

GCE

Chemistry A

H432/02: Synthesis and analytical techniques

Advanced GCE

Mark Scheme for Autumn 2021

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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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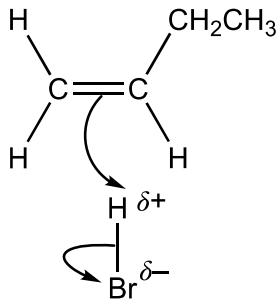
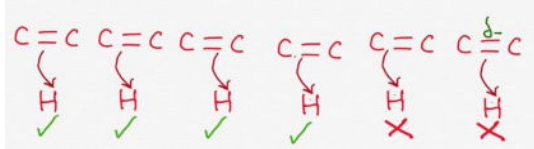
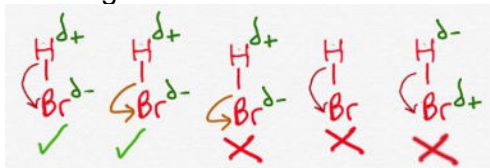
1. Annotations

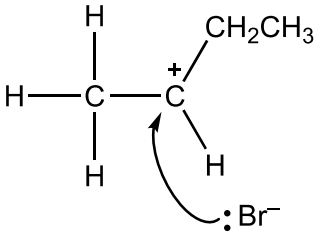
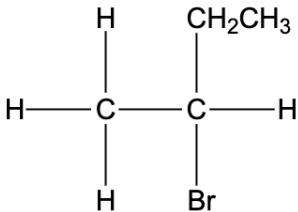
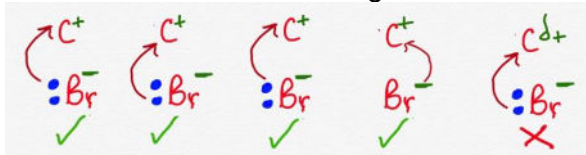
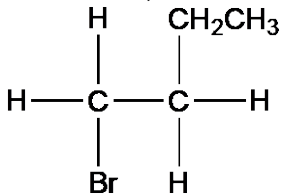
Annotation	Meaning
	Correct response
	Incorrect response
	Omission mark
	Benefit of doubt given
	Contradiction
	Rounding error
	Error in number of significant figures
	Error carried forward
	Level 1
	Level 2
	Level 3
	Benefit of doubt not given
	Noted but no credit given
	Ignore

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

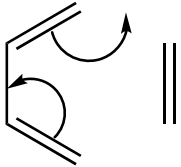
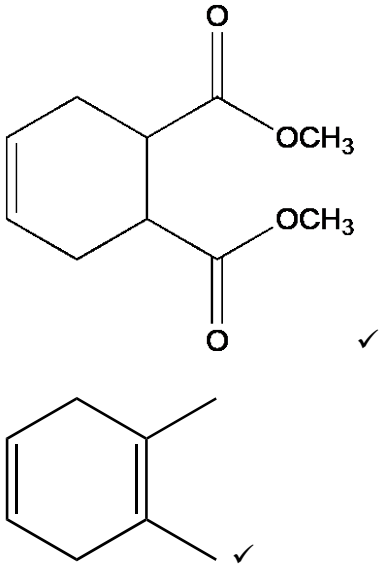
Annotation	Meaning
DO NOT ALLOW	Answers which are not worthy of credit
IGNORE	Statements which are irrelevant
ALLOW	Answers that can be accepted
()	Words which are not essential to gain credit
—	Underlined words must be present in answer to score a mark
ECF	Error carried forward
AW	Alternative wording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

