OCR
Oxford Cambridge and RSA

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.

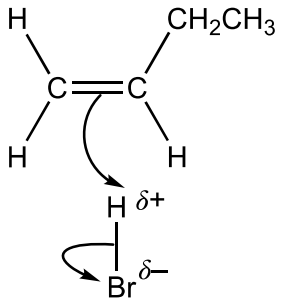
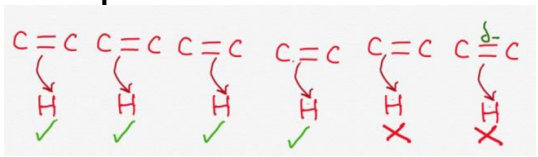
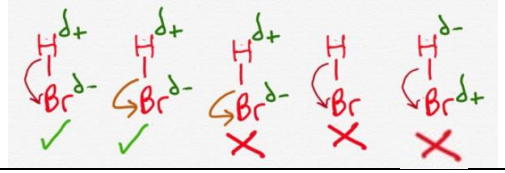
1. Annotations

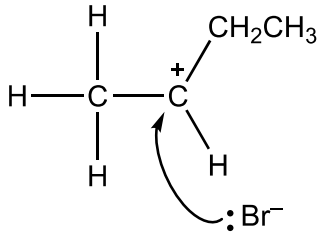
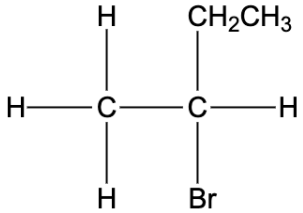
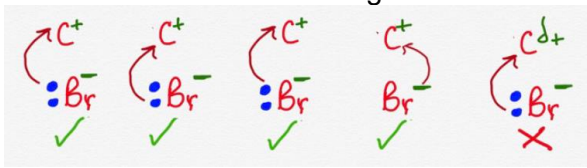
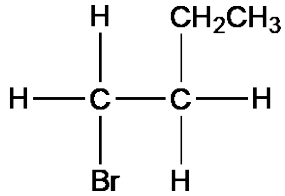
Annotation	Meaning
	Correct response
	Incorrect response
	Omission mark
	Benefit of doubt given
	Contradiction
	Rounding error
	Error in number of significant figures
	Error carried forward
	Level 1
	Level 2
	Level 3
	Benefit of doubt not given
	Noted but no credit given
	Ignore

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

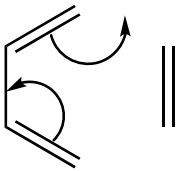
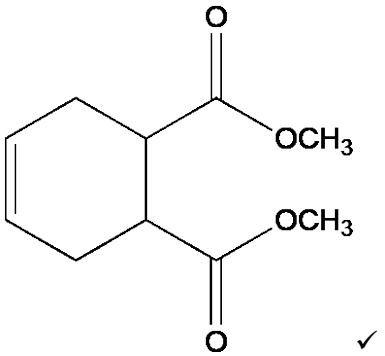
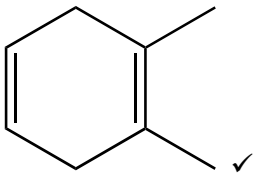
Annotation	Meaning
DO NOT ALLOW	Answers which are not worthy of credit
IGNORE	Statements which are irrelevant
ALLOW	Answers that can be accepted
( )	Words which are not essential to gain credit
__	Underlined words must be present in answer to score a mark
ECF	Error carried forward
AW	Alternative wording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

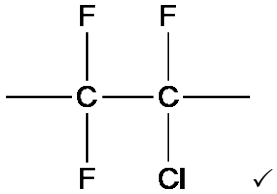
Question	Answer	Marks	AO element	Guidance
1	C	1	AO2.1	**ALLOW** 4 (This is the number of structural isomers)
2	B	1	AO1.2	
3	C	1	AO2.2	
4	C	1	AO2.6	
5	D	1	AO2.1	
6	B	1	AO1.2	
7	A	1	AO1.2	
8	C	1	AO2.1	
9	C	1	AO1.2	
10	A	1	AO2.1	
11	D	1	AO2.5	
12	B	1	AO2.1	
13	B	1	AO2.1	
14	C	1	AO1.1	
15	A	1	AO1.2	
	Total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

