PEARSON EDEXCEL A-LEVEL CHEMISTRY · 9CH0

# CHEMISTRY



## MARK SCHEME

### TOPIC 19: MODERN ANALYTICAL TECHNIQUES II

| SCORE | PERCENTAGE |
| --- | --- |
| /217 | % |

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(iii) Give the formula of a fragment ion, with its *m*/*z* value, that you would expect to be present in the mass spectrum of

benzoic acid but **not** in the mass spectrum of phenol or the mass spectrum of phenylmethanol.

**(2)**

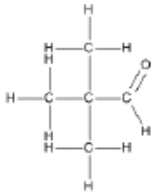
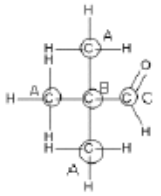
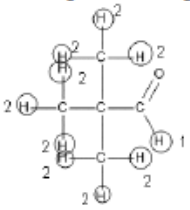
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**(Total for question = 10 marks)**

## Mark Scheme

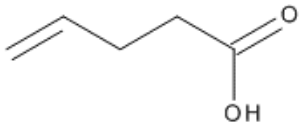
Q1.

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| | An answer that makes reference to the following points:<br><br>• displayed formula of aldehyde (1)<br><br>• three different carbon environments indicated (1)<br><br>• two different proton environments indicated (1)<br><br>• no splitting as there are no hydrogens on the adjacent carbon atom(s) | Example of displayed formula:<br><br>Allow $CH_3$ groups but aldehyde group must be displayed<br><br>Example of three carbon environments:<br><br>Example of two proton environments:<br><br>Stand alone mark | (4) |

Q2.

| Question number | Answer | Mark |
|---|---|---|
| (i) | **The only correct answer is D** ($C_5H_8O_2$)<br>*A is incorrect because $C_7H_{16}$ has a molecular ion m / z = 100.1248*<br>*B is incorrect because $C_6H_{12}O$ has a molecular ion m / z = 100.0885*<br>*C is incorrect because $C_6H_{14}N$ has a molecular ion m / z = 100.1123* | (1) |

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| (ii) | • alkene / C=C **(1)**<br><br>• carboxylic acid / COOH **(1)** | The functional groups can be in any order<br>Ignore just 'double bond'<br><br>Ignore just C=O and OH | (2) |

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| (iii) | • skeletal formula of **X** | Example of skeletal formula   Ignore bond lengths and bond angles | (1) |

Q3.

| Acceptable Answers | Additional Guidance | Mark |
|---|---|---|
| This question assesses a student's ability to show a coherent and logically structured answer with linkages and fully-sustained reasoning.<br><br>Marks are awarded for indicative content and for how the answer is structured and shows lines of reasoning.<br><br>The following table shows how the marks should be awarded for indicative content.<br><br>Number of indicative marking points seen in answer / Number of marks awarded for indicative marking points<br>6 / 4<br>5-4 / 3<br>3-2 / 2<br>1 / 1<br>0 / 0<br><br>Guidance on how the mark scheme should be applied:<br>The mark for indicative content should be added to the mark for lines of reasoning. For example, an answer with five indicative marking points that is partially structured with some linkages and lines of reasoning scores 4 marks (3 marks for indicative content and 1 mark for partial structure and some linkages and lines of reasoning).<br>If there are no linkages between points, the same five indicative marking points would yield an overall score of 3 marks (3 marks for indicative content and no marks for linkages).<br><br>The following table shows how the marks should be awarded for structure and lines of reasoning. | | (6) |

| | | | | |
|---|---|---|---|---|
| | | Number of marks awarded for structure of answer and sustained line of reasoning | | |
| | Answer shows a coherent and logical structure with linkages and fully sustained lines of reasoning demonstrated throughout. | 2 | | |
| | Answer is partially structured with some linkages and lines of reasoning. | 1 | | |
| | Answer has no linkages between points and is unstructured. | 0 | | |
| | **Comment:**<br>Look for the indicative marking points first, then consider the mark for structure of answer and sustained line of reasoning<br>. | | In general it would be expected that 5 or 6 indicative points would get 2 reasoning marks, and 3 or 4 indicative points would get 1 mark for reasoning, and 0, 1 or 2 indicative points would score zero marks for reasoning. | |

| | | | |
|---|---|---|---|
| | **Indicative content**<br><br>• **IP1 -** Similarity<br>**both** $^{1}$H NMR spectra have a peak (which is a singlet with relative peak area 1) for OH<br><br>• **IP2 -** $^{13}$C spectra<br>3 peaks for propan-1-ol **and** 2 peaks for propan-2-ol | **General points to note**<br>If there is any incorrect chemistry, deduct mark(s) from the reasoning. If no reasoning mark(s) awarded do not deduct mark(s).<br>e.g.<br>Mention of splitting on the $^{13}$C spectra<br><br>Deduct 1 reasoning mark if the similarity in IP1 has not been explicitly mentioned<br><br>All IP can be shown on clearly labelled diagrams of structures and/or spectra<br><br>Allow carbon environments for peaks<br>Ignore any reference to peak areas | |

| | | | |
|---|---|---|---|
| | • **IP3 -** $^{1}$H spectra number of peaks<br>4 peaks for propan-1-ol **and** 3 peaks for propan-2-ol<br><br>• **IP4 -** $^{1}$H spectra relative peak areas<br>(relative) peak areas 3 : 2 : 2 : 1 for propan-1-ol,<br>6 : 1 : 1 for propan-2-ol<br><br>• **IP5 -** $^{1}$H splitting pattern for propan-1-ol<br>2 triplets, 1 sextet / split into 6 and 1 singlet<br><br>• **IP6 -** $^{1}$H splitting pattern for propan-2-ol<br>1 doublet, 1 septet / split into 7 and 1 singlet | Allow ratios in any order e.g. 1 : 2 : 2 :3<br><br>Allow hextet for sextet<br>Ignore missing singlet if this has been given in similarity<br><br>Allow heptet for septet<br>Ignore missing singlet if this has been given in similarity | |

Q4.

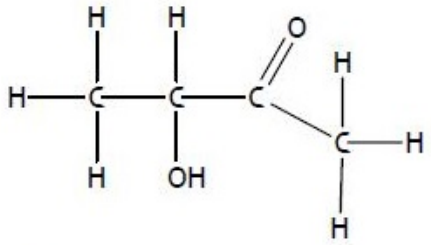
| Question Number | Acceptable Answers | Reject | Mark |
|---|---|---|---|
| **(a)(i)** | C : H : O<br>Mole ratio / mol $\frac{54.5}{12}$ : $\frac{9.1}{1}$ : $\frac{36.4}{16}$ **(1)**<br><br>= 4.5417 : 9.1 : 2.275<br>= 1.996 : 4 : 1<br>= 2 : 4 : 1<br>$C_2H_4O$ **(1)**<br><br>Correct empirical formula of $C_2H_4O$, with or without working, scores **(2)** | | **2** |

| Question Number | Acceptable Answers | Reject | Mark |
|---|---|---|---|
| **(a)(ii)** | **First mark:**<br><br>Any mention of **44** or of doubling $C_2H_4O$ **(1)**<br><br>**Second mark:**<br><br>Any mention of **88 in the context of the mass spectrum** eg mentions 'molecular ion' / $M^+$ / heaviest peak / peak furthest to the right / annotation at 88 on the mass spectrum itself / highest $\frac{m}{z}$ value **(1)** | **88** obtained **just** by adding up the relative atomic masses in $C_4H_8O_2$ scores **(0)** for 2nd scoring point | **2** |

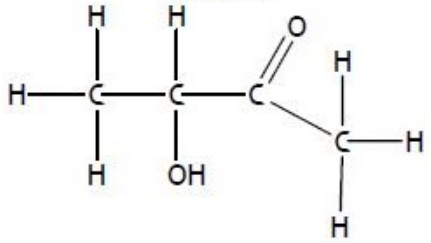
| Question Number | Acceptable Answers | Reject | Mark |
|---|---|---|---|
| **(b)** | (Peak at 3500 $cm^{-1}$) **O—H** **(1)**<br>Allow OH<br><br>(Peak at 1700 $cm^{-1}$) **C=O** **(1)**<br><br>**Penalise extra extension bond on an otherwise correct answer once only**<br>(eg —O—H **and** —C=O scores (1))<br><br>**IGNORE**<br>any names for the bonds suggested even if incorrect | —O—H / —OH<br><br>C—O / —C=O / CO | **2** |

