



Oxford Cambridge and RSA

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

StemUp Model Solution

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 CCl_4
- B CDCl_3
- C D_2O
- D $\text{Si}(\text{CH}_3)_4$

Your answer

C

[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 CH_3COCHO
- D $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$

Your answer

A

[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?

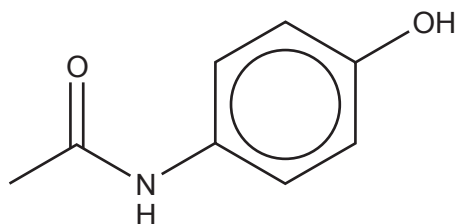
- A $\text{C}_n\text{H}_{2n-4}$
- B $\text{C}_n\text{H}_{2n-2}$
- C C_nH_{2n}
- D $\text{C}_n\text{H}_{2n+2}$

Your answer

B

[1]

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



Paracetamol

Which functional groups are present in paracetamol?

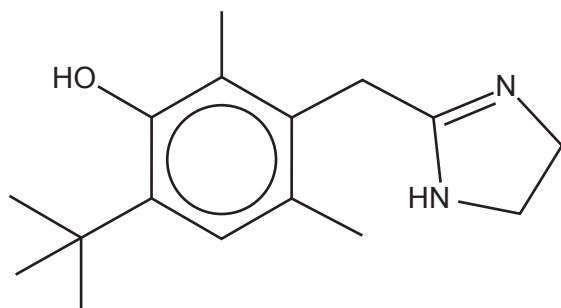
- A alcohol, amide
- B alcohol, arene, ketone, amine
- C phenol, amide
- D phenol, ketone, amine

Your answer

C

[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

B

[1]

6 Which statement supports the delocalised model of benzene and **not** the Kekulé model?

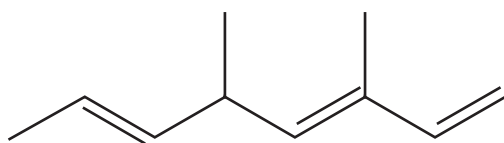
- A Sigma bonds overlap to form a π -system.
- B The carbon-carbon bond lengths are all the same.
- C The enthalpy change of hydrogenation is more exothermic than expected.
- D Benzene is more reactive than alkenes with bromine.

Your answer

B

[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

A

[1]

8 For complete combustion, 0.100 mol of an alkane requires 22.8 dm³ of O₂, measured at RTP.

Which alkane has undergone complete combustion?

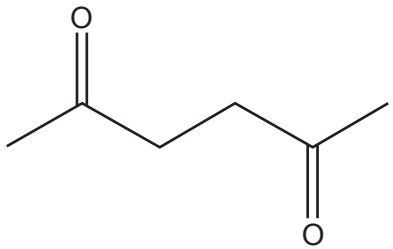
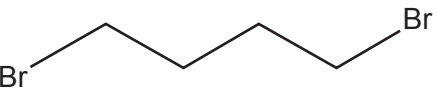
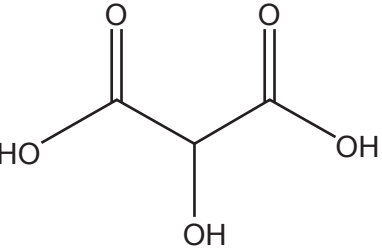
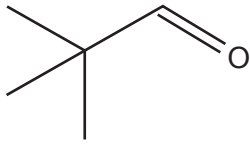
- A pentane
- B hexane
- C heptane
- D octane

Your answer

B

[1]

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

A	
B	
C	
D	

Your answer

C

[1]

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

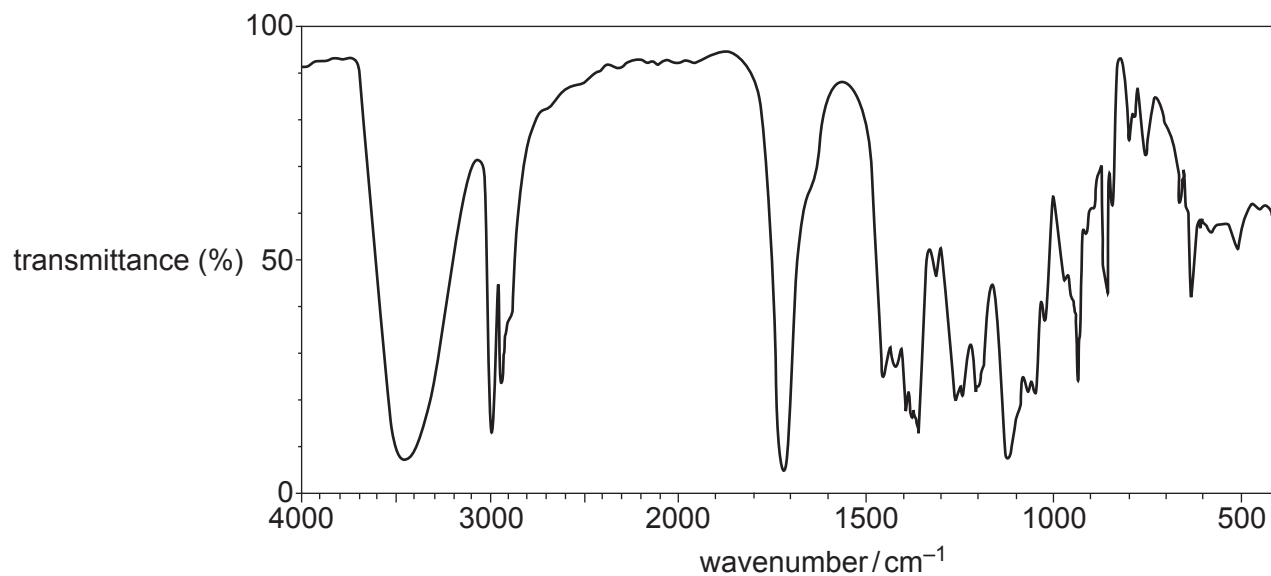
A	$\begin{array}{c} \text{OH} \quad \text{O} \\ \quad \\ \text{H}_3\text{C}-\text{C}-\text{C}-\text{O}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$
B	$\text{HO}-\text{CH}_2-\overset{\text{O}}{\overset{ }{\text{C}}}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_3$
C	$\begin{array}{c} \text{OH} \quad \text{O}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

