# GCE

# Chemistry A

**H432/02:** Synthesis and analytical techniques

Advanced GCE

## Mark Scheme for June 2019

OCR (Oxford Cambridge and RSA) is a leading UK awarding body, providing a wide range of qualifications to meet the needs of candidates of all ages and abilities. OCR qualifications include AS/A Levels, Diplomas, GCSEs, Cambridge Nationals, Cambridge Technicals, Functional Skills, Key Skills, Entry Level qualifications, NVQs and vocational qualifications in areas such as IT, business, languages, teaching/training, administration and secretarial skills.

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This mark scheme is published as an aid to teachers and students, to indicate the requirements of the examination. It shows the basis on which marks were awarded by examiners. It does not indicate the details of the discussions which took place at an examiners' meeting before marking commenced.

All examiners are instructed that alternative correct answers and unexpected approaches in candidates' scripts must be given marks that fairly reflect the relevant knowledge and skills demonstrated.

Mark schemes should be read in conjunction with the published question papers and the report on the examination.

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Annotations available in RM Assessor

| Annotation | Meaning |
|---|---|
|  | Correct response |
|  | Incorrect response |
|  | Omission mark |
|  | 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.

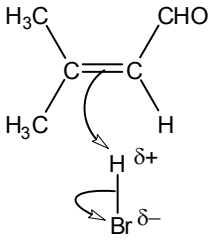
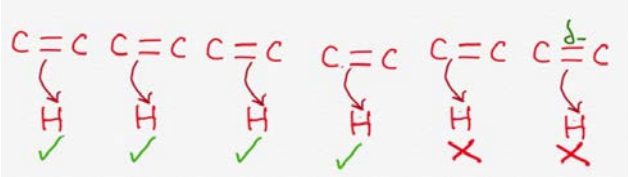
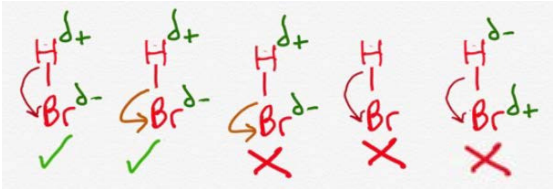
You should ensure also that you are familiar with the administrative procedures related to the marking process. These are set out in the OCR booklet **Instructions for Examiners**. If you are examining for the first time, please read carefully **Appendix 5 Introduction to Script Marking: Notes for New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

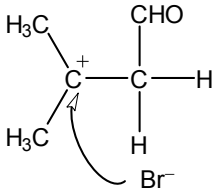
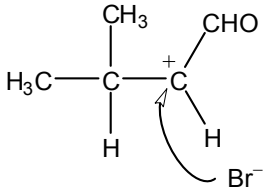
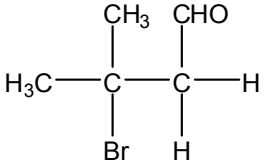
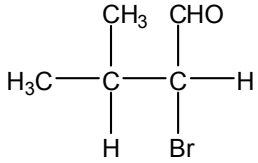
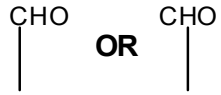
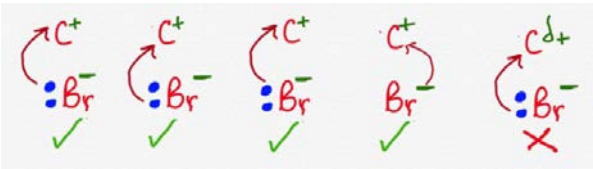
Please ask for help or guidance whenever you need it. Your first point of contact is your Team Leader.

## 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** | | |

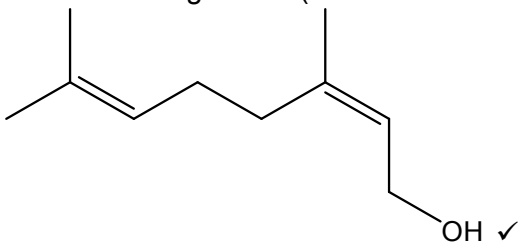
## SECTION B

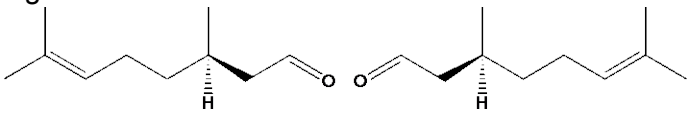
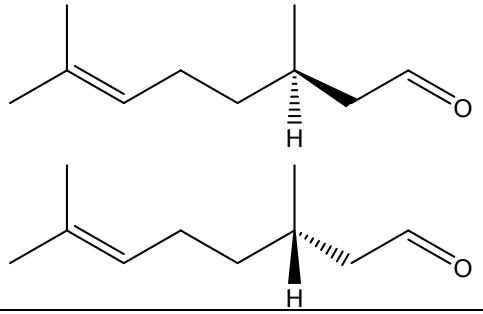
| Question | | | Answer | Marks | AO element | Guidance |
|---|---|---|---|---|---|---|
| 16 | (a) | (i) | **ANNOTATE ANSWER WITH TICKS AND CROSSES**<br><br><br>Curly arrow from C=C bond to H of H–Br ✓<br>**DO NOT ALLOW** partial charge on C=C<br><br>Correct dipole shown on H–Br<br>**AND** curly arrow showing breaking of H–Br bond ✓ | 4 | AO1.2<br><br>AO1.2 | **NOTE**: curly arrows can be straight, snake-like, etc.<br>but **NOT** double headed or half headed arrows<br><br>**1st curly arrow must**<br>• go to the H atom of H–Br<br>**AND**<br>• start from, **OR** be traced back to **any point across width** of C=C<br><br>**2nd curly arrow must**<br>• start from, **OR** be traced back to **any part of** $^{\delta+}$H–Br$^{\delta-}$ bond<br>**AND**<br>• go to Br$^{\delta-}$<br> |

