

Chemistry A

Advanced GCE

Unit **F324**: Rings, Polymers and Analysis

Mark Scheme for January 2012

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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 Scoris.

Annotation	Meaning
	Benefit of doubt given
	Contradiction
	Incorrect response
	Error carried forward
	Ignore
	Not answered question
	Benefit of doubt not given
	Power of 10 error
	Omission mark
	Rounding error
	Error in number of significant figures
	Correct response

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

Annotations should be placed to clearly show where they apply within the body of the text (i.e. not in margins) for:

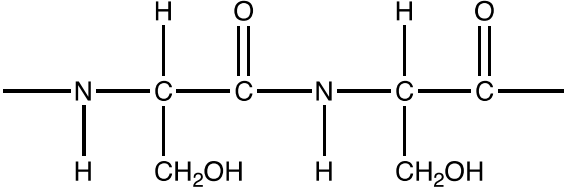
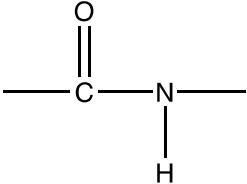
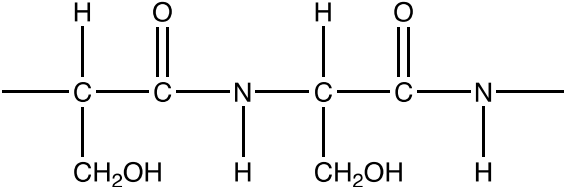
Question 1 c(iii)

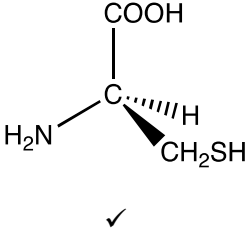
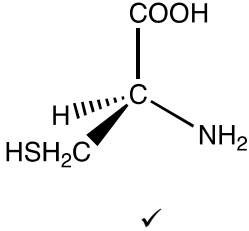
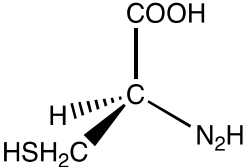
Question 2 a(i), (b)

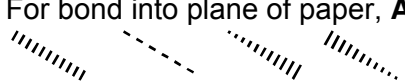

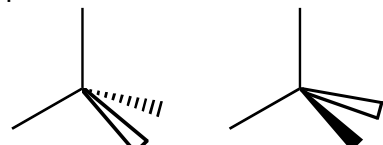
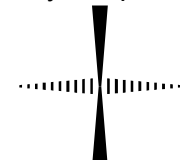
Question 3 a(i), a(ii), b(i)

Question 4 b(ii), (c)

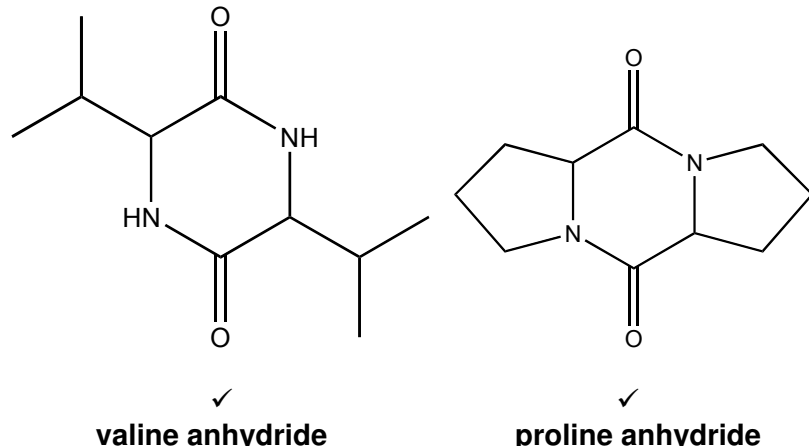
Question	Answer	Mark	Guidance
1 (a) (i)	The pH OR point at which the zwitterion exists ✓	1	<p>ALLOW pH/point at which there is no overall/net charge</p> <p>IGNORE pH/point at which there is no charge/ neutral charge <i>ie overall/net is required</i></p> <p>ALLOW pH/point at which contains COO^- AND NH_3^+</p>
	(ii)	2	<p>ALLOW $\text{CH}_3\text{CH}(\text{NH}_3^+)\text{COO}^-$</p> <p>ALLOW $\text{CH}_3\text{CH}(\text{NH}_3^+)\text{COOH}$</p> <p>ALLOW CO_2^- and CO_2H</p> <p>ALLOW + charge on N or H: ie $^+\text{NH}_3$ or NH_3^+</p> <p>DO NOT ALLOW '-' charge on C: ie ^-COO</p> <p>DO NOT ALLOW H or CH_3 missing</p> <p>ALLOW correct structural OR displayed OR skeletal formula</p> <p>ALLOW combination of formulae as long as unambiguous</p>

