

# **Chemistry A**

Advanced GCE

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

## **Mark Scheme for June 2011**

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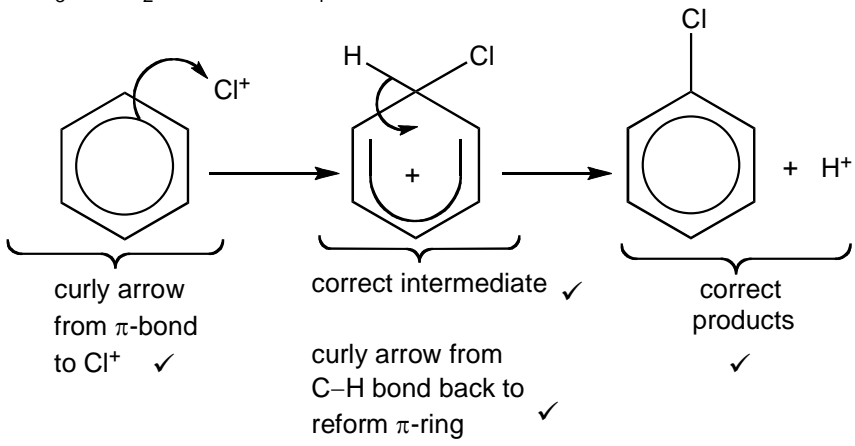
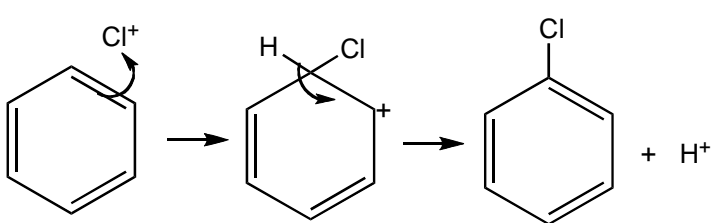
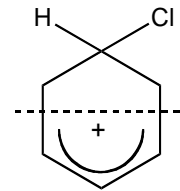
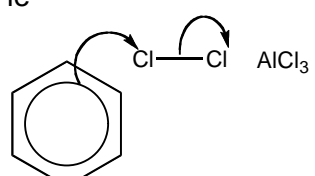
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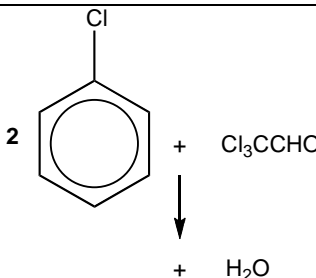
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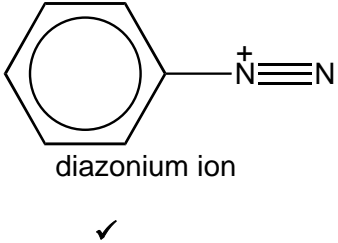
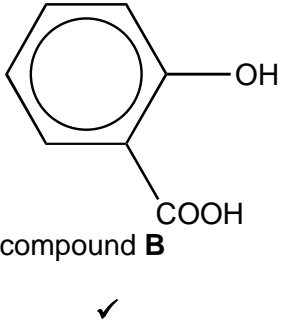
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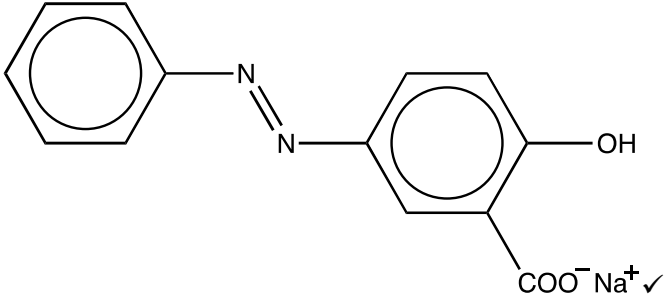
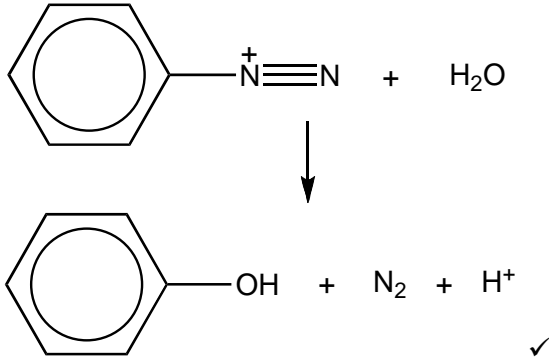
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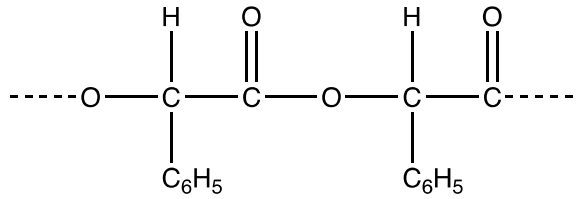
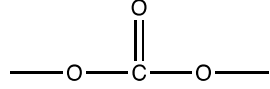
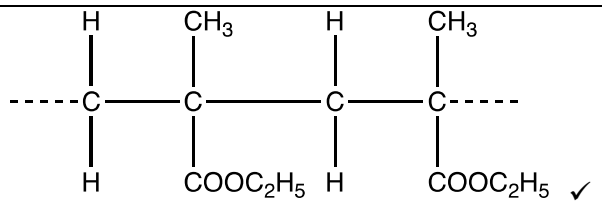
## ALLOW Kekulé structures throughout