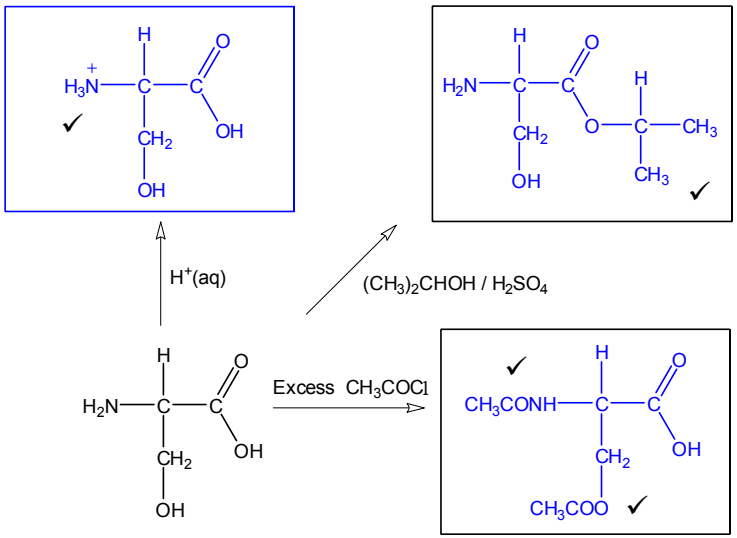
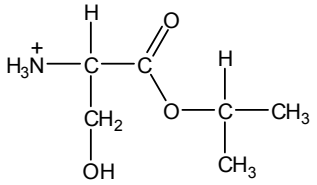
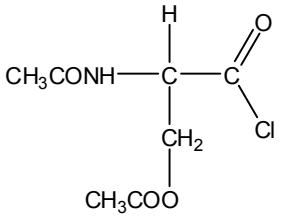
| Question | | | Answer | Marks | AO element | Guidance |
|---|---|---|---|---|---|---|
| | | | Correct carbocation<br>**AND** curly arrow from $Br^-$ to $C^+$ of carbocation ✓<br>**DO NOT ALLOW** $\delta+$ on C of carbocation<br> **OR** <br>---<br>Correct product ✓<br> **OR**  | | AO2.5<br><br>AO2.5 | **IGNORE** connectivity of CHO and $CH_3$ groups in carbocation and product<br>e.g. **ALLOW**<br><br>**ALLOW** COH for CHO *(reaction does not involve this group)*<br><br>**3rd curly arrow must**<br>• go to the C+ of carbocation<br>**AND**<br>• start from, **OR** be traced back to **any point across width** of lone pair on **:**$Br^-$<br>• **OR** start from – charge of $Br^-$ ion<br><br>*(Lone pair **NOT** needed if curly arrow shown from – charge of $Br^-$ ion)*<br><br>**IF** $Br_2$ is used instead of HBr contact your Team Leader |
| | **(a)** | **(ii)** | (major product forms from) most/more stable | **2** | | For carbocation, |

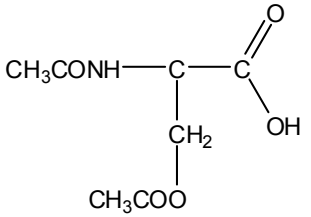
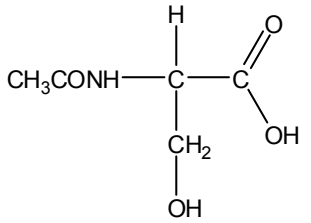
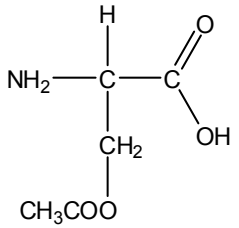
| Question | | | Answer | Marks | AO element | Guidance |
|---|---|---|---|---|---|---|
| | | | intermediate/carbocation ✓<br><br>(major product forms from a) tertiary carbocation<br>**OR** carbocation bonded to more C atoms / more alkyl groups<br>**OR** carbocation bonded to no H atoms ✓ | | AO1.1<br><br>AO1.2 | **ALLOW** carbonium ion or cation<br><br>**IGNORE** descriptions of the major/minor product in terms of Markownikoff's rule<br>e.g. H atom joins to C with most H<br><br>**IGNORE** references to stability of the product<br><br>---<br>**ALLOW ORA**, i.e.<br><br>(minor product forms from) least/less stable intermediate/carbocation ✓<br><br>(minor product forms from a) secondary carbocation<br>**OR** carbocation bonded to fewer C atoms / more alkyl groups<br>**OR** carbocation bonded to H atoms ✓<br>--- |
| | **(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<br><br>**IGNORE** references to acidified dichromate reacting with **both** compounds<br><br>---<br>**ALLOW** 2,4-DNP/2,4-DNPH<br>**ALLOW** Brady's reagent ✓<br><br>Yellow/orange/red precipitate with citronellal/aldehyde/carbonyl group ✓<br>---<br><br>**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<br>**AND**<br>Different **structural** formulae ✓<br><br>**OR**<br><br>Both (geraniol and citronellal) have the molecular formula $C_{10}H_{18}O$<br>**AND**<br>Different **structural** formulae ✓ | **1** | AO1.1 | Same formula is **not** sufficient<br>*(no reference to molecular)*<br>Different arrangement of atoms is **not** sufficient<br>*(no reference to structure/structural)*<br><br>For structural formulae,<br>**ALLOW** structure/displayed/skeletal formulae/ functional groups<br><br>**DO NOT ALLOW** any reference to spatial/space<br><br>**ALLOW ECF** from incorrect molecular formula in **(b)(ii)** |
| | | **(iv)** | Same structural formula | **1** | AO1.1 | **ALLOW** structure/displayed/skeletal formula |

