

GCE

Chemistry A

H432/02: Synthesis and analytical techniques

A Level

Mark Scheme for June 2023

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It is also responsible for developing new specifications to meet national requirements and the needs of students and teachers. OCR is a not-for-profit organisation; any surplus made is invested back into the establishment to help towards the development of qualifications and support, which keep pace with the changing needs of today's society.

This mark scheme is published as an aid to teachers and students, to indicate the requirements of the examination. It shows the basis on which marks were awarded by examiners. It does not indicate the details of the discussions which took place at an examiners' meeting before marking commenced.

All examiners are instructed that alternative correct answers and unexpected approaches in candidates' scripts must be given marks that fairly reflect the relevant knowledge and skills demonstrated.

Mark schemes should be read in conjunction with the published question papers and the report on the examination.

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MARKING INSTRUCTIONS**PREPARATION FOR MARKING****RM ASSESSOR**

1. Make sure that you have accessed and completed the relevant training packages for on-screen marking: *RM Assessor Online Training*; *OCR Essential Guide to Marking*.
2. Make sure that you have read and understood the mark scheme and the question paper for this unit.
3. Log-in to RM Assessor and mark the **required number** of practice responses ("scripts") and the **required number** of standardisation responses.

MARKING

1. Mark strictly to the mark scheme.
2. Marks awarded must relate directly to the marking criteria.
3. The schedule of dates is very important. It is essential that you meet the RM Assessor 50% and 100% (traditional 50% Batch 1 and 100% Batch 2) deadlines. If you experience problems, you must contact your Team Leader (Supervisor) without delay.
4. If you are in any doubt about applying the mark scheme, consult your Team Leader by telephone, email or via the RM Assessor messaging system.
5. Work crossed out:

Crossed Out Responses

Where a candidate has crossed out a response and provided a clear alternative then the crossed out response is not marked. Where no alternative response has been provided, examiners may give candidates the benefit of the doubt and mark the crossed out response where legible.

Rubric Error Responses – Optional Questions

Where candidates have a choice of question across a whole paper or a whole section and have provided more answers than required, then all responses are marked and the highest mark allowable within the rubric is given. Enter a mark for each question answered into RM assessor, which will select the highest mark from those awarded. *(The underlying assumption is that the candidate has penalised themselves by attempting more questions than necessary in the time allowed.)*

Multiple Choice Question Responses

When a multiple choice question has only a single, correct response and a candidate provides two responses (even if one of these responses is correct), then no mark should be awarded (as it is not possible to determine which was the first response selected by the candidate).

When a question requires candidates to select more than one option/multiple options, then local marking arrangements need to ensure consistency of approach.

Contradictory Responses

When a candidate provides contradictory responses, then no mark should be awarded, even if one of the answers is correct.

Short Answer Questions (requiring only a list by way of a response, usually worth only **one mark per response**)

Where candidates are required to provide a set number of short answer responses then only the set number of responses should be marked. The response space should be marked from left to right on each line and then line by line until the required number of responses have been considered. The remaining responses should not then be marked. Examiners will have to apply judgement as to whether a 'second response' on a line is a development of the 'first response', rather than a separate, discrete response. *(The underlying assumption is that the candidate is attempting to hedge their bets and therefore getting undue benefit rather than engaging with the question and giving the most relevant/correct responses.)*

Short Answer Questions (requiring a more developed response, worth **two or more marks**)

If the candidates are required to provide a description of, say, three items or factors and four items or factors are provided, then mark on a similar basis – that is downwards (as it is unlikely in this situation that a candidate will provide more than one response in each section of the response space.)

Longer Answer Questions (requiring a developed response)

Where candidates have provided two (or more) responses to a medium or high tariff question which only required a single (developed) response and not crossed out the first response, then only the first response should be marked. Examiners will need to apply professional judgement as to whether the second (or a subsequent) response is a 'new start' or simply a poorly expressed continuation of the first response.

6. Always check the pages (and additional objects if present) at the end of the response in case any answers have been continued there. If the candidate has continued an answer there then add a tick to confirm that the work has been seen.
7. There is a NR (No Response) option. Award NR (No Response)
- if there is nothing written at all in the answer space
 - OR if there is a comment which does not in any way relate to the question (e.g. 'can't do', 'don't know')
 - OR if there is a mark (e.g. a dash, a question mark) which isn't an attempt at the question.

Note: Award 0 marks – for an attempt that earns no credit (including copying out the question).

8. The RM Assessor **comments box** is used by your Team Leader to explain the marking of the practice responses. Please refer to these comments when checking your practice responses. **Do not use the comments box for any other reason.**

If you have any questions or comments for your Team Leader, use the phone, the RM Assessor messaging system, or email.

9. Assistant Examiners will send a brief report on the performance of candidates to their Team Leader (Supervisor) via email by the end of the marking period. The report should contain notes on particular strengths displayed as well as common errors or weaknesses. Constructive criticism of the question paper/mark scheme is also appreciated.

10. For answers marked by levels of response:

Read through the whole answer from start to finish, using the Level descriptors to help you decide whether it is a strong or weak answer. The indicative scientific content in the Guidance column indicates the expected parameters for candidates' answers, but be prepared to recognise and credit unexpected approaches where they show relevance. Using a 'best-fit' approach based on the skills and science content evidenced within the answer, first decide which set of level descriptors, Level 1, Level 2 or Level 3, best describes the overall quality of the answer.

Once the level is located, award the higher or lower mark:

The higher mark should be awarded where the level descriptor has been evidenced and all aspects of the communication statement (in *italics*) have been met.

The lower mark should be awarded where the level descriptor has been evidenced but aspects of the communication statement (in *italics*) are missing.

In summary:

The skills and science content determines the level.

The communication statement determines the mark within a level.

Level of response questions on this paper are **19** and **23**

The only annotation on a level of response question should be the indication of the level.

A level annotation should be used where all marks for a level have been achieved.

e.g. if a candidate has 6 marks, they would have this annotation on their script:

L3

If a candidate has achieved 5 marks then they have reached Level 3 but will not have met the communication statement.

They should have the following annotations on their scripts:

L3



The same principle should be applied to Level 2 and Level 1.
















No marks (0) should have a cross: ✖

Place the annotations alongside the mark for the question.