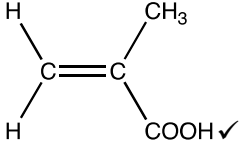
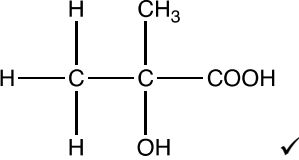
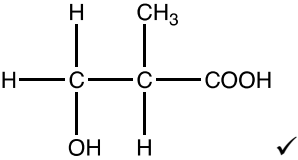
Question	Answer	Mark	Guidance
1 (a)	<p><math>\text{AlCl}_3 + \text{Cl}_2 \longrightarrow \text{AlCl}_4^- + \text{Cl}^+ \checkmark</math></p>  <p>curly arrow from <math>\pi</math>-bond to <math>\text{Cl}^+</math> <math>\checkmark</math></p> <p>correct intermediate <math>\checkmark</math></p> <p>curly arrow from C-H bond back to reform <math>\pi</math>-ring <math>\checkmark</math></p> <p>correct products <math>\checkmark</math></p> <p><math>\text{H}^+ + \text{AlCl}_4^- \longrightarrow \text{AlCl}_3 + \text{HCl} \checkmark</math></p> <p><b>Note:</b> 1st curly arrow should start within the ring or on the ring</p> <hr/> <p><b>Note:</b> ALLOW mechanism using Kekulé structures:</p> 	6	<p><b>ANNOTATIONS MUST BE USED</b></p> <p><b>DO NOT ALLOW</b> the following intermediate:</p>  <p><math>\pi</math>-ring must be more than 1/2 way up  <b>AND</b>  'horseshoe' the right way up,  <i>ie</i> gap towards C with Cl</p> <p><b>ALLOW</b> + sign anywhere inside the 'hexagon' of intermediate</p> <p><b>ALLOW</b> 1st curly arrow starting within the hexagon</p> <p><b>ALLOW</b> mechanism with <math>\text{Cl}-\text{Cl} \cdots \text{AlCl}_3</math> for 1st 2 marks, <i>ie</i></p>  <p>Second curly arrow to either <math>-\text{Cl}</math> or <math>\text{AlCl}_3</math></p> <p><b>Note:</b> If <math>\text{Br}^+</math> is used, <b>DO NOT ALLOW</b> 1st mechanism mark but all other marks available by <b>ECF</b></p>

