PEARSON EDEXCEL IAL CHEMISTRY · YCH11

# CHEMISTRY



## EXAM QUESTION PACK

### UNIT 4: CARBOXYLIC ACIDS

| SCORE | PERCENTAGE |
| --- | --- |
| /137 | % |

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Q1.

**Answer the question with a cross in the box you think is correct ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.**

Butanoic acid may be prepared by the acid hydrolysis of

☒ **A** butyl ethanoate

☒ **B** 1-chlorobutane

☒ **C** ethyl butanoate

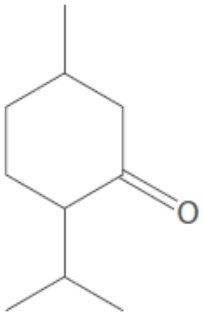
☒ **D** propanenitrile

**(Total for question = 1 mark)**

Q2.

This question is about carbonyl compounds.

(a) The skeletal formula of menthone is shown.




Give the molecular formula of menthone.

**(1)**

.....

(b) Ethanal, $CH_3CHO$ , reacts with hydrogen cyanide in the presence of cyanide ions to form 2-hydroxypropanenitrile.

Draw the mechanism for this reaction.
Include curly arrows, and any relevant lone pairs and dipoles.

**(4)**

(c) A carbonyl compound, **F**, has the molecular formula $C_6H_{12}O$ .

(i) **F** reacts with iodine in an alkaline solution to give a pale yellow precipitate.

Give the name or formula of the group in **F** identified by this test.

**(1)**

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(ii) Draw the **skeletal** formulae of the four possible structures of carbonyl compound **F**.

**(2)**

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|---|---|
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| | |

(iii) The carbon-13 ($^{13}C$) NMR spectrum of **F** has four peaks.

Identify **F** by drawing its **displayed** formula.
Justify your answer by labelling the carbon atoms or groups of carbon atoms responsible for the four peaks in the spectrum.

**(2)**

*(d) Explain, in terms of all the intermolecular forces involved, why butanal has a higher boiling temperature than pentane but a lower boiling temperature than propanoic acid.

| Substance | Boiling temperature / °C |
|---|---|
| butanal | 76 |
| pentane | 36 |
| propanoic acid | 141 |

**(6)**

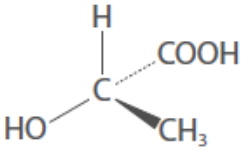
**(Total for question = 16 marks)**

Q3.

This question is about carboxylic acids and their derivatives.

(a) Lactic acid, $CH_3CH(OH)COOH$ , is produced in muscles as a result of anaerobic respiration.

(i) The structure of lactic acid is




Give a reason why lactic acid shows optical isomerism.

**(1)**

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(ii) A laboratory sample of lactic acid does **not** rotate the plane of plane-polarised monochromatic light.

Give a reason for this observation.

**(1)**

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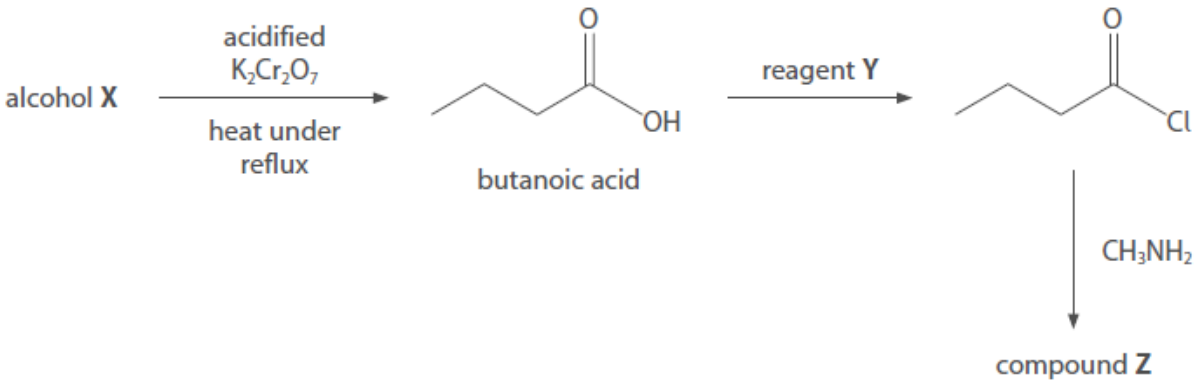
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(iii) Give the structure of the organic product formed when lactic acid reacts with concentrated phosphoric(V) acid, $H_3PO_4$ .

**(1)**

(b) A reaction scheme involving butanoic acid is shown.

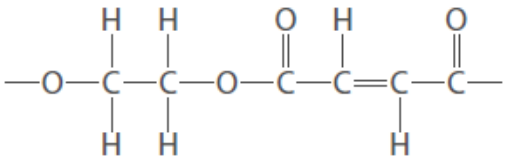



Identify **X**, **Y** and **Z** by name or formula.

**(3)**

| |
|---|
| Alcohol **X** |
| Reagent **Y** |
| Compound **Z** |

(c) The repeat unit of a polyester is shown.



Give the structures of the two monomers that could form this polyester.

**(2)**

| Monomer 1 | Monomer 2 |
|---|---|
| | |

(d) An organic compound **E** contains carbon, hydrogen and oxygen only.

(i) The accurate relative atomic masses, $A_r$ , of the three elements in **E** are shown in the table.

| Element | $A_r$ |
|---|---|
| hydrogen | 1.0078 |
| carbon | 12.0000 |
| oxygen | 15.9949 |

**E** contains five carbon atoms and gives a molecular ion peak at $m / z = 102.0678$ in its mass spectrum.

Deduce the molecular formula of **E**.

**(1)**

(ii) Aqueous sodium hydrogencarbonate is added to a sample of **E**.
No effervescence occurs.

State what can be deduced by this observation.

**(1)**

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.....

(iii) The infrared spectrum of **E** has an absorption in the range 1750 – 1735 $cm^{-1}$.

Name the functional group in **E**.

**(1)**

.....

(iv) Data from the high resolution proton NMR spectrum of **E** is shown.

| Peak | Chemical shift, δ / ppm for TMS | Splitting pattern | Relative peak area |
|---|---|---|---|
| **A** | 4.02 | triplet | 2 |
| **B** | 2.05 | singlet | 3 |
| **C** | 1.65 | sextet | 2 |
| **D** | 0.95 | triplet | 3 |

Deduce the structure of **E**.
Justify your answer by labelling the protons responsible for each peak.

**(3)**

**(Total for question = 14 marks)**

Q4.

Which of these reacts directly with ethanoic acid to form ethanoyl chloride?

☒ **A** chlorine

☒ **B** chloroethane

☒ **C** hydrogen chloride

☒ **D** phosphorus(V) chloride

**(Total for question = 1 mark)**

Q5.

Esters are used in flavourings and perfumes.
They can be made by reactions involving alcohols.

(a) A flask containing a mixture of 0.200 mol of ethanoic acid and 0.150 mol of ethanol was left at 25 °C, in the presence of a catalyst, until equilibrium had been established.

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

The ethanoic acid present in the equilibrium mixture required 34.8 $cm^3$ of a 2.50 mol $dm^{-3}$ solution of sodium hydroxide for complete neutralisation.

(i) Calculate the value of the equilibrium constant, $K_c$, for this reaction at 25 °C.

**(4)**

(ii) The enthalpy change for this reaction is small.

Explain, by reference to the type and number of bonds being broken and made, how this might have been predicted.

**(2)**

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(b) An ester which smells of raspberries can be formed by either of two different reactions.

Reaction **1**

$$HCOOH + (CH_3)_2CHCH_2OH \overset{\text{catalyst}}{\rightleftharpoons} HCOOCH_2CH(CH_3)_2 + H_2O$$

Reaction **2**

$$HCOCl + (CH_3)_2CHCH_2OH \rightarrow HCOOCH_2CH(CH_3)_2 + HCl$$

(i) **Name** the carboxylic acid, alcohol and catalyst used in Reaction **1**.

**(2)**

$HCOOH$ .....  catalyst .....

$(CH_3)_2CHCH_2OH$ .....

(ii) Explain **one** advantage and **one** disadvantage of using Reaction **2** rather than Reaction **1**.

**(4)**

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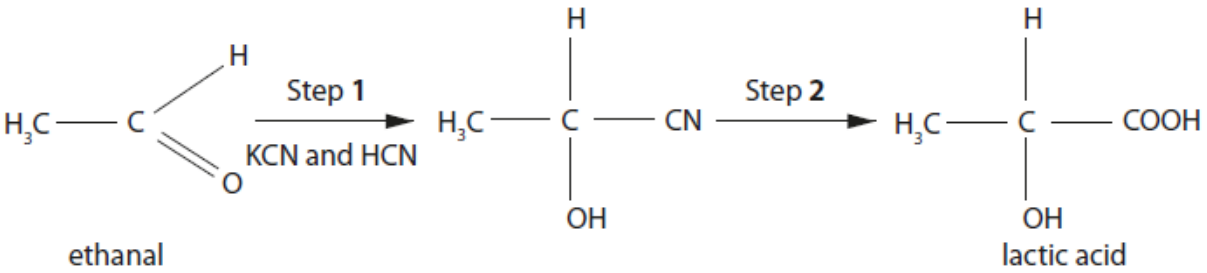
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**(Total for question = 12 marks)**

Q6.

The compound lactic acid can be synthesised from ethanal in two steps.




ethanal

lactic acid

(a) (i) Give the mechanism for Step **1**. Include curly arrows, and any relevant lone pairs and dipoles.

**(4)**

(ii) A student predicted that the product of Step **1** would rotate the plane of plane-polarised light.

Comment on this prediction.

**(3)**

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(iii) Complete the table that summarises information about Step **2**.
State symbols are not required for the equation.

