
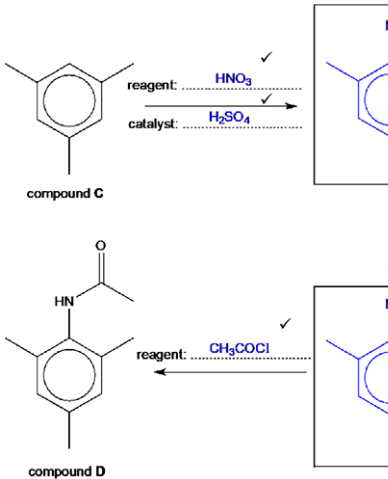


Mark scheme - Spectroscopy

Question	Answer/Indicative content	Marks	Guidance
1 a	<p>Please refer to the marking instructions on page 4 of this mark scheme for guidance on how to mark this question.</p> <p>Level 3 (5–6 marks) Structure I has a viable chemical structure of C₆H₉NO₂ which has the key features consistent with spectral data AND Most of the data analysed</p> <p><i>There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.</i></p> <p>Level 2 (3–4 marks) Compound I has a viable chemical structure of C₆H₉NO₂ with most of the key features consistent with spectral data AND Some of the spectral data analysed.</p> <p><i>There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.</i></p> <p>Level 1 (1–2 marks) Correct determination of empirical formula and/or molecular formula. OR Analyses some of the IR and NMR data. OR Analyses most of the NMR data.</p> <p><i>There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.</i></p> <p>0 marks No response or no response worthy of credit.</p>	6 (AO3. 1 × 4) (AO3. 2 × 2)	<p>Indicative scientific points: Empirical and Molecular Formulae</p> $\begin{array}{cccc} \text{C} & : & \text{H} & : & \text{N} & : & \text{O} \\ = & \frac{56.69}{12.0} & : & \frac{7.09}{1.0} & : & \frac{11.02}{14.0} & : & \frac{25.20}{16.0} \\ \text{OR} & 4.72 & : & 7.09 & : & 0.787 & : & 1.575 \\ = & 6 & : & 9 & : & 1 & : & 2 \end{array}$ <ul style="list-style-type: none"> Empirical formula = C₆H₉NO₂ m/z = 127.0 and empirical formula mass (127) used to determine molecular formula as C₆H₉NO₂ <p>Structures of compound I</p> <p>OR</p> <p>OR</p> <p>ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</p> <p>Key features</p> <ul style="list-style-type: none"> C≡N C=O in aldehyde, ketone, ester, amide, acid anhydride CH₃ group that would give a doublet CH₃ group that would give a triplet CH₂ group that would give a quartet <p>¹H NMR and IR analysis</p> <p>¹H NMR spectrum</p> <ul style="list-style-type: none"> δ = 4.2 ppm, quartet, 2H CH₃–CH₂–O δ = 2.9 ppm, quartet, 1H CO–CH–CH₃ δ = 1.7 ppm, doublet, 3H CO–CH–CH₃ δ = 1.3 ppm, triplet, 3H CH₃–CH₂ <p>IR spectrum</p> <ul style="list-style-type: none"> peak at 1750 (cm⁻¹) is C=O peak at 2280 (cm⁻¹) is C≡N <p>ALLOW ranges from <i>Data Sheet</i> IGNORE references to C–O peaks</p> <p>Examiner's Comments</p> <p>Candidates achieving Level 2 had most of the key features, e.g. CN,</p>

6.3.2 Spectroscopy

				<p>C=O bond and a methyl group but did not consider the splitting patterns seen in the NMR. Most candidates could correctly work out the empirical and molecular formula but then did not use their analysis of the NMR and IR data to suggest a structure. This limited their response to Level 1. The IR spectrum had no O-H peak from an alcohol or carboxylic acid, but candidates often included these groups in their suggested structures.</p>						
	b	<p>CDCl₃ used as a solvent ✓</p> <p>D₂O used to identify OH OR NH protons ✓</p>	<p>2 (AO1. 1×2)</p>	<p>Example and use required for each mark</p> <p>ALLOW for 1 mark, D₂O as a solvent</p> <p>Examiner's Comments</p> <p> Misconception</p> <p>The use of deuterated compounds in NMR analysis was often explained the use in terms of lack of spin but did not give examples (e.g. CDCl₃ as a solvent or D₂O as for identifying OH/NH protons)</p>						
		Total	8							
2	i	<table border="1"> <thead> <tr> <th></th> <th>Compound C</th> <th>Compound D</th> </tr> </thead> <tbody> <tr> <td>Number of peaks</td> <td>3 ✓</td> <td>8 ✓</td> </tr> </tbody> </table>		Compound C	Compound D	Number of peaks	3 ✓	8 ✓	<p>2 (AO3. 2)</p>	
	Compound C	Compound D								
Number of peaks	3 ✓	8 ✓								
	i		<p>5 (AO3. 2×5)</p>	<p>ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</p> <p>IGNORE names for organic intermediates (question asks for structures)</p> <p>ALLOW names of reagents and catalyst</p> <p>Around top arrow, ALLOW 1 of 2 marks if HNO₃ and H₂SO₄ swapped. i.e.</p> <p>reagent: $\xrightarrow{\text{H}_2\text{SO}_4}$</p> <p>catalyst: $\xrightarrow{\text{HNO}_3}$</p> <p>IGNORE references to concentration</p> <p>ALLOW (CH₃CO)₂O for left arrow</p> <p>IGNORE CH₃COOH</p> <p>IGNORE acyl chloride</p> <p>DO NOT ALLOW AlCl₃/FeCl₃/Fe₄</p>						
		Total	7							
3	i		<p>5 → 4 max</p>	<p>ANNOTATE WITH TICKS AND CROSSES, etc.</p> <p>----- ALLOW ORA throughout</p>						

6.3.2 Spectroscopy

	<p>Comparison of branching and points of contact e.g. CH₃CH₂CH₂NH₂ has longer chain / straight chain / no branches AND e.g. CH₃CH₂CH₂NH₂ has more points of contact / more surface interaction (between molecules) ✓</p> <p>Relative strength of force e.g. CH₃CH₂CH₂NH₂ has stronger/more induced dipole(–dipole) interactions OR London forces ✓</p> <hr/> <p>Hydrogen bonds CH₃CH₂CH₂NH₂ OR (CH₃)₂CHNH₂ have hydrogen/H bonds OR (CH₃)₃N has no hydrogen/H bonds ✓</p> <p>Relative strength of force Hydrogen bonds are stronger than London forces /permanent dipole interactions ✓</p> <hr/> <p>Comparison of energy required to break force e.g. More energy to break/overcome London forces/intermolecular forces in CH₃CH₂CH₂NH₂ OR More energy is needed to break H bonds (than London forces) ✓</p>	<p>(AO 1.2)</p> <p>(AO 2.1)</p> <p>(AO 1.2)</p> <p>(AO 2.1)</p>	<p>ALLOW 'The straighter the chain, the more points of contact'</p> <p>IGNORE comparison using 'primary', 'secondary' and 'tertiary'. <i>Comparison of branching is required.</i></p> <p>For London forces,</p> <ul style="list-style-type: none"> ALLOW induced dipole(–dipole) interactions IGNORE IDID OR van der Waals' forces/VDW <p>DO NOT ALLOW CH₃CH₂CH₂NH₂ has more electrons <i>(number of electrons are the same)</i></p> <p>DO NOT ALLOW 'more energy to break covalent bonds</p> <p>ALLOW little energy is required to break London forces (compared with H bonds)</p> <p>Examiner's Comments</p> <p>Candidates were expected to explain the different boiling points of three amines. Most candidates linked increased branching with less surface contact between molecules, leading to weaker induced dipole interactions (London forces). Fewer candidates linked the decreasing boiling points to less energy being required to break the intermolecular bonds.</p> <p>The highest performing candidates recognised the large difference between the boiling points of the primary and tertiary amines. They then identified the cause: primary amines form hydrogen bonds but tertiary amines do not.</p> <p>This question was answered reasonably well with fewer candidates than in the past describing relative strengths of covalent bonds, a common misconception.</p>
i	<p>FIRST CHECK MOLECULAR FORMULA and STRUCTURE IF molecular formula = C₅H₁₃N AND correct structure AND evidence of ideal gas equation → 6 marks Correct up to 87 AND C₅H₁₃N → 5 marks Correct up to 87 → 4 marks</p> <hr/>	<p>6</p> <p>(AO 2.2×4)</p>	<p>IF $n = \frac{pV}{RT}$ is omitted, ALLOW when values are substituted into rearranged ideal gas equation.</p>

6.3.2 Spectroscopy

Rearranging ideal gas equation

$$n = \frac{pV}{RT} \checkmark$$

Unit conversion AND substitution into

$$n = \frac{pV}{RT} :$$

- $R = 8.314$ OR 8.31
- $V = 72(.0) \times 10^{-6}$
- T in K: 373 K

e.g.

$$\frac{1.00 \times 10^5 \times 72.0 \times 10^{-6}}{8.314 \times 373} \checkmark$$

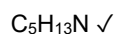
Calculation of n

$$n = 2.32 \times 10^{-3} \text{ (mol)} \checkmark$$

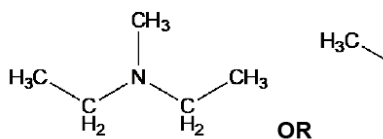
Calculation of M

$$M = \frac{0.202}{2.32 \times 10^{-3}} = 87 \checkmark$$

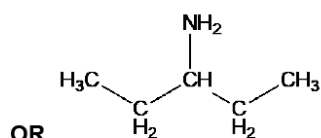
Molecular formula



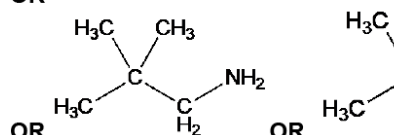
Molecular formula required

Structure of amine A from $\text{C}_5\text{H}_{13}\text{N}$ ✓

OR



OR



OR

Use of 24000

3 marks max possible for use of 72.0 cm^3 OR 0.720 dm^3 by ECF

Calculation

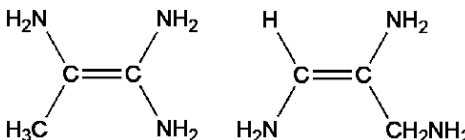
e.g. $n = \frac{72.0}{24000} = 3.00 \times$ **No mark**
(calculati

(AO
3.2)(AO
3.2)Calculator: $n = 2.321740325 \times 10^{-3}$ from 8.314From 8.31, $n = 2.322857889 \times 10^{-3}$

ALLOW elements in any order

ALLOW molecular formula = $\text{C}_3\text{H}_9\text{N}_3$ ALLOW other molecular formulae of an amine that has $M = 87$, e.g. $\text{C}_4\text{H}_9\text{NO}$

ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous

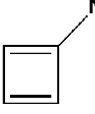
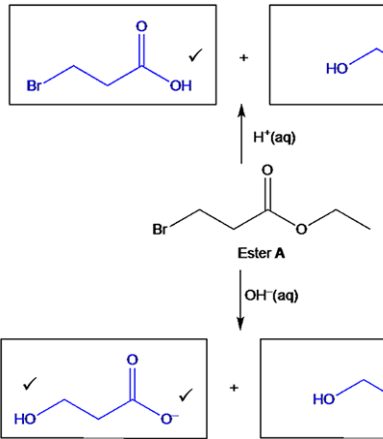
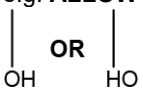

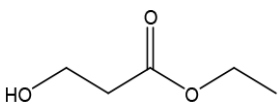
ALLOW structures below from molecular formula = $\text{C}_3\text{H}_9\text{N}_3$ ALLOW ECF but only if structure has calculated M_r AND has 3 peaks in ^{13}C NMR spectrum.Examiner's Comments

Most candidates rearranged the ideal gas equation correctly to make n the subject. They then substituted correct values for p , V , R and T into the equation, with correct unit conversions. Most candidates then calculated n correctly as 2.32×10^{-3} and combined this value with the mass of 0.202 g to derive the molecular formula as 87 .