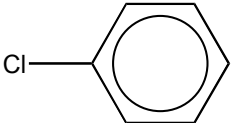
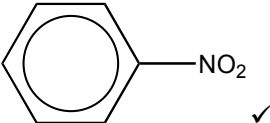
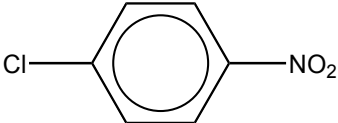
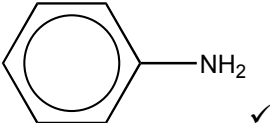
Question	Answer	Mark	Guidance
1 (a) (iii)	<p>pH < 3: COOH ✓</p> <p>pH > 10: NH₂ ✓</p>	2	<p>ALLOW carboxyl group OR carboxylic acid DO NOT ALLOW 'acid' OR just 'carboxylic' (without 'acid')</p> <p>ALLOW amino group OR amine</p> <p>DO NOT ALLOW if give correct formula but wrong name or correct name and wrong formula eg NH₂ and amide</p> <p>IF any carbon chain is shown attached to BOTH functional groups ALLOW 1 mark eg CH₂COOH AND CH₂NH₂ for 1 mark CH₃COOH AND CH₃NH₂ for 1 mark RCOOH AND RNH₂ for 1 mark</p> <p>IF functional groups are shown the wrong way round, ALLOW 1 mark i.e. NH₂ COOH</p>
(b)	<div style="text-align: center;">  </div> <p>peptide link must be fully displayed, i.e.</p> <div style="text-align: center;">  </div> <p>TWO repeat units shown correctly ✓</p>	2	<p>DO NOT ALLOW more repeat units</p> <p>IGNORE brackets and 'n'</p> <p>ALLOW end bonds shown as ----- DO NOT ALLOW if end bonds are missing</p> <p>ALLOW terminal N-H on right (OR C=O on left), <i>ie</i></p> <div style="text-align: center;">  </div> <p>IF peptide bond is shown not displayed, i.e. CONH, 2nd mark can still be awarded</p>