**(4)**

| Conversion of $CH_3CH(OH)CN$ to lactic acid | |
|---|---|
| Reaction type | |
| Reagent | |
| Conditions | |
| Equation | |

(b) Sodium hydrogencarbonate, $NaHCO_3$ , has been used by some athletes to help prevent lactic acid causing muscle pain during exercise.

Write an equation for the reaction between sodium hydrogencarbonate and lactic acid.

**(1)**

(c) Sodium hydrogencarbonate is part of a buffer in the body that controls the pH of blood. Two of the equilibria involved in this process are shown.

Equilibrium 1 $HCO_3^- + H_3O^+ \rightleftharpoons H_2CO_3 + H_2O$

Equilibrium 2 $H_2CO_3 \rightleftharpoons CO_2 + H_2O$

(i) Use the equilibria to explain how the buffer keeps the pH of blood nearly constant when a small increase in the concentration of hydrogen ions occurs.

**(3)**

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(ii) The pH of a blood sample was found to be 7.41.
Calculate the ratio of the concentration of $HCO_3^-$ to $H_2CO_3$ in the blood sample.

$$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$$

$$K_a = 4.50 \times 10^{-7} \text{ mol dm}^{-3}$$

**(3)**

**(Total for question = 18 marks)**

Q7.

This question is about compounds with the molecular formula $C_6H_{12}O_2$.

(a) Hexanoic acid, $C_5H_{11}COOH$, is a weak acid.

(i) Write the equation for the acid dissociation constant, $K_a$, of hexanoic acid.

**(1)**

(ii) Calculate the pH of a 0.100 mol $dm^{-3}$ solution of hexanoic acid.

[p$K_a$ of hexanoic acid = 4.88]

**(4)**

(iii) The solubility of hexanoic acid in water is 1.08 g per 100 g of water.

The isomer of hexanoic acid, butyl ethanoate, $CH_3CO_2C_4H_9$, has a solubility of 0.68 g per 100 g of water.

Explain the differences in these data in terms of the hydrogen bonding between hexanoic acid and water, and between butyl ethanoate and water.

**(3)**

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(b)(i) Compound **A** is thought to be another isomer of hexanoic acid.

10 g of compound **A** is found to contain 6.21 g of carbon and 1.03 g of hydrogen, with the remainder being oxygen.

Use the data to calculate the empirical formula of compound **A**.

You must show **all** your working.

**(3)**

(ii) State how you might use your answer to (b)(i) and a mass spectrum of compound **A** to prove that compound **A** is an isomer of hexanoic acid.

**(1)**

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*(iii) A series of tests was performed on compound **A**.

| | Test | Observation |
|---|---|---|
| 1 | addition of phosphorus(V) chloride | misty fumes |
| 2 | addition of 2,4-dinitrophenylhydrazine | orange precipitate |
| 3 | addition of Benedict's or Fehling's reagent | solution remains blue with no precipitate |
| 4 | addition of acidified potassium dichromate(VI) | solution remains orange |
| 5 | test using polarimetry | plane of plane polarised light is rotated |

Deduce the structure for compound **A**.
Justify your answer by using all the test results.

**(6)**

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(c) Compound **B**, another isomer with the molecular formula $C_6H_{12}O_2$, contains a ring of six carbon atoms.

The carbon-13 NMR spectrum has only two peaks, one of which is at 69 ppm.

Draw the structure of compound **B**.

**(2)**

**(Total for question = 20 marks)**

Q8.

Which compound has the highest boiling temperature?

**(1)**

- ☒ **A** butanal
- ☒ **B** butan-1-ol
- ☒ **C** butanone
- ☒ **D** butanoic acid

**(Total for question = 1 mark)**

Q9.

Carboxylic acids and acyl chlorides both react with alcohols to produce esters.
Acyl chlorides are often preferred to carboxylic acids for this reaction because the yield of the ester is usually higher.
Which of the following statements is the best explanation for the higher yield?

**(1)**

- ☒ **A** acyl chlorides react to remove any water produced
- ☒ **B** the reaction is not reversible
- ☒ **C** the reaction is less exothermic
- ☒ **D** the reaction has a higher atom economy

**(Total for question = 1 mark)**

Q10.

**Answer the question with a cross in the box you think is correct ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.**

The formation of esters and the hydrolysis of esters are reactions that are slow under normal laboratory conditions.

What speeds up these reactions?

| | Esterification | Hydrolysis |
|---|---|---|
| ☒ **A** | acids only | acids only |
| ☒ **B** | acids only | acids and bases |
| ☒ **C** | bases only | bases only |
| ☒ **D** | bases only | acids and bases |

**(Total for question = 1 mark)**

## Mark Scheme

Q1.

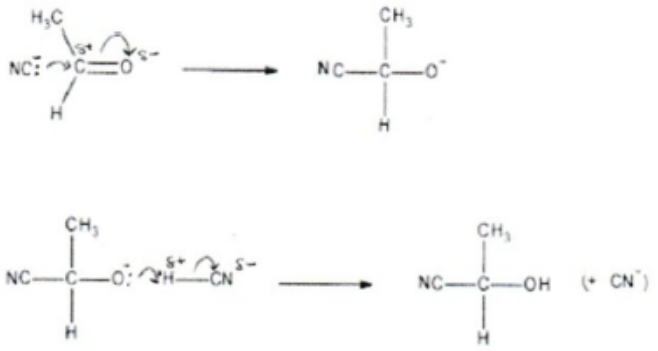
| Question number | Answer | Mark |
|---|---|---|
| | **The only correct answer is C** (ethyl butanoate)<br>*A* *is incorrect because hydrolysis would give ethanoic acid*<br>*B* *is incorrect because hydrolysis would give butan-1-ol*<br>*D* *is incorrect because hydrolysis would give propanoic acid* | **(1)** |

Q2.

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| (a) | • $C_{10}H_{18}O$ | Allow symbols in any order i.e.<br>$C_{10}OH_{18}$ / $H_{18}C_{10}O$ / $H_{18}OC_{10}$ / $OC_{10}H_{18}$ / $OH_{18}C_{10}$<br><br>Allow large numbers e.g. C10H18O<br><br>Do not award superscripts e.g. $C^{10}H^{18}O$ | (1) |

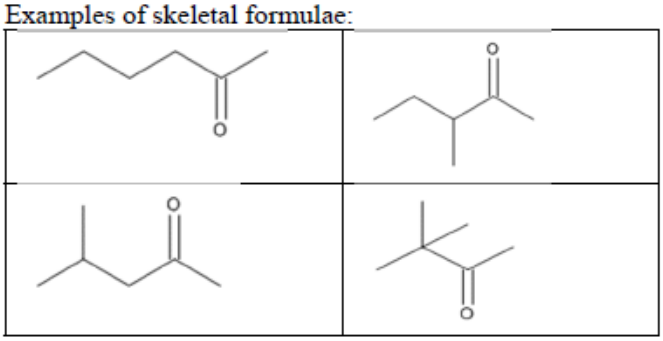
| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| (b) | An answer that makes reference to the following points:<br><br>• curly arrow from lone pair on C of $CN^-$ towards C of aldehyde group (1)<br><br>• curly arrow from C=O to, or just beyond, O **and** dipole on C=O (1)<br><br>• intermediate (1)<br><br>• curly arrow from lone pair on $O^-$ to H **and** curly arrow from H-$\overline{CN}$ bond to anywhere on CN **and** final organic product (1) | Penalise an incorrect dipole in M1 and M4 once only<br>Penalise curly arrow not starting from lone pair once only in M1 and M4<br>Penalise half arrow-heads once only<br><br>Allow $CN^-$ to attack C=O from any angle<br>Allow CN bond displayed<br><br>If M1 lost as curly arrow from N of $CN^-$, allow CN joined to carbon through N<br>Ignore connectivity for vertical CN groups<br><br>Allow curly arrow from lone pair on $O^-$ to $H^+$<br>Ignore missing dipole in HCN | (4) |

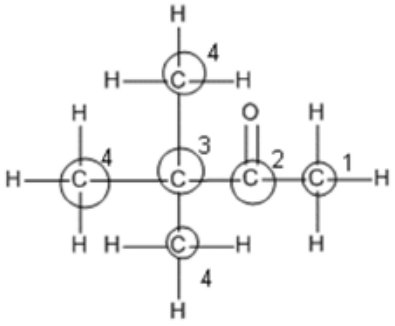
Example of mechanism:



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| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| (c)(i) | • $CH_3CO-$ / $-COCH_3$ / methyl ketone | Allow any combination of structural / displayed formula or skeletal formula<br><br>Allow methyl next to ketone / methyl and ketone / methylcarbonyl<br><br>Allow $CH_3COR$ / $RCOCH_3$<br><br>Ignore missing continuation bond from structures<br><br>Do not award ethanal / methyl secondary alcohol / a specific compound | (1) |

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| (c)(ii) | • any 2 skeletal formulae (1)<br>• remaining 2 skeletal formulae (1) | Examples of skeletal formulae:<br><br>Ignore bond lengths and bond angles<br><br>Allow (1) for 4 correct displayed / structural formulae | (2) |

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| (c)(iii) | • displayed formula of **F** (1)<br>• carbon atoms labelled (1) | Example of displayed formula:<br><br>Allow $CH_3$<br><br>Allow other unambiguous labels for the carbon atoms<br><br>Allow M2 for labels on structural / skeletal formulae, including labels on formulae in (c)(ii)<br><br>Ignore reference to singlet / splitting patterns | (2) |

<table>
<tr><th>Question Number</th><th>Answer</th><th>Additional Guidance</th><th>Mark</th></tr>
<tr>
<td>(d)*</td>
<td>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.
<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>
The following table shows how the marks should be awarded for structure and lines of reasoning.</td>
<td>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).</td>
<td>(6)</td>
</tr>
</table>

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| | 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:**
Look for the indicative marking points first, then consider the mark for structure of answer and sustained line of reasoning

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.

