GCE

Chemistry A

H432/02: Synthesis and analytical techniques

Advanced GCE

Mark Scheme for June 2019

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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.

Annotations available in RM Assessor

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

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

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.

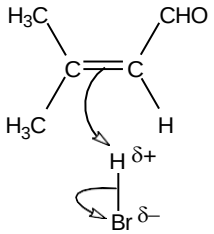
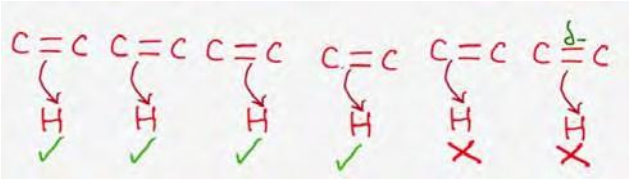
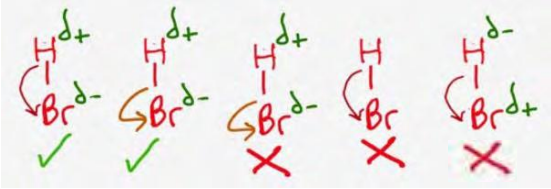
You should ensure also that you are familiar with the administrative procedures related to the marking process. These are set out in the OCR booklet **Instructions for Examiners**. If you are examining for the first time, please read carefully **Appendix 5 Introduction to Script Marking: Notes for New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

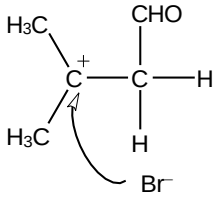
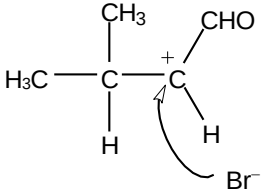
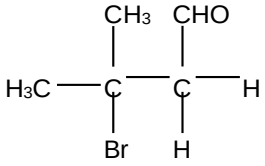
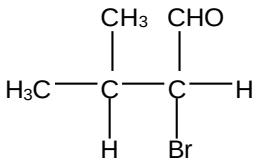
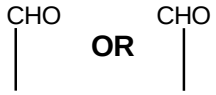
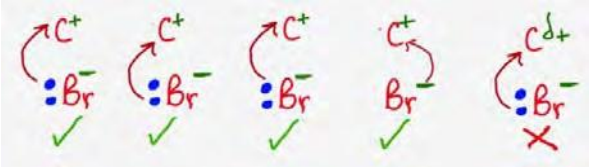
Please ask for help or guidance whenever you need it. Your first point of contact is your Team Leader.

SECTION A

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

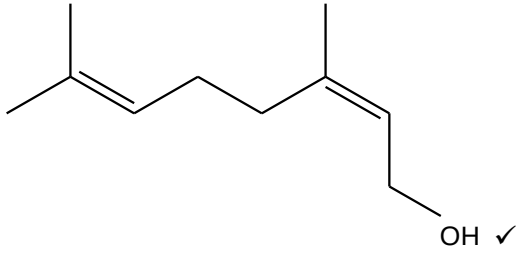
SECTION B

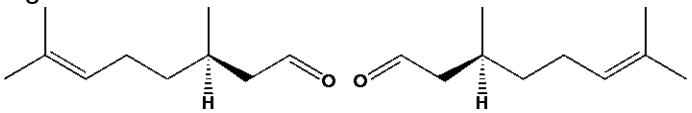
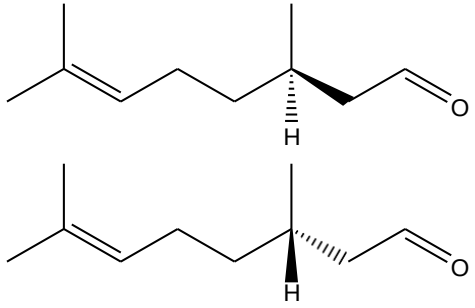
Question			Answer	Marks	AO element	Guidance
16	(a)	(i)	**ANNOTATE ANSWER WITH TICKS AND CROSSES**  Curly arrow from C=C bond to H of H–Br ✓ **DO NOT ALLOW** partial charge on C=C Correct dipole shown on H–Br **AND** curly arrow showing breaking of H–Br bond ✓	4	AO1.2 AO1.2	**NOTE**: curly arrows can 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$^{\delta-}$ 