On additional pages, annotate using

SEEN

11. Annotations available in RM Assessor

Annotation	Meaning
	Correct response
	Incorrect response
	Omission mark
	Benefit of doubt given
	Contradiction
	Rounding error
	Error in number of significant figures
	Error carried forward
	Level 1
	Level 2
	Level 3
	Benefit of doubt not given
	Noted but no credit given
	Ignore
	Blank page

12. Abbreviations, annotations and conventions used in the detailed Mark Scheme (to include abbreviations and subject-specific conventions).

Annotation	Meaning
DO NOT ALLOW	Answers which are not worthy of credit
IGNORE	Statements which are irrelevant
ALLOW	Answers that can be accepted
()	Words which are not essential to gain credit
—	Underlined words must be present in answer to score a mark
ECF	Error carried forward
AW	Alternative wording
ORA	Or reverse argument

13. Subject-specific Marking Instructions

INTRODUCTION

Your first task as an Examiner is to become thoroughly familiar with the material on which the examination depends. This material includes:

- the specification, especially the assessment objectives
- the question paper
- the mark scheme.

You should ensure that you have copies of these materials.

You should ensure also that you are familiar with the administrative procedures related to the marking process. These are set out in the OCR booklet **Instructions for Examiners**. If you are examining for the first time, please read carefully **Appendix 5 Introduction to Script Marking: Notes for New Examiners**.

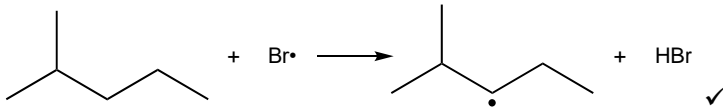
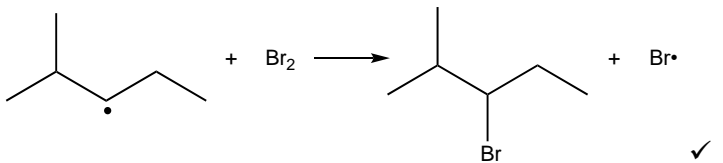
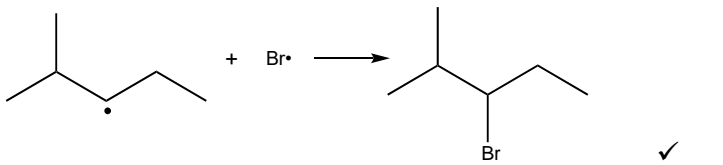
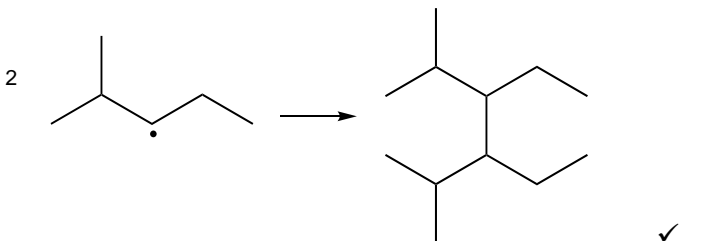
Please ask for help or guidance whenever you need it. Your first point of contact is your Team Leader.

SECTION A

Question	Answer	Marks	AO element	Guidance
1	C	1	AO1.1	
2	A	1	AO1.2	
3	B	1	AO2.1	
4	C	1	AO1.2	
5	B	1	AO1.2	ALLOW 24
6	B	1	AO1.1	
7	A	1	AO1.2	
8	B	1	AO2.2	
9	C	1	AO2.1	
10	B	1	AO2.1	
11	C	1	AO2.1	
12	D	1	AO1.2	
13	B	1	AO1.2	
14	D	1	AO1.2	
15	A	1	AO1.2	
	Total	15		

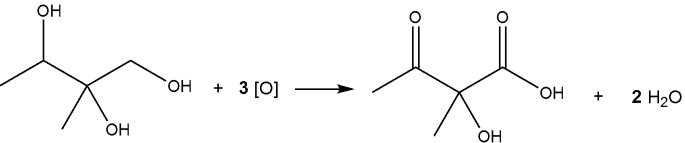
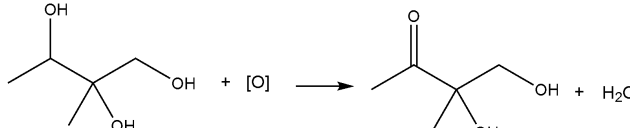
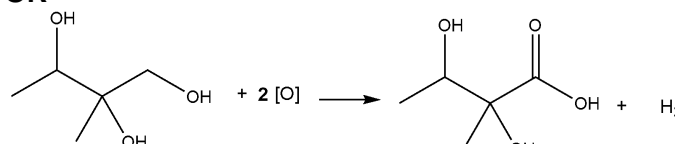
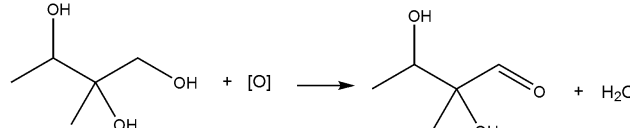
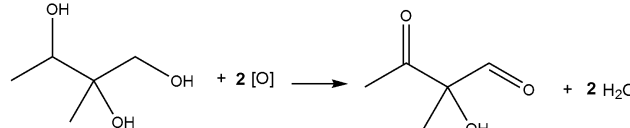
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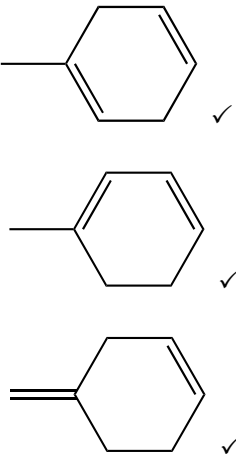
Question			Answer	Marks	AO element	Guidance
16	(a)		<p>Trend for all 3 hydrocarbons (1 mark): Boiling point increases with less branching OR less methyl/alkyl groups/side chains ✓</p> <p>Explanation with comparison (3 marks):</p> <p>Branching and surface contact (Less branching gives) more (surface) contact / interaction (between molecules) ✓</p> <p>Surface contact and London forces (More surface contact) gives more /stronger induced dipole(–dipole) interactions/ London forces ✓</p> <p>Energy and intermolecular forces More energy to break induced dipole(–dipole) interactions/ London forces/intermolecular forces/intermolecular bonds (with less branching) ✓</p>	4	<p>AO1.1</p> <p>AO1.2 X3</p>	<p>ANNOTATE WITH TICKS AND CROSSES Comparisons needed throughout ORA throughout</p> <p>Must have link between rank order of branching and boiling point for all 3. ALLOW Hexane is least branched/straight chain and has highest bp AND 2,2-dimethylbutane is most branched and has lowest bp. IGNORE Chain length</p> <p>Surface area alone is not sufficient, must have idea of contact.</p> <p>DO NOT ALLOW arguments comparing different numbers of electrons (as all have the same number).</p> <p>IGNORE van der Waals'/vdW forces OR IDID OR IDD</p> <p>ALLOW 'more energy to break intermolecular forces' if intermolecular forces are not identified or incorrect. IGNORE harder to overcome/break intermolecular forces (no reference to energy) IGNORE just 'bonds' intermolecular/London forces required</p>