Your answer

B

[1]

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



Which compound could have produced this spectrum?

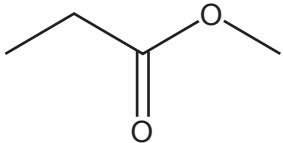
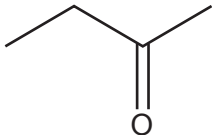
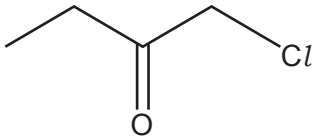
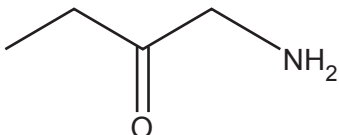
A	
B	
C	
D	

Your answer

C

[1]

12 Which compound reacts with ethanoyl chloride?

A	
B	
C	
D	

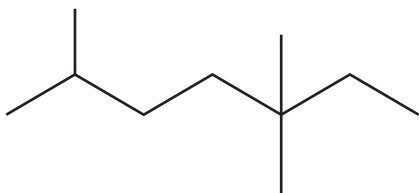
Your answer

D

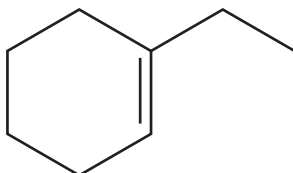
[1]

13 Which compound(s) is/are aliphatic?

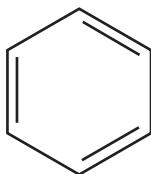
1



2



3



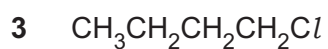
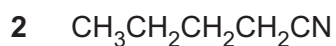
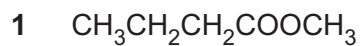
- A** 1, 2 and 3
B Only 1 and 2
C Only 2 and 3
D Only 1

Your answer

B

[1]

14 Which compound(s) is/are hydrolysed by HCl(aq) to produce butanoic acid?



A 1, 2 and 3

B Only 1 and 2

C Only 2 and 3

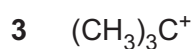
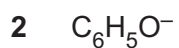
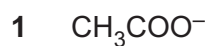
D Only 1

Your answer

D

[1]

15 Which ion(s) contain(s) bond angles of approximately 120° ?



A 1, 2 and 3

B Only 1 and 2

C Only 2 and 3

D Only 1

Your answer

A

[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.

Boiling point increases as branching decreases: hexane (straight chain, no branches) has the highest boiling point and 2,2-dimethylbutane (most branched) has the lowest.

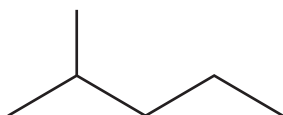
Less branched molecules have more surface contact with each other (they can get closer together), so there is more contact between the molecules.

More surface contact gives more (stronger) induced dipole-dipole interactions (London forces) between the molecules.

So more energy is needed to break the London forces (intermolecular forces) in hexane than in 2-methylpentane, which needs more than 2,2-dimethylbutane.

[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.

Initiation	Equation: $Br_2 \rightarrow 2Br\cdot$ Conditions: <i>ultraviolet (UV) light</i>
Propagation	$+ Br\cdot$ $\longrightarrow$ $+ HBr$ $+ Br_2$ $\longrightarrow$ $+ Br\cdot$
Termination	$Br\cdot + Br\cdot$ $\longrightarrow$ Br_2 $+ Br\cdot$ $\longrightarrow$ 2 $\longrightarrow$

[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.



- (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 cm³
- the molar gas volume is 40.0 dm³ mol⁻¹.