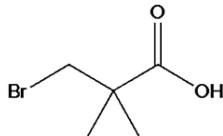
Lower-attaining candidates often made an error in their conversion of cm^3 into m^3 , by multiplying by 10^{-3} rather than 10^{-6} . This error resulted in a value of n as 2.32 and the unrealistic molecular mass of 8.7×10^{-3} , from which a molecular formula is impossible. Candidates in this position are advised to check back at the unit conversions in the working. Very few candidates did not convert 100°C into 373 K .

Candidates with the correct molecular formula of 87 usually suggested

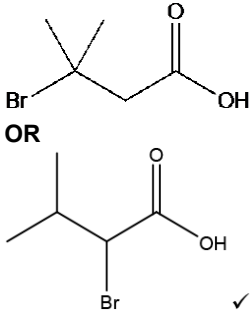
6.3.2 Spectroscopy

		<p>on much simpler)</p> $M = \frac{0.202}{3.00 \times 10^{-3}} = 67.3$ <p>EC ✓ F</p> <p>Molecular formula = C₄H₅N ✓ EC F</p> <p>Structure  ✓ EC F</p>		<p>C₅H₁₃N as the molecular formula. A significant number quoted C₅H₁₁NH₂. This response was not credited as it is not a 'molecular' formula. There are several possible structures of C₅H₁₃N with three ¹³C NMR peaks and any were credited.</p> <p>Error carried forward was applied from a different molecular mass for both the molecular formula and a structure. This emphasises the importance of working within calculation; credit will always be given for a correct method.</p> <p>Instead of using the ideal gas equation, some candidates used the molar gas constant at room temperature and pressure, 24.0 dm³, which gives a molecular mass of 67. This simplified approach could only gain the final 2 marks for this question: a molecular formula (with an error carried forward value of 67, e.g. C₄H₅N) and a structure of an amine with this molecular formula and 3 peaks in the ¹³C NMR spectrum.</p>
		Total	10	
4	a i	ethyl 3-bromopropanoate ✓	1(AO 1.2)	<p>ALLOW one word: ethyl3-bromopropanoate OR more words, e.g. ethyl 3-bromo propanoate</p> <p>IGNORE lack of hyphens, or addition of commas</p> <p>Examiner's Comments</p> <p>This demanding question discriminated well. The most able candidates were able to apply the nomenclature rules to name ester A correctly as ethyl 3-bromopropanoate. Common incorrect responses included ethyl 1-bromopropanoate and ethyl 4-bromopropanoate.</p>
	i		5(AO 2.5 ×5)	<p>ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</p> <p>ALLOW in either order</p> <p>ALLOW any vertical bond to the OH group e.g. ALLOW</p> <p></p> <p>DO NOT ALLOW OH-</p> <p>ALLOW in either order For reaction with OH⁻, ALLOW one mark for</p> <p></p> <p>OR</p> <p></p>

6.3.2 Spectroscopy

				<p>Examiner's Comments</p> <p>This question required candidates to apply their knowledge of hydrolysis reactions to ester A. The majority of candidates were able to show 3-bromopropanoic acid and ethanol in the top two boxes to secure two marks. The organic products from the alkaline hydrolysis proved more difficult. Many candidates identified ethanol as a product in one of the lower boxes but lower ability responses showed the ethoxide ion. Some candidates drew the 3-bromopropanoate ion as the other product. Higher ability candidates realised that the Br atom would be replaced by an OH group and the best responses showed the correct carboxylate ion. Examiners were encouraged by the number of excellent responses seen and the majority of candidates scored 4 or 5 marks.</p>															
	i i i	hydrolysis ✓	1(AO 1.1)	<p>IGNORE 'acid' and 'alkaline'</p> <p>IGNORE nucleophilic substitution</p>															
	b	<table border="1"> <thead> <tr> <th>Proton environment</th> <th>Chemical shift</th> <th>Splitting pattern</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>3.0–4.3</td> <td>Triplet</td> </tr> <tr> <td>2</td> <td>2.0–3.0</td> <td>Triplet</td> </tr> <tr> <td>3</td> <td>3.0–4.3</td> <td>Quartet</td> </tr> <tr> <td>4</td> <td>0.5–1.9</td> <td>Triplet</td> </tr> </tbody> </table> <p>Mark by column Chemical shift: all 4 correct ✓✓ 3 correct ✓ Splitting pattern: all 4 correct ✓✓ 3 correct ✓</p>	Proton environment	Chemical shift	Splitting pattern	1	3.0–4.3	Triplet	2	2.0–3.0	Triplet	3	3.0–4.3	Quartet	4	0.5–1.9	Triplet	4(AO 3.1 × 4)	<p>ALLOW δ values ± 0.2 ppm, as a range or a value within the range</p> <p>ALLOW integers for δ values e.g. 2 is equivalent to 2.0</p> <p>ALLOW quadruplet for quartet</p> <p>ALLOW diagrams to show splitting pattern e.g.</p> <p> for triplet</p> <p> for quartet</p> <p>ALLOW splitting patterns shown as numbers i.e. '3' for triplet, '4' for quartet</p> <p>Examiner's Comments</p> <p>This question was answered well and most candidates scored full marks. A common error was the chemical shift of environment 2, which was sometimes shown as 9.0-10.0. Some candidates gave incorrect splitting patterns for environment 2, stating it would give a singlet, rather than a triplet. This is presumably the result of focusing on the carbon atom to the right of the environment with no H atoms. Candidates should be reminded to consider adjacent carbon atoms on both sides of a particular environment, rather than just looking in one direction.</p>
Proton environment	Chemical shift	Splitting pattern																	
1	3.0–4.3	Triplet																	
2	2.0–3.0	Triplet																	
3	3.0–4.3	Quartet																	
4	0.5–1.9	Triplet																	
	c	 <p>OR</p>	1(AO 3.1)	<p>ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</p> <p>Examiner's Comments</p> <p>This question required candidates to use both pieces of information to deduce that B was a carboxylic acid with two equivalent carbon atoms.</p>															

6.3.2 Spectroscopy

	 <p>Br OR</p> <p>Br ✓</p>		<p>Many candidates were able to suggest a suitable structure. However some candidates did not use all the information and it was common to see responses that showed an ester or a straight chain carboxylic acid.</p>
d	<p>IF answer on answer line = 24018, AWARD 2 marks</p> <p>IF answer on answer line = 27600, AWARD 1 mark</p> <p>-----</p> <p>--</p> <p>Relative mass of 200 molecules = $200 \times 138 = 27600 \checkmark$</p> <p>$M_r$ of polyester = $27600 - 199 \times 18$ $= 24018 \checkmark$</p>	2(AO 2.2 ×2)	<p>ALLOW ECF from incorrect M_r</p> <p>Alternative method based on repeat unit: M_r of 200 repeat units = $200 \times 120 = 24000 \checkmark$ M_r of polymer = $24000 + 1 + 17 = 24018 \checkmark$</p> <p>Examiner's Comments</p> <p>A variety of responses was seen in this demanding question. In general candidates adopted one of two approaches. The most common was to multiply the M_r of 2-hydroxybenzoic acid by 200 and then subtract the mass of the 199 water molecules removed during polymerisation. The other approach used the M_r of the repeat unit. This was multiplied by 200 and the mass of H and OH at each end of the polymer was added to give the final answer. Many candidates were successful with the first step of their approach, but the best responses included the second step taking into account the M_r of water. A significant number of candidates used an incorrect value for the M_r in their first step. Candidates are advised to draw out the structure of a compound before determining the M_r. This is particularly important when only a name is given in the question.</p>
e i	<p><i>* Refer to marking instructions on page 4 of mark scheme for guidance on marking this question.</i></p> <p>Level 3 (5-6 marks) Correct calculation of the mass of $(\text{CH}_3)_2\text{CHCHO}$. AND Planned synthesis includes oxidation of aldehyde and formation of ester C with most of the reagents and conditions identified and equations are mostly correct.</p> <p><i>There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.</i></p> <p>Level 2 (3-4 marks) Calculation of the mass of $(\text{CH}_3)_2\text{CHCHO}$ is partly correct AND Planned synthesis includes</p>	6 (AO 3.3 ×6)	<p>Indicative scientific points may include:</p> <p>Calculation of mass of $(\text{CH}_3)_2\text{CHCHO}$</p> <p>Using moles</p> <ul style="list-style-type: none"> $n(\text{ester}) = \frac{12.75}{102.0}$ $= 0.125 \text{ (mol)}$ $n((\text{CH}_3)_2\text{CHCHO}) = 0.125 \times \frac{100}{40}$ $= 0.3125 \text{ (mol)}$ Mass of $(\text{CH}_3)_2\text{CHCHO} = 72.0 \times 0.3125 = 22.5 \text{ g}$ <p>Using mass</p> <ul style="list-style-type: none"> Theoretical mass of ester = $12.75 \times \frac{100}{40}$ $= 31.875 \text{ (g)}$ Theoretical $n((\text{CH}_3)_2\text{CHCHO}) = \frac{31.875}{102}$ $= 0.3125 \text{ (mol)}$ Mass of $(\text{CH}_3)_2\text{CHCHO} = 72.0 \times 0.3125 = 22.5 \text{ g}$ <p>ALLOW small slip/rounding errors such as errors in M_r e.g. use of 71 instead of 72 for $(\text{CH}_3)_2\text{CHCHO}$</p> <p>-----</p> <p>Examples of partly correct calculations</p> <p>Mass = 3.60 g from $0.125 \times \frac{40}{100} \times 72$</p>

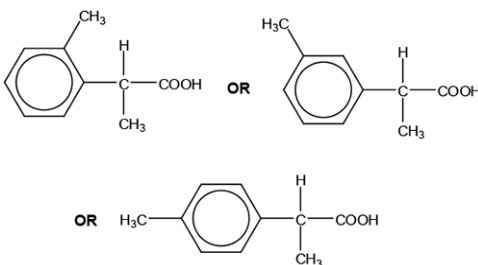
6.3.2 Spectroscopy

	<p>oxidation of aldehyde and formation of ester C with some of the reagents and conditions identified</p> <p>OR</p> <p>Attempts to calculate mass of (CH₃)₂CHCHO but makes little progress</p> <p>AND</p> <p>Planned synthesis includes oxidation of aldehyde and formation of ester C with most of the reagents and conditions identified and equations for each step are mostly correct</p> <p><i>There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.</i></p> <p>Level 1 (1-2 marks)</p> <p>Calculation of the mass of (CH₃)₂CHCHO is partly correct</p> <p>OR</p> <p>Planned synthesis includes both steps with some of the reagents and conditions identified</p> <p>OR</p> <p>Attempts equations for both steps but these may contain errors</p> <p>OR</p> <p>Describes one step of the synthesis with reagents, conditions and equation mostly correct</p> <p><i>There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.</i></p> <p>0 marks</p> <p>No response or no response worthy of credit.</p>		<p style="text-align: right;">(% yield inverted)</p> <p>Mass = 9.00 g from 0.125 × 72</p> <p style="text-align: right;">(% yield omitted)</p> <p><u>Synthesis: reagents and conditions</u></p> <p>Step 1: Oxidation of aldehyde (CH₃)₂CHCHO</p> <ul style="list-style-type: none"> • Reagents: Cr₂O₇²⁻/H⁺ • Conditions: reflux • Equation: (CH₃)₂CHCHO + [O] → (CH₃)₂CHCOOH <p>Step 2: Formation of ester C</p> <ul style="list-style-type: none"> • Reagents: methylpropanoic acid/(CH₃)₂CHCOOH and methanol/CH₃OH • Conditions: acid (catalyst) reflux/heat • Equation: (CH₃)₂CHCOOH + CH₃OH → (CH₃)₂CHCOOCH₃ + H₂O <p>IGNORE attempts to form methanol in synthesis</p> <p><u>Examiner's Comments</u></p> <p>This question was marked using a level of response mark scheme. Most candidates gave a response worthy of at least Level 2 (3-4 marks) by either providing the synthetic steps with reagents and/or equations for the synthesis of ester C as well as calculating the mass of 2-methylpropanal required. Exemplar 3, below, shows a frequently seen Level 2 response. The best performing candidates determined the mass correctly and showed the synthesis efficiently, using equations to communicate the preparation of ester C and received Level 3 (5-6 marks). Some responses focused solely on the 2-methylpropanal and suggested it would be both oxidised and reduced with each of the products being used to form an ester. Others omitted the mass calculation or gave only a partial synthesis. Such responses received Level 1 (1-2 marks).</p> <p>Exemplar 3</p>
--	---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------	--	---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------