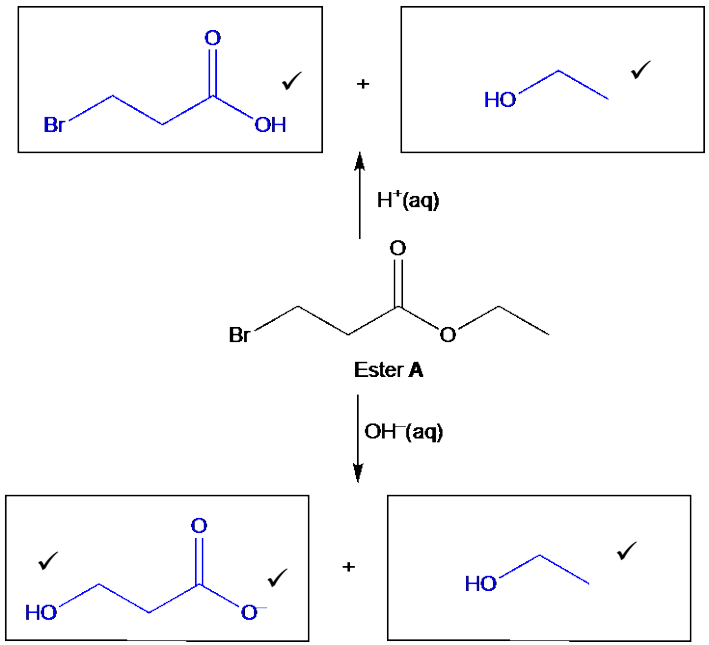
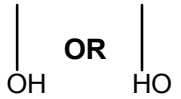
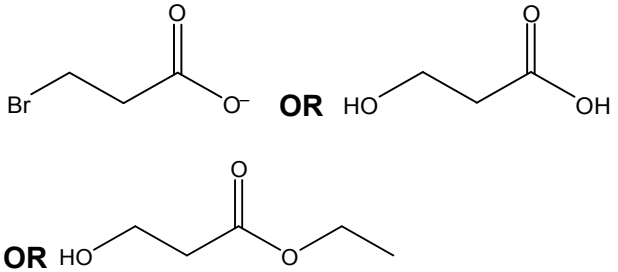
| Question | | | Answer | Marks | AO element | Guidance |
|---|---|---|---|---|---|---|
| | | | **AND**<br>Different arrangement (of atoms) in space<br>**OR** different spatial arrangement (of atoms) ✓ | | | **DO NOT ALLOW** same empirical formula<br>**OR** same general formula<br><br>**IGNORE** same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

| Question | Answer | Marks | AO element | Guidance |
|---|---|---|---|---|
| | **Citronellal**:<br>chiral/asymmetric C at carbon-3<br>**OR** carbon-3 is bonded to 4 different groups<br>**AND**<br>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 ✓<br>e.g.<br> | | AO2.5 | **IGNORE** connectivity of groups around chiral C<br>In citronellal,<br>**ALLOW** $C_6H_{11}$ **OR** R to represent alkenyl chain<br>**ALLOW** $C_2H_3O$ **t**o represent $CH_2CHO$<br>**IF** structural formula of alkenyl chain is used<br>**IGNORE one** small slip in one/both isomers<br>e.g.$(CH_3)_2CHCH_2CH_2$ *(missing carbon-7)*<br>**ALLOW** two 3D structures with 2 groups swapped<br>e.g.<br> |
| | **Total** | **13** | | |

