OCR
RECOGNISING ACHIEVEMENT

GCE

Chemistry A

Advanced GCE

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

Mark Scheme for January 2012

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.

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Annotations available in Scoris.

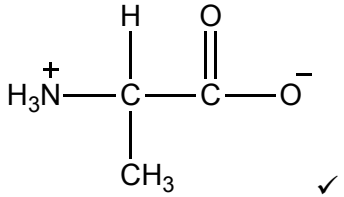
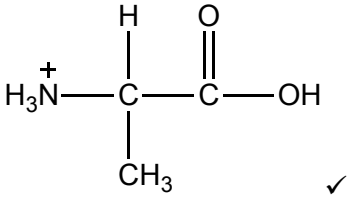
Annotation	Meaning
	Benefit of doubt given
	Contradiction
	Incorrect response
	Error carried forward
	Ignore
	Not answered question
	Benefit of doubt not given
	Power of 10 error
	Omission mark
	Rounding error
	Error in number of significant figures
	Correct response

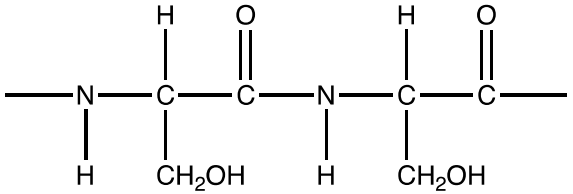
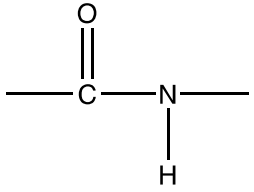
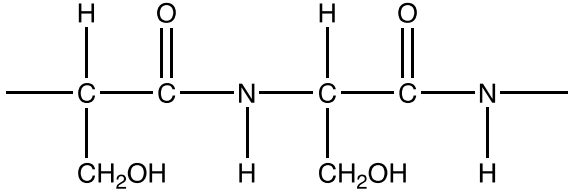
Abbreviations, annotations and conventions used in the detailed Mark Scheme (to include abbreviations and subject-specific conventions).

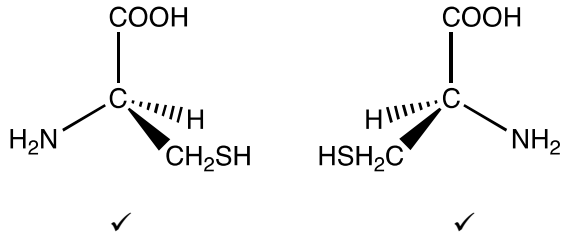
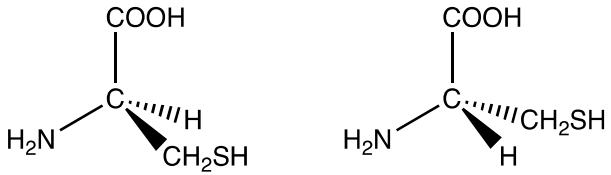
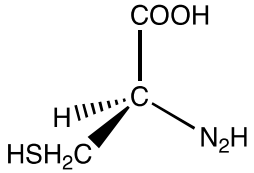
Annotation	Meaning
DO NOT ALLOW	Answers which are not worthy of credit
IGNORE	Statements which are irrelevant
ALLOW	Answers that can be accepted
( )	Words which are not essential to gain credit
__	Underlined words must be present in answer to score a mark
ECF	Error carried forward
AW	Alternative wording
ORA	Or reverse argument

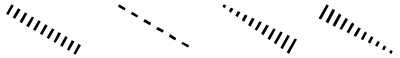
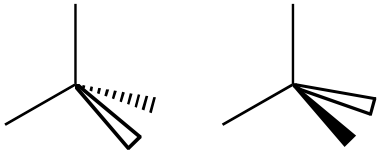
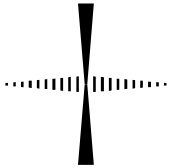
Annotations should be placed to clearly show where they apply within the body of the text (i.e. not in margins) for:

