

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
\checkmark	Correct response
×	Incorrect response
<u>^</u>	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

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	В	1	AO1.2	
3	C	1	AO2.2	
4	C	1	AO2.6	
5	D	1	AO2.1	
6	В	1	AO1.2	
7	Α	1	AO1.2	
8	C	1	AO2.1	
9	С	1	AO1.2	
10	Α	1	AO2.1	
11	D	1	AO2.5	
12	В	1	AO2.1	
13	В	1	AO2.1	
14	C	1	AO1.1	
15	Α	1	AO1.2	
	Total	15		

C	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)	H \downarrow	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 C = C

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Question	Answer	Marks	AO element	Guidance
	Correct carbocation AND curly arrow from Br ⁻ to C ⁺ of carbocation \checkmark DO NOT ALLOW δ + on C of carbocation $H - CH_2CH_3$ $H - CH_2CH_3$ $H - CH_2CH_3$ $H - CH_2CH_3$ $H - CH_2CH_3$			 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 10 C⁺ C⁺ C⁺ C⁺ B⁻ B⁻ B⁻ C⁺ C⁺ B⁻ C⁺ D⁺ C⁺ C⁺ D⁺ D⁺ C⁺ D⁺ D⁺ C⁺ D⁺ D⁺ C⁺ D⁺ D⁺ C⁺ D⁺ D⁺ D⁺ D⁺ D⁺ D⁺ D⁺ D
	Correct product \checkmark H CH ₂ CH ₃ H C C H ₂ CH ₃ H Br			ALLOW ECF for product from incorrect carbocation, i.e. H CH_2CH_3 H $C - C - H$ Br H IF Br ₂ is used instead of HBr contact your Team Leader

Questi	ion	Answer	Marks	AO element	Guidance
	(ii)) (major product forms from) most/more stable intermediate/carbocation ✓	2	AO1.1	For carbocation, ALLOW carbonium ion or cation
		(major product forms from a) secondary carbocation OR carbocation bonded to more C atoms / more alkyl groups OR carbocation bonded to fewer H atoms ✓		AO1.2	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	1	AO3.1	DO NOT ALLOW one side of C=C
		OR C–C bond can rotate ✓			

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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		

Q	Question		Answer	Marks	AO element	Guidance
17	(a)		Formation of Cl • $CClF_3 \rightarrow CF_3 \bullet + Cl \bullet \checkmark$	3	AO2.5	IGNORE dots for formation Cl^{\bullet} , i.e. ALLOW $CClF_3 \rightarrow CF_3 + Cl$
			Breakdown of O_3 $Cl \cdot + O_3 \rightarrow \cdot ClO + O_2 \checkmark$		AO1.1 ×2	DO NOT ALLOW ECF Dots required in this equation
			• $ClO + O \rightarrow Cl \cdot + O_2 \checkmark$			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)	F F CC F CI ✓	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
		(ii)		2	AO2.1	IGNORE brackets IGNORE <i>n</i> Both answers need to be a comparison
			More points of contact / more surface interaction (between molecules) AND Stronger/more dipole(–dipole) interactions ✓		×2	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
			More energy needed to break the intermolecular forces \checkmark			

Question	Answer	Marks	AO element	Guidance
Question (c)	Answer $ \begin{array}{c cccccccccccNH_2 \\ H & H & H & H \\ \hline H &$	Marks 4		Guidance 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. $-C - C - C - C - N - C - O - C - N - C - N - C - N - H$ IGNORE brackets IGNORE n
	Total	10		

C	Question		Answer	Marks	AO element	Guidance
18	(a)	(i)	Non-superimposable mirror images (about a chiral centre) \checkmark	1	AO1.1	
		(ii)	Correct groups attached to chiral C of alanine seen once e.g. CH ₃ HOOC HOOC HOOC HOOC CH ₃ H ₂ N H ₂ N	2	AO2.1 × 2	Each structure must have four central bonds with at least two wedges . For bond into paper accept: $H_{H_{H_{H_{H_{H_{H_{H_{H_{H_{H_{H_{H_{H$

