OCR
RECOGNISING ACHIEVEMENT

GCE

Chemistry A

Advanced GCE

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

Mark Scheme for January 2013

Oxford Cambridge and RSA Examinations

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This mark scheme is published as an aid to teachers and students, to indicate the requirements of the examination. It shows the basis on which marks were awarded by examiners. It does not indicate the details of the discussions which took place at an examiners' meeting before marking commenced.

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.

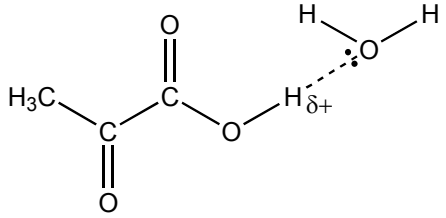
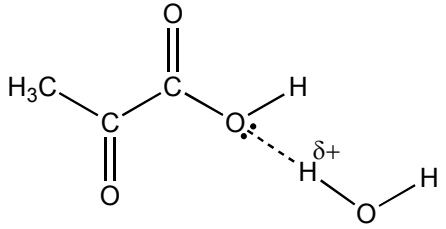
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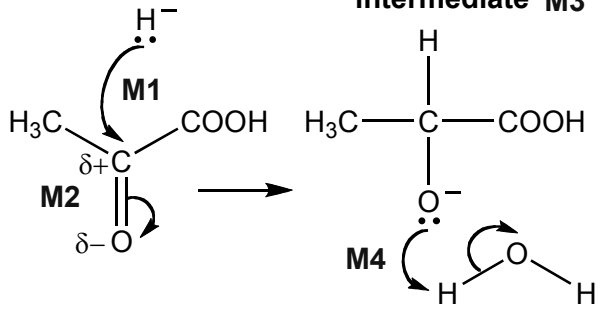
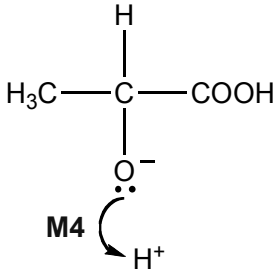
Annotations

Annotation	Meaning
	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

Subject-specific Marking Instructions

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

Question			Answer	Marks	Guidance
1	(a)		**M1 EITHER** in words: (pyruvic acid forms) hydrogen bonds with **water** **OR** correctly **labelled diagram** showing hydrogen bond between pyruvic acid and water ✓ **M2** diagram showing dashed/dotted line between $H^{\delta+}$ in COOH **and lone pair** of electrons on O in H_2O  **OR** diagram showing dashed/dotted line between $H^{\delta+}$ in H_2O and lone pair of electrons on O of OH in COOH ✓ 	2	**FOR M1 only: if use diagram ALLOW a** labelled hydrogen bond to O in C=O **FOR M2 only: IGNORE** a hydrogen bond to C=O, *i.e.* C=O - - - H–O **IGNORE** bond angles Diagram does **not** need to show all of pyruvic acid (**IGNORE** if wrong so allow ethanoic acid) but must have minimum of COOH **MIMIMUM requirement** is a $H^{\delta+}$ (on acid or water) and a lone pair on O (in acid or water) involved in a hydrogen bond ie IGNORE δ-
	(b)		$CH_3CH(OH)CH_2OH + 3[O] \rightarrow CH_3COCOOH + 2H_2O$ four correct formulae ✓ balanced ✓	2	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous (**IGNORE** lack of brackets round 2° alcohol) **DO NOT ALLOW** molecular formulae **IF** propane1,3-diol used score 0

Question			Answer	Marks	Guidance
1	(c)			4	
			M1: 1 mark for curly arrow from H^- to C of C=O ✓		Curly arrow **MUST** start from – sign **OR** lone pair on H^- Lone pair **does not need** to be shown on H^-
			M2: 1 mark for correct dipoles on C=O **AND** curly arrow from double bond to $O^{\delta-}$ ✓		
			M3: 1 mark for correct intermediate with – charge on O ✓		Lone pair **does not need** to be shown on O^-
			M4: 1 mark for curly arrow from O^- of intermediate to H in H_2O **AND** curly arrow from the O—H **bond** to the O in H_2O: **Do not need** to show formation of OH^-		Curly arrow **MUST** start from – sign **OR** from lone pair on O^- of intermediate Lone pair **does not need** to be shown on O^- **For M4,** **ALLOW** mark for curly arrow from O^- of intermediate to H^+ 