Question 1 c(iii)
Question 2 a(i), (b)
Question 3 a(i), a(ii), b(i)
Question 4 b(ii), (c)

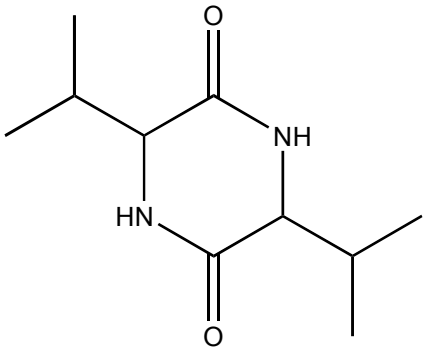
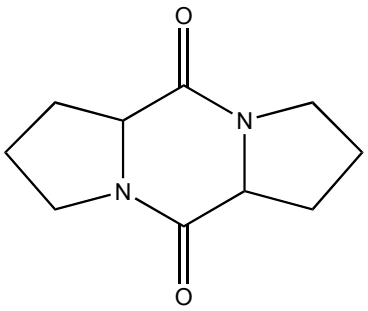
Question			Answer	Mark	Guidance
1	(a)	(i)	The pH **OR** point at which the zwitterion exists ✓	1	**ALLOW** pH/point at which there is no **overall**/**net** charge **IGNORE** pH/point at which there is no charge/ neutral charge *ie overall/net is required* **ALLOW** pH/point at which contains COO^- **AND** NH_3^+
		(ii)	 ✓  ✓	2	**ALLOW** $CH_3CH(NH_3)^+COO^-$ **ALLOW** $CH_3CH(NH_3)^+COOH$ **ALLOW** CO_2^- and CO_2H **ALLOW** + charge on N or H: ie $^+NH_3$ or NH_3^+ **DO NOT ALLOW** '–' charge on C: ie ^-COO **DO NOT ALLOW** H or CH_3 missing **ALLOW** correct structural **OR** displayed **OR** skeletal formula **ALLOW** combination of formulae as long as unambiguous

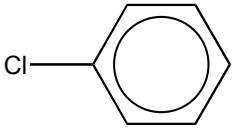
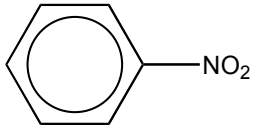
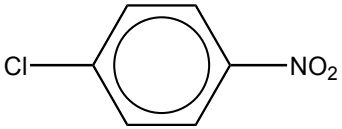
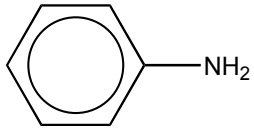
Question			Answer	Mark	Guidance
1	(a)	(iii)	pH < 3: COOH ✓ pH > 10: NH_2 ✓	2	**ALLOW** carboxyl group **OR** carboxylic acid **DO NOT ALLOW** 'acid' **OR** just 'carboxylic' (without 'acid') **ALLOW** amino group **OR** amine **DO NOT ALLOW** if give correct formula but wrong name or correct name and wrong formula eg NH_2 and amide **IF** any carbon chain is shown attached to **BOTH** functional groups **ALLOW** 1 mark eg CH_2COOH **AND** CH_2NH_2 for 1 mark CH_3COOH **AND** CH_3NH_2 for 1 mark RCOOH **AND** RNH_2 for 1 mark **IF** functional groups are shown the wrong way round, **ALLOW** 1 mark i.e. NH_2 COOH
	(b)		 peptide link **must** be fully displayed, i.e.  **TWO** repeat units shown correctly ✓	2	**DO NOT ALLOW** more repeat units **IGNORE** brackets and '*n*' **ALLOW** end bonds shown as ----- **DO NOT ALLOW** if end bonds are missing **ALLOW** terminal N–H on right (OR C=O on left), *ie*  **IF** peptide bond is shown not displayed, i.e. CONH, **2nd mark** can still be awarded

