OCR
RECOGNISING ACHIEVEMENT

GCE

Chemistry A

Advanced GCE **F324**

Mark Scheme for June 2010

Oxford Cambridge and RSA Examinations

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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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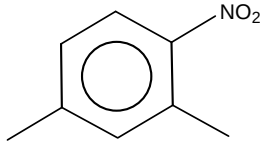
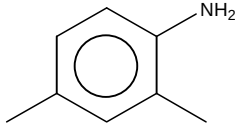
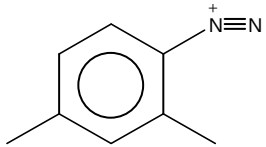
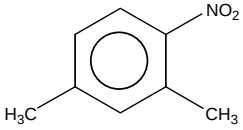
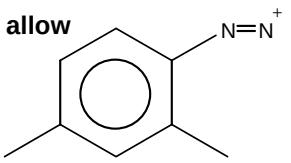
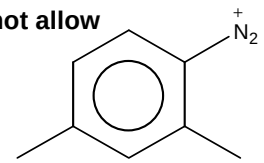
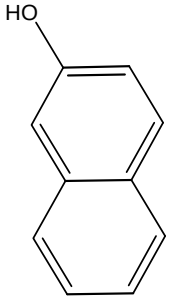
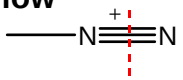
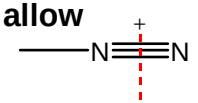
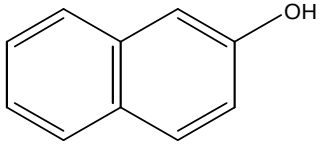
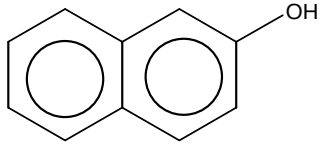
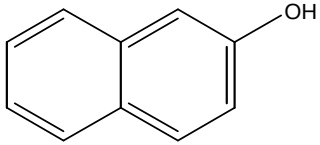
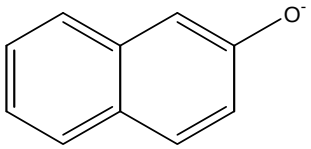
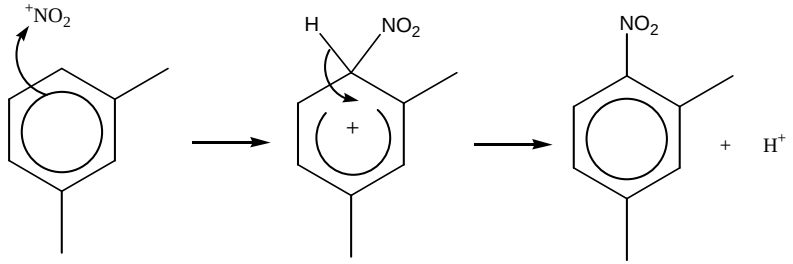
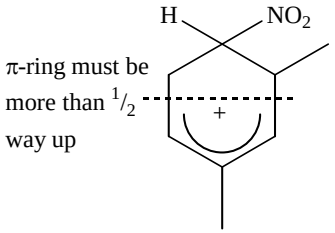
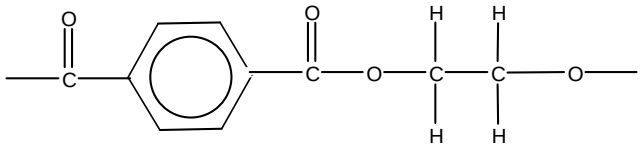
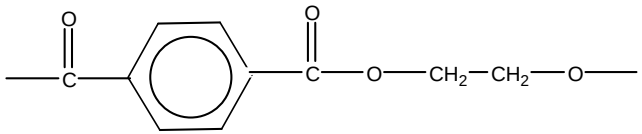
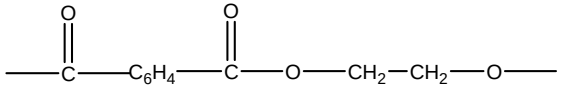
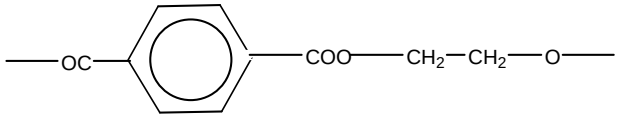
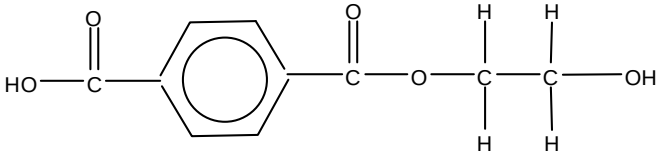
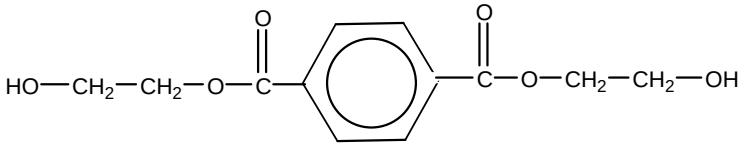
Allow Kekulé structures throughout