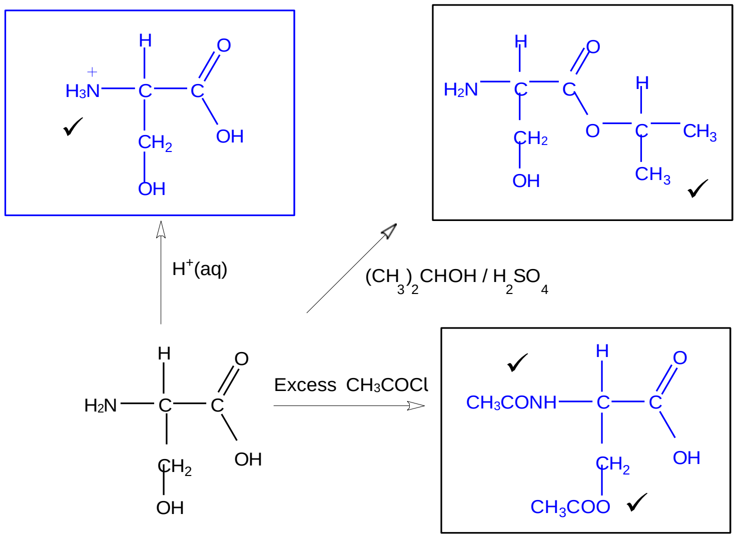
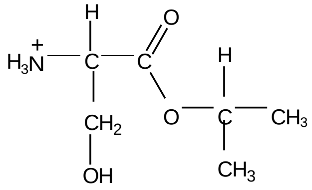
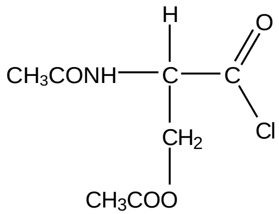
Question			Answer	Marks	AO element	Guidance
			Correct carbocation **AND** curly arrow from Br^- to C^+ of carbocation ✓ **DO NOT ALLOW** δ+ on C of carbocation  **OR**  Correct product ✓  **OR** 		AO2.5 AO2.5	**IGNORE** connectivity of CHO and CH_3 groups in carbocation and product e.g. **ALLOW**  **ALLOW** COH for CHO *(reaction does not involve this group)* **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)* **IF** Br_2 is used instead of HBr contact your Team Leader
	(a)	**(ii)**	(major product forms from) most/more stable	**2**		For carbocation,

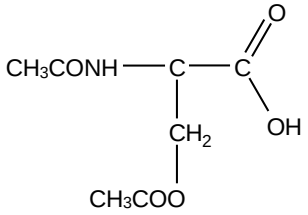
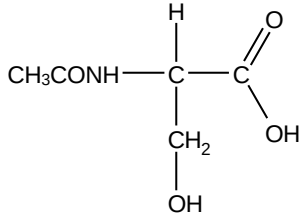
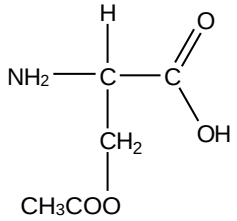
Question			Answer	Marks	AO element	Guidance
			intermediate/carbocation ✓ (major product forms from a) tertiary carbocation **OR** carbocation bonded to more C atoms / more alkyl groups **OR** carbocation bonded to no H atoms ✓		AO1.1 AO1.2	**ALLOW** carbonium ion or cation **IGNORE** descriptions of 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) secondary carbocation **OR** carbocation bonded to fewer C atoms / more alkyl groups **OR** carbocation bonded to H atoms ✓ -
	(b)	**(i)**	Tollens' (reagent) ✓	**2**	AO1.2	**ALLOW** ammoniacal silver nitrate **OR** Ag^{+}/NH_3

Question			Answer	Marks	AO element	Guidance
			Silver (mirror/precipitate/ppt/solid) with citronellal/the aldehyde ✓		×2	**ALLOW** black ppt **OR** grey ppt **IGNORE** references to acidified dichromate reacting with **both** compounds - **ALLOW** 2,4-DNP/2,4-DNPH **ALLOW** Brady's reagent ✓ Yellow/orange/red precipitate with citronellal/aldehyde/carbonyl group ✓ - **IF** other reagents are seen, contact your Team Leader
	(b)	**(ii)**	$C_{10}H_{18}O$ ✓	**1**	AO1.2	**DO NOT ALLOW** $C_{10}H_{17}OH$
	(b)	**(iii)**	Same **molecular** formula **AND** Different **structural** formulae ✓ **OR** Both (geraniol and citronellal) have the molecular formula $C_{10}H_{18}O$ **AND** Different **structural** formulae ✓	**1**	AO1.1	Same formula is **not** sufficient *(no reference to molecular)* Different arrangement of atoms is **not** sufficient *(no reference to structure/structural)* For structural formulae, **ALLOW** structure/displayed/skeletal formulae/ functional groups **DO NOT ALLOW** any reference to spatial/space **ALLOW ECF** from incorrect molecular formula in **(b)(ii)**
		(iv)	Same structural formula	**1**	AO1.1	**ALLOW** structure/displayed/skeletal formula

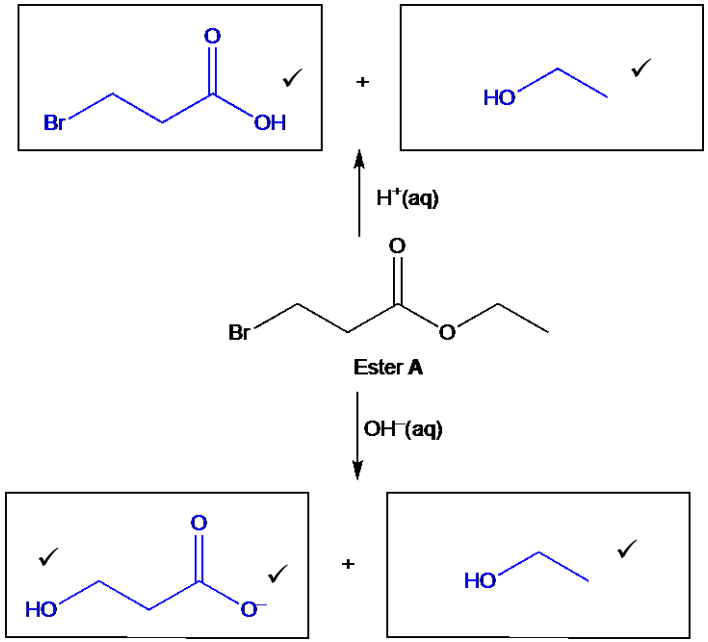
Question			Answer	Marks	AO element	Guidance
			AND Different arrangement (of atoms) in space **OR** different spatial arrangement (of atoms) ✓			**DO NOT ALLOW** same empirical formula **OR** same general formula **IGNORE** same molecular formula Reference to *E*/*Z* isomerism or optical isomerism is **not** sufficient
		(v)	**Geraniol**: (Carbon-carbon) double bond at carbon-2(,3) **AND** *E* **OR** *Z* ✓ Structure of *Z* geraniol (*E* isomer is shown in question)  ✓	**4**	AO1.2 AO2.5	**ANNOTATE ANSWER WITH TICKS AND CROSSES ETC** **CHECK** diagrams of citronellal and geraniol for annotations that may be worthy of credit **DO NOT ALLOW** isomerism at C=C at carbon 6(,-7) **ALLOW** identification of carbon-2(,3) from correct *Z* geraniol isomer if not stated in text or diagram **IGNORE** *cis* **OR** *trans* isomerism *(none of the substituent groups attached to the C=C are the same)* I**GNORE** geometric **ALLOW** type of isomerism from *E*/*Z* labels, even if incorrectly assigned In geraniol, **ALLOW** C_6H_{11} **OR** R to represent alkenyl chain **ALLOW** CH_3O **t**o represent CH_2OH