Question			Answer	Marks	AO element	Guidance
16	(b)	(i)	<p>Initiation</p> $\text{Br}_2 \rightarrow 2\text{Br}\cdot$ AND ultraviolet / UV ✓ <p>Propagation</p>  ✓  ✓ <p>Termination</p> $2\text{Br}\cdot \rightarrow \text{Br}_2$ ✓  ✓ <hr style="border-top: 1px dashed black;"/>  ✓	6	AO1.1 AO2.5 AO2.5 AO2.5 AO3.1	<p>DOT REQUIRED throughout IGNORE temperature and pressure</p> <p>ALLOW ECF for use of $\text{Cl}\cdot$ (from Cl_2) in subsequent propagation and termination steps</p> <p>ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</p> <p>ALLOW 1 mark for propagation for 2 ‘correct’ equations but with dot omitted or in wrong position</p> <p>DO NOT ALLOW ECF from incorrect radical intermediate for termination steps</p>

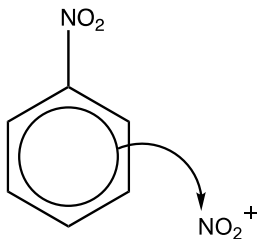
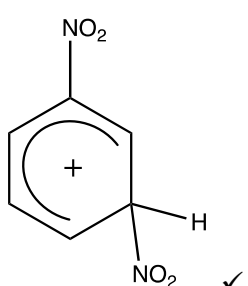
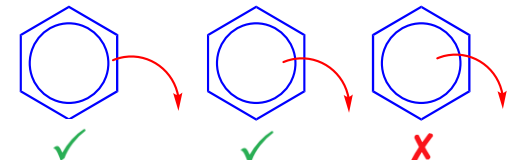
Question			Answer	Marks	AO element	Guidance
16	(b)	(ii)	C_6Br_{14} ✓ Correct balanced equation $\text{C}_6\text{H}_{14} + 14 \text{Br}_2 \rightarrow \text{C}_6\text{Br}_{14} + 14 \text{HBr}$ ✓	2	AO2.6 ×2	ALLOW 1 mark for correct balanced equation using any combination of skeletal OR structural OR displayed formula
	(b)	(iii)	$n(\text{B}) = \frac{72.0}{40000}$ OR $\frac{0.072}{40}$ OR $1.8(0) \times 10^{-3} \text{ (mol)}$ ✓ $M(\text{B}) = \frac{0.8649}{1.8(0) \times 10^{-3}} = 480.5$ ✓ Molecular formula = $\text{C}_6\text{H}_9\text{Br}_5$ ✓	3	AO2.2 ×2 AO3.2	ALLOW 2SF up to calculator value ALLOW ECF from incorrect $n(\text{B})$ ALLOW ECF from incorrect $M(\text{B})$ from $n(\text{B})$ <hr/> COMMON ERROR $n(\text{B}) = \frac{72.0}{24000} = 3 \times 10^{-3} \text{ (mol)}$ ✗ $M(\text{B}) = \frac{0.8649}{3 \times 10^{-3}} = 288.3$✓ Molecular formula = $\text{C}_6\text{H}_{12}\text{Br}_2$ OR $\text{C}_6\text{H}_{11}\text{Br}_3$ ✓ ALLOW ECF for viable molecular formula with C_6 but must be derived from a calculated value for $M(\text{B})$

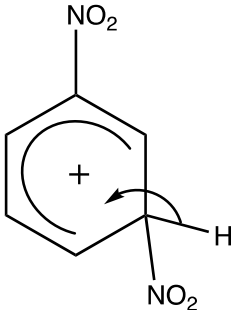
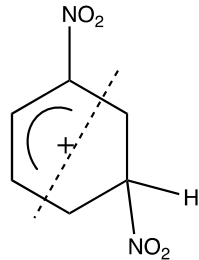
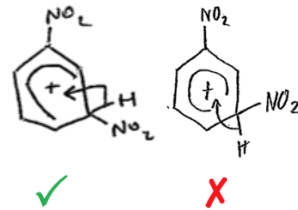
Question			Answer	Marks	AO element	Guidance
17	(a)		$\text{C}_6\text{H}_{11}\text{OH}$ ✓ Correct balanced equation $\text{C}_6\text{H}_{11}\text{OH} + 8\frac{1}{2} \text{O}_2 \rightarrow 6 \text{CO}_2 + 6 \text{H}_2\text{O}$ ✓	2	AO2.6 ×2	For $\text{C}_6\text{H}_{11}\text{OH}$, ALLOW $\text{C}_6\text{H}_{12}\text{O}$ OR any combination of skeletal OR structural OR displayed formula ALLOW multiples IGNORE state symbols ALLOW multiple OH groups in structure for both marks e.g. $\text{C}_6\text{H}_{12}\text{O}_2$ ✓ $\text{C}_6\text{H}_{12}\text{O}_2 + 8 \text{O}_2 \rightarrow 6 \text{CO}_2 + 6 \text{H}_2\text{O}$ ✓