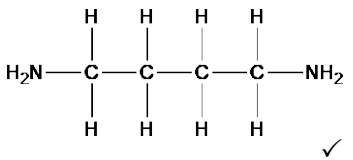
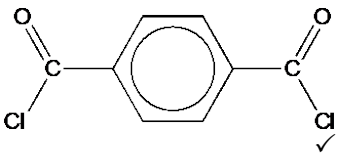
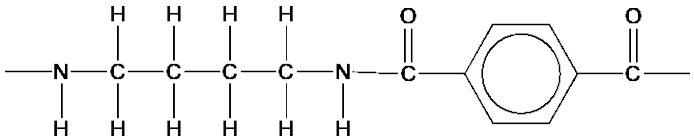
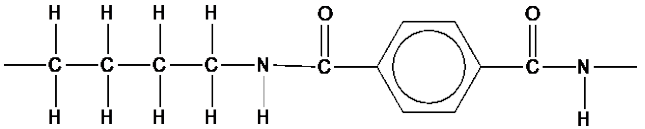
Question			Answer	Marks	AO element	Guidance
16	(a)	(i)	σ-bond: Overlap of **orbitals** between (bonding) atoms ✓ π-bond: **Sideways** overlap of (adjacent) **p-orbitals** ✓	**2**	AO1.1 ×2	**ALLOW** labelled diagrams **IGNORE** the type of orbital for σ-bond **DO NOT ALLOW** pi-orbital
		(ii)	σ-bonds: 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** $^{\delta+}$H–Br$^{\delta-}$ bond **AND** • go to Br$^{\delta-}$ 

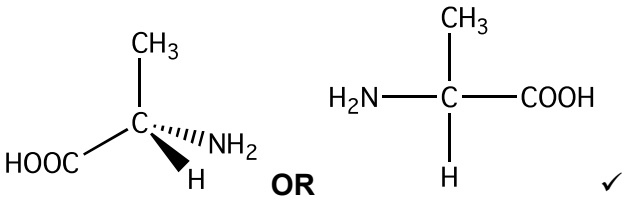
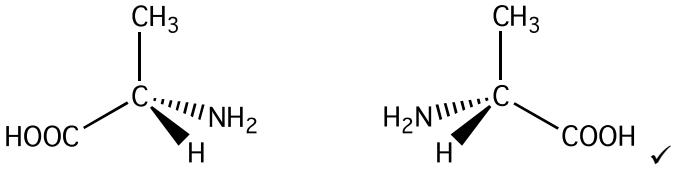
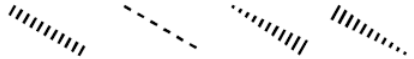
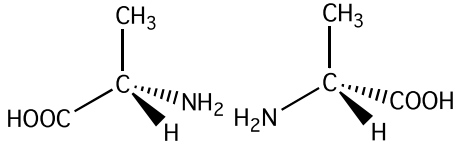
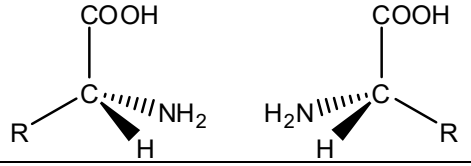
Question	Answer	Marks	AO element	Guidance
	Correct carbocation **AND** curly arrow from Br^- to C^+ of carbocation ✓ **DO NOT ALLOW** δ+ on C of carbocation  Correct product ✓  			**3rd curly arrow must** • go to the C+ of carbocation **AND** • start from, **OR** be traced back to any point across width 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** Br_2 is used instead of HBr contact your Team Leader