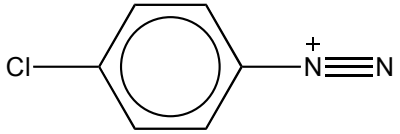
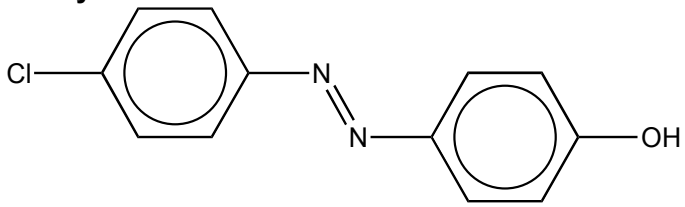
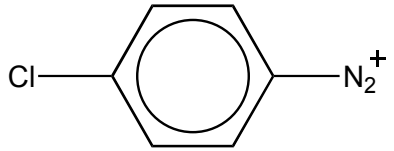
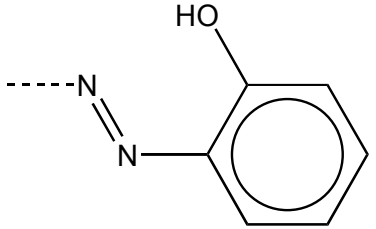
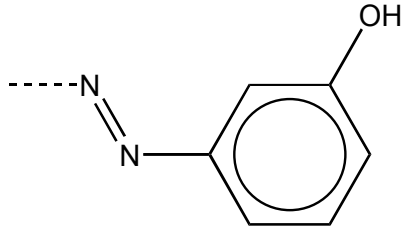
Question			Answer	Mark	Guidance
1	(c)	(i)	There is **no** chiral carbon **OR** there is no asymmetry in the molecule ✓	1	**ALLOW** there is **no** asymmetric carbon **OR** it has **no** non-superimposable mirror image **OR** there are **not** four different atoms/groups of atoms (attached to carbon) **OR** there are only three different atoms/groups of atoms (attached to carbon) **OR** because there are two hydrogen atoms on the carbon
		(ii)	 ✓ ✓	2	**ALLOW** Add the same 3-D structure repeated but with 2 groups 'swapped' as after rotation the 2nd isomer is a mirror image of the first, i.e.  **Connectivity:** Chiral C must be linked to the C of the COOH, the C of the CH_2SH and the N of the NH_2 (ie **connectivity is being tested**) ie, **ALLOW** as in the example but **DO NOT ALLOW** an attempted NH_2 shown as below:  The 2nd mark is for the mirror image of **CORRECT** optical isomer only **CARE**: may be orientated differently **DO NOT** penalise connectivity more than once **Each structure must have four central bonds, with at least one wedge in AND one wedge out**

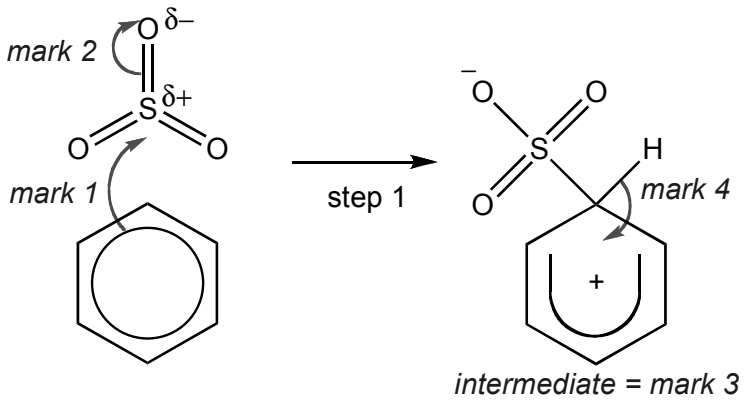
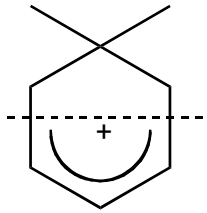
Question			Answer	Mark	Guidance
					--- For bond into plane of paper, **ALLOW**:  For bond out of plane of paper, a solid wedge is expected, either way around:  **ALLOW** a hollow wedge for 'in bond' **OR** an 'out bond', provided it is different from the other in or out wedge eg:  **ALLOW** examples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

