



GCE

Chemistry A

H432/02: Synthesis and analytical techniques

Advanced GCE

Mark Scheme for June 2019

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



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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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

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

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.

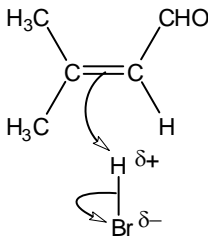
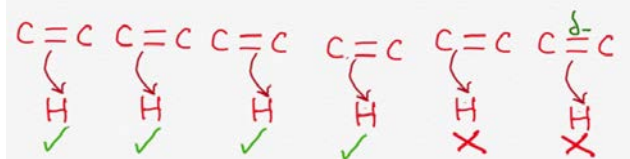
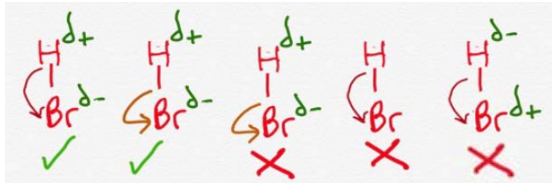
You should ensure also that you are familiar with the administrative procedures related to the marking process. These are set out in the OCR booklet **Instructions for Examiners**. If you are examining for the first time, please read carefully **Appendix 5 Introduction to Script Marking: Notes for New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

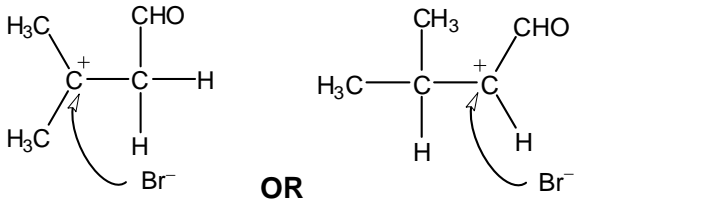
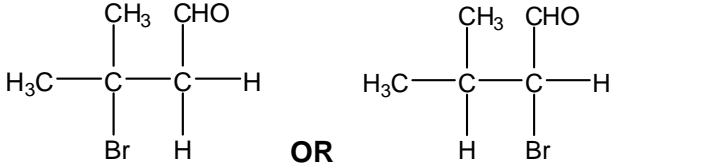

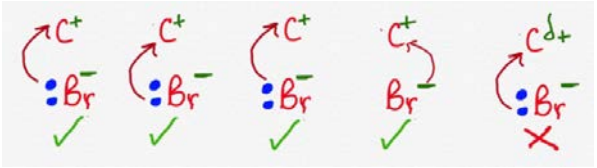
Please ask for help or guidance whenever you need it. Your first point of contact is your Team Leader.

SECTION A

Question	Answer	Marks	AO element	Guidance
1	A	1	AO1.2	
2	D	1	AO2.1	
3	C	1	AO1.2	
4	C	1	AO1.2	ALLOW E (This is the correct term)
5	D	1	AO2.5	
6	A	1	AO2.5	
7	B	1	AO1.2	ALLOW 6 (This is the number of chiral centres)
8	C	1	AO1.2	
9	A	1	AO2.5	
10	B	1	AO2.5	
11	A	1	AO2.4	
12	C	1	AO2.5	
13	C	1	AO1.2	
14	A	1	AO1.1	
15	B	1	AO1.2	
	Total	15		

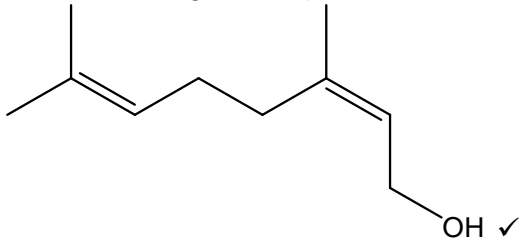
SECTION B

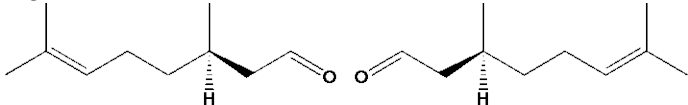
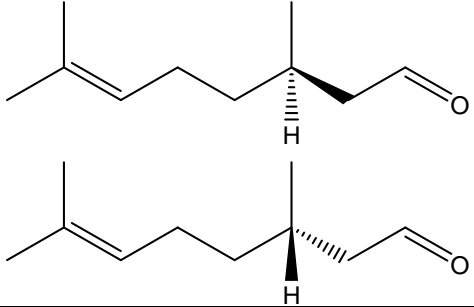
Question			Answer	Marks	AO element	Guidance
16	(a)	(i)	<p>ANNOTATE ANSWER WITH TICKS AND CROSSES</p>  <p>Curly arrow from C=C bond to H of H-Br ✓ DO NOT ALLOW partial charge on C=C</p> <p>Correct dipole shown on H-Br AND curly arrow showing breaking of H-Br bond ✓</p>	4		<p>NOTE: curly arrows can be 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"> go to the H atom of H-Br <p>AND</p> <ul style="list-style-type: none"> start from, OR be traced back to any point across width of C=C  <p>2nd curly arrow must</p> <ul style="list-style-type: none"> start from, OR be traced back to any part of $\delta^+H-Br\delta^-$ bond <p>AND</p> <ul style="list-style-type: none"> go to $Br\delta^-$ 

