spectrum
- The best approach is to look for bonds that are unique to that molecule compared to ethane-1,2–diol

c) The spectrum of ethane-1,2-diol shows:

- There are two peaks which indicate there are <u>two unique ^{1}H /proton environments</u>; [1 mark]
- The integration peaks show the <u>ratio of the ^{1}H / proton environments</u> is 2:1; [1 mark]
- This matches the structure of ethane-1,2-diol which has two identical -OH protons and four identical C-H protons; [1 mark]
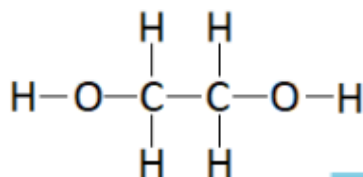
[Total: 3 marks]

- You must distinguish between the number of protons and proton environments
- It would be incorrect to state there are two protons in one environment and one in another environment - it is a ratio, not the actual numbers

d) The number of peaks and splitting pattern for ethanedioic acid:

- One peak / signal; [1 mark]
- There would be no splitting / a singlet; [1 mark]

[Total: 2 marks]

- Ethanedioic acid is a highly symmetrical molecule with only two protons in a chemically identical environment
- The single C-C is capable of rotating so the most sterically favourable position is with the two hydroxyl groups opposite each other:
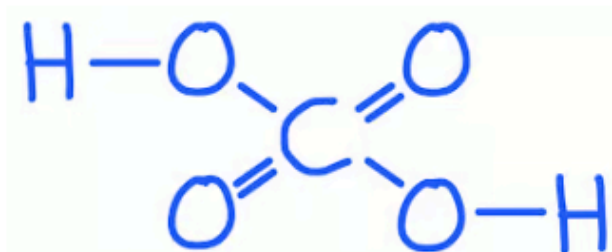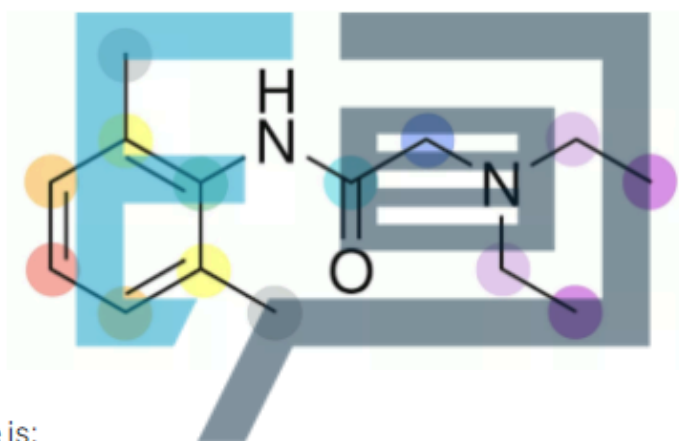
Answer 5.

a) The number of peaks in the carbon–13 NMR spectrum of lidocaine is:

- Nine / 9; [1 mark]

[Total: 1 mark]

- **Careful:** Lidocaine has 2 symmetrical sections; one in the aromatic ring and one in the tertiary amine at the end of the molecule


b) The completed table is:

δ / ppm	environment of proton	number of ^1H atoms responsible for the peak	splitting pattern
1.2	methyl groups next to CH_2	6	triplet
2.3	methyl groups attached to the aromatic ring	6	singlet
3.0	CH next to carbonyl group	1	singlet
7.1 – 7.4	attached to the aromatic ring	3	overlapping peaks
9.0	amide	1	singlet

- Each correct row; [1 mark]

[Total: 3 marks]

