

**GCE**

**Chemistry**

Advanced GCE **2814/01**

Chains, Rings and Spectroscopy

**Mark Scheme for June 2010**

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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.

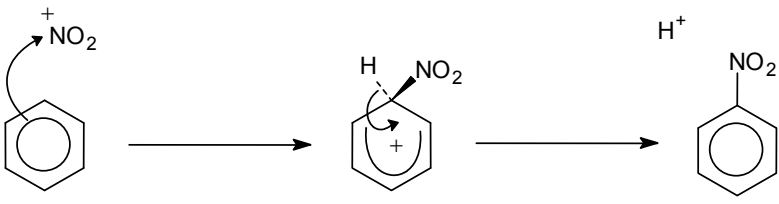
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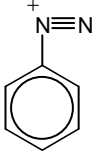
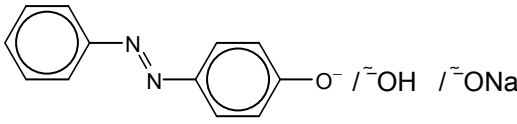
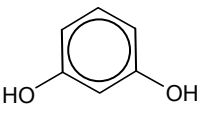
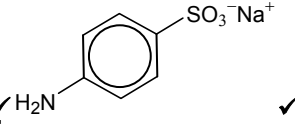
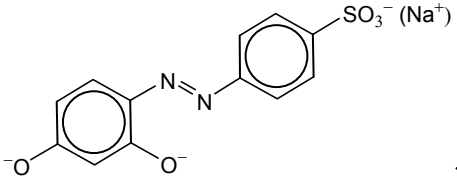
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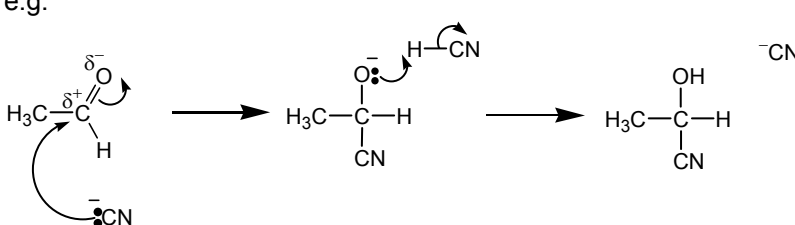
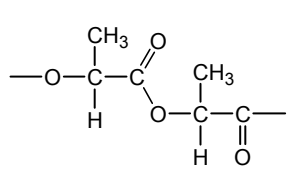
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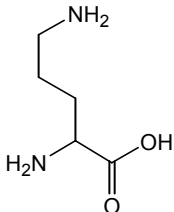
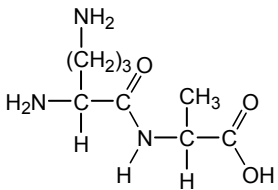
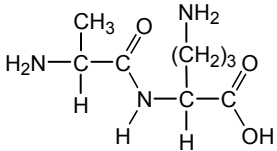
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Qu.	Expected Answers	Marks
1 (a) (i)	$\text{HNO}_3 + \text{H}_2\text{SO}_4$ ✓ (both acids) conc ✓ 50–60°C ✓	3
(ii)	$\text{NO}_2$ ✓	1
(iii)	$\text{H}_2\text{SO}_4 + \text{HNO}_3 \longrightarrow \text{NO}_2^+ + \text{H}_2\text{O} + \text{HSO}_4^-$ / $2\text{H}_2\text{SO}_4 + \text{HNO}_3 \longrightarrow \text{NO}_2^+ + \text{H}_3\text{O}^+ + 2\text{HSO}_4^-$ ✓	1
(iv)	 <p>             curly arrow from <math>\pi</math> bond to electrophile ✓              intermediate ✓              curly arrow from C–H bond to <math>\pi</math> bond ✓              correct products ✓           </p>	4
(v)	moles benzene = $3.9/78 = 0.050$ ✓  actual moles of nitrobenzene formed = $4.9/123 = 0.040$ / 0.0398 <b>or</b> theoretical mass nitrobenzene = $0.050 \times 123 = 6.15$ (g) ✓  $\% \text{ yield} = \frac{\text{actual}}{\text{theoretical}} \text{ mass/moles} = 79.67\% = 80\%$ ✓	80% without working only scores 1 mark   3
(b) (i)	$\text{AlBr}_3$ / Fe / $\text{FeBr}_3$ ✓	ALLOW $\text{AlCl}_3$ 1
(ii)	bromine decolourised ✓ white/cream solid/ppt. ✓ 2,4,6-tribromophenol identified by name/structure ✓  lone pair from O (of O–H ) is delocalised into the ring (or orbital diagram to show) ✓ increases the ( $\pi$ ) electron density(around the ring) ✓ Br–Br more polarised / more attracted ✓	ora for benzene 6
QWC	for correct use of <b>one</b> of the terms <b>electrophile</b> / <b>electrophilic</b> / <b>activation</b>	1
[Total: 20 ]		