6.3.2 Spectroscopy

		<p>① Oxidation of 2-methylpropanal to form 2-methylpropanoic acid using $K_2Cr_2O_7/H^+$ under reflux.</p> $CH_3C(CH_3)_2CHO + [O] \rightarrow CH_3C(CH_3)_2COOH$ <p>② Esterification of 2-methylpropanoic acid with methanol to form ester C.</p> $CH_3C(CH_3)_2COOH + CH_3OH \rightarrow CH_3C(CH_3)_2COOCH_3 + H_2O$ <p>Ester C: 2-methylpropanoate O:4; 1</p> <p>\therefore 2-methylpropanal mass required = $\frac{12.75}{0.4} = 31.875g$ $= 31.88g$ (to 2 s.p.)</p> <p>This response includes an excellent description of the synthesis of ester C. Each step is labelled clearly with the most of the reagents and conditions stated and correct equations. The candidate makes little progress with the calculation of the mass of 2-methylpropanal required, completing only the first step. This response satisfies the Level 2 criteria. The information is provided is relevant and presented with a clear logical structure and was therefore given the upper mark within the level and achieved four marks.</p> <p>The presentation of the synthesis by equations rather than words is an excellent strategy. Candidates are advised to adopt such an approach in questions like this as it allows them develop and clear line of reasoning without the need to write lots of unnecessary text.</p>
i	<p>Y (43) = $(CH_3)_2CH^+$ ✓</p> <p>Z (71) $(CH_3)_2CHCO^+$ ✓</p> <p>If '+' charge is missing/incorrect but the structures of both fragments are correct, award one mark</p>	<p>ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</p> <p>ALLOW positive charge to be anywhere on the structure</p> <p>For Y and Z, ALLOW structure of a feasible fragment ion formed from ester C</p> <div style="text-align: center;"> <p>Ester C</p> </div> <p>e.g. Y (43) = CH_3OC^+ Z (71) = $^+CCOOCH_3$</p> <p>ALLOW 1 mark if both correct ions are shown but in the incorrect columns</p> <p>ALLOW 1 mark for both correct ions if one or both have an 'end bond'</p> <p>ALLOW 1 mark if both ions are shown using correct molecular formulae</p> <p>Examiner's Comments</p> <p>Most candidates were able to provide a correct structure for each of the ions responsible for the peaks labelled Y and Z. Some candidates omitted the charge, or included 'end bonds'. These responses were able</p>

6.3.2 Spectroscopy

				to achieve one mark if both fragments were correct. So the majority of candidates scored one or two marks in this part.
		Total	22	
5		<p><i>* Please refer to the marking instructions on page 4 of this mark scheme for guidance on how to mark this question.</i></p> <p>Level 3 (5–6 marks) Structure is <chem>CH3C6H4CH(CH3)COOH</chem> AND Most of the data analysed.</p> <p><i>There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.</i></p> <p>Level 2 (3–4 marks) A viable aromatic structure of <chem>C10H12O2</chem> that contains C=O AND most key features consistent with spectral data AND Some of the spectral data analysed</p> <p><i>There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.</i></p> <p>Level 1 (1–2 marks) Correct determination of empirical formula and/or molecular formula. OR Analyses some of the IR and NMR data. OR Analyses most of the NMR data.</p> <p><i>There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.</i></p> <p>0 marks No response or no response worthy of credit.</p>	<p>Indicative scientific points:</p> <p>Empirical and Molecular Formulae</p> <ul style="list-style-type: none"> $C : H : O = \frac{73.17}{12.0} : \frac{7.32}{1.0} : \frac{19.51}{16.0}$ $= 6.10 : 7.32 : 1.22$ $= 5 : 6 : 1$ Empirical formula = <chem>C5H6O</chem> uses $m/z = 164.0$ to determine molecular formula as <chem>C10H12O2</chem> <p>Structure ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</p> <p>Key features of an aromatic structure consistent with spectral data</p> <ul style="list-style-type: none"> COOH group 4 aromatic H atoms single H atom that would give a quartet CH₃ group that would give a doublet CH₃ group that would give a singlet <p>Correct Structure</p> <ul style="list-style-type: none"> <chem>CH3C6H4CH(CH3)COOH</chem> ALLOW 2-, 3- OR 4- substitution of ring i.e.  <p>Spectral analysis</p> <p>¹H NMR</p> <ul style="list-style-type: none"> $\delta = 1.6$ ppm, doublet, 3H CH₃-CH- $\delta = 2.3$ ppm, singlet, 3H Ar-CH₃ $\delta = 2.7$ ppm, quartet, 1H CO-CH-CH₃ OR Ar-CH-CH₃ / C₆H₅-CH-CH₃ $\delta = 7.1-7.5$ ppm, multiplet, 4H C₆H₄- <p>ALLOW approximate values for chemical shifts.</p> <p>IR:</p>	

- peak at 2300–3700 (cm^{-1}) is O–H
- peak at ~ 1720 (cm^{-1}) is C=O
- unknown is a carboxylic acid

ALLOW ranges from *Data Sheet*

IGNORE references to C–O peaks

Examiner's Comments

Candidates are confident in tackling questions requiring spectral analysis. Most candidates were able to determine the empirical and molecular formula of the unknown compound and analyse the IR and NMR data. A number of excellent responses were seen which included interpretation of the peak splitting in the NMR spectrum. However, many candidates were unable to suggest a structure that matched their spectral analysis. The majority of structures seen were aromatic but not all contained the carboxylic acid group. Some candidates focused on the NMR data and suggested a structure that was consistent with some of these peaks and included a two substituents of the ring or a degree of chain branching. Lower ability responses often showed a simpler structure of a monosubstituted ring with a straight chain. Stronger responses were able to use all the data to suggest a correct structure as demonstrated in Exemplar 9. Examiners were impressed with the problem solving ability shown by candidates and a significant proportion of responses were given six marks.

Exemplar 8

C: 73.17	H: 7.32	O: 19.51
$\times 12$	$\times 1$	$\times 16$
= 60975	= 7.32	= 1.219375
$\div 1.219375$	$\div 1.219375$	$\div 1.219375$
= 5	= 6	= 1

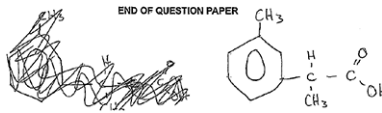
Empirical = $\text{C}_5\text{H}_6\text{O}$ The molecular mass is 164.20
The molecular formula is $\text{C}_{10}\text{H}_{12}\text{O}_2$

The sharp peak at 1700 cm^{-1} is due to a C=O group.
The broad peak at 2300 cm^{-1} is due to a O-H. This suggests a carboxylic acid is present.

Additional answer space if required

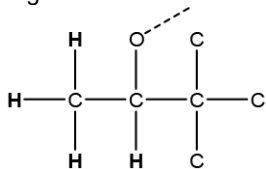
Peak at 1.5 ppm is due to a CH_3 group. It is a doublet due to being adjacent to 1 proton. Peak at 2.4 ppm is due to a CH_2 group. It is a singlet due to being adjacent to 0 protons. Peak at 7.2 ppm is due to a benzene ring. The peak at 2.7 ppm is due to a $\text{HC}-\text{C}$ group. It is a quartet due to being adjacent to 3 protons.

END OF QUESTION PAPER



This candidate starts their analysis by determining the empirical and molecular formula of the unknown compound. Next the IR and NMR data

6.3.2 Spectroscopy

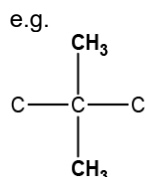
				is analysed in a clear, logical fashion. Although not shown in this report, the candidate had annotated the spectra, a good strategy. At the end of the response the candidate has determined a possible structure. Notice how the candidate has crossed out the first attempt at a structure. This is much better than rubbing out a pencil diagram and re-drawing over the space as this often leads to unclear images that are difficult for examiners to read. This candidate received full marks in this question.
		Total	6	
6		<p><i>Please refer to the marking instructions on page 5 of this mark scheme for guidance on how to mark this question.</i></p> <p>Level 3 (5–6 marks) Compound is a structure of C₆H₁₂O₃ that is consistent with splitting pattern and chemical shifts in NMR spectrum. AND Comprehensive reasoning with most of the data analysed.</p> <p><i>There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.</i></p> <p>Level 2 (3–4 marks) Compound has a feasible chemical structure that is consistent with the splitting pattern in NMR spectrum but may have incorrect molecular formula. AND Reasoning provided with some of the data analysed.</p> <p><i>There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.</i></p> <p>Level 1 (1–2 marks) Correct determination of empirical formula and/or molecular formula. OR Analyses most of the NMR data. OR Attempts to determine empirical and/or molecular formula AND analyses some of the NMR data.</p>	6	<p>Indicative scientific points:</p> <p>Empirical and Molecular Formula</p> <p>• C : H : O = 54.54/12 : 9.10/1 : 36.36/16 4.545 : 9.10 : 2.273 2 : 4 : 1</p> <p>• Empirical formula = C₂H₄O • uses <i>m/z</i> = 132.0 to determine molecular formula as C₆H₁₂O₃</p> <p><u>¹H NMR analysis</u></p> <p>Spectrum:</p> <ul style="list-style-type: none"> • δ = 4.0 ppm, quartet, 1H, CH₃–CH–O • δ = 1.3 ppm, singlet, 6H, (CH₃)₂–C • δ = 1.2 ppm, doublet, 3H, CH₃–CH– <p>Without D₂O:</p> <ul style="list-style-type: none"> • Peak at 11.0 ppm COOH or OH • peak at 3.6 ppm OH <p>Note: Data Sheet shows O–H chemical shift can occur around 11.0 ppm</p> <p>Structure ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</p> <p>Contains</p> <ul style="list-style-type: none"> • region that gives doublet and quartet <p>e.g.</p>  <ul style="list-style-type: none"> • region that gives singlet

6.3.2 Spectroscopy

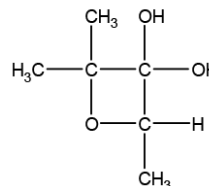
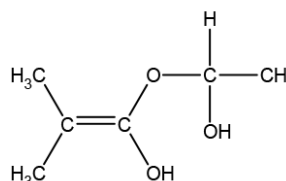
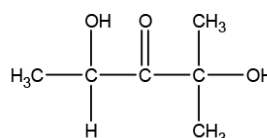
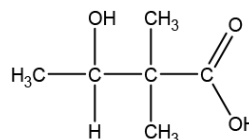
There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.

0 marks

No response or no response worthy of credit.