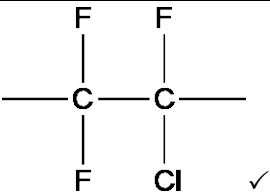
Question	Answer	Marks	AO element	Guidance
1	C	1	AO2.1	ALLOW 4 (This is the number of structural isomers)
2	B	1	AO1.2	
3	C	1	AO2.2	
4	C	1	AO2.6	
5	D	1	AO2.1	
6	B	1	AO1.2	
7	A	1	AO1.2	
8	C	1	AO2.1	
9	C	1	AO1.2	
10	A	1	AO2.1	
11	D	1	AO2.5	
12	B	1	AO2.1	
13	B	1	AO2.1	
14	C	1	AO1.1	
15	A	1	AO1.2	
	Total	15		

Question			Answer	Marks	AO element	Guidance
16	(a)	(i)	σ -bond: Overlap of orbitals between (bonding) atoms ✓ π -bond: Sideways overlap of (adjacent) p-orbitals ✓	2	AO1.1 ×2	ALLOW labelled diagrams IGNORE the type of orbital for σ -bond DO NOT ALLOW pi-orbital
		(ii)	σ -bonds: 9 ✓ π -bonds: 2 ✓	2	AO1.2 ×2	
	(b)	(i)	 Curly arrow from C=C bond to H of H-Br ✓ DO NOT ALLOW partial charge on C=C Correct dipole shown on H-Br AND curly arrow showing breaking of H-Br bond ✓	4	AO1.2 ×2 AO2.5 ×2	NOTE: curly arrows can be straight, snake like, etc. but NOT double headed or half headed arrows 1st curly arrow must - go to the H atom of H-Br AND - start from, OR be traced back to any point across width of C=C  2nd curly arrow must - start from, OR be traced back to any part of $\delta^+ \text{H}-\text{Br}^{\delta-}$ bond AND - go to $\text{Br}^{\delta-}$ 

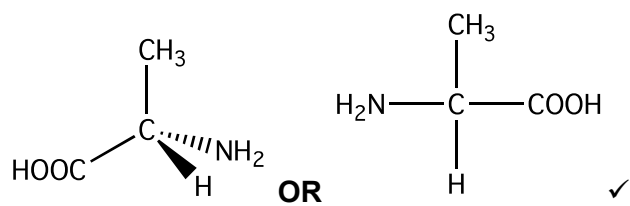
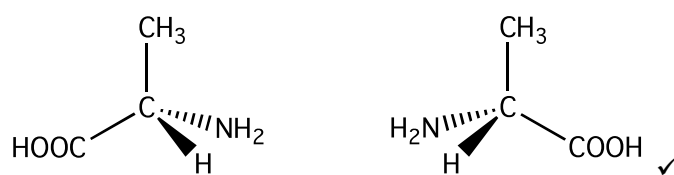
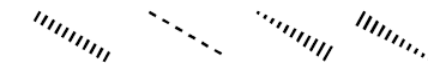
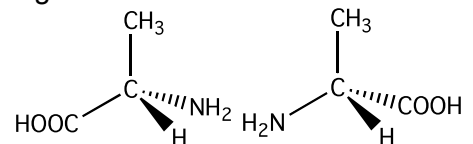
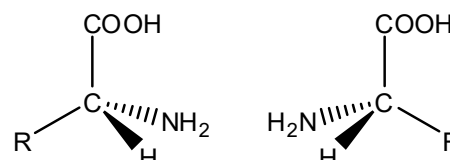
Question	Answer	Marks	AO element	Guidance
	Correct carbocation AND curly arrow from Br⁻ to C⁺ of carbocation ✓ DO NOT ALLOW δ⁺ on C of carbocation  Correct product ✓ 			3rd curly arrow must - go to the C⁺ of carbocation AND - start from, OR be traced back to any point across width of lone pair on :Br⁻ OR start from – charge of Br⁻ ion  (Lone pair NOT needed if curly arrow shown from – charge of Br⁻ ion) ALLOW ECF for product from incorrect carbocation, i.e.  IF Br₂ is used instead of HBr contact your Team Leader