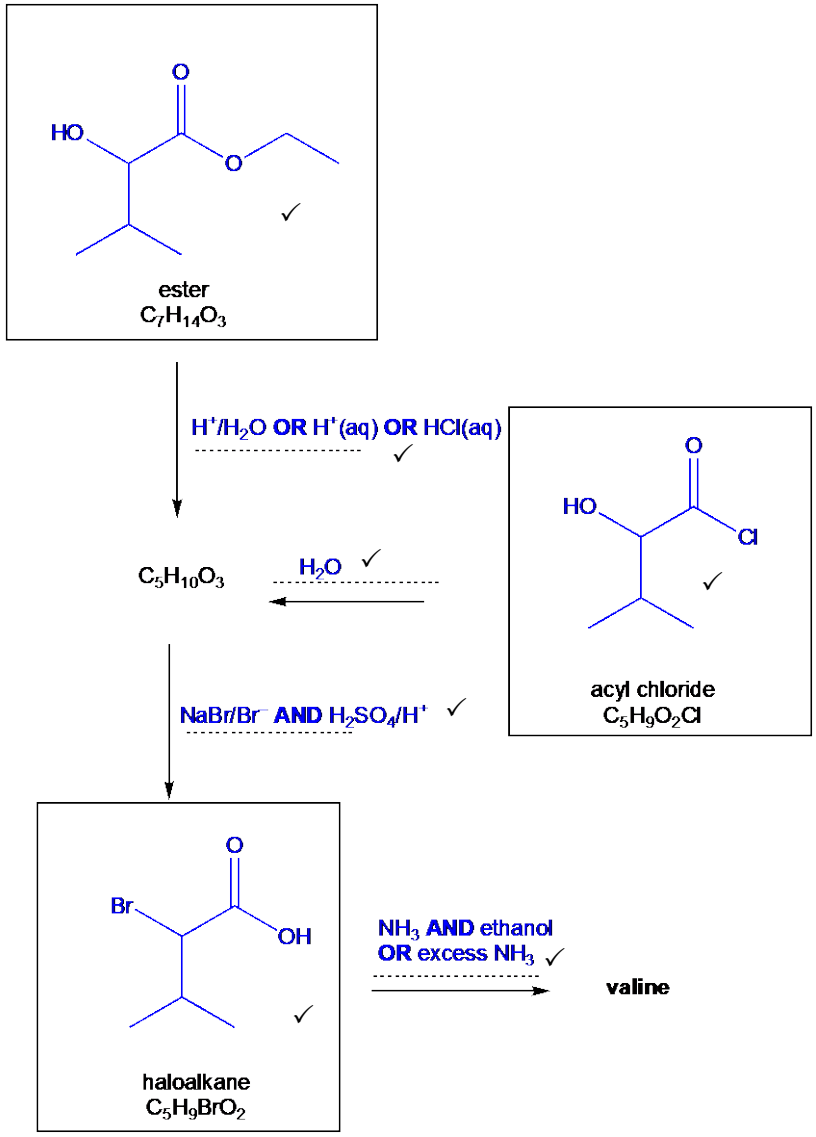
Question			Answer	Marks	AO element	Guidance
		(ii)	(major product forms from) most/more stable intermediate/carbocation ✓ (major product forms from a) secondary carbocation **OR** carbocation bonded to more C atoms / more alkyl groups **OR** carbocation bonded to fewer H atoms ✓	**2**	AO1.1 AO1.2	For 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 *E*/*Z* 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

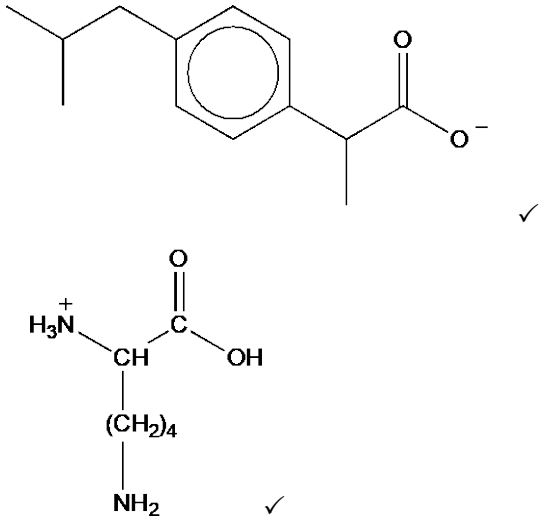
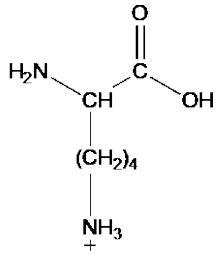
Question			Answer	Marks	AO element	Guidance
	(d)	(i)	 1 mark for each curly arrow ✓✓	2	AO2.5 ×2	**IGNORE** any dipoles shown **NOTE**: curly arrows can be straight, snake-like, etc. but **NOT** half headed or double headed arrows **Curly arrow** from C=C bond must start from, **OR** be traced back to, **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**		