Question	Answer	Marks	AO element	Guidance
	Citronellal: chiral/asymmetric C at carbon-3 **OR** carbon-3 is bonded to 4 different groups **AND** optical isomerism ✓		AO1.2	**ALLOW** identification of carbon-3 from 3D structure citronellal if not stated in text or diagram
	Two 3D structures of citronellal that are mirror images ✓ e.g. 		AO2.5	**IGNORE** connectivity of groups around chiral C In citronellal, **ALLOW** C_6H_{11} **OR** R to represent alkenyl chain **ALLOW** C_2H_3O **t**o represent CH_2CHO **IF** structural formula of alkenyl chain is used **IGNORE one** small slip in one/both isomers e.g.$(CH_3)_2CHCH_2CH_2$ *(missing carbon-7)* **ALLOW** two 3D structures with 2 groups swapped e.g. 
	Total	**13**		

Question			Answer	Marks	AO element	Guidance
17	(a)	(i)	 	4	AO2.5 ×4	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **ALLOW** protonation of NH_2 group in reaction with $(CH_3)_2CHOH$ i.e.  **ALL** structures must be based on serine For reaction with excess CH_3COCl, **IGNORE** reaction of COOH to form an acid anhydride - **ALLOW** 1 mark for  *(both NH and OH groups reacted but acyl chloride instead of COOH)* **OR**

Question			Answer	Marks	AO element	Guidance
						 *(both NH and OH groups reacted but H missing from α C atom)* **OR**  *(NH group reacted correctly but rest of serine unchanged)* **OR**  *(OH group reacted correctly but rest of serine unchanged)*
		(ii)	**IF M_r(amino acid) = 131 from titration analysis AWARD**	**4**		

Question			Answer	Marks	AO element	Guidance
			first 3 marks **ALLOW 3SF** or more throughout **IGNORE** trailing zeroes, e.g. **ALLOW** 0.044 for 0.0440 --- n(HCl) $= 0.150 \times \frac{25.0}{1000}$ **OR** 3.75×10^{-3} (mol) ✓ n(**amino acid**) in 250 cm^3 $= 3.75 \times 10^{-3} \times \frac{250.0}{21.30}$ **OR** 0.0440 (mol) ✓ M(**amino acid**) $= \frac{5.766}{0.0440} = 131$ (g mol^{-1}) ✓ Amino acid = $(CH_3)_2CHCH_2CH(NH_2)COOH$/leucine **AND** working to show R = 57 to justify choice **OR** evidence to show M_r leucine = 131 to justify choice ✓		AO2.8 AO2.8 AO2.8 AO3.2	**ALLOW** alternative approaches **Calculator:** 0.04401408451 **ALLOW ECF** from incorrect n(HCl) **ALLOW ECF** from incorrect n(**amino acid**) **ALLOW ECF** from incorrect M(**amino acid)** **i.e. ECF** for alkyl group closest to calculated M(alkyl group), e.g. for M(alkyl group) = 15, **ALLOW** $CH_3CH(NH_2)COOH$ **Note:** evidence may be shown with table
	(b)	**(i)**	R_f value in range 0.33 – 0.35 ✓	**1**	AO1.1	**ALLOW** 2 SF or more. But ignore digits after second sig fig **ALLOW** $0.\dot{3}$ for 0.33…..
		(ii)	gly(cine) ✓ Amino acid matches (leu(cine) and) glycine in Solvent **W** **AND** Amino acid matches (ala(nine) and) glycine in Solvent **X** ✓	**2**	AO2.3 ×2	 **ALLOW** glycine has the same/similar R_f as the unknown in both solvents/chromatograms **ALLOW** suitable alternatives for R_f e.g. moves same distance
			Total	**11**		

Question			Answer	Marks	AO element	Guidance
18	(a)	(i)	ethyl 3-bromopropanoate ✓	1	AO1.2	**ALLOW** one word: ethyl3-bromopropanoate **OR** more words, e.g. ethyl 3-bromo propanoate **IGNORE** lack of hyphens, or addition of commas
		(ii)		5	AO2.5 ×5	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **ALLOW** in either order **ALLOW** any vertical bond to the OH group e.g. **ALLOW** OH **OR** HO **DO NOT ALLOW** OH– **ALLOW** in either order For reaction with OH^-, **ALLOW** one mark for Br O⁻ **OR** HO OH **OR** HO O