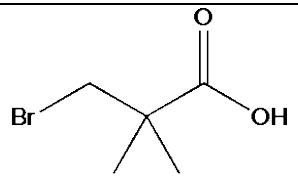
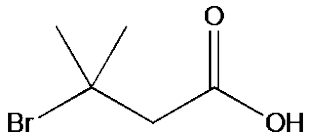
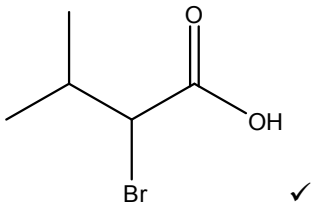
| Question | | | Answer | Marks | AO element | Guidance |
|---|---|---|---|---|---|---|
| 17 | (a) | (i) |   | 4 | AO2.5 ×4 | **ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous<br><br>**ALLOW** protonation of $NH_2$ group in reaction with $(CH_3)_2CHOH$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

| Question | | | Answer | Marks | AO element | Guidance |
|---|---|---|---|---|---|---|
| | | | | | | <br>*(both NH and OH groups reacted but H missing from $\alpha$ C atom)*<br><br>**OR**<br><br><br>*(NH group reacted correctly but rest of serine unchanged)*<br><br>**OR**<br><br><br>*(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**<br>**ALLOW 3SF** or more throughout<br>**IGNORE** trailing zeroes, e.g. **ALLOW** 0.044 for 0.0440<br>---<br>$n$(HCl) $= 0.150 \times \frac{25.0}{1000}$ **OR** $3.75 \times 10^{-3}$ (mol) ✓<br><br>$n$(**amino acid**) in 250 $cm^3$<br>$= 3.75 \times 10^{-3} \times \frac{250.0}{21.30}$ **OR** 0.0440 (mol) ✓<br><br>$M$(**amino acid**) $= \frac{5.766}{0.0440} = 131$ (g $mol^{-1}$) ✓<br><br>Amino acid = $(CH_3)_2CHCH_2CH(NH_2)COOH$/leucine<br>**AND** working to show R = 57 to justify choice<br>**OR** evidence to show $M_r$ leucine = 131 to justify choice ✓ | | AO2.8<br><br>AO2.8<br><br>AO2.8<br><br>AO3.2 | **ALLOW** alternative approaches<br><br>**Calculator:** 0.04401408451<br>**ALLOW ECF** from incorrect $n$(HCl)<br><br>**ALLOW ECF** from incorrect $n$(**amino acid**)<br><br>**ALLOW ECF** from incorrect $M$(**amino acid)**<br>**i.e. ECF** for alkyl group closest to calculated $M$(alkyl group),<br>e.g. for $M$(alkyl group) = 15, **ALLOW** $CH_3CH(NH_2)COOH$<br>**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<br><br>**ALLOW** $0.\dot{3}$ for 0.33….. |
| | | **(ii)** | gly(cine) ✓<br><br>Amino acid matches (leu(cine) and) glycine in Solvent **W**<br>**AND**<br>Amino acid matches (ala(nine) and) glycine in Solvent **X** ✓ | **2** | AO2.3 ×2 | <br><br>**ALLOW** glycine has the same/similar $R_f$ as the unknown in both solvents/chromatograms<br><br>**ALLOW** suitable alternatives for $R_f$<br>e.g. moves same distance |
| | | | **Total** | **11** | | |

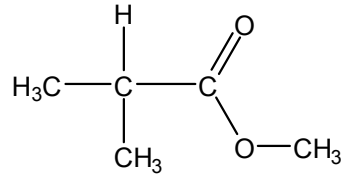
| Question | | | Answer | Marks | AO element | Guidance |
|---|---|---|---|---|---|---|
| 18 | (a) | (i) | ethyl 3-bromopropanoate ✓ | 1 | AO1.2 | **ALLOW** one word: ethyl3-bromopropanoate<br>**OR** more words, e.g. ethyl 3-bromo propanoate<br><br>**IGNORE** lack of hyphens, or addition of commas |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

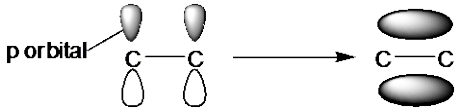
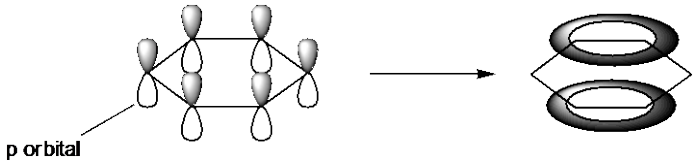
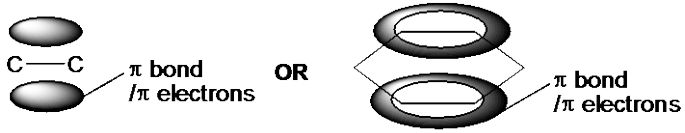
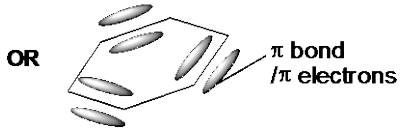
<table>
<tr><th colspan="3">Question</th><th>Answer</th><th>Marks</th><th>AO element</th><th>Guidance</th></tr>
<tr><td></td><td></td><td>(iii)</td><td>hydrolysis ✓</td><td>1</td><td>AO1.1</td><td>IGNORE ‘acid’ and ‘alkaline’’<br>IGNORE nucleophilic substitution</td></tr>
<tr><td></td><td>(b)</td><td></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<br>Chemical shift: all 4 correct ✓✓<br>3 correct ✓<br><br>Splitting pattern: all 4 correct ✓✓<br>3 correct ✓</td><td>4</td><td>AO3.1<br>× 4</td><td>ALLOW δ values ± 0.2 ppm, as a range or a value within the range<br><br>ALLOW integers for δ values<br>e.g. 2 is equivalent to 2.0<br><br>ALLOW quadruplet for quartet<br><br>ALLOW diagrams to show splitting pattern<br>e.g.<br> for triplet<br><br> for quartet<br><br>ALLOW splitting patterns shown as numbers<br>i.e. ‘3’ for triplet, ‘4’ for quartet</td></tr>
</table>