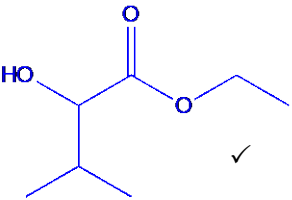
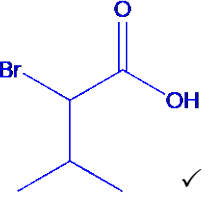
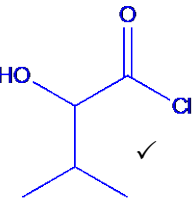
Question			Answer	Marks	AO element	Guidance
		(ii)	(major product forms from) most/more stable intermediate/carbocation ✓ (major product forms from a) secondary carbocation OR carbocation bonded to more C atoms / more alkyl groups OR carbocation bonded to fewer H atoms ✓	2	AO1.1 AO1.2	For carbocation, ALLOW carbonium ion or cation IGNORE descriptions of the major/minor product in terms of Markownikoff's rule e.g. H atom joins to C with most H IGNORE references to stability of the product ALLOW ORA, i.e. (minor product forms from) least/less stable intermediate/carbocation ✓ (minor product forms from a) primary carbocation OR carbocation bonded to less C atoms / less alkyl groups OR carbocation bonded to more H atoms ✓
		(iii)	3 ✓	1	AO1.2	
	(c)	(i)	Same structural formula AND Different arrangement (of atoms) in space OR different spatial arrangement (of atoms) ✓	1	AO1.1	ALLOW structure/displayed/skeletal formula DO NOT ALLOW same empirical formula OR same general formula IGNORE same molecular formula Reference to <i>E/Z</i> isomerism or optical isomerism is not sufficient
		(ii)	Student is not correct AND 2 groups on one carbon atom (of C=C) are the same OR C–C bond can rotate ✓	1	AO3.1	DO NOT ALLOW one side of C=C

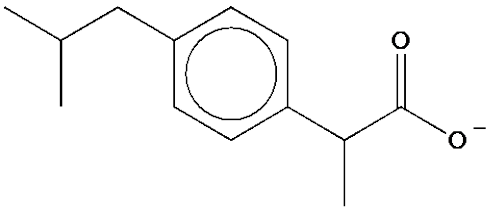
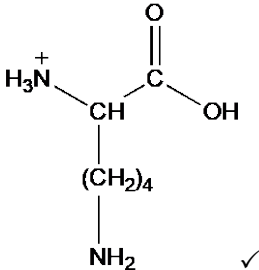
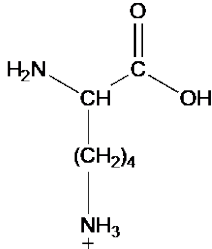
Question			Answer	Marks	AO element	Guidance
	(d)	(i)	 1 mark for each curly arrow ✓✓	2	AO2.5 ×2	IGNORE any dipoles shown NOTE: curly arrows can be straight, snake-like, etc. but NOT half headed or double headed arrows Curly arrow from C=C bond must start from, OR be traced back to, Lower left: any part of C=C bond and go to C–C Upper left: any part of C=C bond and go to gap between C=C and C=C
		(ii)		2	AO3.2 ×2	
			Total	17		

Question			Answer	Marks	AO element	Guidance
17	(a)		Formation of Cl• $\text{CClF}_3 \rightarrow \text{CF}_3\cdot + \text{Cl}\cdot \checkmark$ Breakdown of O₃ $\text{Cl}\cdot + \text{O}_3 \rightarrow \cdot\text{ClO} + \text{O}_2 \checkmark$ $\cdot\text{ClO} + \text{O} \rightarrow \text{Cl}\cdot + \text{O}_2 \checkmark$	3	AO2.5 AO1.1 ×2	IGNORE dots for formation Cl•, i.e. ALLOW $\text{CClF}_3 \rightarrow \text{CF}_3 + \text{Cl}$ DO NOT ALLOW ECF Dots required in this equation IGNORE $\text{O} + \text{O}_3 \rightarrow 2\text{O}_2$ ALLOW 1 mark if both equations are correct by atom but dot(s) missing or incorrect
	(b)	(i)		1	AO2.5	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous 'End bonds' MUST be shown DO NOT ALLOW more than 1 repeat unit IGNORE brackets IGNORE <i>n</i>
		(ii)	More points of contact / more surface interaction (between molecules) AND Stronger/more dipole(–dipole) interactions $\checkmark$ More energy needed to break the intermolecular forces $\checkmark$	2	AO2.1 ×2	Both answers need to be a comparison IGNORE surface area ALLOW more electrons ALLOW induced/permanent dipole interactions ALLOW London forces ALLOW van der Waals' forces (as permanent dipole-dipole and induced dipole-dipole interactions are present within this polymer) IGNORE IDID

