



GCE

Chemistry A

Advanced GCE F324

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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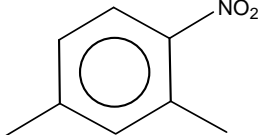
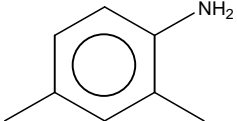
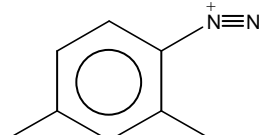
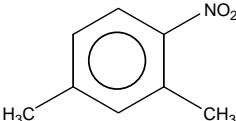
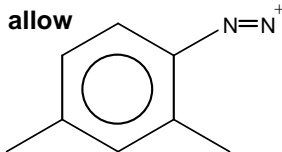
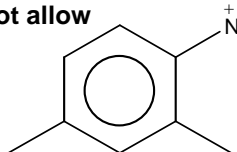
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F324

Mark Scheme

June 2010

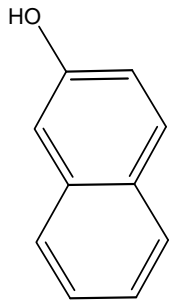
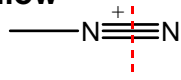
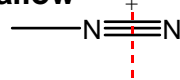
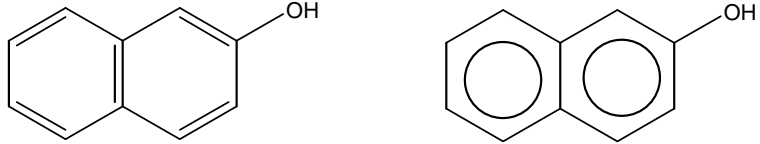
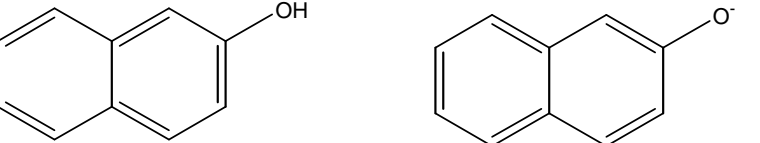
Allow Kekulé structures throughout

Question		Expected Answers	Marks	Additional Guidance
1	a	<p>Bond length intermediate between/different from (short) C=C and (long) C–C ✓</p> <p>ΔH hydrogenation less exothermic than expected (when compared to ΔH hydrogenation for cyclohexene) ✓</p> <p>Only reacts with Br₂ at high temp or in presence of a halogen carrier / resistant to electrophilic attack ✓</p> <p>Please annotate, use ticks to show where marks are awarded</p>	3	<p>ALLOW all carbon–carbon bonds the same length</p> <p>ALLOW ΔH hydrogenation less (negative) than expected</p> <p>ALLOW ΔH hydrogenation different from that expected</p> <p>DO NOT ALLOW ΔH halogenation/hydration</p> <p>ALLOW doesn't decolourise/react with/polarise Br₂</p> <p>ALLOW doesn't undergo addition reactions (with Br₂)</p>
	b	<p>i</p> <p>compound A</p>  <div style="border: 1px solid black; padding: 5px; display: inline-block; margin-left: 20px;"> <p>if NO₂ in wrong position penalise here and ECF for rest of b(i) and b(ii)</p> </div> <p style="text-align: right;">✓</p> <p>compound B</p>  <p style="text-align: right;">✓</p> <p>compound C</p>  <p style="text-align: right;">✓</p>	4	<p>ALLOW any 4-nitro-1,3-dimethylbenzene drawn in any orientation</p> <p>ALLOW</p>  <p>H₃C drawn in any orientation</p> <p>ALLOW any 4-amino-1,3-dimethylbenzene drawn in any orientation</p> <p>ECF amine of incorrect compound A (e.g. position of NO₂ or lack of methyl sticks/groups)</p> <p>ALLOW diazonium chloride salt of 1,3-dimethylbenzene</p> <p>ECF diazonium salt/compound of incorrect compound B</p> <p>IGNORE Cl[−] ion</p> <p>allow</p>  <p>not allow</p> 

