

GCE

Chemistry A

Unit H432/02: Synthesis and analytical techniques

Advanced GCE

Mark Scheme for June 2018

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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.

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Annotations available in RM Assessor

Annotation	Meaning
~	Correct response
×	Incorrect response
	Omission mark
BOD	Benefit of doubt given
CON	Contradiction
RE	Rounding error
SF	Error in number of significant figures
ECF	Error carried forward
LI	Level 1
L2	Level 2
L3	Level 3
NBOD	Benefit of doubt not given
SEEN	Noted but no credit given
I	Ignore

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

Answers which are not worthy of credit
Statements which are irrelevant
Answers that can be accepted
Words which are not essential to gain credit
Underlined words must be present in answer to score a mark
Error carried forward
Alternative wording
Or reverse argument

Subject-specific Marking Instructions

INTRODUCTION

Your first task as an Examiner is to become thoroughly familiar with the material on which the examination depends. This material includes:

- the specification, especially the assessment objectives
- the question paper
- the mark scheme.

You should ensure that you have copies of these materials.

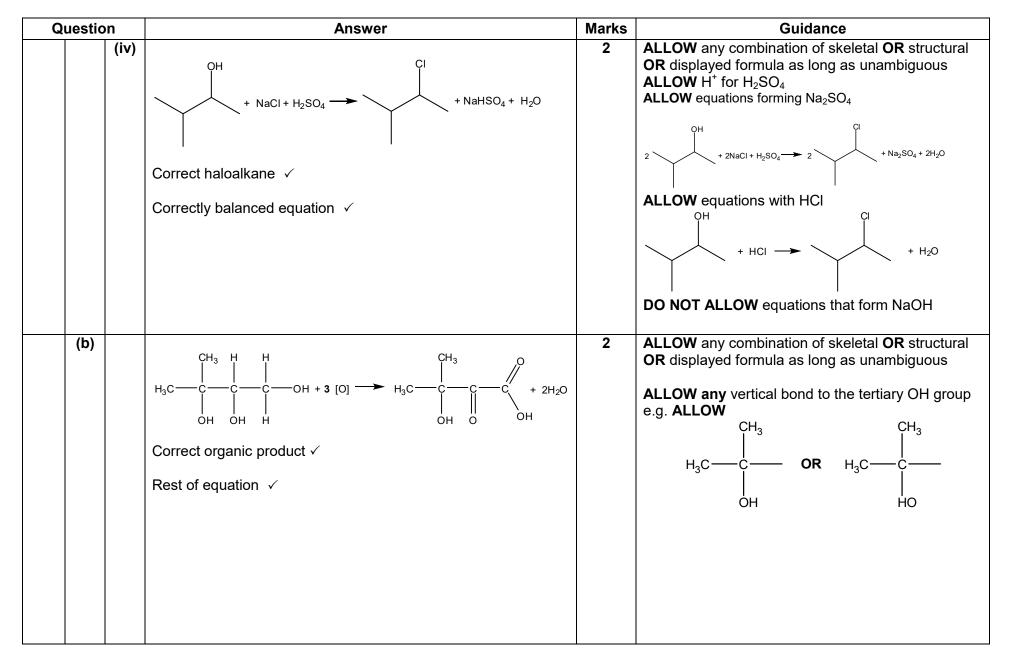
You should ensure also that you are familiar with the administrative procedures related to the marking process. These are set out in the OCR booklet **Instructions for Examiners**. If you are examining for the first time, please read carefully **Appendix 5 Introduction to Script Marking: Notes for New Examiners**.

Please ask for help or guidance whenever you need it. Your first point of contact is your Team Leader.