<table>
<tr><th colspan="3">Question</th><th>Answer</th><th>Marks</th><th>AO element</th><th>Guidance</th></tr>
<tr><td></td><td></td><td>(iii)</td><td>hydrolysis ✓</td><td>1</td><td>AO1.1</td><td>IGNORE ‘acid’ and ‘alkaline’’
IGNORE nucleophilic substitution</td></tr>
<tr><td></td><td>(b)</td><td></td><td>
<table>
<tr><th>Proton environment</th><th>Chemical shift</th><th>Splitting pattern</th></tr>
<tr><td>1</td><td>3.0–4.3</td><td>Triplet</td></tr>
<tr><td>2</td><td>2.0–3.0</td><td>Triplet</td></tr>
<tr><td>3</td><td>3.0–4.3</td><td>Quartet</td></tr>
<tr><td>4</td><td>0.5–1.9</td><td>Triplet</td></tr>
</table>
Mark by column
Chemical shift: all 4 correct ✓✓
3 correct ✓

Splitting pattern: all 4 correct ✓✓
3 correct ✓</td><td>4</td><td>AO3.1
× 4</td><td>ALLOW δ values ± 0.2 ppm, as a range or a value within the range

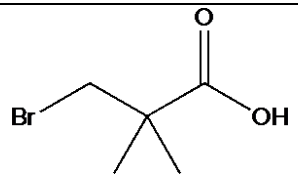
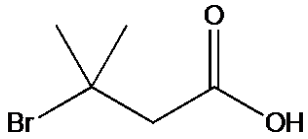
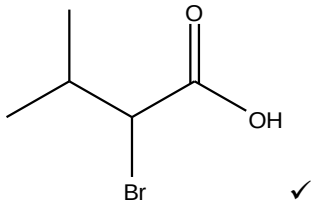
ALLOW integers for δ values
e.g. 2 is equivalent to 2.0

ALLOW quadruplet for quartet

ALLOW diagrams to show splitting pattern
e.g.
  for triplet

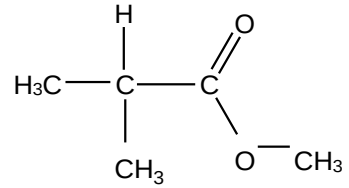
  for quartet

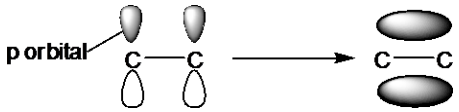
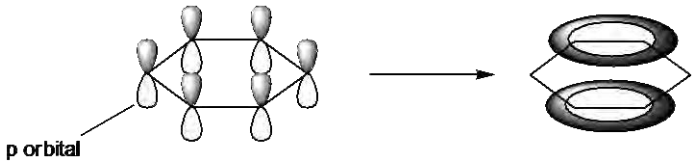
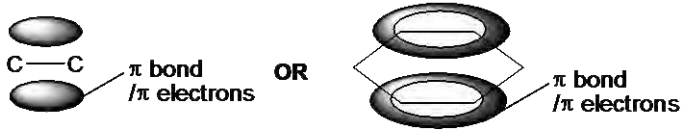
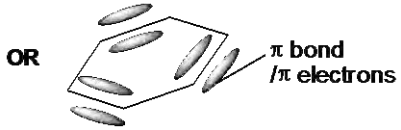
ALLOW splitting patterns shown as numbers
i.e. ‘3’ for triplet, ‘4’ for quartet</td></tr>
</table>

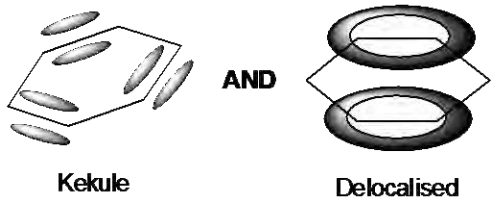
Question			Answer	Marks	AO element	Guidance
	(c)		 **OR**  **OR**  ✓	**1**	AO3.1	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous
	(d)		**IF** answer on answer line = 24018, **AWARD** 2 marks **IF** answer on answer line = 27600, **AWARD** 1 mark --- Relative mass of 200 molecules = 200 × 138 = 27600 ✓ M_r of polyester = 27600 – 199 × 18 = 24018 ✓	**2**	AO2.2 ×2	**ALLOW ECF** from incorrect M_r Alternative method based on repeat unit: M_r of 200 repeat units = 200 x 120 = 24000 ✓ M_r of polymer = 24000 + 1 + 17 = 24018 ✓
	(e)	(i)*	*Refer to marking instructions on page 4 of mark scheme*	**6**	AO3.3	**Indicative scientific points may include:**