F324

Mark Scheme

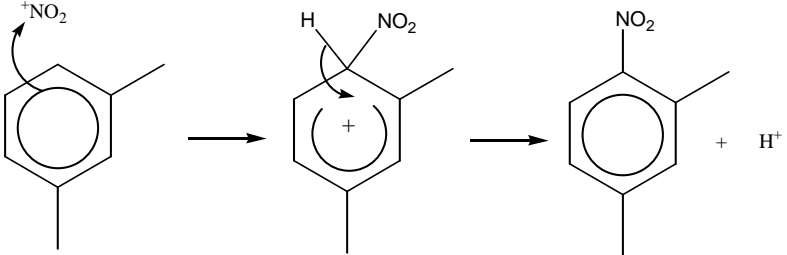
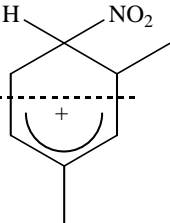
June 2010

Question	Expected Answers	Marks	Additional Guidance
	<p>compound D</p> 	✓	<p>ALLOW if + charge is floating between the two Ns only if it is closer to the correct N</p> <p>allow </p> <p>not allow </p> <p>ALLOW any of</p>   <p>ALLOW O⁻ in place of OH</p>

F324

Mark Scheme

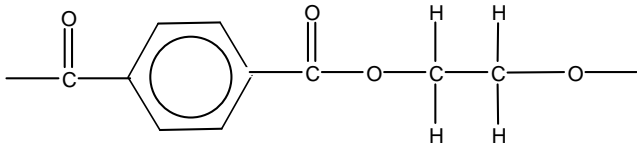
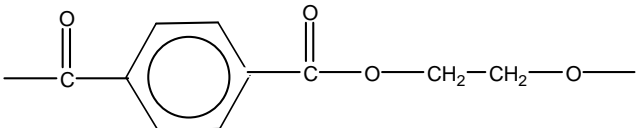
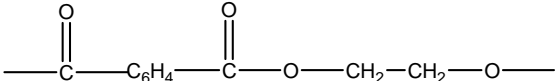
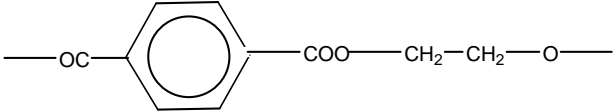
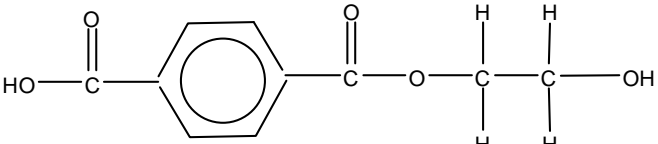
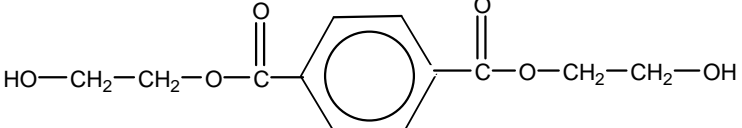
June 2010

Question	Expected Answers	Marks	Additional Guidance
<p data-bbox="69 360 309 627" style="border: 1px solid black; padding: 5px;">If NO₂ is in correct position do not penalise even if compound A in b(i) is not in correct position</p> <p data-bbox="277 209 304 233" style="text-align: center;">ii</p>	<p data-bbox="331 240 1099 272">mark 1 $\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{H}_3\text{O}^+ + 2\text{HSO}_4^- + \text{NO}_2^+ \checkmark$</p> <div data-bbox="338 336 1122 671" style="text-align: center;"> <p data-bbox="555 336 1059 400">mark 4 – curly arrow from C–H bond back to reform π ring AND correct products \checkmark</p>  </div> <p data-bbox="331 687 533 783">mark 2 – curly arrow from π ring to $^+\text{NO}_2 \checkmark$</p> <p data-bbox="591 687 824 807">mark 3 – intermediate with π ring broken in the correct place \checkmark</p> <div data-bbox="846 699 1155 938" style="border: 1px solid black; padding: 5px; margin-left: auto; margin-right: auto;"> <p data-bbox="860 711 1128 911">Link to compound A in part (i) – cannot score full marks [in b(i) & b(ii)] if NO₂ is not adjacent to a methyl</p> </div> <p data-bbox="331 847 808 879">mark 5 - $\text{H}^+ + \text{HSO}_4^- \rightarrow \text{H}_2\text{SO}_4 \checkmark$</p>	5	<p data-bbox="1330 204 2033 312">Equation to show formation of NO₂⁺ ion \checkmark ALLOW $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{HSO}_4^- + \text{NO}_2^+$ $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{HSO}_4^- + \text{H}_2\text{NO}_3^+ \rightarrow \text{H}_2\text{O} + \text{NO}_2^+$</p> <p data-bbox="1330 344 2022 408">ALLOW mark 2 curly arrow must be from 1,3-dimethylbenzene to NO₂⁺ and ECF for marks 3 and 4</p> <p data-bbox="1330 448 1738 480">DO NOT ALLOW intermediate</p> <div data-bbox="1330 520 1659 743" style="text-align: center;">  <p data-bbox="1330 568 1480 671">π-ring must be more than $\frac{1}{2}$ way up</p> </div> <p data-bbox="1330 791 1608 823">ALLOW CH₃s shown</p> <p data-bbox="1330 927 1899 959">ALLOW $\text{H}_3\text{O}^+ + \text{HSO}_4^- \rightarrow \text{H}_2\text{O} + \text{H}_2\text{SO}_4$</p>
<p data-bbox="277 999 304 1023" style="text-align: center;">iii</p>	<p data-bbox="331 999 383 1023">2 \checkmark</p>	1	<p data-bbox="1330 999 1671 1031">No other correct response</p>
Total		13	