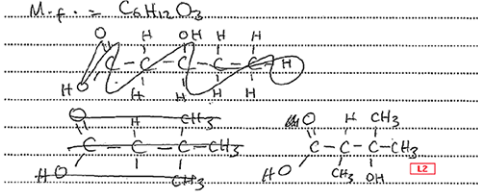
Examples of structures consistent with splitting and chemical shift in NMR



Note: there may be other possible structures that are consistent with the splitting pattern and chemical shifts in NMR – if an alternative structure is seen, please contact your team leader

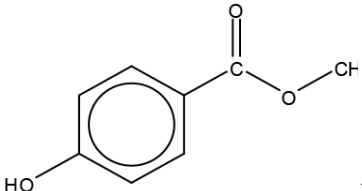
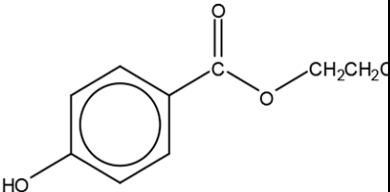
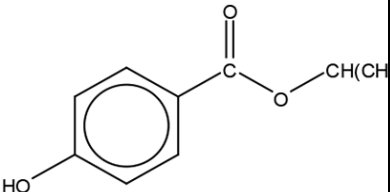
Examiner's Comments

Most candidates were able to determine the empirical and molecular formula of the unknown compound. A number of excellent and clear responses were seen, where the NMR data was explained, including interpretation of the additional peaks observed without D₂O. However many candidates were unable to suggest a structure that matched their NMR interpretation. Some candidates used the quartet, doublet and singlet to suggest a structure that would give rise to this splitting pattern, but which was not consistent with the chemical shifts, see Exemplar 12. Such responses received a level 2 mark (3-4). Stronger responses were able to use all the data to suggest a correct structure. The most common was CH₃CH(OH)C(CH₃)₂COOH although other viable structures, including CH₃CH(OH)COC(CH₃)₂OH, were also seen. Examiners were impressed with the problem solving ability shown by candidates and a significant proportion of responses were credited six marks.

			<p>Exemplar 12</p> <p>C H O 54.54 9.10 36.36 12 1 16 empirical formula = C₆H₁₂O 4.545 9.10 2.2725 Mr = 44 2 4 1 $\frac{132}{44} = 3$ molecular formula = C₆H₁₂O × 3 = C₁₈H₃₆O₃ peak at 1.2 ppm = alk HC-R. H's a doublet so adjacent carbon has 1 H. peak integral of 3 → CH₃ peak at 1.3 ppm = HC-R. Singlet so adjacent C has no protons. Integral of 6 = (CH₂)₂ Peak at 4 ppm indicative of HC-O. Quartet so adjacent C has 3 protons. Integral of 1 = CH Additional answer space if required. D₂O at 11 ppm = $\overset{\text{O}}{\parallel}\text{C}-\text{OH}$ and 3.6 ppm indicative of HC-O. M.f. = C₆H₁₂O₃ </p>
		Total	6
7	i	<p>FIRST CHECK ANSWER ON ANSWER LINE IF answer = 7.5×10^{-4} award 2 marks</p> <p>-----</p> <p>----</p> <p>[K] in mol dm⁻³</p> <p>$\frac{9.13 \times 10^{-2}}{166} = 5.50 \times 10^{-4} \text{ (mol dm}^{-3}\text{)}$</p> <p>[L] from peak areas</p>	<p>2</p> <p>If there is an alternative answer, Apply ECF</p> <p>Alternative method</p> <p>[K] in g dm⁻³ with peak area of 5.9</p> <p>$9.13 \times 10^{-2} \times \frac{5.9}{4.3}$ OR $9.13 \times 10^{-2} \times 1.37$</p> <p>= 0.125 OR 0.13 (g dm⁻³) ✓ Calculator: 0.125272093</p> <p>[L] in mol dm⁻³</p>

This logically presented Level 2 response uses the elemental analysis and mass spectrum data to determine the correct empirical and molecular formula of the unknown compound. The peaks in the NMR spectrum are analysed in detail, with a clear explanation of the splitting patterns. A comment about the two additional peaks observed when the spectrum is run without D₂O is also provided. The response concludes with a structure of C₆H₁₂O₃ that would show a singlet, doublet and quartet in its ¹H NMR spectrum. However, this structure is not consistent with the chemical shift values shown in the spectrum provided. In particular this structure would produce a quartet between 2.0–2.9 ppm, rather than at 4.0 as in the spectrum shown. Consequentially this response does not achieve Level 3. When tackling questions of this type candidates are advised to check that a proposed structure would produce peaks in the correct region of the NMR spectrum to ensure it is totally consistent with the data analysed.

6.3.2 Spectroscopy

	$5.50 \times 10^{-4} \times \frac{5.9}{4.3} \text{ OR } 5.50 \times 10^{-4} \times \frac{1.37}{1.37} \dots$ $= 7.5 \times 10^{-4} \text{ (mol dm}^{-3}\text{)} \checkmark$ <p>2 SF Required</p>		$\frac{0.125}{166} = 7.5 \times 10^{-4}$ <p>OR</p> $\frac{0.13}{166} = 7.8 \times 10^{-4} \text{ (mol dm}^{-3}\text{)} \checkmark$ <p>-----</p> <p>Common errors: Common errors: Award 1 mark for:</p> <ul style="list-style-type: none"> • 0.099 (from $\frac{9.13 \times 10^{-2}}{166} \times 180$) • 6.9×10^{-4} (from $\frac{0.125}{180}$) • 7.2×10^{-4} (from $\frac{0.13}{180}$) • 7.0×10^{-4} (from $\frac{0.25272093}{180}$) <p><u>Examiner's Comments</u></p> <p>This question required candidates to apply their knowledge of gas chromatography and the mole to solve this problem. Most candidates recognised the need to use the relative peak areas to determine the relative proportion of M. Many also realised that division by the molar mass was required to ensure the final answer was given in mol dm⁻³. However, some used molar mass of M rather than K in this step, leading to an answer of 7.0×10^{-4} mol dm⁻³.</p> <p>Answer = 7.5×10^{-4} mol dm⁻³</p>
i i	<p>ester J</p>  <p>esters L and M</p>  	3	<p>ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</p> <p>L and M can be identified either way round</p> <p>IGNORE 'C₃H₇' in L and/or M as ambiguous (<i>question requires structures</i>)</p> <p>IGNORE connectivity of phenol OH group (<i>marks are for structures of alkyl groups</i>)</p> <p><u>Examiner's Comments</u></p> <p>Examiners were encouraged by the number of good responses to this problem solving question. Most candidates achieved at least one mark in this part, often from a correct structure of J. Although many candidates deduced that the R group for both L and M consisted of 3 C atoms and 7 H atoms, only the highest ability candidates were able to join these correctly. A small but significant number of responses showed R groups</p>

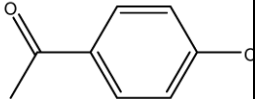
6.3.2 Spectroscopy

				that involved O atoms, despite the prompt that the R represented an alkyl group. Candidates are advised to read questions carefully.
			Total	5
8	i	<p>Number of peaks 2 marks</p> <p>2-nitrophenol AND 3-nitrophenol have six peaks/environments/types of carbon ✓</p> <p>4-nitrophenol has four peaks/environments/types of carbon ✓</p> <p>Statement 1 mark</p> <p>4-nitrophenol can be distinguished OR 2-nitrophenol and 3-nitrophenol cannot be distinguished ✓</p>	3	<p>IGNORE any numbers shown on structures</p> <p>ALLOW 1 mark only IF a response identifies that all the compounds have 6 peaks/environments/types of C</p> <p>OR all the compounds have 4 peaks/environments/types of carbon</p> <p>IGNORE chemical shifts</p> <p>DO NOT ALLOW ECF from an incorrect number of peaks/environments/types of carbon</p> <p><u>Examiner's Comments</u></p> <p>This question required candidates to apply their knowledge of ^{13}C NMR spectroscopy to deduce the number of different carbon environments in each of the nitrophenols shown. The best responses were succinct, stating that it is possible to distinguish 4-nitrophenol from the other two after deducing the correct number of carbon environments for each compound. Lower ability candidates' responses did not identify the symmetry in 4-nitrophenol and suggested all three compounds would produce six peaks, therefore making it impossible to distinguish between them.</p>
	i	<p>(In phenol) a (lone) pair of electrons on O is (partially) delocalised/donated into the π-system / ring ✓</p> <p>Electron density increases/is higher (than benzene) ✓</p> <p>ORA</p> <p>(phenol) is more susceptible to electrophilic attack</p> <p>OR</p> <p>(phenol) attracts/accepts electrophile/HNO_3 more</p> <p>OR</p> <p>(phenol) polarises electrophile/HNO_3 more ✓</p> <p>ORA</p>	3	<p>ALLOW the electron pair in the p-orbitals of the O atom becomes part of the π-system / ring</p> <p>ALLOW diagram to show movement of lone pair into ring</p> <p>ALLOW lone pair of electrons on O is (partially) drawn/ attracted/pulled/ into π-system / ring</p> <p>IGNORE activating</p> <p>IGNORE charge density</p> <p>IGNORE electronegativity</p> <p>IGNORE phenol reacts more readily (<i>no reference to electrophile</i>)</p> <p>ALLOW NO_2^+ for electrophile</p> <p><u>Examiner's Comments</u></p> <p>The relative reactivity of phenol is well known by candidates at this level and the majority scored two or three marks. Candidates who did not score full marks gave imprecise or vague explanations. This included reference to 'higher charge density' or 'higher electronegativity' of the phenol ring, rather than 'higher electron density'.</p>

6.3.2 Spectroscopy

		Total	6	
9	a	<p>Empirical formula</p> <p>Mole Ratio C : H : O = 5.88 : 5.92 : 1.47 ✓</p> <p>Empirical formula = C₄H₄O ✓</p> <p>Molecular formula</p> <p>Molecular formula = C₈H₈O₂</p> <p>AND</p> <p>Evidence of 136 in working or from labelled peak in spectrum ✓</p>	3	<p>ANNOTATE ANSWER WITH TICKS AND CROSSES</p> <p>ALLOW $\frac{70.58}{12.0} : \frac{5.92}{1.0} : \frac{23.50}{16.0}$</p> <p>ALLOW 4:4:1 if linked to C:H:O</p> <p>Alternative method for 3 marks:</p> <p>C: $\frac{136 \times 70.58/100}{12.0} = 8$</p> <p>H: $\frac{136 \times 5.92/100}{1.0} = 8$</p> <p>O: $\frac{136 \times 23.50/100}{16.0} = 2$</p> <p>Examiner Comments</p> <p>The empirical formula was correctly calculated by all but the weakest candidates. The final mark was more difficult to obtain as it required evidence that the molar mass had been determined from the mass spectrum and used in establishing the molecular formula.</p>
	b	<p>Functional groups</p> <p>Phenol AND ketone ✓</p> <p>Explanation</p> <p>Links phenol to (weak) acidity</p> <p>AND</p> <p>no reaction with Na₂CO₃ (so not carboxylic acid) ✓</p> <p>Links 2,4-DNP(H) or Brady's reagent observation to carbonyl</p> <p>AND</p> <p>Tollens' reagent observation (so not an aldehyde) ✓</p>	3	<p>DO NOT ALLOW any other functional groups for first marking point.</p> <p>ALLOW identity of functional groups in the explanation if not stated on functional group prompt line.</p> <p>ALLOW "aldehyde or ketone" in place of carbonyl</p> <p>Examiner Comments</p> <p>Many candidates were able to suggest that the compound contained a ketone but found it more difficult to indicate the presence of phenol. Approximately 20% of the entry obtained all three marks. When explaining the presence of the ketone some failed to indicate that the 2,4-DNP test indicated that the compound must contain a carbonyl and just focused on the lack of reactivity with Tollens'. Answers suggesting the molecule contained a ketone as no reaction was observed with Tollens' did not gain credit when no reference to carbonyl was seen. Those who recognised the presence of a phenol explained that the only acidic functional group that does not react with sodium carbonate is a phenol.</p>
	c	<p>Carbon NMR analysis</p> <p>Peaks between 110–160 ppm are the (four) aromatic (carbon environments) ✓</p> <p>Compound contains a C=O between 190 – 200 ppm</p> <p>AND</p> <p>Compound contains a C-C at 20 –</p>	3	<p>ALLOW peaks to be identified by:</p> <ul style="list-style-type: none"> • Peaks labelled on spectrum • Peaks indicated on a chemical structure • Peaks indicated from within text <p>Note: If identifying aromatic peaks from the spectrum all four peaks should be indicated.</p> <p>ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</p> <p>Examiner Comments</p> <p>When interpreting a carbon-13 NMR spectrum, candidates should be advised to fully label any peaks. Many candidates failed to indicate the</p>