Question	Answer	Marks	AO element	Guidance
17 (b)	 <p>Compound C</p> <p>Correct organic product ✓✓</p> <p>Correct balanced equation ✓</p>	3	<p>AO2.5 ×2</p> <p>AO2.6</p>	<p>ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</p> <p>ALLOW any vertical bond to the OH group e.g. ALLOW</p> <div style="display: flex; align-items: center; justify-content: center;"> <div style="text-align: center;"> OH</div> <div style="margin: 0 10px;">OR</div> <div style="text-align: center;"> HO</div> </div> <p>ALLOW 1 mark for partially oxidised organic product and an additional mark for ECF for correct balanced equation for this product. i.e.</p> <div style="text-align: center;">  <p>Organic product ✓ Correct balanced equation ✓</p> </div> <p>OR</p> <div style="text-align: center;">  </div> <p>OR</p> <div style="text-align: center;">  </div> <p>OR</p> <div style="text-align: center;">  </div>

Question			Answer	Marks	AO element	Guidance
17	(c)	(i)		3	AO2.5 ×3	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous
	(c)	(ii)	NaI / KI AND H ₂ SO ₄ ✓	1	AO1.2	ALLOW HI ALLOW NaI / KI AND H ₃ PO ₄ OR HNO ₃ IGNORE Conc or dilute

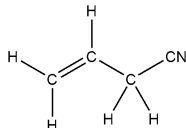
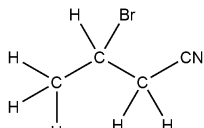
Question			Answer	Marks	AO element	Guidance
17	(d)		<p>Structures 1 mark $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ AND $\text{CH}_3\text{CH}_2\text{CHOHCH}_3$ AND $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$ AND $(\text{CH}_3)_3\text{COH}$ ✓</p> <p>Number of peaks 3 marks $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$/ butan-1-ol OR $\text{CH}_3\text{CH}_2\text{CHOHCH}_3$/ Butan-2-ol have 4 peaks/environments/types of carbon ✓</p> <p>$(\text{CH}_3)_2\text{CHCH}_2\text{OH}$/ (2-)methylpropan-1-ol has 3 peaks/environments/types of carbon ✓</p> <p>$(\text{CH}_3)_3\text{COH}$/(2-)methylpropan-2-ol has 2 peaks/environments/types of carbon ✓</p> <p>Statement 1 mark $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$/(2-)methylpropan-1-ol can be distinguished (from any other isomer) OR $(\text{CH}_3)_3\text{COH}$/(2-)methylpropan-2-ol can be distinguished (from any other isomer) OR $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$/ butan-1-ol AND $\text{CH}_3\text{CH}_2\text{CHOHCH}_3$/ butan-2-ol cannot be distinguished ✓</p>	5	<p>AO2.1</p> <p>AO3.1 ×3</p> <p>AO3.2 ×1</p>	<p>ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</p> <p>Note: all 4 structures are needed for the mark. Additional incorrect structures prevent this mark being awarded.</p> <p>IGNORE chemical shifts</p> <p>IGNORE incorrect name if structure given</p> <p>ALLOW correct number of peaks linked to an incomplete structure e.g. C-C-C-C-OH has 4 peaks (no hydrogens shown)</p> <p>Statement mark can only be awarded if candidate compares at least two isomers and determines correct number of peaks for the isomers referred to.</p> <p>DO NOT ALLOW ECF from an incorrect number of peaks/environments/types of carbon</p>

Question	Answer	Marks	AO element	Guidance
18 (a)	<p>Role of H₂SO₄ catalyst 2 marks</p> <p><i>Forming electrophile</i> $\text{HNO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{H}_2\text{O} + \text{HSO}_4^- + \text{NO}_2^+ \checkmark$</p> <p><i>Reforming catalyst</i> $\text{H}^+ + \text{HSO}_4^- \longrightarrow \text{H}_2\text{SO}_4 \checkmark$</p> <p>Electrophilic attack 1 mark</p> <p>Curly arrow from π-bond to NO_2^+ \checkmark</p>  <hr/> <p>Correct intermediate 1 mark</p> 	5	<p>AO1.2</p> <p>AO1.2</p> <p>AO1.2</p> <p>AO2.5</p>	<p>ANNOTATE ANSWER WITH TICKS AND CROSSES</p> <p>ALLOW $\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{H}_3\text{O}^+ + 2\text{HSO}_4^- + \text{NO}_2^+$</p> <p>ALLOW $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{NO}_3^+ + \text{HSO}_4^-$ then $\text{H}_2\text{NO}_3^+ \rightarrow \text{H}_2\text{O} + \text{NO}_2^+$</p> <p>ALLOW $^+\text{NO}_2$ OR NO_2^+</p> <p>NOTE: curly arrows can be straight, snake-like, etc. but NOT double headed or half headed arrows</p> <p>1st curly arrow must</p> <ul style="list-style-type: none"> start from, OR close to circle of benzene ring <p>AND</p> <ul style="list-style-type: none"> go to anywhere on NO_2^+  <p>DO NOT ALLOW mark for intermediate if additional NO_2 is missing</p>

Question	Answer	Marks	AO element	Guidance
	<p>-----</p> <p>Reforming benzene ring 1 mark</p> <p>Curly arrow from C–H bond to reform π-ring ✓</p>  <p>Curly arrow must start from, OR be traced back to, any part of C–H bond and go inside the ‘hexagon’</p>		AO1.2	<p>IGNORE connectivity to NO₂ groups (<i>mark is for correct substitution position and position of π-ring</i>)</p> <p>DO NOT ALLOW the following intermediate:</p>  <p>π-ring should cover approximately 4 of the 6 sides of the benzene ring structure AND the correct orientation, <i>i.e.</i> gap towards C with NO₂ and H</p>  <p>ALLOW + sign anywhere inside the ‘hexagon’ of intermediate</p>