- The answer to part **(a)** can help guide you when assigning peaks
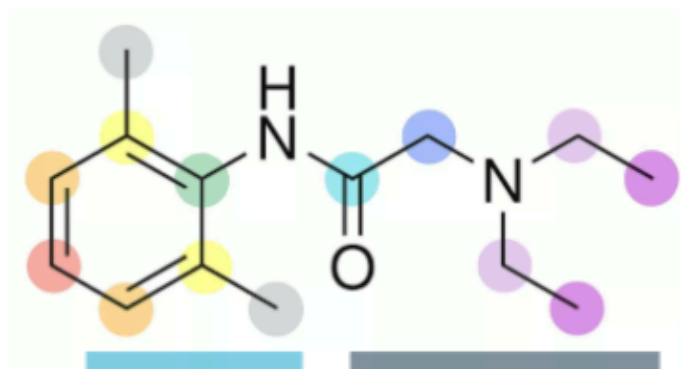
- The following hydrogens are already assigned in the table:
  - The hydrogens directly attached to the aromatic ring (orange and red highlights)
  - The terminal methyl groups (purple highlights)
- The 2 methyl groups (grey highlight) attached to the aromatic ring are identical and have no neighbouring hydrogens
  - This means that they have no splitting pattern and are seen as a singlet accounting for 6 hydrogens
  - The data table suggests that they appear in the range of 2.3 – 3.0
- The CH group (blue highlight) adjacent to the carbonyl group has no neighbouring hydrogens
  - This means that it has no splitting pattern and is seen as a singlet accounting for 1 hydrogen
  - The data table suggests that this should appear in the range of 2.2 – 3.0
- The hydrogen of the NH group (in the middle of the molecule) is an amide hydrogen with no neighbouring hydrogens
  - This means that it has no splitting pattern and is seen as a singlet accounting for 1 hydrogen
  - The data table suggests that this should appear in the range of 5.0 – 12.0

c) Explaining the splitting pattern for the absorption at δ 1.2 ppm:

- There is a neighbouring / adjacent (carbon) atom with has two protons (attached)
  OR
  There is an adjacent CH_2 group; [1 mark]

[Total: 1 mark]

- The 2 methyl groups at the end of the molecule are identical and have 2 neighbouring hydrogens
  - This means that they have a triplet splitting pattern (n + 1 = 3) accounting for 6 hydrogens
  - The data table suggests that they appear in the range of 0.9 – 1.7
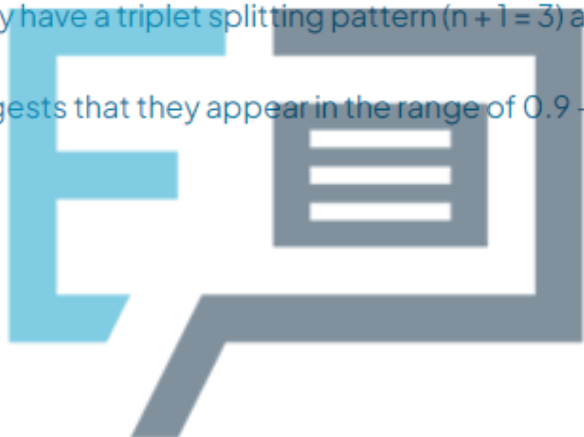
Answer 6.

a) The molecular formula of the compound is:

- Mole ratio $C : H : O = \dfrac{58.82}{12.0} : \dfrac{9.80}{1.0} : \dfrac{31.38}{16.0}$

$$= 4.90 : 9.80 : 1.96; \text{ [1 mark]}$$

- Empirical formula $= C_5H_{10}O_2$; [1 mark]
- Molecular formula $= C_5H_{10}O_2 = (5 \times 12.0) + (10 \times 1.0) + (2 \times 16.0) = 102$

  AND

  Evidence of $m/e = 102$ peak in the spectrum; [1 mark]

ALTERNATIVE

- C: $\dfrac{102 \times \left(\dfrac{58.82}{100}\right)}{12.0} = 5.00$; [1 mark]

- H: $\dfrac{102 \times \left(\dfrac{9.80}{100}\right)}{1.0} = 10.0$

  AND

- O: $\dfrac{102 \times \left(\dfrac{31.37}{100}\right)}{16.0} = 2$; [1 mark]

- Molecular formula $C_5H_{10}O_2$

  AND

  Evidence of $m/e = 102$ peak in the spectrum; [1 mark]

[Total: 3 marks]

- Use all the available information to solve the problem
  - This question gives you two routes to solving the problem if you know the percentage composition and the relative molecular mass
- Showing your steps not only is good practice but also helps you pick up on errors more easily
  - You can then still receive some marks even if you make a mistake

b) The functional groups in compound **P** and reasoning are:

- **P** does not contain a carboxylic acid
  AND
  The Na_2CO_3 (aq) test is negative; [1 mark]
- **P** does not contain an aldehyde or ketone
  AND
  The 2,4–DNP test is negative; [1 mark]
- **P** does not contain an aldehyde group
  AND
  The Tollens' test is negative; [1 mark]
- **P** could be an ester
  OR
  P could be an (insoluble) diol; [1 mark]

[Total: 4 marks]

- It is easier to say what the functional groups are not from the results of the tests
  - Negative results can be just as informative as positive results
- An ester is a good candidate as it has two oxygens and does not respond to any of the tests
  - Although esters are polar, they are not very soluble in water due to an inability to form hydrogen bonds
- Higher alcohols tend to be insoluble, but the presence of two –OH groups would increase the solubility
  - Without more information, it would be hard to say if it is a diol

c) The functional group present in compound **P** is:

- Ester; [1 mark]

Explanation:

- The peak at $\delta = 162$ ppm corresponds to the C=O of a carboxyl group; [1 mark]
- The peak at $\delta = 63$ ppm corresponds to a C–O; [1 mark]

[Total: 3 marks]

- This is simply a case of matching up the spectrum with ranges given in Table 1.2
  - C–O is found at $\delta = 50 - 70$
  - C=O is found at $\delta = 160 - 185$
- An ester is consistent with the information given in parts (a) and (b)
  - Two oxygens are present
  - It is a functional group that does not react with Na_2CO_3, 2,4–DNPH or Tollens' reagent

d) The structure of compound **P** is:

- Correct structure; [1 mark]

$$H_3C \!-\!\!-\!\! CH_2 \!-\!\!-\!\! \overset{\displaystyle O}{\overset{\|}{C}} \!-\!\!-\!\! O \!-\!\!-\!\! CH_2 \!-\!\!-\!\! CH_3$$
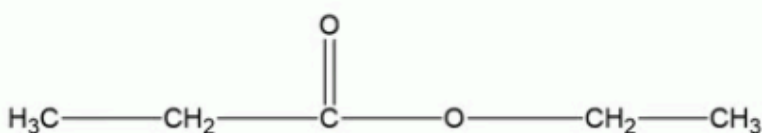
Explanation:

Any **two** from:

- The spectrum shows two quartets and two triplets; [1 mark]
- A quartet and triplet in the same spectrum is indicative of an ethyl / CH_3CH_2 group; [1 mark]
- The spectrum shows two non-identical ethyl groups; [1 mark]

[Total: 3 marks]

- There are several isomeric esters possible with this molecular formula
  - It is the splitting patterns in the proton NMR that allow you to deduce the specific isomer
- Tell-tale patterns like doublets, triplets and quartets enable you to determine neighbouring protons and hence the structure
  - Make sure you know where characteristic functional groups are found in the spectrum as you can also be asked to identify particular peaks in ^{13}C or ^1H NMR spectra
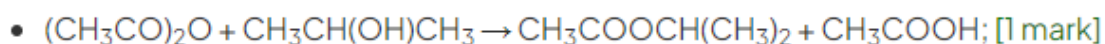
**Answer 7.**

a) The equation, using structural formulae, for the reaction of propan-2-ol and ethanoic anhydride is:

- $(CH_3CO)_2O + CH_3CH(OH)CH_3 \rightarrow CH_3COOCH(CH_3)_2 + CH_3COOH$; [1 mark]

[Total: 1 mark]

- **Remember:** The reaction of an alcohol and an acid anhydride forms an ester and ethanoic acid
  - The most common mistake is to include water as the second product, presumable out of habit of writing "ester + water"
- **Careful:** The question asks for structural formulae, so take your time to get them correct
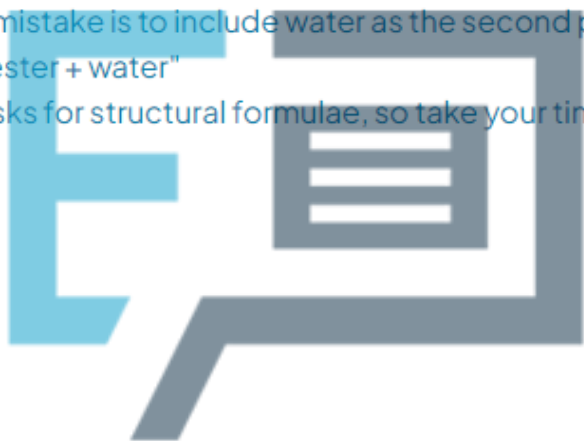
b)

i) A liquid stationary phase separates the organic compounds in a mixture by:

- Their / the compounds relative solubility; [1 mark]

ii) Predicting the separation of these four compounds using the alkane stationary phase, including relative retention times:

- Both esters have the same functional groups
  AND
  They will have similar retention times in the column; [1 mark]
- Alcohols are not soluble in an alkane stationary phase, so will have a short retention time
  AND
  Alkanes are highly soluble in an alkane stationary phase, so will have a long retention time; [1 mark]

[Total: 3 marks]

- **Remember:** Separation in chromatography is due to the solubility of compounds in relation to the other compounds in the mixture
  - The four compounds in the mixture are the two esters and the two contaminants; an alkane and an alcohol
- Retention times are based on the attraction of the compounds to the mobile / stationary phases
  - Non-polar compounds, such as alkane, are more attracted to the non-polar stationary phase resulting in longer retention times
  - Polar compounds, such as esters and alcohols, are less attracted to the non-polar stationary phase resulting in shorter retention times
- Without knowing further information, you can only state that the esters will have similar retention times because they have the same functional groups

c) To identify and draw the ester:

Empirical / molecular formula calculation:

- Mole ratio C : H : O = $\dfrac{66.63}{12.0}$: $\dfrac{11.18}{1.0}$: $\dfrac{22.19}{16.0}$

  OR

  Mole ratio C : H : O = 5.55 : 11.18 : 1.39; [1 mark]

- Empirical ratio C : H : O = $\dfrac{5.55}{1.39}$: $\dfrac{11.18}{1.39}$: $\dfrac{1.39}{1.39}$ **OR** = 4 : 8 : 1
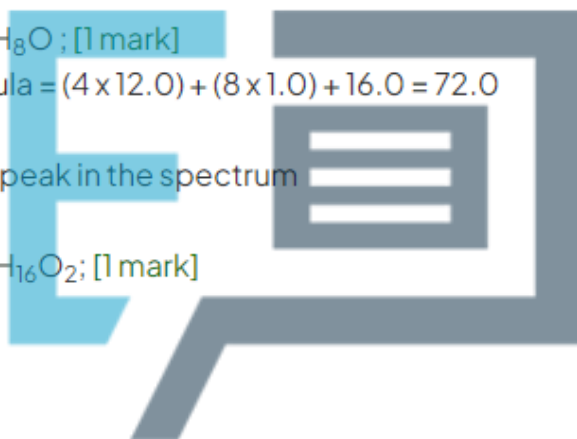
  AND

  Empirical formula = C_4H_8O ; [1 mark]

- Mass of empirical formula = (4 x 12.0) + (8 x 1.0) + 16.0 = 72.0

  AND

  Evidence of m/e = 144 peak in the spectrum

  AND

  Molecular formula = $C_8H_{16}O_2$; [1 mark]

Proton NMR data:

- Peak at ~3.8 ppm: $-CH_2-O$ due to the number of protons indicated on the spectrum
  AND
  Quartet splitting pattern suggests a neighbouring methyl group; [1 mark]
- Peak at ~2.2 ppm: $HC-C=O$
  AND
  Singlet splitting pattern suggests a neighbouring carbon atom <u>with no hydrogens attached</u>; [1 mark]
- Peak at ~1.3 ppm: $R-CH$ as a methyl group due to the number of protons indicated on the spectrum
  AND
  Triplet splitting pattern suggests a neighbouring CH_2 group; [1 mark]
- Peak at ~0.9 ppm: $R-CH$
  AND
  Likely to be $R-(CH_3)_3$ due to the number of protons indicated on the spectrum
  AND
 Singlet splitting pattern suggests a neighbouring carbon atom <u>with no hydrogens attached</u>; [1 mark]

Structure:

 ; [1 mark]
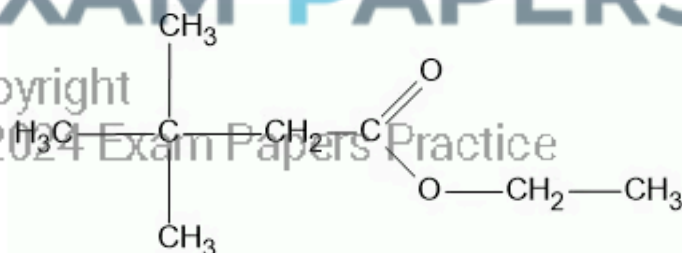
[Total: 8 marks]

- Use all the available information to solve the problem
  - Percentage composition by mass to determine the empirical formula
  - Mass spectrum to determine the molecular formula, in conjunction with your empirical formula calculation
  - NMR data to identify fragments / likely structures with the overall structure
- You **need** to show your working on this type of question as it is relatively easy to make a mistake without realising
  - If you do, you might still gain marks for some of the other points that you make in your answer
- NMR data
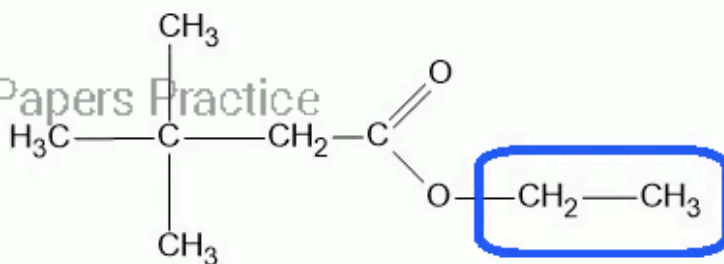 - You know that the compound is an ester
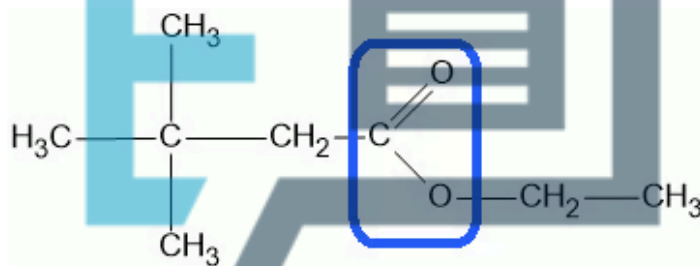
  - From the peaks at ~3.8 and ~1.3 ppm, you know that there is a CH_2 group attached to the oxygen atom AND that the CH_2 has a methyl / CH_3 group attached
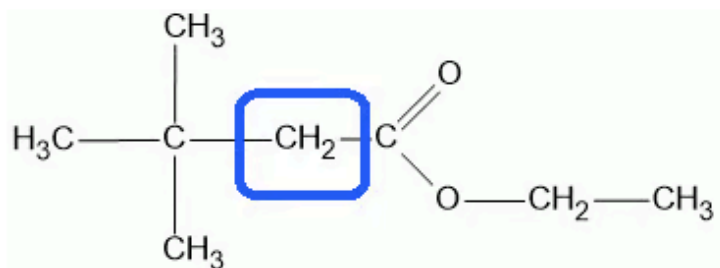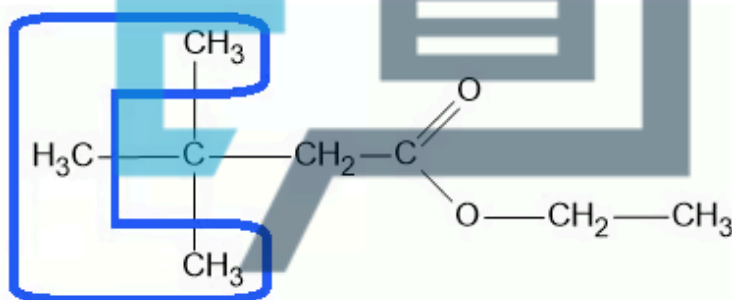
- From the peak at 2.2 ppm, you know that there is a CH_2 with a neighbouring C=O and that it also has a carbon atom with no attached hydrogens

- From the peak at ~0.9 ppm, you know that there are 3 methyl groups attached to a carbon atom with no attached hydrogens