| Question Number | Acceptable Answers | Reject | Mark |
|---|---|---|---|
| **(c)(i)** | **First mark:**<br>(**X** is neutral) so not a (carboxylic) acid **(1)**<br><br>**IGNORE**<br>"**X** doesn't have a charge as it is neutral" / "**X** is not an alkali" / "**X** is not a base"<br><br>**Second mark:**<br><br>(**X** does not react with Tollens') so is **not** an aldehyde / is a ketone **(1)**<br><br>**Third mark:**<br><br>(**X** reacts with $H^+$ / $Cr_2O_7^{2-}$ so) is an alcohol /contains an OH (group) / contains R—OH / contains hydroxyl (group) **(1)**<br><br>**IGNORE**<br>'not an acid' if this is deduced **solely** from the $H^+$ / $Cr_2O_7^{2-}$ information<br><br>**Fourth mark:**<br><br>a primary or a secondary (alcohol)<br>**both needed**<br>**OR**<br>(**X** is) not tertiary (alcohol) **(1)**<br><br>**Mark each point separately**<br><br>**NOTE:**<br><br>'**X** is a primary or a secondary alcohol' scores both the third and fourth marks<br><br>**ALLOW**<br>Correct formulae for the functional groups, instead of their names | **X** is an aldehyde scores **(0)** for this scoring point / **X** is not a ketone scores **(0)** for this scoring point | **4** |

| Question Number | Acceptable Answers | Reject | Mark |
|---|---|---|---|
| **(c)(ii)** | (primary or secondary) alcohol **and** ketone<br><br>**NOTE**<br>**BOTH names** are required here | Just 'hydroxyl for 'alcohol' and/or 'C=O /carbonyl' for ketone/ | **1** |

| Question Number | Acceptable Answers | Reject | Mark |
|---|---|---|---|
| **(d)** | **MARKING ADVICE**<br>Check answer for the suggested structure of X.<br>If the correct structure is shown<br><br>Mark answer according to the following.<br>However if no structure for **X** is shown or an incorrect structure for **X** is proposed, mark answer according to "COMMENTS" scheme below<br><br>**MARKS CAN BE AWARDED FROM SUITABLY ANNOTATED FORMULAE FOR X.**<br><br>**<u>First mark:</u>**<br><br>Four different H / hydrogen / proton environments **(1)**<br><br>**<u>Any five from following seven points</u>:**<br><br>**Either**<br>Application of the (n+1) rule to peak **J** (which is a quartet / splits into **four**)<br>**or**<br>application of the (n+1) rule peak **M** (which is a doublet / splits into **two**) **(1)**<br><br>Any mention to explain **no** splitting for peak **L** as there is no H is attached to the adjacent carbon **(1)** | **Just** 'four different **chemical** environments' | **7** |

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|---|---|---|---|
| | Peak **L**<br>(C**H**$_3$) next to C=O **(1)**<br><br>Peak **M**<br>(C**H**$_3$) next to CH **(1)**<br><br>Peak **K**<br>O**H** **(1)**<br><br>Peak **J**<br>(C**H**) next to $CH_3$ **(1)**<br><br>Any **one** correct δ value quoted within ± 0.2 of the following chemical shifts: 1.4(**M**) or 2.2 (**L**) or 3.7(**K**) or 4.2 (**J**) (ppm) **(1)**<br><br>**Final mark**<br><br>(Compound **X** is) $CH_3CH(OH)COCH_3$<br>**NO** other compound allowed.<br><br>**ACCEPT**<br>any unambiguous formula, e.g. displayed formula<br>**Peak J**<br><br>**Peak M** **Peak K** **Peak L**<br><br>**ACCEPT**<br>3-hydroxybutan-2-one **(1)** | If any incorrect chemical shift **OR A RANGE** of chemical shifts is quoted, this scoring point is not available | |

Q5.

| Question Number | Acceptable Answers | Reject | Mark |
|---|---|---|---|
| **(a)(i)** | Aldehydes often contain (carboxylic) **acid** formed by oxidation (by the oxygen in air) | | **1** |

| Question Number | Acceptable Answers | Reject | Mark |
|---|---|---|---|
| **(a)(ii)** | A larger volume of sodium carbonate solution is neutralized / a larger volume of carbon dioxide forms / faster reaction / more effervescence / more vigorous<br><br>ALLOW reverse argument for impure aldehyde | (The old stock of) aldehyde does not react | **1** |

| Question Number | Acceptable Answers | Reject | Mark |
|---|---|---|---|
| **(a)(iii)** | $Na_2CO_3(aq) + 2C_3H_7COOH(aq) \rightarrow$<br><br>$2C_3H_7COO^{(-)}Na^{(+)}(aq) + CO_2(g) + H_2O(l)$<br><br>Correct balanced equation **(1)**<br>Correct state symbols on correct species **(1)**<br><br>ALLOW<br>$H_2O(aq)$<br>$C_3H_7COO^{(-)}Na^{(+)}(s)$<br>$C_3H_7COOH(l)$ | $NaCO_3$ | **2** |

| Question Number | Acceptable Answers | Reject | Mark |
|---|---|---|---|
| **(a)*(iv)** | 3300 -2500 ($cm^{-1}$) AND O-H (stretching) **(1)**<br><br>1725 – 1700 ($cm^{-1}$) AND C=O (stretching) **(1)**<br>ALLOW single numbers or ranges within these ranges<br>ALLOW<br>1300-1250 ($cm^{-1}$) AND C-O in COOH<br><br>Very broad (O-H) due to hydrogen bonding **(1)** | COOH (group)<br><br>COOH (group)<br><br>Hydrogen Bonding in C=O | **3** |

| Question Number | Acceptable Answers | Reject | Mark |
|---|---|---|---|
| **(a)(v)** | **First mark** (stand alone)<br>4 peaks<br>OR<br>4 hydrogen environments<br><br>ALLOW<br>4 chemical shifts **(1)**<br><br>**Second and Third Marks**<br><br>Splitting pattern:<br><br>($CH_3CH_2CH_2COO\underline{\mathbf{H}}$) singlet /1 line<br><br>($CH_3CH_2C\underline{\mathbf{H_2}}COOH$) triplet / three lines<br><br>($CH_3C\underline{\mathbf{H_2}}CH_2COOH$) sextuplet / sextet / six lines<br><br>($C\underline{\mathbf{H_3}}CH_2CH_2COOH$) triplet / three lines<br><br>All four correct **(2)** any three **(1)**<br><br>ALLOW<br><br>No splits, 2 splits, five splits, 2 splits scores 2<br><br>1,3,6,3 'splits' scores 1 mark | <br><br><br><br><br><br><br><br>1 split<br><br>3 splits<br><br>6 splits<br><br>3 splits | **3** |

| Question Number | Acceptable Answers | Reject | Mark |
|---|---|---|---|
| **(b)** | Start pH at 2.9<br>ALLOW 2—4 **(1)**<br><br>Initial sharp rise to buffer region then vertical section at 25 $cm^3$<br>ALLOW<br>Gradual rise to vertical section at 25 $cm^3$ **(1)**<br><br>Vertical within pH range 6-11<br>**and** 2.5-4 units long **(1)**<br><br>End pH value in range 12-13 **(1)** | <br><br>Horizontal from start<br><br><br><br>deviation from vertical<br><br>maximum before final pH<br>Graph ending before 50$cm^3$ | **4** |

| Question Number | Acceptable Answers | Reject | Mark |
|---|---|---|---|
| **(c)(i)** | White / steamy / misty fumes<br>ALLOW 'gas' for fumes<br>IGNORE correct indicator test on product | White smoke<br>Effervescence<br>Just 'fumes'<br>Just 'gas' | **1** |

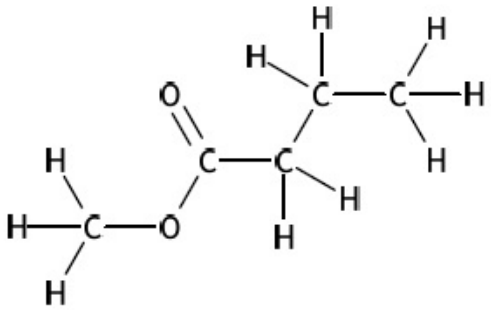
| Question Number | Acceptable Answers | Reject | Mark |
|---|---|---|---|
| **(c)(ii)** | $CH_3CH_2CH_2COCl$ **(1)**<br>ALLOW displayed formula<br><br>butanoyl chloride **(1)**<br>ALLOW Butanyl chloride<br><br>No TE on incorrect structure | $C_3H_7COCL$<br><br><br>Butyl Chloride<br>Buthyl Chloride | **2** |

| Question Number | Acceptable Answers | Reject | Mark |
|---|---|---|---|
| **(d)(i)** | Butan-1-ol<br>OR<br>$CH_3CH_2CH_2CH_2OH$<br><br>If 2 answers are given both must be correct | Butanol<br>Butanal<br>$C_4H_9OH$ | **1** |

| Question Number | Acceptable Answers | Reject | Mark |
|---|---|---|---|
| **(d)(ii)** | (Dry) Ethoxyethane / diethylether / Ether<br><br>OR<br><br>$C_2H_5OC_2H_5$ / $CH_3CH_2OCH_2CH_3$<br><br>If 2 answers are given they must both be correct | | **1** |

| Question Number | Acceptable Answers | Reject | Mark |
|---|---|---|---|
| **(d)(iii)** | The responses are in pairs: a type (1) and an **associated** justification (1)<br><br>Reduction (of butanoic acid) **(1)**<br><br>By addition of hydrogen / loss of oxygen **(1)**<br><br>**OR**<br><br>Oxidation of lithium tetrahydroidaluminate / aluminium hydride / $LiAlH_4$ **(1)**<br><br>By addition of oxygen **(1)**<br><br>**OR**<br><br>(Nucleophilic) addition **(1)**<br><br>of hydride / $H^-$ **(1)**<br><br>**OR**<br><br>Redox **(1)**<br><br>Because butanoic acid has been reduced AND $LiAlH_4$ has been oxidised **(1)** | Any substitution<br>Electrophilic addition | **2** |

| Question Number | Acceptable Answers | Reject | Mark |
|---|---|---|---|
| **(e)(i)** | (Concentrated / dilute) sulfuric / hydrochloric acid<br><br>ALLOW any **strong** acid<br><br>ALLOW 'acid (catalyst)' **(1)**<br><br>(heat or boil under) reflux<br><br>ALLOW Heat / warm **(1)**<br><br>Elevated temp$\leq 65^0$C | Just 'catalyst'<br>Just $H^+$<br>Just 'boil'<br>Just 'distil'<br>High temperature<br><br>Increased concentration | **2** |

| Question Number | Acceptable Answers | Reject | Mark |
|---|---|---|---|
| **(e)(ii)** | <br>All bonds must be shown except<br>ALLOW $CH_3$ at either end of molecule. | Omitted Hydrogen / sticks | **1** |