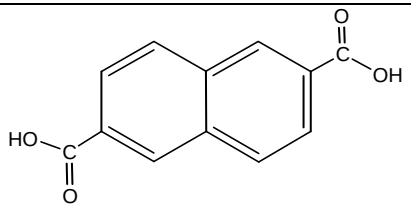
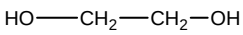
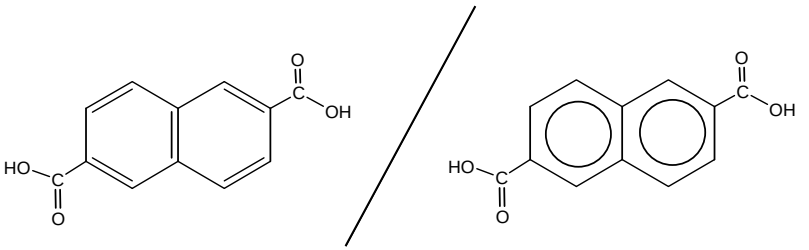
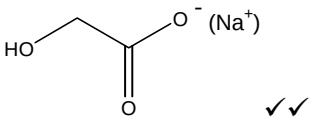
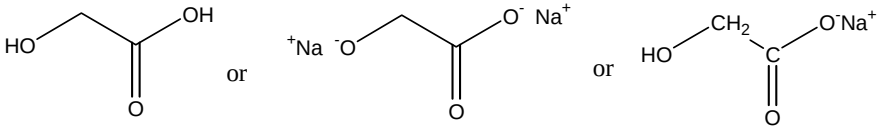
Question			Expected Answers	Marks	Additional Guidance
1	a		Bond length intermediate between/different from (short) C=C and (long) C–C ✓ ΔH hydrogenation less exothermic than expected (when compared to ΔH hydrogenation for cyclohexene) ✓ Only reacts with Br_2 at high temp or in presence of a halogen carrier / resistant to electrophilic attack ✓ **Please annotate, use ticks to show where marks are awarded**	3	**ALLOW** all carbon–carbon bonds the same length **ALLOW** ΔH hydrogenation less (negative) than expected **ALLOW** ΔH hydrogenation different from that expected **DO NOT ALLOW** ΔH halogenation/hydration **ALLOW** doesn't decolourise/react with/polarise Br_2 **ALLOW** doesn't undergo addition reactions (with Br_2)
	b	i	compound **A**  if NO_2 in wrong position penalise here and ECF for rest of **b(i)** and **b(ii)** ✓ compound **B**  ✓ compound **C**  ✓	4	**ALLOW** any 4-nitro-1,3-dimethylbenzene drawn in any orientation **ALLOW**  drawn in any orientation **ALLOW** any 4-amino-1,3-dimethylbenzene drawn in any orientation **ECF** amine of incorrect compound **A** (e.g. position of NO_2 or lack of methyl sticks/groups) **ALLOW** diazonium chloride salt of 1,3-dimethylbenzene **ECF** diazonium salt/compound of incorrect compound **B** **IGNORE** Cl^- ion **allow**  **not allow** 

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

If NO_2 is in correct position do not penalise even if compound **A** in **b(i)** is not in correct position

