

## Monday 19 June 2023 – Afternoon

### A Level Chemistry A

#### H432/02 Synthesis and analytical techniques

Time allowed: 2 hours 15 minutes

**You must have:**

- the Data Sheet for Chemistry A

**You can use:**

- a scientific or graphical calculator
- an HB pencil



Please write clearly in black ink. **Do not write in the barcodes.**

Centre number

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Candidate number

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First name(s)

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Last name

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#### INSTRUCTIONS

- Use black ink. You can use an HB pencil, but only for graphs and diagrams.
- Write your answer to each question in the space provided. If you need extra space use the lined pages at the end of this booklet. The question numbers must be clearly shown.
- Answer **all** the questions.
- Where appropriate, your answer should be supported with working. Marks might be given for using a correct method, even if your answer is wrong.

#### INFORMATION

- The total mark for this paper is **100**.
- The marks for each question are shown in brackets [ ].
- Quality of extended response will be assessed in questions marked with an asterisk (\*).
- This document has **28** pages.

#### ADVICE

- Read each question carefully before you start your answer.

## Section A

You should spend a **maximum** of **20 minutes** on this section.

Write your answer to each question in the box provided.

1 Which compound is used for proton exchange in NMR spectroscopy?

- A  $\text{CCl}_4$
- B  $\text{CDCl}_3$
- C  $\text{D}_2\text{O}$
- D  $\text{Si}(\text{CH}_3)_4$

Your answer

[1]

2 Which compound reacts with 2,4-dinitrophenylhydrazine but does **not** react with Tollens' reagent?

- A  $\text{C}_6\text{H}_5\text{COCOOH}$
- B  $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CHO}$
- C  $\text{CH}_3\text{COCHO}$
- D  $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$

Your answer

[1]

3 Propyne,  $\text{CH}_3\text{C}\equiv\text{CH}$ , is a member of the alkynes homologous series with the  $\text{C}\equiv\text{C}$  functional group.

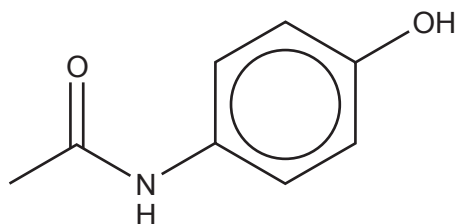
What is the general formula of the alkynes?

- A  $\text{C}_n\text{H}_{2n-4}$
- B  $\text{C}_n\text{H}_{2n-2}$
- C  $\text{C}_n\text{H}_{2n}$
- D  $\text{C}_n\text{H}_{2n+2}$

Your answer

[1]

- 4 The structure of the painkiller paracetamol is shown below.



**Paracetamol**

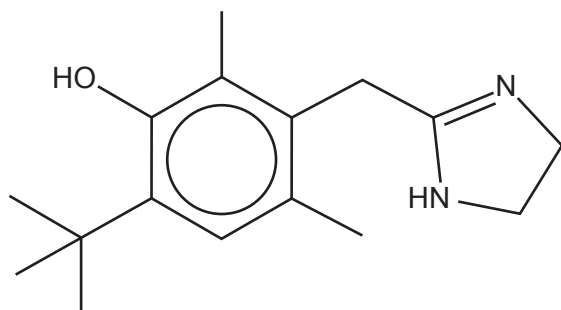
Which functional groups are present in paracetamol?

- A alcohol, amide
- B alcohol, arene, ketone, amine
- C phenol, amide
- D phenol, ketone, amine

Your answer

[1]

- 5 Oxymetazoline, shown below, is used as a decongestant in the treatment of colds.



**Oxymetazoline**

How many H atoms are in one molecule of oxymetazoline?

- A 23
- B 24
- C 25
- D 26

Your answer

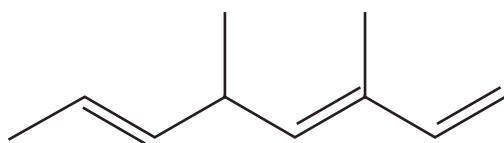
[1]

- 6 Which statement supports the delocalised model of benzene and **not** the Kekulé model?
- A Sigma bonds overlap to form a  $\pi$ -system.
  - B The carbon-carbon bond lengths are all the same.
  - C The enthalpy change of hydrogenation is more exothermic than expected.
  - D Benzene is more reactive than alkenes with bromine.