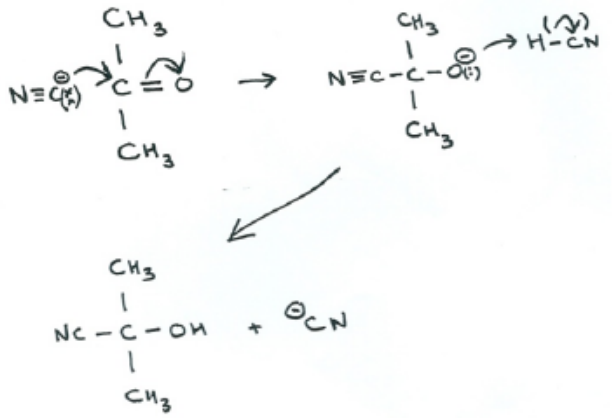
| Question Number | Acceptable Answers | Reject | Mark |
|---|---|---|---|
| **(e)(iii)** | Butanoyl chloride / $CH_3CH_2CH_2COCl$<br>ALLOW Butanyl chloride<br><br>OR<br><br>Butanoic anhydride / $(CH_3CH_2CH_2CO)_2O$<br><br>OR<br><br>Specified alkyl butanoate (not methyl butanoate)<br><br>If name and structure are both given they must both be correct | Butyl Chloride<br>Buthyl Chloride | **1** |

| Question Number | Acceptable Answers | Reject | Mark |
|---|---|---|---|
| **(e)(iv)** | **Advantage** marks are dependent on correct reagent (or near miss e.g. propanoyl chloride) in (iii).<br>No TE on random answer to (iii) eg $H_2SO_4$<br><br>Advantages – any **two** from:<br><br>Higher yield / goes to completion/ not an equilibrium reaction / not reversible<br><br>No heat / no refluxing / less energy needed<br><br>No catalyst needed / faster<br><br>By-product is a gas (so easier to separate) **(2)**<br><br>Disadvantage (marked independently of (e)(iii)) any **one** of:<br><br>(Acyl chloride is) more expensive / corrosive<br>IGNORE<br>Acyl chloride is toxic / hazardous / harmful / difficult to store<br><br>OR<br><br>toxic /corrosive **and** HCl /gas / fumes evolved<br><br>IGNORE harmful/ hazardous/ dangerous<br><br>OR<br><br>has lower atom economy **(1)** | Good yield | **3** |

Q6.

| Question Number | Correct Answer | Reject | Mark |
|---|---|---|---|
| **(a)(i)** | Sodium/potassium dichromate ((VI)) **and** (Dilute/concentrated) sulfuric acid<br><br>OR<br><br>correct formulae / $H^+$ **and** $Cr_2O_7^{2-}$<br><br>ALLOW<br><br>$H^+$ **and** $Cr_2O_7^{2-}$/acidified dichromate((VI))<br><br>**(1)**<br><br>Reflux/distil<br><br>Ignore 'heat', 'warm', and 'boil' alone.<br><br>ALLOW<br><br>Just 'under reflux'<br><br>Just 'under distillation'<br><br>**(1)**<br><br>Second mark depends on mention of dichromate/$Cr_2O_7^{2-}$ in first part<br><br>OR<br><br>$KMnO_4$ and acid with heat<br>**(1)** | Hydrochloric acid | 2 |

| Question Number | Correct Answer | Reject | Mark |
|---|---|---|---|
| **(a)(ii)** | Carbonyl group – addition of 2,4-dinitrophenylhydrazine / 2,4-DNP(H) / Brady's reagent **(1)**<br><br>to give yellow/orange/red precipitate/ppt/ppte/solid/crystals<br><br>ALLOW<br><br>recognisable spelling e.g., percepitate **(1)**<br><br>$CH_3C{=}O$ reaction with iodine in alkali/NaOH/KOH/$OH^-$<br><br>ALLOW<br><br>Iodoform/tri-iodomethane/haloform<br><br>AND<br><br>reaction/test **(1)**<br><br>to form (pale) yellow / cloudy precipitate/solid/crystals **(1)**<br><br>Ignore references to smell<br><br>Ignore heat in either part | 2-DNP/4DNP<br><br>Just DNP<br><br>Brick red ppt | 4 |
| | **Note**<br><br>• In both cases result mark depends on test being recognisably correct even if it did not score a mark<br><br>Examples:<br><br>DNP gives yellow ppt<br><br>Iodine test gives yellow ppt<br><br>Tests for aldehydes with correct results, no marks | | |

| Question Number | Correct Answer | Reject | Mark |
|---|---|---|---|
| **(b)(i)** |  | | 3 |
| | Arrow (from carbon) of $CN^-$ to carbon of C=O | CN without negative charge | |
| | **AND** | | |
| | Arrow from part of C=O double bond to oxygen | | |
| | ALLOW | | |
| | Two steps via a charged canonical form **(1)** | | |
| | Intermediate anion with C-CN bond. **(1)** | | |
| | Arrow from resulting $O^-$ to hydrogen of $HCN/H^+/H_2O$ **(1)** | | |
| | **Note** | …C-NC bond | |
| | Arrow directions must be correct to score each mark | | |
| | Penalise half-headed arrows each time in both parts | | |
| | ALLOW skeletal formulae. | | |

| Question Number | Correct Answer | Reject | Mark |
|---|---|---|---|
| **(c)(i)** | (Acid) hydrolysis<br><br>OR<br><br>Alkaline hydrolysis followed by acidification | Hydration | 1 |

| Question Number | Correct Answer | Reject | Mark |
|---|---|---|---|
| **(b)(ii)** | At low pH very few $CN^-$ ions<br><br>ALLOW<br><br>No $CN^-$ ions<br><br>OR<br><br>No KCN/ only HCN present **(1)**<br><br>At high pH very few $H^+$ / HCN<br><br>ALLOW<br><br>No $H^+$ / HCN<br><br>OR<br><br>Hydroxide reacts with $H^+$ / HCN/ acid **(1)** | | 1 |

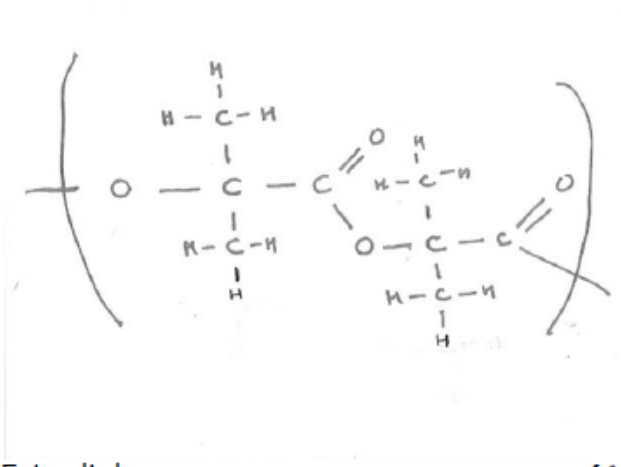
| Question Number | Correct Answer | Reject | Mark |
|---|---|---|---|
| **(c)(ii)** | The O-H absorptions for alcohol and carboxylic acid overlap.<br><br>OR<br><br>OH absorption for an acid is very broad<br><br>OR<br><br>Quote data booklet values which must show some overlap, to include 3300 to 3200.<br><br>ALLOW<br>OH absorptions similar/the same. | Just 'both have OH groups'<br><br>Just 'two OH groups present' | 1 |

| Question Number | Correct Answer | Reject | Mark |
|---|---|---|---|
| **(c)(iii)** | (Chemical shift □) 2.0 - 4.0 (ppm) / any value within this range<br>e.g 3.1/ 3.12/3<br>ALLOW<br><br>Correct number followed by□□,<br><br>eg 3δ | | 1 |

| Question Number | Correct Answer | Reject | Mark |
|---|---|---|---|
| **(c)(iv)** | 3 (peaks) / three | | 1 |

| Question Number | Correct Answer | Reject | Mark |
|---|---|---|---|
| **(c)(v)** | There is no hydrogen atom/proton on the adjacent/neighbouring carbon atom<br><br>ALLOW<br><br>No adjacent/neighbouring hydrogens/protons | | 1 |

| Question Number | Correct Answer | Reject | Mark |
|---|---|---|---|
| **(c)(vi)** | (No)<br><br>2-hydroxy-2-methylpropanoic acid does not have a chiral centre<br><br>OR<br><br>It is not chiral<br><br>OR<br><br>It does not have a mirror image which is non-superimposable<br><br>OR<br><br>Does not have a carbon atom attached to four different groups | Yes... | 1 |

| Question Number | Correct Answer | Reject | Mark |
|---|---|---|---|
| **(d)(i)** | <br><br>Ester linkage **(1)**<br><br>Rest of molecule **(1)**<br><br>ALLOW<br><br>Attached chains as structural formulae<br><br>Ignore n or other numbers outside bracket<br><br>**COMMENT**<br>Check formulae carefully – different carbon frameworks appear. | | 1 |

| Question Number | Correct Answer | Reject | Mark |
|---|---|---|---|
| **(d)(ii)** | Ester | | 1 |

Q7.