Question			Answer	Mark	Guidance
1	(b)	(i)	 <p>2</p> <p>1st mark: reactants, correctly balanced, ✓ ie 2 C<sub>6</sub>H<sub>5</sub>Cl + Cl<sub>3</sub>CCHO</p> <p>2nd mark: product, (correctly balanced) ✓ ie H<sub>2</sub>O</p>	2	<p><b>Each mark is independent of the other</b></p> <p><b>ALLOW</b> C<sub>6</sub>H<sub>5</sub>Cl for chlorobenzene</p> <p><b>ALLOW</b> any unambiguous structure for Cl<sub>3</sub>CCHO, e.g. CCl<sub>3</sub>CHO <b>BUT</b> ..... <b>DO NOT ALLOW</b> CCl<sub>3</sub>COH</p> <p><b>Standalone mark</b></p> <p><b>Standalone mark</b></p>
		(ii)	6 ✓	1	
	(c)		<p>substitution/nitration/NO<sub>2</sub> at different positions (on the ring) <b>OR</b> forms different isomers <b>OR</b> multiple substitution/nitration ✓</p>	1	<p><b>ALLOW</b> examples, e.g. 1-chloro-2-nitrobenzene and 1-chloro-3-nitrobenzene <b>ALLOW</b> 'it' for nitro group</p> <p><b>ALLOW</b> examples, e.g. 1-chloro-2,3-dinitrobenzene <b>IGNORE</b> nitrate/NO<sub>3</sub></p>
	(d)		<p>In phenol, (lone) pair of electrons on O is (partially) <b>delocalised</b> into the ring ✓ <b>QWC</b>: delocalised/delocalized/delocalise, etc must be spelt correctly in the correct context for benzene <b>OR</b> phenol at least once</p> <p>electron density increases/is high ✓ <b>ORA</b></p> <p>Cl<sub>2</sub>/electrophile is (more) polarised ✓ <b>ORA</b></p>	3	<p><b>ANNOTATIONS MUST BE USED</b></p> <p><b>ALLOW</b> diagram to show movement of lone pair into ring but <b>delocalised</b> ring must be mentioned <b>ALLOW</b> lone pair of electrons on O is (partially) drawn/ attracted/pulled into <b>delocalised</b> ring <b>IGNORE</b> 'activates the ring'</p> <p><b>DO NOT ALLOW</b> charge density or electronegativity</p> <p><b>ALLOW</b> Cl<sub>2</sub> is (more) attracted <b>OR</b> Cl<sub>2</sub> is not polarised by benzene <b>OR</b> induces dipoles (in chlorine/electrophile)</p>
<b>Total</b>				<b>13</b>	