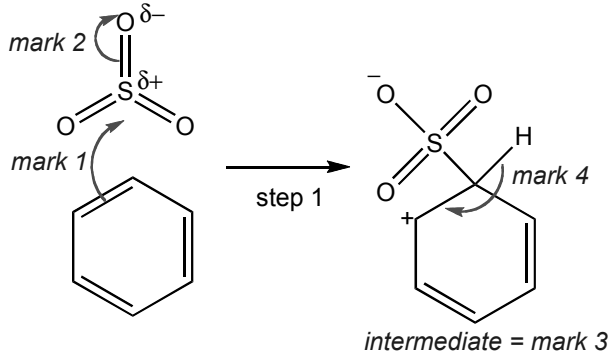
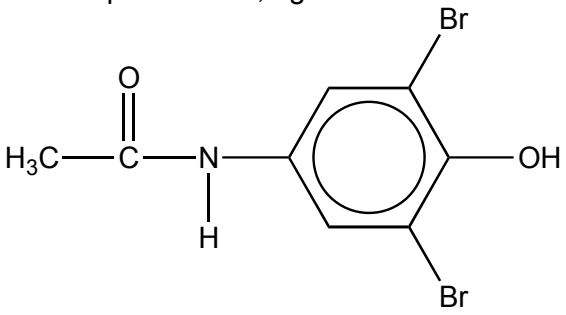
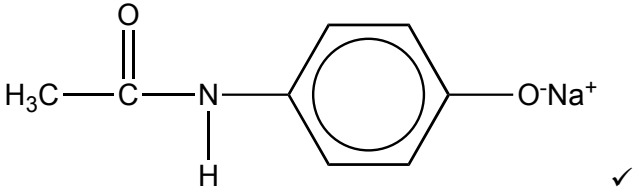
Question			Answer	Mark	Guidance
1	(c)	(iii)	***Disadvantages***: *any **two** from:* • (one stereoisomer might have harmful/adverse) side effects✓ • reduces the (pharmacological) activity/effectiveness ✓ • **cost** of separating stereoisomers **OR** difficulty in separating stereoisomers ✓ ***Synthesis of a single optical isomer*** *any **two** from:* • using enzymes or bacteria ✓ • using (chemical) **chiral** synthesis **OR** using **chiral** catalysts ✓ • using (natural) **chiral** molecules/compounds ✓ ***Quality of Written Communication*** For full marks to be awarded for this question chiral **OR** enzyme **OR** bacteria **OR** catalyst must be spelled correctly at least once in the correct context	2 2	***ANNOTATIONS MUST BE USED*** **IGNORE** harmful/adverse effects only **ALLOW** a response that implies an increased dose **IGNORE** it takes time to separate **ALLOW** biological catalysts **ALLOW chiral** transition metal complex/catalyst **OR stereoselective** transition metal complex/catalyst **ALLOW 'chiral** pool' **OR** L-amino acids / D-sugars

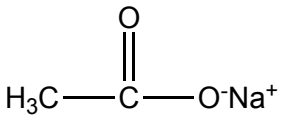
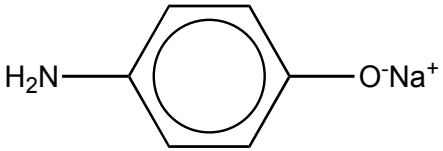
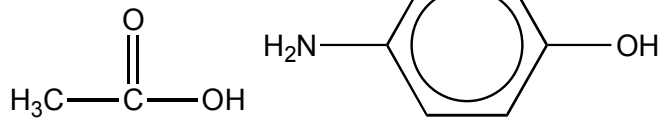
Question			Answer	Mark	Guidance
1	(d)		<table><tr><td>amino acid</td><td>**isoleucine**</td><td>**leucine**</td><td>**tyrosine**</td></tr><tr><td>number of peaks</td><td>6 ✓</td><td>5 ✓</td><td>7 ✓</td></tr></table>	3	1 mark for each number
	(e)		 ✓ **valine anhydride**  ✓ **proline anhydride**	2	**ALLOW** correct structural **OR** displayed **OR** skeletal formula **ALLOW** combination of formulae as long as unambiguous **Common errors:** Look for NH_2 on first structure and NH on second structure
			Total	**19**	