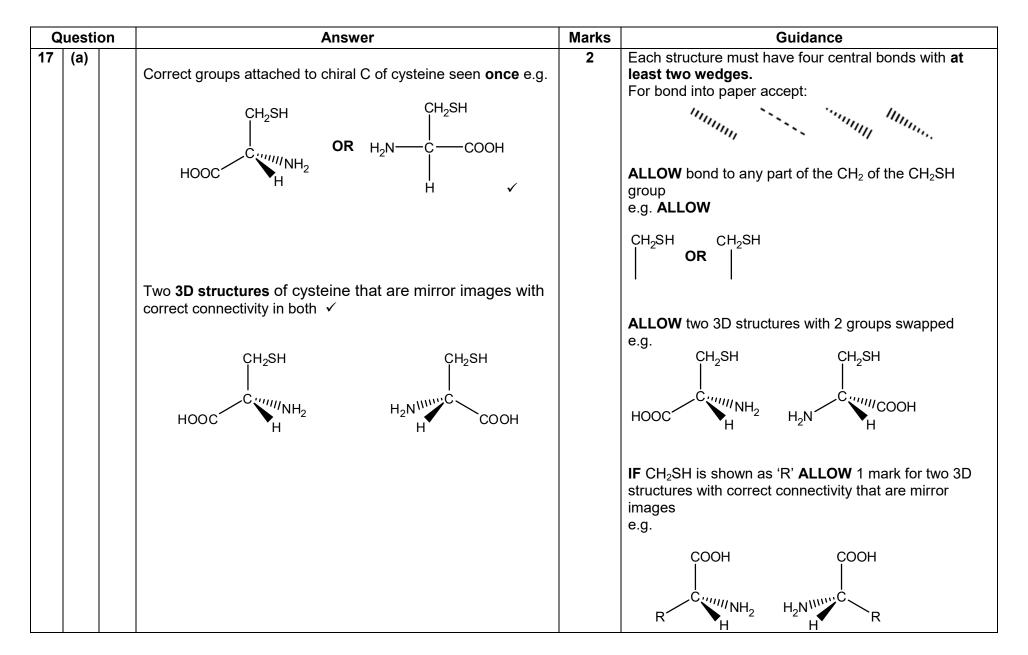
Question	Answer	Marks	Guidance
1	Α	1	
2	C	1	
3	В	1	
4	C	1	
5	В	1	
6	В	1	ALLOW 4 (This is the number of peaks in the NMR spectrum)
7	С	1	
8	D	1	
9	В	1	
10	С	1	
11	В	1	ALLOW 2 (This is the number of straight chain isomers with a chiral C atom)
12	С	1	
13	Α	1	
14	В	1	
15	В	1	
	Total	15	

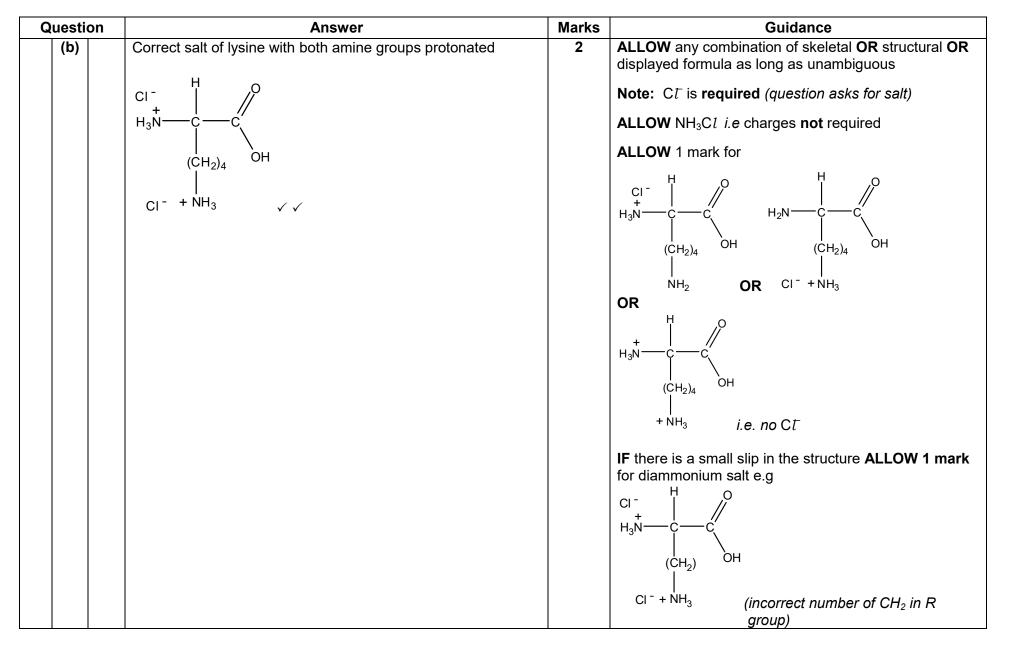
Mark Scheme

Ques	stion	Answer Ma		Guidance
16 (a	a) (i)	3-methylbutan-2-ol ✓	1	IGNORE lack of hyphens or addition of commas ALLOW 3-methylbutane-2-ol DO NOT ALLOW 2-methylbutan-3-ol OR 3-methylbut-2-ol OR 3-methbutan-2-ol OR 3-methybutan-2-ol OR 3-methybutan-2-ol
	(ii)	(CH ₃) ₂ CHCHOHCH ₃ ✓	1	ALLOW brackets around OH e.g. (CH ₃) ₂ CHCH(OH)CH ₃ ALLOW any unambiguous structural formula e.g. CH ₃ CH(CH ₃)CHOHCH ₃ CH ₃ CH(CH ₃)CH(CH ₃)OH
	(iii)	One mark for each correct structure.	2	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous ALLOW in either order