Question	Answer	Marks	AO element	Guidance
	<p>Correct carbocation AND curly arrow from Br⁻ to C⁺ of carbocation ✓ DO NOT ALLOW δ+ on C of carbocation</p>  <p style="text-align: center;">OR</p> <p>-----</p> <p>Correct product ✓</p>  <p style="text-align: center;">OR</p>	2	AO2.5 AO2.5	<p>IGNORE connectivity of CHO and CH₃ groups in carbocation and product e.g. ALLOW</p>  <p style="text-align: center;">OR</p> <p>ALLOW COH for CHO (<i>reaction does not involve this group</i>)</p> <p>3rd curly arrow must</p> <ul style="list-style-type: none"> • go to the C⁺ of carbocation <p>AND</p> <ul style="list-style-type: none"> • start from, OR be traced back to any point across width of lone pair on :Br⁻ • OR start from – charge of Br⁻ ion  <p>(Lone pair NOT needed if curly arrow shown from – charge of Br⁻ ion)</p> <p>IF Br₂ is used instead of HBr contact your Team Leader</p>
(a) (ii)	(major product forms from) most/more stable	2		For carbocation,

Question			Answer	Marks	AO element	Guidance
			<p>intermediate/carbocation ✓</p> <p>(major product forms from a) tertiary carbocation OR carbocation bonded to more C atoms / more alkyl groups OR carbocation bonded to no H atoms ✓</p>		<p>AO1.1</p> <p>AO1.2</p>	<p>ALLOW carbonium ion or cation</p> <p>IGNORE descriptions of the major/minor product in terms of Markownikoff's rule e.g. H atom joins to C with most H</p> <p>IGNORE references to stability of the product</p> <p>-----</p> <p>ALLOW ORA, i.e.</p> <p>(minor product forms from) least/less stable intermediate/carbocation ✓</p> <p>(minor product forms from a) secondary carbocation OR carbocation bonded to fewer C atoms / more alkyl groups OR carbocation bonded to H atoms ✓</p> <p>-----</p>
	(b)	(i)	Tollens' (reagent) ✓	2	AO1.2	ALLOW ammoniacal silver nitrate OR Ag ⁺ /NH ₃

Question			Answer	Marks	AO element	Guidance
			Silver (mirror/precipitate/ppt/solid) with citronellal/the aldehyde ✓		×2	<p>ALLOW black ppt OR grey ppt</p> <p>IGNORE references to acidified dichromate reacting with both compounds</p> <p>-----</p> <p>ALLOW 2,4-DNP/2,4-DNPH ALLOW Brady's reagent ✓</p> <p>Yellow/orange/red precipitate with citronellal/aldehyde/carbonyl group ✓</p> <p>-----</p> <p>IF other reagents are seen, contact your Team Leader</p>
	(b)	(ii)	C ₁₀ H ₁₈ O ✓	1	AO1.2	DO NOT ALLOW C ₁₀ H ₁₇ OH
	(b)	(iii)	<p>Same molecular formula AND Different structural formulae ✓</p> <p>OR</p> <p>Both (geraniol and citronellal) have the molecular formula C₁₀H₁₈O AND Different structural formulae ✓</p>	1	AO1.1	<p>Same formula is not sufficient <i>(no reference to molecular)</i></p> <p>Different arrangement of atoms is not sufficient <i>(no reference to structure/structural)</i></p> <p>For structural formulae, ALLOW structure/displayed/skeletal formulae/functional groups</p> <p>DO NOT ALLOW any reference to spatial/space</p> <p>ALLOW ECF from incorrect molecular formula in (b)(ii)</p>
		(iv)	Same structural formula	1	AO1.1	ALLOW structure/displayed/skeletal formula

