

GCE

Chemistry A

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

Advanced GCE

Mark Scheme for June 2014

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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.

OCR will not enter into any discussion or correspondence in connection with this mark scheme.

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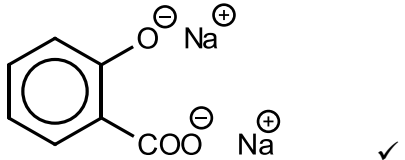
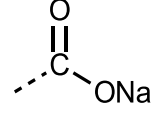
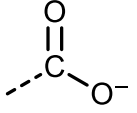
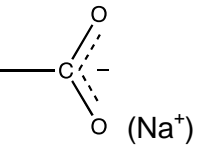
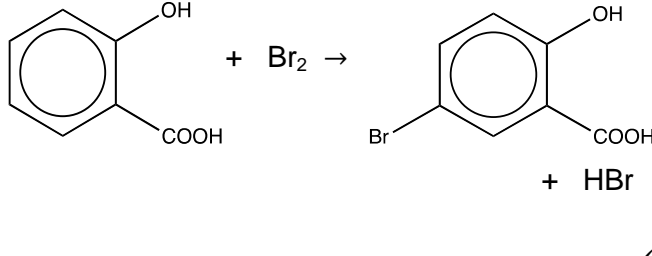
Annotations available in Scoris.

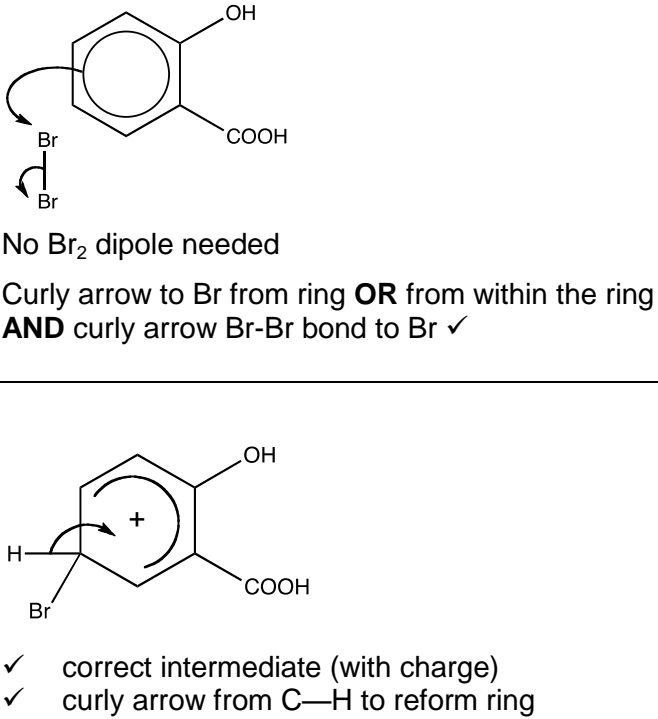
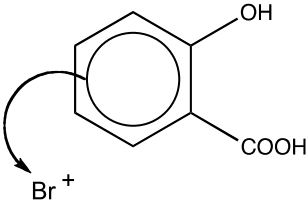
Annotation	Meaning
	Blank Page – this annotation must be used on all blank pages within an answer booklet (structured or unstructured) and on each page of an additional object where there is no candidate response.
	Benefit of doubt given
	Contradiction
	Incorrect response
	Error carried forward
	Ignore
	Not answered question
	Benefit of doubt not given
	Power of 10 error
	Omission mark
	Rounding error
	Error in number of significant figures
	Correct response

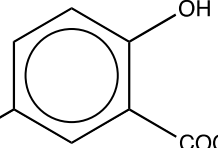
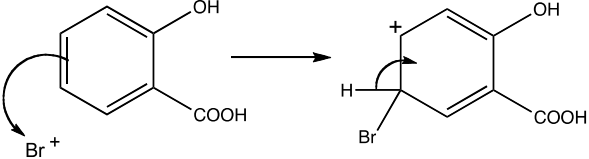
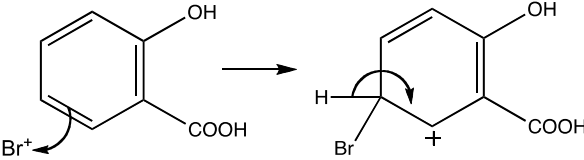
Abbreviations, annotations and conventions used in the detailed Mark Scheme (to include abbreviations and subject-specific conventions).