Question			Answer	Marks	Guidance
1	(d)		***Either:***	3	
			Use Tollens' reagent **AND** correct reference to compound A being oxidised or Tollen's reagent acts as oxidising agent ✓		**ALLOW** $AgNO_3$ in ammonia **OR** ammoniacal $AgNO_3$ **ALLOW** redox reaction
			Observation: silver mirror/precipitate/ppt/solid ✓		**ALLOW** black ppt **OR** grey ppt
			or:		
			Use $K_2Cr_2O_7$ **AND** H_2SO_4 **AND** correct reference to compound A being oxidised or $K_2Cr_2O_7$ acts as oxidising agent ✓		**ALLOW** $Na_2Cr_2O_7$ **OR** $Cr_2O_7^{2-}$ for $K_2Cr_2O_7$ If formulae used, formulae must be correct **ALLOW** acidified dichromate If name given, **ALLOW** dichromate **OR** dichromate(VI) **IGNORE** reference to dilute/conc **ALLOW** H^+
			Observation: turns (dark) green **OR** blue ✓		**ALLOW** $KMnO_4$ **and** H_2SO_4 / acidified manganate(VII)/ permanganate / alkaline manganate(VII) **AND** correct reference to compound A being oxidised or $KMnO_4$ acts as oxidising agent *Observation:* decolourised
			✎ **QWC** oxidised/oxidized/oxidation/redox *etc*. must be spelled **correctly at least ONCE** (*i.e.* **NOT** oxidisation, oxidated) to score 1st mark **UNLESS** 2,4-DNP(H)/Brady's reagent is used, when condensation/addition–elimination must be spelled **correctly at least ONCE**		**ALLOW** Benedict's or Fehling's reagent/solution **AND** correct reference to compound A being oxidised or Benedict's or Fehling's acts as oxidising agent *Observation:* (brick) red ppt **ALLOW** 2,4-DNP(H)/Brady's reagent **AND** measure melting point of derivative **AND** state it is a condensation reaction/addition-elimination reaction *Observation:* orange/yellow/red **precipitate** **ALLOW** solid **OR** crystals **OR** ppt as alternatives for precipitate

<table>
<tr><th colspan="3">Question</th><th>Answer</th><th>Marks</th><th>Guidance</th></tr>
<tr><td></td><td></td><td></td><td>$HOOCCH_2COOH$ ✓</td><td></td><td>ALLOW correct structural OR displayed OR skeletal formulae OR combination of above as long as unambiguous

ALLOW COO^- if used Tollens' or Fehling's or Benedict's

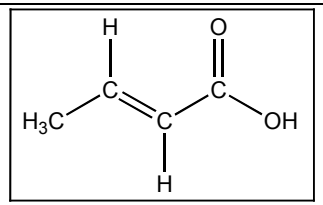
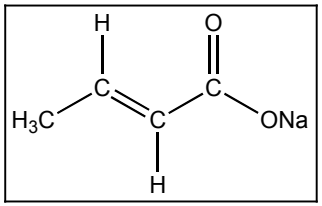
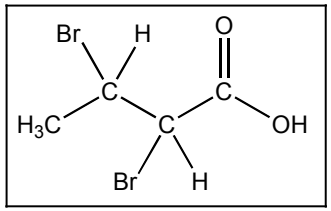
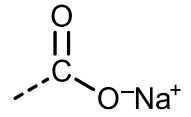
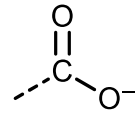
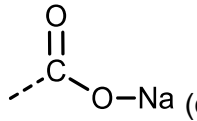
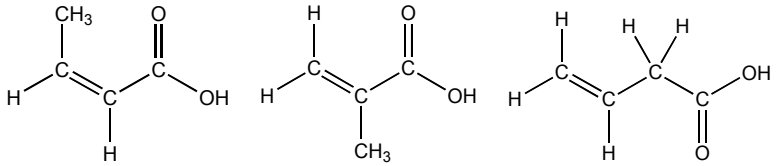
ALLOW correct unambiguous name:
propan(e-1,3-)dioic acid