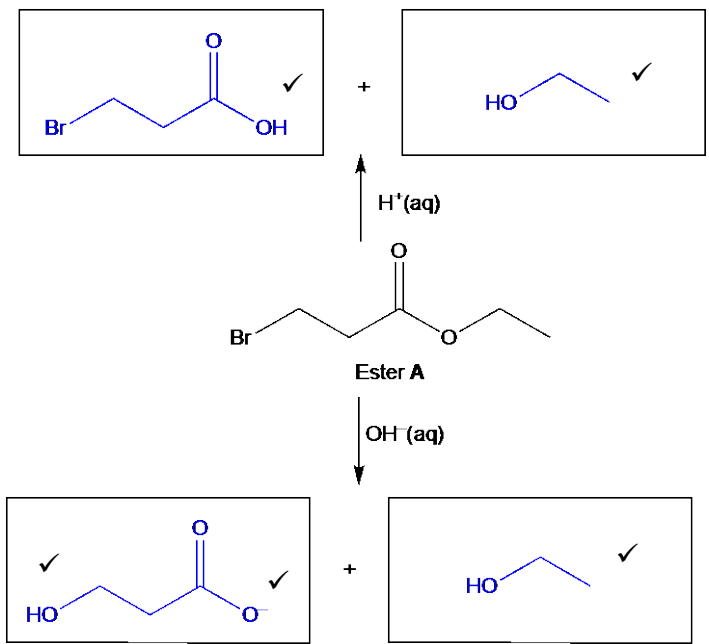


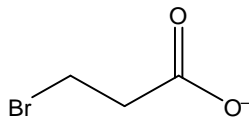
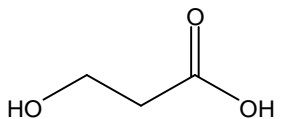
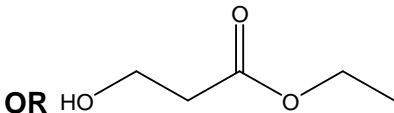
Question	Answer	Marks	AO element	Guidance
	<p>AND Different arrangement (of atoms) in space OR different spatial arrangement (of atoms) ✓</p>			<p>DO NOT ALLOW same empirical formula OR same general formula</p> <p>IGNORE same molecular formula</p> <p>Reference to <i>E/Z</i> isomerism or optical isomerism is not sufficient</p>
(v)	<p>Geraniol: (Carbon-carbon) double bond at carbon-2(,3) AND <i>E</i> OR <i>Z</i> ✓</p> <p>Structure of <i>Z</i> geraniol (<i>E</i> isomer is shown in question)</p>  <p style="text-align: right;">OH ✓</p>	4	<p>AO1.2</p> <p>AO2.5</p>	<p>ANNOTATE ANSWER WITH TICKS AND CROSSES ETC</p> <p>CHECK diagrams of citronellal and geraniol for annotations that may be worthy of credit</p> <p>DO NOT ALLOW isomerism at C=C at carbon 6(,-7)</p> <p>ALLOW identification of carbon-2(,3) from correct <i>Z</i> geraniol isomer if not stated in text or diagram</p> <p>IGNORE <i>cis</i> OR <i>trans</i> isomerism (<i>none of the substituent groups attached to the C=C are the same</i>)</p> <p>IGNORE geometric</p> <p>ALLOW type of isomerism from <i>E/Z</i> labels, even if incorrectly assigned</p> <p>In geraniol, ALLOW C₆H₁₁ OR R to represent alkenyl chain ALLOW CH₃O to represent CH₂OH</p>



Question	Answer	Marks	AO element	Guidance
	<p>Citronellal: chiral/asymmetric C at carbon-3 OR carbon-3 is bonded to 4 different groups AND optical isomerism ✓</p> <p>Two 3D structures of citronellal that are mirror images ✓</p> <p>e.g.</p> 		<p>AO1.2</p> <p>AO2.5</p>	<p>ALLOW identification of carbon-3 from 3D structure citronellal if not stated in text or diagram</p> <p>IGNORE connectivity of groups around chiral C</p> <p>In citronellal, ALLOW C₆H₁₁ OR R to represent alkenyl chain ALLOW C₂H₃O to represent CH₂CHO</p> <p>IF structural formula of alkenyl chain is used IGNORE one small slip in one/both isomers e.g. (CH₃)₂CHCH₂CH₂ (<i>missing carbon-7</i>)</p> <p>ALLOW two 3D structures with 2 groups swapped e.g.</p> 
	Total	13		

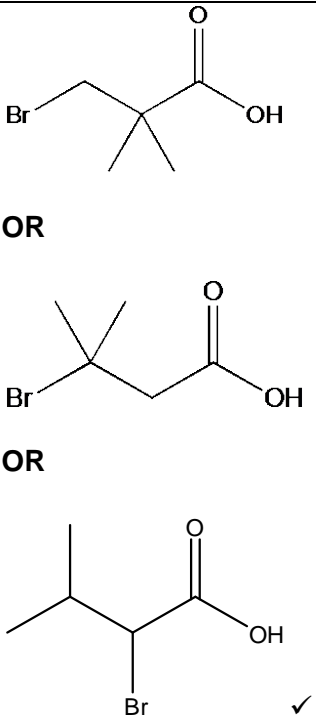
Question	Answer	Marks	AO element	Guidance
17 (a) (i)	<p> <chem>NC(CO)C(=O)O</chem> $\xrightarrow{H^+(aq)}$ <chem>[NH3+](C(CO)C(=O)[O-])</chem> </p> <p> <chem>NC(CO)C(=O)O</chem> $\xrightarrow{(CH_3)_2CHOH / H_2SO_4}$ <chem>NC(C(OC(C)C)C(OC(C)C)C(=O)O</chem> </p> <p> <chem>NC(CO)C(=O)O</chem> $\xrightarrow{\text{Excess } CH_3COCl}$ <chem>CC(=O)NC(CO)C(=O)O</chem> <chem>CC(=O)OC(CO)C(=O)O</chem> </p>	4	AO2.5 ×4	<p>ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</p> <p>ALLOW protonation of NH_2 group in reaction with $(CH_3)_2CHOH$ i.e.</p> <p>ALL structures must be based on serine</p> <p>For reaction with excess CH_3COCl, IGNORE reaction of $COOH$ to form an acid anhydride</p> <p>-----</p> <p>ALLOW 1 mark for</p> <p>(both NH and OH groups reacted but acyl chloride instead of $COOH$)</p> <p>OR</p>