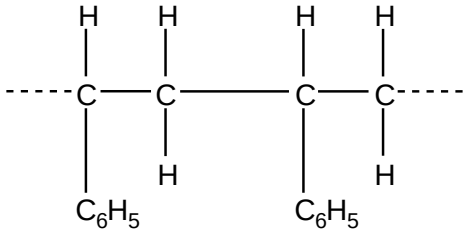
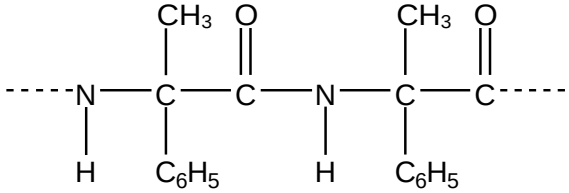
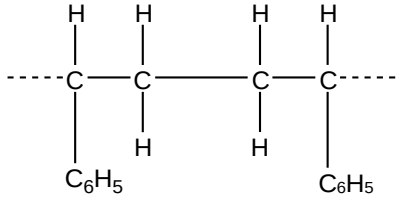
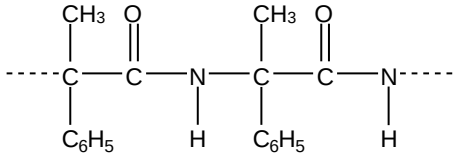
Question	Answer	Marks	AO element	Guidance
	for guidance on marking this question. **Level 3 (5-6 marks**) Correct calculation of the mass of $(CH_3)_2CHCHO$. **AND** Planned synthesis includes oxidation of aldehyde and formation of ester **C** with most of the reagents and conditions identified and equations 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)** Calculation of the mass of $(CH_3)_2CHCHO$ is partly correct **AND** Planned synthesis includes oxidation of aldehyde and formation of ester **C** with some of the reagents and conditions identified **OR** Attempts to calculate mass of $(CH_3)_2CHCHO$ but makes little progress **AND** Planned synthesis includes oxidation of aldehyde and formation of ester **C** with most of the reagents and conditions identified and equations for each step are mostly correct *There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.*		×6	**<u>Calculation of mass of $(CH_3)_2CHCHO$</u>** **Using moles** • $n(\text{ester}) = \frac{12.75}{102.0}$ = 0.125 (mol) • $n((CH_3)_2CHCHO) = 0.125 \times \frac{100}{40}$ = 0.3125 (mol) • Mass of $(CH_3)_2CHCHO = 72.0 \times 0.3125$ = 22.5 g **Using mass** • Theoretical mass of ester = $12.75 \times \frac{100}{40}$ = 31.875 (g) • Theoretical $n((CH_3)_2CHCHO) = \frac{31.875}{102}$ = 0.3125 (mol) • Mass of $(CH_3)_2CHCHO = 72.0 \times 0.3125$ = 22.5 g **ALLOW** small slip/rounding errors such as errors in *M*r e.g. use of 71 instead of 72 for $(CH_3)_2CHCHO$ **----------** ***Examples of partly correct calculations*** Mass = 3.60 g from $0.125 \times \frac{40}{100} \times 72$ (*% yield inverted*) Mass = 9.00 g from 0.125×72 (*% yield omitted*)

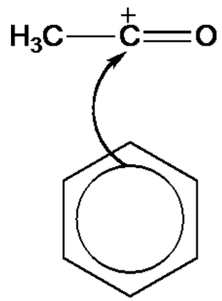
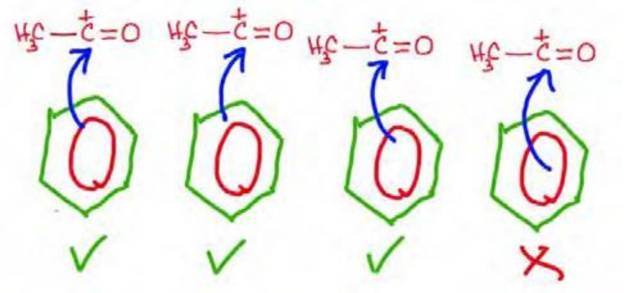
Question			Answer	Marks	AO element	Guidance
			Level 1 (1-2 marks) Calculation of the mass of $(CH_3)_2CHCHO$ is partly correct **OR** Planned synthesis includes both steps with some of the reagents and conditions identified **OR** Attempts equations for both steps but these may contain errors **OR** Describes one step of the synthesis with reagents, conditions 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>** ***Step 1:*** Oxidation of aldehyde $(CH_3)_2CHCHO$ • Reagents: $Cr_2O_7^{2-}/H^+$ • Conditions: reflux • Equation: $(CH_3)_2CHCHO + [O] \rightarrow (CH_3)_2CHCOOH$ ***Step 2:*** Formation of ester C • Reagents**:** methylpropanoic acid/$(CH_3)_2CHCOOH$ and methanol/CH_3OH • Conditions: acid (catalyst) reflux/heat • Equation: $(CH_3)_2CHCOOH + CH_3OH \rightarrow (CH_3)_2CHCOOCH_3 + H_2O$ **IGNORE** attempts to form methanol in synthesis
	(e)	**(ii)**		**2**	AO2.7 × 2	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous

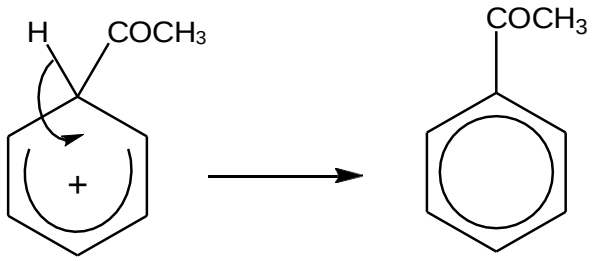
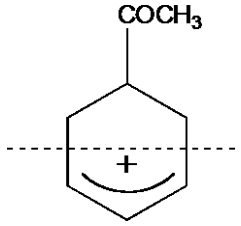
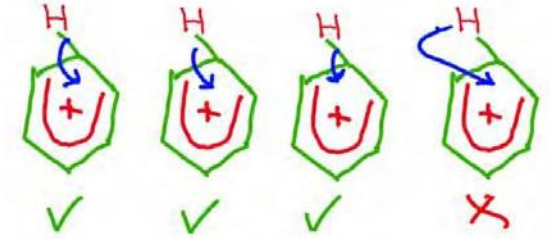
Question			Answer	Marks	AO element	Guidance
			Y (43) = $(CH_3)_2CH^+$ ✓ **Z** (71) $(CH_3)_2CHCO^+$ ✓ *If '+' charge is missing/incorrect but the structures of **both** fragments are correct, award one mark*			**ALLOW** positive charge to be anywhere on the structure For **Y** and **Z**, **ALLOW** structure of a feasible fragment ion formed from ester **C**  **Ester C** e.g. **Y** (43) = CH_3OC^+ **Z** (71) = $^+CCOOCH_3$ **ALLOW** 1 mark if both correct **ions** are shown but in the incorrect columns **ALLOW** 1 mark for both correct **ions** if one or both have an 'end bond' **ALLOW** 1 mark if both **ions** are shown using correct molecular formulae
			Total	**22**		

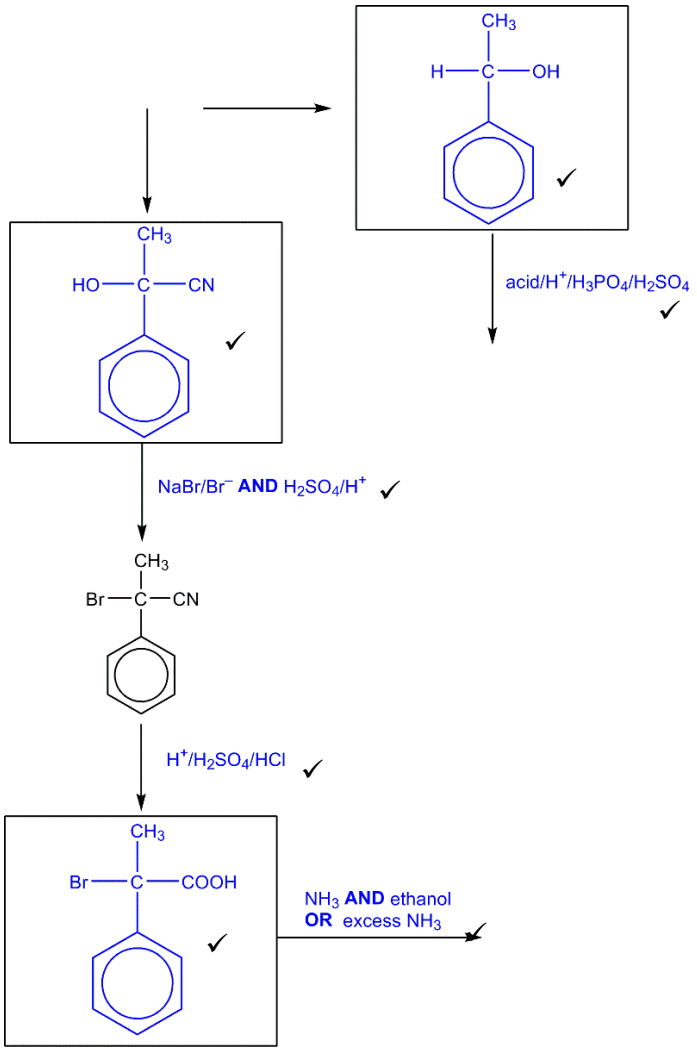
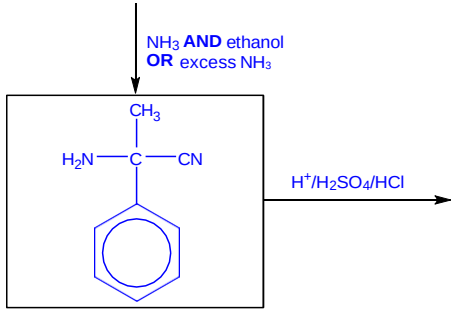
Question			Answer	Marks	AO element	Guidance
19	(a)	(i)	**Similarities** **Orbital overlap** (sideways) overlap of **p** orbitals ✓ **π bond** π bond/system/ring above and below (bonding (C) atoms/ring/plane) ✓	3	AO1.1 × 3	**ANNOTATE ANSWER WITH TICKS AND CROSSES ETC** **ALLOW** diagram showing orbital overlap e.g.  **OR**  p orbital label is **required** for first mark **IGNORE** C=C in diagram showing π bond **IGNORE** reference to s orbital overlap/σ bonds - **ALLOW** from labelled diagram showing π bond e.g.   π bond/π electrons label is **required** for second mark

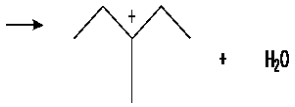
Question			Answer	Marks	AO element	Guidance
			Difference Kekule has: alternating π bonds OR 3 π bonds / localised (π electrons) / overlap in one direction / 2 electrons in π bond **AND** Delocalised has: π ring (system) / all p orbitals overlap OR (π electrons) spread around ring / overlap in both directions / 6 electrons in π bond /			--- **ALLOW** diagram showing π bond in **both** Kekule **AND** delocalised models e.g  π bond labels **not** required for third mark
		(ii)	**Any 2 pieces of evidence from** (✓ ✓) **Bond length** (C–C) bond length is between single (C–C) and double bond (C=C) **OR** all (C–C) bond lengths are the same **Δ*H* hydrogenation** Δ*H* hydrogenation less (exothermic) than expected **Resistance to reaction** Benzene is less reactive than alkenes **OR** bromination of benzene requires a catalyst/halogen carrier **OR** benzene does not react with/decolourise bromine (at room temperature) **OR** benzene reacts by substitution **OR** benzene does not (readily) react by addition	**2**	AO1.1 ×2	**ALLOW (**C–C) bond enthalpy is between single (C–C) and double bond (C=C) **OR** all (C–C) bond enthalpies are the same **IGNORE** enthalpy of hydration Benzene is unreactive is **not** sufficient *(no comparison to alkene)* For halogen carrier, **ALLOW** name or formula of suitable catalyst e.g. Fe, $AlCl_3$, $FeBr_3$