Question		Answer	Marks	AO element	Guidance
18	(b)	<p>FIRST CHECK ANSWER ON ANSWER LINE If answer = 73.2 award 3 marks</p> <p>-----</p> <p>Theoretical moles $n(\text{C}_6\text{H}_5\text{NO}_2)$ OR $n(\text{C}_6\text{H}_4(\text{NO}_2)_2)$ $= \frac{12.5 \times 1.20}{123.0}$ OR 0.12195... (mol) ✓</p> <p>Actual moles $n(\text{C}_6\text{H}_4(\text{NO}_2)_2) = \frac{15.0}{168.0}$ OR 0.0892857(mol) ✓</p> <p>% yield = $\frac{0.0892857...}{0.12195....} \times 100$ = 73.2 % to 3SF ✓</p>	3		<p>ALLOW 3SF up to calculator value throughout working</p> <p>IGNORE rounding errors past 3SF</p> <p>TAKE CARE as value written down may be truncated but with value stored in calculator, depending on rounding, either can be credited.</p> <p>AO2.8 Calculator = 0.1219512195</p> <p>AO2.8 Calculator = 0.08928571429</p> <p>AO1.2 ALLOW ECF except for final mark if value is $\geq 100\%$</p> <p>-----</p> <p>Alternative method using mass</p> <p>1. Theoretical moles = 0.12195.... mol</p> <p>2. Mass = 0.12195... \times 168.0 OR 20.4878... g</p> <p>3. % yield = $\frac{15}{20.4878...} \times 100 = 73.2\%$</p> <p>-----</p> <p>Common errors</p> <p>87.9% → 2 marks</p> <ul style="list-style-type: none"> From $\frac{12.5}{123} = 0.101626....$ (no density)

Question			Answer	Marks	AO element	Guidance
18	(c)		<p><u>Dissolve</u> in the <u>minimum</u> quantity of <u>hot</u> water/solvent ✓</p> <p>Cool (to allow crystals form) AND Then filter (under reduced pressure) ✓</p> <p>(Leave to) <u>dry</u> ✓</p>	3	AO3.3 ×3	<p>ALLOW any solvent</p> <p>IGNORE</p> <ul style="list-style-type: none"> Initial filtering Filtration between dissolving and cooling (implies hot filtration) Washing with cold solvent <p>DO NOT ALLOW use of drying agent (e.g. MgSO₄)</p>

Question	Answer	Marks	AO element	Guidance
19*	<p>Refer to marking instructions on page 4 of mark scheme for guidance on marking this question.</p> <p>Level 3 (5-6 marks) A three stage synthesis in the correct order AND Equations for each stage are mostly correct AND Most reagents 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) Synthesis includes at least two stages in any order OR uses NH_3 and HBr in the correct order (without chain extension) AND some of the reagents and some equations 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) Planned synthesis includes reagents for any two stages OR Describes one stage with reagents 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>	6	AO3.3 ×6	<p>Mark second page as SEEN</p> <p>Indicative scientific points may include:</p> <p>IGNORE conditions</p> <p>Stage 1: Reaction with CN^-</p> <ul style="list-style-type: none"> Reagents: CN^- (in ethanol) Equation: $\text{H}_2\text{C}=\text{CHCH}_2\text{Br} + \text{CN}^- \rightarrow \text{H}_2\text{C}=\text{CHCH}_2\text{CN} + \text{Br}^-$ <p>Intermediate 1</p>  <p>Stage 2: Addition of HBr to $\text{C}=\text{C}$</p> <ul style="list-style-type: none"> Reagents: HBr Equation: $\text{H}_2\text{C}=\text{CHCH}_2\text{CN} + \text{HBr} \rightarrow \text{CH}_3\text{CHBrCH}_2\text{CN}$ <p>Intermediate 2</p>  <p>Stage 3: Reduction of CN</p> <ul style="list-style-type: none"> Reagents: H_2 (with Ni) Equation: $\text{H}_3\text{CCHBrCH}_2\text{CN} + 2\text{H}_2 \rightarrow \text{CH}_3\text{CHBrCH}_2\text{CH}_2\text{NH}_2$ <p>Needs CN^- before HBr – CN^- would react with both Br atoms</p> <p>Needs HBr before H_2 – H_2 would react with $\text{C}=\text{C}$</p>

Question	Answer	Marks	AO element	Guidance
	<p>0 marks No response or no response worthy of credit.</p>			<p><u>Alternative three stage syntheses:</u></p> <p><i>Alternative using LiAlH₄</i> <i>Caution - Can be done as stage 2 or 3</i></p> <ul style="list-style-type: none"> • Reagents: LiAlH₄ • Equation: $\text{H}_2\text{C}=\text{CHCH}_2\text{CN} + 4[\text{H}] \rightarrow \text{H}_2\text{C}=\text{CHCH}_2\text{CH}_2\text{NH}_2$ <p>OR</p> $\text{H}_3\text{CCHBrCH}_2\text{CN} + 4[\text{H}] \rightarrow \text{CH}_3\text{CHBrCH}_2\text{CH}_2\text{NH}_2$ <p><i>Needs CN⁻ before HBr and LiAlH₄</i> <i>Can have HBr and LiAlH₄ in any order</i></p> <p><i>Alternative using radical substitution:</i> <i>Stage 1: Reaction with CN⁻</i></p> <ul style="list-style-type: none"> • Reagents: CN⁻ (in ethanol) • Equation: $\text{H}_2\text{C}=\text{CHCH}_2\text{Br} + \text{CN}^- \rightarrow \text{H}_2\text{C}=\text{CHCH}_2\text{CN} + \text{Br}^-$ <p><i>Stage 2: Reduction of CN and C=C</i></p> <ul style="list-style-type: none"> • Reagents: H₂ (with Ni) • Equation: $\text{H}_2\text{C}=\text{CHCH}_2\text{CN} + 3\text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ <p><i>Stage 3: Reaction with Br₂</i></p> <ul style="list-style-type: none"> • Reagents: Br₂ (with UV) • Equation: $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 + \text{Br}_2 \rightarrow$ $\text{CH}_3\text{CHBrCH}_2\text{CH}_2\text{NH}_2 + \text{HBr}$ <p><i>Needs CN⁻ before H₂</i> <i>Needs H₂ before Br₂</i></p>