Question	Answer	Marks	AO element	Guidance
				<p> $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CONH}-\text{C}-\text{C} \\ \quad \quad \quad \backslash \\ \text{CH}_2 \quad \quad \quad \text{OH} \\ \\ \text{CH}_3\text{COO} \end{array}$ <i>(both NH and OH groups reacted but H missing from α C atom)</i> </p> <p>OR</p> <p> $\begin{array}{c} \text{H} \\ \\ \text{CH}_3\text{CONH}-\text{C}-\text{C} \\ \quad \quad \quad \backslash \\ \text{CH}_2 \quad \quad \quad \text{OH} \\ \\ \text{OH} \end{array}$ <i>(NH group reacted correctly but rest of serine unchanged)</i> </p> <p>OR</p> <p> $\begin{array}{c} \text{H} \\ \\ \text{NH}_2-\text{C}-\text{C} \\ \quad \quad \quad \backslash \\ \text{CH}_2 \quad \quad \quad \text{OH} \\ \\ \text{CH}_3\text{COO} \end{array}$ <i>(OH group reacted correctly but rest of serine unchanged)</i> </p>
(ii)	IF $M_r(\text{amino acid}) = 131$ from titration analysis AWARD	4		

Question		Answer	Marks	AO element	Guidance
		<p>first 3 marks ALLOW 3SF or more throughout IGNORE trailing zeroes, e.g. ALLOW 0.044 for 0.0440</p> <p>-----</p> $n(\text{HCl}) = 0.150 \times \frac{25.0}{1000} \text{ OR } 3.75 \times 10^{-3} \text{ (mol) } \checkmark$ $n(\text{amino acid}) \text{ in } 250 \text{ cm}^3$ $= 3.75 \times 10^{-3} \times \frac{250.0}{21.30} \text{ OR } 0.0440 \text{ (mol) } \checkmark$ $M(\text{amino acid}) = \frac{5.766}{0.0440} = 131 \text{ (g mol}^{-1}\text{) } \checkmark$ <p>Amino acid = $(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{NH}_2)\text{COOH}$/leucine AND working to show $R = 57$ to justify choice OR evidence to show M_r leucine = 131 to justify choice \checkmark</p>		AO2.8 AO2.8 AO2.8 AO3.2	<p>ALLOW alternative approaches</p> <p>Calculator: 0.04401408451 ALLOW ECF from incorrect $n(\text{HCl})$</p> <p>ALLOW ECF from incorrect $n(\text{amino acid})$</p> <p>ALLOW ECF from incorrect $M(\text{amino acid})$ i.e. ECF for alkyl group closest to calculated $M(\text{alkyl group})$, e.g. for $M(\text{alkyl group}) = 15$, ALLOW $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$ Note: evidence may be shown with table</p>
	(b) (i)	R_f value in range 0.33 – 0.35 \checkmark	1	AO1.1	<p>ALLOW 2 SF or more. But ignore digits after second sig fig</p> <p>ALLOW 0.$\dot{3}$ for 0.33.....</p>
	(ii)	gly(cine) \checkmark Amino acid matches (leu(cine) and) glycine in Solvent W AND Amino acid matches (ala(nine) and) glycine in Solvent X \checkmark	2	AO2.3 ×2	<p>ALLOW glycine has the same/similar R_f as the unknown in both solvents/chromatograms</p> <p>ALLOW suitable alternatives for R_f e.g. moves same distance</p>
		Total	11		

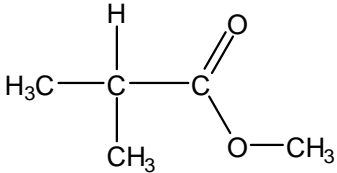
Question	Answer	Marks	AO element	Guidance
18 (a) (i)	ethyl 3-bromopropanoate ✓	1	AO1.2	<p>ALLOW one word: ethyl3-bromopropanoate OR more words, e.g. ethyl 3-bromo propanoate</p> <p>IGNORE lack of hyphens, or addition of commas</p>
	<p>(ii)</p>  <p>Reaction scheme showing Ester A (ethyl 3-bromopropanoate) reacting with $H^+(aq)$ to form 3-bromopropanoic acid and ethanol, and reacting with $OH^-(aq)$ to form 3-bromopropanoate and ethanol. The products are shown in boxes with checkmarks.</p>	5	AO2.5 x5	<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>OR</p>  <p>DO NOT ALLOW OH-</p> <p>ALLOW in either order</p> <p>For reaction with OH^-, ALLOW one mark for</p>  <p>OR</p>  <p>OR</p> 