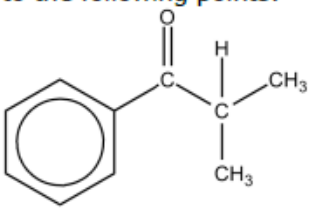
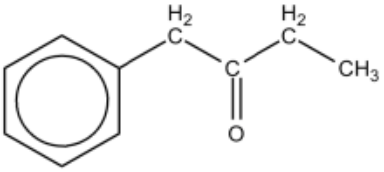
<table>
<tr><th>Question Number</th><th>Acceptable Answer</th><th>Additional Guidance</th><th>Mark</th></tr>
<tr><td>(a)</td><td>• mass of C (1)<br>• mass of H (1)<br>• mass of oxygen <u>and</u> mols of C, H and O (1)<br>• ratio (1)<br>• empirical and use of molar mass to determine molecular formula (1)</td><td><u>Example of calculation</u><br>mass of C = 2.83 x 12/44 = 0.772 g<br>mass of H = 0.693 x 2/18 = 0.077 g<br>mass of oxygen = 0.952 – (0.772 + 0.077) = 0.103 g<br><table><tr><td></td><td>C</td><td>H</td><td>O</td></tr><tr><td>Moles</td><td>0.772/12=0.0643</td><td>0.077/1=0.077</td><td>0.103/16=0.0064</td></tr><tr><td>ratio</td><td>0.0643/0.0063=10</td><td>0.077/0.00643=12</td><td>0.0064/0.0064=1</td></tr></table>Empirical formula = $C_{10}H_{12}O$, this has mass =148<br>so molecular formula = $C_{10}H_{12}O$</td><td>5</td></tr>
</table>

| Question Number | Acceptable Answer | Additional Guidance | Mark |
|---|---|---|---|
| **(i)** | An answer that makes reference to the following point:<br>• contains benzene ring / arene | Ignore comments about alkenes / unsaturated | **1** |

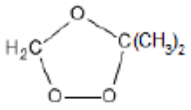
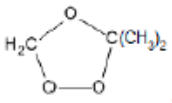
| Question Number | Acceptable Answer | Additional Guidance | Mark |
|---|---|---|---|
| **(ii)** | • is an aldehyde or ketone / is a carbonyl compound | Both aldehyde and ketone required for first alternative | **1** |

| Question Number | Acceptable Answer | Additional Guidance | Mark |
|---|---|---|---|
| **(iii)** | • (**Q** is a) ketone | Allow 'not an aldehyde' if first alternative given in (b)(ii) | **1** |

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| Question Number | Acceptable Answer | Additional Guidance | Mark |
|---|---|---|---|
| **(c)** | An answer that makes reference to the following points:<br><br>(2)<br>• **Chemical shift**<br>(1)<br>peak at 7.5 ppm indicates a benzene ring <u>and</u> peak at 2.55 ppm indicates H on carbon adjacent to C=O <u>and</u> peak at 1.25 ppm indicates alkyl hydrogens<br>• **Splitting pattern**<br>(2)<br>Any 2 from 3:<br>– complex multiplet indicates a benzene ring<br>– septuplet indicates 6 equivalent protons on adjacent carbons<br>– doublet indicates one hydrogen on adjacent carbon<br>• **Area under peak**<br>(2)<br>Any 2 from 3:<br>– five H's indicate $C_6H_5$ / monosubstituted benzene ring<br>– one H indicates one H on C next to carbonyl group<br>– six H's indicates six H's on two methyl groups | Award 1 mark for any structure of $C_{10}H_{12}O$ which includes a benzene ring and a ketone<br>e.g.<br> | **7** |

Q8.

| Question Number | Acceptable Answer | Additional Guidance | Mark |
|---|---|---|---|
| | An answer that makes reference to the following points:<br><br>• **K** is HCHO/methanal because it is the (only) carbonyl with $M_r$ 30<br>(1)<br><br>• the $M_r$ of **L** is 58 so it could be $CH_3COCH_3$/propanone or $CH_3CH_2CHO$/propanal<br>**or**<br>• a carbonyl compound with 3 carbon atoms<br>(1)<br><br>• 2 peaks on the $^{13}C$ NMR spectrum show 2 different carbon environments so it must be propanone (as propanal would have 3 different carbon environments<br><br>(1) | | **5** |
| | • **J** is methylpropene/$CH_2=C(CH_3)_2$ / <br>(1)<br><br>• $CH_2=C(CH_3)_2 + O_3 \rightarrow$ <br> $+ H_2O \rightarrow HCHO + O=C(CH_3)_2 + H_2O_2$<br><br>**both** equations correct<br>(1) | | |

Q9.

| Question Number | Answer | Mark |
|---|---|---|
| (i) | **The only correct answer is B** (alkaline iodine solution)<br><br>***A*** *is not correct because this oxidising agent would react with phenylethanal and not with phenylethanone which is the wrong way round*<br><br>***C*** *is not correct because test is for aldehydes and so would react with phenylethanal and not with phenylethanone which is the wrong way round*<br><br>***D*** *is not correct because test is for aldehydes and so would react with phenylethanal and not with phenylethanone which is the wrong way round* | **(1)** |

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| (ii) | An answer that makes reference to the following points:<br><br>• formation of yellow/orange/red (crystalline) precipitate **(1)**<br><br>• (Filter then) recrystallisation of products **(1)**<br><br>• determination of melting temperature **(1)**<br><br>• comparison (and hence identification) from use of database/known values **(1)** | Colour and state are both required<br>Allow solid for ppt<br>Ignore any conditions given with the use of 2,4-DNPH<br><br>Penalise M3 if any reference to boiling temperature<br><br>Award only in the context of melting temperature of the hydrazones or as a TE of boiling temperature<br><br>Max 3 out of 4 if test is only carried out with one of the carbonyls | **(4)** |

<table>
<tr><th>Question Number</th><th>Answer</th><th>Additional Guidance</th><th>Mark</th></tr>
<tr>
<td>* (iii)</td>
<td>
This question assesses the student's ability to show a coherent and logically structured answer with linkages and fully sustained reasoning.<br><br>
Marks are awarded for indicative content and for how the answer is structured and shows lines of reasoning.<br><br>
The following table shows how the marks should be awarded for indicative content.
<table>
<tr><th>Number of indicative marking points seen in answer</th><th>Number of marks awarded for indicative marking points</th></tr>
<tr><td>6</td><td>4</td></tr>
<tr><td>5-4</td><td>3</td></tr>
<tr><td>3-2</td><td>2</td></tr>
<tr><td>1</td><td>1</td></tr>
<tr><td>0</td><td>0</td></tr>
</table>
<br>
The following table shows how the marks should be awarded for structure and lines of reasoning
<table>
<tr><th></th><th>Number of marks awarded for structure of answer and sustained lines of reasoning</th></tr>
<tr><td>Answer shows a coherent logical structure with linkages and fully sustained lines of reasoning demonstrated throughout</td><td>2</td></tr>
<tr><td>Answer is partially structured with some linkages and lines of reasoning</td><td>1</td></tr>
<tr><td>Answer has no linkages between points and is unstructured</td><td>0</td></tr>
</table>
</td>
<td>
Guidance on how the mark scheme should be applied: The mark for indicative content should be added to the mark for lines of reasoning. For example, a response with four indicative marking points that is partially structured with some linkages and lines of reasoning scores 4 marks (3 marks for indicative content and 1 mark for partial structure and some linkages and lines of reasoning).<br>
If there were no linkages between the points, then the same indicative marking points would yield and overall score of 3 marks (3 marks for indicative content and zero marks for linkages).<br><br>
In general it would be expected that 5 or 6 indicative points would get 2 reasoning marks, and 3 or 4 indicative points would get 1 mark for reasoning, and 0, 1 or 2 indicative points would score zero marks for reasoning. If there is any incorrect chemistry, deduct mark(s) from the reasoning. If no reasoning mark(s) awarded do not deduct mark(s).<br><br>
If there is no mention of protons/hydrogens in the response then deduct one structure and reasoning mark
</td>
<td>(6)</td>
</tr>
</table>