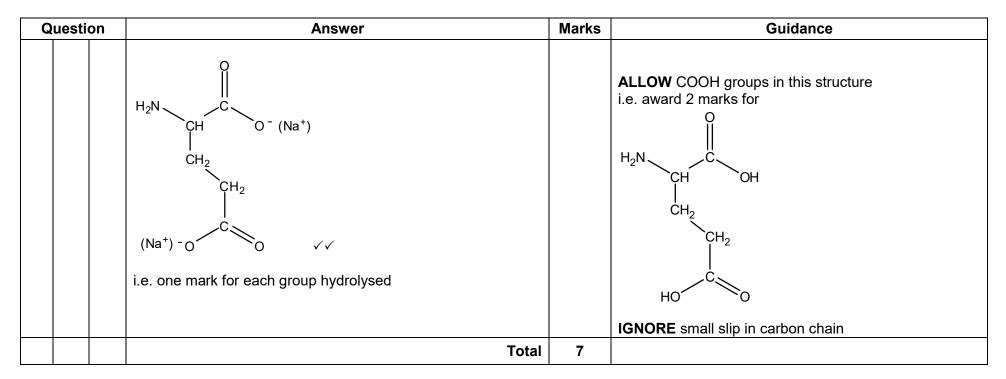
Question	Answer	Marks	Guidance
(c)	Product from excess CH ₃ OH/H ₂ SO₄ H ₃ COOC	3	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous e.g OOC IGNORE connectivity in each product ALLOW the <i>E</i> or <i>Z</i> isomer as product from excess CH ₃ OH/H ₂ SO ₄
	Product from steam, H_3PO_4 HOOC \downarrow COOH \downarrow OH \checkmark		
	H COOH HOOC COOH H COOH HOOC COOH C C H C H H HOOC H HOOC H H		'End bonds' MUST be shown (do not have to be dotted) IGNORE brackets IGNORE <i>n</i> ALLOW more than one repeat unit but has to be a whole number of repeat units
	Total	11	





Question	Answer	Marks	Guidance
			OR CI^{-} $H_{3}N^{-}$ C^{-} C^{-} O $(CH_{2})_{4}$ OH $CI^{-} + NH_{3}$ (H missing from α C atom)
(c)	$HO - CH_2 + HO - CH_2 + HO - CH_2 + HO - CH_2 + CH - CH$	3	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous IGNORE NH ₃ (question asks for organic products) ALLOW $-COO^-$ OR $-COONa$ DO NOT ALLOW negative charge on C atom DO NOT ALLOW negative charge on C atom DO NOT ALLOW $-COO-Na$ (covalent bond) BUT ALLOW ECF if seen in subsequent structures DO NOT ALLOW COOH in this structure DO NOT ALLOW (sodium) salt of alcohol group i.e. $-O - CH_2 - CH_2$