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

$$n(B) = 72.0 \div 40\,000 = 1.80 \times 10^{-3} \text{ mol}$$

$$M(B) = 0.8649 \div 1.80 \times 10^{-3} = 480.5 \text{ g mol}^{-1}$$

$$C_6H_{14-x}Br_x: 86.0 + 78.9x = 480.5, \text{ so } x = 5$$

$$\text{check: } C_6H_9Br_5 = 72.0 + 9.0 + 399.5 = 480.5$$

molecular formula = ... $C_6H_9Br_5$ [3]

17 This question is about alcohols.

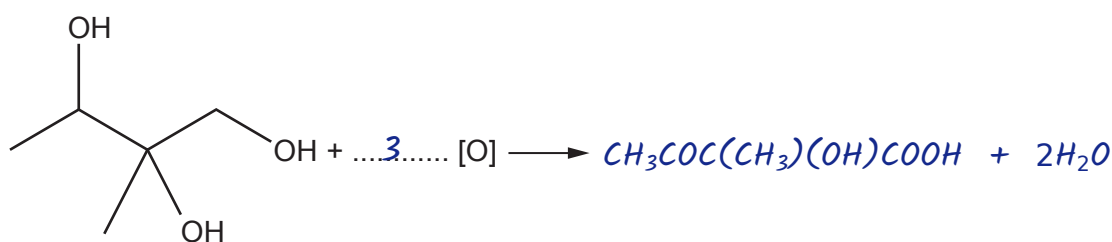
- (a) An **unsaturated** alcohol has 6 carbon atoms and contains **one** C=C bond.

Construct an equation for the complete combustion of this alcohol.



- (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

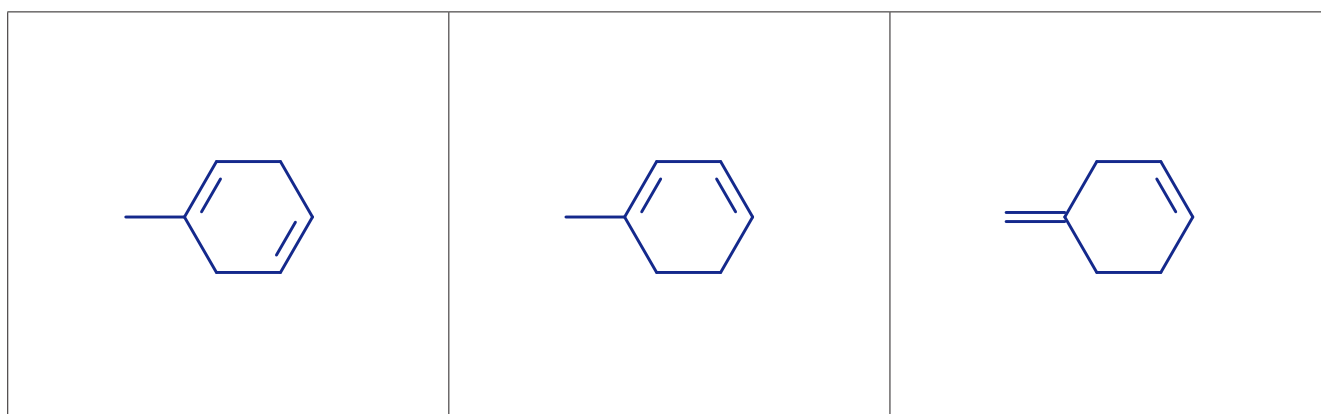
[3]

- (c) Compound **D**, shown below, is refluxed with H_2SO_4 , as an acid catalyst, to form a mixture of three isomers with the molecular formula C_7H_{10} .



Compound D

- (i) Draw the structures of the **three** isomers of C_7H_{10} formed from compound **D**.



[3]

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

Suggest suitable reagents for this reaction.



- (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.

The four alcohols are butan-1-ol $CH_3CH_2CH_2CH_2OH$, butan-2-ol $CH_3CH_2CH(OH)CH_3$, 2-methylpropan-1-ol $(CH_3)_2CHCH_2OH$ and 2-methylpropan-2-ol $(CH_3)_3COH$.

Butan-1-ol and butan-2-ol: each has 4 different carbon environments, so 4 peaks. 2-methylpropan-1-ol: the two CH_3 carbons are equivalent, so 3 environments, 3 peaks. 2-methylpropan-2-ol: the three CH_3 carbons are equivalent, so 2 environments, 2 peaks.

So the student is only partly correct: 2-methylpropan-1-ol and 2-methylpropan-2-ol can be distinguished from all the others, but butan-1-ol and butan-2-ol (both 4 peaks) cannot be distinguished.

[5]

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

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

Step 1 12.5 cm³ of nitrobenzene (density = 1.20 g cm⁻³) is refluxed with concentrated nitric acid in the presence of concentrated sulfuric acid as a catalyst.