Your answer

[1]

- 7 What is the systematic name for the compound below?



- A 3,5-dimethylocta-1,3,6-triene
- B 3,5-dimethylocta-2,5,7-triene
- C 4,6-dimethylocta-1,3,6-triene
- D 4,6-dimethylocta-2,5,7-triene

Your answer

[1]

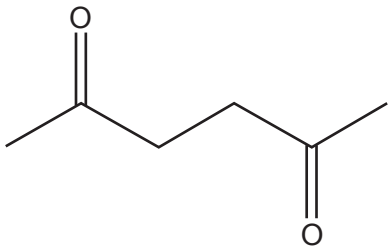
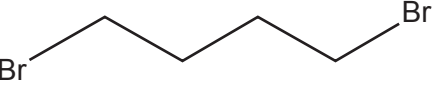
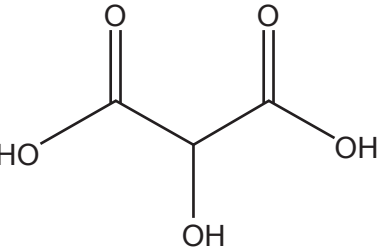
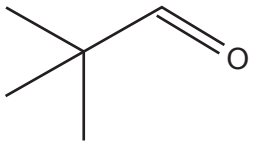
- 8 For complete combustion, 0.100 mol of an alkane requires 22.8 dm<sup>3</sup> of O<sub>2</sub>, measured at RTP.  
Which alkane has undergone complete combustion?

- A pentane
- B hexane
- C heptane
- D octane

Your answer

[1]

9 Which compound has the greatest number of peaks in its proton NMR spectrum?

<b>A</b>	
<b>B</b>	
<b>C</b>	
<b>D</b>	

Your answer

[1]

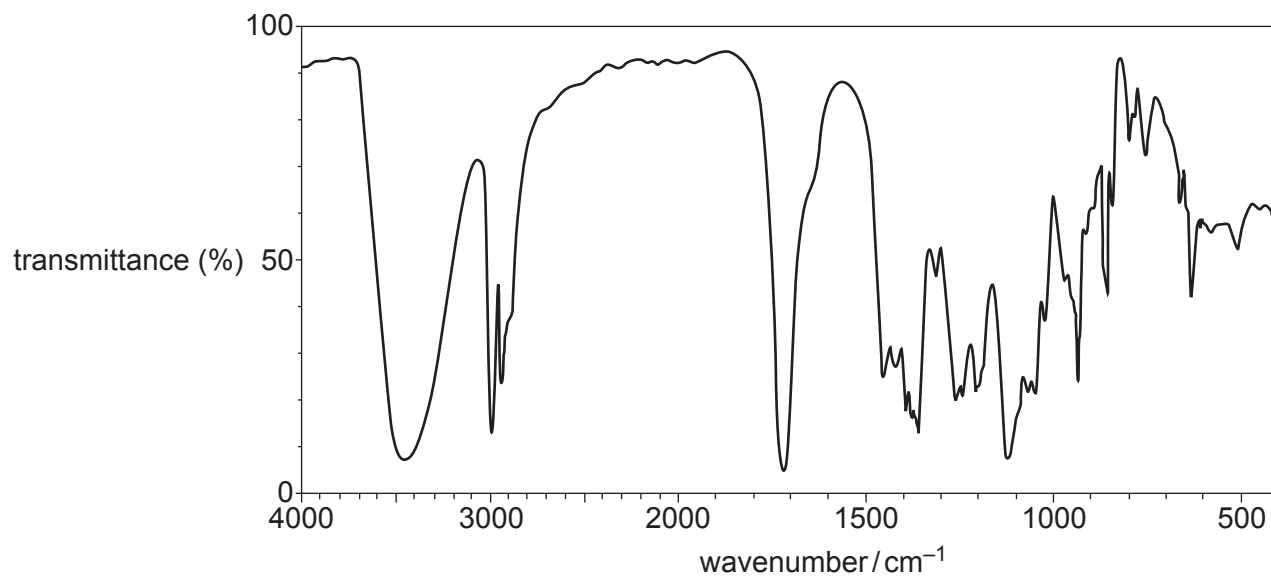
10 Which ester is most likely to produce a mass spectrum with a fragment ion at  $m/z = 43$ ?