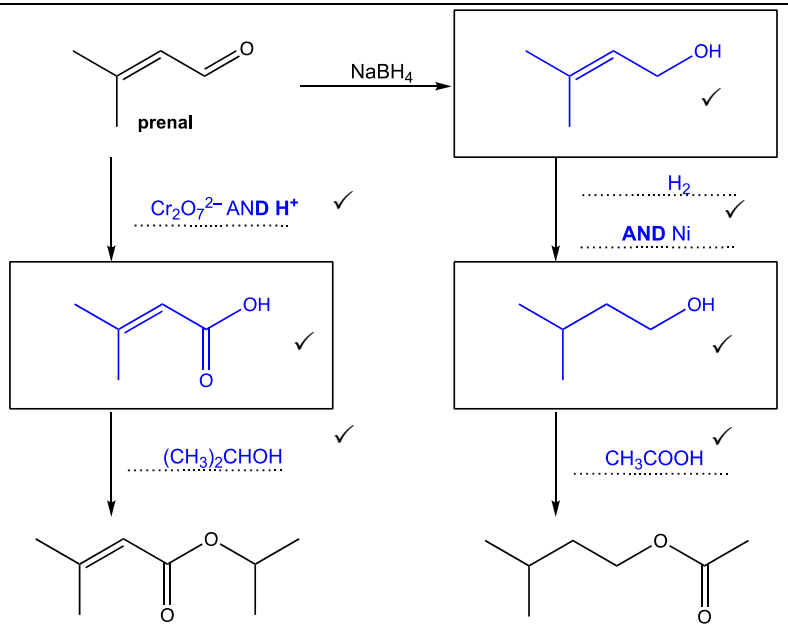
Question			Answer	Marks	AO element	Guidance
17	(a)		**Formation of C*l*•** $CCl F_3 \rightarrow CF_3 \bullet + Cl \bullet$ ✓ **Breakdown of O_3** $Cl \bullet + O_3 \rightarrow \bullet ClO + O_2$ ✓ $\bullet ClO + O \rightarrow Cl \bullet + O_2$ ✓	3	AO2.5 AO1.1 ×2	**IGNORE** dots for formation C*l*•, i.e. **ALLOW** $CCl F_3 \rightarrow CF_3 + Cl$ **DO NOT ALLOW** ECF Dots **required** in this equation **IGNORE** $O + O_3 \rightarrow 2O_2$ **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** *n*
		(ii)	More points of contact / more surface interaction (between molecules) **AND** Stronger/more dipole(–dipole) interactions ✓ More energy needed to break the intermolecular forces ✓	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)	 ✓  ✓  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** *n*
	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.  **OR** ✓ 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** CH_3 is shown as 'R' **ALLOW** 1 mark for two 3D structures with correct connectivity that are mirror images e.g. 

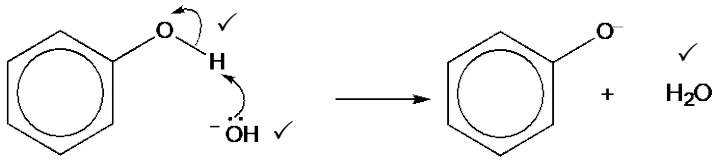
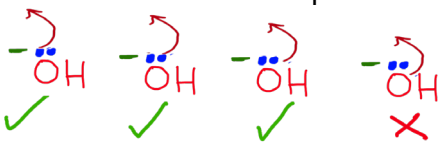
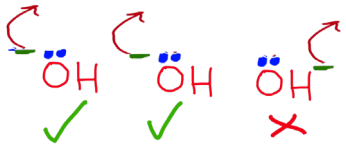
Question			Answer	Marks	AO element	Guidance
		(iii)	4 ✓	1	AO2.2	
	(b)			7	AO1.2 × 4 AO2.5 × 3	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **ALLOW** names of reagents **DO NOT ALLOW** OH– for HO– but **ALLOW ECF** for subsequent use in **(b)** 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/H_2SO_4

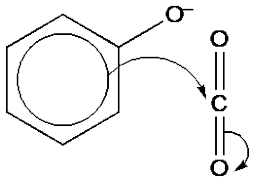
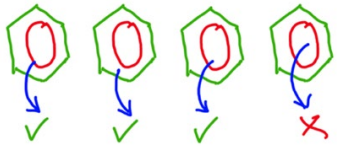
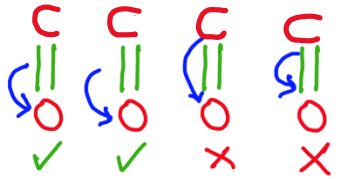
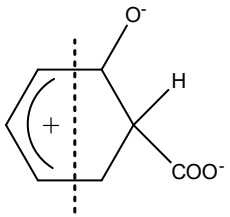
Question			Answer	Marks	AO element	Guidance
	(c)	(i)	$C_{13}H_{18}O_2$ ✓	1	AO2.1	**ALLOW** C, H and O in any order
		(ii)	**FIRST CHECK ANSWER ON THE ANSWER LINE** **If answer = 1.17×10^{21} award 3 marks** *M*(ibuprofen) = 206 ✓ n(ibuprofen) = $\frac{400 \div 1000}{206}$ = 1.94×10^{-3} (mol) ✓ Number 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*(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		