Additional incorrect chemistry loses a structure and lines of reasoning mark (if 1 or 2 have been awarded).

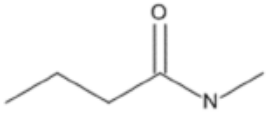
| | | | |
|---|---|---|---|
| | **Indicative content**<br><br>• **IP1 London forces**<br>Pentane (only) has London forces / all have London forces<br>• **IP2 Butanal**<br>Butanal (also) has (permanent) dipole-dipole interactions<br>• **IP3 Propanoic acid**<br>Propanoic acid (also) has (dipole-dipole and) hydrogen bonding<br>• **IP4 Intermolecular forces**<br>The London forces have about the same strength as they have a similar number of electrons / pentane has 42, butanal has 40 (and propanoic acid has 40 electrons)<br>**or**<br>butanal has dipole-dipole interactions because it is polar / has a dipole on C=O<br>**or**<br>propanoic acid has hydrogen bonding because it contains OH / COOH group<br><br>• **IP5 Butanal and pentane**<br>Dipole-dipole interactions are stronger than London forces **or** more energy is needed to overcome the dipole-dipole interactions than London forces<br>• **IP6 Butanal and propanoic acid**<br>Hydrogen bonding is stronger than dipole-dipole interactions<br>**or**<br>more energy is needed to overcome hydrogen bonding than dipole-dipole interactions | Allow dispersion forces / van der Waals' forces / forces between an instantaneous dipole and an induced dipole for London forces throughout answer<br>Do not award IP1 if any other forces mentioned<br><br>Allow dipole-dipole forces / attractions / bonds<br>Do not award IP2 if hydrogen bonding included<br><br>Allow similar relative molecular masses (butanal 72, pentane 72, propanoic acid 74)<br><br>Do not award incorrect numbers of electrons / relative molecular masses<br><br>Allow dipole-dipole interactions linked to C=O<br><br>Allow diagram of hydrogen bond between two molecules<br>Ignore formation of dimer<br><br>Allow London forces are the weakest (intermolecular force)<br>Do not award if covalent bonds broken or explanation is about intermolecular forces with water<br><br>Allow hydrogen bonding is the strongest (intermolecular force)<br>Do not award if covalent bonds broken or explanation is about intermolecular forces with water | **(6)** |

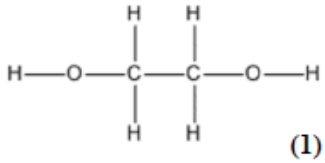
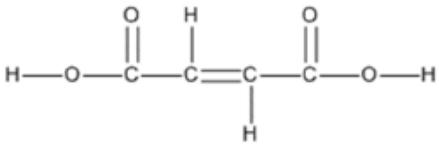
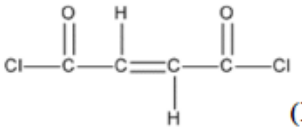
Q3.

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| (a)(i) | An answer that makes reference to the following point:<br>• it / lactic acid is non-superimposable on its mirror image | Allow there are four different atoms / groups attached to a carbon (atom)<br>Allow it is chiral / has a chiral centre / has a chiral carbon (atom) / has an asymmetric carbon (atom)<br><br>Ignore rotates the plane of plane-polarised light<br><br>Do not award four different molecules attached to a carbon (atom) | (1) |

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| (a)(ii) | An answer that makes reference to the following point:<br>• it is a racemic mixture<br>**or**<br>contains equal amounts of the two enantiomers / (optical) isomers | Allow rotations caused by both enantiomers / isomers cancel<br><br>Ignore just contains two enantiomers / isomers<br><br>Do not award plane-polarised light cannot pass through the solution | (1) |

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| (a)(iii) | • $CH_2$=CHCOOH | Allow any combination of structural or displayed formulae or skeletal formulae / $COOHCH=CH_2$ | (1) |

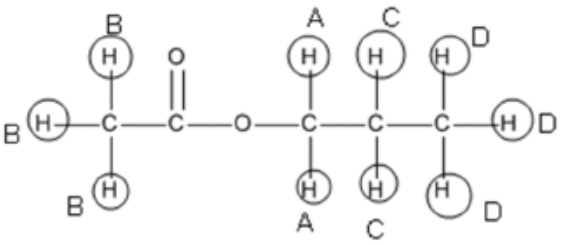
| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| (b) | • **X**: butan-1-ol<br>**or**<br><br>**or** $CH_3CH_2CH_2CH_2OH$ / $CH_3(CH_2)_2CH_2OH$ **(1)**<br>• **Y**: phosphorus(V) chloride / phosphorus pentachloride / $PCl_5$ **(1)**<br>• **Z**: *N*-methylbutanamide<br>**or**<br><br>**or** $CH_3CH_2CH_2CONHCH_3$ / $CH_3(CH_2)_2CONHCH_3$ **(1)** | Mark independently<br>If names and formulae are given, both must be correct but penalise missing H from carbon chain displayed formulae once only<br><br>Allow any combination of skeletal, structural or displayed formulae<br><br>Ignore molecular formulae for **X**, **Y** and **Z**<br><br>Ignore butanol / $C_4H_9OH$<br>Do not award $CH_3CH_2CH_2CH_3O$<br>Do not award butanal<br><br>Allow phosphorus(III) chloride / $PCl_3$ / thionyl chloride / $SOCl_2$<br>Do not award hydrochloric acid / HCl<br><br>Ignore methylbutanamide / butanamide in addition to a correct structure<br><br>Allow NH in skeletal formula<br><br>Do not award $CH_3CH_2CH_2COHNCH_3$ / $CH_3CH_2CH_2COCH_3NH$ | (3) |

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| (c) | • Monomer 1<br><br>(1)<br>• Monomer 2<br><br>or<br><br>(1) | Allow monomers in either order<br>Allow any combination of structural or displayed formulae / skeletal formulae<br>Allow OH<br><br>Ignore bond lengths and bond angles<br><br>Penalise OH-C on left of molecules once only<br>Penalise missing H from carbon chain displayed formulae once only<br><br>Accept cis isomers | (2) |

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| (d)(i) | • $C_5H_{10}O_2$ | Allow symbols in any order<br><br>Ignore any working<br>Ignore + charge | (1) |

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| (d)(ii) | • **E** is not a carboxylic acid<br>or does not contain COOH (group) | If name and formula are given, both must be correct<br><br>Allow **E** is not an acid<br><br>Do not award additional functional groups | (1) |

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| (d)(iii) | • **E** is an ester | Ignore saturated / -COO- / C=O<br><br>Do not award additional functional groups | (1) |

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| (d)(iv) | • structure of **E** (1)<br>• 2 or 3 proton environments correct (1)<br>• 4th proton environment correct (1) | Example of structure:<br><br>Protons can be circled and labelled or just labelled<br>Allow labels using data from the table<br>Only 1 proton from each group needs to be labelled<br>Allow whole groups to be labelled, including the carbon atom | (3) |

Q4.

| Question Number | Answer | Mark |
|---|---|---|
| | The only correct answer is **D** (phosphorus(V) chloride)<br>*A is incorrect as chlorine will not react with ethanoic acid to form ethanoyl chloride*<br>*B is incorrect as chloroethane will not react with ethanoic acid to form ethanoyl chloride*<br>*C is incorrect as hydrogen chloride will not react with ethanoic acid to form ethanoyl chloride* | 1 |

Q5.

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| **(a)(i)** | • calculates moles of acid present in the mixture **(1)**<br>• calculates moles of ester and water present in the mixture **(1)**<br>• calculates moles of ethanol present in the mixture **(1)**<br>• expression for $K_c$ and final answer | Example calculation<br>mol of acid = mol of NaOH = $\frac{34.8}{1000}$ x 2.50 = 0.087 (mol)<br>mol of ester = mol of water = 0.2 – 0.087 = 0.113(mol)<br>mol of ethanol = 0.150 – 0.113 = 0.037<br>If the expression for Kc is incorrect, e.g. no water, allow TE on M1-3 for example not calculating moles of water as well as ester<br>$K_c = \frac{0.113/V \times 0.113/V}{0.087/V \times 0.037/V}$ = 3.9668 / 4.0 (no units)<br>OR<br>$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$ = 3.9668 / 4.0 **and** statement that volumes cancel<br>Do not penalise lack of square brackets in equilibrium expression<br>Assumption that 0.087 is moles of acid used gives moles ethanol = 0.063 moles ester = water = 0.087<br>Kc = 1.0632 scores max (3)<br>Calculation of acid moles at equilibrium larger than acid moles at the start can score M4 only<br>If no other mark is scored Award (1) for calculation of 0.087(mol) however it is used, Ignore SF | **(4)** |

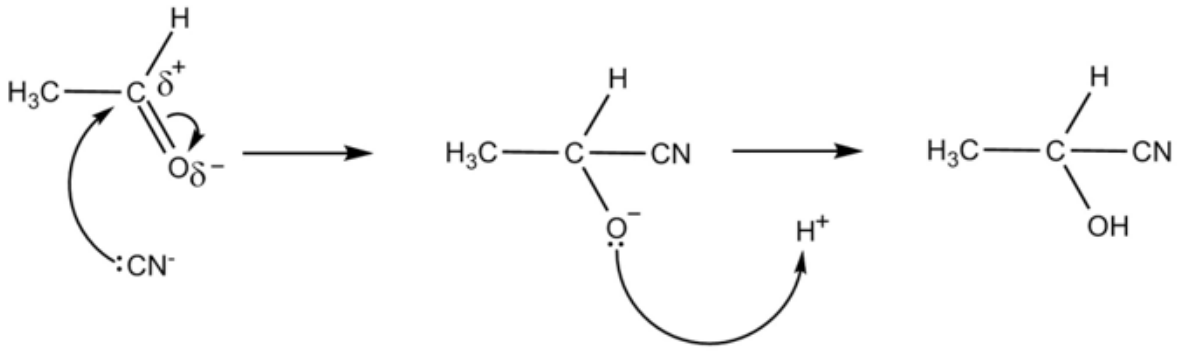
| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| **(a)(ii)** | An answer that makes reference to the following points:<br><br>• same type of / similar bonds being broken and made **(1)**<br><br>• same number of each type of bond being broken and made **(1)** | Allow O-H and C-O bonds being broken and made<br>Allow the same bond being broken and made<br>Allow C-OH<br>Ignore C-O-H and COH<br>Ignore CO without the bond shown<br><br>Award 2 marks for a complete list of the bonds being broken and made e.g.<br>Bonds broken and made are 1 x C-O and 1 x O-H scores 2<br><br>Allow ester link as C-O<br><br>If no other mark is scored award 1 mark for 1 O-H bond is broken and made<br>Or<br>1 C-O bond is broken and made<br><br>If no other mark is scored allow the energy required to break the bonds is similar to the energy released making the bonds for (1) | **(2)** |