Qu.	Expected Answers	Marks
2 (a)	<p><b>step 1</b>  <math>\text{HNO}_2 + \text{HCl} / \text{NaNO}_2 + \text{HCl} \checkmark</math>  below <math>10^\circ\text{C} \checkmark</math></p> <p><b>step 2</b>  add to phenol in alkaline conditions / <math>\text{NaOH}</math> (below <math>10^\circ\text{C}</math>) <math>\checkmark</math></p> <div style="display: flex; align-items: center;"> <div style="text-align: center;">  <p><math>\checkmark</math></p> </div> <div style="text-align: center; margin: 0 20px;">  <p><math>\checkmark</math></p> </div> <div style="margin-left: 20px;"> <p><b>ALLOW</b> <math>\text{C}_6\text{H}_5</math> not displayed</p> <p><b>ALLOW</b> any substitution position in the dye</p> </div> </div>	5
(b) (i)	$\text{N}=\ddot{\text{N}}$ circled $\checkmark$	1
(ii)	12 carbons $\checkmark$ 9 hydrogens $\checkmark$	2
(iii)	<div style="display: flex; align-items: center;"> <div style="text-align: center;">  <p><math>\checkmark</math></p> </div> <div style="text-align: center; margin: 0 20px;">  <p><math>\checkmark</math></p> </div> </div> <p><b>DO NOT ALLOW</b> connection errors here</p> <p><b>ALLOW</b> <math>-\text{SO}_3\text{H}</math></p>	2
(c)	<div style="text-align: center;">  <p><math>\checkmark</math></p> </div> <p><b>ALLOW</b> just one <math>\ddot{\text{O}}</math></p>	1
<b>[Total: 11]</b>		

Qu.	Expected Answers	Marks
3 (a) (i)	<p><b>mechanism</b></p> <p>arrow from <b>C</b> of CN<sup>-</sup> to C ✓</p> <p>dipole and curly arrow breaking π-bond on C=O ✓</p> <p>structure of the intermediate ✓</p> <p>curly arrow to H of HCN / H<sub>2</sub>O / H<sup>+</sup> ✓</p> <p>e.g.</p>  <p><b>ALLOW</b> NaOH / HCN</p> <p><b>reagents:</b> HCN + KCN / H<sub>2</sub>SO<sub>4</sub> + KCN ✓</p>	5
(ii)	<p><b>type of reaction:</b> hydrolysis ✓</p> <p><b>equation:</b> – e.g.</p> $\text{CH}_3\text{CH}(\text{OH})\text{CN} + 2\text{H}_2\text{O} \longrightarrow \text{CH}_3\text{CH}(\text{OH})\text{COOH} + \text{NH}_3 \quad /$ $\text{CH}_3\text{CH}(\text{OH})\text{CN} + 2\text{H}_2\text{O} + \text{H} \longrightarrow \text{CH}_3\text{CH}(\text{OH})\text{COOH} + \text{NH}_4^+$ <p>H<sub>2</sub>O / NH<sub>3</sub> ✓ rest of the equation and balancing ✓</p>	3
(b)	<p>lactic acid has a chiral centre / optical isomers ✓</p> <p>laboratory sample has both optical isomers / stereoisomers</p> <p>fermentation would contain only one optical isomer <b>AW</b> ✓</p> <p><b>DO NOT ALLOW</b> just 'isomers'</p>	2
(c) (i)	 <p>ester link ✓ rest of structure also correct ✓</p>	2
(ii)	<p><b>renewable</b> = made from plants that can be grown <b>AW</b></p> <p><b>biodegradable</b> = broken down by bacteria etc <b>AW</b></p> <p><b>reason linked to biodegradability</b></p> <p>e.g. less landfill / less harm to animals / broken down by hydrolysis / no need to burn so no harmful gases etc <b>AW ora</b></p> <p><b>reason linked to renewability</b></p> <p>e.g. does not increase atmospheric CO<sub>2</sub> <b>AW ora</b></p> <p><b>ANY two for ✓✓</b></p>	2
(d)	<p><b>2CH<sub>3</sub>CH(OH)COOH</b> <math>\longrightarrow</math> <b>C<sub>6</sub>H<sub>8</sub>O<sub>4</sub> + 2H<sub>2</sub>O</b></p> <p>H<sub>2</sub>O as product / 2x lactic acid as reactants ✓</p> <p>rest of the equation correct and balanced ✓</p> <p><b>ALLOW</b> any combination of molecular or structural formulae</p>	2
<b>[Total: 16 ]</b>		