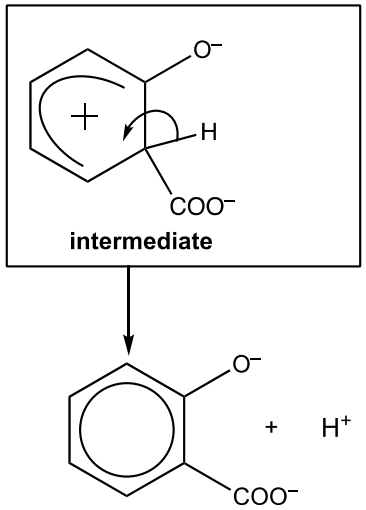
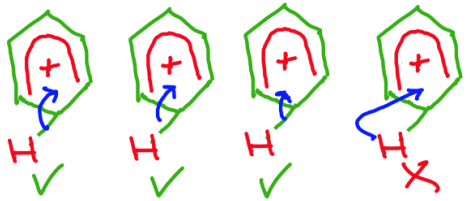
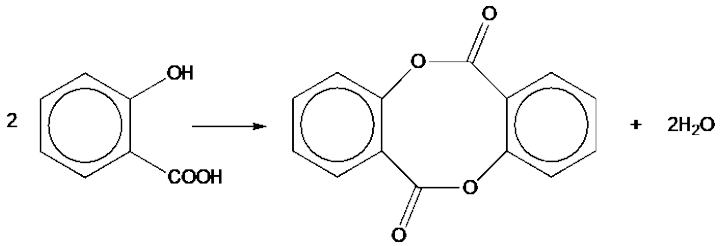
Question			Answer	Marks	AO element	Guidance
19	(a)	(i)	3-methylbut-2-enal ✓	1	AO1.2	**IGNORE** lack of hyphens, or addition of commas
		(ii)		7	AO1.2 ×4 AO2.5 ×3	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **ALLOW** names of reagents and catalyst For oxidation, **ALLOW** $K_2Cr_2O_7$ for $Cr_2O_7^{2-}$ **ALLOW** H_2SO_4 for H^+ For left hand side esterification **IGNORE** C_3H_7OH **IF** esterification is given instead of hydrogenation contact your Team Leader

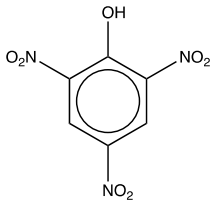
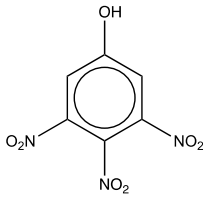
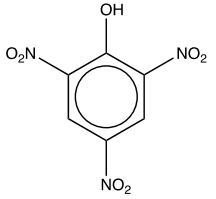
Question	Answer	Marks	AO element	Guidance
(b)*	*Refer to marking instructions on page 5 of mark scheme for guidance on marking this question.* **Level 3 (5-6 marks**) Correct calculation of the mass of $C_6H_5CH_2Cl$ **AND** Planned synthesis to form the intermediate $C_6H_5CH_2CN$ followed by hydrolysis to form **A** with most of the reagents identified and equations are mostly correct. *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)** Correct calculation of the mass of $C_6H_5CH_2Cl$ **AND** Planned synthesis to form the intermediate $C_6H_5CH_2CN$ with most of the reagents identified and equation is mostly correct **OR** Calculation of the mass of $C_6H_5CH_2Cl$ is partly correct **AND** Planned synthesis includes formation of the intermediate $C_6H_5CH_2CN$ followed by hydrolysis to form **A** with some of the reagents identified **OR** Attempts to calculate mass of $C_6H_5CH_2Cl$ but makes little progress **AND** Planned synthesis includes formation of the intermediate $C_6H_5CH_2CN$ 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 $C_6H_5CH_2Cl$</u>** **Using moles** • $n(\mathbf{A}) = \frac{5.44}{136}$ = 0.04(00) (mol) • $n(C_6H_5CH_2Cl) = 0.0400 \times \frac{100}{25}$ = 0.16(0) (mol) • Mass of $C_6H_5CH_2Cl = 126.5 \times 0.16$ = 20.2(4) g **Using mass** • Theoretical mass of ester = $5.44 \times \frac{100}{25}$ = 21.76 (g) • Theoretical $n(C_6H_5CH_2Cl) = \frac{21.76}{136}$ = 0.16(0) (mol) • Mass of $C_6H_5CH_2Cl = 126.5 \times 0.160$ = 20.2(4) g **ALLOW** small slip/rounding errors such as errors in M_r e.g. use of 137 instead of 136 for $C_6H_5CH_2COOH$ --- *Examples of partly correct calculations* 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*)