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| **(b)(i)** | • methanoic acid<br><br>• (concentrated) sulfuric acid<br><br>• 2-methylpropan-1-ol | All three correct scores (2)<br>Any two correct scores (1)<br><br>Allow hydrochloric acid / $H_2SO_4$ / HCl<br>Ignore $H^+$<br>Ignore (aq) after formulae<br>Ignore hydrogen chloride in words<br><br>Allow methylpropan-1-ol<br>Allow 2-methyl-1-propanol<br>Allow methyl-1-propanol<br>Do not award 2-methylpropanol | **(2)** |

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| **(b)(ii)** | Any one advantage:<br>• no heat required / works at room temperature **(1)**<br>• so reduces energy cost **(1)**<br>or<br>• no catalyst required **(1)**<br>• reducing product purification costs / making purification easier / no need to recover catalyst **(1)**<br>or<br>• reaction is not an equilibrium / reaction goes to completion **(1)**<br>• so produces a higher yield **(1)**<br>Any one disadvantage:<br>• hydrogen chloride produced is acidic / corrosive **(1)**<br>• corrosion resistant plant/equipment required (which is more expensive) **(1)**<br>or<br>• HCl is toxic<br>• use a fume cupboard / clean exhaust gases / capture the gas (for sale) | • Accept the reaction is (much) faster<br>• so no energy required<br>Ignore just lower cost<br>Ignore more product<br>Allow reactants are not wasted<br>Ignore reference to atom economy | **(4)** |

Q6.

| Q | Acceptable Answers | Additional Guidance | Mark |
|---|---|---|---|
| (a)(i) | • arrow from lone pair on carbon of cyanide ion to carbonyl carbon **(1)**<br>• dipoles on carbon and oxygen in carbonyl bond **and** arrow from carbonyl bond to oxygen or just beyond **(1)**<br>• structure of intermediate, including charge **(1)**<br>• arrow from lone pair of oxygen in intermediate to hydrogen ion / H in HCN **(1)** | Penalise absence of lone pair only once in M1, M3 and M4<br>If HCN used to protonate in step 2, dipole on HCN and curly arrow to break HCN bond are **not** required<br>Ignore product | 4 |



| Q | Acceptable Answers | Additional Guidance | Mark |
|---|---|---|---|
| (a)(ii) | The prediction is incorrect because<br><br>• ethanal is planar around the carbonyl carbon atom / planar around the CHO **(1)**<br><br>• (so in Step 1) the (carbonyl) carbon can be attacked from above or below **(1)**<br><br>• hence both stereoisomers (of intermediate / product) will form in equal amounts<br>**or**<br>so product mixture is racemic / rotates the plane of plane-polarised light equally in both directions **(1)** | Accept planar at the site of the nucleophilic attack / planar about C=O<br><br>Do not award planar molecule / cation / intermediate<br><br>Allow attack from any direction / either side<br><br>Ignore 'has no effect on the plane of plane-polarised light'<br><br>Ignore comments related to SN1 or SN2<br><br>If no other mark scored allow 1 mark for idea that product will rotate plane of plane polarised light as it has a chiral centre / carbon | **3** |

| Q | Acceptable Answers | Additional Guidance | Mark |
|---|---|---|---|
| (a)(iii) | • hydrolysis **(1)**<br><br>• (dilute) hydrochloric acid / HCl((aq)) **(1)**<br><br>• heat (under reflux) / reflux **(1)**<br><br>• $CH_3CH(OH)CN + 2H_2O + H^+ \rightarrow CH_3CH(OH)COOH + NH_4^+$ **(1)**<br>OR<br>$CH_3CH(OH)CN + 2H_2O \rightarrow CH_3CH(OH)COOH + NH_3$<br>OR<br>$CH_3CH(OH)CN + 2H_2O + HCl \rightarrow CH_3CH(OH)COOH + NH_4Cl$<br>OR<br>$CH_3CH(OH)CN + H_2O + OH^- \rightarrow CH_3CH(OH)COO^- + NH_3$<br>**and**<br>$CH_3CH(OH)COO^- + H^+ \rightarrow CH_3CH(OH)COOH$ | Allow any strong acid by name or formula<br><br>Allow sodium hydroxide **followed by** any (strong) acid<br>Ignore conc / concentrated<br><br>Allow 'boil' for heat<br><br>Allow NaOH for $OH^-$<br>Allow HCl for $H^+$<br><br>Ignore state symbols even if incorrect | **4** |

| Q | Acceptable Answers | Additional Guidance | Mark |
|---|---|---|---|
| (b) | • $CH_3CH(OH)COOH + NaHCO_3 \rightarrow CH_3CH(OH)COO^-Na^+ + H_2O + CO_2$<br><br>OR<br><br>$H^+ + HCO_3^- \rightarrow H_2O + CO_2$ | Allow $CH_3CH(OH)COONa$<br>Allow $H_2CO_3$<br><br>Ignore state symbols even if incorrect<br>Do not award if covalent bond shown between O and Na | **1** |

| Q | Acceptable Answers | Additional Guidance | Mark |
|---|---|---|---|
| (c)(i) | • (large concentration of) $HCO_3^-$ react with (extra) $H^+$ ions **(1)**<br><br>• equilibrium 1 moves to the RHS to keep concentration of $H^+$ ions constant / $H_2CO_3$ forms to keep concentration of $H^+$ ions constant **(1)**<br><br>• equilibrium 2 moves to RHS to form $CO_2$ (which can be excreted from the body) / $H_2CO_3$ then forms $CO_2$ (and water) **(1)** | Allow ratio of $[HCO_3^-]$ to $[H_2CO_3]$ remains constant / ratio of [salt] to [acid] remains constant<br><br>Allow $H_3O^+$ for $H^+$<br>Allow equilibrium 1 moves to the RHS to remove excess $H^+$ ions / $H_2CO_3$ forms to remove excess $H^+$ ions<br><br>If no reference to $H^+$ and $CO_2$ in M2 and M3 but direction of movement of equilibria are correct in both cases, allow 1 mark | 3 |

| Q | Acceptable Answers | Additional Guidance | Mark |
|---|---|---|---|
| (c)(ii) | • calculation of $[H^+]$ / $[H_3O^+]$ **(1)**<br>• $K_a$ expression **(1)**<br><br>• rearrangement of $K_a$ expression and calculation of $[HCO_3^-] : [H_2CO_3]$ **(1)**<br><br>OR<br>• calculation of p$K_a$ **(1)**<br><br>• Henderson Hasselbach expression **(1)**<br>• rearrangement of $K_a$ expression and calculation of $[HCO_3^-] : [H_2CO_3]$ **(1)** | $[H^+] = 10^{-7.41}$ / = $3.8905 \times 10^{-8}$<br><br>$K_a = \frac{[HCO_3^-][H^+]}{[H_2CO_3]}$ Allow $[H_3O^+]$ in $K_a$<br><br>Do not award $[H_2O]$ in $K_a$ expression<br><br>$[HCO_3^-] : [H_2CO_3]$<br>$= 4.5 \times 10^{-7} \div 3.8905 \times 10^{-8} = 11.567 : 1 = 11.6 (: 1)$<br>Ignore SF except 1<br>Allow correct rounding of $[H^+]$ to $3.9 \times 10^{-8}$<br>Allow 1 : 0.086444 if it's clear that 1 relates to $[HCO_3^-]$<br>p$K_a = -\log 4.5 \times 10^{-7} = 6.3468$<br><br>pH = p$K_a$ + log($[HCO_3^-] \circ [H_2CO_3]$)<br><br>7.41 - 6.3468 = log($[HCO_3^-] \circ [H_2CO_3]$)<br>$[HCO_3^-] : [H_2CO_3] = 11.567 (: 1)$<br>Correct answer with no working scores (3)<br>If final answer close, check for and allow correct rounding | 3 |
| | | **(Total for Question = 18 marks)** | |

Q7.