Mark Scheme



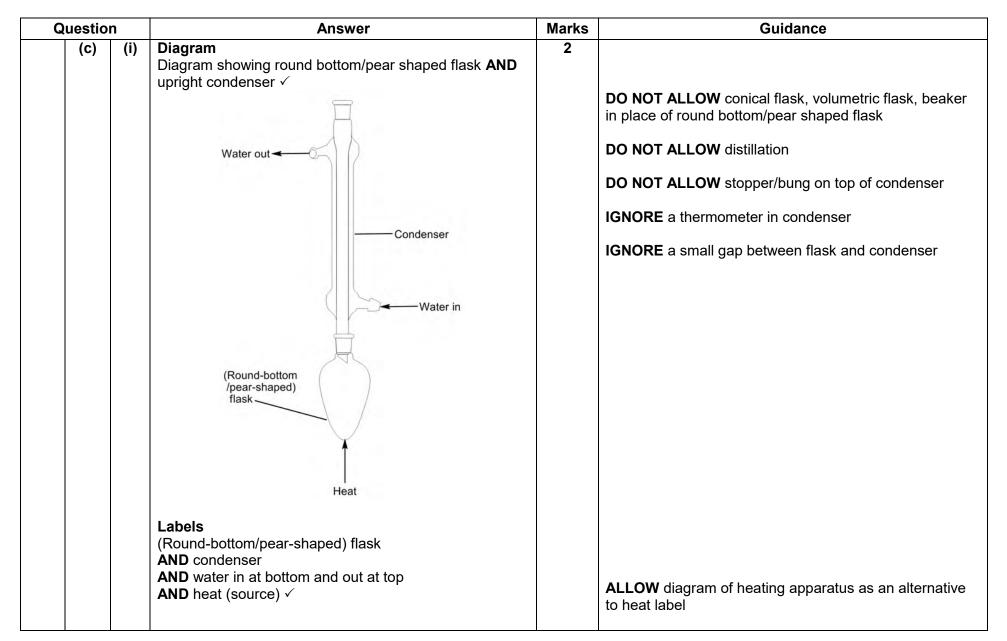
Questi	on	Answer		Guidance	
18 (a)	(i)	Number of peaks2 marks2-nitrophenol AND 3-nitrophenol have six peaks/environments/types of carbon ✓4-nitrophenol has four peaks/environments/types of carbon ✓Statement1 mark4-nitrophenol can be distinguished OR 2-nitrophenol and 3-nitrophenol cannot be distinguished with the statement of th	3	IGNORE any numbers shown on structures ALLOW 1 mark only IF a response identifies that all the compounds have 6 peaks/environments/types of C OR all the compounds have 4 peaks/environments/ types of carbon IGNORE chemical shifts DO NOT ALLOW ECF from an incorrect number of	
	(ii)	 (In phenol) a (lone) pair of electrons on O is(partially) delocalised/donated into the π-system / ring ✓ Electron density increases/is higher (than benzene) ✓ ORA (phenol) is more susceptible to electrophilic attack OR (phenol) attracts/accepts electrophile/HNO₃ more OR (phenol) polarises electrophile/HNO₃ more ✓ ORA 	3	peaks/environments/types of carbon ALLOW the electron pair in the p-orbitals of the O atom becomes part of the π -system / ring ALLOW diagram to show movement of lone pair into ring ALLOW lone pair of electrons on O is (partially) drawn/attracted/pulled/ into π -system / ring IGNORE activating IGNORE charge density IGNORE electronegativity IGNORE phenol reacts more readily (<i>no reference to</i> <i>electrophile</i>) ALLOW NO ₂ ⁺ for electrophile	

Question	Answer	Marks	Guidance
	Curly arrow from π -bond to S in SO ₃ AND curly arrow from the S=O bond to O atom \checkmark \bigcirc_{H_3} $\bigcirc_{S_4}^{H_5}$	3	ANNOTATE WITH TICKS AND CROSSES NOTE: curly arrows can be straight, snake-like, etc. but NOT double headed or half headed arrows 1st curly arrow must • go to the S of SO ₃ AND • start from, OR close to circle of benzene ring \overrightarrow{O} \overrightarrow{O} \overrightarrow{O} \overrightarrow{O} \overrightarrow{O} 2nd curly arrow must start from, OR be traced back to, any part of S=O bond and go to O \overrightarrow{S} \overrightarrow{S} \overrightarrow{S} \overrightarrow{S} ALLOW 2nd curly arrow from S=O to any O in SO ₃
			Intermediate must have correct SO ₃ ⁻ structure fully displayed

Question	Answer	Marks	Guidance
	Correct intermediate \checkmark Curly arrow from C-H bond to reform π -ring \checkmark		DO NOT ALLOW the following intermediate: \downarrow + + + + + + + + + + + + + + + + + + +
		Total 9	

Q	uestion	Answer	Marks	Guidance
19	(a)	Links rate of reaction to strength of bond/bond enthalpy ✓ e.g. the weaker the bond the faster the reaction stronger bond takes longer to break lower bond enthalpy reacts faster	2	Each marking point must be a comparison
		Correct comparison of rate of reaction for at least two C– Hal bonds e.g. C–F bond is hydrolysed slow est C–I bond is hydrolysed faster than C–Br C–Br has shorter reaction time than C–CI OR		IGNORE references to halogens as elements: <i>i.e.</i> chlorine is less reactive than bromine etc. DO NOT ALLOW chloride, bromide and iodide
		Correct comparison of C–Hal bond strength/enthalpy of at least two of C–Hal bonds e.g. C–I bond is the weak est C–I has lower bond enthalpy than C–Br C–Br is broken more easily/readily than C–CI C–Hal bond strength decreases down group (7) ✓		IGNORE references to bond length, polarity and electronegativity