F324

Mark Scheme

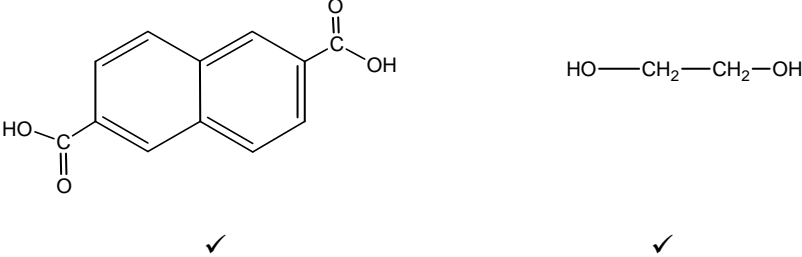
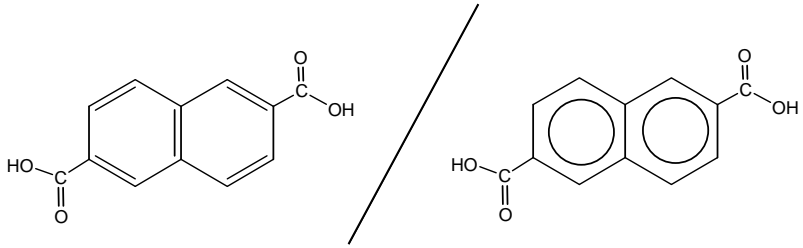
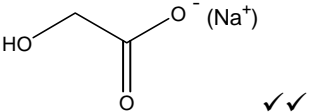
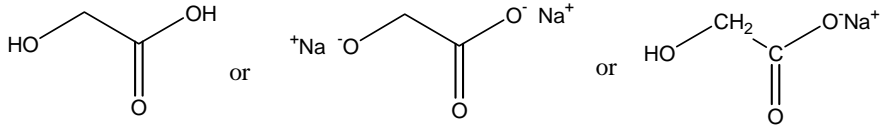
June 2010

Question	Expected Answers	Marks	Additional Guidance
2 a i	 <p>✓✓ Ester group must be displayed to get both marks and must contain 4 Os</p>	2	<p>ALLOW for both marks</p>  <p>ALLOW for one mark</p>  <p>ALLOW for one mark</p>  <p>ALLOW Kekulé structure / (CH₂)₂ ALLOW one mark if end bonds missing ALLOW 1 mark if the CH₂CH₂ is drawn skeletally ALLOW for</p>  <p>ALLOW <u>1 mark</u> if repeat unit shows a displayed ester group and contains a benzene ring and two other carbons</p> <p>DO NOT ALLOW -OCC₆H₄COOCH₂CH₂O-</p>
	 <p>✓</p>	1	<p>ALLOW Kekulé structure/ (CH₂)₂ CO₂ for ester groups C₆H₄ if already penalised in a(i)</p>