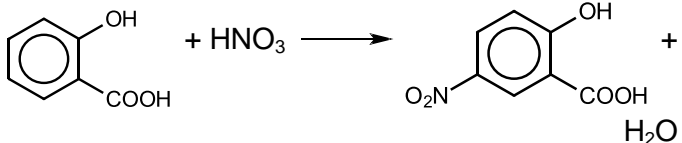
Annotation	Meaning
DO NOT ALLOW	Answers which are not worthy of credit
IGNORE	Statements which are irrelevant
ALLOW	Answers that can be accepted
()	Words which are not essential to gain credit
—	Underlined words must be present in answer to score a mark
ECF	Error carried forward
AW	Alternative wording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

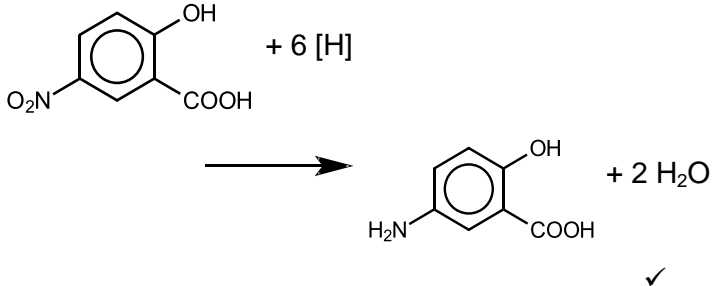
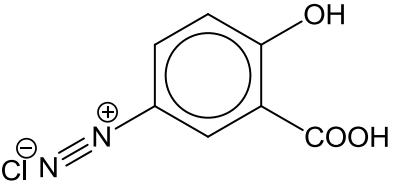
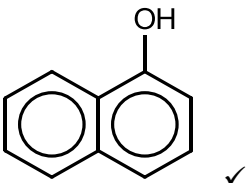
The following questions should be annotated with ticks to show where marks have been awarded in the body of the text:

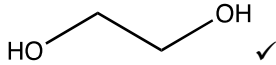
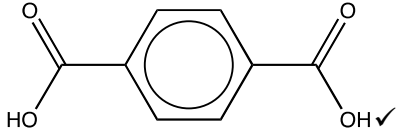
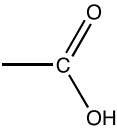
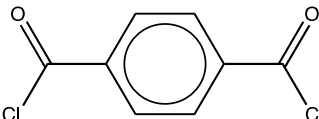
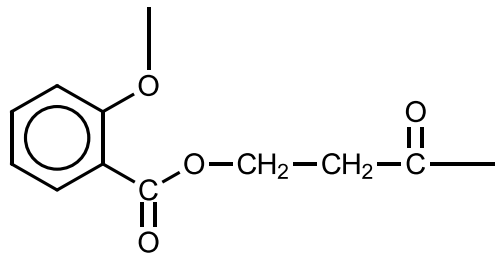
Question	Answer	Mark	Guidance
Where circles have been placed round charges, this is for clarity only and does not indicate a requirement			
1 (a) (i)		1	<p>ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous</p> <p>DO NOT ALLOW —O—Na OR -COO-Na (covalent bond)</p> <p>ALLOW —O⁻</p> <p>ALLOW —ONa ALLOW —COONa OR  OR </p> <p>ALLOW delocalised carboxylate</p>  (Na ⁺)
1 (a) (ii)	<p>(Bromine) would be decolourised/turn (from orange/red/yellow/brown) to colourless</p> <p>OR white precipitate/solid/emulsion (formed) ✓</p>	1	<p>IGNORE goes clear</p> <p>DO NOT ALLOW other colours for bromine</p> <p>IGNORE cream precipitate</p> <p>DO NOT ALLOW salicylic acid turns colourless/decolourised</p> <p>IGNORE temperature/fumes</p>
1 (a) (iii)		1	<p>ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous</p> <p>MUST be all correct to score mark</p> <p>ALLOW molecular formulae, i.e. C₇H₆O₃ + Br₂ → C₇H₅O₃Br + HBr</p>