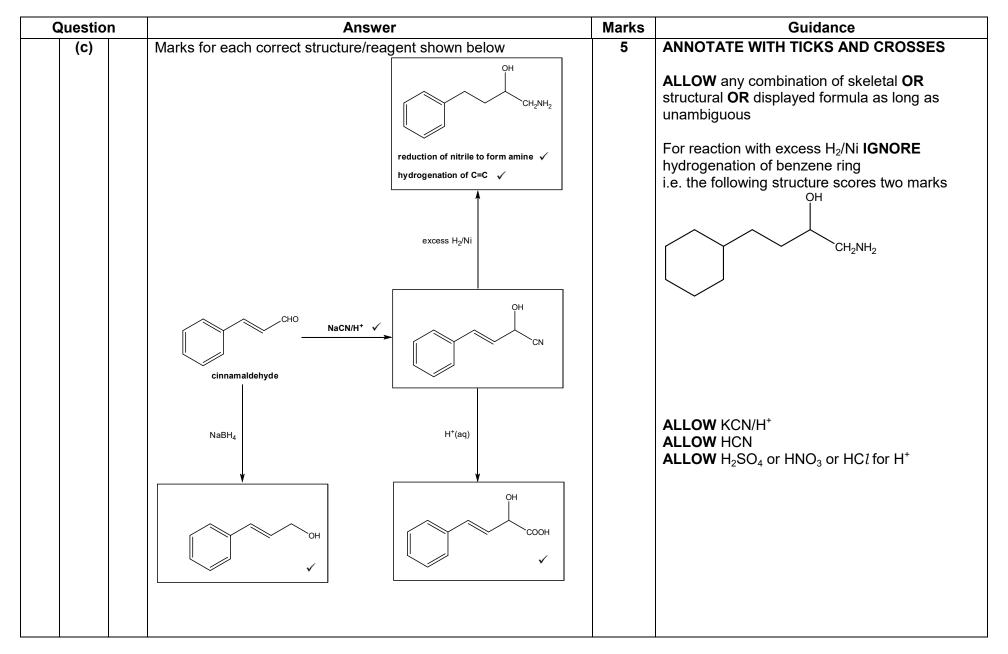
Question	Answer	Marks	Guidance
Question (b)	AnswerCurly arrow from HO ⁻ to carbon atom of C–CI bond \checkmark Dipole shown on C–CI bond, C^{δ^+} and Cl^{δ^-} AND curly arrow from C–CI bond to CI atom \checkmark $\overbrace{OH^-}$ IGNORE presence of Na ⁺ but OH ⁻ needed i.e. Na ⁺ OH ⁻ can be allowed if criteria metCorrect organic product AND Cl ⁻ \checkmark IGNORE presence of Na ⁺ but Cl ⁻ needed i.e. Na ⁺ OH ⁻ can be allowed 	Marks 3	Guidance ANNOTATE ANSWER TICKS AND CROSSES NOTE: curly arrows can be straight, snake-like, etc. but NOT double headed or half headed arrows 1st curly arrow must • go to the C of C-Cl AND • start from, OR be traced back to any point across width of lone pair on O of OH ⁻ • OR start from - charge on O of ⁻ OH ion • OR start from - charge on O of ⁻ OH ion • OH OH OH • OH Curly arrow must start from, OR be traced back to, any part of C-Cl bond and go to Cl



Question	Answer	Marks	Guidance
(c) (ii)	Precipitate G 1 mark silver bromide/AgBr AND $M = 1.88/0.01 = 188 \text{ (g mol}^{-1})$ 188 - 107.9 = 80.1 (so halide is Br ⁻)/	3	 ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous Note: working is required for first mark ALLOW use of 108 as A_r of Ag
	Alcohol F and Haloalkane E 2 marks		
	E and F clearly identified F/alcohol: butan-2-ol H OH $H_{3}C - C - C - CH_{3}$ H H		Note: E and F can be identified by correct name or structure BUT IGNORE incorrect names
	 E/haloalkane: E is haloalkane of C₄H₉X with same halogen as G AND same carbon chain as F ✓ 		
	Total	10	