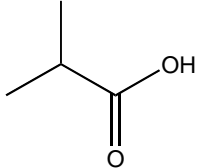
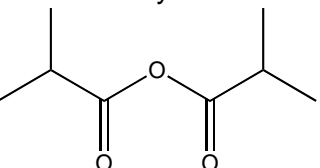
Question		Answer	Mark	Guidance
2	(a)	(i)		
		donates a lone pair (on N) <b>OR</b> accepts a proton/H <sup>+</sup> ✓	1	<b>IGNORE</b> 'forms a dative covalent bond' (no direction of lone pair) <b>ALLOW</b> 'forms a dative covalent bond with/to H <sup>+</sup> ' <b>ALLOW</b> mark for N:→H <sup>+</sup> (can be from correct equation)
		(ii)		
		$(\text{C}_2\text{H}_5\text{NH}_3^+)_2\text{SO}_4^{2-}$ ✓  $\text{C}_2\text{H}_5\text{NH}_3^+ \text{CH}_3\text{COO}^-$ ✓	2	<b>ALLOW</b> $(\text{C}_2\text{H}_5\text{NH}_3)_2 \text{SO}_4$ <b>DO NOT ALLOW</b> $(\text{C}_2\text{H}_5\text{NH}_3) \text{HSO}_4$ <b>OR</b> $(\text{C}_2\text{H}_5\text{NH}_3^+) \text{HSO}_4^-$ <i>brackets not required</i>  <b>ALLOW</b> $(\text{C}_2\text{H}_5\text{NH}_3) (\text{CH}_3\text{COO})$ <b>OR</b> $(\text{C}_2\text{H}_5\text{NH}_3^+) (\text{CH}_3\text{COO}^-)$ <i>brackets not required</i> <b>ALLOW</b> separate ions with or without a '+' sign between them, e.g. $\text{C}_2\text{H}_5\text{NH}_3^+ + \text{CH}_3\text{COO}^-$
	(b)	(i)		
		 diazonium ion ✓		
		 compound B ✓	2	In diazonium ion, <b>IGNORE</b> Cl <sup>-</sup> <b>ALLOW</b> '+' sign up to halfway along triple bond from left-hand N  In compound B, <b>ALLOW</b> -OH ionised as -O <sup>-</sup> <b>ALLOW</b> -COOH ionised as COO <sup>-</sup>
		(ii)		
		conditions = alkaline /OH <sup>-</sup>  <b>AND</b> use = dye/pigment/colouring ✓	1	<b>BOTH</b> responses required for one mark  <b>ALLOW</b> named alkali, e.g. NaOH/KOH <b>ALLOW</b> base  <b>IGNORE</b> references to temperature  <b>ALLOW</b> use = indicator

Question		Answer	Mark	Guidance
2	(b) (iii)	Organic product:  Other products: CO <sub>2</sub> AND H <sub>2</sub> O ✓	2	IGNORE phenoxide: O <sup>-</sup> OR O <sup>-</sup> Na <sup>+</sup>  ALLOW COO <sup>-</sup> OR COONa  ALLOW H <sub>2</sub> CO <sub>3</sub> Note: must be formulae and not names (in question)
	(c)		1	ALLOW N <sub>2</sub> <sup>+</sup> on structural formula ALLOW C <sub>6</sub> H <sub>5</sub> N <sub>2</sub> <sup>+</sup> + H <sub>2</sub> O → C <sub>6</sub> H <sub>5</sub> OH + N <sub>2</sub> + H <sup>+</sup> ALLOW C <sub>6</sub> H <sub>5</sub> N <sub>2</sub> Cl + H <sub>2</sub> O → C <sub>6</sub> H <sub>5</sub> OH + N <sub>2</sub> + HCl  If + charge shown, IGNORE its position
<b>Total</b>			<b>9</b>	

Question		Answer	Mark	Guidance
3	(a)	<p><b>monomers</b> join/bond/add/react/form polymer/form chain  <b>AND</b> another product/small molecule e.g. H<sub>2</sub>O/HCl ✓</p> <p><b>QWC</b> must spell <b>AND</b> use 'monomer(s)' correctly throughout</p>	1	<p><b>IGNORE</b> 'two' when referring to monomers, ie (two) monomers .....</p>
	(b) (i)	 <p>ester link ✓  <b>Note:</b> Any ester link shown <b>must</b> be correct  rest of the structure ✓</p>	2	<p><b>ALLOW</b> correct structural <b>OR</b> displayed <b>OR</b> skeletal formula  <b>OR</b> mixture of the above (as long as unambiguous)</p> <p><b>ALLOW</b> benzene ring for C<sub>6</sub>H<sub>5</sub></p> <p>'End bonds' <b>MUST</b> be shown (do not have to be dotted)</p> <p><b>ALLOW one</b> or more repeat units but has to have a whole number of repeat units (<i>ie</i> does not have to be two)</p> <p>For ester, <b>DO NOT ALLOW</b> </p> <p><b>ALLOW</b> structure with no O at left end and COO at right end</p> <p><b>IGNORE</b> brackets  <b>IGNORE</b> <i>n</i></p>
	(ii)	 <p>✓</p>	1	<p><b>ALLOW</b> correct structural <b>OR</b> displayed <b>OR</b> skeletal formula  <b>OR</b> mixture of the above (as long as unambiguous)</p> <p><b>ALLOW one</b> or more repeat units but has to have a whole number of repeat units (<i>ie</i> does not have to be two)</p> <p>'End bonds' <b>MUST</b> be shown (do not have to be dotted)</p> <p><b>IGNORE</b> brackets  <b>IGNORE</b> <i>n</i></p>