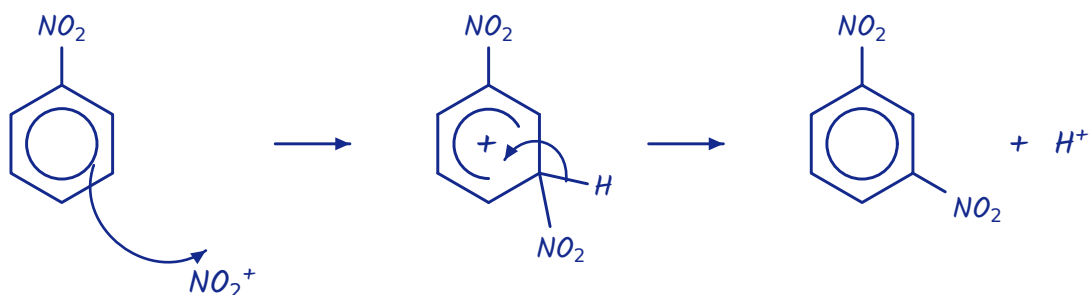
Step 2 The mixture is cooled. Impure crystals of 1,3-dinitrobenzene appear.

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

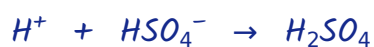
The chemist obtains 15.0 g of pure 1,3-dinitrobenzene.

(a) Outline the mechanism for this reaction, including the role of H₂SO₄ as a catalyst.

Generating the electrophile:



Regenerating the catalyst:



H₂SO₄ is used up making NO₂⁺ but is re-formed at the end, so it is a catalyst.

[5]

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

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

$$\text{mass of nitrobenzene} = 12.5 \times 1.20 = 15.0 \text{ g}$$

$$n(\text{C}_6\text{H}_5\text{NO}_2) = 15.0 \div 123.0 = 0.12195 \text{ mol}$$

$$= \text{theoretical } n(\text{C}_6\text{H}_4(\text{NO}_2)_2) \text{ (1 : 1)}$$

$$\text{actual } n(\text{C}_6\text{H}_4(\text{NO}_2)_2) = 15.0 \div 168.0 = 0.089286 \text{ mol}$$

$$\% \text{ yield} = 0.089286 \div 0.12195 \times 100 = 73.2 \%$$

$$\text{percentage yield} = \dots\dots\dots 73.2 \dots\dots\dots \% \text{ [3]}$$

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

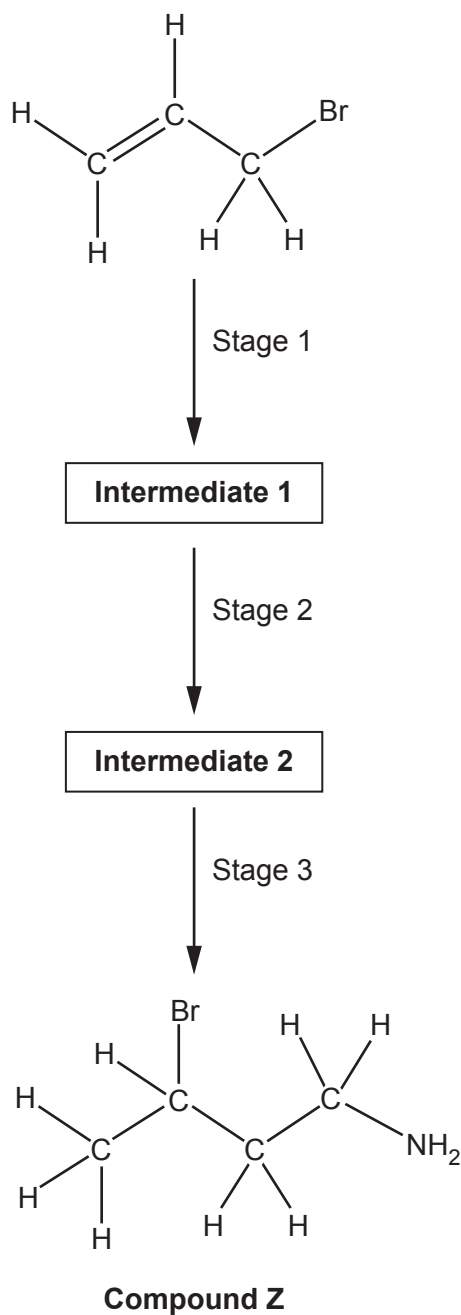
Dissolve the impure crystals in the minimum volume of hot solvent (e.g. hot ethanol).

Leave the solution to cool so crystals form, then filter under reduced pressure (Buchner funnel).

Leave the crystals to dry.

..... [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]

Stage 1: react with KCN (CN⁻) in ethanol (nucleophilic substitution); this adds
one carbon to the chain.



Intermediate 1: $\text{H}_2\text{C}=\text{CHCH}_2\text{CN}$ (but-3-enenitrile)

Stage 2: react with HBr (electrophilic addition to the C=C). Br adds to C2 (the

major product) via the more stable secondary carbocation.



Intermediate 2: $\text{CH}_3\text{CHBrCH}_2\text{CN}$ (3-bromobutanenitrile)

Stage 3: reduce the nitrile with H_2 and a Ni catalyst (reduction of CN to CH_2NH_2).



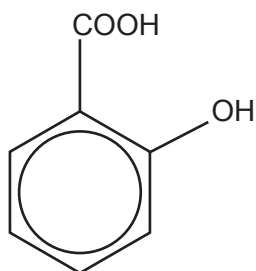
Order of stages: CN^- must be used before HBr, because after adding HBr there would be two Br atoms and CN^- would substitute both of them.