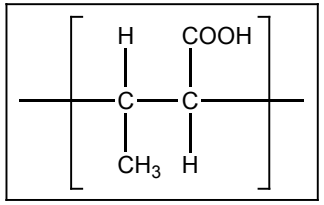
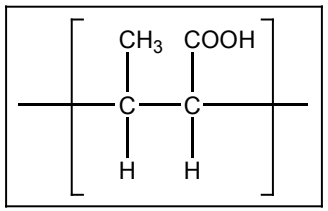
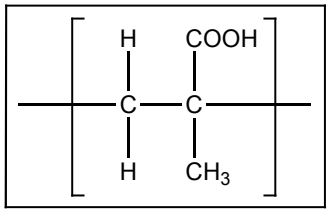
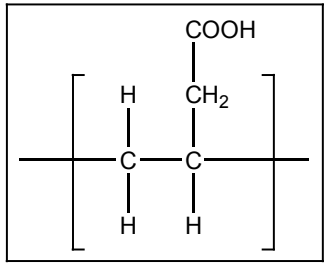
IGNORE dipropanoic acid
DO NOT ALLOW propan(e-1,3-)dicarboxylic acid

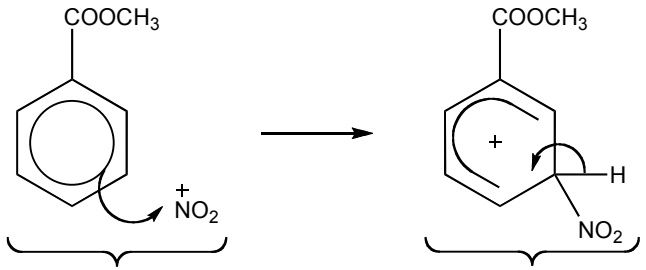
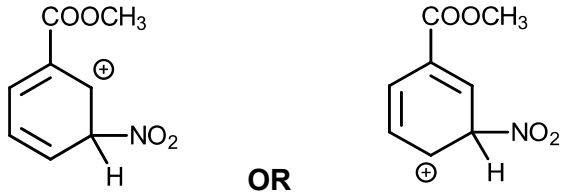
if used 2,4-DNP(H):
ALLOW correct hydrazone structure or name
ALLOW "(2,4-dinitrophenyl)hydrazone" (derivative)</td></tr>
<tr><td>1</td><td>(e)</td><td>(i)</td><td><table><tr><td></td><td>C</td><td>H</td><td>O</td></tr><tr><td>%</td><td>55.81%</td><td>7.02%</td><td>37.17%</td></tr><tr><td>mol</td><td>4.65</td><td>7.02</td><td>2.32</td></tr><tr><td>ratio</td><td>2</td><td>3</td><td>1</td></tr></table>empirical formula = C_2H_3O ✓

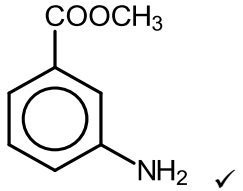
molecular formula = $C_4H_6O_2$ ✓</td><td>2</td><td>Alternative method scores 2 marks:
0.0702/1 x 86 = 6; 0.3717/16 x 86 = 2; 0.5581/12 x 86 = 4