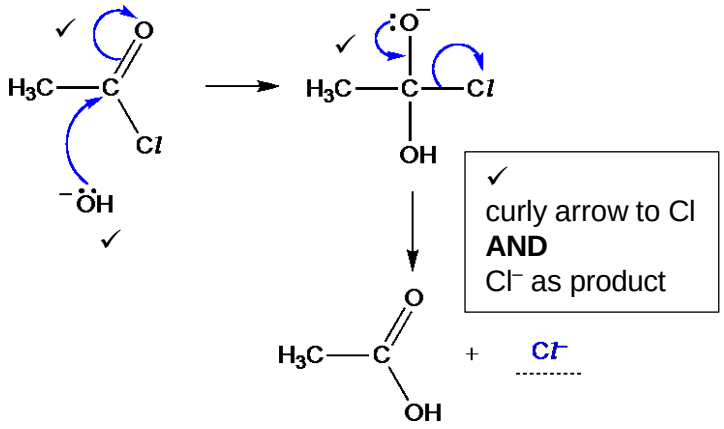
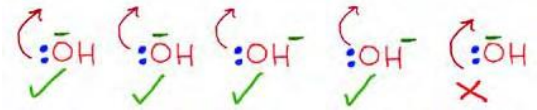
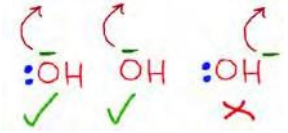
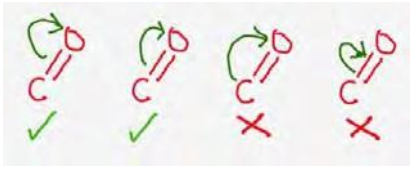
Question			Answer	Marks	AO element	Guidance
	(b)	(i)	**Polymer from D**  ✓ **Polymer from E**  Amide link ✓ 2 repeat units of correct polymer ✓	3	AO2.5 AO1.2 AO2.5	--- For **BOTH** structures, **ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous 'End bonds' **MUST** be shown **BUT ALLOW ECF IF** end bonds omitted in both structures **DO NOT ALLOW** more than 2 repeat units **BUT ALLOW ECF** in subsequent structure **IGNORE** connectivity of C_6H_5 --- **CARE**: **ALLOW** any consistent repeat unit: C_6H_5 and H groups can alternate or be on opposite sides of chain e.g.  end –NH– may be at either side e.g.  **IGNORE** brackets **IGNORE** *n*

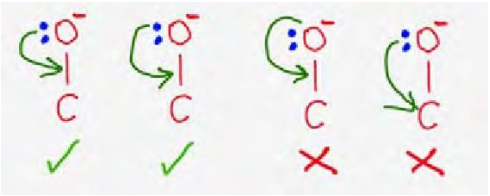
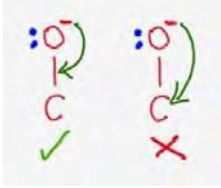
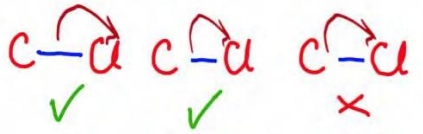
Question	Answer	Marks	AO element	Guidance
(ii)	**D** Addition / polyalkene **AND** **E**: Condensation / polyamide ✓	1	AO1.1	**DO NOT ALLOW** 'additional'
(iii)	**Formation of electrophile** $CH_3COCl + AlCl_3 \rightarrow CH_3–C^+=O + AlCl_4^-$ ✓ **Mechanism** Curly arrow from π-bond to $CH_3C^+=O$ ✓  -	5	 AO2.5 AO2.5	**ANNOTATE ANSWER WITH TICKS AND CROSSES** **ALLOW** '+' charge anywhere on CH_3C^+O *i.e.* CH_3CO^+ **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=O **AND** • start from, **OR** close to **circle of benzene ring**  **IGNORE** curly arrow shown on C=O

Question	Answer	Marks	AO element	Guidance
	Correct intermediate ✓ Curly arrow from C–H bond to reform π-ring ✓  **Regeneration of catalyst** $H^+ + AlCl_4^- \longrightarrow AlCl_3 + HCl$ ✓		AO3.1 AO2.5 AO1.2	**DO NOT ALLOW** the following intermediate:  π-ring should cover approximately 4 of the 6 sides of the benzene ring structure **AND** the correct orientation, *i.e.* gap towards C with $COCH_3$ **ALLOW** + sign anywhere inside the 'hexagon' of intermediate **curly arrow** must start from, **OR** be traced back to, **any part of** C-H bond and go inside the 'hexagon' 