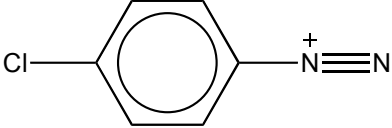
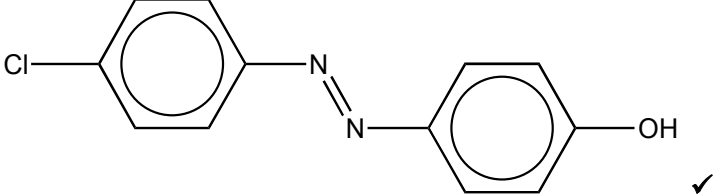
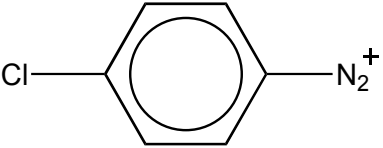
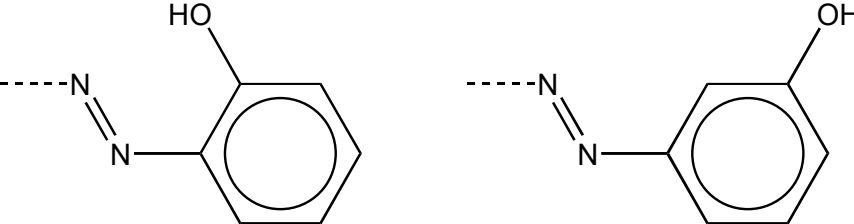
Question	Answer	Mark	Guidance
1 (c) (i)	There is no chiral carbon OR there is no asymmetry in the molecule ✓	1	<p>ALLOW there is no asymmetric carbon OR it has no non-superimposable mirror image OR there are not four different atoms/groups of atoms (attached to carbon) OR there are only three different atoms/groups of atoms (attached to carbon) OR because there are two hydrogen atoms on the carbon</p>
	(ii)	2	<p>ALLOW Add the same 3-D structure repeated but with 2 groups 'swapped' as after rotation the 2nd isomer is a mirror image of the first, i.e.</p> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  </div> <div style="text-align: center;">  </div> </div> <p>Connectivity: Chiral C must be linked to the C of the COOH, the C of the CH₂SH and the N of the NH₂ (ie connectivity is being tested)</p> <p>ie, ALLOW as in the example but DO NOT ALLOW an attempted NH₂ shown as below:</p> <div style="text-align: center;">  </div> <p>The 2nd mark is for the mirror image of CORRECT optical isomer only CARE: may be orientated differently</p> <p>DO NOT penalise connectivity more than once Each structure must have four central bonds, with at least one wedge in AND one wedge out</p>

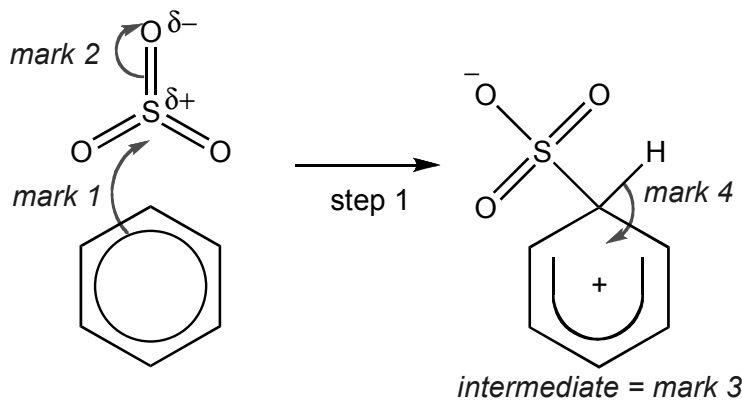
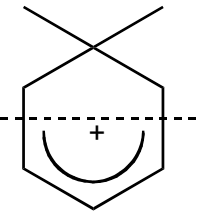
Question	Answer	Mark	Guidance
			<p>-----</p> <p>For bond into plane of paper, ALLOW:</p>  <p>For bond out of plane of paper, a solid wedge is expected, either way around:</p>  <p>ALLOW a hollow wedge for 'in bond' OR an 'out bond', provided it is different from the other in or out wedge eg:</p>  <p>ALLOW examples of other 3-D representations provided they are possible: i.e.</p>  <p>CARE: This is a 3-D representation so this is possible and the bonds are clearly not 90° to one another</p>

