1. Study the reaction scheme below, then answer the questions that follow.

(a) (i) Butanal contains a carbonyl group. State a chemical test for a carbonyl group and describe the result of the test.

Test .................................................................................................................................

Result ................................................................................................................................

(ii) An isomer of butanal also possesses a carbonyl group, but cannot be oxidised by acidified sodium dichromate(VI). Give the structural formula of this isomer and its name.

Structural formula ...........................................................................................................

Name ................................................................................................................................

(iii) Another isomer of butanal contains a carbonyl group and can be oxidised by acidified sodium dichromate(VI). Draw the displayed formula of this isomer.

(1)
(b) Compound X is a colourless liquid that smells of pineapples.

(i) To what class of compounds does X belong?

................................................................................................................................................. (1)

(ii) Ethanol, C₂H₅OH, reacts with butanoic acid to form compound X. Complete the diagram below to show the structural formula of X and the other product.

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{O}–\text{CH}_2\text{CH}_3 \]

................................................................................................................................................. (1)

(iii) Give the name of compound X.

................................................................................................................................................. (1)

(iv) What type of attacking species is ethanol in this reaction?

................................................................................................................................................. (1)
(c) Describe what you would expect to see during Reaction 2.

(1)

(d) Explain why Reaction 4 is far more vigorous than Reaction 3.

(2) (Total 12 marks)

2. This question is about compounds with the molecular formula C₄H₈O.

(a) (i) Draw the displayed formulae of TWO isomers, A and B, which are both aldehydes. Give their systematic names.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
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<tbody>
<tr>
<td>Name</td>
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(4)
(ii) Suggest an instrumental method by which these isomers, A and B, could be distinguished.

Outline how the results would differ.

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(2)

(b) Substance C, butanone, is another isomer of C₄H₈O.

(i) Name a reagent which results in the same observation when it reacts with all three isomers, A, B and C.

Reagent ................................................................................................................................
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Observation .........................................................................................................................
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(2)

(ii) Name a reagent where the resulting observation for C would be different from that for A and B.

Reagent ................................................................................................................................
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Observation with C .............................................................................................................
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Observation with A and B .................................................................................................
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(3)
(c)  

(i) Suggest structural formulae for TWO more isomers of C$_4$H$_8$O, D and E, which are cyclic and react with sodium to give off hydrogen.

\[ \text{D} \quad \text{E} \]  

(ii) Both A and B can be oxidised to carboxylic acids. These acids will then react with either of the isomers D or E in the presence of a strong acid as a catalyst.

What is the name given to the products of this type of reaction? 
.........................................................................................................................................................................................

(iii) For one of the carboxylic acids formed from A or B and one of the isomers D or E, draw a displayed formula of the product formed when they react together.

(Total 16 marks)
3. Name the following organic compound

HCHO

...........................................................................................................................................

(Total 1 mark)

4. (a) Draw the displayed formula of a branched chain ketone containing five carbon atoms.

(b) Give the systematic name for this ketone.

...........................................................................................................................................

(1)

(c) What is the molecular formula of the alcohol this ketone could be made from?

...........................................................................................................................................

(1)
(d) An alcohol can be converted into a ketone by oxidation with sodium dichromate(VI) and sulphuric acid.

Explain why refluxing the mixture first, rather than immediately distilling the product over from the beginning, results in a higher yield of the ketone.

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(Total 5 marks)

5. Ethanal, \( \text{CH}_3\text{CHO} \), can be converted into 2-hydroxypropanoic acid, \( \text{CH}_3\text{CH(OH)}\text{COOH} \).

State the reagents and conditions needed for each step in this synthesis.

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(Total 4 marks)

6. (a) Name the homologous series to which the compound \( \text{CH}_3\text{CH}_2\text{CHO} \) belongs.

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(1)
(b) Describe what you would see if a sample of CH\textsubscript{3}CH\textsubscript{2}CHO was warmed with Benedict’s solution.