HBr must be added before the H_2/Ni reduction, because H_2/Ni would also hydrogenate the $\text{C}=\text{C}$ bond, leaving nothing for HBr to add to.

Additional answer space if required.

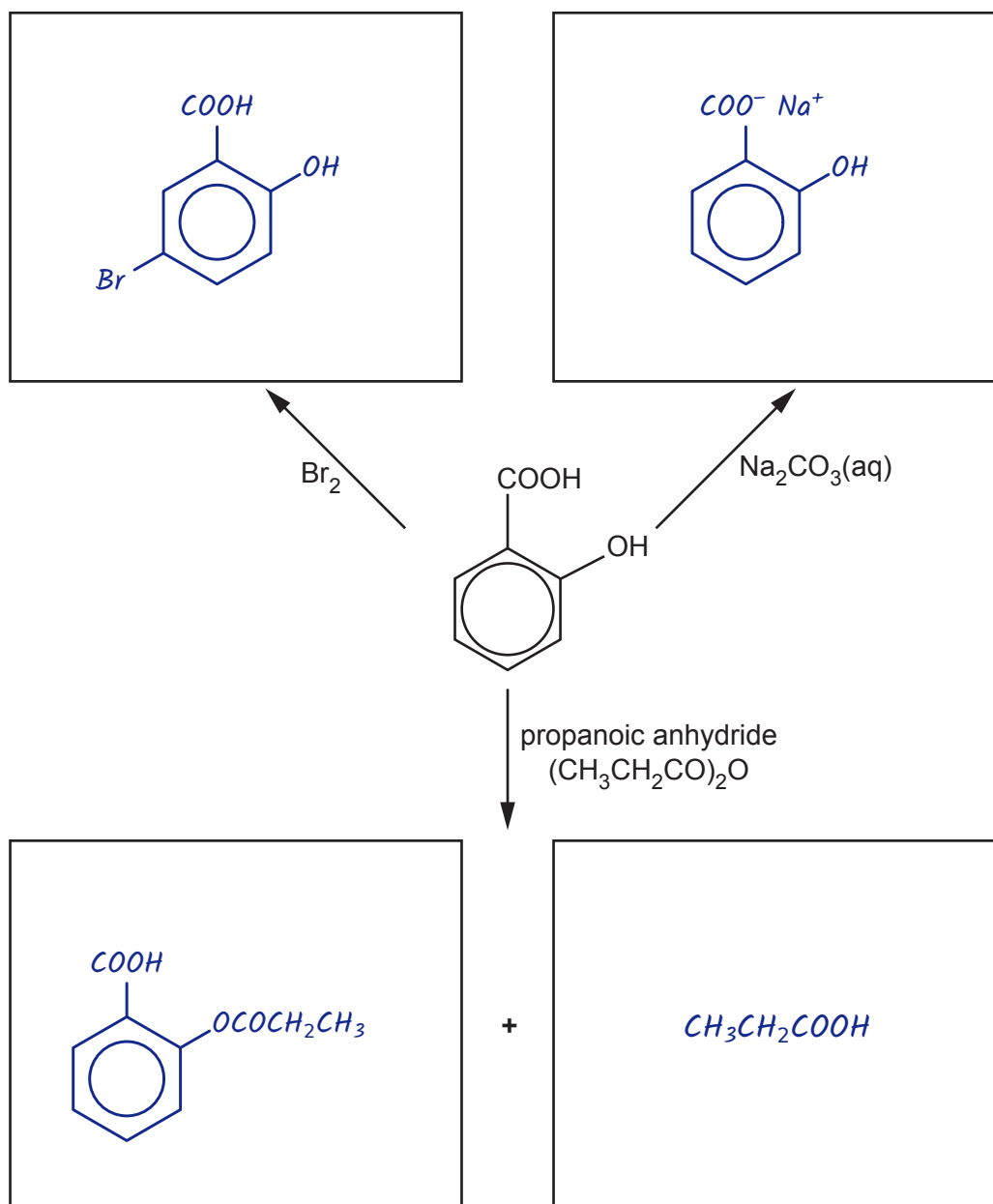
20 This question is about aromatic compounds containing the -COOH and -OH functional groups.

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



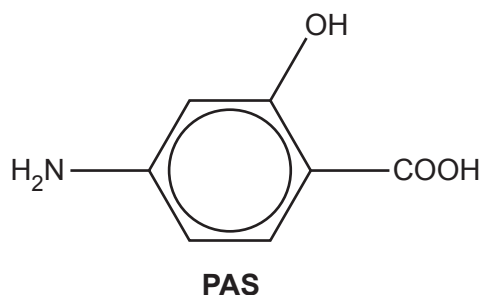
Salicylic acid

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



[4]

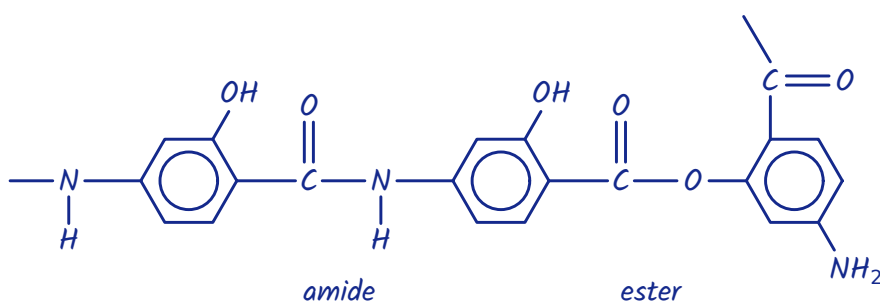
- (b) PAS, shown below, is an antibiotic used to treat several diseases including tuberculosis (TB).