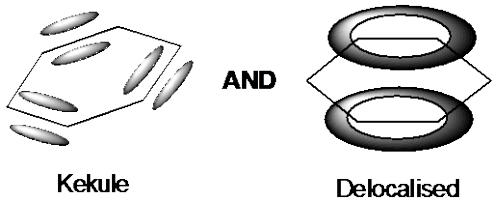
| Question | | | Answer | Marks | AO element | Guidance |
|---|---|---|---|---|---|---|
| | (c) | | <br>**OR**<br><br>**OR**<br> ✓ | **1** | AO3.1 | **ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous |
| | (d) | | **IF** answer on answer line = 24018, **AWARD** 2 marks<br>**IF** answer on answer line = 27600, **AWARD** 1 mark<br>---<br>Relative mass of 200 molecules = 200 × 138 = 27600 ✓<br><br>$M_r$ of polyester = 27600 – 199 × 18 = 24018 ✓ | **2** | AO2.2 ×2 | **ALLOW ECF** from incorrect $M_r$<br><br>Alternative method based on repeat unit:<br>$M_r$ of 200 repeat units = 200 x 120 = 24000 ✓<br><br>$M_r$ 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:** |

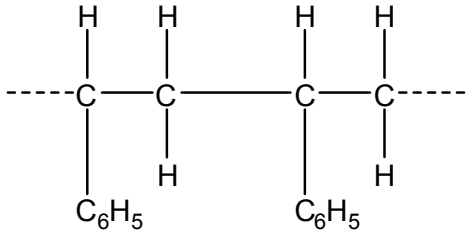
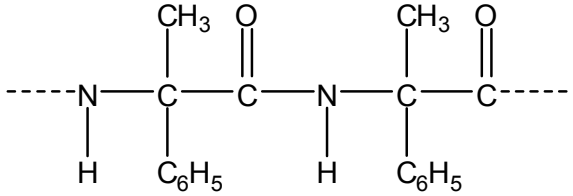
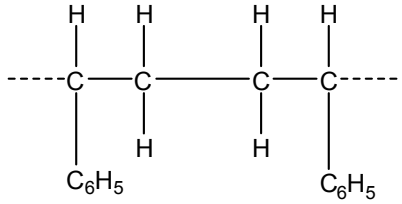
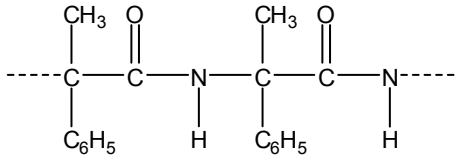
| Question | | | Answer | Marks | AO element | Guidance |
|---|---|---|---|---|---|---|
| | | | *for guidance on marking this question.*<br><br>**Level 3 (5-6 marks**)<br>Correct calculation of the mass of $(CH_3)_2CHCHO$.<br>**AND**<br>Planned synthesis includes oxidation of aldehyde and formation of ester **C** with most of the reagents and conditions identified and equations are mostly correct.<br><br>*There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.*<br><br>**Level 2 (3-4 marks)**<br>Calculation of the mass of $(CH_3)_2CHCHO$ is partly correct<br>**AND**<br>Planned synthesis includes oxidation of aldehyde and formation of ester **C** with some of the reagents and conditions identified<br>**OR**<br>Attempts to calculate mass of $(CH_3)_2CHCHO$ but makes little progress<br>**AND**<br>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<br><br>*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>**<br>**Using moles**<br>• $n$(ester) = $\frac{12.75}{102.0}$<br>= 0.125 (mol)<br>• $n((CH_3)_2CHCHO) = 0.125 \times \frac{100}{40}$<br>= 0.3125 (mol)<br>• Mass of $(CH_3)_2CHCHO = 72.0 \times 0.3125$<br>= 22.5 g<br><br>**Using mass**<br>• Theoretical mass of ester = $12.75 \times \frac{100}{40}$<br>= 31.875 (g)<br>• Theoretical $n((CH_3)_2CHCHO) = \frac{31.875}{102}$<br>= 0.3125 (mol)<br>• Mass of $(CH_3)_2CHCHO = 72.0 \times 0.3125$<br>= 22.5 g<br><br>**ALLOW** small slip/rounding errors such as errors in *Mr* e.g. use of 71 instead of 72 for $(CH_3)_2CHCHO$<br><br>**----------**<br>***Examples of partly correct calculations***<br>Mass = 3.60 g from $0.125 \times \frac{40}{100} \times 72$<br>(*% yield inverted*)<br><br>Mass = 9.00 g from $0.125 \times 72$<br>(*% yield omitted*) |