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| | | | |
|---|---|---|---|
| | **Indicative content**<br><br>**Similarities** | Ignore references to $C^{13}$ nmr<br>Accept annotations on a structure towards crediting the following IPs<br>Allow either a single chemical shift value or a range within the stated values<br>Penalise incorrect chemical shifts | |
| | • **IP1**: aromatic hydrogens will give similar/same peaks | Both have peaks in the range 6.5-8.4 (ppm)<br>Ignore any splitting description | |
| | • **IP2**: both have a peak in the range 1.7-3.0 (ppm) (due to the hydrogen of the H–C–C=O type) | Ignore any splitting pattern given for this peak to award this mark | |
| | **Differences**<br>• **IP3** (Hydrogen environments): Phenylethanone has one less peak/hydrogen environment than phenylethanal | Allow any difference of one in the number of peaks stated | |
| | • **IP4** (Splitting patterns): a singlet for phenylethanone but a doublet and a triplet in phenylethanal | All these splitting patterns required for this IP | |
| | • **IP5** (Peak area ratios): relative peak (area) ratio in phenylethanone is 3 but in phenylethanal the peak (area) ratio is 2 to 1 | Ignore the splitting pattern for this IP and ignore any peak areas given for the aryl hydrogens | |
| | • **IP6** (Chemical shifts): (Only) phenylethanal has an aldehyde (hydrogen) peak in the range 9 – 10.1 (ppm) | Ignore the splitting pattern for this IP | |

Q10.

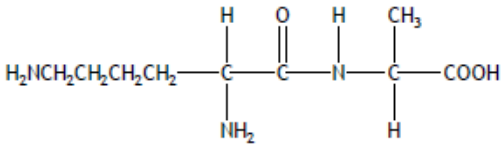
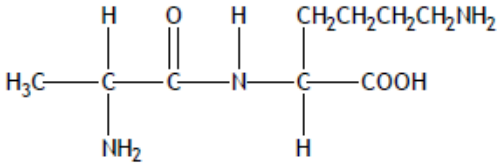
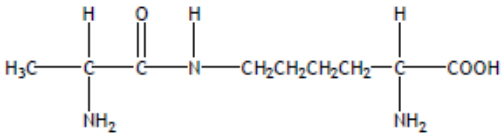
| Question Number | Acceptable Answer | Additional Guidance | Mark |
|---|---|---|---|
| **(a)** | An explanation that makes reference to the following points:<br><br>• **A** no because the two substances have the same molecular formula/ relative molecular mass (1)<br><br>• **B** yes because only 2-aminopropanal is chiral (1)<br><br>• **C** no because both substances react with Fehling's solution (to produce a red precipitate) (1) | Allow no because 3-aminopropanal is not chiral and 2-aminopropanal could be a racemic mixture | **3** |

| Question Number | Acceptable Answer | Additional Guidance | Mark |
|---|---|---|---|
| ***(b)** | This question assesses a student's ability to show a coherent and logically structured answer with linkages and fully-sustained reasoning.<br><br>Marks are awarded for indicative content and for how the answer is structured and shows lines of reasoning.<br><br>The following table shows how the marks should be awarded for indicative content.<br><br>Number of indicative marking points seen in answer / Number of marks awarded for indicative marking points<br>6 / 4<br>5–4 / 3<br>3–2 / 2<br>1 / 1<br>0 / 0<br><br>The following table shows how the marks should be awarded for structure and lines of reasoning. | Guidance on how the mark scheme should be applied:<br>The mark for indicative content should be added to the mark for lines of reasoning. For example, an answer with five indicative marking points that is partially structured with some linkages and lines of reasoning scores 4 marks (3 marks for indicative content and 1 mark for partial structure and some linkages and lines of reasoning).<br>If there are no linkages between points, the same five indicative marking points would yield an overall score of 3 marks (3 marks for indicative content and no marks for linkages). | |

| | Number of marks awarded for structure of answer and sustained line of reasoning |
|---|---|
| Answer shows a coherent and logical structure with linkages and fully sustained lines of reasoning demonstrated throughout. | 2 |
| Answer is partially structured with some linkages and lines of reasoning. | 1 |
| Answer has no linkages between points and is unstructured. | 0 |

| | | | |
|---|---|---|---|
| | **Indicative content**<br>• both have 4 different proton environments/ peaks will be at same chemical shift<br>• peak areas are 1:1:2:3 in 2-aminopropanal<br>• peak areas are 1:2:2:2 in 3-aminopropanal<br>• explanation or use of the (n+1) rule for any splitting pattern<br>• 2-aminopropanal has 1 singlet ($NH_2$), 2 doublets (C**H**O), and ($CH_3$), 1 pentuplet (C**H**)<br>• 3-aminopropanal has 1 singlet ($NH_2$), 2 triplets (C**H**O), and ($CH_2$-$NH_2$), 1 quartet ($CH_2$) | Allow ratios in any order for the second and third marking points<br>Only penalise use of peak heights instead of peak areas once | **6** |

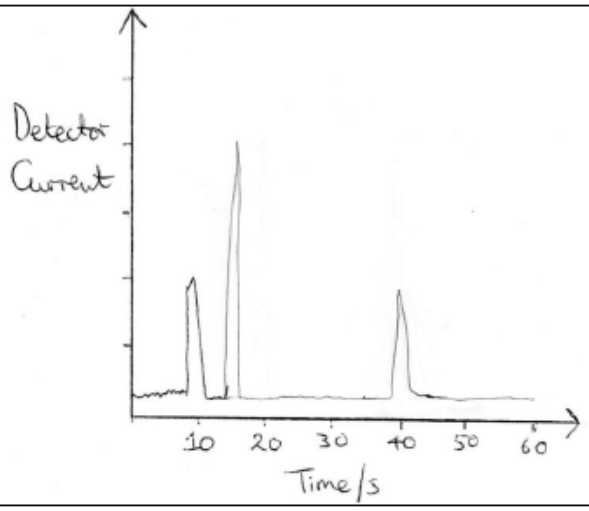
Q11.

| Question Number | Acceptable Answers | Additional Guidance | Mark |
|---|---|---|---|
| (a) | Any one of:<br><br>OR<br><br>OR<br> | Must be the dipeptide and not the repeat unit<br>Allow $-CO_2H$<br>Allow $-H_2N$<br>Allow –CONH– / -COHN- unless C-H-N<br>Allow zwitterions or cyclic dipeptides<br>Allow skeletal / part-skeletal formulae | **(1)** |

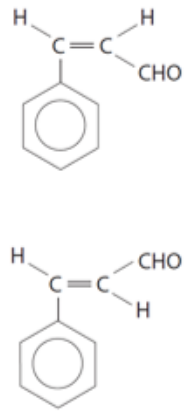
| Question Number | Acceptable Answers | Additional Guidance | Mark |
|---|---|---|---|
| **(b)** | An explanation that makes reference to the following points:<br><br>• (In acidic conditions) lysine (ion) has two positive charges (whereas alanine has only one) **(1)**<br><br>• (So lysine ion has) has greater attraction for the stationary phase **(1)** | Ignore comments on retention time, solubility, polarity, dipoles or intermolecular forces<br><br>Allow 'greater positive charge'<br>Allow lysine has 2 $NH_2$ groups that can be protonated<br><br>Allow<br>'greater affinity for stationary phase'<br>'adheres better to stationary phase'<br>'better adsorption onto stationary phase'<br><br>Allow<br>'polar phase' for 'stationary phase'<br><br>Allow reverse argument for alanine<br><br>Mark points M1 and M2 independently | **(2)** |

Q12.

| Question Number | Acceptable Answer | Additional guidance | Mark |
|---|---|---|---|
| (i) | A statement that makes reference to<br><br>• gases are inert / do not react (with the components of the mixture) | Ignore references to intermolecular bonding / stability<br>Do not award for not an oxidising agent | (1) |

| Question Number | Acceptable Answer | Additional guidance | Mark |
|---|---|---|---|
| (ii) | A sketch that includes<br><br>• peak at 15 seconds and 40 seconds **(1)**<br><br>• (peak at 15 seconds) with height at approximately twice that of the peak at 10 seconds **(1)**<br><br>• (peak at 40 seconds with) height at approximately the same height as that of the peak at 10 seconds<br><br>**(1)**<br><br>Exemplar sketch | Penalise additional peaks<br>Max 1 for the differences in height if both peaks are not at correct positions | (3) |
| |  | | |

Q13.

| Question Number | Answer | Additional guidance | Mark |
|---|---|---|---|
| (b)(i) | • contains C=C/alkene | | 1 |
| (b)(ii) | • contains carbonyl group/ aldehyde or ketone | C=O alone | 1 |
| (b)(iii) | • aldehyde/ -CHO | | 1 |
| (c)(i) | • 77 $C_6H_5^+$ (1)<br>• 103 $C_8H_7^+$ (1) | Must show a charge but only penalise omission once<br>Allow structural, displayed or skeletal formulae | 2 |
| (c)(ii) | <br> | Allow non-displayed benzene C-Hs | 2 |
| (c)(iii) | • The peak is due to the presence of an atom of a ($^{13}C$) isotope | Allow reference to other named isotope of H or O | 1 |

Q14.

| Question Number | Correct Answer | Reject | Mark |
|---|---|---|---|
| | C | | 1 |

Q15.

| Question Number | Answer | Mark |
|---|---|---|
| | **The only correct answer is B** (6)<br><br>***A*** *is not correct because four carbon atoms in the aromatic ring are non-equivalent and not just three, so the correct total of non-equivalent carbon atoms and therefore peaks is six*<br><br>***C*** *is not correct because there are two sets of equivalent carbon atoms in the aromatic ring and not just one which means that the correct total of non-equivalent carbon atoms and therefore peaks is six*<br><br>***D*** *is not correct because this is the total number of carbon atoms in antifebrin but carbon atoms 2 and 6 in the aromatic ring are equivalent, as are 3 and 5, which gives a correct total of six non-equivalent carbon atoms and therefore six peaks* | **(1)** |

Q16.

| Question Number | Correct Answer | Reject | Mark |
|---|---|---|---|
| | C | | 1 |

Q17.