$C_4H_6O_2$ answer alone worth 2 marks</td></tr>
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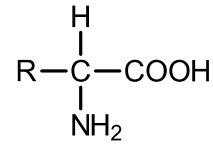
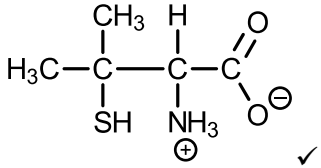
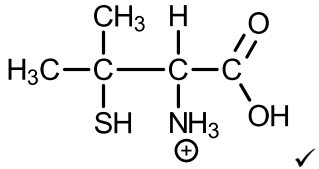
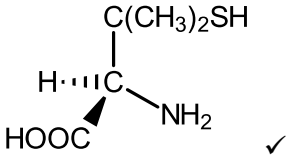
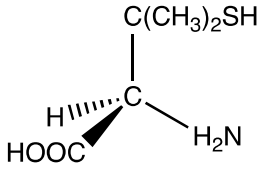
Question			Answer	Marks	Guidance
1	(e)	(ii)	 **compound B** ✓  **compound C** ✓  **compound D** ✓	4	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous eg COOH does not have to be displayed E/trans stereoisomer is needed **For compound C,** **ALLOW**  **OR**  If charges shown on both O and Na then both must be correct **DO NOT ALLOW**  (covalent bond) **ALLOW ECF** for **C** and **D** if **B** is identified as one of the following three structures: 

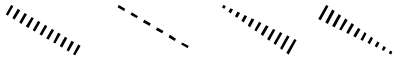
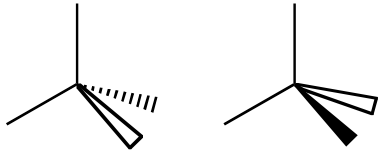
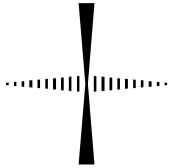
Question	Answer	Marks	Guidance
	 **one repeat unit of polymer E** ✓		**For polymer E**, brackets **not** required **IGNORE** n Free rotation so CH_3 can be shown at top, next to COOH **IF** more than one repeat unit has been drawn a single repeat unit **MUST** be identified by brackets or clear label **The only polymers to ALLOW as ECF from incorrect B are:**   
	Total	**17**	

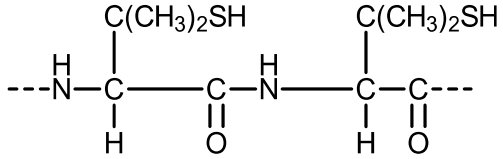
Question			Answer	Marks	Guidance
2	(a)	(i)	**M1**: $HNO_3 + H_2SO_4 \rightarrow H_2O + HSO_4^- + NO_2^+$ ✓  **M2:** curly arrow from ring to NO_2^+ **M2** ✓ **M3:** correct intermediate **M4:** curly arrow from C-H bond back to reform ring **M3** ✓ **M4** ✓ --- **Note**: **ALLOW M2 AND M4** for benzene **OR ANY** substituted benzene compound For **M3**, credit **ONLY** the **correct** intermediate --- **M5** $H^+ + HSO_4^- \rightarrow H_2SO_4$ ✓	5	**ALLOW** $HNO_3 + 2H_2SO_4 \rightarrow H_3O^+ + 2HSO_4^- + NO_2^+$ **ALLOW** $HNO_3 + H_2SO_4 \rightarrow HSO_4^- + H_2NO_3^+$ then $H_2NO_3^+ \rightarrow H_2O + NO_2^+$ **ALLOW** $^+NO_2$ **OR** NO_2^+ **ALLOW** first curly arrow from the ring **OR** from within the ring to any part of the NO_2^+ including the + charge **DO NOT ALLOW** intermediate with broken ring covering less than half the ring **DO NOT ALLOW incorrect orientation of horseshoe** **ALLOW** non-delocalized (Kekulé) structures **ALLOW** carbocation on either side of H/NO_2 substituents:  **IF** NO_2 is shown in incorrect position or $COOCH_3$ has been omitted in intermediate **DO NOT AWARD** M3 but can award other marks **(max 4)**
		(ii)	electrophilic substitution ✓	1	

Question			Answer			Marks	Guidance
2	(b)	(i)	 ✓			1	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous
		(ii)	Reaction **1**	Sn **AND concentrated** HCl	✓	4	**IGNORE** temperature and reaction type/purpose of reagents
			Reaction **2**	HNO_2 **OR** $NaNO_2$ with (dil) HCl < 10°C	✓ ✓		**IGNORE** reference to concentration
			Reaction **4**	hot/heated **aqueous** NaOH	✓		**ALLOW** (heat under) reflux for 'hot' **IGNORE** warm/alkaline if temp stated accept 50º or greater **MUST** have aq or water or any stated concentration