- (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.

$$\text{mass of PAS} = 300 \text{ mg} \times 20.0 = 6000 \text{ mg} = 6.00 \text{ g}$$

$$M(\text{PAS}) = M(\text{C}_7\text{H}_7\text{NO}_3) = 153.0 \text{ g mol}^{-1}$$

$$n(\text{PAS}) = 6.00 \div 153.0 = 0.039216 \text{ mol}$$

$$\text{number} = 0.039216 \times 6.02 \times 10^{23} = 2.36 \times 10^{22}$$

number of PAS molecules = ... 2.36×10^{22}

[3]

21 This question is about α -amino acids.

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

Most α -amino acids show optical isomerism.

Explain the term **optical isomerism**.

Optical isomers are non-superimposable mirror images of each other; they arise when a molecule has a chiral centre (a carbon with four different groups attached).

[1]

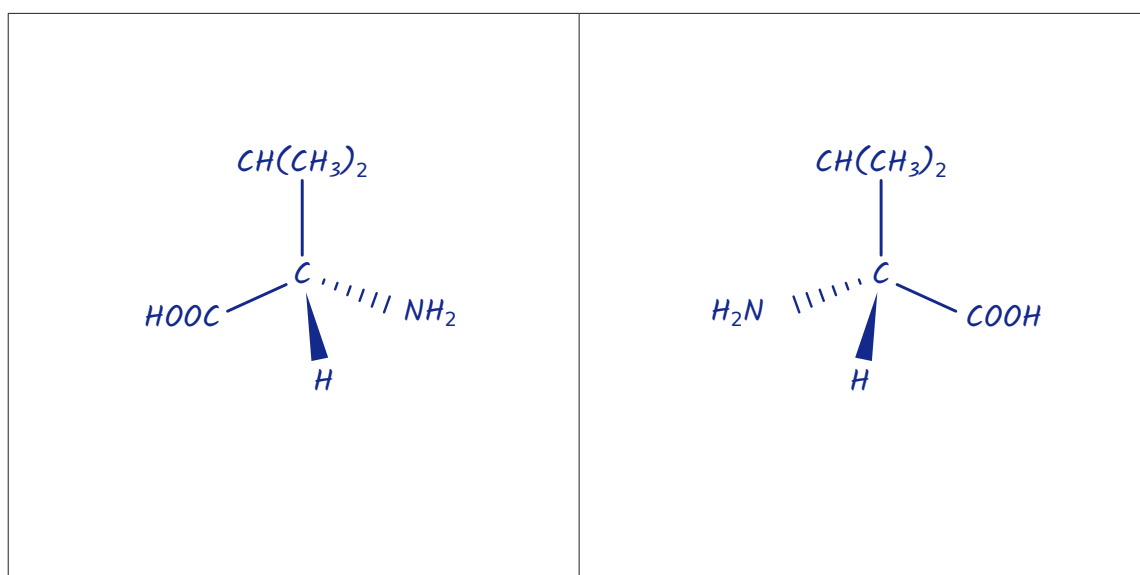
(b) The α -amino acid valine has the R group of $-\text{CH}(\text{CH}_3)_2$.

(i) What is the systematic name of valine?

2-amino-3-methylbutanoic acid

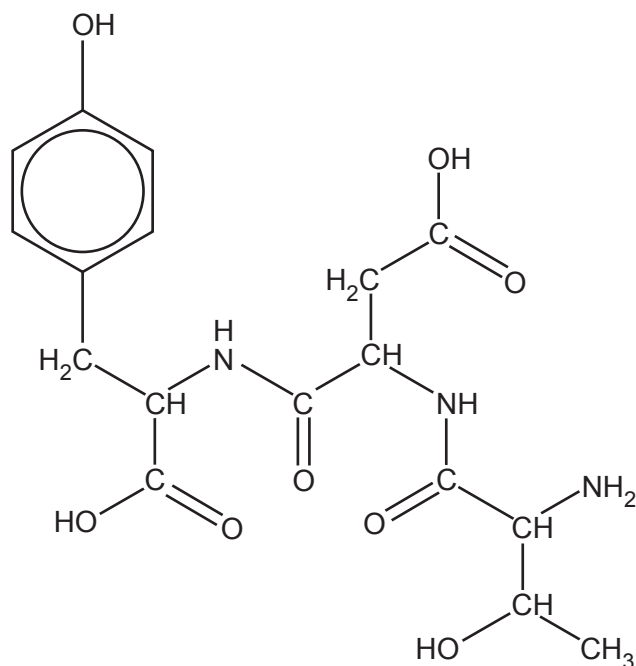
[1]

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



[2]

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



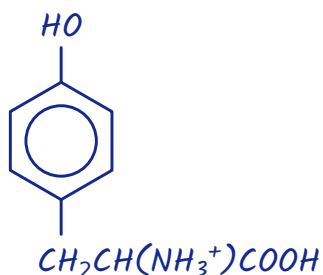
Compound E

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

16 [1]

(ii) A student hydrolyses compound **E** with dilute hydrochloric acid, HCl(aq) .