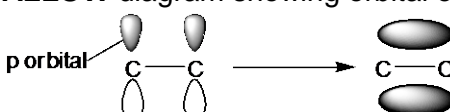
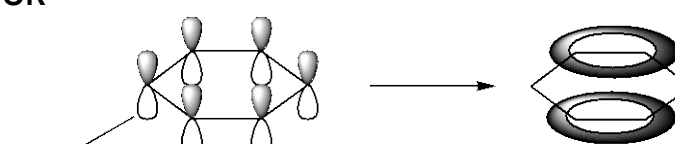
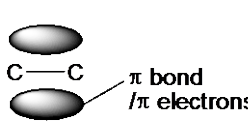
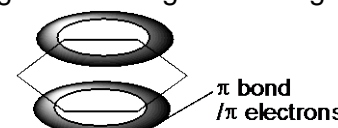
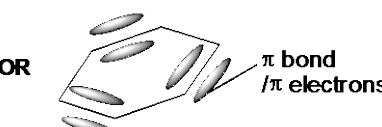
Question		Answer	Marks	AO element	Guidance															
	(iii)	hydrolysis ✓	1	AO1.1	IGNORE 'acid' and 'alkaline' IGNORE nucleophilic substitution															
	(b)	<table border="1"> <thead> <tr> <th>Proton environment</th> <th>Chemical shift</th> <th>Splitting pattern</th> </tr> </thead> <tbody> <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 ✓</p> <p>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	AO3.1 × 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>
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																		

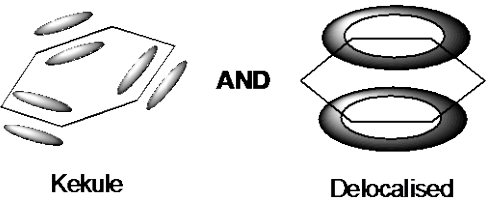
Question		Answer	Marks	AO element	Guidance
	(c)	 <p>OR</p> <p>OR</p>	1	AO3.1	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous
	(d)	<p>IF answer on answer line = 24018, AWARD 2 marks IF answer on answer line = 27600, AWARD 1 mark</p> <p>-----</p> <p>Relative mass of 200 molecules = $200 \times 138 = 27600$ ✓</p> <p>M_r of polyester = $27600 - 199 \times 18 = 24018$ ✓</p>	2	AO2.2 ×2	ALLOW ECF from incorrect M_r Alternative method based on repeat unit: M_r of 200 repeat units = $200 \times 120 = 24000$ ✓ M_r of polymer = $24000 + 1 + 17 = 24018$ ✓
(e)	(i)*	Refer to marking instructions on page 4 of mark scheme	6	AO3.3	Indicative scientific points may include:

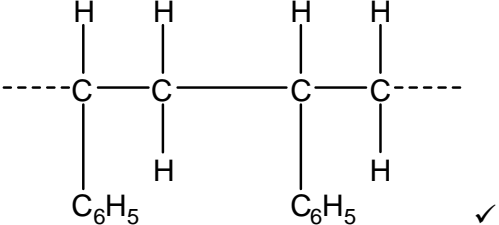
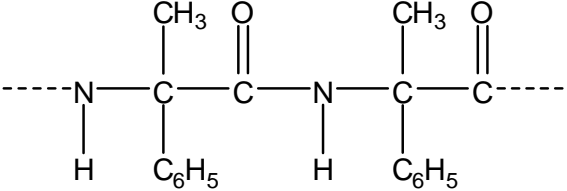
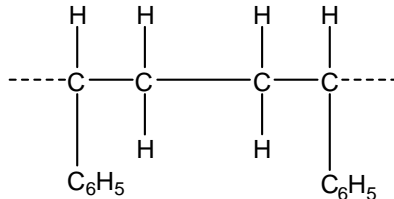
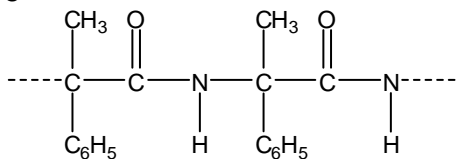
Question	Answer	Marks	AO element	Guidance
	<p><i>for guidance on marking this question.</i></p> <p>Level 3 (5-6 marks) Correct calculation of the mass of (CH₃)₂CHCHO. AND Planned synthesis includes oxidation of aldehyde and formation of ester C with most of the reagents and conditions identified and 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 (CH₃)₂CHCHO is partly correct AND Planned synthesis includes oxidation of aldehyde and formation of ester C with some of the reagents and conditions identified OR Attempts to calculate mass of (CH₃)₂CHCHO but makes little progress AND 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>		×6	<p>Calculation of mass of (CH₃)₂CHCHO 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 (CH₃)₂CHCHO = 72.0 × 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 (CH₃)₂CHCHO = 72.0 × 0.3125 $= 22.5 \text{ g}$ <p>ALLOW small slip/rounding errors such as errors in Mr e.g. use of 71 instead of 72 for (CH₃)₂CHCHO</p> <p>-----</p> <p>Examples of partly correct calculations</p> <p>Mass = 3.60 g from $0.125 \times \frac{40}{100} \times 72$ (% yield inverted)</p> <p>Mass = 9.00 g from 0.125×72 (% yield omitted)</p>