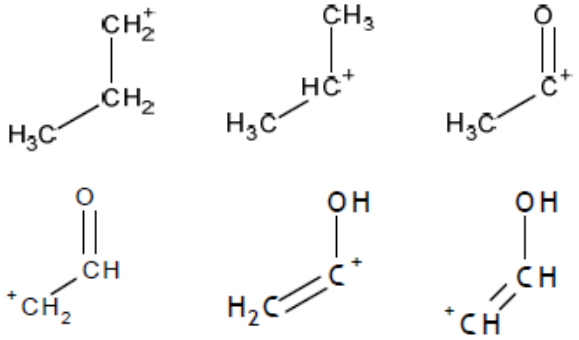
| Question Number | Acceptable Answers | Reject | Mark |
|---|---|---|---|
| **(a)(i)** | So that only the water formed in the combustion is absorbed by X / measured.<br><br>ALLOW<br>'reacts with X' for 'absorbed by X'<br><br>OR<br>Otherwise the mass / amount of the water measured will be too high | Reacts with A<br><br>References to Y | **1** |

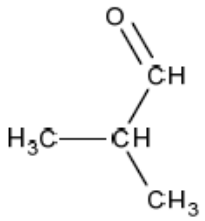
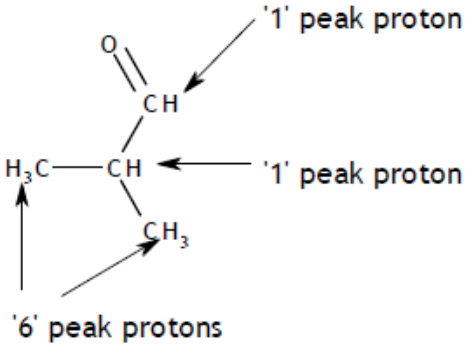
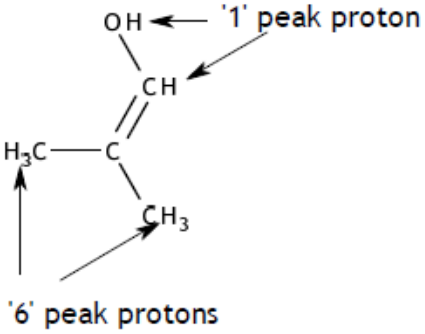
| Question Number | Acceptable Answers | Reject | Mark |
|---|---|---|---|
| **(a)(ii)** | (Anhydrous) Calcium chloride / $CaCl_2$ / Magnesium sulphate / $MgSO_4$ / silica gel / sodium sulphate / $Na_2SO_4$<br><br>ALLOW<br>Phosphorus(V) oxide / phosphorus pentoxide / $P_4O_{10}$ / $P_2O_5$ / Silica beads | Sulfuric acid<br>Calcium oxide<br>Silica / $SiO_2$<br>anhydrous copper(II) sulfate | **1** |

| Question Number | Acceptable Answers | Reject | Mark |
|---|---|---|---|
| **(a)(iii)** | Soda lime<br><br>OR<br><br>calcium hydroxide / $Ca(OH)_2$<br>**and**<br>sodium hydroxide / NaOH<br><br>ALLOW<br>sodium hydroxide / NaOH / potassium hydroxide / KOH / Calcium oxide / CaO | Limewater | **1** |

| Question Number | Acceptable Answers | Reject | Mark |
|---|---|---|---|
| **(a)(iv)** | The methods below illustrate the allocation of marks. But the first four marks may be scored by any correct method.<br><br>**Method 1**<br><br>mol $CO_2$ = 8.8/44 = 0.2 (= mol C) **(1)**<br><br>mol $H_2O$ = 3.6/18 = 0.2<br>mol H = 2 x mol $H_2O$ = 0.4 **(1)**<br><br>mass O = 3.6 – (12 x 0.2 + 1 x 0.4)<br>= 0.8 (g) **(1)**<br><br>mol O = 0.8/16 = 0.05 **(1)**<br><br>**Method 2**<br><br>Mass H = 3.60 x 2/18 = 0.40 (g)<br>= 0.40 / 1 = 0.40 (mol) **(1)**<br><br>Mass C = 8.80 x 12/44 = 2.4 (g)<br>= 2.4 / 12 = 0.20 (mol) **(1)**<br><br>Mass O = 3.60 – (0.40 + 2.4) = 0.80(g) **(1)**<br>= 0.80 / 16 = 0.05 (mol) **(1)** | | **5** |
| | Empirical formula = $C_4H_8O$ **(1)**<br><br>TE on incorrect moles but the ratio **must** be whole number<br><br>IGNORE use of $O_2$ for O in the 'words'<br><br>Correct empirical formula with some working at each stage scores full marks<br>**but**<br>Correct empirical formula with **no** working or **unclear and non-scoring** working scores final mark only | | |

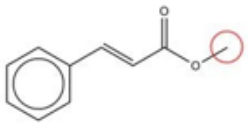
| Question Number | Acceptable Answers | Reject | Mark |
|---|---|---|---|
| **(b)(i)** | (Molecular ion is m/e =) 72 (= $M_r$ of **A**)**(1)**<br><br>Molecular formula = $C_4H_8O$ **(1)**<br><br>No TE on incorrect molecular ion | Structural Or Displayed Or Molecular ion | **2** |

| Question Number | Acceptable Answers | Reject | Mark |
|---|---|---|---|
| **(b)(ii)** | Any three of (1 mark for each structure)<br><br>ALLOW structural formulae (eg $CH_3CO^+$)<br><br>IGNORE Position of positive charge<br><br>Penalise omission of charge or negative charge once<br>$C_3H_7^+$ and /or $C_2H_3O^+$ scores 1 if no scoring structure | | **3** |

| Question Number | Acceptable Answers | | Reject | Mark |
|---|---|---|---|---|
| *(c) | Structure of **A** (1)<br><br>Three (proton/H) environments (1)<br>**Identify** the 6 protons in one environment and 1 each in the other two (1)<br>No TE on incorrect structures except propan-2-ol : scores MP3 only | OR diagram (1)<br><br><br>6 proton label (1) **both** 1 proton labels (1)<br>ALLOW enol structure<br><br><br>6 proton label (1) **both** 1 proton labels (1) | | **3** |

Q18.

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| (i) | An answer that makes reference to the following points:<br>• peak due to tetramethylsilane (1)<br>• so (chemical) shifts (due to other hydrogen atoms) can be compared (1) | Allow TMS / $Si(CH_3)_4$<br>Name must be correct if given<br>Allow<br>"a reference" / "a standard"<br>"calibration"<br>Ignore<br>"to allow other molecules to be compared" | (2) |

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| (ii) | An answer that makes reference to the following points:<br><br>• **M1** circle around $-CH_3$ group in $-OCH_3$ (1)<br><br>• **M2** singlet as no neighbouring hydrogen atoms (1)<br><br>• **M3** peak area of 3 means there are 3 hydrogen atoms in this environment (1) | Allow 'protons' for hydrogen atoms<br><br><br>Award whole $-OCH_3$ circled<br>Do not award if C=O included in circle<br>M1 is a stand alone mark<br><br>Award "has no adjacent hydrogen atoms"<br>Award "no hydrogens on adjacent carbon"<br>Ignore "there is no adjacent C atom"<br><br>Award "(relative) peak area of three for a $-CH_3$ group"<br>For M3 must relate to (relative) peak area / integral<br>Ignore references to chemical shift value for ester $\delta$ = 3.0 to 4.0 (ppm)<br><br>Ignore references to relative heights of peaks<br><br>**Comment**<br>M2 and / or M3 dependent on $-CH_3$ group being included in the circled group | (3) |

Q19.