Question		Answer	Mark	Guidance
3	(c)	<p>compound <b>C</b></p>  <p>compound <b>D</b> and compound <b>E</b></p>  	3	<p><b>ALLOW</b> correct structural <b>OR</b> displayed <b>OR</b> skeletal formula  <b>OR</b> mixture of the above (as long as unambiguous)  <b>ALLOW</b> CH<sub>2</sub>C(CH<sub>3</sub>)COOH</p> <p><b>ALLOW D</b> and <b>E</b> by <b>ECF</b> from an incorrect structure of <b>C</b> provided that <b>C</b> contains a double bond and molecular formulae of <b>D</b> and <b>E</b> is C<sub>4</sub>H<sub>8</sub>O<sub>3</sub> with H<sub>2</sub>O added across double bond</p>
	(d)	(i)		<p><b>ALLOW</b> correct structural <b>OR</b> displayed <b>OR</b> skeletal formula  <b>OR</b> mixture of the above (as long as unambiguous)  e.g. (CH<sub>3</sub>)<sub>2</sub>CHOH</p> <p><b>DO NOT ALLOW</b> –HO</p> <p><b>IGNORE</b> working (<i>ie</i> other structures) provided correct structure of propan-2-ol is shown</p> <p><b>IGNORE</b> name (even if wrong)</p>



Question	Answer	Mark	Guidance
3 (d) (ii)	 <p>OR acid anhydride:</p> 	1	<p><b>ALLOW</b> correct structural <b>OR</b> displayed <b>OR</b> skeletal formula  <b>OR</b> mixture of the above (as long as unambiguous)  <b>OR</b> (2-)methylpropanoic acid</p> <p><b>DO NOT ALLOW</b> incorrect name  (will CON a correct structure)</p> <p><b>ALLOW</b> acyl chloride: <math>(\text{CH}_3)_2\text{CHCOCl}</math></p> <p><b>IGNORE</b> working provided correct structure of propan-2-ol is shown</p>
	<p>(iii)</p> <p>Hydrogen bonds form <b>with</b> water ✓  <b>Note:</b> Can be shown in diagram as dashed line, <i>ie</i> ---- (no label required)</p> <p><b>DO NOT CON</b> 'hydrogen bond' from an incorrect hydrogen bond in diagram</p> <p>Mandelic acid forms more hydrogen bonds (with water) ✓  <b>ORA</b></p> <p>Mandelic acid has an extra OH  <b>OR</b> 2 OH groups  <b>OR</b> has a COOH group ✓  <b>ORA</b></p>	3	<p><b>ANNOTATIONS MUST BE USED</b></p> <p><b>ALLOW</b> a diagram showing hydrogen bonds with water, dipole and lone pair are not required  <b>ALLOW</b> a hydrogen bond to C=O, <i>ie</i> C=O---H-O  <b>IGNORE</b> bond angles  Diagram does <b>not</b> need to show all of mandelic acid  <b>(IGNORE if wrong)</b></p> <p><b>ALLOW</b> any comparison of numbers of hydrogen bonds provided that mandelic acid has more hydrogen bonds</p> <p><b>DO NOT ALLOW</b> 'No -OH groups in ester (as there are)'  <b>DO NOT ALLOW</b> reference to <math>\text{-OH}^-</math> / hydroxide</p> <p><b>IGNORE</b> reference to carbon chain and van der Waals' forces</p> <p><b>Note:</b> If a response compares <b>Ester 1</b> with <b>Ester 2</b> rather than with mandelic acid, maximum of 2 marks:  <b>1st mark</b> hydrogen bonds  <b>2nd mark</b> <b>Ester 2</b> has more Os/oxygens  <b>OR</b> <b>Ester 2</b> forms more hydrogen bonds</p>