Qu.	Expected Answers	Marks
4 (a) (i)	$\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ / ringed on structure ✓ <b>IGNORE</b> 'propylamine' but 'con' if named as an amide	1
(ii)	 <p>two <math>-\text{NH}_2</math> and skeletal <math>-\text{COOH}</math> ✓  rest of the molecule correct ✓  <b>ALLOW</b> ecf from non-skeletal <math>\text{COOH}</math></p>	2
(b) (i)	$^+\text{H}_3\text{NCH}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3^+)\text{COOH}$ one $\text{NH}_2$ protonated ✓ both $\text{NH}_2$ protonated ✓ <b>IGNORE</b> $\text{Cl}^-$ <b>ALLOW</b> $-\text{NH}_3\text{Cl}$	2
(ii)	$\text{H}_2\text{NCH}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)\text{COO}^-$ ✓ <b>IGNORE</b> $\text{Na}^+$ <b>ALLOW</b> $\text{COONa}$ <b>ALLOW</b> ecf from (i) on minor structural errors	1
(c)	$\text{PCl}_5 \longrightarrow \text{POCl}_3 + \text{HCl}$ / $\text{SOCl}_2 \longrightarrow \text{SO}_2 + \text{HCl}$ ✓ ✓ ✓ ✓ ✓ ✓ (allow $\text{PCl}_3 \longrightarrow \text{H}_3\text{PO}_3$ for the first two marks)	3
(d)	<p>one peptide linkage correct ✓  <b>ALLOW</b> <math>\text{CONH}</math> not displayed</p> <div style="display: flex; justify-content: space-around; align-items: flex-start;"> <div style="text-align: center;">  </div> <div style="text-align: center;">  </div> </div> <p>max one mark if <math>\text{COONH}</math> linkage  <b>ALLOW</b> ornithine linked by either <math>\text{NH}_2</math> group  <b>ALLOW</b> <math>\text{C}_3\text{H}_6\text{NH}_2</math> for the side chain</p> <p>one correct dipeptide ✓  second dipeptide with R groups swapped ✓  <b>ALLOW</b> ecf for last mark for idea of swapping side chains as long as a peptide is attempted</p>	3
<b>[Total: 12]</b>		

Qu.	Expected Answers	Marks
5 (a)	hex-3-en ..... al ✓ ✓ <b>ALLOW</b> 'ene' <b>ALLOW</b> '-1-al'	2
(b)	<div style="text-align: center;"><div style="border: 1px solid black; padding: 10px; margin: 10px auto; width: 200px;"><math display="block">\begin{array}{c} \text{Br} \quad \text{Br} \\   \quad   \\ \text{CH}_3\text{CH}_2-\text{C}-\text{C}-\text{CH}_2\text{CHO} \\   \quad   \\ \text{H} \quad \text{H} \end{array}</math></div><div style="display: flex; justify-content: space-around; align-items: center; margin: 10px 0;"><div style="text-align: center;"><math>\xleftarrow[\text{LiAlH}_4 + \text{ether}]{\text{NaBH}_4}</math></div><div style="text-align: center;"><math>\xrightarrow[\text{H}^+ / \text{Cr}_2\text{O}_7^{2-}]{\text{Br}_2}</math></div></div><div style="border: 1px solid black; padding: 10px; margin: 10px auto; width: 200px;"><math display="block">\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{COOH}</math></div><div style="text-align: center; margin: 10px 0;"><math>\downarrow</math> polymerisation</div><div style="border: 1px solid black; padding: 10px; margin: 10px auto; width: 300px;"><math display="block">\begin{array}{cccc} \text{CH}_3 &amp; \text{CHO} &amp; \text{CH}_3 &amp; \text{CHO} \\   &amp;   &amp;   &amp;   \\ \text{CH}_2 &amp; \text{CH}_2 &amp; \text{CH}_2 &amp; \text{CH}_2 \\   &amp;   &amp;   &amp;   \\ -\text{C} &amp; -\text{C} &amp; -\text{C} &amp; -\text{C}- \\   &amp;   &amp;   &amp;   \\ \text{H} &amp; \text{H} &amp; \text{H} &amp; \text{H} \end{array}</math></div></div> <p>addition polymer attempted with two repeats ✓ correct side chains ✓</p>	5
(c)	<div style="display: flex; justify-content: space-around; align-items: flex-start;"><div style="text-align: center;"><math display="block">\begin{array}{c} \text{CH}_3\text{CH}_2 \quad \text{CH}_2\text{CHO} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H} \quad \text{H} \end{array}</math><p>cis ✓</p></div><div style="text-align: center;"><math display="block">\begin{array}{c} \text{CH}_3\text{CH}_2 \quad \text{H} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H} \quad \text{CH}_2\text{CHO} \end{array}</math><p>trans ✓</p></div></div> <p><b>ALLOW</b> one mark for two correct structures with incorrect labels</p> <p><b>ALLOW</b> ecf on minor side chain errors</p>	2
<b>[Total: 9]</b>		