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| | • 4 (additional) peaks drawn (1)<br>• Splitting marks (ignore chemical shift at this point) (2)<br>- p, q and s are triplets and r is quartet scores 2 marks<br>- two or three splitting patterns correctly shown scores 1 mark<br>• area under curve (1)<br>- total shown by candidate = (2+2+2+3) = 9<br>• chemical shifts (2)<br>- Peak at 0-2 ppm due to protons on s<br>- Peak at 2-3 ppm due to protons on r<br>- Peak at 3-4 ppm due to protons on q<br>- Peak at 1.6-2.8 ppm due to protons on p | Peaks can be shown as separate lines<br>Ignore whether values are linked to correct peak<br>All peaks at correct chemical shift score 2 marks<br>Two or three at correct chemical shift peaks score 1 mark | 6 |

Q20.

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| | An explanation that makes reference to the following points:<br>EITHER<br>• retention time depends on the polarity **or** attraction / affinity / solubility / of the component for the stationary phase (1)<br>• The greater attraction / affinity / solubility / of the component for the stationary phase the greater the retention time (1)<br>OR<br>• retention time depends on the boiling temperature of the compound (1)<br>• higher boiling temperature compounds spend less time in the gas phase / mobile phase so have longer retention time (1) | Allow 'solid phase' or 'liquid phase' for 'stationary phase'<br>Allow 'retention time depends interaction with stationary phase'<br>Ignore attractions to the mobile / gas phase<br>Ignore comments related to mass of compounds | **(2)** |

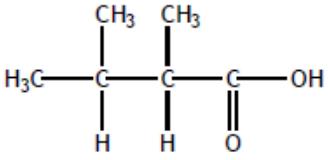
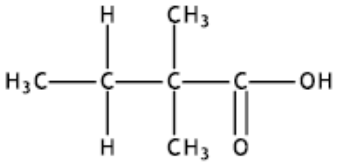
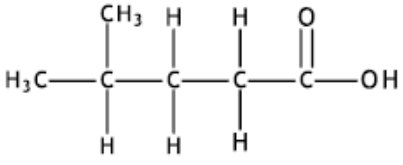
Q21.

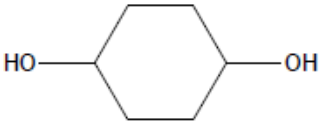
| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| | C | | 1 |

Q22.

| Question Number | Correct Answer | Reject | Mark |
|---|---|---|---|
| | B | | **1** |

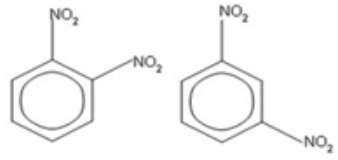
Q23.

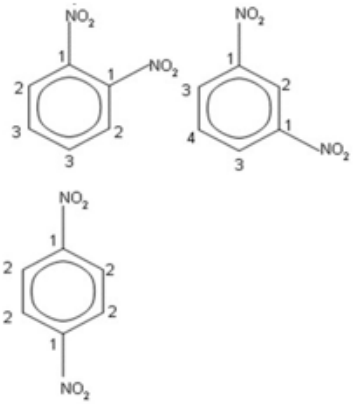
| Question Number | Acceptable Answers | Additional Guidance | Mark |
|---|---|---|---|
| **(i)** | Any two of the following<br><br>$(CH_3)_2CHCH(CH_3)COOH$ /<br><br>**(1)**<br><br>$CH_3CH_2C(CH_3)_2COOH$ /<br><br>**(1)**<br><br>$(CH_3)_2CHCH_2CH_2COOH$ /<br><br>**(1)** | Allow displayed or skeletal formulae | **(2)** |

| Question Number | Acceptable Answers | Additional Guidance | Mark |
|---|---|---|---|
| (ii) |   | Do not award other types of structure | (1) |

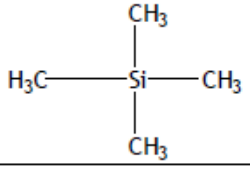
Q24.

| Question Number | Acceptable Answers | Additional Guidance | Mark |
|---|---|---|---|
| (i) | $C_6H_4^{+}$ | Allow $H_4C_6^{+}$<br><br>Do not award just $C_6H_4$ | (1) |

| Question Number | Acceptable Answers | Additional Guidance | Mark |
|---|---|---|---|
| (ii) | • 3 correct formulae (2) | Examples of formulae<br><br><br><br>Allow (1) for any 2 correct formulae<br><br>Allow (2) for three disubstituted benzenes with incorrect substituents / (1) for any two disubstituted benzenes with incorrect substituents<br><br>Allow incorrectly displayed formulae of $NO_2$ groups<br><br>**In (c)(ii) and (iii):**<br>Allow Kekule structures<br>Allow hydrogen atoms shown on benzene<br>Ignore connectivity of $NO_2$ groups<br>Penalise missing circle in benzene once only | (2) |

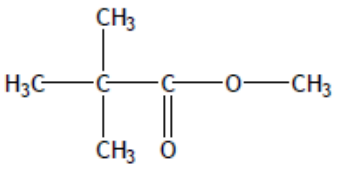
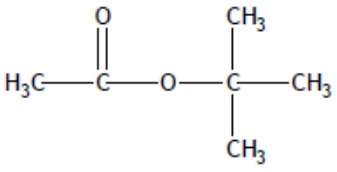
| Question Number | Acceptable Answers | Additional Guidance | Mark |
|---|---|---|---|
| **(iii)** | • **D** identified as 1,3-dinitrobenzene **and** 4 different carbon environments labelled **(1)**<br>• 3 different carbon environments labelled on 1,2-dinitrobenzene **(1)**<br>• 2 different carbon environments labelled on 1,4-dinitrobenzene **(1)** | <br><u>Examples of identification</u><br>These labels may be shown on the structures in (c)(ii)<br>The identification of **D** can be assumed if it is the only structure with 4 carbon environments labelled<br>Allow any form of identification of the carbon environments e.g. numbers, letters, equivalent carbon environments circled<br>TE on disubstituted benzene substituents in (ii)<br>Penalise only half the carbon environments labelled once only | **(3)** |

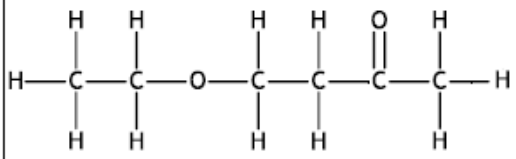
Q25.

| Question Number | Acceptable Answers | Additional Guidance | Mark |
|---|---|---|---|
| **(i)** | $(CH_3)_4Si$ | Allow partially or fully displayed formula<br>Ignore connectivity<br> | **(1)** |

| Question Number | Acceptable Answers | Additional Guidance | Mark |
|---|---|---|---|
| (ii) | An answer that makes reference to any **two** of the following:<br>• single peak / all H or all C in same environment / no splitting pattern **(1)**<br>• (TMS) peak to the right / upfield / out of the way of other peaks / peak doesn't overlap with other peaks **(1)**<br>• (TMS) low boiling temperature / volatile / can be easily removed **(1)**<br>• gives a strong signal so only a small amount needed **(1)** | Allow 12 H or 4 C in the same environment<br>Ignore references to inertness / non-toxicity / cost / non-polar(ity)<br>Ignore chemical shift = 0<br>12 H / 4 C are equivalent so gives a strong signal scores 2 marks | **(2)** |

Q26.

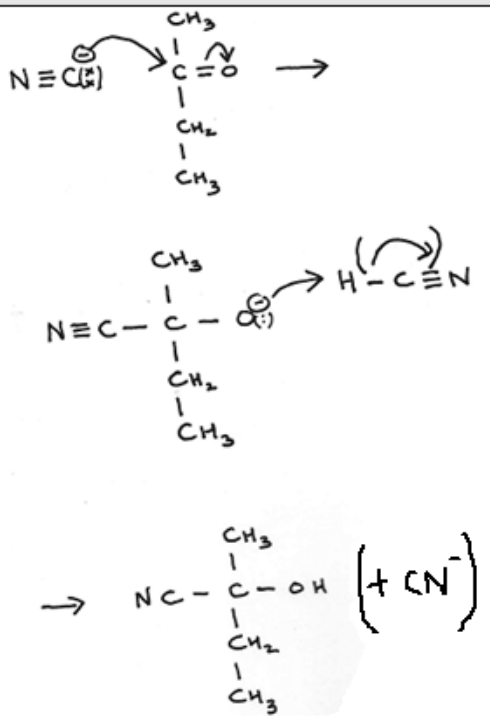
| Question Number | Acceptable Answers | Additional Guidance | Mark |
|---|---|---|---|
| (i) | $C(CH_3)_3COOCH_3$<br>**or**<br><br>**(1)**<br>$CH_3COOC(CH_3)_3$<br>**or**<br><br>**(1)** | Allow displayed or skeletal formulae | **(2)** |

| Question Number | Acceptable Answers | Additional Guidance | Mark |
|---|---|---|---|
| (ii) | An answer that makes reference to the following points:<br><br>• the chemical shift δ 2.2 identified **(1)**<br><br>• four remaining chemical shifts identified **(2)**<br><br>• two splitting patterns given **and** explained **(2)** | $CH_3C{=}O$ / methyl attached to C=O<br><br>Identifies 2 or 3 chemical shifts correctly scores 1<br><br>δ 1.2 3.5 3.8 2.6 (2.2)<br><br><br><br>1 specific splitting patterns explained scores 1 | **(5)** |