Question			Answer	Marks	Guidance
2	(b)	(iii)	In **amine**, (lone) **pair** of electrons on N is (partially) **delocalised** into the ring ✓ ✎ **QWC** delocalised/delocalized/delocalise, *etc*. must be spelled correctly in the correct context **at least once** for 1st mark electron density is high(er) / increases ✓ great(er) attraction (from aromatic ring) for electrophile/diazonium ion ✓	3	**ALLOW** diagram to show movement of (lone) pair into ring but **delocalised** ring must be mentioned **ALLOW** (lone) pair of electrons on N is (partially) drawn/attracted/pulled into **delocalised** ring **ALLOW** electron density low(er) for benzene **IGNORE** 'activates the ring' **IGNORE** charge density alone but **ALLOW** electron charge density **DO NOT ALLOW** electronegativity **ALLOW** less/low attraction from benzene for electrophile/diazonium ion **ALLOW** amine is a **better** nucleophile/**more** susceptible to electrophilic attack **DO NOT ALLOW** reference to dipole induced in diazonium ion **DO NOT ALLOW** reference to bromine as electrophile
			Total	**14**	

Question			Answer	Marks	Guidance
3	(a)		Both NH_2 and COOH are attached to the same carbon ✓	1	**ALLOW** amine/amino and carboxyl(ic) **ALLOW** (it has the structure)  **ALLOW** $RCH(NH_2)COOH$ in any order but C and H must be adjacent (to each other)
	(b)	(i)	 ✓	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous **ALLOW** NH_3^+ **ALLOW** delocalised carboxylate
		(ii)	 ✓	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous **ALLOW** NH_3^+
	(c)		 ✓	1	**Connectivity is being tested:** Chiral C **must** be linked to the C of the COOH, the C of the $C(CH_3)_2SH$ and the N of the NH_2 **eg DO NOT ALLOW** an attempted NH_2 shown as below: 

Question			Answer	Marks	Guidance
					The structure must have four central bonds, with at least one wedge in AND one wedge out --- For bond into plane of paper, **ALLOW**:  For bond out of plane of paper, a solid wedge is expected, either way around:  **ALLOW** a hollow wedge for 'in bond' OR an 'out bond', provided it is different from the other in or out wedge e.g.:  **ALLOW** examples of other 3D representations provided they are possible: i.e.  **CARE**: This is a 3D representation so this is possible and the bond are clearly not 90º to one another

Question			Answer	Marks	Guidance
3	(d)	(i)	CH_2CI_2 ✓	1	**ALLOW** CH_2Br_2 **OR** CH_2I_2 **OR** CH_2F_2 **OR** other dihalogenated methane derivatives eg CH_2BrCl **IGNORE** names
		(ii)	 peptide link ✓ rest of structure ✓	2	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous **ALLOW** —NH— at other end 'End bonds' **MUST** be shown (solid or dotted) **IGNORE** brackets and/or *n* around **two** repeat units 1st mark does not require amide group fully displayed ie **ALLOW** –CONH– **DO NOT ALLOW 2nd** mark if amide/peptide link wrong If more than 2 repeat units only first mark (peptide link) can be awarded
	(e)	(i)	penicillamine = 4 ✓ methionine = 5 ✓	2	
		(ii)	(CO)O**H**, N**H**/N**H**$_2$ **AND** S**H** ✓ all undergo proton exchange ✓	2	**ALLOW** (CO)O**D**, N**D**/N**D**$_2$, S**D**, **ALLOW** H (atoms/protons/ions) replaced by D (atoms/ions)