<b>A</b>	$\begin{array}{c} \text{OH} \quad \text{O} \\   \quad    \\ \text{H}_3\text{C}-\text{C}-\text{C}-\text{O}-\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$
<b>B</b>	$\text{HO}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_3$
<b>C</b>	$\begin{array}{c} \text{OH} \quad \text{O} \\   \quad    \\ \text{H}_3\text{C}-\text{CH}-\text{CH}_2-\text{C}-\text{O}-\text{CH}_3 \end{array}$
<b>D</b>	$\begin{array}{c} \text{OH} \quad \text{O} \\   \quad    \\ \text{CH}_3\text{CH}_2-\text{C}-\text{C}-\text{O}-\text{CH}_2\text{CH}_2\text{OH} \\   \\ \text{CH}_3 \end{array}$

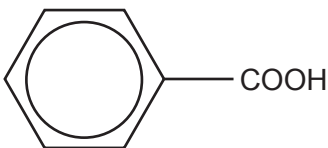
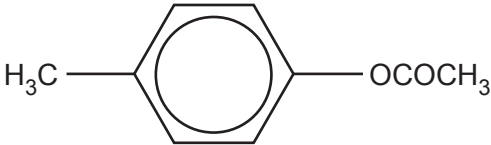
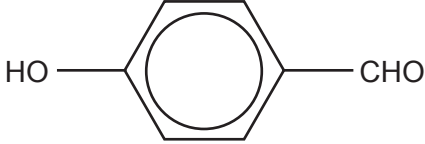
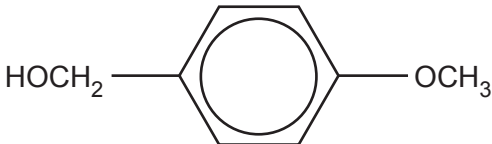
Your answer

[1]

11 The infrared spectrum of an organic compound is shown below.



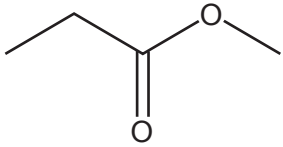
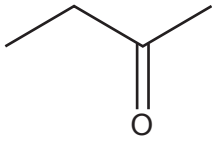
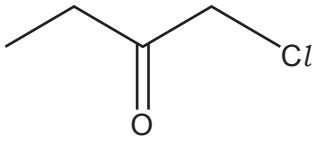
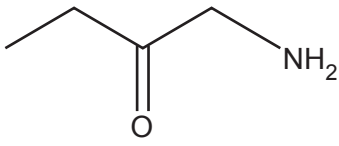
Which compound could have produced this spectrum?

<b>A</b>	
<b>B</b>	
<b>C</b>	
<b>D</b>	

Your answer

[1]

12 Which compound reacts with ethanoyl chloride?

<b>A</b>	
<b>B</b>	
<b>C</b>	
<b>D</b>	

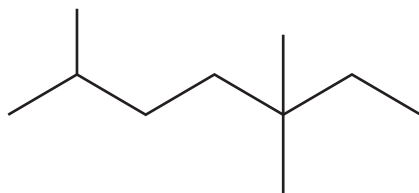
Your answer

[1]

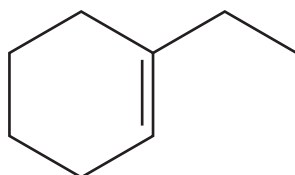


13 Which compound(s) is/are aliphatic?

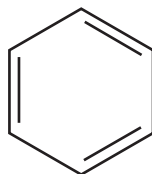
1



2



3



A 1, 2 and 3

B Only 1 and 2

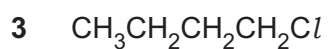
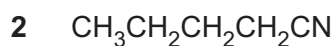
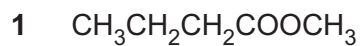
C Only 2 and 3

D Only 1

Your answer

[1]

14 Which compound(s) is/are hydrolysed by  $\text{HCl}(\text{aq})$  to produce butanoic acid?



A 1, 2 and 3

B Only 1 and 2

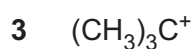
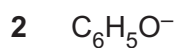
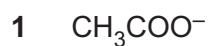
C Only 2 and 3

D Only 1

Your answer

[1]

15 Which ion(s) contain(s) bond angles of approximately  $120^\circ$ ?



A 1, 2 and 3

B Only 1 and 2

C Only 2 and 3

D Only 1

Your answer

[1]

11  
Section B

16 This question is about hydrocarbons.

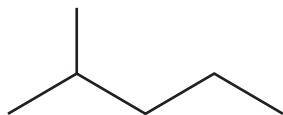
(a) The boiling points of some hydrocarbons containing 6 carbon atoms are shown below.