Qu.	Expected Answers	Marks																
6 (a)	<p><b>To confirm aldehyde or ketone</b></p> <p>2,4-dinitrophenylhydrazine / Brady's reagent ✓ red / orange / yellow ... solid / ppt / crystals ✓</p> <p><b>To distinguish between aldehyde or ketone</b></p> <p>warm with ✓ ammoniacal silver nitrate / Tollens' reagent ✓ → silver (mirror) ✓ / acidified Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> ; → green</p> <p><b>DO NOT ALLOW</b> recrystallise etc for the 2nd mark</p> <p><b>ALLOW</b> any other suitable tests e.g. Fehlings, MnO<sub>4</sub></p>	5																
(b) (i)	M written next to the peak at m/e = 106 ✓	1																
(ii)	C <sub>7</sub> H <sub>6</sub> O / C <sub>6</sub> H <sub>5</sub> CHO                      C = 7 ✓ H = 6 and O ✓	2																
(c)	<table border="1"><tr><td><math display="block">\begin{array}{ccccccc} &amp; \text{H} &amp; \text{H} &amp; \text{H} &amp; \text{H} &amp; &amp; \\ &amp;   &amp;   &amp;   &amp;   &amp; &amp; \\ \text{H} &amp; - \text{C} &amp; - \text{C} &amp; - \text{C} &amp; - \text{C} &amp; - \text{CHO} \\ &amp;   &amp;   &amp;   &amp;   &amp; &amp; \\ &amp; \text{H} &amp; \text{H} &amp; \text{H} &amp; \text{H} &amp; &amp; \end{array}</math> ✓</td><td><math display="block">\begin{array}{ccccccc} &amp; \text{H} &amp; \text{H} &amp; \text{H} &amp; &amp; &amp; \\ &amp;   &amp;   &amp;   &amp; &amp; &amp; \\ \text{H} &amp; - \text{C} &amp; - \text{C} &amp; - \text{C} &amp; - \text{CHO} \\ &amp;   &amp;   &amp;   &amp; &amp; &amp; \\ &amp; \text{H} &amp; \text{CH}_3 &amp; \text{H} &amp; &amp; &amp; \end{array}</math> ✓</td></tr><tr><td><math display="block">\begin{array}{ccccccc} &amp; \text{H} &amp; \text{H} &amp; \text{H} &amp; &amp; &amp; \\ &amp;   &amp;   &amp;   &amp; &amp; &amp; \\ \text{H} &amp; - \text{C} &amp; - \text{C} &amp; - \text{C} &amp; - \text{CHO} \\ &amp;   &amp;   &amp;   &amp; &amp; &amp; \\ &amp; \text{H} &amp; \text{H} &amp; \text{CH}_3 &amp; &amp; &amp; \end{array}</math> ✓</td><td><math display="block">\begin{array}{ccccccc} &amp; \text{H} &amp; &amp; \text{CH}_3 &amp; &amp; &amp; \\ &amp;   &amp; &amp;   &amp; &amp; &amp; \\ \text{H} &amp; - \text{C} &amp; - &amp; \text{C} &amp; - \text{CHO} \\ &amp;   &amp; &amp;   &amp; &amp; &amp; \\ &amp; \text{H} &amp; &amp; \text{CH}_3 &amp; &amp; &amp; \end{array}</math> ✓</td></tr></table>	$\begin{array}{ccccccc} & \text{H} & \text{H} & \text{H} & \text{H} & & \\ &   &   &   &   & & \\ \text{H} & - \text{C} & - \text{C} & - \text{C} & - \text{C} & - \text{CHO} \\ &   &   &   &   & & \\ & \text{H} & \text{H} & \text{H} & \text{H} & & \end{array}$ ✓	$\begin{array}{ccccccc} & \text{H} & \text{H} & \text{H} & & & \\ &   &   &   & & & \\ \text{H} & - \text{C} & - \text{C} & - \text{C} & - \text{CHO} \\ &   &   &   & & & \\ & \text{H} & \text{CH}_3 & \text{H} & & & \end{array}$ ✓	$\begin{array}{ccccccc} & \text{H} & \text{H} & \text{H} & & & \\ &   &   &   & & & \\ \text{H} & - \text{C} & - \text{C} & - \text{C} & - \text{CHO} \\ &   &   &   & & & \\ & \text{H} & \text{H} & \text{CH}_3 & & & \end{array}$ ✓	$\begin{array}{ccccccc} & \text{H} & & \text{CH}_3 & & & \\ &   & &   & & & \\ \text{H} & - \text{C} & - & \text{C} & - \text{CHO} \\ &   & &   & & & \\ & \text{H} & & \text{CH}_3 & & & \end{array}$ ✓	4												
$\begin{array}{ccccccc} & \text{H} & \text{H} & \text{H} & \text{H} & & \\ &   &   &   &   & & \\ \text{H} & - \text{C} & - \text{C} & - \text{C} & - \text{C} & - \text{CHO} \\ &   &   &   &   & & \\ & \text{H} & \text{H} & \text{H} & \text{H} & & \end{array}$ ✓	$\begin{array}{ccccccc} & \text{H} & \text{H} & \text{H} & & & \\ &   &   &   & & & \\ \text{H} & - \text{C} & - \text{C} & - \text{C} & - \text{CHO} \\ &   &   &   & & & \\ & \text{H} & \text{CH}_3 & \text{H} & & & \end{array}$ ✓																	
$\begin{array}{ccccccc} & \text{H} & \text{H} & \text{H} & & & \\ &   &   &   & & & \\ \text{H} & - \text{C} & - \text{C} & - \text{C} & - \text{CHO} \\ &   &   &   & & & \\ & \text{H} & \text{H} & \text{CH}_3 & & & \end{array}$ ✓	$\begin{array}{ccccccc} & \text{H} & & \text{CH}_3 & & & \\ &   & &   & & & \\ \text{H} & - \text{C} & - & \text{C} & - \text{CHO} \\ &   & &   & & & \\ & \text{H} & & \text{CH}_3 & & & \end{array}$ ✓																	
(d)	<table border="1"><thead><tr><th></th><th>D</th><th>E</th><th>F</th></tr></thead><tbody><tr><td><b>No of peaks and areas</b></td><td>3 peaks ratio 3:1:6 ✓</td><td>4 peaks ratio: 3:2:2:3 ✓</td><td>2 peaks ratio: 2:3 / 4:6 ✓</td></tr><tr><td><b>chemical shifts (ppm)</b></td><td>2.0–2.9 (×2) 0.7–1.6 ✓</td><td>2.0–2.9 (×2) 0.7–1.6 1.2–1.4 ✓</td><td>2.0–2.9 0.7–1.6 ✓</td></tr><tr><td><b>splitting AW to describe</b></td><td>singlet doublet / 1:1 ✓ (multiplet)</td><td>singlet 2 x triplet / 1:2:1 ✓ (multiplet)</td><td>triplet / 1:2:1 quartet 1:3:3:1 ✓</td></tr></tbody></table> <p>on D and E, <b>IGNORE</b> any splitting given for the multiplet</p>		D	E	F	<b>No of peaks and areas</b>	3 peaks ratio 3:1:6 ✓	4 peaks ratio: 3:2:2:3 ✓	2 peaks ratio: 2:3 / 4:6 ✓	<b>chemical shifts (ppm)</b>	2.0–2.9 (×2) 0.7–1.6 ✓	2.0–2.9 (×2) 0.7–1.6 1.2–1.4 ✓	2.0–2.9 0.7–1.6 ✓	<b>splitting AW to describe</b>	singlet doublet / 1:1 ✓ (multiplet)	singlet 2 x triplet / 1:2:1 ✓ (multiplet)	triplet / 1:2:1 quartet 1:3:3:1 ✓	9
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<b>QWC</b>	For at least <b>two</b> relevant sentences in which the meaning is clear with correct spelling, punctuation and grammar ( <b>ALLOW</b> bullet points and note form where appropriate).	1																

Total: 22



**OCR (Oxford Cambridge and RSA Examinations)**  
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