Question	Expected Answers	Marks	Additional Guidance
ii	***mark 1*** $HNO_3 + 2H_2SO_4 \rightarrow H_3O^+ + 2HSO_4^- + NO_2^+$ ✓ ***mark 4*** – curly arrow from C–H bond back to reform π ring **AND** correct products ✓  ***mark 2*** – curly arrow from π ring to $^+NO_2$ ✓ ***mark 3*** – intermediate with π ring broken in the correct place ✓ ***mark 5*** - $H^+ + HSO_4^- \rightarrow H_2SO_4$ ✓ Link to compound **A** in part **(i)** – cannot score full marks [in **b(i)** & **b(ii)**] if NO_2 is not adjacent to a methyl	5	Equation to show formation of NO_2^+ ion ✓ **ALLOW** $HNO_3 + H_2SO_4 \rightarrow H_2O + HSO_4^- + NO_2^+$ $HNO_3 + H_2SO_4 \rightarrow HSO_4^- + H_2NO_3^+ \rightarrow H_2O + NO_2^+$ **ALLOW** mark 2 curly arrow must be from 1,3-dimethylbenzene to NO_2^+ and **ECF** for marks 3 and 4 **DO NOT ALLOW** intermediate  **ALLOW** CH_3s shown **ALLOW** $H_3O^+ + HSO_4^- \rightarrow H_2O + H_2SO_4$
iii	2 ✓	1	No other correct response
	Total	**13**	

Question			Expected Answers	Marks	Additional Guidance
2	a	i	 ✓✓ Ester group must be displayed to get both marks and must contain 4 Os	2	**ALLOW** for both marks  **ALLOW** for one mark  **ALLOW** for one mark  **ALLOW** Kekulé structure / $(CH_2)_2$ **ALLOW** one mark if end bonds missing **ALLOW** 1 mark if the CH_2CH_2 is drawn skeletally **ALLOW** for  **ALLOW** <u>1 mark</u> if repeat unit shows a displayed ester group and contains a benzene ring and two other carbons **DO NOT ALLOW** $-OCC_6H_4COOCH_2CH_2O-$
		ii	 ✓	1	**ALLOW** Kekulé structure/ $(CH_2)_2$ CO_2 for ester groups C_6H_4 if already penalised in **a(i)**

Question			Expected Answers	Marks	Additional Guidance
	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	  ✓ ✓ **Penalise incorrect bond linkage in 2b(ii) only. Do not penalise elsewhere on the paper**	2	**ALLOW** $COOH/CO_2H$ **ALLOW**  **ALLOW** $HO(CH_2)_2OH$
	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**	

<table>
<tr><th colspan="3">Question</th><th colspan="2">Expected Answers</th><th>Marks</th><th>Additional Guidance</th></tr>
<tr><td rowspan="3">3</td><td rowspan="3">a</td><td rowspan="3"></td><td colspan="2">Alternative approaches</td><td rowspan="3">4</td><td rowspan="3">ALLOW ammoniacal $AgNO_3$/ $Ag^+(NH_3)_2$ / $Ag^+(NH_3)$
ALLOW acidified dichromate OR Fehlings as an alternative to Tollens – observation ‘turn green’ OR ‘red precipitate’ respectively
ALLOW acidified manganagate(VII) and observation as either brown precipitate/decolourised/pale pink
ALLOW Brady’s (reagent)
ALLOW orange/red/yellow for colour of the 2,4-DNP(H) precipitate
ALLOW solid/crystals in place of precipitate
IGNORE any reference to melting points
ALLOW PCl_5 as a test for the acid – observation would be ‘white fumes (of HCl)’

ALLOW detection of (carboxylic) acid by reacting with an alcohol to make an ester but no mark for the observation.

DO NOT ALLOW detection of (carboxylic) acid by pH or indicator

Please annotate, use ticks to show where marks are awarded</td></tr>
<tr><td>Tollens’ test AND ‘silver precipitate/mirror’ ✓
is the aldehyde ✓

react with 2,4-DNP(H) and ‘orange precipitate’ ✓

must be the ketone ✓</td><td>Tollens’ test AND ‘silver precipitate/mirror’ ✓
is the aldehyde ✓

react with carbonate/ hydrogencarbonate/ Na/Mg and ‘fizzes/ bubbles/ effervesces/ gas evolved ✓

must be the (carboxylic) acid ✓</td></tr>
<tr><td>2,4-DNP(H) AND orange precipitate ✓
is either aldehyde OR ketone ALLOW carbonyl OR C=O✓

Tollens’ test & ‘silver ppt/mirror’ ✓
is the aldehyde ✓</td><td>2,4-DNP(H) and no orange precipitate ✓
is the (carboxylic) acid ✓