6.3.2 Spectroscopy

		30 ppm ✓ Structure		presence of four aromatic peaks yet produced a structure containing a benzene ring. In some cases candidates did not link their answer to part (a) of the question giving structures that did not match their molecular formula.
		Total	9	
1 0		<p><i>Please refer to marking instructions on page 4 of mark scheme for guidance on how to mark this question.</i></p> <p>Level 3 (5–6 marks) A comprehensive analysis of the information available with through explanations linked to the evidence. Acid C identified as a tricarboxylic acid with a tertiary –OH group and the correct molecular formula of C₆H₈O₇.</p> <p><i>There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated</i></p> <p>Level 2 (3–4 marks) Analysis of the information available but explanations may be incomplete or there may be mistakes in calculations, although the method may be sound.</p> <p><i>There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.</i></p> <p>Level 1 (1–2 marks) A simple analysis of the information available and limited explanations which may or may not be explicitly linked to the evidence.</p> <p><i>The information is basic and communicated in an unstructured way. The information is supported by limited evidence and the relationship to the evidence may not be clear.</i></p> <p>0 marks – No response worthy of credit.</p>	6	<p>Indicative scientific points may include Identification of functional groups</p> <ul style="list-style-type: none"> • Tribasic acid → three –COOH groups <i>From 1 mol C requires 3 mol NaOH</i> • Tertiary alcohol <i>From no colour change with hot acidified dichromate(VI)</i> <p>Determination of molecular formula of C</p> <ul style="list-style-type: none"> • $M(\mathbf{C}) = \frac{2.323}{1.21 \times 10^{-2}} = 192 \text{ (g mol}^{-1}\text{)}$ <i>From 1.21 × 10⁻² mol C has a mass of 2.323 g.</i> • $192 - 3 \times 45 \text{ (3} \times \text{COOH)} - 16 \text{ (O)} = 41 \text{ 41} \rightarrow \text{C}_3\text{H}_5 \text{ (or evidence of working)}$ • Molecular formula = C₆H₈O₇ <p>Structure of citric acid</p> <ul style="list-style-type: none"> • 4 peaks in ¹³C NMR → 4 types of carbon • Correct structure of C matching evidence. <p style="text-align: center;"> $\begin{array}{c} \text{COOH} \\ \\ \text{HOOC}-\text{CH}_2-\text{C}-\text{CH}_2-\text{COOH} \\ \\ \text{OH} \end{array}$ </p> <p>NOTE: Structure below match all evidence except for ¹³C NMR. See Level 3 criteria.</p> <p style="text-align: center;"> $\begin{array}{c} \text{COOH} \\ \\ \text{HO}-\text{C}-\text{CH}_2-\text{CH}_2-\text{COOH} \\ \\ \text{COOH} \end{array} \quad \begin{array}{c} \text{COOH} \\ \\ \text{HOOC}-\text{C}-\text{CH}-\text{COOH} \\ \quad \\ \text{OH} \quad \text{CH}_3 \end{array}$ </p>

6.3.2 Spectroscopy

		Total	6	
1	a	<p>Reagent and observation</p> <p>sodium carbonate AND Fizzing/effervescence/bubbling ✓</p> <p>Equation Correctly balanced equation ✓</p> <p>e.g. $2\text{RCOOH} + \text{Na}_2\text{CO}_3 \rightarrow 2\text{RCOONa} + \text{CO}_2 + \text{H}_2\text{O}$</p>	2	<p>Note: both reagent and observation are required for first mark</p> <p>ALLOW name or formula for any suitable carbonate e.g. NaHCO_3, potassium carbonate etc.</p> <p>ALLOW reagent from equation if not stated elsewhere</p>
	i	<p>Reagent and observation</p> <p>Tollens' (reagent) AND Silver (mirror) ✓</p> <p>Equation $\text{RCHO} + [\text{O}] \rightarrow \text{RCOOH}$ ✓</p>	2	<p>Note: both reagent and observation are required for first mark</p> <p>ALLOW ammoniacal silver nitrate OR Ag^+/NH_3</p> <p>ALLOW $\text{H}^+/\text{Cr}_2\text{O}_7^{2-}$ OR acidified (potassium/sodium) dichromate AND Orange to green (<i>this would identify the aldehyde from the carboxylic acid, ketone and esters</i>)</p>
	b	<p>2,4-dinitrophenylhydrazine AND Orange/yellow/red precipitate ✓</p>	1	<p>ALLOW errors in spelling ALLOW 2,4(-)DNP OR 2,4(-)DNPH ALLOW Brady's reagent or Brady's Test ALLOW solid OR crystals OR ppt as alternatives for precipitate</p>
	c	<p>$\text{CH}_3\text{COOC}(\text{CH}_3)_3 + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + (\text{CH}_3)_3\text{COH}$</p> <p>$\text{CH}_3\text{COONa}$ ✓ Rest of equation correct ✓</p> <p>OR $(\text{CH}_3)_3\text{CCOOCH}_3 + \text{NaOH} \rightarrow (\text{CH}_3)_3\text{CCOONa} + \text{CH}_3\text{OH}$</p> <p>$(\text{CH}_3)_3\text{CCOONa}$ ✓ Rest of equation correct ✓</p>	2	<p>Note: the hydrolysis of either ester may be given</p> <p>ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</p> <p>DO NOT ALLOW molecular formulae of products (<i>question requires structures of products to be shown</i>)</p>
	i	<p>Reagent and observation</p> <p>$\text{H}^+/\text{Cr}_2\text{O}_7^{2-}$ OR acidified (potassium/sodium) dichromate AND Orange to green (with CH_3OH) ✓</p> <p>Equation</p>	2	

6.3.2 Spectroscopy

		$\text{CH}_3\text{OH} + [\text{O}] \rightarrow \text{HCHO} + \text{H}_2\text{O}$ OR $\text{CH}_3\text{OH} + 2[\text{O}] \rightarrow \text{HCOOH} + \text{H}_2\text{O}$ ✓		ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous DO NOT ALLOW molecular formulae (<i>question requires structures of organic compounds to be shown</i>)
	i i i	^{13}C NMR (1 mark) (It is) not possible to identify (the esters) with ^{13}C NMR AND (both) spectra would contain four peaks (with similar chemical shifts) ✓ ^1H NMR (2 marks) (It is) possible to identify (the esters) with ^1H NMR (^1H NMR spectrum of) $\text{CH}_3\text{COOC}(\text{CH}_3)_3$ has a singlet/peak between 2.0–3.0 (ppm) (^1H NMR spectrum of) $(\text{CH}_3)_3\text{CCOOCH}_3$ has a singlet/peak between 3.0–4.3 (ppm) All three correct statements ✓✓ Any two correct statements ✓	3	ALLOW 'same number of peaks' in place of 'four peaks' ALLOW any value or range of values within 2.0–3.0 ALLOW any value or range of values within 3.0–4.3
	d	<u>Possible structures for ketone (2 marks)</u> $\begin{array}{c} \text{O} \\ \\ \text{CH}_3 - \text{C} - \text{CH}_2\text{CH}_2\text{CH}_3 \end{array}$ $\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{CH}_2 - \text{C} - \text{CH}_2\text{CH}_3 \end{array}$ $\begin{array}{c} \text{O} \\ \\ \text{CH}_3 - \text{C} - \text{CH} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$ All three correct ✓✓ Any two correct ✓	5	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous IGNORE names of ketones

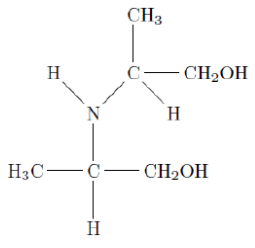
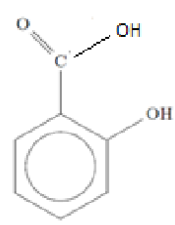
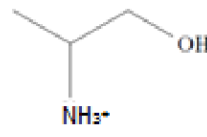
6.3.2 Spectroscopy

		<p>Aldehyde (3 marks)</p> <p>Peak at (δ) 1.2 shows HC–R AND No H on adjacent C atom as peak is singlet ✓</p> <p>Peak at (δ) 9.6 shows H–C=O AND No H on adjacent C atom as peak is singlet ✓</p> $ \begin{array}{c} \text{CH}_3 \quad \text{O} \\ \quad \parallel \\ \text{H}_3\text{C}-\text{C}-\text{C}-\text{H} \\ \\ \text{CH}_3 \end{array} $ <p>OR (2,2-)dimethylpropanal ✓</p>		
Total		17		
1 2		<p><i>*Please refer to the marking instructions on page 4 of this mark scheme for guidance on how to mark this question.</i></p> <p>Level 3 (5–6 marks) Structure of J identified as $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{CN}$ AND/OR A comprehensive analysis with most of the spectral data analysed and few omissions.</p> <p><i>There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.</i></p> <p>Level 2 (3–4 marks) Analysis may be incomplete and structure of J identified. OR Thorough analysis of one aspect of the information given in question and structure of J may be incorrectly identified.</p> <p><i>There is a line of reasoning presented with some structure. The information presented is</i></p>	6	<p>LOOK ON THE SPECTRA for labelled peaks. Indicative scientific points may include:</p> <p>Empirical and Molecular Formula of J</p> $ \begin{array}{r} \text{C : H : N} = \quad 74.17/12 \quad : \quad 11.41/1 \quad : \quad 14.42/14 \\ \qquad \qquad \qquad 6.18 \quad : \quad 11.41 \quad : \quad 1.03 \\ \circ \qquad \qquad \qquad 6 \quad : \quad 11 \quad : \quad 1 \end{array} $ <p>\circ Empirical formula of J = $\text{C}_6\text{H}_{11}\text{N}$</p> <ul style="list-style-type: none"> uses $m/z = 97.0$ and empirical formula to determine molecular formula of J as $\text{C}_6\text{H}_{11}\text{N}$ <p><u>^1H NMR spectrum</u></p> <ul style="list-style-type: none"> $\delta = 0.9$ ppm, triplet, $\text{CH}_3-\text{CH}_2-(\text{C}-)$ $\delta = 1.4$ ppm, singlet, $(\text{CH}_3)_2\text{C}-$ $\delta = 1.6$ ppm, quartet, $\text{CH}_3-\text{CH}_2-(\text{C}-)$ <p><u>IR Spectrum and Structure of J</u></p> <p>\circ peak at $2220-2260$ (cm^{-1}) is $\text{C}\equiv\text{N}$</p>

6.3.2 Spectroscopy

		<p><i>relevant and supported by some evidence.</i></p> <p>Level 1 (1–2 marks) An attempt at a simple analysis.</p> <p>OR Explains one scientific point thoroughly with a few omissions.</p> <p><i>The information is basic and communicated in an unstructured way. The information is supported by limited evidence and the relationship to the evidence may not be clear.</i></p> <p>0 marks No response or no response worthy of credit.</p>		<p>○ Correct structure of J</p> $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}_2-\text{C}-\text{CN} \\ \\ \text{CH}_3 \end{array}$ <p>ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</p>										
		Total	6											
1 3	a i	<table border="1"> <thead> <tr> <th colspan="2">¹H NMR spectrum for 2-aminop</th> </tr> <tr> <th>Chemical shift, δ/ppm</th> <th>Relative peak area</th> </tr> </thead> <tbody> <tr> <td>0.8 – 2.0</td> <td>3</td> </tr> <tr> <td>2.3 – 3.0</td> <td>1</td> </tr> <tr> <td>3.3 – 4.2</td> <td>2</td> </tr> </tbody> </table> <p style="text-align: right;">✓✓✓</p>	¹ H NMR spectrum for 2-aminop		Chemical shift, δ/ppm	Relative peak area	0.8 – 2.0	3	2.3 – 3.0	1	3.3 – 4.2	2	3	<p>One mark for each correct row ALLOW δ values as a range or a value within the specified range. ALLOW δ values +/- 0.2 ppm. ALLOW a response that implies a splitting into two for a doublet etc. ALLOW sextet/hextet/six (or more than 5) as alternative to multiplet Relative peak area = CH /3H etc. penalise once</p> <p>Examiner's Comments</p> <p>Although it could be argued that this question tested the same skill three times, the full range of marks was awarded and errors were seen in the chemical shift, relative peak area and splitting pattern. Fully correct responses included either a chemical shift value within the range specified on the data sheet or a range that matched the one given on the data sheet.</p>
¹ H NMR spectrum for 2-aminop														
Chemical shift, δ/ppm	Relative peak area													
0.8 – 2.0	3													
2.3 – 3.0	1													
3.3 – 4.2	2													
	i i	<p>M⁺ peak at 75 (peak 1) CH₃CH(NH₂)CH₂OH⁺/C₃H₉NO⁺ ✓</p> <p>Fragment peak at 44 (peak 2) CH₃CH(NH₂)⁺/C₂H₆N⁺ ✓</p>	2	<p>ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous</p> <p>Positive charge is essential but ALLOW maximum of one mark if both formulae are correct AND neither species has a positive charge</p> <p>Examiner's Comments</p> <p>Although peak 2 was often correct, the species responsible for the M⁺ peak was often missing a positive charge. Possibly students have learned that the particles become charged as part of the fragmentation process and don't realise that only charged particles can be detected by a mass spectrometer.</p>										