Question			Answer	Mark	Guidance
3	(d)	(iv)	To test for (adverse) side effects <b>OR</b> to test toxicity <b>OR</b> to test for irritation ✓	1	<b>ALLOW</b> a stated adverse side effect, eg allergy, carcinogenic, etc  <b>IGNORE</b> references to optical isomers, chirality, etc  <b>IGNORE</b> vague statements such as harmful to skin, dangerous to skin, corrosive to skin, reacts with skin  <b>ALLOW</b> company liable to litigation/damages
			<b>Total</b>	<b>13</b>	

Question	Answer	Mark	Guidance
4	<p><b>Equations</b>  <math>\text{CH}_3\text{COCHO} + 4[\text{H}] \longrightarrow \text{CH}_3\text{CHOHCH}_2\text{OH} \checkmark</math>  <math>\text{CH}_3\text{COCHO} + [\text{O}] \longrightarrow \text{CH}_3\text{COCOOH} \checkmark</math></p> <p><b>Reduction reagents and observation</b>  Methylglyoxal is <b>reduced</b> by <math>\text{NaBH}_4 \checkmark</math></p> <p><b>Oxidation reagents and observation</b>  Methylglyoxal is <b>oxidised</b> by <math>\text{H}_2\text{SO}_4</math> <b>AND</b> <math>\text{K}_2\text{Cr}_2\text{O}_7 \checkmark</math>  Observation: turns green <b>OR</b> blue <math>\checkmark</math></p> <p><b>OR</b>  Methylglyoxal is <b>oxidised</b> by Tollens' reagent <math>\checkmark</math>  Observation: Silver (mirror) <math>\checkmark</math></p>	<p>1</p> <p>1</p> <p>1</p> <p>2</p>	<p><b>ANNOTATIONS MUST BE USED</b>  Throughout question, <b>ALLOW</b> correct structural <b>OR</b> displayed <b>OR</b> skeletal formula  <b>DO NOT ALLOW</b> molecular formulae</p> <p><b>ALLOW</b> partial reduction (ie reduction of either C=O group)  [H] implies reduction  [O] implies oxidation</p> <p>reduced <b>AND</b> reagent are <b>both</b> required for the mark  <b>ALLOW</b> link to equation with [H] for reduction  <b>ALLOW</b> <math>\text{LiAlH}_4</math> as alternative for <math>\text{NaBH}_4</math>  <b>ALLOW</b> any recognisable attempt at name  <b>IGNORE</b> any reference to acids</p> <p>oxidised <b>AND</b> reagent are <b>both</b> required for the mark  <b>ALLOW</b> link to equation with [O] for oxidation  <b>ALLOW</b> <math>\text{Na}_2\text{Cr}_2\text{O}_7</math> instead of <math>\text{K}_2\text{Cr}_2\text{O}_7</math>  <b>ALLOW</b> <math>\text{H}^+</math> <b>AND</b> <math>\text{Cr}_2\text{O}_7^{2-}</math> <b>OR</b> <math>\text{H}^+</math> <b>AND</b> <math>\text{CrO}_4^{2-}</math></p> <p>If name given, <b>ALLOW</b> dichromate <b>OR</b> dichromate(VI)  <b>ALLOW</b> acidified dichromate  <b>ALLOW</b> any strong acid  If formulae used, formulae must be correct</p> <p><b>ALLOW</b> <math>\text{AgNO}_3</math> in ammonia <b>OR</b> ammoniacal <math>\text{AgNO}_3</math></p> <p><b>ALLOW oxidised</b> by manganate  Observation: decolourised</p> <p><b>Note:</b> If one reaction is identified as oxidation, assume the other is reduction (and vice versa)</p>
	<b>Total</b>	<b>5</b>	