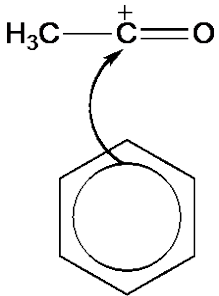
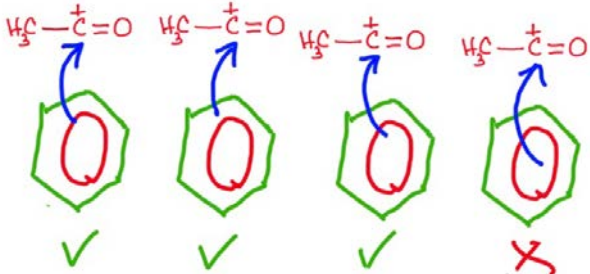
Question		Answer	Marks	AO element	Guidance
		<p>Level 1 (1-2 marks) Calculation of the mass of $(\text{CH}_3)_2\text{CHCHO}$ is partly correct OR Planned synthesis includes both steps with some of the reagents and conditions identified OR Attempts equations for both steps but these may contain errors OR 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 No response or no response worthy of credit.</p>			<p><u>Synthesis: reagents and conditions</u></p> <p>Step 1: Oxidation of aldehyde $(\text{CH}_3)_2\text{CHCHO}$</p> <ul style="list-style-type: none"> • Reagents: $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$ • Conditions: reflux • Equation: $(\text{CH}_3)_2\text{CHCHO} + [\text{O}] \rightarrow (\text{CH}_3)_2\text{CHCOOH}$ <p>Step 2: Formation of ester C</p> <ul style="list-style-type: none"> • Reagents: methylpropanoic acid/$(\text{CH}_3)_2\text{CHCOOH}$ and methanol/CH_3OH • Conditions: acid (catalyst) reflux/heat • Equation: $(\text{CH}_3)_2\text{CHCOOH} + \text{CH}_3\text{OH} \rightarrow (\text{CH}_3)_2\text{CHCOOCH}_3 + \text{H}_2\text{O}$ <p>IGNORE attempts to form methanol in synthesis</p>
(e)	(ii)		2	AO2.7 × 2	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous

Question	Answer	Marks	AO element	Guidance
	<p>Y (43) = $(\text{CH}_3)_2\text{CH}^+$ ✓</p> <p>Z (71) $(\text{CH}_3)_2\text{CHCO}^+$ ✓</p> <p><i>If '+' charge is missing/incorrect but the structures of both fragments are correct, award one mark</i></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) = $^+\text{CCOOCH}_3$</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>
	Total	22		

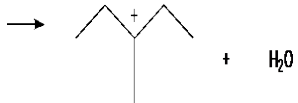
Question			Answer	Marks	AO element	Guidance
19	(a)	(i)	<p>Similarities</p> <p>Orbital overlap (sideways) overlap of p orbitals ✓</p> <p>π bond</p> <p>π bond/system/ring above and below (bonding (C) atoms/ring/plane) ✓</p>	3	AO1.1 × 3	<p>ANNOTATE ANSWER WITH TICKS AND CROSSES ETC</p> <p>ALLOW diagram showing orbital overlap e.g.</p>  <p>OR</p>  <p>p orbital label is required for first mark</p> <p>IGNORE C=C in diagram showing π bond</p> <p>IGNORE reference to s orbital overlap/σ bonds</p> <p>-----</p> <p>ALLOW from labelled diagram showing π bond e.g.</p>  <p>OR</p>  <p>OR</p>  <p>π bond/π electrons label is required for second mark</p>

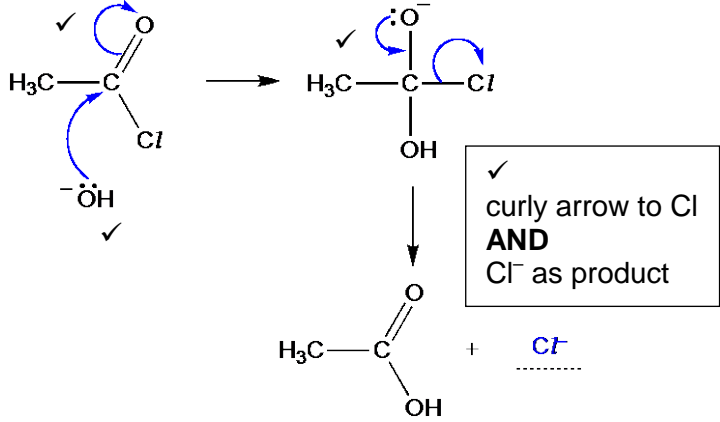
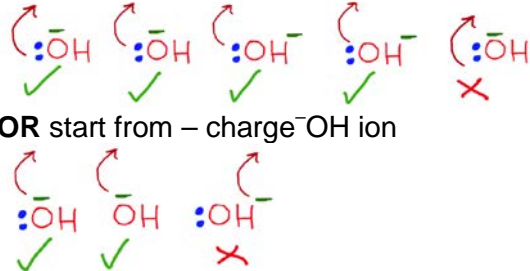
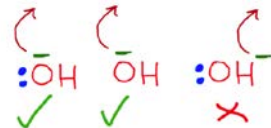
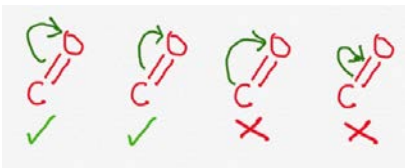
Question	Answer	Marks	AO element	Guidance
	<p>Difference</p> <p>Kekule has: alternating π bonds OR 3 π bonds / localised (π electrons) / overlap in one direction / 2 electrons in π bond</p> <p>AND</p> <p>Delocalised has: π ring (system) / all p orbitals overlap OR (π electrons) spread around ring / overlap in both directions / 6 electrons in π bond /</p>			<p>-----</p> <p>ALLOW diagram showing π bond in both Kekule AND delocalised models e.g</p> <div style="text-align: center;">  <p style="display: flex; justify-content: space-around; width: 100%;"> Kekule Delocalised </p> </div> <p>π bond labels not required for third mark</p>
(ii)	<p>Any 2 pieces of evidence from (✓ ✓)</p> <p>Bond length (C–C) bond length is between single (C–C) and double bond (C=C) OR all (C–C) bond lengths are the same</p> <p>ΔH hydrogenation ΔH hydrogenation less (exothermic) than expected</p> <p>Resistance to reaction Benzene is less reactive than alkenes OR bromination of benzene requires a catalyst/halogen carrier OR benzene does not react with/decolourise bromine (at room temperature) OR benzene reacts by substitution OR benzene does not (readily) react by addition</p>	2	AO1.1 ×2	<p>ALLOW (C–C) bond enthalpy is between single (C–C) and double bond (C=C) OR all (C–C) bond enthalpies are the same</p> <p>IGNORE enthalpy of hydration</p> <p>Benzene is unreactive is not sufficient (no comparison to alkene)</p> <p>For halogen carrier, ALLOW name or formula of suitable catalyst e.g. Fe, AlCl₃, FeBr₃</p>