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(2)
(Total 3 marks)

7. The drug ibuprofen can be synthesised from benzene by the route shown below.

(a) Name the type and mechanism of the reaction in Step A, and suggest a suitable reagent and catalyst.

Type and mechanism ..................................................................................................................

Name of the reagent for Step A .................................................................................................

Catalyst .....................................................................................................................................

(3)
(b) Step C is a reduction.

Give ONE reason why lithium tetrahydridoaluminate, LiAlH$_4$, is preferred to hydrogen as a reducing agent in this reaction.

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(2)

(c) A sample of the final product was analysed by combustion. 1.00 g was burnt in oxygen. It produced 2.78 g carbon dioxide and 0.786 g water.

State the molecular formula of ibuprofen and show that these results are consistent with it.
(d) Ibuprofen can be analysed by instrumental methods. The infrared spectra of ibuprofen and two other drugs, aspirin and paracetamol, not necessarily in that order, are shown opposite.

Ibuprofen has the formula

Aspirin has the formula

Paracetamol has the formula

(i) Explain, referring to the structure of each molecule, why infrared spectroscopy is not a good technique to distinguish aspirin from ibuprofen.

..........................................................................................................................
(ii) Deduce which of X, Y or Z is the infrared spectrum of paracetamol, giving a piece of evidence from the spectrum you select.
(iii) Ibuprofen and aspirin can be distinguished using their mass spectra.

A line at mass/charge ratio 57 occurs only in the mass spectrum of ibuprofen. Give the formula of the ion which produces this line.

Suggest the mass/charge ratio of one line which occurs in the mass spectrum of aspirin but not ibuprofen, and the formula of the species which produces it.

8. (a) (i) Add Brady’s Reagent / 2,4-dinitrophenylhydrazine (1) Yellow/orange precipitate / crystals/ solid produced (1) 2
(ii) CH₃CH₂COCH₃ (1) Butanone (1) 2
(iii)  

(b) (i) Esters (1) 1
(ii) CH₃CH₂CH₂CO₂CH₂CH₃ + H₂O (1) 1
(iii) Ethyl butanoate (1) 1
(iv) Nucleophile/ nucleophilic (1) 1
(c) Cloudy/misty/steamy fumes/vapour/gas

(d) Cl is more electron withdrawing/electronegative (1)
Which makes carbonyl carbon more electrophilic/positive/susceptible to nucleophilic attack
OR Cl is a better leaving group (than OH)
as Cl⁻ is more stable (than −H) (1)

[12]

9. (a) (i) H—C—C—C—C≡O (1) Butanal / butan-1-al (1)

(ii) Any one from
Infrared spectra (1)
different in ‘fingerprint’
OR differences in frequencies/wavelengths absorbed
OR different peak/trough patterns (1)
NOT different peaks/troughs
Measure Boiling point (1)
Different boiling points and suggest why e.g. straight chain higher boiling point (1)

nmr spectra (1)
A + B would have a different number of peaks (1)

Mass spec (1)
Different fragmentation pattern (1)
X-ray diffraction (1)
Electron density maps identify branching (1)
Prepare 2,4-dinitrophenylhydrazone (1)
and measure melting point (1)

NOT measure melting point

(b) (i) 2,4-dinitrophenylhydrazone / 2,4-DNP(h) / Brady’s reagent (1)
orange/yellow/orange-red/yellow-orange precipitate/crystals
[a solid must be mentioned] (1)
NOT ‘Red’
2nd mark dependent on 1st

(ii) (Heat with) Benedict’s reagent/Fehling’s reagent (1)
Result for C remains blue (1)
ALLOW no change if blue mentioned somewhere
Result for A and B orange/red/green/yellow/brown precipitate/crystals [a solid must be mentioned] (1)
OR
Acidified dichromate (1)
Result for C remains orange (1)
Result for A + B green/blue (1)
Same rules as above but precipitate not needed
2nd and 3rd marks dependent on 1st