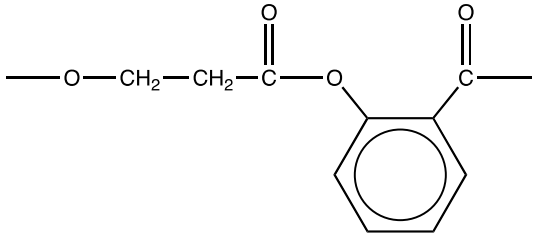
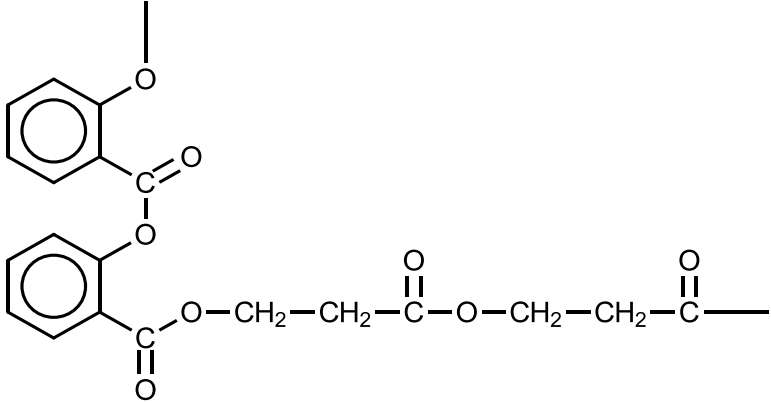
Question			Answer	Mark	Guidance
1	(a)	(iv)	$(\text{CH}_3)_2\text{CHOH}/\text{CH}_3\text{CH}(\text{OH})\text{CH}_3/\text{propan(-)2(-)ol}$ AND acid/ $\text{H}^+/\text{H}_2\text{SO}_4$ (catalyst) ✓	1	ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous ALLOW 2-propanol DO NOT ACCEPT incorrect name or incorrect formula of alcohol IGNORE reflux/concentrated (acid)
1	(b)	(i)	 <p>No Br_2 dipole needed</p> <p>Curly arrow to Br from ring OR from within the ring AND curly arrow Br-Br bond to Br ✓</p> <p>✓ correct intermediate (with charge) ✓ curly arrow from C—H to reform ring</p>	4	ALLOW mechanism with Br^+ electrophile (Maximum 3 marks)  <p>IGNORE any equations involving a halogen carrier</p> <p>BUT DO NOT ALLOW intermediate with π-system covering less than half of ring:</p> <p>ALLOW + charge anywhere inside the 'horseshoe' Horseshoe must have open end towards Br</p> <p>Apply ecf to error in structure of intermediate (M2)</p>

Question	Answer	Mark	Guidance
	 $+ \text{HBr} / \text{H}^+ + \text{Br}^-$ ✓ Correct products (Br ⁻ may be shown in the first step)		<p>ALLOW Kekulé mechanism as shown (Maximum 3 marks if Br⁺ is the electrophile)</p>  <p>ALLOW double bonds in alternate arrangement</p> 