Q27.

| Question Number | Correct Answer | Reject | Mark |
|---|---|---|---|
| **(a)(i)** | Sodium/potassium dichromate ((VI)) **and** (Dilute/concentrated) sulfuric acid<br><br>OR<br><br>correct formulae / $H^+$ **and** $Cr_2O_7^{2-}$<br><br>ALLOW<br><br>$H^+$ **and** $Cr_2O_7^{2-}$/acidified dichromate((VI)) **(1)**<br><br>Reflux/distil<br><br>Ignore 'heat', 'warm', and 'boil' alone.<br><br>ALLOW<br><br>Just 'under reflux'<br><br>Just 'under distillation' **(1)**<br><br>Second mark depends on mention of dichromate/$Cr_2O_7^{2-}$ in first part<br><br>OR<br><br>$KMnO_4$ and acid with heat **(1)** | Hydrochloric acid | **2** |

| Question Number | Correct Answer | Reject | Mark |
|---|---|---|---|
| **(a)(ii)** | Carbonyl group – addition of 2,4-dinitrophenylhydrazine / 2,4-DNP(H) / Brady's reagent **(1)**<br><br>to give yellow/orange/red precipitate/ppt/ppte/solid/crystals<br><br>ALLOW<br><br>recognisable spelling e.g., percepitate **(1)**<br><br>$CH_3C{=}O$ reaction with iodine in alkali/NaOH/KOH/$OH^-$<br><br>ALLOW<br><br>Iodoform/tri-iodomethane/haloform<br><br>AND<br><br>reaction/test **(1)**<br><br>to form (pale) yellow / cloudy precipitate/solid/crystals **(1)** | 2-DNP/4DNP<br><br>Just DNP<br><br>Brick red ppt | **4** |
| | Ignore references to smell<br><br>Ignore heat in either part<br><br>**Note**<br><br>• In both cases result mark depends on test being recognisably correct even if it did not score a mark<br><br>Examples:<br><br>DNP gives yellow ppt<br><br>Iodine test gives yellow ppt<br><br>• Tests for aldehydes with correct results, no marks | | |

| Question Number | Correct Answer | Reject | Mark |
|---|---|---|---|
| **(b)(i)** | <br>Arrow (from carbon) of $CN^-$ to carbon of C=O<br><br>AND<br><br>Arrow from part of C=O double bond to oxygen<br><br>ALLOW | CN without negative charge | **3** |
| | Two steps via a charged canonical form **(1)**<br><br>Intermediate anion with C-CN bond. **(1)**<br><br>Arrow from resulting $O^-$ to hydrogen of $HCN/H^+/H_2O$ **(1)**<br><br>**Note**<br><br>Arrow directions must be correct to score each mark<br>Penalise half-headed arrows each time in both parts<br>ALLOW skeletal formulae. | ...C-NC bond | |

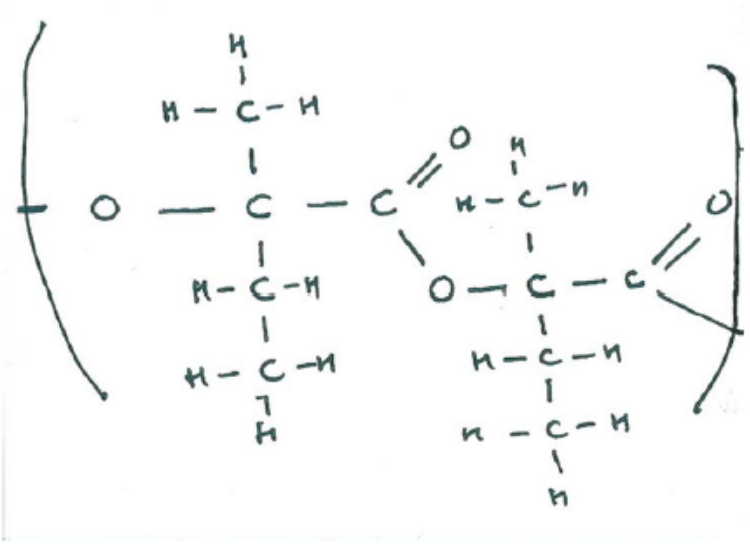
| Question Number | Correct Answer | Reject | Mark |
|---|---|---|---|
| **(b)(ii)** | Forms a racemic mixture **(1)**<br><br>Because bonds around C=O are planar<br><br>OR<br><br>Carbonyl group/reaction site is (trigonal) planar<br><br>OR<br><br>Bonds around carbonyl carbon are planar **(1)**<br><br>Cyanide can attack from either side / above or below **(1)** | Butanone/molecule/it is planar<br><br>C=O is planar<br><br>Carbonyl bond is planar<br><br>Intermediate is planar | **3** |

| Question Number | Correct Answer | Reject | Mark |
|---|---|---|---|
| **(c)(i)** | (Acid) hydrolysis<br><br>OR<br><br>Alkaline hydrolysis followed by acidification | Hydration | **1** |

| Question Number | Correct Answer | Reject | Mark |
|---|---|---|---|
| **(c)(ii)** | The O-H absorptions for alcohol and carboxylic acid overlap.<br><br>OR<br>OH absorption for an acid is very broad<br><br>OR<br>Quote data booklet values which must show some overlap, to include 3300 to 3200.<br><br>ALLOW<br>OH absorptions similar/the same. | Just 'both have OH groups'<br><br>Just 'two OH groups present' | **1** |

| Question Number | Correct Answer | Reject | Mark |
|---|---|---|---|
| **(c)(iii)** | (Chemical shift δ) 2.0 - 4.0 (ppm) / any value within this range<br><br>ALLOW<br>Correct number followed by δ,<br>eg 3δ | | **1** |

| Question Number | Correct Answer | Reject | Mark |
|---|---|---|---|
| **(c)(iv)** | There is no hydrogen atom/proton on the adjacent/neighbouring carbon atom<br><br>ALLOW<br>No adjacent/neighbouring hydrogens/protons | | **1** |

| Question Number | Correct Answer | Reject | Mark |
|---|---|---|---|
| **(d)** | <br>Ester linkage **(1)**<br>Rest of molecule **(1)**<br><br>ALLOW<br>Attached chains as structural formulae<br>Ignore n or other numbers outside bracket | | **2** |

Q28.

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| | • number of peaks in first product (1)<br>• number of peaks in second product (1) | Number of peaks in the $^{13}C$ NMR spectrum: 4, 6 | (2) |

Q29.

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| (i) | An answer that makes reference to<br><br>• **(M1)** (similarity) all have arene C–H absorptions<br>Either 3030 ($cm^{-1}$)<br>**or**<br>750 and/or 700 ($cm^{-1}$)<br>**(1)**<br><br>• **(M2)** only phenol and phenylmethanol have O–H<br>3750 - 3200 ($cm^{-1}$)<br>**(1)**<br><br>• **(M3)** only benzoic acid has O–H<br>3300 - 2500 ($cm^{-1}$)<br>**(1)**<br><br>• **(M4)** only benzoic acid has C=O 1700 - 1680 ($cm^{-1}$)<br>**(1)**<br><br>• **(M5)** only phenylmethanol has alkane C–H absorptions<br>either<br>2962 - 2853 ($cm^{-1}$)<br>or<br>1485 - 1365 ($cm^{-1}$)<br>**(1)** | Bond and wavenumber ranges necessary for each mark<br><br>Do not award 880/830/780 ($cm^{-1}$)<br><br>Do not award –OH / C–OH by penalising once only in M2 and M3<br><br>All 5 correct bonds with no wavenumber ranges scores (3) 4 correct etc scores (2) and 3 correct etc scores (1)<br><br>All 5 correct wavenumber ranges with no bonds or incorrect bonds scores (3) 4 correct etc scores (2) and 3 correct etc scores (1)<br><br>Penalise any additional peaks once only<br><br>Ignore references to different fingerprint regions | **(5)** |

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| (ii) | An answer that makes reference to<br><br>• five peaks (in the $^{13}C$ NMR spectrum)<br>**(1)**<br><br>• (four) aromatic peaks within the chemical shift range of 165 - 105 (ppm)<br>**(1)**<br><br>• (one) peak (for the C-OH) within the chemical shift range of 75 - 55 (ppm)<br>**(1)** | Allow any range within the stated ranges<br>Penalise single values as opposed to ranges once only<br>Accept annotations on diagram<br><br>Penalise additional peaks once only when three or more types of peak are stated | **(3)** |

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| (iii) | An answer that makes reference to<br><br>• suitable formula of fragment ion **(1)**<br><br>• matching *m*/*z* value **(1)** | <u>Example of a suitable formula</u><br><br>$C_6H_5COO^+$ or $C_6H_5CO^+$<br>Do not award $C_7H_5O_2^+$ or $C_7H_5O^+$<br><br>*m*/*z* = 121 or 105<br><br>Allow<br>$COOH^+$ (1)<br>Do not award bond to the fragment, e.g. –$COOH^+$<br><br>*m*/*z* = 45 (1)<br><br>No TE on incorrect fragment ions such as $CH_3^+$ | **(2)** |