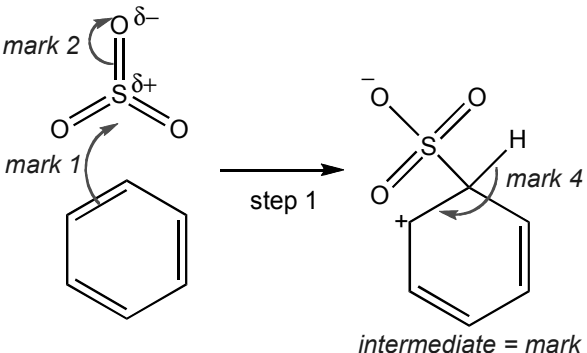
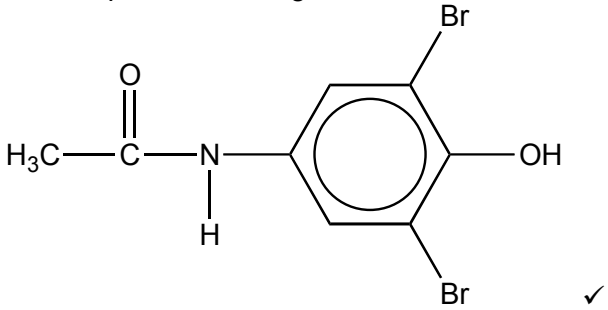
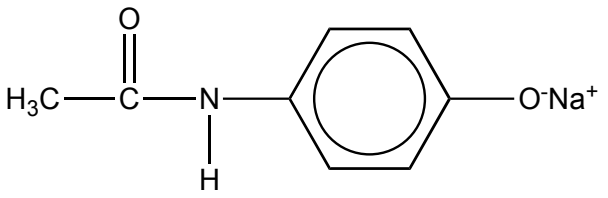
Question			Answer	Mark	Guidance
1	(c)	(iii)	<p>Disadvantages: any two from:</p> <ul style="list-style-type: none"> • (one stereoisomer might have harmful/adverse) side effects ✓ • reduces the (pharmacological) activity/effectiveness ✓ • cost of separating stereoisomers OR difficulty in separating stereoisomers ✓ <p>Synthesis of a single optical isomer any two from:</p> <ul style="list-style-type: none"> • using enzymes or bacteria ✓ • using (chemical) chiral synthesis OR using chiral catalysts ✓ • using (natural) chiral molecules/compounds ✓ <p>Quality of Written Communication For full marks to be awarded for this question chiral OR enzyme OR bacteria OR catalyst must be spelled correctly at least once in the correct context</p>	2	<p>ANNOTATIONS MUST BE USED</p> <p>IGNORE harmful/adverse effects only</p> <p>ALLOW a response that implies an increased dose</p> <p>IGNORE it takes time to separate</p> <p>ALLOW biological catalysts</p> <p>ALLOW chiral transition metal complex/catalyst OR stereoselective transition metal complex/catalyst</p> <p>ALLOW 'chiral pool' OR L-amino acids / D-sugars</p>

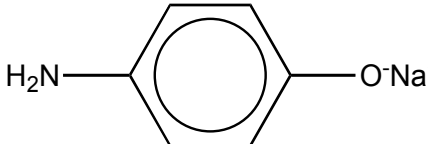
Question		Answer				Mark	Guidance								
1	(d)	<table border="1"> <tr> <td>amino acid</td> <td>isoleucine</td> <td>leucine</td> <td>tyrosine</td> </tr> <tr> <td>number of peaks</td> <td>6 ✓</td> <td>5 ✓</td> <td>7 ✓</td> </tr> </table>				amino acid	isoleucine	leucine	tyrosine	number of peaks	6 ✓	5 ✓	7 ✓	3	1 mark for each number
amino acid	isoleucine	leucine	tyrosine												
number of peaks	6 ✓	5 ✓	7 ✓												
	(e)	 <p style="text-align: center;"> ✓ valine anhydride </p> <p style="text-align: center;"> ✓ proline anhydride </p>				2	<p>ALLOW correct structural OR displayed OR skeletal formula</p> <p>ALLOW combination of formulae as long as unambiguous</p> <p>Common errors: Look for NH₂ on first structure and NH on second structure</p>								
Total					19										