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| **(a)(i)** | An answer that makes reference to the following points:<br>• $K_a = \frac{[C_5H_{11}COO^-][H^+]}{[C_5H_{11}COOH]}$ | Accept $[CH_3CH_2CH_2CH_2CH_2CO_2^-]$ and $[CH_3CH_2CH_2CH_2CH_2CO_2H]$<br>Accept $[H_3O^+]$ instead of $[H^+]$<br>Accept other representations of the chain of hexanoic acid / hexanoate ion, such as $[CH_3(CH_2)_4COO^-]$<br>Ignore equation for dissociation<br>Do not award $[H^+]^2/[C_5H_{11}COOH]$<br>Do not award brackets that are not square brackets<br>Do not award molecular formulae | **(1)** |

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| **(a)(ii)** | • uses expression for $pK_a$ **(1)**<br>• use of $K_a$ expression **(1)**<br>• rearrange and solve for $H^+$ **(1)**<br>• find pH | Example calculation<br>$K_a = 10^{-pK_a}$ / $K_a = 10^{-4.88}$ / $pK_a = -\log_{10}K_a$ / 4.88 = $-\log_{10}K_a$ / $K_a$ = 0.000013183 / 1.3183 x $10^{-5}$<br>$10^{-4.88}$ / 1.3183 x $10^{-5}$ / $0.000013183 = \frac{[H^+]^2}{0.1}$<br>$[H^+] = \sqrt{0.000013183 \times 0.1}$ = 0.0011482 / 0.00115 / 1.1482 x $10^{-3}$<br>/ 1.15 x $10^{-3}$ (mol $dm^{-3}$)<br>pH = $-\log_{10}[H^+]$ = 2.94 / 2.9400<br>Do not award M4 with units<br>Final correct answer with no working scores (4)<br>Final correct answer scores (4)<br>Allow TE at each stage<br>Omitting the square root gives 5.88 scores (3)<br>Use of 4.88 for $K_a$ gives 0.1558 scores (3)<br>Ignore SF except 1 SF | **(4)** |

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| **(a)(iii)** | An answer that makes reference to the following points:<br><br>• hexanoic acid forms more hydrogen bonds (per molecule) with water than butyl ethanoate does **(1)**<br><br>**(1)**<br><br>• hexanoic acid has an -OH group which forms hydrogen bonds (with water) **(1)**<br><br>• butyl ethanoate / hexanoic acid has a C=O group which forms hydrogen bonds (with water) | All marks may be scored with a diagram or diagrams<br><br>Allow hexanoic forms two hydrogen bonds per molecule but butyl ethanoate forms only one<br><br>Ignore references to the strength of the hydrogen bonds<br>Ignore all references to other intermolecular forces | **(3)** |

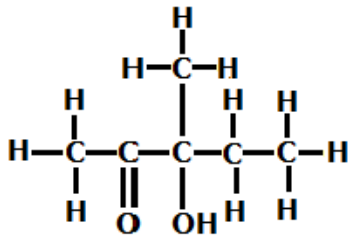
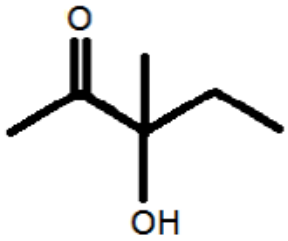
| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| **(b)(i)** | • calculate mass of oxygen **(1)**<br><br>**(1)**<br>• divides masses by atomic mass<br><br>• divides by smallest to find the simplest ratio **(1)**<br><br>**and**<br><br>correct empirical formula | Example calculation<br><br>Mass of O = 10 - 6.21 - 1.03 = 2.76(g)<br><br>Element / Mass / Mass / Atomic Mass / Ratio<br>C: 6.21 / 6.21 / 12 = 0.5175 / 3<br>H: 1.03 / 1.03 / 1 = 1.03 / 6<br>O: 2.76 / 2.76 / 16 = 0.1725 / 1<br><br>$C_3H_6O$<br><br>Correct answer with mass/atomic mass ratios calculated scores (3)<br><br>Do not award $C_6H_{12}O_2$ stated as empirical formula<br><br>Ignore SF<br><br>Ignore reference to $C_6H_{12}O_2$ after finding empirical formula<br><br>Allow 1 mark for $CH_2$ deduced without finding the mass of oxygen<br><br>Allow max 1 mark for incorrect masses of oxygen divided correctly by atomic mass<br><br>Correct answer with no working scores (1) | **(3)** |

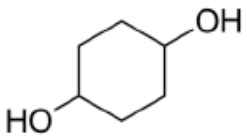
| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| **(b)(ii)** | An answer that makes reference to the following points:<br><br>• molecular ion peak / peak at highest mass will be at twice the mass of the empirical formula / will be at 116 | Ignore references to n.m.r or i.r. | **(1)** |

| Question Number | Answer | Additional guidance | Mark |
|---|---|---|---|
| **(b)(iii)** | 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: 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>In general, an answer with 5 or 6 IPs would score 2 reasoning marks, 3 or 4 IPs would score 1 reasoning mark, 0, 1 or 2 IPs would score 0 reasoning marks. | **(6)** |

| | | |
|---|---|---|
| | <table><tr><td></td><td>Number of marks awarded for structure of answer and sustained line of reasoning</td></tr><tr><td>Answer shows a coherent and 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> | 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>Candidates may treat each test separately or may build on each test. Accept statements in any order. |

| | | | |
|---|---|---|---|
| | **Indicative content**<br><br>• **IP1** Misty fumes suggest OH group present<br><br>• **IP2** Orange precipitate suggests a carbonyl group is present (so no carboxylic acid, must be alcohol)<br><br>• **IP3** (Negative) Benedict's / Fehling's reagent suggests no aldehyde group present / a ketone is present | Accept alcohol or carboxylic acid group present (must state both)<br><br>Accept ketone or aldehyde present (must state both Ignore C=O is present<br><br>Accept just 'no oxidisable groups present / cannot be oxidised' in either IP3 or IP4 but not both<br><br>Allow tertiary alcohol is present | |

| | | | |
|---|---|---|---|
| | • **IP4** Acidified potassium dichromate(VI) suggests not a primary, a secondary alcohol or an aldehyde present | Accept just no primary or secondary alcohol present<br>Ignore references to ketone and carboxylic acid giving no result | |
| | • **IP5** Polarimetry indicates a chiral centre is present / it is a chiral molecule | Ignore $S_N2$<br>Allow 4 different groups on a carbon<br>Allow optically active<br>Allow contains a single enantiomer | |
| | • **IP6** Structure of 3-hydroxy-3-methylpentan-2-one<br><br> | Allow the correct name<br>Allow displayed or structural formula or combinations<br>Allow contractions such as $CH_3$- $C_2H_5$- | |

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| **(c)** | An answer that makes reference to the following points:<br>• a structure containing **two** –OH groups **(1)**<br>• correct structure **(1)** | Do not award an –OH group and a -COOH group<br>Award this mark even if the structure does not contain a ring of six atoms.<br><br>Structure may be skeletal or displayed or a mixture, as long as it is clear. Allow, for example, a displayed formula with condensed $CH_2$.<br>Ignore connectivity of -OH | **(2)** |

Q8.

| Question number | Answer | Mark |
|---|---|---|
| | D butanoic acid | 1 |

Q9.

| Question number | Answer | Mark |
|---|---|---|
| | B the reaction is not reversible | 1 |

Q10.

| Question number | Answer | Mark |
|---|---|---|
| | **The only correct answer is B** (acids only ;acids and bases)<br>***A*** *is incorrect because bases also speed up hydrolysis*<br>***C*** *is incorrect because bases do not speed up esterification and acids also speed up hydrolysis*<br>***D*** *is incorrect because bases do not speed up esterification* | **(1)** |

Q1.

The compound HOOCCH=CHCOOH reacts with excess sodium hydroxide solution.

What is the organic product formed in the reaction?

☒ **A** NaOOCCH=CHCOONa

☒ **B** HOOCCH=CHCOONa

☒ **C** NaOOCC(OH)HC(OH)HCOONa

☒ **D** NaOOCCH=CHCHO

**(Total for question = 1 mark)**

Q2.

This question concerns six isomers each with the molecular formula $C_5H_{10}O_2$.

(a) Isomers **A**, **B**, **C** and **D** are structural isomers that all react with aqueous sodium carbonate to produce carbon dioxide.

Isomer **A** is a straight-chain compound.

Isomer **B** has only two peaks in its high resolution proton NMR spectrum, both of which are singlets.

Isomer **C** contains a chiral centre but isomer **D** does not.

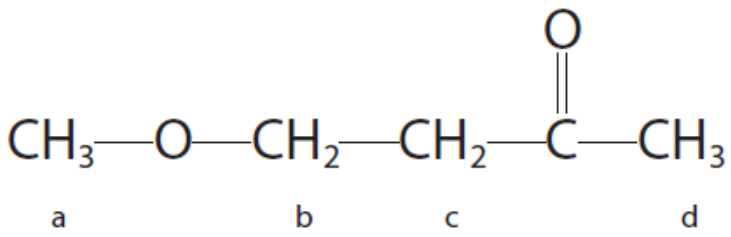
Give the structures of these **four** isomers.

**(4)**

| A | B |
|---|---|
| | |

| C | D |
|---|---|
| | |

(b) (i) Isomer **E** contains an ether functional group (R-O-R) and a ketone functional group. The **low** resolution proton NMR spectrum of isomer **E** has four peaks. The displayed formula of isomer **E** is




The four hydrogen environments responsible for the four peaks are labelled. Complete the table of information regarding these peaks including the splitting pattern in the **high** resolution spectrum.

**(3)**

| Peak | a | b | c | d |
|---|---|---|---|---|
| Relative peak area | 3 | | | |
| Chemical shift range, δ / ppm | 2.9 – 4.2 | | | |
| Splitting | singlet | | | |

(ii) State the number of peaks in the carbon-13 ($^{13}C$) NMR spectrum of **E**.

**(1)**

.....

(c) Isomer **F** is a neutral compound that smells of pears.

It can be formed by the reaction between compounds **V** and **W** in the presence of concentrated sulfuric acid.

Compound **V** has an absorption in its infrared spectrum at 1720 $cm^{-1}$ and a broad absorption around 3050 $cm^{-1}$.

Compound **W** can be formed directly from propanal.

(i) Identify, by name or formula, compounds **V**, **W** and **F**.

Justify your answer by using **all** the available information.

**(4)**

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(ii) State the conditions required and the reagent needed to form compound **W** from propanal.

**(1)**

.....

(iii) State the role of sulfuric acid in the formation of **F**.

**(1)**

.....

(d) State which one of the isomers **A**, **E** and **F** has the highest boiling temperature.

Justify your answer.