Question		Answer	Marks	AO element	Guidance
(c)		$\begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{H} \\ & & & \\ \text{H}_2\text{N}-\text{C}-\text{C}-\text{C}-\text{C}-\text{NH}_2 \\ & & & \\ \text{H} & \text{H} & \text{H} & \text{H} \end{array}$ ✓ ✓ Amide link: ✓ 1 repeat unit of correct polymer: ✓	4	AO2.5 ×2 AO1.2 AO2.5	For polymer, DO NOT ALLOW > 1 repeat unit 'End bonds' MUST be shown (do not have to be dotted) ALLOW –NH– at either end i.e. IGNORE brackets IGNORE <i>n</i>
Total			10		

Question			Answer	Marks	AO element	Guidance
18	(a)	(i)	Non-superimposable mirror images (about a chiral centre) ✓	1	AO1.1	
		(ii)	Correct groups attached to chiral C of alanine seen once e.g.  Two 3D structures of alanine that are mirror images AND correct connectivity in both i.e. 	2	AO2.1 × 2	Each structure must have four central bonds with at least two wedges. For bond into paper accept:  ALLOW two 3D structures with 2 groups swapped e.g.  IF CH₃ is shown as 'R' ALLOW 1 mark for two 3D structures with correct connectivity that are mirror images e.g. 

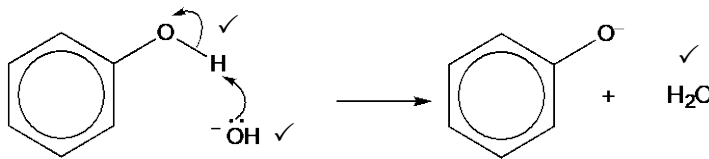
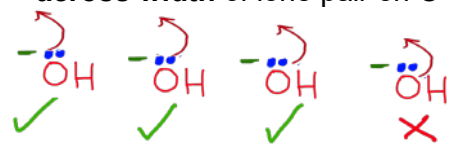
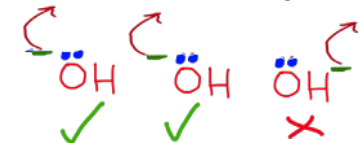
Question	Answer	Marks	AO element	Guidance
(iii)	4 ✓	1	AO2.2	
(b)	 ester C₇H₁₄O₃ H⁺/H₂O OR H⁺(aq) OR HCl(aq) ✓ C₅H₁₀O₃ H₂O ✓ NaBr/Br⁻ AND H₂SO₄/H⁺ ✓  haloalkane C₅H₉BrO₂ NH₃ AND ethanol OR excess NH₃ ✓ valine  acyl chloride C₅H₉O₂Cl	7	AO1.2 × 4 AO2.5 × 3	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous ALLOW names of reagents DO NOT ALLOW OH⁻ for HO⁻ but ALLOW ECF for subsequent use in (b) For hydrolysis, ALLOW dilute acid ALLOW alkaline conditions followed by protonation of carboxylate i.e. NaOH(aq)/OH⁻(aq) AND H⁺(aq)/HCl(aq) ALLOW HBr for NaBr/H₂SO₄