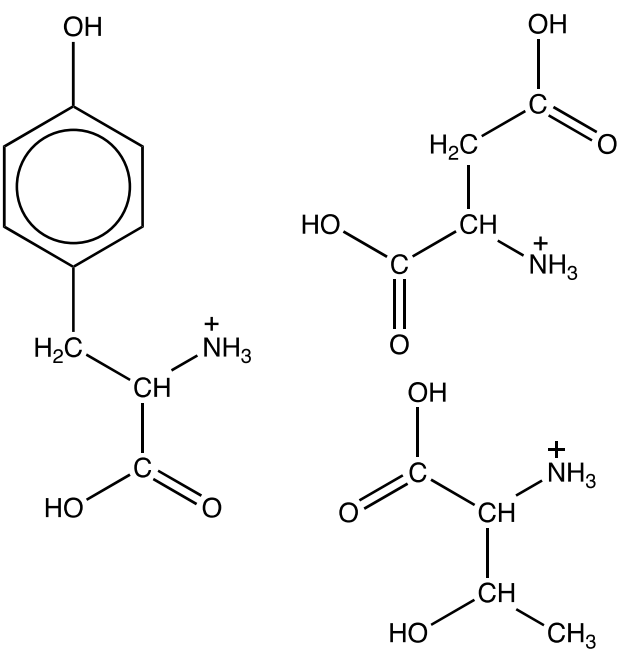
Question	Answer	Marks	AO element	Guidance
				<p>Two stage synthesis using NH_3 and HBr forming product with no lengthening of carbon chain</p> <p>Stage 1: Reaction of NH_3</p> <ul style="list-style-type: none"> • Reagents: NH_3 (in ethanol) • Equation: $\text{H}_2\text{C}=\text{CHCH}_2\text{Br} + \text{NH}_3 \rightarrow \text{H}_2\text{C}=\text{CHCH}_2\text{NH}_2 + \text{HBr}$ OR 2 $\text{NH}_3 \rightarrow \text{NH}_4\text{Br}$ <p>Stage 2: Addition of HBr to $\text{C}=\text{C}$</p> <ul style="list-style-type: none"> • Reagents: HBr • Equation: $\text{H}_2\text{C}=\text{CHCH}_2\text{NH}_2 + \text{HBr} \rightarrow \text{CH}_3\text{CHBrCH}_2\text{NH}_2$ <p>Needs NH_3 before HBr – HBr would react with $\text{C}=\text{C}$</p>

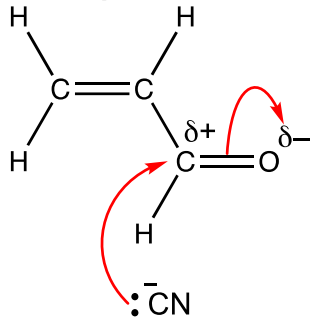
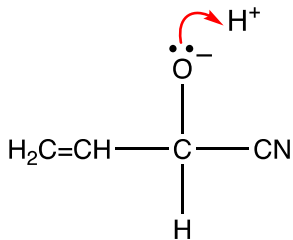
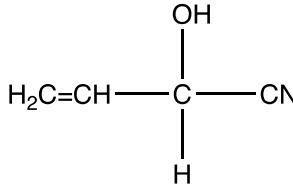
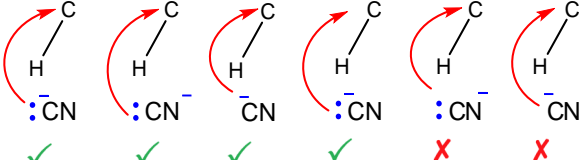
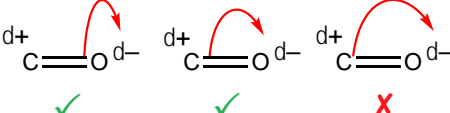
Question	Answer	Marks	AO element	Guidance
20 (a)		4	AO2.5 ×4	<p>IGNORE connectivity of phenol OH group and COOH group throughout (<i>marks are for correct conversions</i>)</p> <p>Br₂ ALLOW Br substitution at any position on ring ALLOW up to 4 Br atoms onto ring</p> <p>Na₂CO₃ ALLOW COO⁻ OR COONa</p> <p>(CH₃CH₂CO)₂O IGNORE reaction of COOH to form an acid anhydride</p> <p>ALLOW structures in bottom 2 boxes in either order</p>

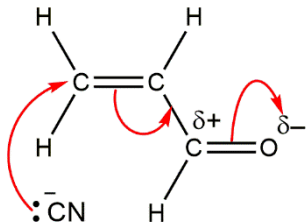
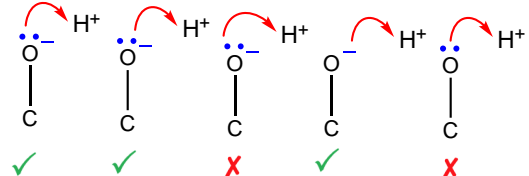
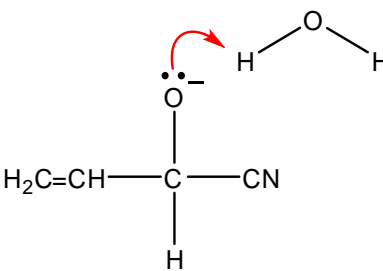
Question			Answer	Marks	AO element	Guidance
20	(b)	(i)	<p>Section contains</p> <p>A displayed amide linkage between 2 benzene rings ✓</p> <p>A displayed ester linkage between 2 benzene rings ✓</p> <p>Section with at least one 'end bond' and correct positioning of all 3 groups on each benzene ✓</p>	3	<p>AO1.2 ×2</p> <p>AO3.2</p>	<p>Marking point 3 is dependent on first 2 marks Check bonding around each benzene so C=O position 1, C-O position 2 and C-NH position 4.</p> <p>ALLOW 'end bonds' (with either a solid or dashed line') OR terminal ends e.g. -O- or -OH</p> <p>ALLOW any combination of 'end bonds' as showing a section not a repeat unit</p> <p>IGNORE connectivity of OH and NH₂ groups to benzene</p>