0	Questio	n	Answer	Marks	Guidance
20	(a)		priority groups/atoms are on different/opposite sides \checkmark High(est) priority groups are C ₆ H ₅ AND CHO OR Lowest priority groups are H and CH ₃ \checkmark	2	 ALLOW suitable alternatives to 'priority' e.g. groups with highest atomic number or more important groups etc. ALLOW high priority groups are diagonal(ly across) IGNORE references to relative mass of groups, <i>A</i>_r, <i>M</i>_r, ALLOW identification by name e.g aldehyde for CHO phenyl/benzene group for C₆H₅ alkyl for CH₃ ALLOW response in terms that O has higher priority than H in context of –CH₃ and –CHO IF 'priority' is not mentioned ALLOW 1 mark for
	(b)	(i)	Bromine/ Br₂ AND goes colourless/decolourised ✓	1	 'C₆H₅ and CHO are on different sides' OR H and CH₃ are on different sides Note: both reagent and observation are required ALLOW bromine water/ Br₂(aq)
		(ii)	Tollens' (reagent) AND Silver (mirror/precipitate/ppt/solid) ✓	1	 Note: both reagent and observation are required for the mark. ALLOW ammoniacal silver nitrate OR Ag⁺/NH₃ ALLOW black ppt OR grey ppt

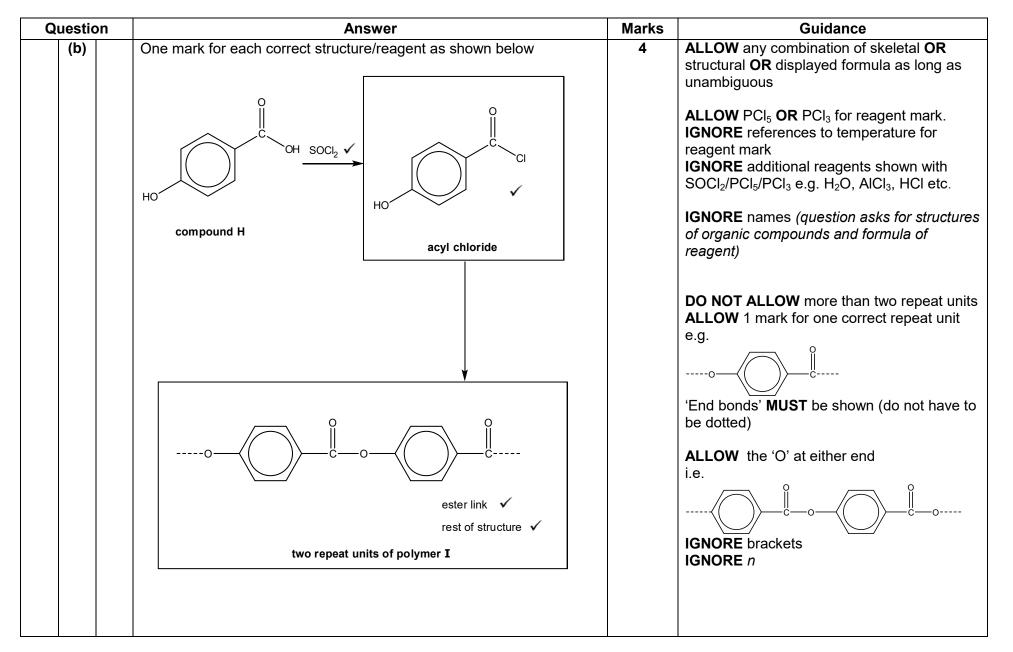
Question	Answer	Marks	Guidance
(iii)	(Add) 2,4-dinitrophenylhydrazine AND orange/yellow/red precipitate√	3	ALLOW errors in spelling ALLOW 2,4(-)DNP OR 2,4(-)DNPH ALLOW Brady's reagent or Brady's Test ALLOW solid OR crystals OR ppt as alternatives for precipitate
	Take melting point (of crystals) ✓ Compare to known values/database ✓		Mark second and third points independently of response for first marking point DO NOT ALLOW 2 nd and 3 rd marks for taking and comparing boiling points OR chromatograms