**(3)**

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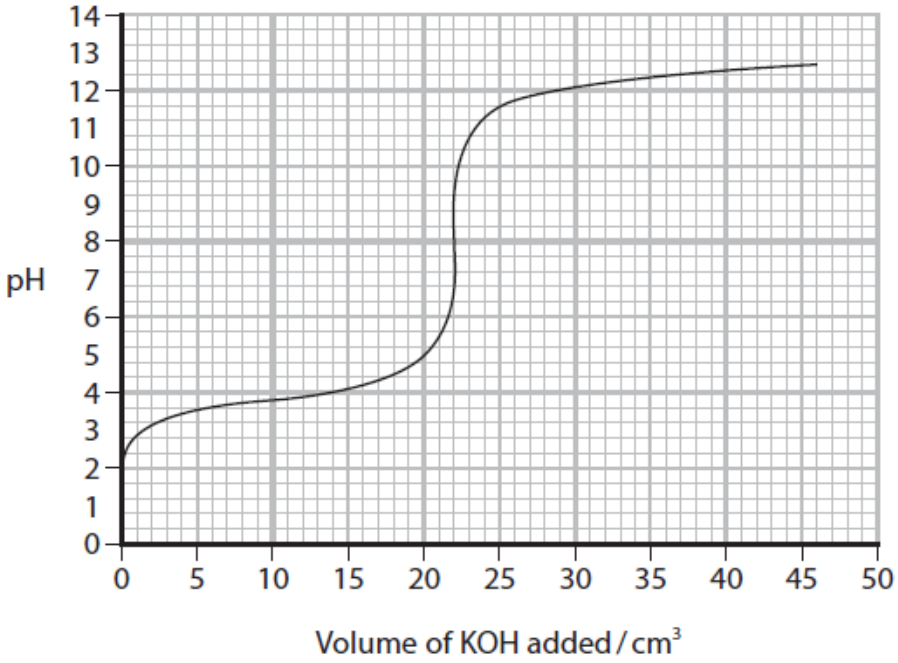
**(Total for question = 17 marks)**

Q3.

This question is about methanoic acid and propanoic acid.

(a) A student carried out a titration to find the concentration of an aqueous solution of potassium hydroxide.

25.00 $cm^3$ of 0.150 mol $dm^{-3}$ aqueous methanoic acid was pipetted into a conical flask. Potassium hydroxide was added from a burette while measuring the pH. The titration curve is shown.




(i) Complete the equation for the reaction taking place in this titration. State symbols are not required.

**(1)**

HCOOH +

(ii) Calculate the concentration of the potassium hydroxide solution, using your equation in (i) and the titration curve.

**(2)**

(iii) Use the titration curve to determine a value for the acid dissociation constant, $K_a$, of methanoic acid.

**(3)**

(b) A student prepared a buffer by mixing together equimolar aqueous solutions of propanoic acid, $CH_3CH_2COOH$, and sodium propanoate, $CH_3CH_2COONa$.

The acid dissociation constant, $K_a$, for propanoic acid is $1.3 \times 10^{-5}$ mol $dm^{-3}$.

Calculate the volume ratio of propanoic acid to sodium propanoate needed to produce a buffer solution
with a pH of 4.6

**(2)**

**(Total for question = 8 marks)**

Q4.

**Answer the question with a cross in the box you think is correct ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.**

An organic compound that reacts with **both** lithium tetrahydridoaluminate(III) (lithium aluminium hydride) **and** magnesium could be

☒ **A** an aldehyde

☒ **B** a carboxylic acid

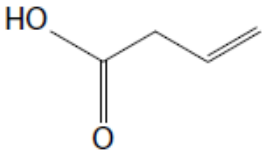
☒ **C** a ketone

☒ **D** a tertiary alcohol

**(Total for question = 1 mark)**

Q5.

Lithium tetrahydridoaluminate(III), $LiAlH_4$, is used to reduce the compound shown.




The product formed is:

**(1)**

☒ **A** a saturated alcohol

☒ **B** a saturated carboxylic acid

☒ **C** an unsaturated alcohol

☒ **D** an unsaturated ketone

**(Total for question = 1 mark)**

Q6.

Which reaction does **not** produce a carboxylic acid?

**(1)**

☒ **A** hydrolysis of an acyl chloride with cold water

☒ **B** hydrolysis of an ester by refluxing with dilute hydrochloric acid

☒ **C** hydrolysis of a nitrile by refluxing with aqueous potassium hydroxide

☒ **D** oxidation of a primary alcohol by refluxing with excess acidified potassium dichromate

**(Total for question = 1 mark)**

Q7.

**Answer the question with a cross in the box you think is correct ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.**

Which reaction cannot form a carboxylic acid?

☒ **A** oxidation of primary alcohol

☒ **B** acidic hydrolysis of a nitrile

☒ **C** alkaline hydrolysis of an ester

☒ **D** acyl chloride reacting with water

**Use this space for any rough working. Anything you write in this space will gain no credit.**

**(Total for question = 1 mark)**

Q8.

**For each question, select one answer from A to D and put a cross in the box ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.**

Compound **X**, $C_4H_{10}O$, is oxidised to form compound **Y**.

Compound **Y** reacts with ethanol in the presence of concentrated sulfuric acid to give an ester, **Z**.

Which of these could be the formula of **Z**?

☒ **A** $CH_3COOC(CH_3)_3$

☒ **B** $CH_3CH_2COO(CH_2)_3CH_3$

☒ **C** $(CH_3)_2CHCOOCH_2CH_3$

☒ **D** $CH_3CH_2COOCH_2CH(CH_3)_2$

**(Total for question = 1 mark)**

Q9.

Compound **X** is used by mammals as an alternative energy source to sugars.
**X** is a compound of carbon, hydrogen and oxygen only.

(a) Complete combustion of a 2.50 g sample of **X** in dry oxygen produced 4.31 g of carbon dioxide and 1.32 g of water as the only products.

(i) Give a reason why the oxygen used must be dry.

**(1)**

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.....

.....

(ii) Show that the empirical formula of **X** is $C_4H_6O_3$. You **must** show your working.

**(5)**

(b) Compound **X** gave an orange precipitate with Brady's reagent (2,4-dinitrophenylhydrazine) but no reaction with Tollens' reagent.

When **X** was added to a solution of sodium hydrogencarbonate, effervescence occurred and the gas evolved turned limewater cloudy.

The carbon-13 NMR spectrum of **X** had only four peaks.

(i) Deduce the **two** possible structures of **X**, showing how this information supports your answer.

**(6)**

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(ii) Give a **chemical** test which would allow you to distinguish between the two compounds you have given in (b)(i). Include the reagents required and the result for each of the compounds.

**(3)**

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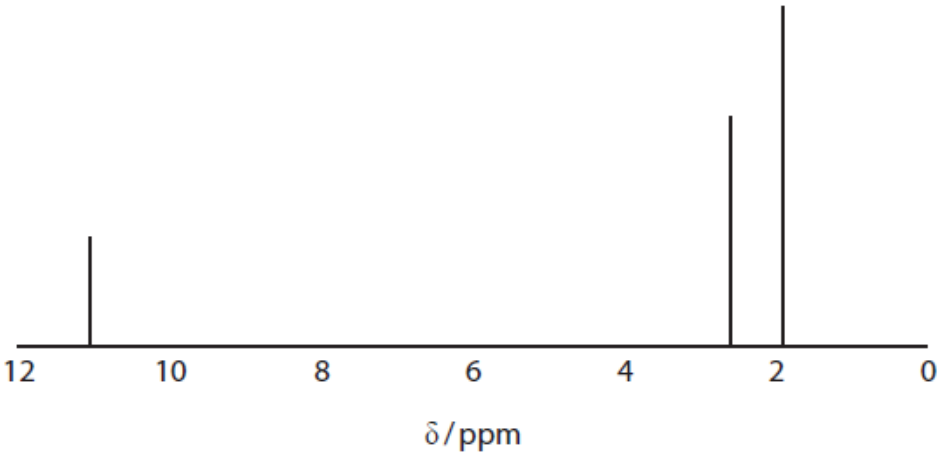
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(c) A simplified **high** resolution proton ($^1$H) NMR spectrum of compound **X** is shown.




Explain how the number of peaks in the $^{1}$H NMR spectrum, together with their relative heights, their chemical shifts and their splitting patterns, may be used to confirm the structure of **X**. Use the chemical shifts given in your Data Booklet.

**(5)**

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**(Total for question = 20 marks)**

Q10.

**For each question, select one answer from A to D and put a cross in the box ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.**

But-2-ene-1,4-diol may be converted into 2-oxobutanedioic acid in a two-step synthesis through an intermediate compound **W**.