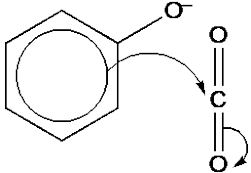
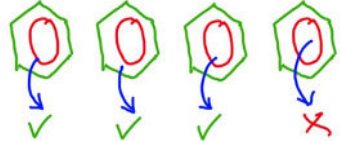
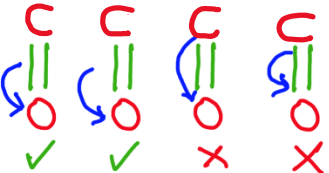
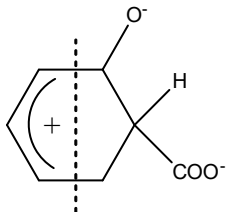
Question			Answer	Marks	AO element	Guidance
	(c)	(i)	$C_{13}H_{18}O_2$ ✓	1	AO2.1	ALLOW C, H and O in any order
		(ii)	FIRST CHECK ANSWER ON THE ANSWER LINE If answer = 1.17×10^{21} award 3 marks $M(\text{ibuprofen}) = 206$ ✓ $n(\text{ibuprofen}) = \frac{400 \div 1000}{206} = 1.94 \times 10^{-3} \text{ (mol)}$ ✓ Number of molecules = $1.94 \times 10^{-3} \times 6.02 \times 10^{23}$ = 1.17×10^{21} to 3 SF ✓	3	AO2.2 × 3	ALLOW ECF from (c)(i) Calculator: $1.941747573 \times 10^{-3}$ ALLOW ECF from $n(\text{ibuprofen})$ 3 SF essential
	(d)	(i)	 ✓  ✓	2	AO3.2 × 2	IGNORE small slip in carbon chains ALLOW 
		(ii)	More soluble in water ✓	1	AO3.1	Answer must be a comparison ALLOW dissolve faster/quicker IGNORE absorbed more quickly (given in question)
			Total	18		

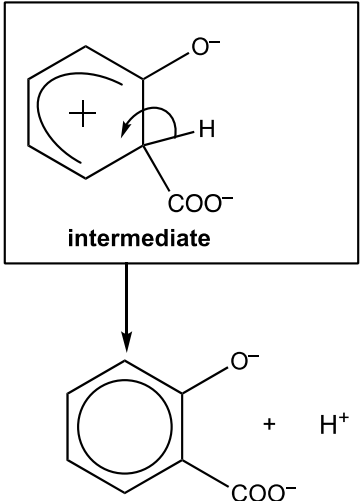
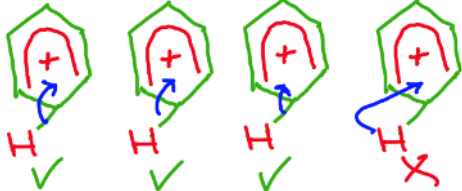
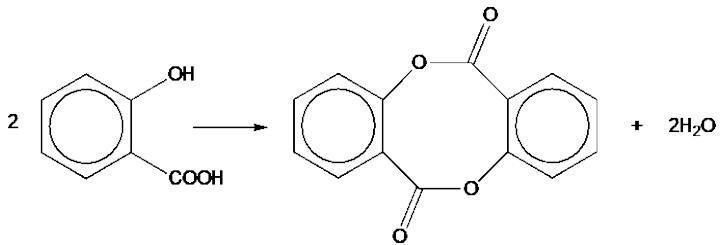
Question			Answer	Marks	AO element	Guidance
19	(a)	(i)	3-methylbut-2-enal ✓	1	AO1.2	IGNORE lack of hyphens, or addition of commas
		(ii)	Reaction scheme for part (ii): Prenal (3-methylbut-2-enal) is the starting material. Pathway 1 (Left): - Prenal is reduced by NaBH_4 to 3-methylbut-2-en-1-ol (marked with a blue check). 3-methylbut-2-en-1-ol is oxidized by $\text{Cr}_2\text{O}_7^{2-}$ AND H^+ (marked with a blue check) to 3-methylbut-2-enoic acid (marked with a blue check). 3-methylbut-2-enoic acid reacts with $(\text{CH}_3)_2\text{CHOH}$ (marked with a blue check) to form 3-methylbut-2-enoic isopropyl ester. Pathway 2 (Right): - Prenal is reduced by NaBH_4 to 3-methylbut-2-en-1-ol (marked with a blue check). 3-methylbut-2-en-1-ol is hydrogenated by H_2 AND Ni (marked with a blue check) to 3-methylbutan-1-ol (marked with a blue check). 3-methylbutan-1-ol reacts with CH_3COOH (marked with a blue check) to form 3-methylbutyl acetate.	7	AO1.2 ×4 AO2.5 ×3	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous ALLOW names of reagents and catalyst For oxidation, ALLOW $\text{K}_2\text{Cr}_2\text{O}_7$ for $\text{Cr}_2\text{O}_7^{2-}$ ALLOW H_2SO_4 for H^+ For left hand side esterification IGNORE $\text{C}_3\text{H}_7\text{OH}$ IF esterification is given instead of hydrogenation contact your Team Leader