Question			Answer	Mark	Guidance
2	(a)	(i)	Response requires three stages • chlorination • nitration • reduction Reduction must be **a later stage** than nitration **Mark according to which sequence chosen.** **Stage 1** **organic product:**  **OR**  ✓ **chemicals:** Cl_2 **AND** $AlCl_3$ **OR** HNO_3 **AND** H_2SO_4 ✓ **Stage 2** **organic product:**  **OR**  ✓ **chemicals:** HNO_3 **AND** H_2SO_4 **OR** Sn **AND** HCl ✓ **Stage 3** **chemicals:** Cl_2 **AND** $AlCl_3$ **OR** Sn **AND** HCl ✓	5	Acceptable sequence of stages are: • nitration, reduction, chlorination • nitration, chlorination, reduction, • chlorination, nitration, reduction For organic products, **ALLOW** $C_6H_5NO_2$ **OR** C_6H_5Cl **OR** $C_6H_5NH_2$ **ALLOW** NO_2– **AND** NH_2– **DO NOT ALLOW** $ClC_6H_4NO_2$ (formula ambiguous) **DO NOT ALLOW** molecular formulae **IGNORE** any **additional** structures shown eg 2- (*ortho*) and 3- (*meta*) substituted isomers In chemicals boxes, **IGNORE** temperatures **IGNORE '**catalyst' For **chlorination** chemicals, **ALLOW** Cl_2 **AND** $FeCl_3$ **OR** Cl_2 **AND** Fe **OR** Cl_2 **AND** halogen carrier For **nitration** chemicals, 'concentrated' **not** required for HNO_3 OR H_2SO_4 **BUT** ... **DO NOT ALLOW** 'dilute' For **reduction** chemicals, 'concentrated' HCl **not** required but **DO NOT ALLOW** 'dilute' For Sn/HCl **ALLOW** addition of NaOH also **IF** it is clear that it is a second step **BUT** ……. **DO NOT ALLOW** Sn **AND** HCl **AND** NaOH **IGNORE** catalyst

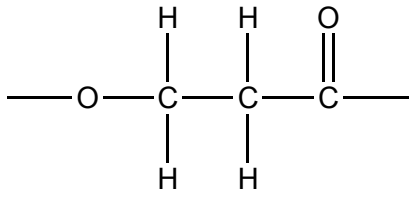
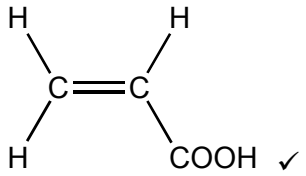
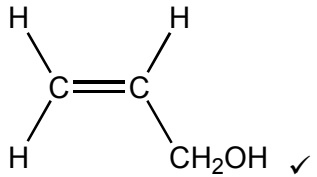
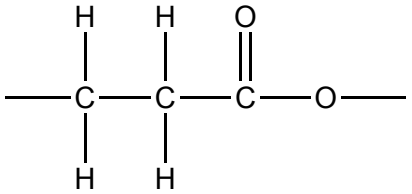
Question			Answer	Mark	Guidance
2	(a)	(ii)	**diazonium ion**  ✓ –N≡N group **MUST** be displayed **azo dye**  ✓ –N=N– group **MUST** be displayed	2	**ALLOW** '+' sign up to halfway along triple bond from left-hand N **IGNORE** presence of Cl^- **DO NOT ALLOW** Cl^-– substituent on benzene ring **DO NOT ALLOW:**  **In azo dye,** **ALLOW** as alternative to phenol OH group: O^- **OR** O^-Na^+ **OR** ONa **ALLOW** phenol part substituted at any carbon (ie 2,3 or 4 position for –OH) i.e.   **IGNORE** geometry/shape, i.e. **ALLOW** —N=N— **Mark independently** **DO NOT ALLOW** if Cl– is missing from benzene ring in **EITHER** structure