Tollens’ test & ‘silver ppt/mirror’ ✓
is the aldehyde ✓</td></tr>
<tr><td></td><td>b</td><td></td><td colspan="2">Peak in range 2500–3300 (cm^{-1}) or (around) 3000 shows O–H ✓
[need wavenumber (or range) <u>and</u> O–H bond]</td><td>1</td><td>DO NOT ALLOW single peak quoted within range 2500–3300 other than 3000 (cm^{-1}) for OH
DO NOT ALLOWrange 3200–3550 (cm^{-1})
IGNORE any reference to C-O or C=O</td></tr>
</table>

<table>
<tr><th colspan="3">Question</th><th>Expected Answers</th><th>Marks</th><th>Additional Guidance</th></tr>
<tr><td></td><td>c</td><td></td><td>Alternative approaches depending on whether or not the aldehyde is correct
<table><tr><td>Doublet indicates adjacent C is bonded to only 1H
OR
(relative) peak area indicates 2 x CH_3 (in the same environment) ✓

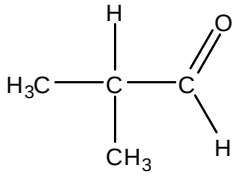
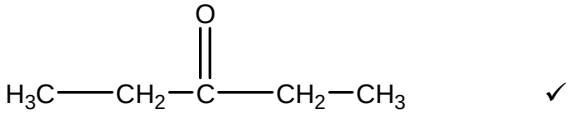
If aldehyde is correct
$(CH_3)_2CH$——CH_2—CHO
✓ ✓
If aldehyde is correct only need to explain doublet OR peak areas</td><td>Doublet indicates adjacent C is bonded to only 1H✓
AND
(relative) peak area indicates 2 x CH_3 (in the same environment) ✓

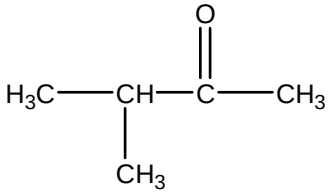
If aldehyde identified is incorrect ×

if aldehyde is incorrect must explain both doublet or peak areas</td></tr></table></td><td></td><td>ALLOW 3-methylbutanal , any correct unambiguous structure
ALLOW two marks for correct aldehyde with no explanation

ALLOW doublet/peak at 0.9ppm due to R–CH
ALLOW the splitting shows adjacent to CH/environment that contains 1 H/proton

ALLOW 6 Hs/ protons in same environment
DO NOT ALLOW 6 Hs in same environment next to CHO

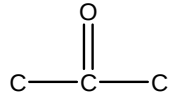
e.g. 
would score two marks if the doublet and the peak areas were correctly explained</td></tr>
<tr><td></td><td>d</td><td>i</td><td>  ✓
ketone 3</td><td>1</td><td>ALLOW displayed/skeletal formulae</td></tr>
<tr><td></td><td></td><td>ii</td><td>There are 4 (different C) environments ✓

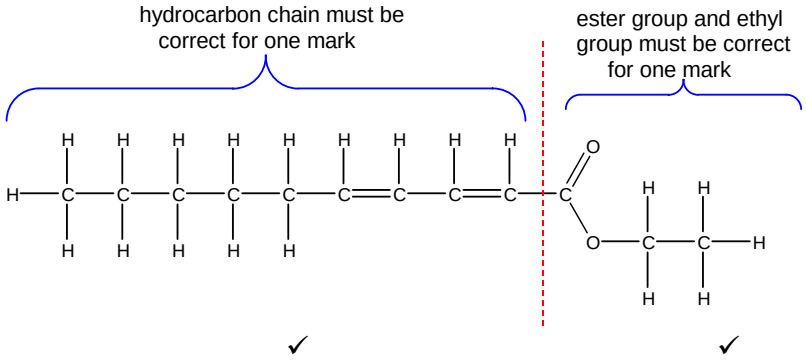
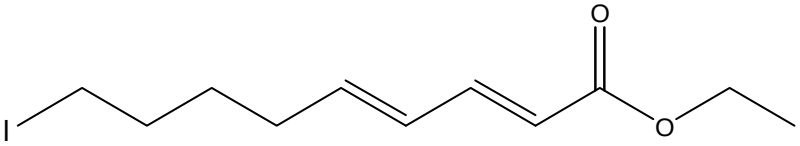
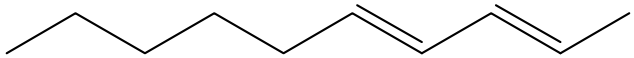
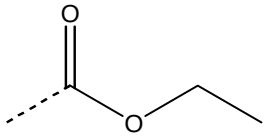
(therefore) it is ketone 2 l
  ✓