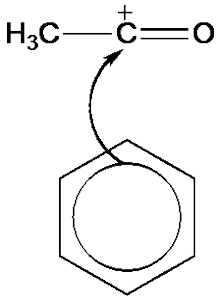
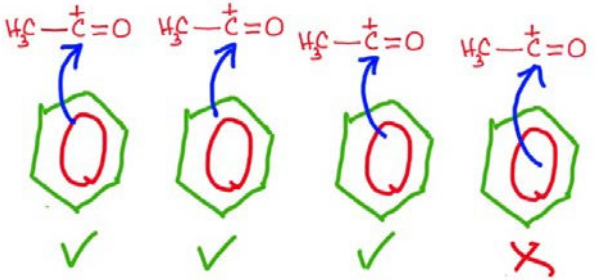
| Question | | | Answer | Marks | AO element | Guidance |
|---|---|---|---|---|---|---|
| | | | **Level 1 (1-2 marks)**<br>Calculation of the mass of $(CH_3)_2CHCHO$ is partly correct<br>**OR**<br>Planned synthesis includes both steps with some of the reagents and conditions identified<br>**OR**<br>Attempts equations for both steps but these may contain errors<br>**OR**<br>Describes one step of the synthesis with reagents, conditions and equation mostly correct<br><br>*There is an attempt at a logical structure with a line of reasoning. The information is in the most part relevant.*<br><br>**0 marks**<br>No response or no response worthy of credit. | | | **<u>Synthesis: reagents and conditions</u>**<br><br>***Step 1:*** Oxidation of aldehyde $(CH_3)_2CHCHO$<br>• Reagents: $Cr_2O_7^{2-}/H^+$<br>• Conditions: reflux<br>• Equation:<br>$(CH_3)_2CHCHO + [O] \rightarrow (CH_3)_2CHCOOH$<br><br>***Step 2:*** Formation of ester C<br>• Reagents**:** methylpropanoic acid/$(CH_3)_2CHCOOH$ and methanol/$CH_3OH$<br>• Conditions: acid (catalyst) reflux/heat<br>• Equation:<br>$(CH_3)_2CHCOOH + CH_3OH \rightarrow (CH_3)_2CHCOOCH_3 + H_2O$<br>**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 |

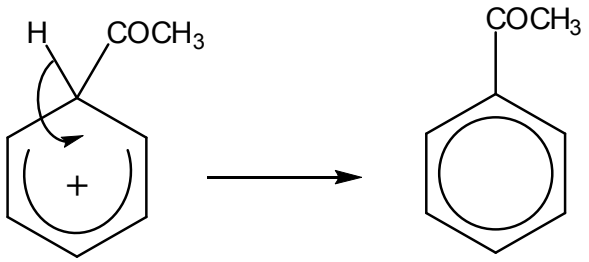
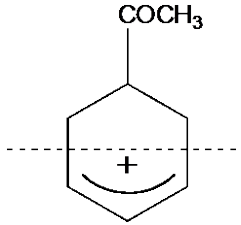
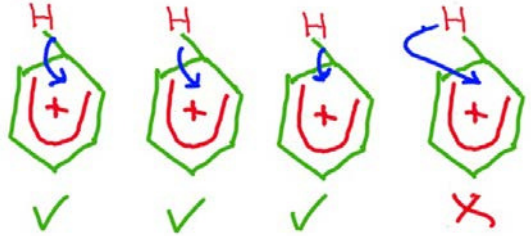
| Question | | | Answer | Marks | AO element | Guidance |
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| | | | **Y** (43) = $(CH_3)_2CH^+$ ✓<br><br>**Z** (71) $(CH_3)_2CHCO^+$ ✓<br><br>*If '+' charge is missing/incorrect but the structures of **both** fragments are correct, award one mark* |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