Question	Answer	Mark	Guidance
2 (a) (i)	<p>Response requires three stages</p> <ul style="list-style-type: none"> chlorination nitration reduction <p>Reduction must be a later stage than nitration</p> <p>Mark according to which sequence chosen.</p> <p>Stage 1 organic product:</p> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  </div> <div style="text-align: center;">OR</div> <div style="text-align: center;">  </div> </div> <p>✓</p> <p>chemicals: Cl₂ AND AlCl₃ OR HNO₃ AND H₂SO₄</p> <p>Stage 2 organic product:</p> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  </div> <div style="text-align: center;">OR</div> <div style="text-align: center;">  </div> </div> <p>✓</p> <p>chemicals: HNO₃ AND H₂SO₄ OR Sn AND HCl ✓</p> <p>Stage 3 chemicals: Cl₂ AND AlCl₃ OR Sn AND HCl ✓</p>	5	<p>Acceptable sequence of stages are:</p> <ul style="list-style-type: none"> nitration, reduction, chlorination nitration, chlorination, reduction, chlorination, nitration, reduction <p>For organic products, ALLOW C₆H₅NO₂ OR C₆H₅Cl OR C₆H₅NH₂ ALLOW NO₂- AND NH₂- DO NOT ALLOW ClC₆H₄NO₂ (formula ambiguous) DO NOT ALLOW molecular formulae IGNORE any additional structures shown eg 2- (<i>ortho</i>) and 3- (<i>meta</i>) substituted isomers</p> <p>In chemicals boxes, IGNORE temperatures IGNORE 'catalyst'</p> <p>For chlorination chemicals, ALLOW Cl₂ AND FeCl₃ OR Cl₂ AND Fe OR Cl₂ AND halogen carrier</p> <p>For nitration chemicals, 'concentrated' not required for HNO₃ OR H₂SO₄ BUT ... DO NOT ALLOW 'dilute'</p> <p>For reduction chemicals, 'concentrated' HCl not required but DO NOT ALLOW 'dilute'</p> <p>For Sn/HCl ALLOW addition of NaOH also IF it is clear that it is a second step BUT DO NOT ALLOW Sn AND HCl AND NaOH</p> <p>IGNORE catalyst</p>

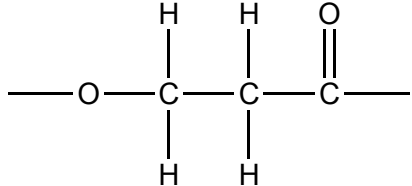
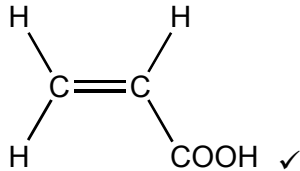
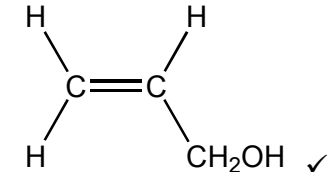
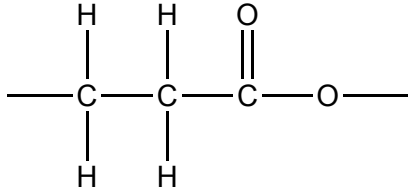
Question	Answer	Mark	Guidance
2 (a) (ii)	<p>diazonium ion</p>  <p>✓</p> <p>-N≡N group MUST be displayed</p> <p>azo dye</p>  <p>✓</p> <p>-N=N- group MUST be displayed</p>	2	<p>ALLOW '+' sign up to halfway along triple bond from left-hand N</p> <p>IGNORE presence of Cl⁻</p> <p>DO NOT ALLOW Cl⁻ substituent on benzene ring</p> <p>DO NOT ALLOW:</p>  <p>In azo dye,</p> <p>ALLOW as alternative to phenol OH group: O⁻ OR O⁻Na⁺ OR ONa</p> <p>ALLOW phenol part substituted at any carbon (ie 2,3 or 4 position for -OH) i.e.</p>  <p>IGNORE geometry/shape, i.e. ALLOW —N=N—</p> <p>Mark independently</p> <p>DO NOT ALLOW if Cl⁻ is missing from benzene ring in EITHER structure</p>