Identify the intermediate compound **W** and the reagent for Step **2**.

| | | Compound **W** | Reagent for Step **2** |
|---|---|---|---|
| ☒ | **A** | $HOCH_2CH(OH)CH_2CH_2OH$ | $LiAlH_4$ in dry ether |
| ☒ | **B** | $HOOCH_2CH{=}CHCOOH$ | $LiAlH_4$ in dry ether |
| ☒ | **C** | $OHCCH(OH)CH_2CHO$ | hot acidified $K_2Cr_2O_7$ |
| ☒ | **D** | $HOCH_2CH(OH)CH_2CH_2OH$ | hot acidified $K_2Cr_2O_7$ |

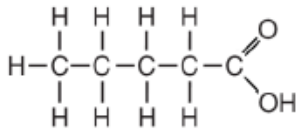
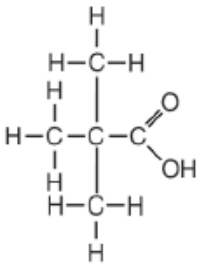
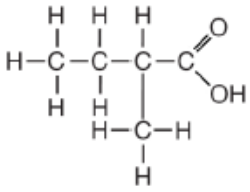
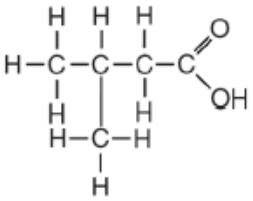
**(Total for question = 1 mark)**

## Mark Scheme

Q1.

| Question Number | Answer | Mark |
|---|---|---|
| | The only correct answer is **A** (NaOOCCH=CHCOONa)<br><br>*B is incorrect as only one of the -COOH groups has reacted*<br>*C is incorrect as OH groups have added across the double bond*<br>*D is incorrect as only one of the -COOH groups has reacted, and a -COOH group has been reduced* | 1 |

Q2.

| Question Number | Answer | Additional guidance | Mark |
|---|---|---|---|
| (a) | • Structure A **(1)**<br>• Structure B **(1)**<br>• Structure C **(1)**<br>• Structure D **(1)** | A<br><br>B<br><br>C<br><br>D<br><br>Allow condensed or skeletal formulae<br>If Structure B has not been scored allow this structure as a correct answer for Structure D<br>Penalise OH−C connectivity once only to horizontal bonds<br>Ignore connectivity on vertical bonds to OH and all bonds to $CH_3$ groups.<br>Penalise incorrect names also given once only | **(4)** |

| Question Number | Answer | Additional guidance | Mark |
|---|---|---|---|
| (b)(i) | • 3, 4 or 5 correct boxes **(1)**<br>• 6, 7 or 8 correct boxes **(2)**<br>• Nine correct boxes **(3)** | <table><tr><td>b</td><td>c</td><td>d</td></tr><tr><td>2</td><td>2</td><td>3</td></tr><tr><td>2.7 – 4.2</td><td>1.5 – 2.9</td><td>1.5 – 2.9</td></tr><tr><td>triplet</td><td>triplet</td><td>singlet</td></tr></table><br>Allow a value or range within the range<br>Allow triple / single 3lines / 1 line | **(3)** |

| Question Number | Answer | Additional guidance | Mark |
|---|---|---|---|
| (b)(ii) | • Five / 5 (peaks) | | **(1)** |

| Question Number | Answer | Additional guidance | Mark |
|---|---|---|---|
| (c)(i) | • Identifies isomer **F** (1)<br><br>• Identifies compound **V** and compound **W** (1)<br><br>• Two points of justification for identification of isomer **F**, compound **V** and compound **W** (2) | Penalise use of $C_3H_7$ for formulae once only<br><br>**F** is propyl ethanoate / $CH_3COOCH_2CH_2CH_3$<br>Allow TE on incorrect alcohol or carboxylic acid for V and W<br>If name and formula is given both must be correct<br><br>Compound **V** is ethanoic acid / $CH_3COOH$<br>and<br>Compound **W** is propan-1-ol / $CH_3CH_2CH_2OH$<br>Ignore just 'propanol'<br><br>Any two from:<br><br>Compound **V** is a carboxylic acid justified by infra-red<br>Award for correct identification of the bond responsible for either peak?<br><br>Compound **W** is propan-1-ol / an alcohol / propanol justified by reduction of propanal<br>Allow propanol here but not in M2<br><br>Compound **V** or **W** justified by reaction with the other to form an ester<br><br>Compound **F** is an ester justified by smell / neutral compound | (4) |

| Question Number | Answer | Additional guidance | Mark |
|---|---|---|---|
| (c)(ii) | • (Lithium tetrahydridoalumate(III) / lithium aluminium hydride) / $LiAlH_4$ **AND** in dry ether / diethyl ether / ethoxyethane (solvent) | ALLOW<br>Lithal<br><br>ALLOW<br>Sodium tetrahydridoborate / sodium borohydride<br>AND<br>Water / ethanol solvent | (1) |

| Question Number | Answer | Additional guidance | Mark |
|---|---|---|---|
| (c)(iii) | • Catalyst | Ignore mention of acid / homogeneous / proton donor<br><br>Ignore additional words<br><br>Do not award just 'proton donor' or donates hydrogen ions | (1) |

| Question Number | Answer | Additional guidance | Mark |
|---|---|---|---|
| (d) | An explanation that makes reference to the following points:<br><br>• Isomer A (has the highest boiling temperature) (1)<br><br>• (Isomer A has the) **only** molecules held together by hydrogen bonding / Isomer A forms hydrogen bonds but E and F do not (1)<br><br>• Hydrogen bonds are the strongest intermolecular forces (1) | In general ignore reference to other intermolecular forces (but see below)<br><br>Allow it forms hydrogen bonds<br>Ignore it forms hydrogen bonds with other compounds/substances<br>Ignore comments about straight chain so stronger London forces<br><br>Allow hydrogen bonding is stronger than London forces and/or permanent dipoles<br>Allow just 'forms strong hydrogen bonds' | (3) |

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Q3.

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| (a)(i) | An answer that makes reference to the following point:<br>• $HCOOH + KOH \rightarrow HCOOK + H_2O$ | Allow $HCOO^- K^+ / HCOO^- + K^+$<br>Allow $HCOOH + OH^- \rightarrow HCOO^- + H_2O$<br>Allow Na in place of K<br>Ignore state symbols even if incorrect<br>Do not award HCOO – K | (1) |

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| (a)(ii) | • correct volume read off the graph (1)<br>• correct concentration (1) | Example of calculation<br>22 ($cm^3$)<br>This may be noted on the graph<br>$25.0 \times 0.15/22.0 = 0.17045$ (mol $dm^{-3}$)<br>Ignore SF except 1SF<br>Allow TE on wrong volume<br>Correct answer scores 2 | (2) |

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| (a)(iii) | An answer that makes reference to the following points:<br><br>• volume at half-neutralisation **(1)**<br><br>• pH value at half-neutralisation **(1)**<br><br>• calculation of $K_a$ **(1)** | <br><br>11 $cm^3$ (Allow TE from volume in (a)(ii))<br><br>pH = 3.8 (± 0.1)<br><br>(Hydrogen ion concentration = $10^{-3.8}$)<br>$K_a = 1.5849 \times 10^{-4}$ / 0.00015849 ($mol\ dm^{-3}$)<br>Correct answer with no working scores 3<br><br>Allow TE throughout<br>Ignore SF<br><br>If 3.9 used<br>(Hydrogen ion concentration = $10^{-3.9}$)<br>$K_a = 1.2589 \times 10^{-4}$ / 0.00012589 ($mol\ dm^{-3}$)<br><br>If 3.7 used<br>(Hydrogen ion concentration = $10^{-3.7}$)<br>$K_a = 1.9953 \times 10^{-4}$ / 0.00019953 ($mol\ dm^{-3}$)<br><br>Allow TE from wrong pH | **(3)** |
| | Alternative method 1<br><br>• pH at half-neutralisation **(1)**<br><br>• p $K_a$ value **(1)**<br><br>• calculation of $K_a$ **(1)** | <br><br>3.8 (± 0.1)<br><br>3.8 (± 0.1)<br><br>$K_a = 10^{-3.8}$<br>$= 1.5849 \times 10^{-4}$ / 0.00015849 ($mol\ dm^{-3}$)<br>Correct answer with no working scores 3<br><br>If 3.9 used<br>Hydrogen ion concentration = $10^{-3.9}$<br>$= 1.2589 \times 10^{-4}$ / 0.00012589 ($mol\ dm^{-3}$)<br>$= K_a$<br><br>If 3.7 used<br>Hydrogen ion concentration = $10^{-3.7}$<br>$= 1.9953 \times 10^{-4}$ / 0.00019953 ($mol\ dm^{-3}$)<br>$= K_a$<br><br>Allow TE from wrong pH for M2 and M3 | |

| | | | |
|---|---|---|---|
| | Alternative method 2 (using pH of the methanoic acid at the start)<br><br>• pH at the start **(1)**<br><br>• convert pH into $H^+$ concentration **(1)**<br><br>• calculation of $K_a$ **(1)**<br><br>2.0 gives a value of $6.667 \times 10^{-4}$ (mol dm$^{-3}$)<br>2.1 gives a value of $4.206 \times 10^{-4}$ (mol dm$^{-3}$)<br>2.2 gives a value of $2.654 \times 10^{-4}$ (mol dm$^{-3}$)<br>2.3 gives a value of $1.674 \times 10^{-4}$ (mol dm$^{-3}$)<br>2.4 gives a value of $1.057 \times 10^{-4}$ (mol dm$^{-3}$)<br>2.5 gives a value of $3.162 \times 10^{-3}$ (mol dm$^{-3}$) | 2.3<br>Allow 2.0-2.5<br><br>Hydrogen ion concentration = $10^{-2.3}$<br>= $5.0119 \times 10^{-3}$ / 0.0050119 (mol dm$^{-3}$)<br><br>$K_a = \frac{(5.0119 \times 10^{-3})^2}{0.15}$<br>= $1.6746 \times 10^{-4}$ / 0.00016746 (mol dm$^{-3}$)<br><br>Correct answer with no working scores 3<br><br>Allow TE from wrong pH<br>(i.e. not in the range of 2.0-2.5)<br><br>Ignore SF | |

| Question Number | Answer | Additional Guidance | Mark |
|---|---|---|---|
| **(b)** | An answer that makes reference to the following points:<br><br>• calculation of $[H^+]$ **(1)**<br><br>• correct ratio **(1)** | Example of calculation<br><br>$[H^+] = K_a \times \frac{[HA]}{[A^-]}$ OR $\frac{[H^+]}{K_a} = \frac{[HA]}{[A^-]}$<br><br>$2.5119 \times 10^{-5}$ / 0.000025119<br><br>$\frac{[HA]}{[A^-]} = \frac{2.5118864 \times 10^{-5}}{1.3 \times 10^{-5}} = 1.9322:1$<br><br>Correct answer with no working scores 2<br><br>Allow just 1.9322<br>Allow rounding to 2:1<br><br>Ignore SF<br><br>Reciprocal ratio correctly identified 0.5175:1 scores 2<br>Correct answer with no working scores 2<br><br>Allow Henderson-Hasselbach equation<br><br>$pH = pKa - \log \frac{[HA]}{[A^-]}$<br>$4.6 = 4.8861 - \log \frac{[HA]}{[A^-]}$ **(1)**<br>$\frac{[HA]}{[A^-]} = 1.9322:1$ **(1)**<br>Allow just 1.9322<br>Ignore SF<br><br>Reciprocal ratio correctly identified 0.5175:1 scores 2 | **(2)** |

Q4.

| Question Number | Answer | Mark |
|---|---|---|
| | **The only correct answer is B** (a carboxylic acid)<br><br>*A is incorrect because this will not react with magnesium*<br><br>*C is incorrect because this will not react with magnesium*<br><br>*D is incorrect because this will not react with lithium tetrahydridoaluminate(III) or magnesium* | (1) |

Q5.

| Question number | Answer | Mark |
|---|---|---|
| | C an unsaturated alcohol | 1 |

Q6.

| Question number | Answer | Mark |
|---|---|---|
| | C hydrolysis of a nitrile by refluxing with aqueous potassium hydroxide | 1 |

Q7.

| Question Number | Answer | Mark |
|---|---|---|
| | **The only correct answer is C** (alkaline hydrolysis of an ester)<br><br>*A is not correct because this reaction will produce a carboxylic acid*<br><br>*B is not correct because this reaction will produce a carboxylic acid*<br><br>*D is not correct because this reaction will produce a carboxylic acid* | (1) |

Q8.