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



(each as its chloride salt, NH_3^+Cl^-)

[4]

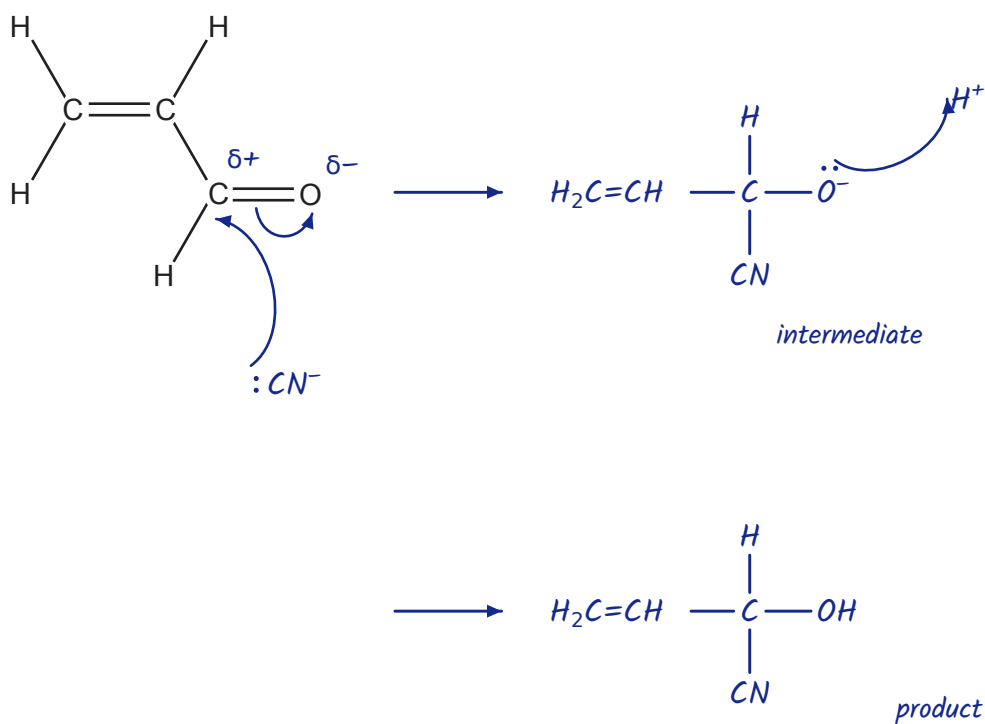
22 This question is about reactions of acrolein, $\text{H}_2\text{C}=\text{CHCHO}$.

(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]

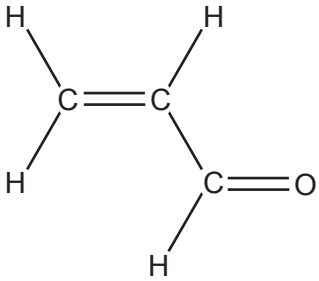
- (ii) Name this type of mechanism.

nucleophilic addition

[1]

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

$H_2C=CHCH_2OH$ unsaturated alcohol	reagent(s) ..steam, $H_2O(g)$..... catalyst ..H_3PO_4..(acid).....	$CH_3CH(OH)CH_2OH$ diol (major product)
---	--	---



acrolein

reagent(s)
.. $H^+ / Cr_2O_7^{2-}$

$H_2C=CHCOOH$ carboxylic acid	reagent(s) ..$SOCl_2$.....
---	---

$$\begin{array}{cccc} H & CHO & H & CHO \\ | & | & | & | \\ -C- & -C- & -C- & -C- \\ | & | & | & | \\ H & H & H & H \end{array}$$

polymer (2 repeat units)

$H_2C=CHCOCl$
acyl chloride

[9]

23* An unknown organic compound is analysed.

The results are shown below.