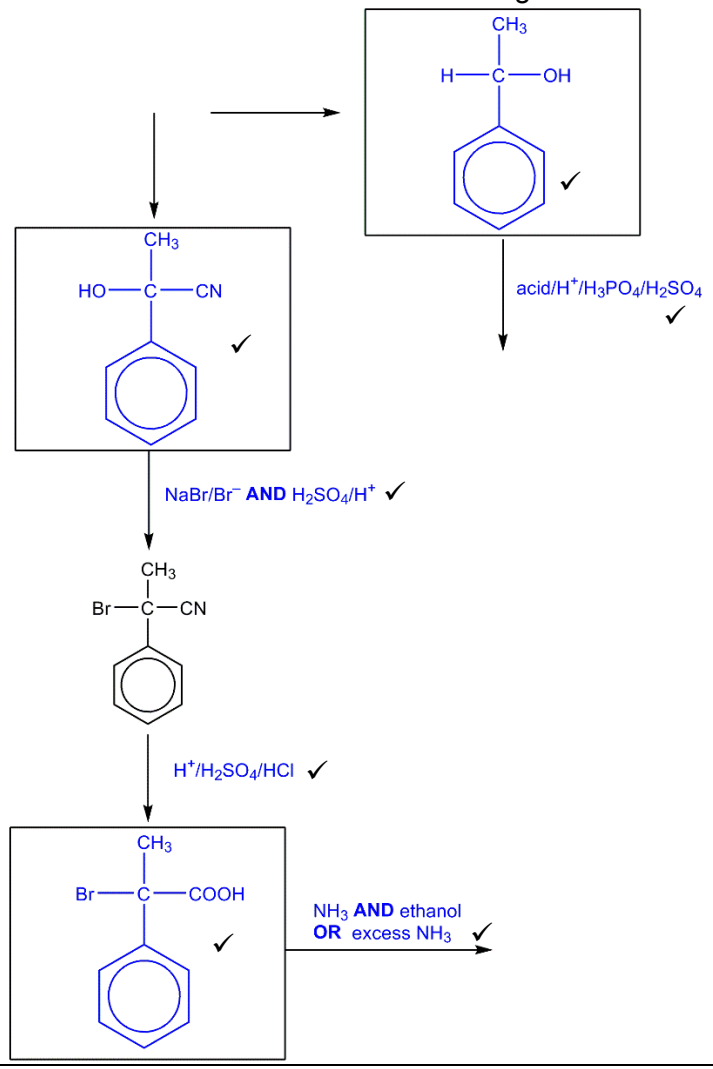
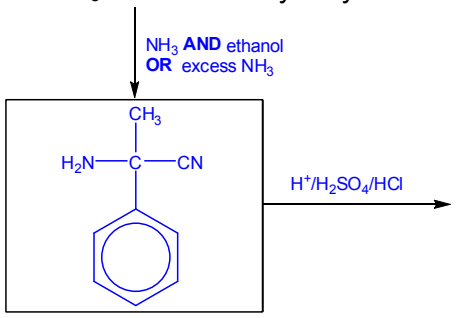
| Question | | | Answer | Marks | AO element | Guidance |
|---|---|---|---|---|---|---|
| 19 | (a) | (i) | **Similarities**<br><br>**Orbital overlap**<br>(sideways) overlap of **p** orbitals ✓<br><br>**π bond**<br><br>π bond/system/ring above and below (bonding (C) atoms/ring/plane) ✓ | 3 | AO1.1 × 3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

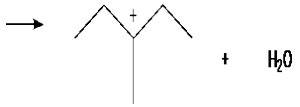
| Question | | | Answer | Marks | AO element | Guidance |
|---|---|---|---|---|---|---|
| | | | **Difference**<br><br>Kekule has: alternating π bonds OR 3 π bonds / localised (π electrons) / overlap in one direction / 2 electrons in π bond<br>**AND**<br>Delocalised has: π ring (system) / all p orbitals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

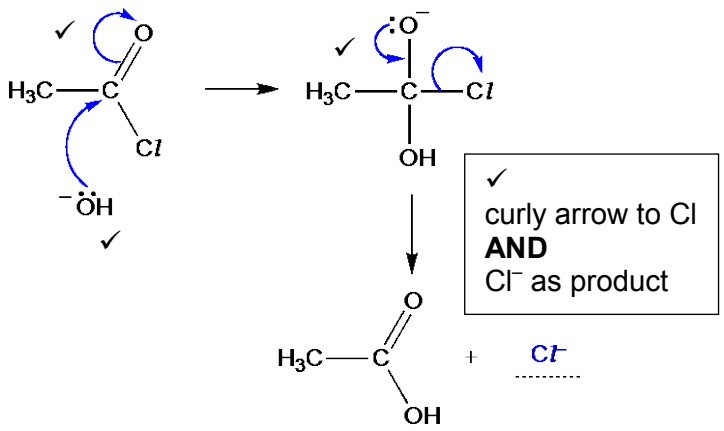
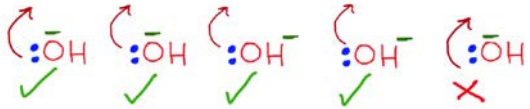
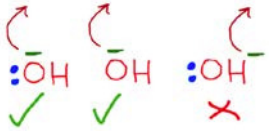
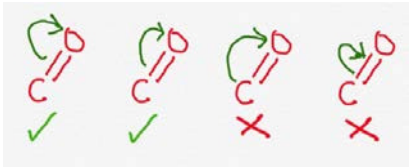
| Question | | | Answer | Marks | AO element | Guidance |
|---|---|---|---|---|---|---|
| | (b) | (i) | **Polymer from D**<br><br>✓<br><br>**Polymer from E**<br><br>Amide link ✓<br><br>2 repeat units of correct polymer ✓ | 3 | AO2.5<br><br>AO1.2<br><br>AO2.5 | ---<br>For **BOTH** structures,<br>**ALLOW**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