(c)  (i)

\[
\begin{align*}
\text{Any two} \\
&\text{ALLOW fully displayed} \\
\text{ALLOW } \text{CH}_2\text{CH}_2\text{CH}_2\text{CHOH} \\
\text{ALLOW } \text{OH} \quad \text{NOT} \quad \text{OH} \\
\text{NOT } \text{CH}_2\text{CH}_2\text{CH}_2\text{CHOH etc}
\end{align*}
\]

(ii) Esters
NOT esterification
(iii) e.g.  

\[ \text{CH}_3\text{C}(-\text{C})\text{C}-\text{C}(-\text{C})\text{C}(-\text{O})\text{H} \]

ester group - must be displayed (1)  
rest of molecule - need not be fully displayed (1)  
- 2\(^{nd}\) mark dependent on 1\(^{st}\)  

ALLOW TE from CH\(_2\)CH\(_2\)CH\(_2\)CHOH etc in (c)(i) for 2 marks in (iii)

If enol in (c)(i) max 2 (out of 5) for (c) ie (ii) and ester displayed in (iii) can be awarded 2

10. methanal

Accept formaldehyde  
Accept metanal  
Reject methanol  
Reject methone

11. (a)  

\[ \text{H}-\text{C}(-\text{C})\text{C}(-\text{C})\text{C}(-\text{C})\text{H}\]

Ketone + five carbon atoms (could be straight chain) (1)  
Branched chain + rest of molecule (1)  

Allow 1 CH\(_3\) group not displayed  
Reject aldehyde  
Reject if any hydrogen atoms missing (1 max)
(b) 2-methylbutan(e)-3-one/
3-methylbutan(e)-2-one
Ignore punctuation

Accept 2-methylbutanone
Accept 3-methylbutanone
Allow TE from (a) provided it is a ketone
e.g. pentan-2-one, pentan-3-one

Reject 2-methylbuta(-3)one
Reject 2-methylbut(-3)one
Reject 2-methylbutan-2-one
Reject methylbutanone

(c) C$_5$H$_{12}$O

Accept C$_5$H$_{11}$OH
Reject structural or displayed formula

(d) The reactants don’t distil over before they can react
    
    Accept higher % of alcohol will be oxidised/not all of the alcoholic will react/maximum chance of oxidising
    Accept more time to oxidise to condense (any evaporated) reactants
    Reject BP of alcohol low
    Reject explanation of what happens during refluxing
    Reject to get a higher yield
    Reject discussion of rate of reaction
12. **First two marks:**

For correct **reagent** (ignore all state symbols) (1)

For correct **condition(s)**, but only if with matching reagent (1)

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCN</td>
<td>Catalyst of CN&lt;sup&gt;-&lt;/sup&gt;</td>
</tr>
<tr>
<td>HCN</td>
<td>KCN</td>
</tr>
<tr>
<td>KCN</td>
<td>HCN</td>
</tr>
<tr>
<td>HCN or KCN</td>
<td>any stated pH or pH range between 5 and 9</td>
</tr>
<tr>
<td>KCN</td>
<td>+ (named) acid / H&lt;sup&gt;+&lt;/sup&gt;</td>
</tr>
<tr>
<td>HCN</td>
<td>+ (named) base / OH&lt;sup&gt;-&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

[Note: The intermediate compound CH<sub>3</sub>CH(OH)CN does not have to be identified.]