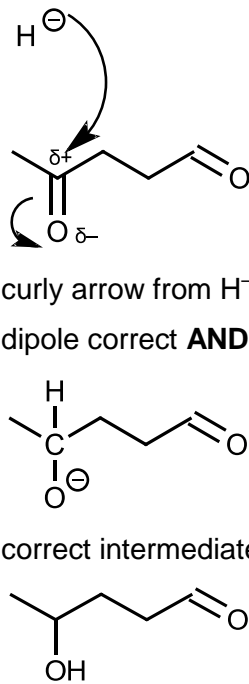
Question			Answer	Mark	Guidance
1	(b)	(ii)	<p>(In salicylic acid)</p> <p>lone pair/pair of electrons on O(H)/phenol is ~ (partially) delocalised into the ring ✓</p> <p>electron density increases/is high ORA ✓</p> <p>Br₂/electrophile is (more) polarised ORA ✓</p> <p> QWC: delocalised/delocalized/delocalise etc. must be spelled correctly in the correct context at least once</p>	3	<p>ALLOW diagram to show movement of lone pair into ring but delocalised ring must be mentioned</p> <p>ALLOW lone pair/pair of electrons on O(H)/phenol is (partially) drawn/attracted/pulled into delocalised ring</p> <p>IGNORE 'activates the ring'</p> <p>ALLOW more electron rich</p> <p>DO NOT ALLOW charge density or electronegativity</p> <p>ALLOW (salicylic acid) attracts electrophiles more/more susceptible to electrophilic attack</p> <p>ALLOW Br₂ is (more) attracted OR Br₂ is not polarised by benzene OR induces dipoles (in bromine/electrophile)</p> <p>Delocalise(d) needed to score the first marking point</p>
1	(c)	(i)	<p>Step 1</p> <p>Add HNO₃ ✓</p> 	4	<p>ALLOW reagent mark if HNO₃ in equation</p> <p>IGNORE H₂SO₄ (NOTE: H₂SO₄ not required with phenols)</p> <p>IGNORE concentrations of acids/temperature</p> <p>ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous</p> <p>Equations MUST be completely correct for one mark each</p>

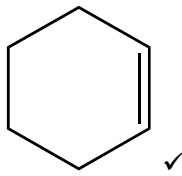
Question			Answer	Mark	Guidance
			<p>Step 2</p> <p>Tin AND concentrated HCl ✓</p> 		DO NOT ALLOW 3H ₂
1	(c)	(ii)	<p>Nitrogen electron pair OR nitrogen lone pair accepts a proton/H⁺ ✓</p>	1	<p>DO NOT ALLOW nitrogen/N lone pair accepts hydrogen (proton/H⁺ required)</p> <p>ALLOW nitrogen donates an electron pair/lone pair to H⁺</p> <p>IGNORE NH₂ group donates electron pair</p>
1	(c)	(iii)	<p>compound A ✓</p>  <p>compound B ✓</p> 	2	<p>ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous</p> <p>ALLOW —N₂Cl OR —N₂⁺Cl⁻</p> <p>DO NOT ALLOW —N≡N⁺ OR —N≡N⁺ Cl⁻</p> <p>DO NOT ALLOW —N₂-Cl (covalent bond)</p>

Question			Answer	Mark	Guidance
1	(d)	(i)	<p>monomers join/bond/add/react/form polymer/form chain AND another product/small molecule/H₂O/HCl ✓</p>	1	IGNORE specific reference to number of molecules
1	(d)	(ii)	<p>   </p> <p>Connectivity is penalised only in this question</p>	2	<p>DO NOT ALLOW –HO (penalise connectivity once only) Both structures must be skeletal DO NOT ALLOW stray sticks (skeletal means CH₃ attached) DO NOT ALLOW structure with a C shown, e.g.</p> <p>  </p> <p>ALLOW</p> <p>  </p>
1	(d)	(iii)	<p>  </p> <p>ester link MUST be fully displayed ✓</p> <p>OR</p>	1	ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous

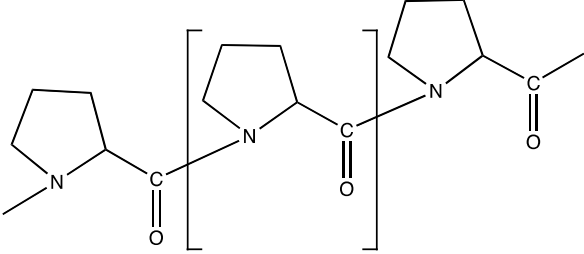
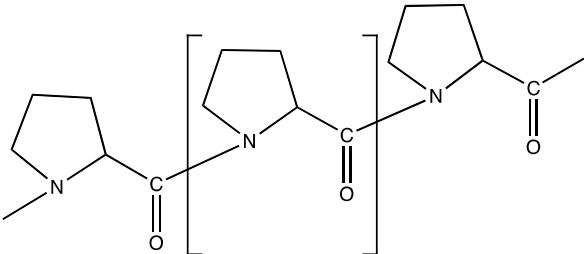
Question	Answer	Mark	Guidance
			<p>ALLOW</p>  <p>IGNORE bond angles</p> <p>DO NOT ALLOW more than one repeat unit unless correct repeat unit is indicated</p> <p>IGNORE brackets with <i>n</i></p> <p>ALLOW any correct repeat unit</p> <p>ALLOW end bonds shown as - - - -</p> <p>DO NOT ALLOW if structure has no end bonds</p>
	Total	22	