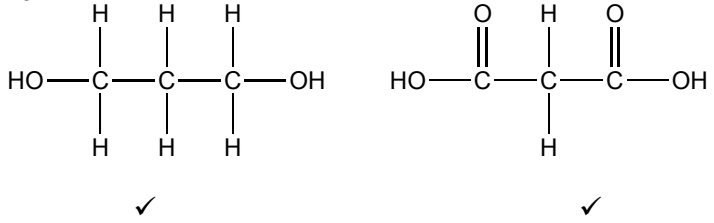
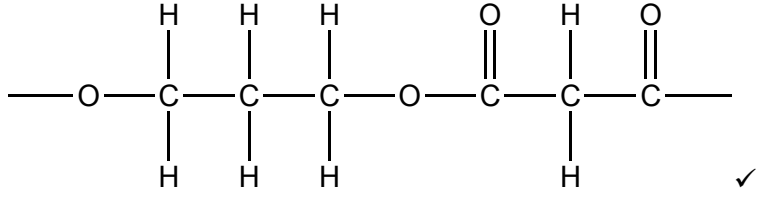
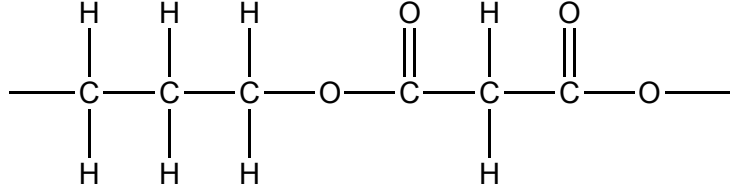
Question	Answer	Mark	Guidance
2 (b)	 <p style="text-align: center;">intermediate = mark 3</p>	4	<p>ANNOTATIONS MUST BE USED</p> <p>mark 1 – curly arrow from π-delocalised ring in benzene to $S^{\delta+}$ in SO_3 ✓ ALLOW curly arrow from the ring OR from within the ring</p> <p>mark 2 – curly arrow from one $S=O$ double bond to the O (to produce a $S-O^-$) ✓ ALLOW curly arrow to any O in SO_3</p> <p>mark 3 – intermediate showing delocalisation over 5 carbons ✓ Intermediate must have correct SO_3^- structure FULLY displayed DO NOT ALLOW intermediate with broken ring less than halfway up in correct orientation:</p>  <p>mark 4 – curly arrow from C–H bond reforming π- delocalised ring in benzene ✓ Stand alone mark</p> <p>IGNORE responses after STEP 2</p>

Question	Answer	Mark	Guidance
			<p>ALLOW Kekulé mechanism</p>  <p>ALLOW double bonds shown in other Kekulé arrangement</p>
2 (c) (i)	<p>Various possibilities, eg:</p> 		<p>ALLOW 1, 2, 3 or 4 Br atoms substituted on phenol ring at carbon atoms 2, 3, 5 or 6 BUT -OH must be in correct position shown DO NOT ALLOW O⁻ or ONa</p> <p>ALLOW for side chain: CH₃CONH but aromatic part of structure must be shown</p> <p>IGNORE any additional inorganic products in boxes (even if incorrect)</p>
	<p>Reaction with Na</p> 	2	<p>ALLOW ONa OR O⁻ as alternative to O⁻Na⁺ DO NOT ALLOW O-Na OR O⁻Na (i.e. Na without charge)</p> <p>-ONa must be in correct position shown</p> <p>ALLOW for side chain: CH₃CONH but aromatic part of structure must be shown</p> <p>IGNORE any additional inorganic products in boxes (even if incorrect)</p>

Question		Answer	Mark	Guidance
2	(c) (ii)	<p>Hydrolysis with NaOH(aq)</p> $\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^-\text{Na}^+ \quad \checkmark$  <p>Mark independently</p>	2	<p>On BOTH structures, ALLOW ONa OR O⁻ as alternative to O⁻Na⁺ DO NOT ALLOW O-Na OR O⁻Na (i.e. Na without charge)</p> <p>-ONa must be in correct position shown on 2nd structure</p> <p>ALLOW CH₃COONa/ CH₃CO₂Na OR CH₃COO⁻/ CH₃CO₂⁻</p> <p>ALLOW one mark for carboxylic acid AND phenol, rather than sodium salts:</p> $\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH} \quad \text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{OH}$ <p>ALLOW NH₂-, CH₃-</p> <p>IGNORE any additional inorganic products in boxes (even if incorrect)</p>
Total			15	