<table>
<tr><th colspan="3">Question</th><th>Answer</th><th>Marks</th><th>Guidance</th></tr>
<tr><td>3</td><td>(e)</td><td>(iii)</td><td>
<table>
<tr><th colspan="4">^{1}H NMR spectrum for methionine</th><th></th></tr>
<tr><th>Type of proton(s)</th><th>Chemical shift</th><th>Splitting pattern</th><th>Relative peak area</th><th></th></tr>
<tr><td>NH$_2$</td><td>4.5</td><td>singlet</td><td>2</td><td></td></tr>
<tr><td>H$_3$C-S-</td><td>2.1</td><td>singlet</td><td>3</td><td>✓</td></tr>
<tr><td>-S-CH$_2$-</td><td>2.4</td><td>triplet</td><td>2</td><td>✓</td></tr>
<tr><td>S-CH$_2$-CH$_2$</td><td>0.7–2.0</td><td>multiplet OR quartet</td><td>2</td><td>✓</td></tr>
<tr><td>CHNH$_2$</td><td>2.0–3.0</td><td>triplet</td><td>1</td><td>✓</td></tr>
<tr><td>OH</td><td>11–12</td><td>singlet</td><td>1</td><td>✓</td></tr>
</table>
Rows can be in any order
IGNORE extra rows
Do not need to show bonds between atoms
</td><td>5</td><td>
ALLOW any value within ranges given for δ /ppm on the Data Sheet
IGNORE reference to NH$_2$ signals (given as example)

GUIDANCE
• mark by rows
• ALL data in row must be correct for each mark
• ALLOW “triplet of doublets” or “doublet of triplets” for multiplet/quartet signal from —CH$_2$CH$_2$S—

ALLOW quadruplet

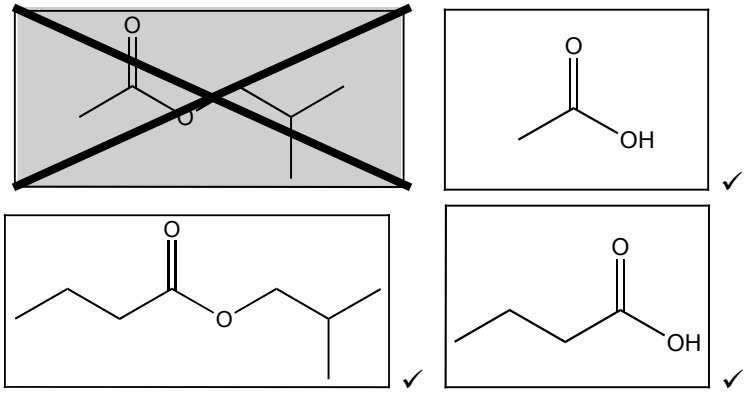
ALLOW a response that implies a single peak OR ‘no splitting’

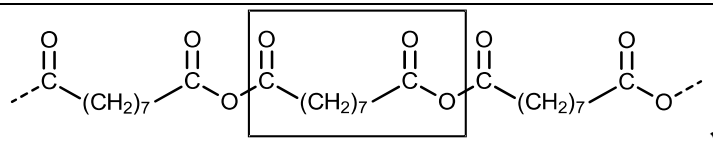
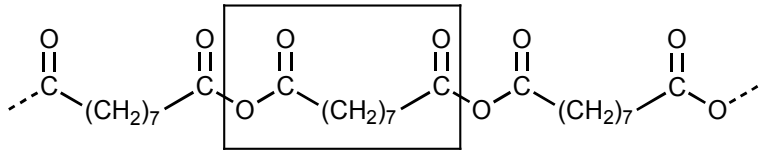
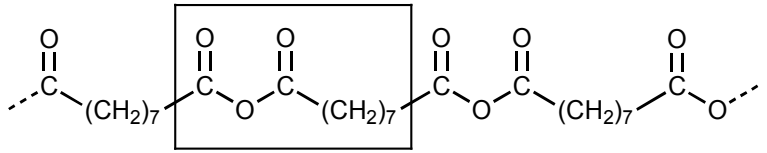
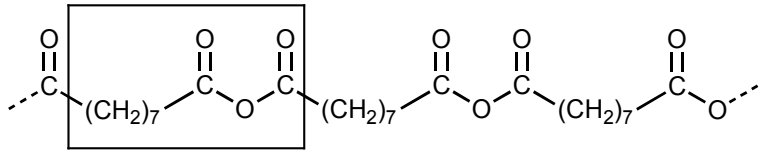
ALLOW a response that implies a splitting into three for a triplet/into four for a quartet