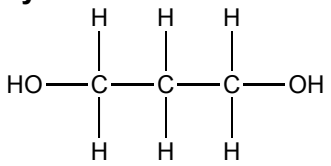
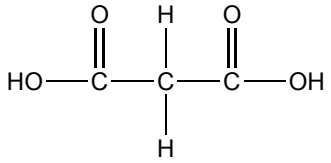
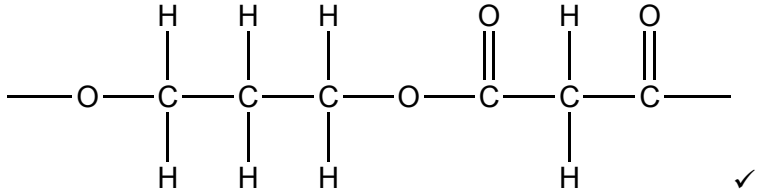
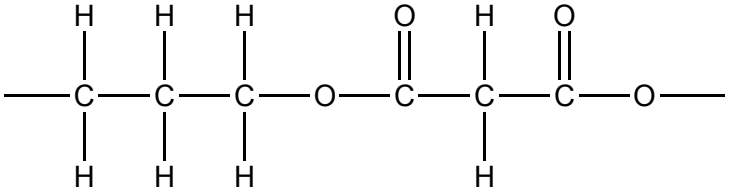
Question	Answer	Mark	Guidance
2 (b)		4	***ANNOTATIONS MUST BE USED*** **mark 1** – curly arrow from π-delocalised ring in benzene to $S^{\delta+}$ in SO_3 ✓ **ALLOW** curly arrow from the ring **OR** from within the ring **mark 2** – curly arrow from **one** S=O double bond to the O (to produce a $S–O^-$) ✓ **ALLOW** curly arrow to any O in SO_3 **mark 3** – intermediate showing delocalisation over 5 carbons ✓ Intermediate must have correct SO_3^- structure **FULLY** displayed **DO NOT ALLOW** intermediate with broken ring less than halfway up in correct orientation:  **mark 4** – curly arrow from C–H bond reforming π- delocalised ring in benzene ✓ **Stand alone mark** **IGNORE** responses after **STEP 2**

Question			Answer	Mark	Guidance
					ALLOW Kekulé mechanism  **ALLOW** double bonds shown in other Kekulé arrangement
2	(c)	(i)	Various possibilities, eg:  ✓		**ALLOW** 1, 2, 3 or 4 Br atoms substituted on phenol ring at carbon atoms 2, 3, 5 or 6 **BUT** –OH must be in correct position shown **DO NOT ALLOW** O^- or ONa **ALLOW** for side chain: CH_3CONH but aromatic part of structure must be shown **IGNORE** any additional inorganic products in boxes (even if incorrect
			Reaction with Na  ✓	2	**ALLOW** ONa **OR** O^- as alternative to O^-Na^+ **DO NOT ALLOW** O–Na **OR** O^-Na (i.e. Na without charge) –ONa must be in correct position shown **ALLOW** for side chain: CH_3CONH but aromatic part of structure must be shown **IGNORE** any additional inorganic products in boxes (even if incorrect)