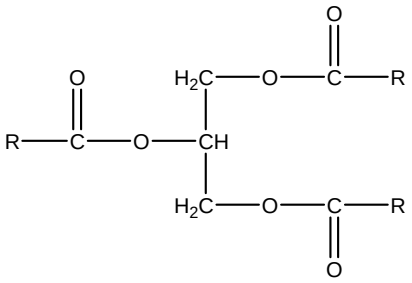
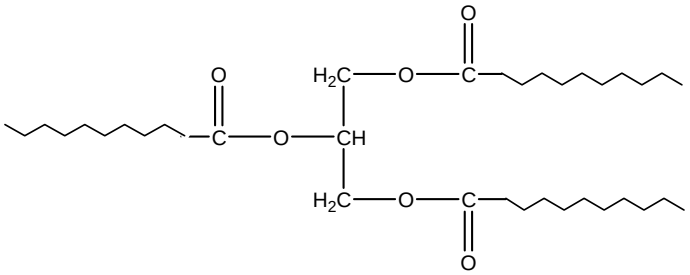
(C responsible for peak at δ = 210 ppm) is C=O/carbonyl carbon ✓</td><td>3</td><td>ALLOW 2 Cs are in same environment/equivalent

ALLOW 3-methylbutan(-2-)one/ any correct unambiguous structure

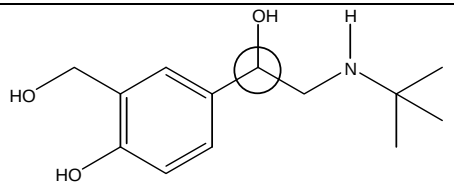
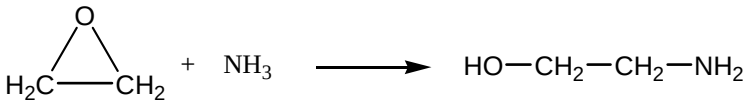
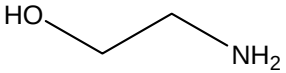
ALLOW 2-methylbutan-3-one

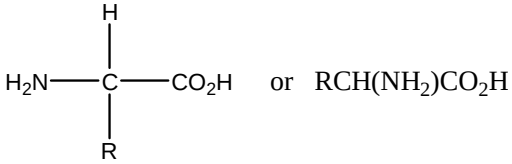
ALLOW
  </td></tr>
<tr><td></td><td></td><td></td><td>Total</td><td>12</td><td></td></tr>
</table>

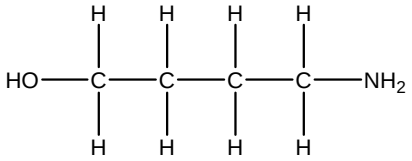
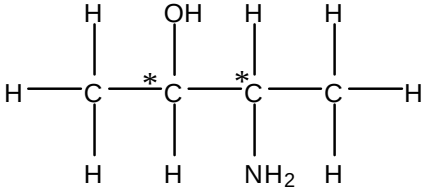
Question			Expected Answers	Marks	Additional Guidance
4	a	i	The time (from the injection of the sample) for the component to leave the column ✓	1	**ALLOW** time from injection to detection **ALLOW** time spent in column **ALLOW** time taken to reach detector
		ii	They have similar retention times ✓	1	**ALLOW** both are esters therefore partition/adsorption/retention times will be very similar **ALLOW ECF** if they describe R_f values in part **a(i)** **ALLOW** same retention times
		iii	Butylbutanoate ✓	1	**ALLOW** butyl butanoate **ALLOW** but-1-yl butanoate **DO NOT ALLOW** butanyl butanoate
	b	i	 ✓ ✓	2	**ALLOW** any correct unambiguous structure/ $CH_3(CH_2)_4CHCHCHCHCOOCH_2CH_3$ / $CH_3(CH_2)_4CHCHCHCHCOOC_2H_5$ $CH_3(CH_2)_4(CH)_4COOCH_2CH_3$ **DO NOT ALLOW** $C_5H_{11}CHCHCHCHCOOCH_2CH_3$ etc **ALLOW** CO_2 for ester  **ALLOW** 1 mark for correct 2,4-decadiene structure e.g.  **ALLOW** 1 mark for correct ethyl … oate structure e.g.  or —$CO_2C_2H_5$ or —$COOC_2H_5$