Question		Answer	Mark	Guidance
5	(a)	idea of separating (the components/compounds) ✓ idea of (identifying compounds) by comparison with a (spectral) database ✓	2	<b>ALLOW</b> (identifies compounds) using fragmentation (patterns)/fragment ions (but <b>IGNORE</b> molecular ions) ✓ <b>Note:</b> Each marking point does <b>not</b> need to be linked to GC or MS (The question asks about GC–MS as a combined technique)
	(b)	(i) 54.2% of 118 <b>OR</b> $54.2/118 \times 100 = 64/63.96$ (hence there are 4 oxygens) ✓  118 – 64 = 54 hence 4 carbon (48) and 6 hydrogen (6) ✓	2	<b>IGNORE</b> calculation that proves that $C_4H_6O_4$ has a molar mass of 118 (ie $12 \times 4 + 6 \times 1 + 16 \times 4$ ) <b>ALLOW</b> $64/118 \times 100 = 54.2\%$ for 1st mark <b>IGNORE</b> method using empirical formula  <b>ALLOW</b> any reasonable working leading to 4C  <b>Note:</b> $54.2(\%) \div 16$ would <b>not</b> get the 1st mark but the answer could be used to get the 2nd mark
		(ii) carboxyl group <b>OR</b> carboxylic acid ✓ must be <b>name</b> (in question)	1	<b>IGNORE</b> working, e.g. O–H, C=O, C–O on IR spectrum



Question		Answer	Mark	Guidance
6	(a) (i)	<p style="text-align: right;">✓</p>	1	<p>Circles can be around C <b>OR</b> CH atoms but must <b>not</b> include other atoms</p> <p><b>ALLOW</b> any suitable way of highlighting chiral carbons, e.g. asterisk, *</p> <p><b>Note:</b> Mark the circles and ignore other working on diagram</p>
	(ii)	<p>carboxyl <b>OR</b> carboxylic acid, amine, amide, ester must be <b>names</b></p> <p>2 marks for 4 correct functional groups ✓✓ 1 mark for 3 correct functional groups ✓</p>	2	<p><b>ALLOW</b> peptide for amide</p>
	(b)	<p>1 mark for left-hand amino acid with NH<sub>3</sub><sup>+</sup> <b>OR</b> NH<sub>2</sub> ✓ 1 mark for right-hand amino acid with NH<sub>3</sub><sup>+</sup> <b>OR</b> NH<sub>2</sub> ✓ 1 mark for <b>both</b> amino acids shown with NH<sub>3</sub><sup>+</sup> ✓</p>	4	<p><b>ALLOW</b> correct structural <b>OR</b> displayed <b>OR</b> skeletal formula <b>OR</b> mixture of the above (as long as unambiguous)</p> <p><b>ALLOW</b> + charge on H of NH<sub>3</sub> groups, ie NH<sub>3</sub><sup>+</sup></p> <p><b>Note:</b> If there are more than three structures shown, credit any correct structures and ignore incorrect structures</p>

Question		Answer	Mark	Guidance
6	(c)	(adverse) side effects OR toxicity OR irritation ✓	1	<p><b>ALLOW</b> a stated adverse side effect, eg allergy, carcinogenic, hyperactivity etc</p> <p><b>IGNORE</b> references to optical isomers, chirality, etc</p> <p><b>IGNORE</b> vague statements such as harmful to body, dangerous to body</p> <p><b>DO NOT ALLOW</b> obesity, corrosive to body</p> <p><b>ALLOW</b> company liable to litigation/damages</p> <p><b>Note:</b> Scroll down to bottom of page to check for any further writing</p>
			<b>Total</b>	<b>8</b>

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