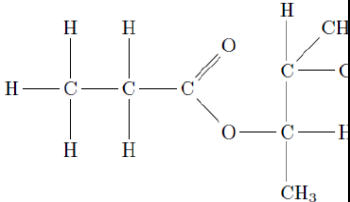
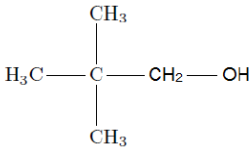
6.3.2 Spectroscopy

	b	i	Ethanolic ammonia OR ammonia/NH ₃ AND ethanol ✓	1	ALLOW ammonia in a sealed tube ALLOW dilute ethanolic ammonia/NH ₃ IGNORE heat ALLOW alcohol for ethanol DO NOT ALLOW any reference to water or hydroxide ions Examiner's Comments A well answered question. Some candidates forgot to use a solvent or suggested the use of aqueous ammonia.
		i	(compound D) 	1	ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous Examiner's Comments This question discriminated well. Although there were very few blank pages, many incorrect structures were seen. ✓
	c	i	Alcohol AND Amide/peptide ✓	1	IGNORE phenol IGNORE hydroxyl/hydroxy IGNORE attempts to classify alcohol or amide as primary, secondary or tertiary DO NOT ALLOW hydroxide Examiner's Comments Generally well answered but incorrect functional groups included carbonyl and amine.
		i	 	2	ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous ALLOW + on N or H i.e. ⁺ NH ₃ or NH ₃ ALLOW NH ₃ ⁺ Cl ⁻ Examiner's Comments Many candidates were able to score one mark for this question but the amine group was often not protonated and it was surprisingly common to see the amine group as NH ₂ ⁺ .
			Total	10	
1 4	a		<u>Reducing agent</u> NaBH ₄ / sodium tetrahydridoborate(III) / sodium borohydride ✓ <u>Equation</u>	1	ALLOW LiAlH ₄ /lithium tetrahydridoaluminate(III)/lithium aluminium hydride ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above

6.3.2 Spectroscopy

	$\text{CH}_3(\text{CH}_2)_3\text{CHO} + 2[\text{H}] \rightarrow \text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{OH} \checkmark$		<p>ALLOW $\text{C}_4\text{H}_9\text{CHO} + 2[\text{H}] \rightarrow \text{C}_5\text{H}_{11}\text{OH}$</p> <p>ALLOW molecular formulae: $\text{C}_5\text{H}_{10}\text{O} + 2[\text{H}] \rightarrow \text{C}_5\text{H}_{12}\text{O}$</p> <p>DO NOT ALLOW $-\text{COH}$ for aldehyde</p> <p>Examiner's Comments</p> <p>Very well answered. The most common error was an incorrect formula for the aldehyde.</p>
b	<p>M1 Compound F structure is a secondary alcohol with the formula $\text{C}_5\text{H}_{11}\text{OH} \checkmark$</p> <p>M2 Compound F $= \text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{CH}_3)\text{CH}_3 \checkmark$</p> <p>M3 Compound G = $\text{CH}_3\text{COCH}(\text{CH}_3)\text{CH}_3 \checkmark$</p> <p>M4 $n(\text{NaOH}) = (0.125 \times 22.8/1000) = 0.00285 \text{ (mol)} \checkmark$</p> <p>M5 $M(\text{compound H}) = (0.211/0.00285) = 74.0 \text{ (g mol}^{-1}\text{)} \checkmark$</p> <p>M6 Compound H = / $\text{CH}_3\text{CH}_2\text{COOH} \checkmark$</p> <p>M7 Compound I =</p>	7	<p>ANNOTATE WITH TICKS AND CROSSES ETC</p> <p>ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous</p> <p>IGNORE names if structures are given</p> <p>ALLOW 3-methylbutan-2-ol if structure not given</p> <p>ALLOW ECF from an incorrect secondary alcohol for M3 e.g. pentan-2-ol \rightarrow pentan-2-one e.g. pentan-3-ol \rightarrow pentan-3-one</p> <p>ALLOW (3-)methylbutanone if structure not given</p> <p>IGNORE any discussion of the reactions of compound G with 2,4-dinitrophenylhydrazine and/or Tollens' reagent.</p> <p>ALLOW 3 SF up to calculator value correctly rounded</p> <p>IF $M(\text{compound H}) = 74$ award 2 marks (M4 + M5)</p> <p>ALLOW ECF from incorrect calculation of amount of NaOH</p> <p>ALLOW propanoic acid if structure not given</p> <p>ALLOW ECF from incorrect compound F (alcohol) and/or incorrect compound H (carboxylic acid) to form compound I (ester).</p> <p>Compounds F, G, H and I must be placed in the correct box or correctly labelled for M2, M3, M6 and M7</p> <p>Examiner's Comments</p> <p>A high scoring question with many candidates gaining full marks. Although most realised that Compound F was a secondary alcohol, fewer candidates combined this knowledge with the information provided by carbon-13 NMR to deduce the correct structure of the secondary alcohol.</p>

6.3.2 Spectroscopy

						✓
	c		<p>The structural isomer is:</p> 	1	<p>ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above as long as unambiguous</p> <p>ALLOW 2,2-dimethylpropan-1-ol</p> <p>Examiner's Comments</p> <p>A good discriminator but many correct structures were seen.</p>	✓
Total			10			
1 5	a i		Radio (waves) ✓	1	<p>ALLOW a value in the range 60 – 900 MHz</p> <p>Examiner's Comments</p> <p>The interaction of materials with the low-energy radio wave region of the electromagnetic spectrum is described in the specification but this question was surprisingly poorly answered. Infrared, ultraviolet, X-rays and gamma rays were all commonly seen answers in addition to ranges of chemical shift quoted from the data sheet.</p>	
		i i	The solvent does not have any hydrogen / H / protons ✓	1	<p>ALLOW to prevent (¹H nuclei from) the solvent from interfering with the NMR spectrum</p> <p>ALLOW does not show on the spectrum</p> <p>ALLOW no peak / signal (from solvent)</p> <p>IGNORE volatility</p> <p>Examiner's Comments</p> <p>The need for deuterated solvents was well known but some candidates confused the use of this solvent with the use of TMS as the standard for chemical shift measurements or the identification of O—H and N—H protons by proton exchange using D₂O.</p>	
	b		14 ✓	1	<p>Examiner's Comments</p> <p>Almost all candidates scored this mark for counting the peaks in the ¹³C NMR spectrum.</p>	
	c		<p>NMR analysis (5 marks)</p> <p>M1</p>	7	<p>ANNOTATE ANSWER WITH TICKS AND CROSSES ETC</p> <p>IGNORE analysis of ¹³C spectrum</p>	

6.3.2 Spectroscopy

Peaks between (δ) 7.1 and 7.5 (ppm)

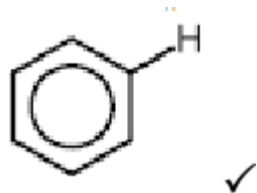
OR

Relative peak area of 7

OR

Multiplet

=



M2

Peak at 5.2/5.3

OR

Relative peak area of 1

= N-H ✓

M3

Peak at 2.3/2.4

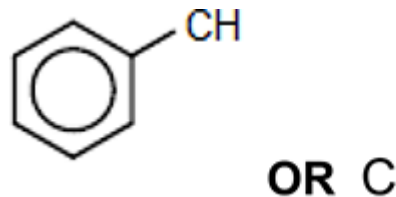
OR

Relative peak area of 2

OR

Quartet

=



✓

M4

Peak at 0.7/0.8

OR

Triplet

= R-CH **OR** R-CH₃ ✓

M5

Triplet (at δ 0.7) **AND** quartet (at δ 2.3) = CH₂CH₃

OR triplet at (δ) 0.7 shows (C with) 2 adjacent Hs / protons = CH₂CH₃

OR quartet (at δ 2.3) shows (C with) 3 adjacent Hs / protons = CH₂CH₃ ✓

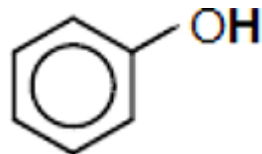
Each peak can be identified from its δ value \pm 0.2 ppm

ALLOW (seven) benzene ring protons **OR** aromatic protons

DO NOT ALLOW benzene ring without reference to protons

ALLOW C₆H₆

IGNORE



IGNORE O-H, CONH **AND** C=CH

ALLOW quadruplet

IGNORE CHC=O **AND** HC-N

DO NOT ALLOW triplet = CH₃ **OR** CH₂CH₃

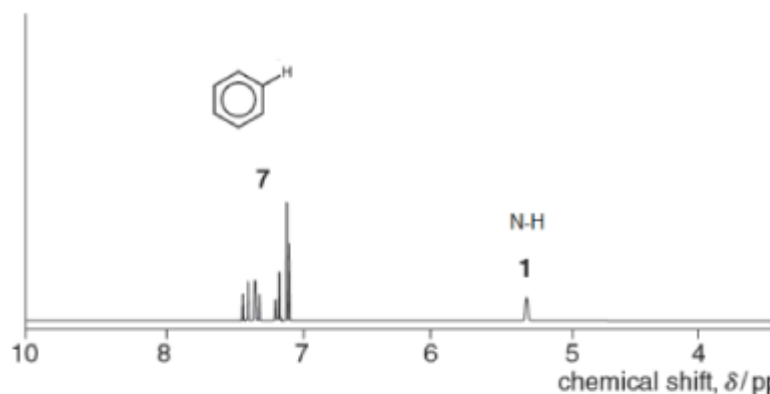
This also scores **M4** if triplet is linked to R-CH₃

ALLOW CH₃CH₂ described as R-CH₃ and 2 adjacent H

OR -CH₂- and 3 adjacent H

The information can be presented on the spectrum or in a table.

6.3.2 Spectroscopy

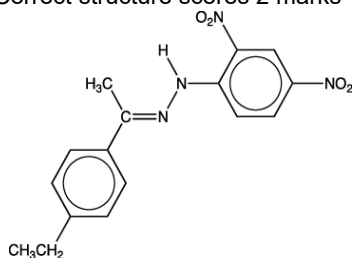


QWC: triplet or quartet spelled correctly in the correct context for **M5**

Identification of **R¹** and **R²** (2 marks)

Orange precipitate **L**

Correct structure scores 2 marks



R¹ or **R²** = -CH₃ ✓

R₁ or **R₂** =

Chemical shift/ppm	Relative peak area	Splitting pattern
7.1 – 7.5	7	Multiple
5.3	1	Singlet
2.3/2.4	2	Quartet
1.7/1.8	3	Singlet
0.7/0.8	3	triplet

IGNORE peak in the range 1.6–2.2 = HC–C=N– because this information is given in the question.