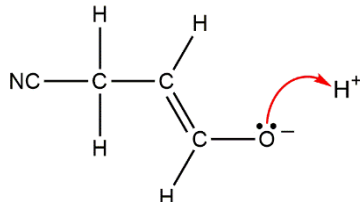
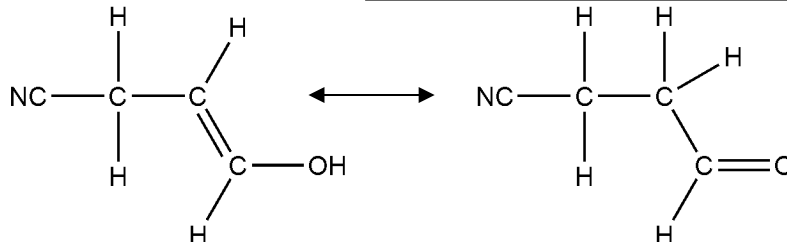
Question			Answer	Marks	AO element	Guidance
20	(b)	(ii)	<p>FIRST CHECK ANSWER ON THE ANSWER LINE If answer = 2.36×10^{22} award 3 marks</p> <p>Calculate moles of PAS:</p> <p>300 mg of PAS contains $\frac{300 \times 10^{-3}}{153}$ OR $1.96 \dots \times 10^{-3}$ (mol) ✓</p> <p>Daily dose of PAS:</p> <p>$n(\text{PAS})$ for 20.0 kg child = $20 \times 1.96 \dots \times 10^{-3}$ (mol) OR 0.0392..... (mol) ✓</p> <p>Use of Avogadro's constant:</p> <p>Number of PAS molecules = $0.0392 \dots \times 6.02 \times 10^{23}$ = 2.36×10^{22} ✓</p>	3	<p>AO3.1 ×2</p> <p>AO3.2 ×1</p>	<p>ALLOW 3SF up to calculator value throughout</p> <p>IGNORE rounding errors past 3SF</p> <p>If there is an alternative answer, apply ECF throughout. Steps can be carried out in any order.</p> <p>Calculator values:</p> <p>$1.960784314 \times 10^{-3}$</p> <p>0.03921568627</p> <p>Common alternative method: $m(\text{PAS})$ for 20.0 kg child = 0.3×20 OR 6.0 (g) ✓ $n(\text{PAS})$ for 20.0 kg child = $6/153$ OR 0.0392...(mol) ✓</p>

[illegible]

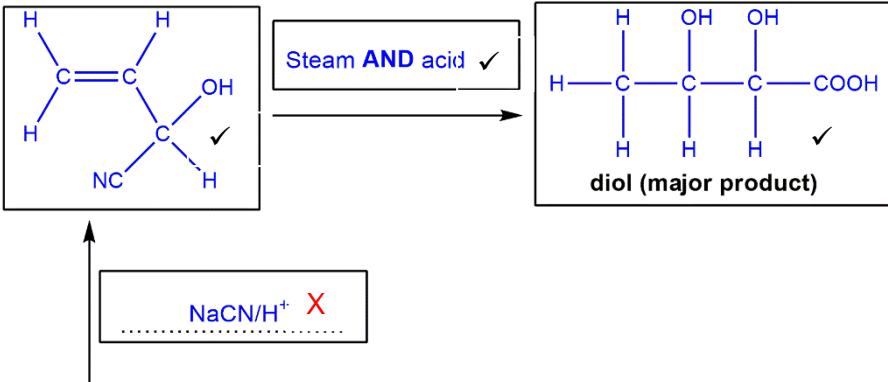
Question			Answer	Marks	AO element	Guidance
21	(c)	(i)	16 ✓	1	AO2.6	
	(c)	(ii)	 <p>1 mark for each correct structure with</p> <ul style="list-style-type: none"> • Either NH_3^+ OR NH_2 ✓✓✓ <p>1 mark for</p> <ul style="list-style-type: none"> • all 3 correct structures with NH_3^+ ✓ 	4	AO2.5 ×4	<p>ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</p> <p>IGNORE connectivity</p> <p>ALLOW + charge on H of NH_3 group, i.e. NH_3^+</p> <p>If structures are shown with NH_3 groups (without the + charge) OR as NH_2^+ groups allow ECF for subsequent use.</p> <p>ALLOW structures shown as correctly balanced salts, e.g. NH_3Cl OR NH_3^+Cl^- all marks can be awarded.</p>

Question	(a)	(i)	Answer	Marks	AO	Guidance
22			<p>NOTE: curly arrows can be straight, snake-like, etc. but NOT double headed or half headed arrows</p> <hr/> <p>Nucleophilic attack 2 marks</p> <div style="display: flex; align-items: center;">  <div style="border: 1px solid black; padding: 5px; margin-left: 10px;"> Curly arrow from :CN^- to C of C=O ✓ Correct dipole shown on C=O AND curly arrow showing breaking of C=O ✓ </div> </div> <hr/> <p>Intermediate 1 mark</p> <div style="display: flex; align-items: center;">  <div style="border: 1px solid black; padding: 5px; margin-left: 10px;"> Correct intermediate AND curly arrow from O^- to H^+ ✓ DO NOT ALLOW δ^- on O of intermediate IGNORE connectivity of $\text{H}_2\text{C=CH-}$ </div> </div> <hr/> <p>Product 1 mark</p> <div style="display: flex; align-items: center;">  <div style="border: 1px solid black; padding: 5px; margin-left: 10px;"> Correct product ✓ </div> </div>	4	AO1.2 ×2 AO2.5 ×2	<p>ANNOTATIONS MUST BE USED</p> <p>1st curly arrow must</p> <ul style="list-style-type: none"> go to the C atom of C=O AND start from, OR be traced back to any point across width of lone pair on C of :CN OR :CN^- OR start from $-$ charge on C of :CN (then lone pair on CN^- does not need to be shown) <div style="display: flex; justify-content: space-around;">  </div> <p>2nd curly arrow must</p> <ul style="list-style-type: none"> start from, OR be traced back to any part of $\delta^+\text{C=O}$ δ^- bond AND go to $\text{O}^{\delta-}$ (across width of $\text{O}^{\delta-}$) <div style="display: flex; justify-content: space-around;">  </div> <p>3rd curly arrow must</p> <ul style="list-style-type: none"> go to H^+ AND start from, OR be traced back to any point across width of lone pair on :O^- OR start from $-$ charge of O^- of intermediate (then lone pair on O^- does not need to be shown)

Question	Answer	Marks	AO	Guidance
	<p>Possible alternative 1,4 (conjugate) addition can be credited as follows (not in specification):</p> <p>-----</p> <p>Nucleophilic attack 2 marks</p> <div style="display: flex; align-items: center;">  <div style="border: 1px solid black; padding: 5px; margin-left: 10px;"> <p>Curly arrow from CN^- to C of CH_2 of $\text{C}=\text{C}$ ✓</p> <p>Curly arrow from $\text{C}=\text{C}$ to $\text{C}-\text{C}$ AND curly arrow showing breaking of $\text{C}=\text{O}$ ✓</p> </div> </div> <p>-----</p>			 <p>NOTE: For arrow to H^+ ALLOW arrow to H of H_2O i.e.</p>  <p>IGNORE attempt to draw curly arrow showing breaking of $\text{H}-\text{O}$ in H_2O</p> <p>IGNORE lack of dipole on H_2O</p> <p>IGNORE absence of OH^- as 2nd product Otherwise this more difficult mechanism could cost 2 marks</p>