F324

Mark Scheme

June 2010

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	b i	$C_7H_5O_2$	1	ALLOW any order of elements ALLOW $C_{14}H_{10}O_4 \rightarrow C_7H_5O_2$ or $C_{14}H_{10}O_4 = C_7H_5O_2$
	ii	 <p>Penalise incorrect bond linkage in 2b(ii) only. Do not penalise elsewhere on the paper</p>	2	ALLOW COOH/CO ₂ H ALLOW  ALLOW HO(CH ₂) ₂ OH
	c i		2	ALLOW any of the following for 1 mark  DO NOT ALLOW any other response
	ii	(PGA is) <u>(bio)degradable</u> OR <u>photodegradable</u> OR <u>hydrolysed</u> (but hydrocarbon based polymers are non-biodegradable) ✓ One of (bio)degradable OR photodegradable OR hydrolysed must be spelt correctly – if one spelt correctly and another incorrectly spelt – ALLOW mark	1	ALLOW broken down by <u>bacteria</u> (must be spelt correctly) ALLOW degrade as alternative to degradable ALLOW undergoes hydrolysis as alternative to hydrolysed IGNORE any additional information if the additional information is correct e.g. biodegradable and doesn't produce toxic gases DO NOT ALLOW any additional information if the additional information is incorrect e.g. biodegradable and can be recycled
Total			9	

F324

Mark Scheme

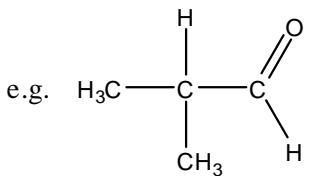
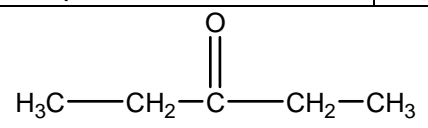
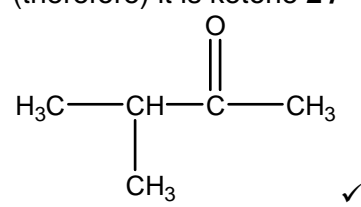
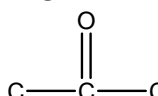
June 2010

Question		Expected Answers		Marks	Additional Guidance
3	a	Alternative approaches		4	<p>ALLOW ammoniacal AgNO_3 / $\text{Ag}^+(\text{NH}_3)_2$ / $\text{Ag}^+(\text{NH}_3)$</p> <p>ALLOW acidified dichromate OR Fehlings as an alternative to Tollens – observation ‘turn green’ OR ‘red precipitate’ respectively</p> <p>ALLOW acidified manganate(VII) and observation as either brown precipitate/decolourised/pale pink</p> <p>ALLOW Brady’s (reagent)</p> <p>ALLOW orange/red/yellow for colour of the 2,4-DNP(H) precipitate</p> <p>ALLOW solid/crystals in place of precipitate</p> <p>IGNORE any reference to melting points</p> <p>ALLOW PCl_5 as a test for the acid – observation would be ‘white fumes (of HCl)’</p> <p>ALLOW detection of (carboxylic) acid by reacting with an alcohol to make an ester but no mark for the observation.</p> <p>DO NOT ALLOW detection of (carboxylic) acid by pH or indicator</p> <p>Please annotate, use ticks to show where marks are awarded</p>
		<p>Tollens’ test AND ‘silver precipitate/mirror’ ✓ is the aldehyde ✓</p> <p>react with 2,4-DNP(H) and ‘orange precipitate’ ✓</p> <p>must be the ketone ✓</p>	<p>Tollens’ test AND ‘silver precipitate/mirror’ ✓ is the aldehyde ✓</p> <p>react with carbonate/hydrogencarbonate/Na/Mg and ‘fizzes/bubbles/ effervesces/ gas evolved’ ✓</p> <p>must be the (carboxylic) acid ✓</p>		
	b	<p>2,4-DNP(H) AND orange precipitate ✓ is either aldehyde OR ketone ALLOW carbonyl OR $\text{C}=\text{O}$ ✓</p> <p>Tollens’ test & ‘silver ppt/mirror’ ✓ is the aldehyde ✓</p>	<p>2,4-DNP(H) and no orange precipitate ✓ is the (carboxylic) acid ✓</p> <p>Tollens’ test & ‘silver ppt/mirror’ ✓ is the aldehyde ✓</p>	1	<p>DO NOT ALLOW single peak quoted within range 2500–3300 other than 3000 (cm^{-1}) for OH</p> <p>DO NOT ALLOW range 3200–3550 (cm^{-1})</p> <p>IGNORE any reference to C-O or C=O</p>