Question			Answer	Mark	Guidance
3	(a)	(i)	<p>One mark is for positive carbonyl test (Add) 2,4-dinitrophenylhydrazine AND orange/yellow/red precipitate ✓</p> <p>One mark is for negative aldehyde test EITHER (Add) Tollens' reagent/Tollens' test AND no change OR no reaction OR no silver (mirror)</p> <p>OR (Add) H₂SO₄ AND K₂Cr₂O₇ AND no change OR no reaction OR no green colour ✓</p>	2	<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> <p>ALLOW AgNO₃/NH₃ (Formulae must be correct) OR ammoniacal silver nitrate</p> <p>ALLOW Fehling's solution OR Benedict's solution AND no (brick-red) precipitate</p> <p>ALLOW any response that implies that nothing happens ie no change OR no reaction OR no silver (mirror)</p> <p>ALLOW 'the aldehyde/pentanal gives a silver mirror'</p> <p>ALLOW H⁺ AND Cr₂O₇²⁻ (Formulae must be correct)</p> <p>ALLOW any response that implies that nothing happens</p> <p>IGNORE responses using NaBH₄ (as no observations)</p> <p>NOTE: a(ii) is marked completely independently of a(i)</p>
		(ii)	<p>1st mark Take melting point of orange crystals/derivative/product from 2,4-DNP ✓</p> <p>2nd mark Compare melting point with known values OR compare melting point with value in database/reference book ✓</p>	2	<p>Mark independently of response for 1st mark</p> <p>DO NOT ALLOW 1st or 2nd marks for taking and comparing boiling points OR chromatograms</p>

Question	Answer	Mark	Guidance
3 (b) (i)	<p>Synthesis 1</p>  <p>Ester linkage must be fully displayed ✓</p> <p>Synthesis 2</p>  	6	<p>NOTE: ALL Structures MUST have Hs shown IGNORE bond angles</p> <p>DO NOT ALLOW more than one repeat unit IGNORE brackets and 'n'</p> <p>ALLOW terminal O— on right (OR C=O on left), i.e.</p>  <p>ALLOW end bonds shown as ---- DO NOT ALLOW if structure has no end bonds</p>

Question			Answer	Mark	Guidance
			<p>Synthesis 3</p>  		<p>Mark each structure independently</p> <p>HO- must be connected correctly on BOTH structures</p> <p>DO NOT ALLOW more repeat units IGNORE brackets and 'n'</p> <p>ALLOW terminal O— on right (OR C=O on left), i.e.</p>  <p>ALLOW end bonds shown as ----- DO NOT ALLOW if structure has no end bonds</p> <p>DO NOT ALLOW ECF from wrong structure in previous boxes</p>
3	(b)	(ii)	<p>Synthesis 1: condensation AND Synthesis 2: addition AND Synthesis 3: condensation ✓</p>	1	All three correct responses required for the mark
			Total	11	

Question		Answer	Mark	Guidance	
4	(a)	$(\text{CH}_3\text{CO})_2\text{O} + \text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ $\rightarrow \text{CH}_3\text{COOCH}(\text{CH}_3)_2 + \text{CH}_3\text{COOH}$ 1st mark Correct structure of ester: $\text{CH}_3\text{COOCH}(\text{CH}_3)_2$ ✓ 2nd mark Equation contains correct formulae for $(\text{CH}_3\text{CO})_2\text{O}$, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ AND CH_3COOH ✓	2	ALLOW correct structural OR displayed OR skeletal formula ALLOW combination of formulae as long as unambiguous DO NOT ALLOW molecular formulae ALLOW $(\text{CH}_3)_2\text{CHOOCCH}_3$ OR $(\text{CH}_3)_2\text{CHOCOCH}_3$	
	(b)	(i)	(relative) solubility ✓	1	IGNORE partition DO NOT ALLOW adsorption OR absorption
		(ii)	The esters would have similar retention times AND similar structures/molecules OR same functional groups OR similar polarities OR similar solubilities ✓ Alcohol would have short retention time AND alkane would have long retention time ✓	2	IGNORE similar properties