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Question	Answer	Marks	AO element	Guidance
(iii) (b)	4 ✓	1 7	AO2.2 AO1.2	
	0 		× 4 AO2.5 × 3	ALLOW any combination of skeletal OR structural OR displayed formula as long as unambiguous
	HOOO		Ŭ	ALLOW names of reagents
	ester			DO NOT ALLOW OH– for HO– but ALLOW ECF for subsequent use in (b)
	$\begin{array}{c} C_{7}H_{14}O_{3} \\ H^{+}/H_{2}O \text{ OR } H^{+}(aq) \text{ OR } HCl(aq) \\ HO \\ HO \\ HO \\ CI \end{array}$			For hydrolysis, ALLOW dilute acid ALLOW alkaline conditions followed by protonation of carboxylate i.e. NaOH(aq)/OH ⁻ (aq) AND H ⁺ (aq)/HCI(aq)
	$C_{5}H_{10}O_{3} \xrightarrow{H_{2}O} \checkmark$ $acyl chloride$ $C_{5}H_{9}O_{2}Cl$			ALLOW HBr for NaBr/H ₂ SO ₄
	$\begin{tabular}{ c c c c } \hline & & & & & \\ \hline & & & & \\ \hline & & & & \\ \hline & & & &$			

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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	3	AO2.2 × 3	
	M (ibuprofen) = 206 \checkmark			ALLOW ECF from (c)(i)
	$n(\text{ibuprofen}) = \frac{400 \div 1000}{206} = 1.94 \times 10^{-3} \text{ (mol)} \checkmark$			Calculator: 1.941747573 × 10 ⁻³
	Number of molecules = $1.94 \times 10^{-3} \times 6.02 \times 10^{23}$ = 1.17×10^{21} to 3 SF \checkmark			ALLOW ECF from <i>n</i> (ibuprofen) 3 SF essential
(d) (i)		2	AO3.2 × 2	IGNORE small slip in carbon chains
	$ \begin{array}{c c} & & & \\ &$			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		

0	Questi	on	Answer	Mark	AO element	Guidance
19	(a)	(i)	3-methylbut-2-enal √	1	AO1.2	IGNORE lack of hyphens, or addition of commas
		(ii)	$ \begin{array}{c} & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & $		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 K₂Cr₂O₇ for Cr₂O₇²⁻ ALLOW K₂Cr₂O₇ for Cr₂O₇²⁻ ALLOW H₂SO₄ for H⁺ For left hand side esterification IGNORE C₃H₇OH 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 $C_6H_5CH_2CI$ ANDPlanned synthesis to form the intermediate $C_6H_5CH_2CN$ followed by hydrolysis to form A with most of the reagents 	6	AO2.4 ×2 AO2.7 ×2 AO3.3 ×2	Indicative scientific points may include: <u>Calculation of mass of C₆H₅CH₂Cl</u> Using moles • $n(A) = \frac{5.44}{136}$ = 0.04(00) (mol) • $n(C_6H_5CH_2Cl) = 0.0400 \times \frac{100}{25}$ = 0.16(0) (mol) • Mass of C ₆ H ₅ CH ₂ Cl = 126.5 × 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 ₆ H ₅ CH ₂ Cl = 126.5 × 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 $C_6H_5CH_2COOH$

Question	Answer	Marks	AO element	Guidance
	There is a line of reasoning presented with some structure.The information presented is relevant and supported bysome evidence.Level 1 (1-2 marks)Calculation of the mass of $C_6H_5CH_2Cl$ is partly correctORAttempts to calculate mass of $C_6H_5CH_2Cl$ but makes littleprogressANDPlanned synthesis includes formation of the intermediateC $_6H_5CH_2CN$ with the reagent identifiedORPlanned synthesis includes both steps with some of thereagents identifiedORPlanned synthesis includes both steps with some of thereagents identifiedORDescribes one step of the synthesis with reagent(s) andequation mostly correctThere is an attempt at a logical structure with a line ofreasoning. The information is in the most part relevant.O marksNo response or no response worthy of credit.			Synthesis: reagents and conditionsStage 1: Formation of intermediate, $C_6H_5CH_2CN$ • Reagents: $CN^-(/ethanol)$ • Equation: $C_6H_5CH_2CI + CN^- \rightarrow C_6H_5CH_2CN + CI^-$ OR $C_6H_5CH_2CI + NaCN \rightarrow C_6H_5CH_2CN + NaCl$ (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 $C_6H_5CH_2CN + 2H_2O + HCI \rightarrow C_6H_5CH_2COOH + NH_4CI$
	Total	18		