Question			Expected Answers	Marks	Additional Guidance
		ii		1	**ALLOW**  any orientation of the three fatty acids
	c		**1.** react phenylethanal with $H_2SO_4/K_2Cr_2O_7$ ✓ **2.** to get phenylethanoic acid/$C_6H_5CH_2COOH$ ✓ mark **2** can be scored if dichromate is used without being acidified **3.** react phenylethanal with $NaBH_4$ ✓ **4.** to get 2-phenylethanol/$C_6H_5CH_2CH_2OH$ ✓ mark **3** must be correct to score mark **4** **5.** react phenylethanoic acid with 2-phenylethanol. If both already correctly named **ALLOW** acid and alcohol✓ **6.** H_2SO_4 if linked to the reaction of an alcohol and acid✓ **7.** reflux in either **(1)** or **(5)** or catalyst used in **(5)** ✓ QWC must spell catalyst or reflux correctly	7	**ALLOW** H^+ & $Cr_2O_7^{2-}$ or $H_2SO_4/Na_2Cr_2O_7$ - any other oxidising agent or other named acid – please consult with TL **ALLOW** $LiAlH_4$ as alternative to $NaBH_4$ phenylethanoic acid & phenylethanol must be unambiguously identified by either name or formula **DO NOT ALLOW** or oxidised to form(a carboxylic) acid or reduced to form alcohol for marks 2 and 4 **ALLOW** conc H_2SO_4 **DO NOT ALLOW** dilute or H_2SO_4(aq) **DO NOT ALLOW** just acid catalyst **DO NOT ALLOW** HCl, HNO_3 **Please annotate, use ticks to show where marks are awarded**
			Total	**13**	

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

Question			Expected Answers	Marks	Additional Guidance
5	a	i	 ✓	1	**ALLOW** * in place of circle **ALLOW** if circle extends to include OH
		ii	**Mark 1** – production of a single isomer is more expensive/difficult **OR** separation of the single isomer is expensive/difficult✓ **Mark 2** – one of the isomers is more (pharmacologically) active or one of the isomers might have adverse/harmful/nasty side effects ✓ **Marks 3 and 4** – problems are overcome by using: 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
	b	i	 ✓	1	**ALLOW**  **ALLOW** epoxy ethane as C_2H_4O, $(CH_2)_2O$, CH_2OCH_2 **ALLOW** product as $HO(CH_2)_2NH_2$ **DO NOT ALLOW** product as C_2H_7NO
		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

Question			Expected Answers	Marks	Additional Guidance
	c	i	$HO—CH_2—CH_2—NH_3^+ Cl^-$ Must show Cl^- ion ✓	1	**ALLOW** $HOCH_2CH_2NH_3Cl$ if formula is correct and both charges not shown **ALLOW** $(CH_2)_2$/ any correct unambiguous structure **DO NOT ALLOW** ions joined by covalent bonds
		ii	$HO—CH_2—CH_2—NH_3^+ HS^-$ Must show HS^- ion ✓	1	**ALLOW** if formula is correct and both charges not shown **ALLOW** $(CH_2)_2$/ any correct unambiguous structure **ALLOW** $\left(HO—CH_2—CH_2—NH_3^+\right)_2 S^{2-}$
	d	i	Both NH_2 and COOH are joined to the same C ✓	1	**ALLOW**  or $RCH(NH_2)CO_2H$ The 4 groups/atoms attached to the C can be in any order but CH must be adjacent. ( ) not essential
		ii	$HO—CH_2—CH_2—NH_2 + 2[O] \longrightarrow HO—\overset{\overset{O}{\|\|}}{C}—CH_2—NH_2 + H_2O$ ✓	1	**ALLOW** $(CH_2)_2$ **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**		

Question			Expected Answers	Marks	Additional Guidance
	e	i	Isomer **F**  ✓ Isomer **G**  * not required ✓	2	**ALLOW** $HO(CH_2)_4NH_2$/ **ALLOW** any correct unambiguous structure of 1-aminobutan-4-ol **ALLOW** $CH_3CH(OH)CH(NH_2)CH_3$ **ALLOW** any correct unambiguous structure of 2-aminobutan-3-ol.
			Total	**13**	

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