F324

Mark Scheme

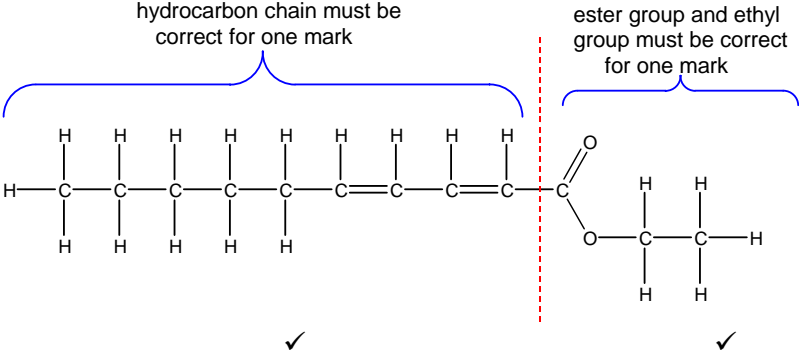
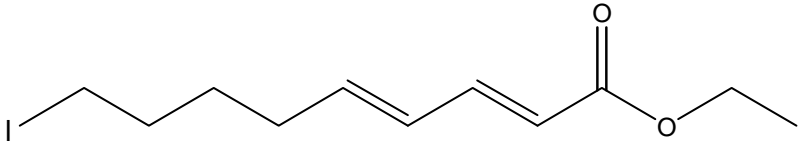
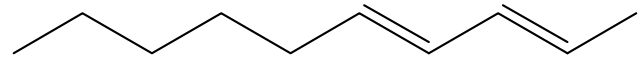
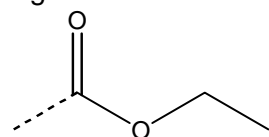
June 2010

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c		<p>Alternative approaches depending on whether or not the aldehyde is correct</p> <p>Doublet indicates adjacent C is bonded to only 1H OR (relative) peak area indicates 2 x CH₃ (in the same environment) ✓</p> <p>If aldehyde is correct (CH₃)₂CH—CH₂—CHO ✓✓</p> <p><i>If aldehyde is correct only need to explain doublet OR peak areas</i></p>		<p>ALLOW 3-methylbutanal , any correct unambiguous structure ALLOW two marks for correct aldehyde with no explanation</p> <p>ALLOW doublet/peak at 0.9ppm due to R—CH ALLOW the splitting shows adjacent to CH/environment that contains 1 H/proton</p> <p>ALLOW 6 Hs/ protons in same environment DO NOT ALLOW 6 Hs in same environment next to CHO</p>
		<p>Doublet indicates adjacent C is bonded to only 1H ✓ AND (relative) peak area indicates 2 x CH₃ (in the same environment) ✓</p> <p>If aldehyde identified is incorrect ✗</p> <p><i>if aldehyde is incorrect must explain both doublet or peak areas</i></p>		<p>e.g. </p> <p>would score two marks if the doublet and the peak areas were correctly explained</p>
d	i	<p> ✓</p> <p>ketone 3</p>	1	ALLOW displayed/skeletal formulae
	ii	<p>There are 4 (different C) environments ✓ (therefore) it is ketone 2 /</p> <p> ✓</p> <p>(C responsible for peak at δ = 210 ppm) is C=O/carbonyl carbon ✓</p>	3	<p>ALLOW 2 Cs are in same environment/equivalent</p> <p>ALLOW 3-methylbutan(-2-)one/ any correct unambiguous structure</p> <p>ALLOW 2-methylbutan-3-one</p> <p>ALLOW</p> <p></p>
Total			12	

F324

Mark Scheme

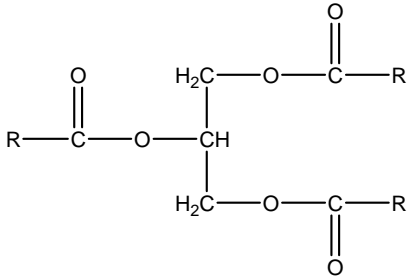
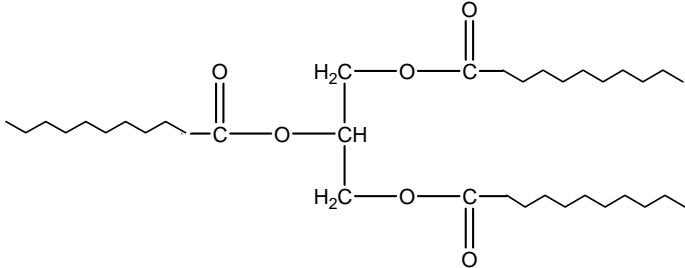
June 2010