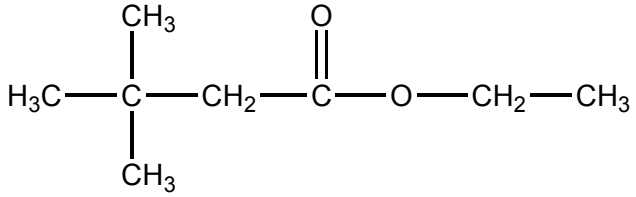
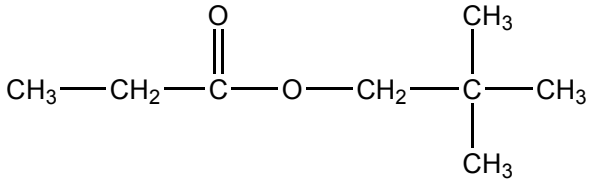
Question			Answer	Mark	Guidance
2	(c)	(ii)	**Hydrolysis with NaOH(aq)**  ✓  ✓ **Mark independently**	2	On **BOTH** structures, **ALLOW** ONa **OR** O^- as alternative to O^-Na^+ **DO NOT ALLOW** O–Na **OR** O^-Na (i.e. Na without charge) –ONa must be in correct position shown on 2nd structure **ALLOW** CH_3COONa/ CH_3CO_2Na **OR** CH_3COO^-/ $CH_3CO_2^-$ **ALLOW** one mark for carboxylic acid **AND** phenol, rather than sodium salts:  **ALLOW** NH_2–, CH_3– **IGNORE** any additional inorganic products in boxes (even if incorrect)
			Total	**15**	

Question			Answer	Mark	Guidance
3	(a)	(i)	One mark is for positive carbonyl test (Add) 2,4-dinitrophenylhydrazine **AND** orange/yellow/red precipitate ✓		**ALLOW** errors in spelling **ALLOW** 2,4(-)DNP **OR** 2,4(-)DNPH **ALLOW** Brady's reagent or Brady's Test **ALLOW** solid **OR** crystals **OR** ppt as alternatives for precipitate
			One mark is for negative aldehyde test **EITHER** (Add) Tollens' reagent/Tollens' test **AND** **no** change **OR no** reaction **OR no** silver (mirror)		**ALLOW** $AgNO_3/NH_3$ (Formulae must be correct) **OR** ammoniacal silver nitrate **ALLOW** Fehling's solution **OR** Benedict's solution **AND no** (brick-red) precipitate **ALLOW** any response that implies that nothing happens **ie no** change **OR no** reaction **OR no** silver (mirror) **ALLOW** 'the aldehyde/pentanal gives a silver mirror'
			OR (Add) H_2SO_4 **AND** $K_2Cr_2O_7$ **AND** **no** change **OR no** reaction **OR no** green colour ✓	2	**ALLOW** H^+ **AND** $Cr_2O_7^{2-}$ (Formulae must be correct) **ALLOW** any response that implies that nothing happens **IGNORE** responses using $NaBH_4$ (as no observations)
		(ii)	**1st mark** Take melting point of orange crystals/derivative/product from 2,4-DNP ✓ **2nd mark** Compare melting point with known values **OR** compare melting point with value in database/reference book ✓	2	**NOTE**: **a(ii)** is marked completely independently of **a(i)** **Mark independently of response for 1st mark** **DO NOT ALLOW** 1st or 2nd marks for taking and comparing boiling points **OR** chromatograms

Question			Answer	Mark	Guidance
3	(b)	(i)	**Synthesis 1**  ✓ Ester linkage **must** be fully displayed **Synthesis 2**  ✓  ✓	6	**NOTE: ALL** Structures **MUST** have Hs shown **IGNORE** bond angles **DO NOT ALLOW** more than one repeat unit **IGNORE** brackets and '*n*' **ALLOW** terminal O— on right (**OR** C=O on left), i.e.  **ALLOW** end bonds shown as ----- **DO NOT ALLOW** if structure has **no** end bonds

Question			Answer	Mark	Guidance
			Synthesis 3  ✓  ✓  ✓		**Mark each structure independently** HO– **must** be connected correctly on **BOTH** structures **DO NOT ALLOW** more repeat units **IGNORE** brackets and '*n*' **ALLOW** terminal O— on right (**OR** C=O on left), i.e.  **ALLOW** end bonds shown as ----- **DO NOT ALLOW** if structure has **no** end bonds **DO NOT ALLOW ECF** from wrong structure in previous boxes
3	(b)	(ii)	**Synthesis 1**: condensation **AND** **Synthesis 2**: addition **AND** **Synthesis 3**: condensation ✓	1	**All** three correct responses required for the mark
			Total	**11**	