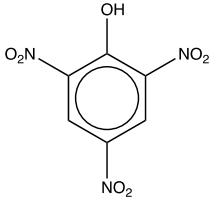
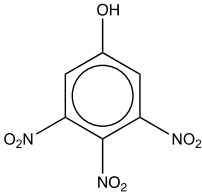
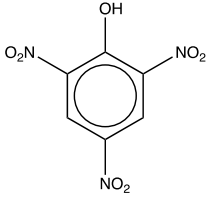
Question	Answer	Marks	AO element	Guidance
(b)*	<i>Refer to marking instructions on page 5 of mark scheme for guidance on marking this question.</i> Level 3 (5-6 marks) Correct calculation of the mass of C₆H₅CH₂Cl AND Planned synthesis to form the intermediate C₆H₅CH₂CN followed by hydrolysis to form A with most of the reagents identified and equations are mostly correct. <i>There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.</i> Level 2 (3-4 marks) Correct calculation of the mass of C₆H₅CH₂Cl AND Planned synthesis to form the intermediate C₆H₅CH₂CN with most of the reagents identified and equation is mostly correct OR Calculation of the mass of C₆H₅CH₂Cl is partly correct AND Planned synthesis includes formation of the intermediate C₆H₅CH₂CN followed by hydrolysis to form A with some of the reagents identified OR Attempts to calculate mass of C₆H₅CH₂Cl but makes little progress AND Planned synthesis includes formation of the intermediate C₆H₅CH₂CN followed by hydrolysis to form A with most of the reagents identified and equations are mostly correct	6	AO2.4 ×2 AO2.7 ×2 AO3.3 ×2	Indicative scientific points may include: <u>Calculation of mass of C₆H₅CH₂Cl</u> Using moles $n(\text{A}) = \frac{5.44}{136}$ $= 0.04(00) \text{ (mol)}$ $n(\text{C}_6\text{H}_5\text{CH}_2\text{Cl}) = 0.0400 \times \frac{100}{25}$ $= 0.16(0) \text{ (mol)}$ - Mass of C₆H₅CH₂Cl = 126.5 × 0.16 $= 20.2(4) \text{ g}$ Using mass - Theoretical mass of ester = $5.44 \times \frac{100}{25}$ $= 21.76 \text{ (g)}$ - Theoretical $n(\text{C}_6\text{H}_5\text{CH}_2\text{Cl}) = \frac{21.76}{136}$ $= 0.16(0) \text{ (mol)}$ - Mass of C₆H₅CH₂Cl = 126.5 × 0.160 $= 20.2(4) \text{ g}$ ALLOW small slip/rounding errors such as errors in <i>M_r</i> e.g. use of 137 instead of 136 for C₆H₅CH₂COOH ----- <i>Examples of partly correct calculations</i> Mass = 1.265 g from $0.0400 \times \frac{25}{100} \times 126.5$ (% yield inverted) Mass = 5.06 g from 0.0400×126.5 (% yield omitted)