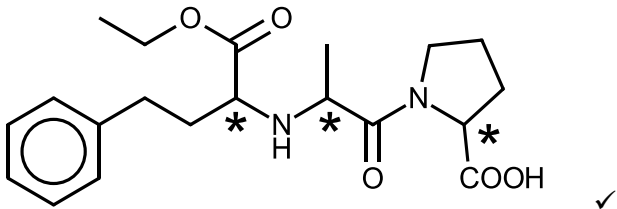
Question	Answer	Mark	Guidance
2 (a)	<p>FIRST react all with Tollens' reagent AND silver mirror/ppt/solid (formed) with compound D</p> <p>OR with Fehling's/Benedict's solutions AND (brick-red/orange) solid/precipitate (formed) with compound D ✓</p> <p>NOTE: eliminates D</p> <div data-bbox="324 608 1070 756" style="border: 1px solid black; padding: 5px; margin: 10px 0;"> </div> <p>✓</p> <p>THEN react C and E with $\text{H}_2\text{SO}_4/\text{H}^+$ AND $\text{K}_2\text{Cr}_2\text{O}_7/ \text{Cr}_2\text{O}_7^{2-}/\text{Na}_2\text{Cr}_2\text{O}_7$ AND colour change OR green colour with compound C</p> <p>OR <u>no</u> change OR <u>no</u> reaction OR no green colour with compound E ✓</p> <div data-bbox="324 1059 1084 1177" style="border: 1px solid black; padding: 5px; margin: 10px 0;"> </div> <p>✓</p>	4	<p>ALLOW ammonia + silver nitrate for reagent ALLOW black solid/ppt ALLOW 'the aldehyde gives a silver mirror' ALLOW solid OR crystals OR ppt as alternatives for precipitate ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous</p> <p>DO NOT ALLOW molecular formulae for organic structures</p> <p>IGNORE all references to 2,4-dinitrophenylhydrazine/Brady's</p> <p>ACCEPT acidified dichromate ALLOW blue/green blue IGNORE equation for oxidation of D</p> <p>ALLOW equation for partial oxidation</p> <div data-bbox="1240 1082 1984 1161" style="border: 1px solid black; padding: 5px; margin: 10px 0;"> </div>

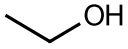
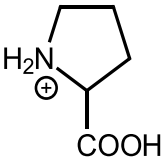
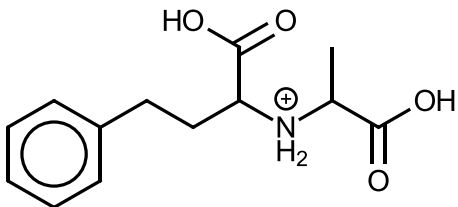


Question	Answer	Mark	Guidance
			<p>ALLOW alternative sequences e.g. FIRST react all with H_2SO_4 AND $\text{K}_2\text{Cr}_2\text{O}_7$ colour change with C and D <i>eliminates E</i></p> <p>At least one correct equation and structure of one product from either reaction required for the second mark. NB several possible products for the oxidation of D</p> <p>THEN react C and D with Tollens' <i>distinguishes between C and D</i></p>
2 (b)	 <p>curly arrow from H^- to $\text{C}^{(\delta+)}$ of correct $\text{C}=\text{O}$ group ✓</p> <p>dipole correct AND curly arrow from $\text{C}=\text{O}$ bond to $\text{O}^{(\delta-)}$ ✓</p> <p>correct intermediate with negative charge on O ✓</p> <p>correct product ✓</p>	4	<p>ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous</p> <p>First curly arrow must come from either a lone pair on H or negative charge on H</p> <p>IF aldehyde reduced OR both carbonyls reduced DO NOT AWARD first mark (second, third and fourth marks can be awarded ECF)</p> <p>IGNORE lack of $\text{C}-\text{H}$ if entirely skeletal</p> <p>IGNORE curly arrows in second stage</p> <p>Apply ecf to error in structure e.g. CH_2 missing from the chain or $-\text{COOH}/-\text{COH}$ instead of $-\text{CHO}$</p> <p>IGNORE other products</p>