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4	a	i	1	<p>ALLOW time from injection to detection</p> <p>ALLOW time spent in column</p> <p>ALLOW time taken to reach detector</p>
		ii	1	<p>ALLOW both are esters therefore partition/adsorption/retention times will be very similar</p> <p>ALLOW ECF if they describe R_f values in part a(i)</p> <p>ALLOW same retention times</p>
		iii	1	<p>ALLOW butyl butanoate</p> <p>ALLOW but-1-yl butanoate</p> <p>DO NOT ALLOW butanyl butanoate</p>
	b	i	2	<p>ALLOW any correct unambiguous structure/ $\text{CH}_3(\text{CH}_2)_4\text{CHCHCHCHCOOCH}_2\text{CH}_3$ / $\text{CH}_3(\text{CH}_2)_4\text{CHCHCHCHCOOC}_2\text{H}_5$ $\text{CH}_3(\text{CH}_2)_4(\text{CH})_4\text{COOCH}_2\text{CH}_3$ DO NOT ALLOW $\text{C}_5\text{H}_{11}\text{CHCHCHCHCOOCH}_2\text{CH}_3$ etc ALLOW CO_2 for ester</p> <p>hydrocarbon chain must be correct for one mark</p> <p>ester group and ethyl group must be correct for one mark</p>  <p>ALLOW 1 mark for correct 2,4-decadiene structure e.g.</p>  <p>ALLOW 1 mark for correct ethyl ... oate structure e.g.</p>  <p>or $-\text{CO}_2\text{C}_2\text{H}_5$ or $-\text{COOC}_2\text{H}_5$</p> 

F324

Mark Scheme

June 2010

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ii		1	<p>ALLOW</p>  <p>any orientation of the three fatty acids</p>
c	<p>1. react phenylethanal with $\text{H}_2\text{SO}_4/\text{K}_2\text{Cr}_2\text{O}_7$ ✓</p> <p>2. to get phenylethanoic acid/$\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$ ✓</p> <p>mark 2 can be scored if dichromate is used without being acidified</p> <p>3. react phenylethanal with NaBH_4 ✓</p> <p>4. to get 2-phenylethanol/$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OH}$ ✓</p> <p>mark 3 must be correct to score mark 4</p> <p>5. react phenylethanoic acid with 2-phenylethanol. If both already correctly named ALLOW acid and alcohol ✓</p> <p>6. H_2SO_4 if linked to the reaction of an alcohol and acid ✓</p> <p>7. reflux in either (1) or (5) or catalyst used in (5) ✓</p> <p>QWC must spell catalyst or reflux correctly</p>	7	<p>ALLOW H^+ & $\text{Cr}_2\text{O}_7^{2-}$ or $\text{H}_2\text{SO}_4/\text{Na}_2\text{Cr}_2\text{O}_7$ - any other oxidising agent or other named acid – please consult with TL</p> <p>ALLOW LiAlH_4 as alternative to NaBH_4</p> <p>phenylethanoic acid & phenylethanol must be unambiguously identified by either name or formula</p> <p>DO NOT ALLOW or oxidised to form (a carboxylic) acid or reduced to form alcohol for marks 2 and 4</p> <p>ALLOW conc H_2SO_4 DO NOT ALLOW dilute or $\text{H}_2\text{SO}_4(\text{aq})$ DO NOT ALLOW just acid catalyst DO NOT ALLOW HCl, HNO_3</p> <p>Please annotate, use ticks to show where marks are awarded</p>
Total		13	

if either phenylethanoic acid or 2-phenylethanol not prepared – automatically lose two marks