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C	Question		Answer	Marks	AO element	Guidance
20	(a)	(i)	Stage 1	6		ANNOTATE WITH TICKS AND CROSSES
			$ \begin{array}{c} $		AO1.1 AO1.2 AO2.5	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 ⁻ \overrightarrow{OH} \overrightarrow{OH} \overrightarrow{OH} \overrightarrow{OH} • OR start from - charge ⁻ OH ion \overrightarrow{OH} \overrightarrow{OH} \overrightarrow{OH} 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 ⁺

Mark Scheme

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 \checkmark \swarrow		AO2.5	 1st curly arrow must go to the C of CO₂ AND start from, OR close to circle of benzene ring ing ing ing 2nd curly arrow must start from, OR be traced back to, any part of C=O bond and go to O ind ind
	Correct intermediate ✓ Curly arrow from C–H bond to reform π-ring AND H ⁺ formed ✓		AO2.5 AO1.2	DO NOT ALLOW the following intermediate: $ \begin{array}{c} $

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Q	luesti	ion	Answer	Marks	AO element	Guidance
			$\begin{array}{c} & & & \\ & & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ &$			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 ✓	2	AO2.1 ×2	ALLOW alkali IGNORE 'nucleophile', 'donates electron pair'
			CO_2 : electrophile OR electron pair acceptor \checkmark			IGNORE lone pair acceptor (No lone pair involved)
		(iii)	Ŏ	3	AO3.1	
			OH O		AO3.2	
			$2 \qquad \qquad$		AO2.6	
			One ester link in organic product \checkmark			
			Correct structure of organic product \checkmark			
			Correct equation AND balanced ✓			

Quest	ion	Answer	Marks	AO element	Guidance
(b)	(i)	Dissolve in hot water/solvent ✓	3	AO3.3 ×3	ALLOW any solvent
		Minimum amount of solvent ✓			IGNORE Initial filtering
		Cool AND Filter AND (leave to) dry ✓ All three needed			 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	AO1.2	ALLOW alternative approach for empirical formula and evidence that 229 is equal to $C_6H_3N_3O_7$
		6:3:3:7 OR		× 2	
		C ₆ H ₃ N ₃ O ₇ ✓			DO NOT ALLOW ECF from the empirical formula
		Molecular formula = $C_6H_3N_3O_7$ AND use of <i>M</i> = 229.0 (directly linked to molecular formula) \checkmark		AO3.1	with the wrong molar ratio
		Any trisubstituted –NO ₂ substituted phenol that is consistent with $M = 229.0 \checkmark$		AO3.2	
					O ₂ N NO ₂
		Evidence for substitution 2,4,6 OR 3,4,5 substituted phenol AND 4 peaks/ C environments from ¹³ C NMR ✓		AO3.1 ×2	^Ν ο ₂ Νο ₂ 2,4,6 3,4,5
		2,4,6 substituted phenol AND directing effects of –OH ✓			
					^{NO} 2 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.	6	AO3.1 ×4	Indicative scientific points may include: Observations from Test-tube tests
	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		AO3.2 ×2	2,4 DNPD has no C=O E and F have C=O presentH*/Cr2O72- D is primary OR secondary alcohol E and F are ketones (negative test shows not aldehydes)Br2D, E and F have no C=C/are saturated $13C$ NMR analysisD: • 3 carbon environments/types of C • $\delta = 24, 36$ ppmC-C • $\delta = 73$ ppm,C-O
	 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 			• $\delta = 7.5 \text{ ppm},$ • $C=0$ 1 H NMR analysisE:• $\delta = 2.4 \text{ ppm},$ quartet $CH_3-CH_2-C=0$ • $\delta = 1.1 \text{ ppm},$ triplet CH_3-CH_2-F • $\delta = 2.6 \text{ ppm},$ heptet/multiplet $(CH_3)_2-CH-C=0$ • $\delta = 2.1 \text{ ppm},$ singlet, $CH_3-C=0$ • $\delta = 1.1 \text{ ppm},$ doublet CH_3-CH- StructuresALLOW any combination of skeletal OR structuralOR displayed formula as long as unambiguous OH
	Analyses most of the NMR data. OR Analyses some of the observations and NMR data			

Mark Scheme

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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