Question		Answer	Mark	Guidance								
2	(c)	<table border="1"> <thead> <tr> <th>Compound</th> <th>C</th> <th>D</th> <th>E</th> </tr> </thead> <tbody> <tr> <td>Number of peaks</td> <td>5</td> <td>5</td> <td>4</td> </tr> </tbody> </table> <p style="text-align: right;">all correct ✓</p>	Compound	C	D	E	Number of peaks	5	5	4	1	
Compound	C	D	E									
Number of peaks	5	5	4									
2	(d) (i)	<ul style="list-style-type: none"> • pent-2-ene <table style="display: inline-table; vertical-align: middle; margin-left: 10px;"> <tr> <td style="text-align: center; padding-right: 10px;"> $\begin{array}{c} \text{H}_3\text{C} \\ \\ \text{C}=\text{O} \\ \\ \text{H} \end{array}$ </td> <td style="text-align: center; vertical-align: middle;">AND</td> <td style="text-align: center; padding-left: 10px;"> $\begin{array}{c} \text{H} \\ \\ \text{O}=\text{C} \\ \\ \text{CH}_2\text{CH}_3 \end{array}$ ✓ </td> </tr> </table> • hexa-2,4-diene <table style="display: inline-table; vertical-align: middle; margin-left: 10px;"> <tr> <td style="text-align: center; padding-right: 10px;"> $\begin{array}{c} \text{H}_3\text{C} \\ \\ \text{C}=\text{O} \\ \\ \text{H} \end{array}$ ✓ </td> <td style="text-align: center; vertical-align: middle;">O=C-C=O</td> <td style="text-align: center; padding-left: 10px;"> $\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{O}=\text{C}-\text{C}=\text{O} \\ \quad \\ \text{H} \quad \text{H} \end{array}$ ✓ </td> </tr> </table> 	$\begin{array}{c} \text{H}_3\text{C} \\ \\ \text{C}=\text{O} \\ \\ \text{H} \end{array}$	AND	$\begin{array}{c} \text{H} \\ \\ \text{O}=\text{C} \\ \\ \text{CH}_2\text{CH}_3 \end{array}$ ✓	$\begin{array}{c} \text{H}_3\text{C} \\ \\ \text{C}=\text{O} \\ \\ \text{H} \end{array}$ ✓	O=C-C=O	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{O}=\text{C}-\text{C}=\text{O} \\ \quad \\ \text{H} \quad \text{H} \end{array}$ ✓	3	<p>ALLOW correct structural OR displayed OR skeletal formulae</p> <p>OR combination of above as long as unambiguous</p> <p>ALLOW C₂H₅CHO and CH₃CHO</p>		
$\begin{array}{c} \text{H}_3\text{C} \\ \\ \text{C}=\text{O} \\ \\ \text{H} \end{array}$	AND	$\begin{array}{c} \text{H} \\ \\ \text{O}=\text{C} \\ \\ \text{CH}_2\text{CH}_3 \end{array}$ ✓										
$\begin{array}{c} \text{H}_3\text{C} \\ \\ \text{C}=\text{O} \\ \\ \text{H} \end{array}$ ✓	O=C-C=O	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{O}=\text{C}-\text{C}=\text{O} \\ \quad \\ \text{H} \quad \text{H} \end{array}$ ✓										
2	(d) (ii)		1	<p>ALLOW correct structural OR displayed OR skeletal formulae</p> <p>OR combination of above as long as unambiguous</p>								
Total			13									