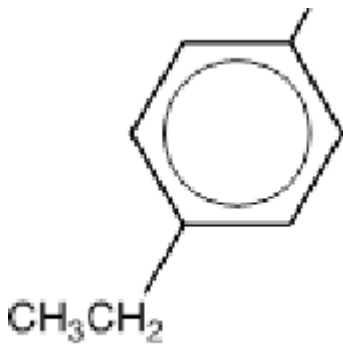
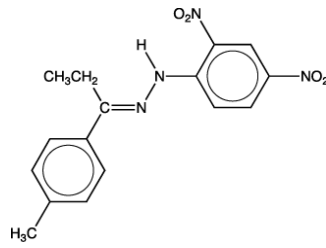
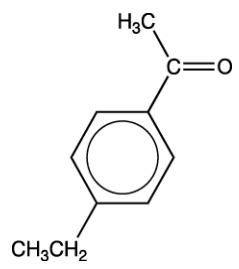
H₃C–C=N– scores one mark for the identification of **R¹** or **R²** (see below)

ALLOW correct structural **OR** displayed **OR** skeletal formulae **OR** a combination of above as long as unambiguous

Marks are for structure of **R¹** and **R²**

IGNORE errors in the rest of the structure

ALLOW 1 mark for CH₃ and CH₃CH₂ swapped, i.e. the following structure

			 <p>ALLOW $\text{H}_3\text{C}-\text{C}=\text{N}-$</p> <p>MUST BE 1,4-disubstituted (14 carbon environments in the ^{13}C NMR spectrum)</p> <p>Examiner's Comments</p> <p>Although the use of 2,4-dinitrophenylhydrazine to detect the presence of a carbonyl group in an organic compound and to identify a carbonyl compound from the melting point of the derivative is required in the specification, the equation for this reaction and the structure of the derivative was not required in the question. The equation for the reaction and the structure of the derivative, with R^1 and R^2 groups from the original carbonyl compound, was given in the question. The structure of carbonyl K was similar in complexity to structures featured in previous papers. The mark scheme was constructed so that at least two of the first five marks awarded for the analysis were easily accessible by comparing the chemical shifts in the ^1H NMR spectrum with those displayed in the data sheet. These marks were often achieved by the construction of a clearly labelled and well organised table or by annotating the spectrum. Splitting patterns were well understood but one problem for candidates was the difficulty in associating the peak at $\delta = 2.3/2.4$ ppm with a benzylic hydrogen; many candidates focused more on coupling than on chemical shifts and missed a chance to solve the structure. Of the two marks available for identifying R^1 and R^2, one could be derived quickly by linking information given in the question with one of the peaks in the ^1H NMR spectrum. The second identification mark required careful analysis of both the ^1H NMR and ^{13}C NMR data. Overall, most candidates were able to score marks on this question and completely correct answers were achieved by the most able candidates.</p>
d	<p>Carbonyl compound K</p>  <p style="text-align: center;">✓</p>	1	<p>ALLOW ECF from incorrect compound L Must be a correct carbonyl structure</p> <p>Examiner's Comments</p> <p>It was not possible to score a mark for this question unless a structure had been drawn for compound L. However, many candidates were able to score this mark as error carried forward from structures that had failed to gain any credit in the previous question were allowable.</p>
	Total	11	

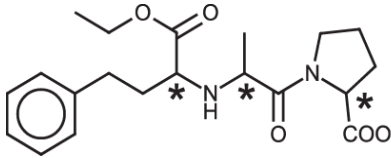
6.3.2 Spectroscopy

1 6	a	<p>TMS / tetramethylsilane</p> <p>(which is the) standard (for chemical shift measurements) ✓</p>	1	<p>ALLOW (CH₃)₄Si</p> <p>ALLOW TMS is the reference OR TMS has $\delta = 0$ (ppm) OR for calibration OR for comparison</p> <p>IGNORE solvent, unreactive, volatile, it gives a sharp peak</p> <p>Examiner's Comments</p> <p>This was well answered by the majority of candidates.</p>
	b	<p>NMR analysis = 5 marks</p> <p>M1: Peak(s) at (δ) 9.7 = CHO ✓</p> <p>M2: Peak(s) at (δ) 7.1 = C₆H₄ ✓</p> <p>M3: Triplet at (δ) 1.3 / peak at 1.3 AND quartet (at δ 2.6) / peak at 2.6 = CH₂CH₃ ✓</p> <p>M4: Triplet at (δ) 9.7 / peak at 9.7 AND doublet (at δ 3.7) / peak at 3.7 = CH₂CHO ✓</p> <p>M5: (n+1 rule) Any one of the following</p> <ul style="list-style-type: none"> ○ triplet at (δ) 1.3 shows (C with) 2 adjacent Hs / protons OR adjacent CH₂ (<i>because of splitting: so triplet</i>) 	9	<p>NOTE: Each peak can be identified from:</p> <ul style="list-style-type: none"> • its δ value • a range, e.g. "the peak between 0.8 and 2.0" • its relative peak area (beware two peaks with 2 protons) • its splitting (beware two triplets) • labelling on the spectrum <p>ALLOW CH₂CHO / aldehyde IGNORE reference to phenol</p> <p>ALLOW (four) benzene ring proton(s) IGNORE reference to phenol</p> <p>M3 and M4 Look for a clear link (using words or diagrams) between the two peaks</p> <p>ALLOW a response that implies a splitting into three for a triplet / into two for a doublet etc.</p> <p>ALLOW "neighbouring" Hs for "adjacent to" Hs</p> <p>IGNORE other comments about splitting once M5 has been awarded</p>

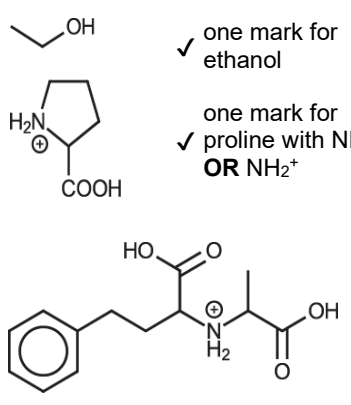
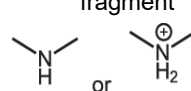

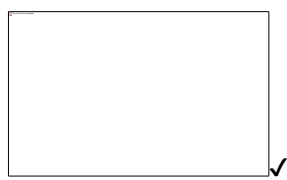
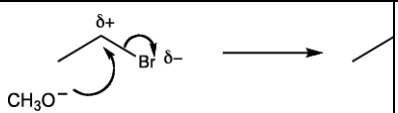
6.3.2 Spectroscopy

	<ul style="list-style-type: none"> ○ quartet at (δ 2.6 shows) (C with) 3 adjacent Hs / protons OR adjacent CH_3 ○ triplet at (δ) 9.7 shows (C with) 2 adjacent Hs / protons OR adjacent CH_2 • doublet at (δ 3.7 shows) (C with) 1 adjacent H / proton OR adjacent CH <p style="text-align: right;">✓</p> <p>QWC: triplet spelled correctly in the correct context once</p> <p>Aldehyde structure = 4 marks</p> <p style="text-align: right;">✓✓</p> <p>✓✓</p>		<p>DO NOT ALLOW one of M3 or M4 or M5 if triplet not seen</p>
			<p>ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous</p> <p>IF structure contains C_6H_4 ✓</p> <p>IF structure contains C_6H_4 AND the organic structure contains CH_3CH_2 directly attached to the benzene ring OR contains CH_2CHO directly attached to the benzene ring ✓✓</p> <p>IF structure has formula $\text{C}_{10}\text{H}_{12}\text{O}$ AND structure contains C_6H_4 AND the structure contains CH_3CH_2 AND contains CH_2CHO AND 1,2 OR 1,3 substituted ✓✓✓</p> <p>IF structure has formula $\text{C}_{10}\text{H}_{12}\text{O}$ AND structure contains C_6H_4 AND the structure contains CH_3CH_2 AND contains CH_2CHO AND 1,4 substituted ✓✓✓✓ (use of ^{13}C data)</p> <p>Examiner's Comments</p> <p>Good discrimination was achieved in this question. Nearly all could score at least one mark from the first two marking points by identifying the peak associated with the proton in the aldehyde group, or the peak given by</p>

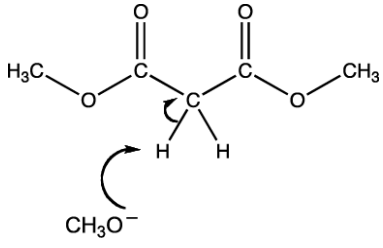
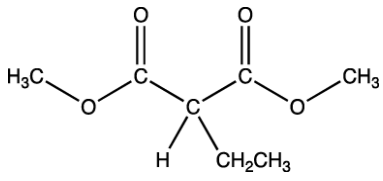
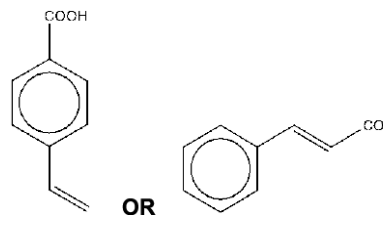
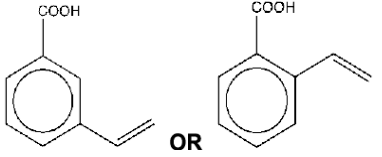
6.3.2 Spectroscopy

				<p>benzene ring protons. Many gave a good explanation of a splitting pattern to score the fifth marking point. These marks were often achieved by the construction of a clearly labelled and well organised table.</p> <p>Many were able to suggest a structure for compound H. The best candidates included a 1,4 substituted benzene ring after correctly interpreting the information from the carbon-13 NMR spectrum. Candidates should avoid drawing several different structures and not indicating which one they wish to have marked.</p>							
			Total	10							
1 7			<table border="1"> <thead> <tr> <th>Compound</th> <th>C</th> <th>D</th> </tr> </thead> <tbody> <tr> <td>Number of peaks</td> <td>5</td> <td>5</td> </tr> </tbody> </table> <p style="text-align: center;">all correct ✓</p>	Compound	C	D	Number of peaks	5	5	1	<p>Examiner's Comments</p> <p>The interpretation of carbon-13 NMR spectra seems to be very well understood and the vast majority of candidates were able to correctly predict the number of peaks for all three compounds.</p>
Compound	C	D									
Number of peaks	5	5									
			Total	1							
1 8	a		<p style="text-align: center;">¹H NMR spectrum for se</p> <table border="1"> <thead> <tr> <th>chemical shift, δ /ppm</th> <th>relative peak area</th> </tr> </thead> <tbody> <tr> <td>2.0 to 3.0</td> <td>1</td> </tr> <tr> <td>3.3 to 4.2</td> <td>2</td> </tr> </tbody> </table> <p>One mark for each correct row ✓✓</p>	chemical shift, δ /ppm	relative peak area	2.0 to 3.0	1	3.3 to 4.2	2	2	<p>ALLOW δ values ± 0.2 ppm, as a range or a value within the range</p> <p>ALLOW a response that implies a splitting into three for a triplet / into two for a doublet</p> <p>Examiner's Comments</p> <p>Many candidates did not have the skills required to score marks on this question. Errors were made in all three columns and most often in assigning appropriate shift values from the data sheet.</p>
chemical shift, δ /ppm	relative peak area										
2.0 to 3.0	1										
3.3 to 4.2	2										
	b	i		1	<p>ALL correct for one mark</p> <p>Examiner's Comments</p> <p>This part was answered well by many candidates. Some missed the chiral centre on the proline moiety or added an asterisk to a carbonyl carbon.</p>						
		i	<p>any two from:</p> <p>no / fewer side effects</p> <p>increases the (pharmacological) activity / effectiveness</p> <p>Reduces / stops the need for / cost / difficulty in separating stereoisomers / optical isomers ✓✓</p>	2	<p>IGNORE toxic / harmful</p> <p>IGNORE a response that implies a reduced dose</p> <p>IGNORE "it takes (less) time to separate"</p> <p>Examiner's Comments</p> <p>Most candidates gained this mark by stating that the use of a single stereoisomer results in fewer side effects and increased pharmacological activity. Vague answers and comments about a reduced dose did not score marks.</p>						