Question	Answer	Marks	AO element	Guidance
(b) (i)	<p>Polymer from D</p>  <p>Polymer from E</p>  <p>Amide link ✓</p> <p>2 repeat units of correct polymer ✓</p>	3	AO2.5 AO1.2 AO2.5	<p>-----</p> <p>For BOTH structures, ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous</p> <p>'End bonds' MUST be shown BUT ALLOW ECF IF end bonds omitted in both structures</p> <p>DO NOT ALLOW more than 2 repeat units BUT ALLOW ECF in subsequent structure</p> <p>IGNORE connectivity of C₆H₅</p> <p>-----</p> <p>CARE: ALLOW any consistent repeat unit: C₆H₅ and H groups can alternate or be on opposite sides of chain e.g.</p>  <p>end -NH- may be at either side e.g.</p>  <p>IGNORE brackets IGNORE <i>n</i></p>

Question	Answer	Marks	AO element	Guidance
(ii)	<p>D Addition / polyalkene AND E: Condensation / polyamide ✓</p>	1	AO1.1	DO NOT ALLOW 'additional'
(iii)	<p>Formation of electrophile $\text{CH}_3\text{COCl} + \text{AlCl}_3 \rightarrow \text{CH}_3\text{-C}^+=\text{O} + \text{AlCl}_4^-$ ✓</p> <p>Mechanism Curly arrow from π-bond to $\text{CH}_3\text{C}^+=\text{O}$ ✓</p> <div style="text-align: center;">  </div> <hr style="border-top: 1px dashed black;"/>	5	AO2.5 AO2.5	<p>ANNOTATE ANSWER WITH TICKS AND CROSSES</p> <p>ALLOW '+' charge anywhere on $\text{CH}_3\text{C}^+\text{O}$ <i>i.e.</i> CH_3CO^+</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"> go to the C of $\text{C}=\text{O}$ <p>AND</p> <ul style="list-style-type: none"> start from, OR close to circle of benzene ring <div style="text-align: center;">  </div> <p>IGNORE curly arrow shown on $\text{C}=\text{O}$</p>

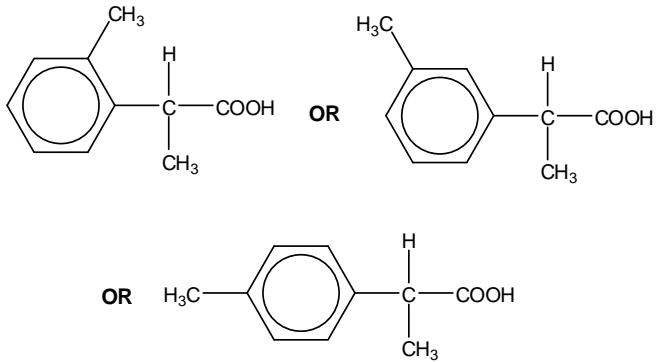
Question	Answer	Marks	AO element	Guidance
(iv)	<p>one mark for each correct structure/reagent</p> <p> CH_3 $\text{HO}-\text{C}-\text{CN}$ $\text{Br}-\text{C}-\text{CN}$ $\text{Br}-\text{C}-\text{COOH}$ $\text{H}-\text{C}-\text{OH}$ </p> <p> Reagents: NH_3 AND ethanol OR excess NH_3 ✓ $\text{H}^+/\text{H}_2\text{SO}_4/\text{HCl}$ ✓ NaBr/Br^- AND $\text{H}_2\text{SO}_4/\text{H}^+$ ✓ acid/$\text{H}^+/\text{H}_3\text{PO}_4/\text{H}_2\text{SO}_4$ ✓ </p>	7	AO2.5 x7	<p>ALLOW any vertical bond to the OH OR NH_2 groups e.g. ALLOW</p> <p> $\begin{array}{c} \\ \text{OH} \end{array}$ OR $\begin{array}{c} \\ \text{HO} \end{array}$ AND $\begin{array}{c} \\ \text{NH}_2 \end{array}$ OR $\begin{array}{c} \\ \text{H}_2\text{N} \end{array}$ </p> <p>DO NOT ALLOW OH^-, OR NH_2^- but ALLOW ECF for subsequent use in this part</p> <p>For elimination, IGNORE 'concentrated', 'dilute' with acids BUT DO NOT ALLOW $\text{H}_2\text{O}/\text{steam}/(\text{aq})$</p> <p>ALLOW HBr for $\text{NaBr}/\text{H}_2\text{SO}_4$</p> <p>For hydrolysis. IGNORE missing (aq) ALLOW HNO_3 for hydrolysis but DO NOT ALLOW 'HNO_3 and H_2SO_4'</p> <p>ALLOW final 2 stages in opposite order i.e. NH_3 before acid hydrolysis</p> <p> CH_3 $\text{H}_2\text{N}-\text{C}-\text{CN}$ $\text{Br}-\text{C}-\text{COOH}$ </p> <p> Reagents: NH_3 AND ethanol OR excess NH_3 $\text{H}^+/\text{H}_2\text{SO}_4/\text{HCl}$ </p>
	Total	23		