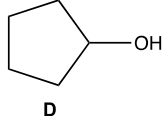
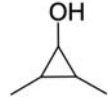
Question	Answer	Marks	AO element	Guidance
	<i>There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.</i> Level 1 (1-2 marks) Calculation of the mass of C₆H₅CH₂Cl is partly correct OR Attempts to calculate mass of C₆H₅CH₂Cl but makes little progress AND Planned synthesis includes formation of the intermediate C₆H₅CH₂CN with the reagent identified OR Planned synthesis includes both steps with some of the reagents identified OR Attempts equations for both steps but these may contain errors OR Describes one step of the synthesis with reagent(s) and equation mostly correct <i>There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.</i> 0 marks No response or no response worthy of credit.			<u>Synthesis: reagents and conditions</u> Stage 1: Formation of intermediate, C₆H₅CH₂CN - Reagents: CN⁻(/ethanol) - Equation: $\text{C}_6\text{H}_5\text{CH}_2\text{Cl} + \text{CN}^- \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CN} + \text{Cl}^-$ OR $\text{C}_6\text{H}_5\text{CH}_2\text{Cl} + \text{NaCN} \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CN} + \text{NaCl}$ (OR use of KCN) Stage 2: Formation of A, C₆H₅CH₂COOH - Reagents: H⁺/H₂O (ALLOW 'acid hydrolysis') - Equation: $\text{C}_6\text{H}_5\text{CH}_2\text{CN} + 2\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{COOH} + \text{NH}_4^+$ OR $\text{C}_6\text{H}_5\text{CH}_2\text{CN} + 2\text{H}_2\text{O} + \text{HCl} \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{COOH} + \text{NH}_4\text{Cl}$
	Total	18		

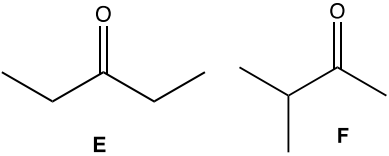
Question	Answer	Marks	AO element	Guidance
20 (a) (i)	Stage 1  1 mark for each curly arrow as shown.	6	AO1.1 AO1.2 AO2.5	ANNOTATE WITH TICKS AND CROSSES NOTE: curly arrows can be straight, snake-like, etc. but NOT double headed or half headed arrows Curly arrow from OH⁻ must - go to the H of O-H AND - start from, OR be traced back to any point across width of lone pair on O of OH⁻  OR start from – charge⁻OH ion  Curly arrow from O–H bond must start from, OR be traced back to, any part of O–H bond and go to O IGNORE dipoles on O–H bond IGNORE Na⁺

Question	Answer	Marks	AO element	Guidance
	Stage 2 Curly arrow from π-ring to C in CO_2 AND curly arrow from the C=O bond to O atom ✓  Correct intermediate ✓ Curly arrow from C–H bond to reform π-ring AND H^+ formed ✓		AO2.5 1st curly arrow must - go to the C of CO_2 AND - start from, OR close to circle of benzene ring  2nd curly arrow must start from, OR be traced back to, any part of C=O bond and go to O  ALLOW 2nd curly arrow from C=O to any O in CO_2 DO NOT ALLOW the following intermediate:  π-ring must cover more than half of the benzene ring structure AND the correct orientation, <i>i.e.</i> gap towards C with CO_2^- ALLOW + sign anywhere inside the 'hexagon' of the intermediate.	AO2.5 AO1.2