Question	Answer	Marks	Guidance
(d)*	Please refer to marking instructions on page 5 of mark scheme for guidance on how to mark this question. Level 3 (5–6 marks) An outline of the mechanism for the formation of either product which is mostly correct. AND Major and minor products identified with a correct explanation of which product is most/least likely to be formed. There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated. Level 2 (3–4 marks) An outline of the mechanism for the formation of either product but with a few omissions/errors. AND Identifies major/minor product correctly OR Explanation of which product is most/least likely to be formed. There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence. Level 1 (1–2 marks) A basic outline of the mechanism for the formation of either product is attempted. OR Basic explanation of which of the products is most/least likely to be formed. There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.	6	Please check all of page 23 which is included with this response. If this page is blank please annotate with SEEN Throughout: ALLOW correct structural OR displayed OR skeletal formulae OR a combination of above if unambiguous Indicative scientific points: <u>Mechanism for formation of either product.</u> • Curly arrow from C=C to attack the I atom of the I-C1 • Curly arrow from I-C1 • Curly arrow from I-C1 • Curly arrow from I-C1 • Curly arrow from negative charge on carbon atom • Curly arrow from negative charge on C1 ⁻ or lone pair on C1 ⁻ to carbon atom with positive charge $ \stackrel{+}{ (- + + + + + + + + + + + + + + + + + +$

Question	Answer	Marks	Guidance
Question	Answer 0 marks No response or no response worthy of credit.	Marks	Guidance Organic products Anjor/most likely product Image: Colspan="2">CHO Image: Colspan="2">COLSPANE" Colspan="2">CHO Image: Colspan="2">COLSPANE" Colspan="2">C
		Total 18	OR the – I is attached to the carbon atom with most hydrogens attached

Q	uestio	n Answer	Marks	Guidance
21	(a)	Product from Na ₂ CO ₃ $\downarrow \qquad \qquad$	3	 ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous ALLOW -COO⁻ OR -COONa DO NOT ALLOW negative charge on C atom DO NOT ALLOW -COO-Na (covalent bond) IGNORE connectivity of phenol OH group (marks are for correct conversions)
		Product from NaOH(aq) O O O $O^{-}(Na^{+})$ $(Na^{+})^{-}O$		ALLOW 1 mark if top two structures are shown in wrong boxes
		Product from Br ₂ Br e.g. HO		 ALLOW substitution of any H from benzene ring ALLOW multiple substitution, <i>i.e.</i> di-, tri- and tetrabromo products. IGNORE connectivity of phenol OH group (marks are for correct conversions)



Question	Answer	Marks	Guidance
Question (C) (i		Marks 2	If there is an alternative answer, Apply ECF Alternative method [K] in g dm ⁻³ with peak area of 5.9 $9.13 \times 10^{-2} \times \frac{5.9}{4.3}$ OR $9.13 \times 10^{-2} \times 1.37$ $= 0.125$ OR 0.13 (g dm ⁻³) \checkmark Calculator: 0.125272093 [L] in mol dm ⁻³ $\frac{0.125}{166} = 7.5 \times 10^{-4}$ OR $\frac{0.13}{166} = 7.8 \times 10^{-4}$ (mol dm ⁻³) \checkmark Common errors: Award 1 mark for: • 0.099(from $\frac{9.13 \times 10^{-2}}{166} \times 180$) • 6.9 $\times 10^{-4}$ (from $\frac{0.125}{180}$)
			• 7.2×10^{-4} (from $\frac{0.13}{180}$) • 7.0×10^{-4} (from $\frac{0.25272093}{180}$)

Question	Answer	Marks	Guidance
Question (ii)	ester J HO H	Marks 3	Guidance ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous L and M can be identified either way round IGNORE 'C ₃ H ₇ ' in L and/or M as ambiguous (question requires structures) IGNORE connectivity of phenol OH group (marks are for structures of alkyl groups)
	но		
	Total	12	

Q	Question	Answer	Marks	Guidance
22	(a)	$C_7H_{16} + 7^1/_2O_2 \rightarrow 7CO + 8H_2O$ OR $C_7H_{16} + 4O_2 \rightarrow 7C + 8H_2O \checkmark$	1	ALLOW multiples IGNORE state symbols ALLOW equations for incomplete combustion that give CO and/or C with CO ₂ e.g C ₇ H ₁₆ + 9O ₂ \rightarrow 4CO + 3CO ₂ + 8H ₂ O C ₇ H ₁₆ + 6O ₂ \rightarrow 4CO + 3C + 8H ₂ O
	(b)	Heptane compared to hexane heptane (has a longer chain so) has more points of contact / more surface interaction (between molecules) ✓	4	ANNOTATE WITH TICKS AND CROSSES ALLOW ORA throughout
		heptane has stronger/more induced dipole(–dipole) interactions \checkmark		ALLOW heptane has more electrons IGNORE IDID
		Pentan-1-ol compared to heptane and/or hexane pentan-1-ol has hydrogen bonds that are strong(er than induced dipole–dipole interactions) OR		ALLOW stronger/more London forces IGNORE van der Waals' forces/VDW for induced dipole– dipole interactions (<i>ambiguous as this term refers to both</i> <i>permanent dipole–dipole interactions and induced</i> <i>dipole–dipole interactions</i>)
		 (alcohols have) hydrogen bonds and induced dipole(-dipole) interactions/London forces ✓ Energy required to break forces 		IGNORE 'pentan-1-ol can form hydrogen bonds with water'
		More energy is required to break induced dipole(–dipole) interactions in heptane than hexane OR More energy is required to break hydrogen bonds ✓		 ALLOW 'more energy to break intermolecular forces' if intermolecular forces are not stated. IGNORE it is harder to break the intermolecular forces <i>no reference to energy</i>) IGNORE more energy needed to separate molecules IGNORE more energy is needed to break bonds