Addition of 2,4-DNP

No visible change

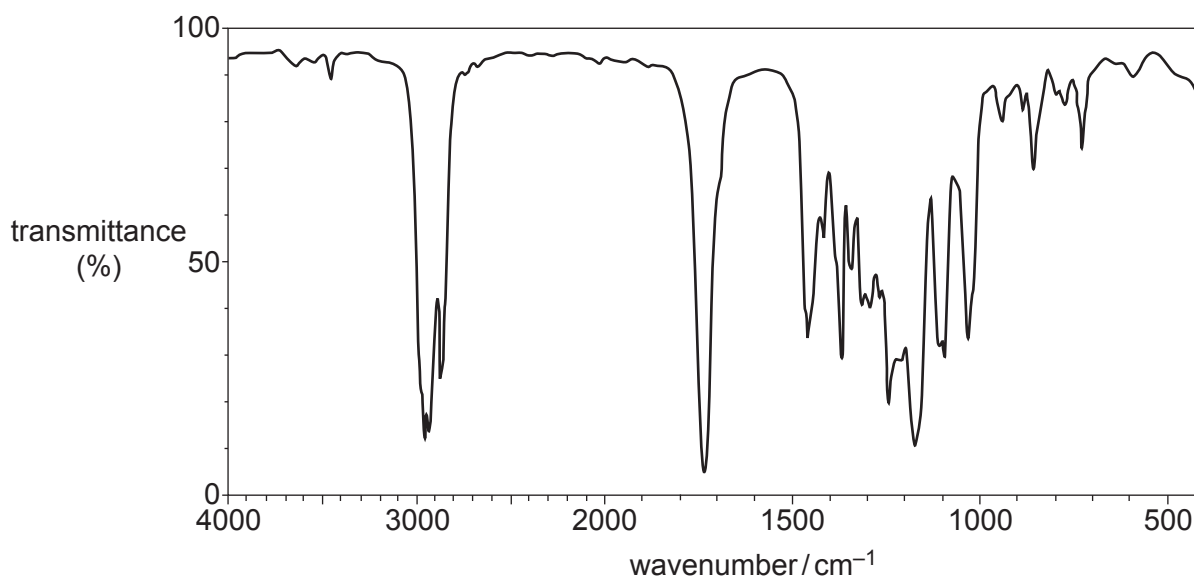
Elemental analysis by mass

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

Mass spectrum

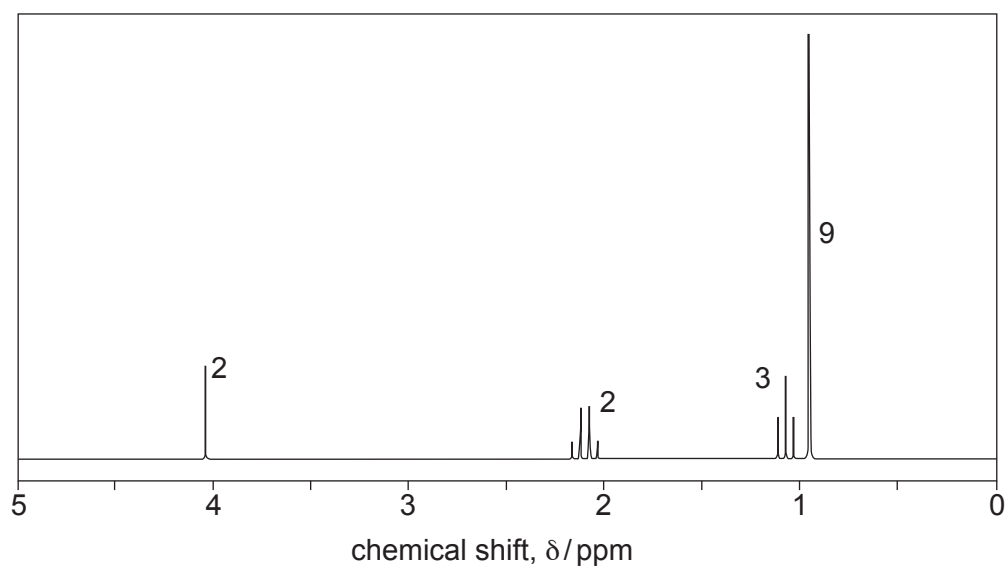
Molecular ion peak at $m/z = 144.0$

IR spectrum



Proton NMR spectrum

The numbers by each peak are the relative peak areas.



Use the information to identify the organic compound.

Show **all** your reasoning.

Empirical formula: $C : H : O = 66.63/12.0 : 11.18/1.0 : 22.19/16.0 = 5.55 :$

$11.18 : 1.39 = 4 : 8 : 1$, so C_4H_8O ($M = 72.0$).

Molecular ion at $m/z = 144.0 = 2 \times 72.0$, so the molecular formula is $C_8H_{16}O_2$.

IR: strong absorption at about 1740 cm^{-1} shows $C=O$; there is no broad $O-H$

absorption (3200 to 3600 cm^{-1}), so it is not an acid or alcohol. No change with

2,4-DNP means it is not an aldehyde or ketone, so with two O atoms and $C=O$

the compound is an ester.

Proton NMR (4 environments):

$\delta = 0.9$ ppm, singlet, 9H: $C(CH_3)_3$, no H on the adjacent carbon.

$\delta = 1.1$ ppm, triplet, 3H: CH_3 next to a CH_2 (CH_3CH_2).

$\delta = 2.2$ ppm, quartet, 2H: CH_2 next to CH_3 and next to $C=O$ ($CH_3CH_2C=O$).

$\delta = 4.0$ ppm, singlet, 2H: $O-CH_2$, next to the oxygen of the ester and to a C with no H ($C(CH_3)_3$).

The compound is $CH_3CH_2COOCH_2C(CH_3)_3$, 2,2-dimethylpropyl propanoate ($C_8H_{16}O_2$,

$M = 144.0$).

[6]

Additional answer space if required.

END OF QUESTION PAPER

[illegible]

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