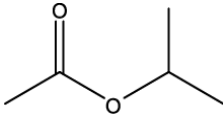
6.3.2 Spectroscopy

		 <p>✓ one mark for ethanol</p> <p>✓ one mark for proline with NH OR NH₂⁺</p> <p>i i i</p> <p>with  or </p> <p>✓ one mark for remaining fragment</p> <p>Fourth mark for structure of both ions shown correctly with NH₂⁺</p>	4	<p>ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous</p> <p>ALLOW + charge on H of NH₂ groups, <i>i.e.</i> NH₂⁺</p> <p>IGNORE negative (counter) ions</p> <p>Examiner's Comments</p> <p>This question discriminated well. Most candidates were able to score one mark for the formula of ethanol. Only a small number of able candidates scored full marks for including the correct formulae for the protonated amine groups formed during acid hydrolysis.</p>
		<p>idea of separating (the components / compounds)</p> <p>i v</p> <p>AND idea of (identifying compounds by) comparison with a (spectral) database ✓</p>	1	<p>ALLOW (identifies compounds) using fragmentation (patterns) / fragment ions (but IGNORE molecular ions)</p> <p>IGNORE retention times</p> <p>Examiner's Comments</p> <p>To get the mark for this question candidates had to include points about the separation of the mixture and identification of the compounds. Answers based on identification using retention times or measurement of molar mass did not score the mark.</p>
		Total	10	
19	a		1	
	b i	$2\text{Na} + 2\text{CH}_3\text{OH} \rightarrow 2\text{Na}^+ + 2\text{CH}_3\text{O}^- + \text{H}_2$ ✓	1	ALLOW $2\text{Na} + 2\text{CH}_3\text{OH} \rightarrow 2\text{CH}_3\text{ONa} + \text{H}_2$
		 <p>i i</p> <p>Curly arrow from CH₃O⁻ to carbon atom of C-Br bond ✓</p> <p>Dipole shown on C-Br bond, C^{δ+} and Br^{δ-}</p> <p>AND curly arrow from C-Br bond to the Br atom ✓</p>	3	<p>ALLOW correct structural OR skeletal OR displayed formula OR mixture of the above as long as non-ambiguous.</p> <p>The curly arrow must start from O atom of CH₃O⁻</p> <p>AND must start either from a lone pair or from the negative charge.</p> <p>No need to show lone pair if curly arrow comes from negative charge.</p> <p>ALLOW S_N1</p> <p>Dipole shown on C-Br bond, C^{δ+} and Br^{δ-}, and curly arrow from C-Br bond to the Br atom.</p> <p>Correct carbocation drawn.</p>

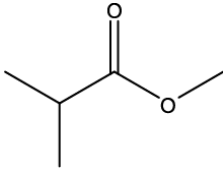
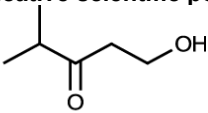
6.3.2 Spectroscopy

		Products of reaction (must not be ambiguous) ✓		AND curly arrow from CH_3O^- to carbocation. The curly arrow must start from the oxygen atom of the CH_3O^- , and must start either from a lone pair or from the negative charge.																				
	i i i	CH_3O^- donates an electron pair AND heterolytic fission ✓	1	ASSUME 'it' refers to CH_3O^-																				
	c	<table border="1"> <thead> <tr> <th>Chemical shift, δ/ppm</th> <th>Relative peak area</th> <th>Splitting pattern</th> <th></th> </tr> </thead> <tbody> <tr> <td>0.5–1.9</td> <td>3</td> <td>Triplet</td> <td>✓</td> </tr> <tr> <td>3.0–4.3</td> <td>2</td> <td>Quartet</td> <td>✓</td> </tr> <tr> <td>0.5–1.9</td> <td>6</td> <td>Doublet</td> <td>✓</td> </tr> <tr> <td>3.0–4.3</td> <td>1</td> <td>Heptet</td> <td>✓</td> </tr> </tbody> </table>	Chemical shift, δ/ppm	Relative peak area	Splitting pattern		0.5–1.9	3	Triplet	✓	3.0–4.3	2	Quartet	✓	0.5–1.9	6	Doublet	✓	3.0–4.3	1	Heptet	✓	4	ALLOW δ values ± 0.2 ppm, as a range or a value within the range ALLOW multiplet for heptet
Chemical shift, δ/ppm	Relative peak area	Splitting pattern																						
0.5–1.9	3	Triplet	✓																					
3.0–4.3	2	Quartet	✓																					
0.5–1.9	6	Doublet	✓																					
3.0–4.3	1	Heptet	✓																					
	d i	 <p>Curly arrow from CH_3O^- to H of CH_2 ✓ Curly arrow from C–H bond to C of CH_2 ✓</p>  <p>✓</p>	3	The curly arrow must start from O atom of CH_3O^- AND must start either from a lone pair or from the negative charge. No need to show lone pair if curly arrow comes from negative charge. ALLOW any unambiguous structure, skeletal, displayed, structural or combination.																				
	i i	CH_3O^- accepted a proton ✓	1	ASSUME 'it' refers to CH_3O^-																				
		Total	14																					
2 0		<p>Electrophilic substitution means benzene ring</p> <p>Electrophilic addition means alkene / $\text{C}=\text{C}$</p> <p>Isomer of $\text{C}_9\text{H}_8\text{O}_2$ containing $\text{C}=\text{C}$, benzene ring AND COOH Correct isomer:</p>  <p>OR</p>	5	<p>Concluded using data provided and conclusions from 1st two marks.</p> <p>ALLOW 1 mark for:</p>  <p>(does not gain final justification mark)</p>																				

6.3.2 Spectroscopy

		justification in terms of number of carbon environments																														
		Total	5																													
2 1		<p>Elemental analysis and molecular formula</p> <p>Use of percentages to give empirical formula C₅H₁₀O₂</p> <p>Evidence of using empirical formula AND 102 to give molecular formula = C₅H₁₀O₂</p> <p>IR Spectrum Peak at ~1750 OR 1630–1820 (cm⁻¹) AND C=O</p> <p>NMR analysis</p> <p>Peak(s) at (δ) 4.9 shows HC–O AND 1 H in environment (peak area) OR 6H on adjacent C as peak is multiplet / heptet / septet</p> <p>Peak at (δ) 2.2 shows HC–C=O AND 3 H in environment (peak area) OR No H on adjacent C as peak is singlet</p> <p>Peak(s) at (δ) 1.3 shows HC–R AND 6 H (or 2 × CH₃) in environment (peak area) OR 1H on adjacent C as peak is doublet</p> <p>Structure Correct structure:</p>  <p>Allow one mark for</p>	8	<p>ANNOTATE ANSWER WITH TICKS AND CROSSES</p> <table border="1" data-bbox="703 539 1449 723"> <tr> <td>C : H : O</td> <td>=</td> <td>58.80 / 12</td> <td>:</td> <td>9.87 / 1</td> <td>:</td> <td>31.33 / 16</td> </tr> <tr> <td></td> <td></td> <td>4.90</td> <td>:</td> <td>9.87</td> <td>:</td> <td>1.96</td> </tr> <tr> <td></td> <td></td> <td>2.5</td> <td>:</td> <td>5.04</td> <td>:</td> <td>1</td> </tr> <tr> <td></td> <td></td> <td>5</td> <td>:</td> <td>10</td> <td>:</td> <td>2</td> </tr> </table> <p>Alternative method: carbon: (102 × 58.80 / 100)/12 = 5 hydrogen: (102 × 9.87 / 100)/1 = 10 oxygen: (102 × 31.33 / 100)/16 = 2</p> <p>ALLOW C=O peak labelled on spectrum</p> <p>IGNORE reference to C–O peak</p> <p>NOTE each peak can be identified from:</p> <ul style="list-style-type: none"> its δ value a range e.g. 'the peak between 1.3–1.4' its relative peak area its splitting labelling on spectrum <p>ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</p> <p>DO NOT ALLOW ECF from incorrect molecular formula</p>	C : H : O	=	58.80 / 12	:	9.87 / 1	:	31.33 / 16			4.90	:	9.87	:	1.96			2.5	:	5.04	:	1			5	:	10	:	2
C : H : O	=	58.80 / 12	:	9.87 / 1	:	31.33 / 16																										
		4.90	:	9.87	:	1.96																										
		2.5	:	5.04	:	1																										
		5	:	10	:	2																										

6.3.2 Spectroscopy

														
		Total	8											
2 2		<p>* Please refer to the marking instruction point 10 for guidance on how to mark this question.</p> <p>Level 3 (5–6 marks) Structure correct AND Analysed all ^1H NMR signals with at least two supporting statements made.</p> <p><i>The analysis is clear and logically structured. The supporting statements are relevant to the correct structure drawn.</i></p> <p>Level 2 (3–4 marks) Structure has correct molecular formula AND C=O AND OH but in incorrect positions AND Analysed at least three ^1H NMR signals with one or two supporting statements made.</p> <p><i>The analysis is presented with some structure. The supporting statements are in the most-part relevant to the structure drawn.</i></p> <p>Level 1 (1–2 marks) Structure has correct molecular formula AND C=O OR OH but in incorrect positions. AND Analysed at least two ^1H NMR signals with no or one supporting statements made.</p> <p><i>The analysis is basic and communicated in an unstructured way. The relationship of the supporting evidence to the structure may not be clear.</i></p> <p>0 marks No response or no response worthy of credit.</p>	6	<p>Indicative scientific points may be included: Structure</p>  <p>L =</p> <p>^1H NMR spectrum</p> <table> <tbody> <tr> <td>$\delta = 3.8$ ppm, triplet, 2H</td> <td>$\text{CH}_2\text{—CH}_2\text{—O}$</td> </tr> <tr> <td>$\delta = 3.7$ ppm, singlet, 1H</td> <td>O—H</td> </tr> <tr> <td>$\delta = 3.1$ ppm, triplet, 2H</td> <td>$\text{CH}_2\text{—CH}_2\text{C=O}$</td> </tr> <tr> <td>$\delta = 2.7$ ppm, septet, 1H</td> <td>$(\text{CH}_3)_2\text{CHC=O}$</td> </tr> <tr> <td>$\delta = 1.0$ ppm, doublet, 6H</td> <td>$(\text{CH}_3)_2\text{CH}$</td> </tr> </tbody> </table> <p>Supporting statements $\delta = 3.7$ ppm lost after D_2O, indicating —OH $\delta = 213$ ppm in ^{13}C NMR but no $\delta = 9\text{--}10$ ppm in ^1H NMR so ketone, not aldehyde $M_r(\text{C}_3\text{H}_6\text{O}) = 58 \quad 116/58 = 2 \rightarrow \text{C}_6\text{H}_{12}\text{O}_2$</p>	$\delta = 3.8$ ppm, triplet, 2H	$\text{CH}_2\text{—CH}_2\text{—O}$	$\delta = 3.7$ ppm, singlet, 1H	O—H	$\delta = 3.1$ ppm, triplet, 2H	$\text{CH}_2\text{—CH}_2\text{C=O}$	$\delta = 2.7$ ppm, septet, 1H	$(\text{CH}_3)_2\text{CHC=O}$	$\delta = 1.0$ ppm, doublet, 6H	$(\text{CH}_3)_2\text{CH}$
$\delta = 3.8$ ppm, triplet, 2H	$\text{CH}_2\text{—CH}_2\text{—O}$													
$\delta = 3.7$ ppm, singlet, 1H	O—H													
$\delta = 3.1$ ppm, triplet, 2H	$\text{CH}_2\text{—CH}_2\text{C=O}$													
$\delta = 2.7$ ppm, septet, 1H	$(\text{CH}_3)_2\text{CHC=O}$													
$\delta = 1.0$ ppm, doublet, 6H	$(\text{CH}_3)_2\text{CH}$													
		Total	6											