Hydrocarbon	Boiling point/°C
2,2-dimethylbutane	50
2-methylpentane	60
hexane	69

State and explain the trend in boiling points shown by these hydrocarbons.

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.....  
..... [4]

(b) 2-methylpentane reacts with bromine by radical substitution.



**2-methylpentane**

A mixture of organic products is formed, including 3-bromo-2-methylpentane, and compounds **A** and **B**.

(i) Complete the table below to show the mechanism for the formation of 3-bromo-2-methylpentane and **three** possible equations for termination.

In your equations, use **structural** or **skeletal formulae** and 'dots' (•) for the position of radicals.

<b>Initiation</b>	Equation: .....
	Conditions: .....
<b>Propagation</b>	→
	→
<b>Termination</b>	→
	→

[6]

- (ii) Organic compound **A** is formed by the substitution of **all** 14 H atoms in 2-methylpentane by Br atoms.

Write the equation, using **molecular formulae**, for the formation of compound **A** from 2-methylpentane.

..... [2]

- (iii) Organic compound **B** is formed by the substitution of **some** of the 14 H atoms in 2-methylpentane by Br atoms.

0.8649 g of compound **B** is heated until it is vaporised.

Under the conditions used:

- compound **B** has a volume of 72.0 cm<sup>3</sup>
- the molar gas volume is 40.0 dm<sup>3</sup> mol<sup>-1</sup>.

Determine a possible molecular formula of compound **B**.

molecular formula = ..... [3]

17 This question is about alcohols.

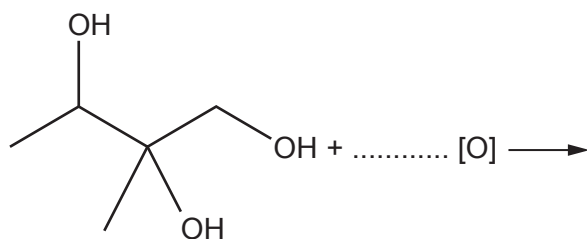
- (a) An **unsaturated** alcohol has 6 carbon atoms and contains **one** C=C bond.

Construct an equation for the complete combustion of this alcohol.

..... [2]

- (b) Compound **C**, shown below, is refluxed with excess acidified potassium dichromate(VI) to form a single organic product and one other product.

Complete the equation for this reaction.



**Compound C**

[3]

- (c) Compound **D**, shown below, is refluxed with  $\text{H}_2\text{SO}_4$ , as an acid catalyst, to form a mixture of three isomers with the molecular formula  $\text{C}_7\text{H}_{10}$ .



**Compound D**

- (i) Draw the structures of the **three** isomers of  $\text{C}_7\text{H}_{10}$  formed from compound **D**.

--	--	--

[3]

- (ii) A student converts compound **D** into a diiodoalkane.

Suggest suitable reagents for this reaction.

..... [1]

(d) There are 4 structural isomers of  $C_4H_{10}O$  that are alcohols.

A student predicts that these structural isomers could be distinguished using carbon-13 NMR spectroscopy.

Explain whether the student is correct.

In your answer, show how the peaks in the carbon-13 NMR spectra are linked to the structure of each alcohol isomer.

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..... [5]

18 1,3-dinitrobenzene is a solid at room temperature.

A chemist prepares 1,3-dinitrobenzene as outlined below.

**Step 1** 12.5 cm<sup>3</sup> of nitrobenzene (density = 1.20 g cm<sup>-3</sup>) is refluxed with concentrated nitric acid in the presence of concentrated sulfuric acid as a catalyst.

**Step 2** The mixture is cooled. Impure crystals of 1,3-dinitrobenzene appear.

**Step 3** The impure crystals are purified to obtain pure 1,3-dinitrobenzene.

The chemist obtains 15.0 g of pure 1,3-dinitrobenzene.