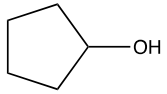
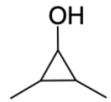
Question			Answer	Marks	AO element	Guidance
			There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence. **Level 1 (1-2 marks)** Calculation of the mass of $C_6H_5CH_2Cl$ is partly correct **OR** Attempts to calculate mass of $C_6H_5CH_2Cl$ but makes little progress **AND** Planned synthesis includes formation of the intermediate $C_6H_5CH_2CN$ 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 *There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.* **0 marks** No response or no response worthy of credit.			**<u>Synthesis: reagents and conditions</u>** ***Stage 1**:* Formation of intermediate, $C_6H_5CH_2CN$ • Reagents: CN^-(/ethanol) • Equation: $C_6H_5CH_2Cl + CN^- \rightarrow C_6H_5CH_2CN + Cl^-$ **OR** $C_6H_5CH_2Cl + NaCN \rightarrow C_6H_5CH_2CN + NaCl$ ***(OR** use of KCN)* ***Stage 2**:* Formation of **A**, $C_6H_5CH_2COOH$ • Reagents: H^+/H_2O (**ALLOW** 'acid hydrolysis' • Equation: $C_6H_5CH_2CN + 2H_2O + H^+ \rightarrow C_6H_5CH_2COOH + NH_4^+$ **OR** $C_6H_5CH_2CN + 2H_2O + HCl \rightarrow C_6H_5CH_2COOH + NH_4Cl$
			Total	**18**		

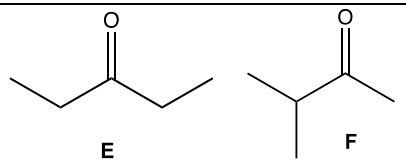
Question			Answer	Marks	AO element	Guidance
20	(a)	(i)	**Stage 1**  1 mark for each curly arrow as shown.	6	AO1.1 AO1.2 AO2.5	**ANNOTATE WITH TICKS AND CROSSES** **NOTE**: curly arrows can be straight, snake-like, etc. but **NOT** double headed or half headed arrows **Curly arrow** from OH^- must • go 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 AO2.5 AO1.2	**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.e.* gap towards C with CO_2^- **ALLOW** + sign anywhere inside the 'hexagon' of the intermediate.

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 ✓ CO_2: electrophile **OR** electron pair acceptor ✓	**2**	AO2.1 ×2	**ALLOW** alkali **IGNORE** 'nucleophile', 'donates electron pair' **IGNORE** lone pair acceptor (*No lone pair involved)*
(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 ✓ *All three needed*	**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** $C_6H_3N_3O_7$ ✓ Molecular formula = $C_6H_3N_3O_7$ **AND** use of M = 229.0 (directly linked to molecular formula) ✓ Any trisubstituted $–NO_2$ substituted phenol that is consistent with M = 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 $C_6H_3N_3O_7$ **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*			*Refer to marking instructions on page 5 of mark scheme for guidance on marking this question.* **Level 3 (5–6 marks)** Compounds **D, E AND F** correctly identified **AND** Most of the observations and NMR data analysed. *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)** Most of compounds **D, E AND F** correctly identified **AND** Some of the observations and NMR 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)** 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:** **Observations from Test-tube tests** 2,4 DNP **D** has no C=O **E** and **F** have C=O present $H^+/Cr_2O_7^{2-}$ **D** is primary **OR** secondary alcohol **E** and **F** are ketones *(negative test shows not aldehydes)* Br_2 **D**, **E** and **F** have no C=C/are saturated **^{13}C NMR analysis** **D:** • 3 carbon environments/types of C • δ = 24, 36 ppm **C**–**C** • δ = 73 ppm, **C**–O **^{1}H NMR analysis** **E:** • δ = 2.4 ppm, quartet CH_3–**CH_2**–C=O • δ = 1.1 ppm, triplet **CH_3**–CH_2– **F:** • δ = 2.6 ppm, heptet/multiplet $(CH_3)_2$–**CH**–C=O • δ = 2.1 ppm, singlet, **CH_3**–C=O • δ = 1.1 ppm, doublet **CH_3**–CH– **Structures** **ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous  D **OR** 

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

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