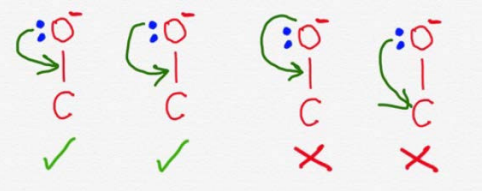
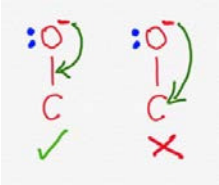
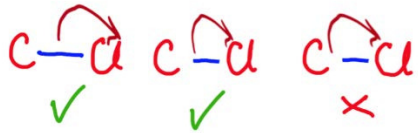
| Question | | | Answer | Marks | AO element | Guidance |
|---|---|---|---|---|---|---|
| | | (ii) | **D** Addition / polyalkene<br>**AND**<br>**E**: Condensation / polyamide ✓ | 1 | AO1.1 | **DO NOT ALLOW** 'additional' |
| | | (iii) | **Formation of electrophile**<br>$CH_3COCl + AlCl_3 \rightarrow CH_3–C^+=O + AlCl_4^-$ ✓<br>**Mechanism**<br>Curly arrow from π-bond to $CH_3C^+=O$ ✓<br><br>---------- | 5 | AO2.5<br>AO2.5 | **ANNOTATE ANSWER WITH TICKS AND CROSSES**<br>**ALLOW** '+' charge anywhere on $CH_3C^+O$<br>*i.e.* $CH_3CO^+$<br>**NOTE**: curly arrows can be straight, snake-like, etc. but **NOT** double headed or half headed arrows<br>**1st curly arrow** must<br>• go to the C of C=O<br>**AND**<br>• start from, **OR** close to **circle of benzene ring**<br><br>**IGNORE** curly arrow shown on C=O |

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

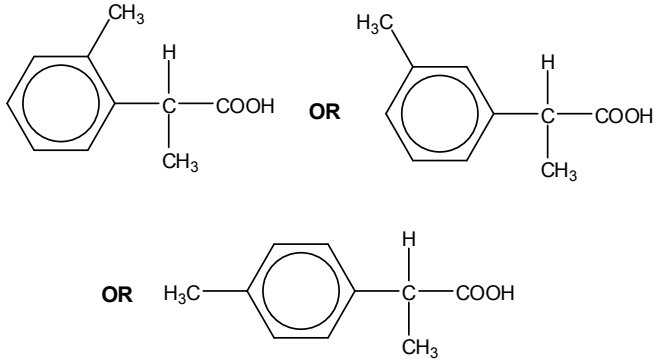
| Question | Answer | Marks | AO element | Guidance |
|---|---|---|---|---|
| (iv) | **one** mark for each correct structure/reagent<br><br> | 7 | AO2.5 ×7 | **ALLOW** any vertical bond to the OH **OR** $NH_2$ groups<br>e.g. **ALLOW**<br><br><br>**DO NOT ALLOW** OH–, **OR** $NH_2$– but **ALLOW ECF**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

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

| Question | | | Answer | Marks | AO element | Guidance |
|---|---|---|---|---|---|---|
| | (b) | (i) |  | **4** | AO3.2 ×4 | **IGNORE** any dipoles shown<br><br>**NOTE**: curly arrows can be straight, snake-like, etc. but **NOT** double headed or half headed arrows<br><br>**Curly arrow** from $OH^-$ must<br>• go to the C of C=O<br>**AND**<br>• start from, **OR** be traced back to **any point across width** of lone pair on O of $OH^-$<br><br>• **OR** start from – charge$^-$OH ion<br><br><br>**Curly arrow** from C=O bond must start from, **OR** be traced back to, **any part of** C=O bond and go to O<br><br><br>**Curly arrow** from $O^-$ must |

| Question | | | Answer | Marks | AO element | Guidance |
|---|---|---|---|---|---|---|
| | | | | | | • go to C=O bond<br>**AND**<br>• start from, **OR** be traced back to, **any point across width** of lone pair<br><br>• **OR** start from '–' charge of $O^-$<br><br>Curly arrow from C–Cl bond must start from, **OR** be traced back to, **any part of** C–Cl bond and go to Cl<br> |
| | **(b)** | **(ii)** | ($OH^-$) donates an electron pair/lone pair<br>**OR**<br>($OH^-$ 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.*<br><br>**Level 3 (5–6 marks)**<br>Structure is $CH_3C_6H_4CH(CH_3)COOH$<br>**AND**<br>Most of the data analysed.<br><br>*There is a well-developed line of reasoning which is clear and logically structured. The information presented is relevant and substantiated.*<br><br>**Level 2 (3–4 marks)**<br>A viable aromatic structure of $C_{10}H_{12}O_2$ that contains C=O **AND** most key features consistent with spectral data<br>**AND**<br>Some of the spectral data analysed<br><br>*There is a line of reasoning presented with some structure. The information presented is relevant and supported by some evidence.* | 6 | AO1.2 × 2<br>AO3.1 × 2<br>AO3.2 × 2 | **Indicative scientific points:**<br><br>**Empirical and Molecular Formulae**<br>• C : H : O = $\frac{73.17}{12.0} : \frac{7.32}{1.0} : \frac{19.51}{16.0}$<br>= 6.10 : 7.32 : 1.22<br>= 5 : 6 : 1<br><br>• Empirical formula = $C_5H_6O$<br>• uses *m/z* = 164.0 to determine molecular formula as $C_{10}H_{12}O_2$<br><br>**Structure**<br>**ALLOW** any combination of skeletal **OR** structural **OR** displayed formula as long as unambiguous<br><br>**Key features of an aromatic structure consistent with spectral data**<br>• COOH group<br>• 4 aromatic H atoms<br>• single H atom that would give a quartet<br>• $CH_3$ group that would give a doublet<br>• $CH_3$ group that would give a singlet |

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

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