Hydrolysis of −CN group to −COOH group:

*IGNORE MENTION OF “HEAT / REFLUX”*

---

13. (a) Aldehyde(s) 1
14. (a) Electrophilic substitution (1)
IGNORE extras eg Friedel Craft, alkylation UNLESS contradictory
1-chloro-(2)-methylpropane (1)
IGNORE punctuation
Accept (2)-methyl-1-chloropropane
Accept CH₃CH(CH₃)CH₂Cl/CH(CH₃)₂CH₂Cl
Accept “Bromo”/”iodo” for “chloro”
Reject 1-methyl-2-chloropropane
Reject missing “1” from position of Cl in name

Catalyst
AlCl₃/aluminium chloride (1)
Accept Al₂Cl₆, AlBr₃, FeBr₃

(b) LiAlH₄ is a source of H⁻/hydride ion (1)
Hydrogen might reduce/attack benzene ring/ H⁻ won’t attack region of negative charge/ H⁻ can attack (δ⁺) C in keto group (1)
Reject comments on conditions or safety eg temperature, pressure
Reject LiAlH₄/H⁻ is a more powerful reducing agent
Reject H⁻ is a nucleophile/a stronger nucleophile
Reject any mention of attack on carboxylate ion (for 2nd mark)
(c) **Note:** although many candidates have calculated the empirical formula, this is not required.

Molecular formula of ibuprofen = $\text{C}_{13}\text{H}_{18}\text{O}_2$ (1)

*Allow if given at end*

Allow marks for masses and number of moles if answers are rounded to 2 SF in “OR” but method is correct.

**EITHER**

$M_r = 206$ (1)

\[ 1 \text{ g} = \frac{1}{216} \text{ mol} = 4.854 \times 10^{-3} \text{ mol} \]

mass $\text{CO}_2$ produced from 13 C
\[ = 13 \times 44 \times 4.854 \times 10^{-3} = 2.78 \text{ g} \text{ (1)} \]

mass $\text{H}_2\text{O}$ from 18 H
\[ = 9 \times 18 \times 4.854 \times 10^{-3} = 0.787 \text{ g} \text{ (1)} \]

**OR**

Mass C = \[ \frac{(2.78 \times 12)}{44} = 0.758 \text{ g} \text{ (1)} \]

Mass H = \[ \frac{(0.786)}{9} = 0.0873 \text{ g} \text{ (1)} \]

Moles C = \[ \frac{(0.758)}{12} = 0.0632 \text{ (1)} \]

Moles H = 0.0873 (1)

Ratio C:H = 0.0632: 0.0873 = 13:18 (1) 4

(d) **(i)** (Aspirin and ibuprofen) both contain same (types of)

**bond(s)** (so absorb at same frequency/wavenumber) 1

Accept list of at least 4 bonds which are present in both

Reject “groups” for “bonds”

(ii) Data is required for mark

Y = paracetamol
Peak at 3500–3300 (N–H)
IGNORE mention of amine

OR 3500–3140 (N–H or amide)

OR 3750–3200 ((phenolic) O–H)

OR Only Y has peaks above 3000 cm$^{-1}$ (so must contain different type of bond to X and Z) 1

Reject C–H in arene = 3030 as present in both

Reject 1700–1630 (amide)
(iii) 57 in Ibuprofen
\[ \text{C}_4\text{H}_9^+/\text{CH}_3\text{CH(CH}_3\text{)CH}_2^+/\text{CH}(	ext{CH}_3)_2\text{CH}_2^+ \]
OR
\[ \text{C}_2\text{O}_2\text{H}^+/\text{CCO}_2\text{H}^+ (1) \]

Accept structural or displayed formulae

Do not allow lines at
15 (CH\(_3\)^+)
76 (C\(_6\)H\(_4\)^+)
43 (C\(_3\)H\(_7\)^+ or CH\(_3\)CO\(^+\))
45 (COOH\(^+\))
as present in both

Aspirin
59 (1) OCOCH\(_3\)^+/C\(_2\)H\(_3\)O\(_2^+\) (1)
OR
121 (1) C\(_6\)H\(_4\)CO\(_2\)H\(^+\) (1)
OR
180 (1) C\(_9\)H\(_8\)O\(_4^+\) (parent ion) (1)
OR
137 (1) C\(_6\)H\(_4\)(CO\(_2\)H)O\(^+\) (1)

Penalise no/wrong charges once only