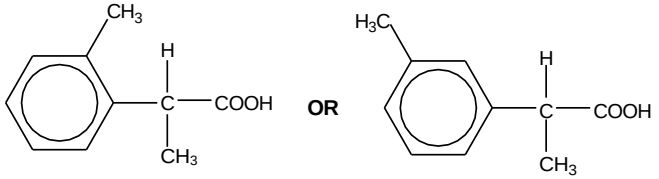
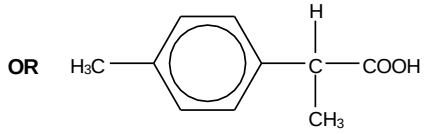
Question	Answer	Marks	AO element	Guidance
(iv)	**one** mark for each correct structure/reagent  	7	AO2.5 ×7	**ALLOW** any vertical bond to the OH **OR** NH_2 groups e.g. **ALLOW**  **DO NOT ALLOW** OH^-, **OR** NH_2^- but **ALLOW ECF** for subsequent use in this part For elimination, **IGNORE** 'concentrated', 'dilute' with acids **BUT DO NOT ALLOW** H_2O/steam/(aq) **ALLOW** HBr for $NaBr/H_2SO_4$ For hydrolysis. **IGNORE** missing (aq) **ALLOW** HNO_3 for hydrolysis but **DO NOT ALLOW** 'HNO_3 and H_2SO_4' **ALLOW** final 2 stages in opposite order i.e. NH_3 before acid hydrolysis 
	Total	**23**		

Question			Answer	Marks	AO element	Guidance
20	(a)	(i)	Movement of an electron **pair** ✓	1	AO1.1	For electron pair, **ALLOW** lone pair **OR** bonding pair **OR** 2 electrons
	(a)	(ii)	 Correct carbon skeleton ✓ '+' charge on correct carbon skeleton ✓	2	AO3.1 ×2	**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **IGNORE** any other products
	(a)	(iii)	**Heterolytic** one (bonded) atom/O receives both/2 electrons ✓ **Fission** Breaking of a **covalent** bond **OR** breaking of C-O bond ✓	2	AO1.2 AO1.1	**ALLOW** 2 electrons go to one (bonded) atom/O **IGNORE** formation of ions/radicals For O atom, **ALLOW** species **DO NOT ALLOW** element **OR** molecule 'Bond breaking' is **not** sufficient *(no reference to covalent)*

Question			Answer	Marks	AO element	Guidance
	(b)	(i)	 ✓ curly arrow to Cl **AND** Cl^- as product	4	AO3.2 ×4	**IGNORE** any dipoles shown **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 C of C=O **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 C=O bond must start from, **OR** be traced back to, **any part of** C=O bond and go to O  **Curly arrow** from O^- must

Question			Answer	Marks	AO element	Guidance
						• go to C=O bond **AND** • start from, **OR** be traced back to, **any point across width** of lone pair  • **OR** start from '–' charge of O^-  Curly arrow from C–Cl bond must start from, **OR** be traced back to, **any part of** C–Cl bond and go to Cl 
	(b)	**(ii)**	(OH^-) donates an electron pair/lone pair **OR** (OH^- acts as a) nucleophile ✓	**1**	AO1.2	
			Total	**10**		

Question	Answer	Marks	AO element	Guidance
21*	*Please refer to the marking instructions on page 4 of this mark scheme for guidance on how to mark this question.* **Level 3 (5–6 marks)** Structure is $CH_3C_6H_4CH(CH_3)COOH$ **AND** 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.* **Level 2 (3–4 marks)** A viable aromatic structure of $C_{10}H_{12}O_2$ that contains C=O **AND** most key features consistent with spectral data **AND** Some of the spectral data analysed *There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.*	6	AO1.2 × 2 AO3.1 × 2 AO3.2 × 2	**Indicative scientific points:** **<u>Empirical and Molecular Formulae</u>** • C : H : O = $\frac{73.17}{12.0} : \frac{7.32}{1.0} : \frac{19.51}{16.0}$ = 6.10 : 7.32 : 1.22 = 5 : 6 : 1 • Empirical formula = C_5H_6O • uses *m/z* = 164.0 to determine molecular formula as $C_{10}H_{12}O_2$ **<u>Structure</u>** **ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous **Key features of an aromatic structure consistent with spectral data** • COOH group • 4 aromatic H atoms • single H atom that would give a quartet • CH_3 group that would give a doublet • CH_3 group that would give a singlet

Question	Answer	Marks	AO element	Guidance
	Level 1 (1–2 marks) Correct determination of empirical formula and/or molecular formula. **OR** Analyses some of the IR and NMR data. **OR** Analyses most 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.* **0 marks** No response or no response worthy of credit.			**Correct Structure** • $CH_3C_6H_4CH(CH_3)COOH$ **ALLOW** 2-, 3- **OR** 4- substitution of ring *i.e.*  **OR**  **OR** **<u>Spectral analysis</u>** **^{1}H NMR** • δ = 1.6 ppm, doublet, 3H **CH_3**–CH– • δ = 2.3 ppm, singlet, 3H Ar-C**H_3** • δ = 2.7 ppm, quartet, 1H CO–**CH**–CH_3 **OR** Ar–**CH**–CH_3 / C_6H_5–**CH**–CH_3 • δ = 7.1–7.5 ppm, multiplet, 4H C_6**H_4**– **ALLOW** approximate values for chemical shifts. **IR:** • peak at 2300–3700 (cm^{-1}) is O–H • peak at ~1720 (cm^{-1}) is C=O • unknown is a carboxylic acid **ALLOW** ranges from *Data Sheet* **IGNORE** references to C–O peaks
	Total	**6**		

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