Question			Answer	Mark	Guidance
4	(a)		$(CH_3CO)_2O + CH_3CH(OH)CH_3 \rightarrow CH_3COOCH(CH_3)_2 + CH_3COOH$ **1st mark** Correct structure of ester: $CH_3COOCH(CH_3)_2$✓ **2nd mark** Equation contains correct formulae for $(CH_3CO)_2O$, $CH_3CH(OH)CH_3$ **AND** CH_3COOH ✓	2	**ALLOW** correct structural **OR** displayed **OR** skeletal formula **ALLOW** combination of formulae as long as unambiguous **DO NOT ALLOW** molecular formulae **ALLOW** $(CH_3)_2CHOOCCH_3$ **OR** $(CH_3)_2CHOCOCH_3$
	(b)	(i)	(relative) solubility ✓	1	**IGNORE** partition **DO NOT ALLOW** adsorption **OR** absorption
		(ii)	The esters would have similar retention times **AND** similar structures/molecules **OR** same functional groups **OR** similar polarities **OR** similar solubilities ✓ Alcohol would have short retention time **AND** alkane would have long retention time ✓	2	**IGNORE** similar properties

Question			Answer	Mark	Guidance
4	(c)		**Elemental analysis and molecular formula – 2 marks** Use of percentages (to find EF) **AND** 144 ✓ Molecular formula = $C_8H_{16}O_2$ ✓	2 marks	***ANNOTATIONS MUST BE USED*** *Working* C : H : O = 66.63/12 : 11.18/1 : 22.19/16 5.5525 : 11.18 : 1.386875 4 : 8 : 1 Alternative method: carbon: (144 x 66.63/100)/12 = 8 hydrogen: (144 x 11.18/100)/1 = 16 oxygen: (144 x 22.19/100)/16 = 2
			ester structure – 4 marks  ✓✓✓✓	4 marks	**ALLOW** correct structural **OR** displayed **OR** skeletal formula **ALLOW** combination of formulae as long as unambiguous **NO ECF** from earlier structures If not fully correct award following marks: If structure an ester of formula $C_8H_{16}O_2$ **OR** the organic structure contains $C(CH_3)_3$ ✓ If structure is an ester of formula $C_8H_{16}O_2$ **AND** ester contains $C(CH_3)_3$ ✓✓ If structure is an ester of formula $C_8H_{16}O_2$ **AND** ester contains $O–CH_2C(CH_3)_3$ **AND** ester contains CH_3CH_2COO ✓✓✓ *i.e. If the ester link is reversed*  **IGNORE** any name

Question			Answer	Mark	Guidance
			NMR analysis – 4 marks Triplet (at *δ* 1.3) shows an adjacent CH_2 **OR** triplet (at *δ* 1.3) shows (C with) 2 adjacent Hs/protons ✓ *(because of splitting: so triplet)* Peak at (*δ*) 2.2 shows H adjacent to C=O **AND** adjacent to (C with) no hydrogens ✓ *(because of no splitting: so singlet)* Peak at (*δ*) 4.2 shows H–C–O **AND** adjacent CH_3 OR 3 adjacent Hs/protons ✓ *(because of splitting: so quartet)* Peak at (*δ*) 0.9 show 3 x CH_3 ✓ *(because of singlet and area 9)*	4 marks	**NOTE: Each peak can be identified from:** • its δ value: ± 0.2 ppm • a range, eg 'the peak between 2 and 3' • its relative peak area (CARE two peaks have an area of 2) • its splitting (CARE: two peaks are singlets) • labelling on the spectrum **----------** **QWC: triplet** must be spelled correctly **ALLOW** neighbouring Hs for adjacent to Hs For peak at (*δ*) 2.2 **ALLOW** singlet at (δ) 2.2 **ALLOW** singlet labelled 2 For peak at (*δ*) 4.2 **ALLOW** quartet (labelled 2) **----------** ***Check back for any responses added to spectra*** ***ADD ^ MARK TO THE SPECTRUM PAGE TO SHOW THAT IT HAS BEEN LOOKED AT***
			Total for 4(c)	10	
			Total	**15**	

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