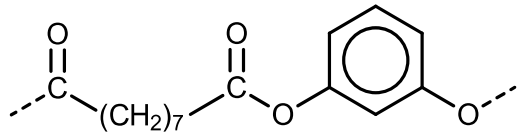
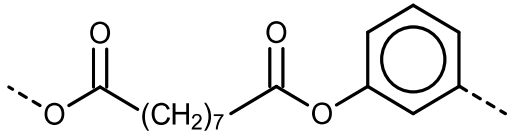
Clear and unambiguous identification of the protons (when more than one type is present) other than by position number should be credited
eg for CHNH$_2$ could be HCCO or CHN or HCN or CH$_2$CH

eg for S-CH$_2$-CH$_2$ could be CH$_2$C(H)NH$_2$ or CCH$_2$C or CH$_2$CH$_2$ or RCH$_2$R or RCHR

eg ‘CH between COOH and NH$_2$’ OR identification by number labels on chemical structures
</td></tr>
<tr><td></td><td></td><td></td><td>Total</td><td>16</td><td></td></tr>
</table>

Question			Answer	Marks	Guidance
4	(a)	(i)	(2-)methylpropan-1-ol ✓	1	**ALLOW** without hyphens
		(ii)	 ✓ ✓ ✓	3	**DO NOT MARK** top left hand structure: (on paper) **ALLOW in any order** **ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous **If use displayed formulae but omit one or more H atoms DO NOT ALLOW each time**
	(b)	(i)	The time (from the injection of the sample) for the component/compound/substance to leave the column ✓	1	**IGNORE** (time for) gas to leave column **DO NOT ALLOW** time in GC/machine/apparatus **ALLOW** time from injection to detection **ALLOW** time spent in column **ALLOW** time taken to reach detector
		(ii)	They have similar retention times **OR** unknown compounds have no reference retention times for comparison ✓	1	**ALLOW** same retention times **ALLOW** both are esters therefore relative solubilities/ partition/adsorption/retention times will be very similar

Question			Answer	Marks	Guidance
4	(c)	(i)	 ✓	1	**IF end repeat unit shown** the line of the box must go through the continuation bond **ALLOW** other possibilities for showing structure with repeat unit displayed, eg repeat unit with O on left and not on right.  Other possibilities:  
		(ii)	Hydrolysis ✓	1	**IGNORE** decomposition/biodegradation **IGNORE** mention of acid/alkali

Question			Answer	Marks	Guidance
4	(c)	(iii)	broad absorption 2500–3300 (cm^{-1}) ✓ (because) (degradation) forms (di)carboxylic acid / COOH ✓	2	**ALLOW** carboxyl group **IGNORE** reference to carbonyl/1640–1750 (cm^{-1}) **IGNORE** reference to C—O/1000–1300 (cm^{-1})
		(iv)	 **M1** ester link ✓ **M2** the two oxygen atoms from benzene-1,3-diol linked at 1,3 positions ✓ **M3** one repeat unit fully correct ✓	3	**ALLOW** correct structural **OR** displayed **OR** skeletal formulae **OR** combination of above as long as unambiguous Ester link does not need to be fully displayed eg accept –COO– **ALLOW** —O— at other end ie  'End bonds' **MUST** be shown (solid or dotted) **DO NOT ALLOW** more repeat units **IGNORE** brackets and/or *n* **IF** more than one repeat unit has been drawn a single repeat unit **MUST** be identified by brackets or clear label
			Total	**13**	

OCR (Oxford Cambridge and RSA Examinations)
1 Hills Road
Cambridge
CB1 2EU

OCR Customer Contact Centre

Education and Learning
Telephone: 01223 553998
Facsimile: 01223 552627
Email: general.qualifications@ocr.org.uk

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Telephone: 01223 552552
Facsimile: 01223 552553

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