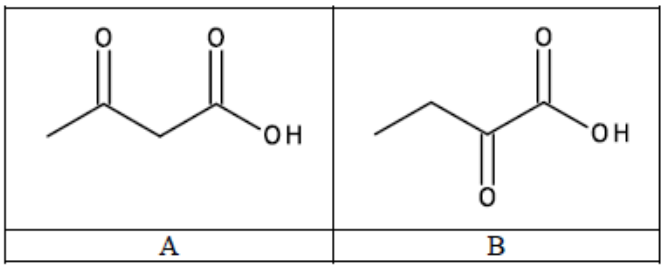
| Question Number | Correct Answer | Mark |
|---|---|---|
| | **The only correct answer is C** ( $(CH_3)_2CHCOOCH_2CH_3$ )<br><br>***A*** *is incorrect because this product could not be formed as compound* ***Y*** *must have 4 carbon atoms and the ester* ***Z*** *must be formed from ethanol*<br><br>***B*** *is incorrect because this product could not be formed as compound* ***Y*** *must have 4 carbon atoms and the ester* ***Z*** *must be formed from ethanol*<br><br>***D*** *is incorrect because this product could not be formed as compound* ***Y*** *must have 4 carbon atoms and the ester* ***Z*** *must be formed from ethanol* | (1) |

Q9.

| Question number | Answer | Additional guidance | Mark |
|---|---|---|---|
| (a)(i) | • otherwise the mass of water from the combustion cannot be measured | Allow any indication that the measurement of water is affected<br>Allow indication that the values of H and O obtained will be affected<br>Ignore just reference to 'the products'<br>Do not award (presence of water) affects the reaction of $O_2$ with X<br>Do not award water reacts with X<br>Do not award water dissolves $CO_2$ | 1 |

<table>
<tr><th>Question number</th><th>Answer</th><th>Additional guidance</th><th>Mark</th></tr>
<tr><td>(a)(ii)</td><td>• moles of $CO_2$ and $H_2O$ (1)<br><br>• masses of C and H (1)<br><br>• mass of O (1)<br><br>• moles of C, H and O (1)<br><br>• ratio (1.33:2:1), ( integer ratio) and empirical formula (1)<br><br>Allow inductive calculation<br><br>• balanced equation (1)</td><td>Example of calculation<br><br>mol $CO_2$ = 4.31 ÷ 44 = 0.097955<br>mol $H_2O$ = 1.32 ÷ 18 = 0.073333<br><br>mass of C = 0.097955 x 12 = 1.1755 g<br>mass of H = 0.073333 x 2 = 0.1467 g<br><br>mass of O = 2.50 − (1.1755 + 0.1467)<br>= 1.1778 g<br><br><table><tr><td></td><td>C</td><td>H</td><td>O</td></tr><tr><td>mol</td><td>0.0980 x 1<br>= 0.0980</td><td>0.0733 x 2<br>= 0.147</td><td>1.178/16<br>= 0.0736</td></tr><tr><td>ratio</td><td>1.33</td><td>2</td><td>1</td></tr><tr><td>integers</td><td>4</td><td>6</td><td>3</td></tr></table><br>$C_4H_6O_3$<br><br>No TE if oxygen mass not calculated<br><br>In M1 and M2 mol $CO_2$ and mass of carbon scores (1)<br><br>mol $H_2O$ and mass of hydrogen scores (1) Example of inductive calculation<br><br>$C_4H_6O_3 + 4O_2 \rightarrow 4CO_2 + 3H_2O$<br><br>Formula mass (4x12 + 6 + 3 x 16) = 102 (g)<br><br>$CO_2$ = 4 x 44 = 176 (g) and $H_2O$ = 3 x 18 = 54 (g)<br><br>2.5 x 176 ÷ 102 = 2.5 (g)</td><td>5</td></tr>
<tr><td></td><td>• Formula mass ($C_4H_6O_3$) (1)<br><br>• Product masses from equation (1)<br><br>• Mass of $CO_2$ from 2.5 g of X (1)<br><br>• Mass of $H_2O$ from 2.5 g of X (1)</td><td>2.5 x 54 ÷ 102 = 1.32 (g)<br><br>Correct answer with any correct method scores (5)<br>Correct answer with no working scores (0)<br><br>TE at each stage<br><br>Ignore SF except 1 SF</td><td></td></tr>
</table>

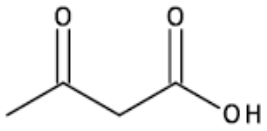
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| Question number | Answer | Additional guidance | Mark |
|---|---|---|---|
| (b)(i) | An answer that makes reference to the following<br><br>• two structures **(2)**<br><br>• $^{13}C$ spectrum shows four different (types of) carbon atom (so molecular formula same as empirical formula) **(1)**<br><br>• reaction with Brady's reagent indicates a carbonyl compound **(1)** | <br><br>A B<br><br>Allow displayed or structural formulae or any combination of skeletal, displayed and structural<br>Penalise incorrect horizontal –OH connectivity once<br>Ignore names even if incorrect<br><br>Accept X has four carbon environments<br>Allow $^{13}C$ spectrum shows X has four types of carbon atom<br>Ignore just 'X has four carbon atoms'<br><br>Ignore just 'X is a ketone' / C=O present<br>Do not award 'acyl'<br><br>Accept COOH (group) | 6 |

| | | | |
|---|---|---|---|
| | • no reaction with Tollens' reagent indicates a ketone (group) / not an aldehyde **(1)**<br><br>• reaction with $NaHCO_3$ (forming $CO_2$) indicates (carboxylic) **acid** **(1)** | | |

| Question number | Answer | Additional guidance | Mark |
|---|---|---|---|
| (b)(ii) | An answer that makes reference to the following<br><br>• reagents for iodoform test<br>**(1)**<br><br>• result for methyl ketone<br>**(1)**<br><br>• result for ethyl ketone<br>**(1)** | iodine / $I_2$<br>**and**<br>sodium hydroxide /NaOH / potassium hydroxide KOH<br><br>Accept NaI / KI **and** NaOCl<br><br>Allow iodine **and** $OH^-$ / alkali<br><br>Ignore 'iodoform test'<br><br>(pale) yellow precipitate<br>Allow<br>yellow solid / ppt /ppte /antiseptic smell<br><br>No change / precipitate<br>Allow<br>no reaction / (pale) yellow precipitate does not form<br><br>M2 and M3 dependent on M1 or a near miss or just 'iodoform test'<br><br>If result not linked to structure max (2)<br><br>e.g NaOH and $I_2$ give yellow ppt (positive) and no reaction (negative) scores (2)<br><br>If no reagent or an incorrect reagent given then both observation marks correct scores (1) | **3** |

| | | | |
|---|---|---|---|
| | | Do not award use of physical methods | |

| Question number | Answer | Additional guidance | Mark |
|---|---|---|---|
| (c) | An answer that makes reference to the following<br><br>• structure of X<br>**(1)**<br><br>• (three) peaks indicate three proton environments **(1)**<br><br>• peak heights / areas indicate environments contain 3, 2 and 1 protons **(1)**<br><br>• all singlets / no splitting so no adjacent proton environments **(1)**<br><br>• identification of proton environments from chemical shifts **(1)** | <br><br>Answers may refer to the diagram<br><br>Allow number of peaks shows number of proton environments<br>Allow if the protons in each environment are clearly labelled e.g. each set circled<br><br>Ignore just 'peak areas are 3:2:1'<br><br>peak at δ about 11.1 is COO**H**<br><br>peak at δ about1.9 is C**H**$_3$CO<br><br>peak at δ about 2.5 is -OCC**H**$_2$COOH<br>Allow 'alkane proton' / **H**-C-C<br>Allow both 1.9 and 2.5 identified as **H**-C-C=O<br><br>Do not award reference to the functional group rather than the proton<br><br>M2, M3 and M5 may be awarded without referring to the structure<br>M2 and M3 are standalone | 5 |

Q10.

| Question Number | Correct Answer | Mark |
|---|---|---|
| | **The only correct answer is D** ($HOCH_2CH(OH)CH_2CH_2OH$ hot acidified $K_2Cr_2O_7$)<br><br>***A*** *is incorrect because the compound* ***W*** *is correct but* $LiAlH_4$ *is a reducing agent*<br><br>***B*** *is incorrect because both the compound* ***W*** *and reagent are incorrect*<br><br>***C*** *is incorrect because the compound* ***W*** *is the wrong compound* | (1) |

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