F324

Mark Scheme

June 2010

Question		Expected Answers	Marks	Additional Guidance			
5	a i	 ✓	1	ALLOW * in place of circle ALLOW if circle extends to include OH			
	ii	<p>Mark 1 – production of a single isomer is more expensive/difficult OR separation of the single isomer is expensive/difficult ✓</p> <p>Mark 2 – one of the isomers is more (pharmacologically) active or one of the isomers might have adverse/harmful/nasty side effects ✓</p> <p>Marks 3 and 4 – problems are overcome by using:</p> <table style="border: none;"> <tr> <td style="border: none;"> Enzymes/bacteria/biological catalyst Chiral synthesis Chiral catalyst or transition metal complex Start with a natural chiral molecule or chiral pool </td> <td style="border: none; vertical-align: middle;"> } } } } </td> <td style="border: none; vertical-align: middle;"> ✓✓ any </td> </tr> </table>	Enzymes/bacteria/biological catalyst Chiral synthesis Chiral catalyst or transition metal complex Start with a natural chiral molecule or chiral pool	} } } }	✓✓ any	4	IGNORE any reference to dosage ALLOW one is more effective/works (better) DO NOT ALLOW use naturally occurring isomer unless stated that it is a chiral compound DO NOT ALLOW transition metal ion DO NOT ALLOW pool synthesis Chiral pool synthesis scores 1 (not 2) marks
Enzymes/bacteria/biological catalyst Chiral synthesis Chiral catalyst or transition metal complex Start with a natural chiral molecule or chiral pool	} } } }	✓✓ any					
	b i	 ✓	1	ALLOW ALLOW epoxy ethane as C ₂ H ₄ O, (CH ₂) ₂ O, CH ₂ OCH ₂ ALLOW product as HO(CH ₂) ₂ NH ₂ DO NOT ALLOW product as C ₂ H ₇ NO			
	ii	HO—CH ₂ —CH ₂ —NH—CH ₂ —CH ₂ —OH ✓	1	ALLOW (CH ₂) ₂ ALLOW displayed/skeletal formula DO NOT ALLOW molecular formula			

F324

Mark Scheme

June 2010

Question		Expected Answers	Marks	Additional Guidance
	c i	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}_3^+ \text{Cl}^-$ Must show Cl^- ion ✓	1	ALLOW $\text{HOCH}_2\text{CH}_2\text{NH}_3\text{Cl}$ if formula is correct and both charges not shown ALLOW $(\text{CH}_2)_2/$ any correct unambiguous structure DO NOT ALLOW ions joined by covalent bonds
	ii	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}_3^+ \text{HS}^-$ Must show HS^- ion ✓	1	ALLOW if formula is correct and both charges not shown ALLOW $(\text{CH}_2)_2/$ any correct unambiguous structure ALLOW $\left(\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}_3^+\right)_2 \text{S}^{2-}$
	d i	Both NH_2 and COOH are joined to the same C ✓	1	ALLOW $\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{N}-\text{C}-\text{CO}_2\text{H} \\ \\ \text{R} \end{array}$ or $\text{RCH}(\text{NH}_2)\text{CO}_2\text{H}$ The 4 groups/atoms attached to the C can be in any order but CH must be adjacent. () not essential
	ii	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}_2 + 2[\text{O}] \longrightarrow \text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{NH}_2 + \text{H}_2\text{O} \checkmark$	1	ALLOW $(\text{CH}_2)_2$ DO NOT ALLOW molecular formula
	e i	Question 5e is followed by two blank lined pages (15 and 16) which candidates can use instead of requesting additional paper. Please check to see whether or not pages 15 or 16 have been used		

F324

Mark Scheme

June 2010

Question		Expected Answers	Marks	Additional Guidance
e	i	<p>Isomer F</p> $\begin{array}{cccc} & \text{H} & \text{H} & \text{H} & \text{H} \\ & & & & \\ \text{HO} & -\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{NH}_2 \\ & & & & \\ & \text{H} & \text{H} & \text{H} & \text{H} \end{array}$ <p style="text-align: right;">✓</p> <p>Isomer G</p> $\begin{array}{cccc} & \text{H} & \text{OH} & \text{H} & \text{H} \\ & & & & \\ \text{H} & -\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{H} \\ & & & & \\ & \text{H} & \text{H} & \text{NH}_2 & \text{H} \end{array}$ <p style="text-align: center;">* not required</p> <p style="text-align: right;">✓</p>	2	<p>ALLOW HO(CH₂)₄NH₂/ ALLOW any correct unambiguous structure of 1-aminobutan-4-ol</p> <p>ALLOW CH₃CH(OH)CH(NH₂)CH₃ ALLOW any correct unambiguous structure of 2-aminobutan-3-ol.</p>
Total			13	

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