Question			Answer	Marks	AO element	Guidance
20	(a)	(i)	Movement of an electron pair ✓	1	AO1.1	For electron pair, ALLOW lone pair OR bonding pair OR 2 electrons
	(a)	(ii)	 <p>Correct carbon skeleton ✓</p> <p>'+' charge on correct carbon skeleton ✓</p>	2	AO3.1 ×2	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous IGNORE any other products
	(a)	(iii)	<p>Heterolytic one (bonded) atom/O receives both/2 electrons ✓</p> <p>Fission Breaking of a covalent bond OR breaking of C-O bond ✓</p>	2	AO1.2 AO1.1	<p>ALLOW 2 electrons go to one (bonded) atom/O</p> <p>IGNORE formation of ions/radicals</p> <p>For O atom, ALLOW species DO NOT ALLOW element OR molecule</p> <p>'Bond breaking' is not sufficient (no reference to covalent)</p>

Question	Answer	Marks	AO element	Guidance
(b) (i)	 <p> $\text{H}_3\text{C}-\text{C}(=\text{O})-\text{Cl} + \text{OH}^- \rightarrow \text{H}_3\text{C}-\text{C}(\text{OH})(\text{O}^-)-\text{Cl} \rightarrow \text{H}_3\text{C}-\text{C}(=\text{O})-\text{OH} + \text{Cl}^-$ </p> <p> ✓ curly arrow to Cl AND Cl⁻ as product </p>	4	AO3.2 ×4	<p>IGNORE any dipoles shown</p> <p>NOTE: curly arrows can be straight, snake-like, etc. but NOT double headed or half headed arrows</p> <p>Curly arrow from OH⁻ must</p> <ul style="list-style-type: none"> go to the C of C=O <p>AND</p> <ul style="list-style-type: none"> start from, OR be traced back to any point across width of lone pair on O of OH⁻  <ul style="list-style-type: none"> OR start from - charge OH⁻ ion  <p>Curly arrow from C=O bond must start from, OR be traced back to, any part of C=O bond and go to O</p>  <p>Curly arrow from O⁻ must</p>

Question			Answer	Marks	AO element	Guidance
						<ul style="list-style-type: none"> go to C=O bond <p>AND</p> <ul style="list-style-type: none"> start from, OR be traced back to, any point across width of lone pair <ul style="list-style-type: none"> OR start from '–' charge of O[–] <p>Curly arrow from C–Cl bond must start from, OR be traced back to, any part of C–Cl bond and go to Cl</p>
(b)	(ii)	(OH [–]) donates an electron pair/lone pair OR (OH [–] acts as a) nucleophile ✓	1	AO1.2		
Total				10		

Question	Answer	Marks	AO element	Guidance
21*	<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 CH₃C₆H₄CH(CH₃)COOH 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 C₁₀H₁₂O₂ 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>	6	AO1.2 × 2 AO3.1 × 2 AO3.2 × 2	<p>Indicative scientific points:</p> <p><u>Empirical and Molecular Formulae</u></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 = C₅H₆O • uses $m/z = 164.0$ to determine molecular formula as C₁₀H₁₂O₂ <p><u>Structure</u> 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

Question	Answer	Marks	AO element	Guidance
	<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>Correct Structure</p> <ul style="list-style-type: none"> • $\text{CH}_3\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{COOH}$ ALLOW 2-, 3- OR 4- substitution of ring <i>i.e.</i>  <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> <ul style="list-style-type: none"> • peak at 2300–3700 (cm⁻¹) is O–H • peak at ~1720 (cm⁻¹) is C=O • unknown is a carboxylic acid <p>ALLOW ranges from <i>Data Sheet</i> IGNORE references to C–O peaks</p>
	Total	6		

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