Question			Answer	Marks	AO	Guidance
			<p>Intermediate 1 mark</p> <div></div> <div><p>Correct intermediate AND curly arrow from O⁻ to H⁺ ✓</p><p>DO NOT ALLOW δ- on O of intermediate</p></div> <p>-----</p> <p>Product 1 mark</p> <div><p>Either tautomer as correct product ✓</p><div></div></div>			<p>Product mark can only be given here if clear from mechanism that there is nucleophilic attack of CH₂ in C=C.</p> <p>Same product could be seen with an attempt at electrophilic addition across C=C.</p>
22	(a)	(ii)	Nucleophilic addition ✓	1	AO1.1	IGNORE just 'addition'

Question		Answer	Marks	AO	Guidance
22	(b)	<p>alcohol</p> <p>diol (major product)</p> <p>carboxylic acid</p> <p>acyl chloride</p> <p>polymer (2 repeat units)</p> <p>acrolein</p> <p>Reagents: NaBH_4, Steam AND acid, H^+ AND $\text{Cr}_2\text{O}_7^{2-}$, SOCl_2</p>	9	AO1.2 x4 AO2.5 x5	<p>ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</p> <p>ALLOW Correct names instead of formula for all reagents throughout e.g. For H^+ and $\text{Cr}_2\text{O}_7^{2-}$, ALLOW acidified dichromate</p> <p>For Steam and acid</p> <ul style="list-style-type: none"> For steam, ALLOW $\text{H}_2\text{O}(\text{g})$ OR H_2O with $T \geq 100^\circ\text{C}$ For acid, ALLOW H^+ OR H_2SO_4 OR H_3PO_4 Note both needed for 1 mark. ALLOW either way round. <p>For NaBH_4</p> <ul style="list-style-type: none"> IGNORE water / aqueous / acid ALLOW LiAlH_4 <p>For SOCl_2, ALLOW PCl_5 OR COCl_2</p> <ul style="list-style-type: none"> IGNORE H^+ OR HCl <p>For H^+ and $\text{Cr}_2\text{O}_7^{2-}$, ALLOW H_2SO_4 AND $\text{K}_2\text{Cr}_2\text{O}_7$ OR $\text{Na}_2\text{Cr}_2\text{O}_7$ ALLOW Tollens' reagent</p> <p>IGNORE connectivity except DO NOT ALLOW -COH for aldehyde</p> <p>For polymer ALLOW alternating side chains. IGNORE brackets and use of 'n' 'End bonds' MUST be shown (solid or dotted)</p>

Question	Answer	Marks	AO	Guidance
	<p>Only possible alternative that can gain credit:</p> <p>Reaction with NaCN/H⁺</p> <div style="text-align: center;">  </div>			<p>IF NaCN/H⁺ reacted with acrolein instead of NaBH₄</p> <ul style="list-style-type: none"> • No mark for NaCN/H⁺ OR HCN • Unsaturated alcohol award mark for product as shown • Final product must have CN hydrolysed as shown

Question	Answer	Marks	AO element	Guidance
23	<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 is either $\text{CH}_3\text{CH}_2\text{COOCH}_2\text{C}(\text{CH}_3)_3$ OR $(\text{CH}_3)_3\text{CCH}_2\text{COOCH}_2\text{CH}_3$ 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) Structure is an ester of $\text{C}_8\text{H}_{16}\text{O}_2$ with some key features present AND Analyses some of the data from at least 3 of the scientific points.</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) Attempts analysis from at least 2 of the scientific points.</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	AO1.2 × 2 AO3.1 × 2 AO3.2 × 2	<p>Mark spectra page as SEEN</p> <p>Indicative scientific points:</p> <p>1. Empirical Formulae</p> $\begin{aligned} \text{C} : \text{H} : \text{O} &= \frac{66.63}{12.0} : \frac{11.18}{1.0} : \frac{22.19}{16.0} \\ &= 5.55 : 11.18 : 1.39 \\ &= 4 : 8 : 1 \end{aligned}$ <ul style="list-style-type: none"> Empirical formula = $\text{C}_4\text{H}_8\text{O}$ <p>2. Molecular Formulae</p> <ul style="list-style-type: none"> uses $m/z = 144.0$ to determine molecular formula as $\text{C}_8\text{H}_{16}\text{O}_2$ <p>3. Functional group From IR, <ul style="list-style-type: none"> → $\text{C}=\text{O}$ from $\sim 1740 \text{ cm}^{-1}$ IGNORE references to $\text{C}-\text{O}$ peaks</p> <p>No reaction with 2,4-DNP <ul style="list-style-type: none"> → no carbonyl/no ketone and aldehyde Likely to be an ester </p> <p>4. ^1H NMR analysis</p> <ul style="list-style-type: none"> $\delta = 0.9 \text{ ppm}$, singlet, 9H $-\text{C}(\text{CH}_3)_3$ $\delta = 1.2 \text{ ppm}$, triplet, 3H CH_3CH_2- $\delta = 2.2 \text{ ppm}$, quartet, 2H $\text{CH}_3\text{CH}_2\text{CO}$ $\delta = 4.1 \text{ ppm}$, singlet, 2H $-\text{OCH}_2-$ <p>ALLOW approximate values for chemical shifts.</p>

Question	Answer	Marks	AO element	Guidance
				<p>Structure ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</p> <p>Key features consistent with chemical shift data and relative peak areas</p> <ul style="list-style-type: none"> • O-CH₂ • C(CH₃)₃ • CH₃CH₂C=O <p>Correct Structure</p> <ul style="list-style-type: none"> • CH₃CH₂COOCH₂C(CH₃)₃ <div style="text-align: center;"> $\begin{array}{ccccccc} & & & \text{O} & & \text{CH}_3 & \\ & & & & & & \\ \text{CH}_3 - & \text{CH}_2 - & \text{C} - & \text{O} - & \text{CH}_2 - & \text{C} - & \text{CH}_3 \\ & & & & & & \\ & & & & & \text{CH}_3 & \end{array}$ </div>

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