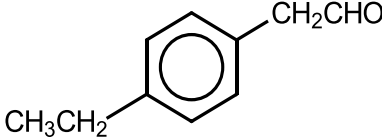
Question			Answer	Mark	Guidance
3	(a)	(i)	$\begin{array}{ccccccc} & \text{H} & \text{O} & & \text{CH}_2\text{OH} & & \\ & & & & & & \\ \text{H}_2\text{N} & -\text{C} & -\text{C} & -\text{N} & -\text{C} & -\text{COOH} & \\ & & & & & & \\ & \text{CH}_3 & & \text{H} & \text{H} & & \end{array}$ $\begin{array}{ccccccc} & \text{H} & \text{O} & & \text{CH}_3 & & \\ & & & & & & \\ \text{H}_2\text{N} & -\text{C} & -\text{C} & -\text{N} & -\text{C} & -\text{COOH} & \\ & & & & & & \\ & \text{HOH}_2\text{C} & & \text{H} & \text{H} & & \end{array}$	2	<p>ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous</p> <p>DO NOT ALLOW peptide chains</p>
3	(a)	(ii)	<p>alanine at pH 6.0</p> $\begin{array}{ccc} & \text{H} & \text{O} \\ & & \\ \text{H}_3\text{N}^{\oplus} & -\text{C} & -\text{C}-\text{O}^{\ominus} \\ & & \\ & \text{CH}_3 & \end{array}$ <p>serine at pH 10.0</p> $\begin{array}{ccc} & \text{H} & \text{O} \\ & & \\ \text{H}_2\text{N} & -\text{C} & -\text{C}-\text{O}^{\ominus} \\ & & \\ & \text{CH}_2\text{OH} & \end{array}$	2	<p>ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous</p> <p>ALLOW + charge on N or H: <i>i.e.</i> $^+\text{NH}_3$ or NH_3^+</p> <p>DO NOT ALLOW ‘-’ charge on C <i>i.e.</i> ^-COO</p> <p>DO NOT ALLOW if structure is incomplete</p>

Question	Answer	Mark	Guidance
3 (a) (iii)		1	<p>ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous</p> <p>IGNORE bond angles</p> <p>DO NOT ALLOW more than one repeat unit</p> <p>ALLOW end bonds shown as - - - -</p> <p>DO NOT ALLOW if structure has no end bonds</p> <p>IGNORE brackets unless they are used to pick out the repeat unit from a polymer chain</p> <p>IGNORE n</p> 

Question			Answer	Mark	Guidance									
3	(b)		<p style="text-align: center;">¹H NMR spectrum for serine</p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>chemical shift, δ /ppm</th> <th>relative peak area</th> <th>splitting pattern</th> </tr> </thead> <tbody> <tr> <td>2.0 to 3.0</td> <td>1</td> <td>triplet</td> </tr> <tr> <td>3.3 to 4.2</td> <td>2</td> <td>doublet</td> </tr> </tbody> </table> <p>One mark for each correct row ✓✓</p>	chemical shift, δ /ppm	relative peak area	splitting pattern	2.0 to 3.0	1	triplet	3.3 to 4.2	2	doublet	2	<p>ALLOW δ values ± 0.2 ppm, as a range or a value within the range</p> <p>ALLOW a response that implies a splitting into three for a triplet/into two for a doublet</p>
chemical shift, δ /ppm	relative peak area	splitting pattern												
2.0 to 3.0	1	triplet												
3.3 to 4.2	2	doublet												
3	(c)	(i)		1	ALL correct for one mark									
3	(c)	(ii)	<p>any two from:</p> <p>no/fewer side effects</p> <p>increases the (pharmacological) activity/effectiveness</p> <p>Reduces/stops the need for/cost/difficulty in separating stereoisomers/optical isomers</p> <p style="text-align: right;">✓✓</p>	2	<p>IGNORE toxic/harmful</p> <p>IGNORE a response that implies a reduced dose</p> <p>IGNORE "it takes (less) time to separate"</p>									