(a) Outline the mechanism for this reaction, including the role of H<sub>2</sub>SO<sub>4</sub> as a catalyst.

[5]



(b) Determine the percentage yield of 1,3-dinitrobenzene.

Give your answer to **3** significant figures.

percentage yield = ..... % **[3]**

(c) Describe how to purify the impure crystals in **Step 3**.

.....

.....

.....

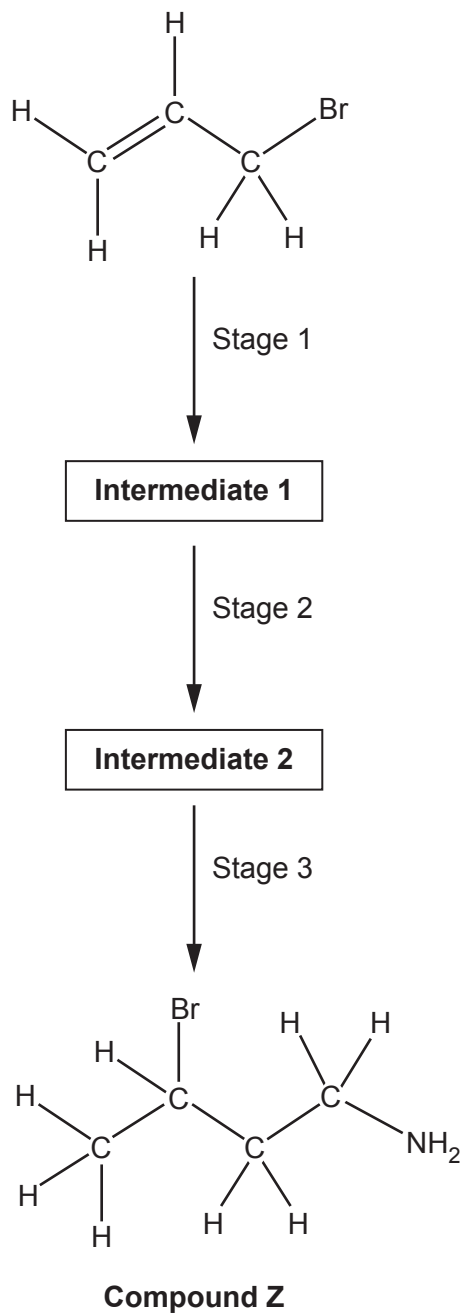
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..... **[3]**

19\* A student intends to synthesise compound **Z**, as shown in the flowchart below.



Plan this synthesis showing reagents, the structures of **intermediate 1** and **intermediate 2**, and equations. [6]

.....

.....

.....