Question	Answer	Mark	Guidance
4 (c)	<p>Elemental analysis and molecular formula – 2 marks</p> <p>Use of percentages (to find EF) AND 144 ✓</p> <p>Molecular formula = C₈H₁₆O₂ ✓</p>	2 marks	<p>ANNOTATIONS MUST BE USED</p> <p><i>Working</i></p> $\begin{array}{rcl} \text{C : H : O} & = & 66.63/12 : 11.18/1 : 22.19/16 \\ & & 5.5525 : 11.18 : 1.386875 \\ & & 4 : 8 : 1 \end{array}$ <p>Alternative method:</p> <p>carbon: (144 x 66.63/100)/12 = 8 hydrogen: (144 x 11.18/100)/1 = 16 oxygen: (144 x 22.19/100)/16 = 2</p>
	<p>ester structure – 4 marks</p> $\begin{array}{ccccccc} & \text{CH}_3 & & \text{O} & & & \\ & & & & & & \\ \text{H}_3\text{C} & - \text{C} & - & \text{CH}_2 & - & \text{C} & - \text{O} - \text{CH}_2 - \text{CH}_3 \\ & & & & & & \\ & \text{CH}_3 & & & & & \end{array}$ <p style="text-align: right;">✓✓✓✓</p>	4 marks	<p>ALLOW correct structural OR displayed OR skeletal formula ALLOW combination of formulae as long as unambiguous NO ECF from earlier structures</p> <p>If not fully correct award following marks:</p> <p>If structure an ester of formula C₈H₁₆O₂ OR the organic structure contains C(CH₃)₃ ✓</p> <p>If structure is an ester of formula C₈H₁₆O₂ AND ester contains C(CH₃)₃ ✓✓</p> <p>If structure is an ester of formula C₈H₁₆O₂ AND ester contains O-CH₂C(CH₃)₃ AND ester contains CH₃CH₂COO ✓✓✓ <i>i.e. If the ester link is reversed</i></p> $\begin{array}{ccccccc} & & & \text{O} & & & \text{CH}_3 \\ & & & & & & \\ \text{CH}_3 & - & \text{CH}_2 & - & \text{C} & - & \text{O} - \text{CH}_2 - & \text{C} & - & \text{CH}_3 \\ & & & & & & & & & \\ & & & & & & & \text{CH}_3 & & \end{array}$ <p>IGNORE any name</p>

Question	Answer	Mark	Guidance
	<p>NMR analysis – 4 marks</p> <p>Triplet (at δ 1.3) shows an adjacent CH_2 OR triplet (at δ 1.3) shows (C with) 2 adjacent Hs/protons ✓ <i>(because of splitting: so triplet)</i></p> <p>Peak at (δ) 2.2 shows H adjacent to $\text{C}=\text{O}$ AND adjacent to (C with) no hydrogens ✓ <i>(because of no splitting: so singlet)</i></p> <p>Peak at (δ) 4.2 shows $\text{H}-\text{C}-\text{O}$ AND adjacent CH_3 OR 3 adjacent Hs/protons ✓ <i>(because of splitting: so quartet)</i></p> <p>Peak at (δ) 0.9 show 3 x CH_3 ✓ <i>(because of singlet and area 9)</i></p>	4 marks	<p>NOTE: Each peak can be identified from:</p> <ul style="list-style-type: none"> its δ value: ± 0.2 ppm a range, eg 'the peak between 2 and 3' its relative peak area (CARE two peaks have an area of 2) its splitting (CARE: two peaks are singlets) labelling on the spectrum <p>-----</p> <p>QWC: triplet must be spelled correctly ALLOW neighbouring Hs for adjacent to Hs</p> <p>For peak at (δ) 2.2 ALLOW singlet at (δ) 2.2 ALLOW singlet labelled 2</p> <p>For peak at (δ) 4.2 ALLOW quartet (labelled 2)</p> <p>-----</p> <p>Check back for any responses added to spectra</p> <p>ADD ^ MARK TO THE SPECTRUM PAGE TO SHOW THAT IT HAS BEEN LOOKED AT</p>
	Total for 4(c)	10	
	Total	15	

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