Question	Answer	Marks	AO element	Guidance
				DO NOT ALLOW mark for intermediate if phenolic O⁻ is missing curly arrow must start from, OR be traced back to, any part of C-H bond and go inside the 'hexagon' 
(ii)	OH⁻: base ✓ CO₂: electrophile OR electron pair acceptor ✓	2	AO2.1 ×2	ALLOW alkali IGNORE 'nucleophile', 'donates electron pair' IGNORE lone pair acceptor (<i>No lone pair involved</i>)
(iii)	 One ester link in organic product ✓ Correct structure of organic product ✓ Correct equation AND balanced ✓	3	AO3.1 AO3.2 AO2.6	

Question			Answer	Marks	AO element	Guidance
	(b)	(i)	Dissolve in hot water/solvent ✓ Minimum amount of solvent ✓ Cool AND Filter AND (leave to) dry ✓ <i>All three needed</i>	3	AO3.3 ×3	ALLOW any solvent IGNORE - Initial filtering - hot filtration to remove insoluble impurities DO NOT ALLOW adding of a drying agent (e.g. MgSO ₄)
		(ii)	C : H : N : O 31.44/12 : 1.31/1 : 18.34/14 : 48.91/16 OR 2.62 : 1.31 : 1.31 : 3.06 ✓ 6:3:3:7 OR C ₆ H ₃ N ₃ O ₇ ✓ Molecular formula = C ₆ H ₃ N ₃ O ₇ AND use of <i>M</i> = 229.0 (directly linked to molecular formula) ✓ Any trisubstituted –NO ₂ substituted phenol that is consistent with <i>M</i> = 229.0 ✓ Evidence for substitution 2,4,6 OR 3,4,5 substituted phenol AND 4 peaks/ C environments from ¹³ C NMR ✓ 2,4,6 substituted phenol AND directing effects of –OH ✓	6	AO1.2 × 2 AO3.1 AO3.2 AO3.1 ×2	ALLOW alternative approach for empirical formula and evidence that 229 is equal to C ₆ H ₃ N ₃ O ₇ DO NOT ALLOW ECF from the empirical formula with the wrong molar ratio  2,4,6  3,4,5  2,4,6
			Total	20		

Question	Answer	Marks	AO element	Guidance
21*	<i>Refer to marking instructions on page 5 of mark scheme for guidance on marking this question.</i> Level 3 (5–6 marks) Compounds D, E AND F correctly identified AND Most of the observations and NMR data analysed. <i>There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.</i> Level 2 (3–4 marks) Most of compounds D, E AND F correctly identified AND Some of the observations and NMR data analysed. <i>There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.</i> Level 1 (1–2 marks) Most of compounds D, E AND F correctly identified OR Some of compounds D, E AND F correctly identified AND Analyses some of the observations or NMR data OR Analyses most of the observations from the test-tube tests. OR Analyses most of the NMR data. OR Analyses some of the observations and NMR data	6	AO3.1 ×4 AO3.2 ×2	Indicative scientific points may include: <u>Observations from Test-tube tests</u> 2,4 DNP D has no C=O E and F have C=O present H⁺/Cr₂O₇²⁻ D is primary OR secondary alcohol E and F are ketones <i>(negative test shows not aldehydes)</i> Br₂ D, E and F have no C=C/are saturated <u>¹³C NMR analysis</u> D: • 3 carbon environments/types of C • δ = 24, 36 ppm C–C • δ = 73 ppm, C–O <u>¹H NMR analysis</u> E: • δ = 2.4 ppm, quartet CH₃–CH₂–C=O • δ = 1.1 ppm, triplet CH₃–CH₂– F: • δ = 2.6 ppm, heptet/multiplet (CH₃)₂–CH–C=O • δ = 2.1 ppm, singlet, CH₃–C=O • δ = 1.1 ppm, doublet CH₃–CH– <u>Structures</u> ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous  OR 

Question			Answer	Marks	AO element	Guidance
			<i>There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.</i> 0 marks No response or no response worthy of credit.			 E F
			Total	6		

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