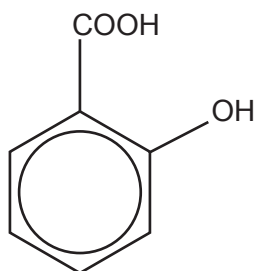
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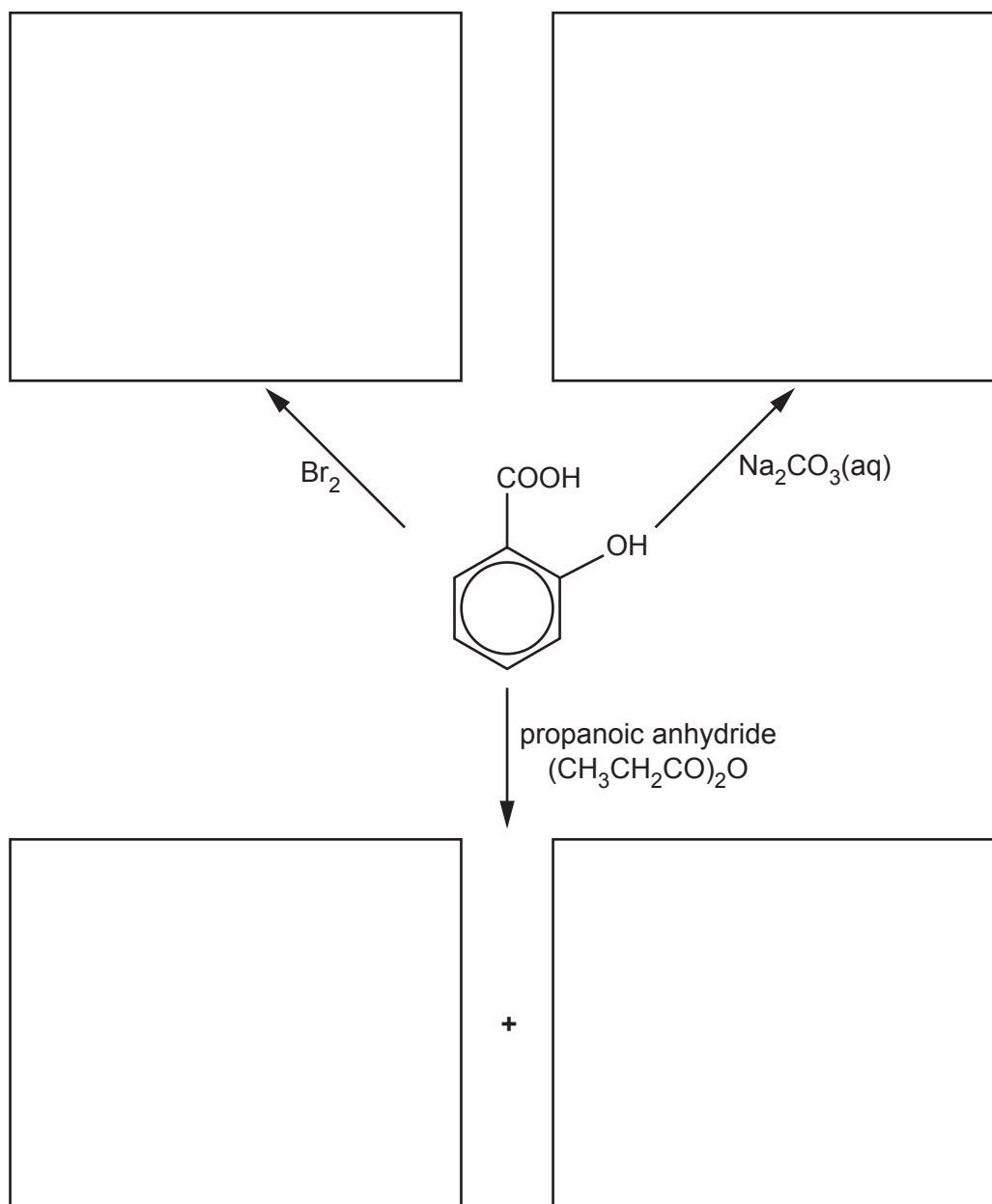
20 This question is about aromatic compounds containing the  $\text{-COOH}$  and  $\text{-OH}$  functional groups.

(a) Salicylic acid, shown below, is used in the manufacture of some important medicines.

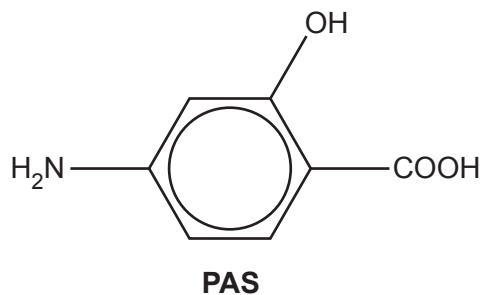


**Salicylic acid**

Complete the flowchart for reactions of salicylic acid, by adding the organic products in each box.



- (b) PAS, shown below, is an antibiotic used to treat several diseases including tuberculosis (TB).



- (i) A student predicts that PAS could polymerise to form a polymer containing **both** ester and amide linkages.

Draw a section of this polymer.

The section should contain **one** amide and **one** ester linkage, which should be displayed.

[3]

- (ii) For the treatment of TB, the maximum daily dosage of PAS that should be prescribed is 300 mg per kg of body mass.

A child weighs 20.0 kg.

Calculate the number of PAS molecules in the maximum daily dosage of PAS for this child.

number of PAS molecules = .....

[3]

21 This question is about  $\alpha$ -amino acids.

(a) The general formula of an  $\alpha$ -amino acid is  $\text{RCH}(\text{NH}_2)\text{COOH}$ .

Most  $\alpha$ -amino acids show optical isomerism.