Question	Answer	Marks	Guidance
(c) (i)	<i>n</i> (CO ₂) = 2.97/44 = 0.0675 (mol) √	5	Consult your team leader if an alternative creditworthy approach is seen
	<i>n</i> (H ₂ O) = 1.62/18 = 0.0900 (mol)√ Ratio of C : H 3 : 8 √		IGNORE ratio of CO_2 to H_2O is 3:4 ALLOW this mark from the correct molecular formula OR a correct structure if not shown in working
	Molecular formula C₃H ₈ O₂√		DO NOT ALLOW an incorrect molecular formula
	Structure any correct structure of $C_3H_8O_2 \checkmark$ e.g. HO C C C C OH HO H H H H H H H OR H C C OC C OH H H H H H H H H H H H H H H		Mark independently from molecular formula but structure MUST contain 3C, 8H and 2O ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous ALLOW any vertical bond to the OH group e.g. ALLOW $\mid OR \mid OR \mid OH$ DO NOT ALLOW OH–

Mark Scheme

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Question	Answer	Marks	Guidance
Question (c) (ii)	Answer $HO \longrightarrow OH + HO \longrightarrow OO + HO \longrightarrow OO + H_2O$ Carbonyl compound identified as propanone \checkmark Rest of equation \checkmark	Marks 2	Guidance ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous

Question	Answer	Marks	Guidance
(d)*	Please refer to the marking instructions on page 5 of this mark scheme for guidance on how to mark this question.	6	Indicative scientific points: Empirical and Molecular Formula
	Level 3 (5–6 marks) Compound is a structure of $C_6H_{12}O_3$ that is consistent with splitting pattern and chemical shifts in NMR spectrum. AND		• $C: H: O = 54.54/12 : 9.10/1 : 36.36/16$ 4.545 : 9.10 : 2.273 2 : 4 : 1
	Comprehensive reasoning with most of the data analysed. There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.		 Empirical formula = C₂H₄O uses <i>m/z</i> = 132.0 to determine molecular formula as C₆H₁₂O₃
	 Level 2 (3–4 marks) Compound has a feasible chemical structure that is consistent with the splitting pattern in NMR spectrum but may have incorrect molecular formula. AND Reasoning provided with some of the data analysed. There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence. Level 1 (1–2 marks) Correct determination of empirical formula and/or molecular 		1 H NMR analysisSpectrum:• $\delta = 4.0$ ppm, quartet, 1H, CH_3 -CH-O• $\delta = 1.3$ ppm, singlet, 6H, $(CH_3)_2$ -C• $\delta = 1.2$ ppm, doublet, 3H, CH_3 -CH-Without D ₂ O:• Peak at 11.0 ppm COOH or OH• peak at 3.6 ppm OHNote: Data Sheet shows O-H chemical shift can occur around 11.0 ppm
	formula. OR Analyses most of the NMR data. OR Attempts to determine empirical and/or molecular formula AND analyses some of the NMR data. There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.		Structure ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous Contains

Question	Answer	Marks	Guidance
	0 marks No response or no response worthy of credit.		• region that gives doublet and quartet e.g. H C C C H C C C • region that gives singlet e.g. C C C C C C C C C C C C C C C
			Examples of structures consistent with splitting and chemical shift in NMR $H_3C - C - C - C - C - C - C - C - C - C -$

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C	Question		Answer	Marks	Guidance
					$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$
					$H_{3C} O - C - CH_{3}$ $H_{3C} O - C - CH_{3}$ $H_{3C} O - C - CH_{3}$
					СН ₃ ОН H ₃ CСОН ОСН
					CH ₃ Note: there may be other possible structures that are consistent with the splitting pattern and chemical shifts in NMR – if an alternative structure is seen, please contact your team leader
			Total	18	

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