Question			Answer	Mark	Guidance
3	(c)	(iii)	   <p>✓ one mark for ethanol</p> <p>✓ one mark for proline with NH OR NH₂⁺</p> <p>✓ one mark for remaining fragment</p> <p>with  or </p> <p>✓ Fourth mark for structure of both ions shown correctly with NH₂⁺</p>	4	<p>ALLOW correct structural OR displayed OR skeletal formulae</p> <p>OR combination of above as long as unambiguous</p> <p>ALLOW + charge on H of NH₂ groups, <i>i.e.</i> NH₂⁺</p> <p>IGNORE negative (counter) ions</p>
3	(c)	(iv)	<p>idea of separating (the components/compounds)</p> <p>AND idea of (identifying compounds by) comparison with a (spectral) database ✓</p>	1	<p>ALLOW (identifies compounds) using fragmentation (patterns)/fragment ions (but IGNORE molecular ions)</p> <p>IGNORE retention times</p>
Total				15	

Question		Answer	Mark	Guidance
4	(a)	TMS/tetramethylsilane (which is the) standard (for chemical shift measurements) ✓	1	ALLOW (CH ₃) ₄ Si ALLOW TMS is the reference OR TMS has $\delta = 0$ (ppm) OR for calibration OR for comparison IGNORE solvent, unreactive, volatile, it gives a sharp peak
4	(b)	NMR analysis = 5 marks M1: Peak(s) at (δ) 9.7 = CHO ✓ M2: Peak(s) at (δ) 7.1 = C ₆ H ₄ ✓ M3: Triplet at (δ) 1.3/peak at 1.3 AND quartet (at δ 2.6)/ peak at 2.6 = CH ₂ CH ₃ ✓ M4: Triplet at (δ) 9.7/peak at 9.7 AND doublet (at δ 3.7)/peak at 3.7 = CH ₂ CHO ✓	9	NOTE: Each peak can be identified from: <ul style="list-style-type: none"> its δ value a range, e.g. "the peak between 0.8 and 2.0" its relative peak area (beware two peaks with 2 protons) its splitting (beware two triplets) labelling on the spectrum ALLOW CH ₂ CHO/aldehyde IGNORE reference to phenol ALLOW (four) benzene ring proton(s) IGNORE reference to phenol M3 and M4 Look for a clear link (using words or diagrams) between the two peaks

Question	Answer	Mark	Guidance
	<p>M5: (n+1 rule) Any one of the following</p> <ul style="list-style-type: none"> • triplet at (δ) 1.3 shows (C with) 2 adjacent Hs/protons OR adjacent CH₂ (because of splitting: so triplet) • quartet at (δ) 2.6 shows (C with) 3 adjacent Hs/protons OR adjacent CH₃ • triplet at (δ) 9.7 shows (C with) 2 adjacent Hs/protons OR adjacent CH₂ • doublet at (δ) 3.7 shows (C with) 1 adjacent H/proton OR adjacent CH <p> QWC: triplet spelled correctly in the correct context once</p>	✓	<p>ALLOW a response that implies a splitting into three for a triplet/into two for a doublet etc.</p> <p>ALLOW “neighbouring” Hs for “adjacent to” Hs</p> <p>IGNORE other comments about splitting once M5 has been awarded</p> <p>DO NOT ALLOW one of M3 or M4 or M5 if triplet not seen</p>
	<p>Aldehyde structure = 4 marks</p> <div style="text-align: center;">  </div> <p style="text-align: right;">✓✓✓✓</p>		<p>ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous</p> <p>IF structure contains C₆H₄ ✓</p> <p>IF structure contains C₆H₄ AND the organic structure contains CH₃CH₂ directly attached to the benzene ring OR contains CH₂CHO directly attached to the benzene ring ✓✓</p> <p>IF structure has formula C₁₀H₁₂O AND structure contains C₆H₄ AND the structure contains CH₃CH₂ AND contains CH₂CHO AND 1,2 OR 1,3 substituted ✓✓✓</p>

Question			Answer	Mark	Guidance
					IF structure has formula $C_{10}H_{12}O$ AND structure contains C_6H_4 AND the structure contains CH_3CH_2 AND contains CH_2CHO AND 1,4 substituted ✓✓✓✓ (use of ^{13}C data)
			Total	10	

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