Explain the term **optical isomerism**.

.....

.....

.....

..... [1]

(b) The  $\alpha$ -amino acid valine has the R group of  $-\text{CH}(\text{CH}_3)_2$ .

(i) What is the systematic name of valine?

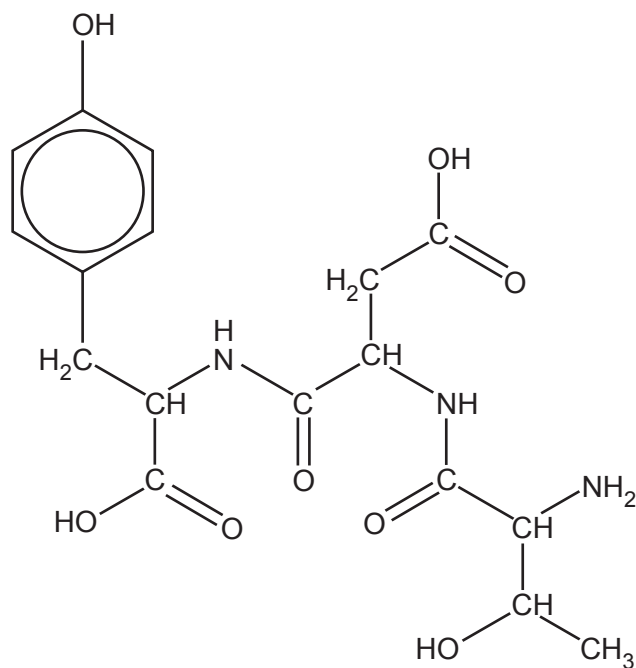
..... [1]

(ii) Draw diagrams to show 3D structures of the optical isomers of valine.

--	--

[2]

(c) Three  $\alpha$ -amino acids can react together to form compound **E**, shown below.



**Compound E**

(i) How many optical isomers are possible for compound **E**?

..... [1]

(ii) A student hydrolyses compound **E** with dilute hydrochloric acid,  $\text{HCl}(\text{aq})$ .

Draw the structures of the organic products formed by this hydrolysis.

[4]

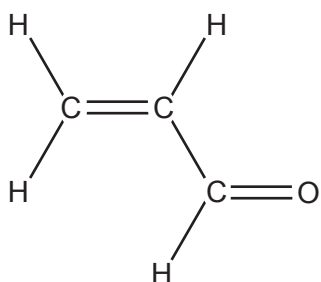
22 This question is about reactions of acrolein,  $\text{H}_2\text{C}=\text{CHCHO}$ .

(a) Acrolein reacts with sodium cyanide in acidic conditions,  $\text{NaCN}(\text{aq})/\text{H}^+(\text{aq})$ .

(i) Outline the reaction mechanism for this reaction, showing the intermediate and the organic product.

The structure of acrolein has been provided.

Include curly arrows and relevant dipoles.



[4]

(ii) Name this type of mechanism.

..... [1]



(b) Complete the flowchart by filling in each box.

Flowchart showing the reactions of acrolein:

Acrolein (structure shown) reacts to form an **unsaturated alcohol** (via reagent(s) and catalyst) and a **carboxylic acid** (via reagent(s)).

The **unsaturated alcohol** further reacts to form a **diol (major product)** (via reagent(s) and catalyst).

The **carboxylic acid** further reacts to form an **acyl chloride** (via reagent(s)).

Acrolein also reacts to form a **polymer (2 repeat units)**.

Reaction boxes for reagents and catalysts are provided for the following steps:

- Acrolein to unsaturated alcohol
- Unsaturated alcohol to diol (major product)
- Acrolein to carboxylic acid
- Carboxylic acid to acyl chloride

[9]

23\* An unknown organic compound is analysed.

The results are shown below.

**Addition of 2,4-DNP**

No visible change

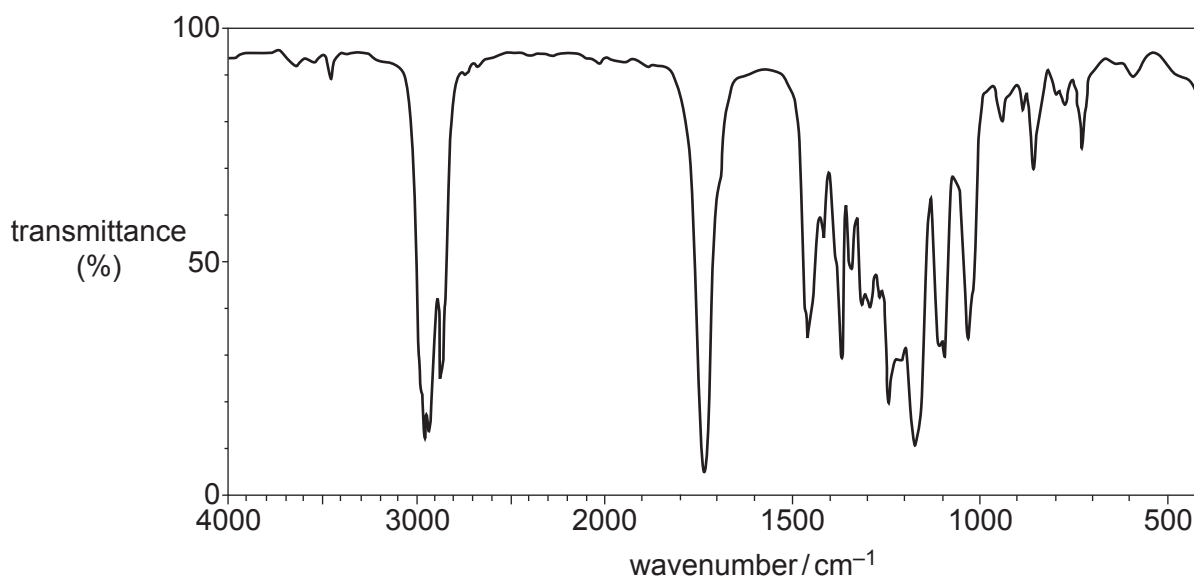
**Elemental analysis by mass**

C, 66.63%; H, 11.18%; O, 22.19%

**Mass spectrum**

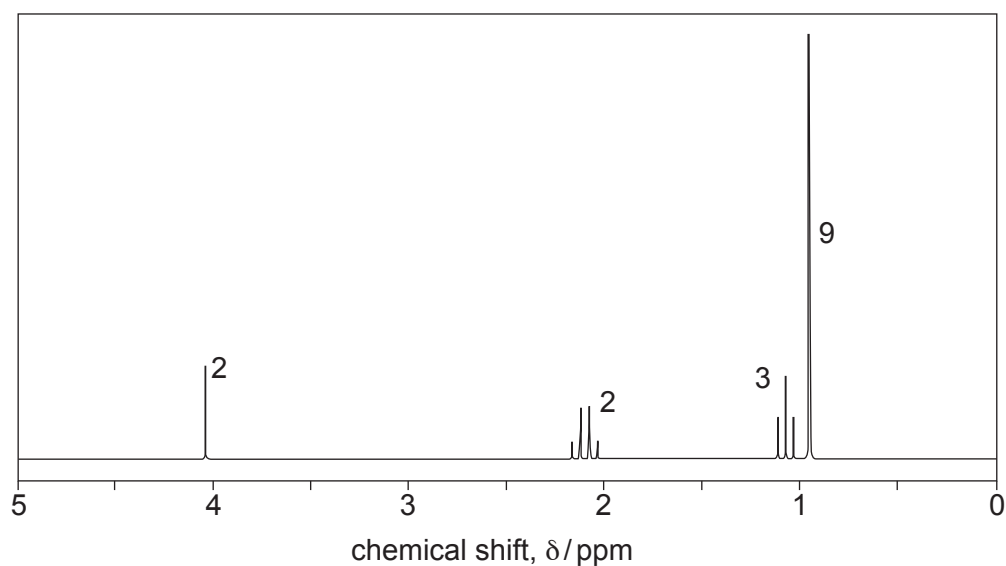
Molecular ion peak at  $m/z = 144.0$

**IR spectrum**



**Proton NMR spectrum**

The numbers by each peak are the relative peak areas.





**ADDITIONAL ANSWER SPACE**

If additional space is required, you should use the following lined page(s). The question number(s) must be clearly shown in the margin(s).

A large rectangular area with a vertical solid line on the left side and horizontal dotted lines across the rest of the page, providing space for writing answers.



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