



Oxford Cambridge and RSA

A Level Chemistry A

H432/02 Synthesis and analytical techniques

Tuesday 12 June 2018 – Afternoon

Time allowed: 2 hours 15 minutes



You must have:

- the Data Sheet for Chemistry A
(sent with general stationery)

You may use:

- a scientific or graphical calculator



First name										
Last name	StemUp Model Solution									
Centre number						Candidate number				

INSTRUCTIONS

- Use black ink. You may use an HB pencil for graphs and diagrams.
- Complete the boxes above with your name, centre number and candidate number.
- Answer **all** the questions.
- Write your answer to each question in the space provided. If additional space is required, use the lined page(s) at the end of this booklet. The question number(s) must be clearly shown.
- Do **not** write in the barcodes.

INFORMATION

- The total mark for this paper is **100**.
- The marks for each question are shown in brackets [].
- Quality of extended responses will be assessed in questions marked with an asterisk (*).
- This document consists of **32** pages.

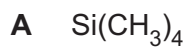
SECTION A

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

Write your answer to each question in the box provided.

Answer **all** the questions.

1 Which compound is used as a standard for NMR chemical shift measurements?

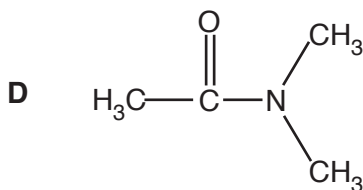
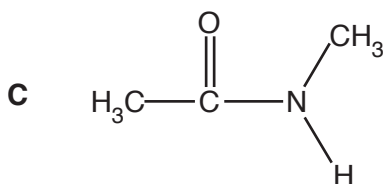
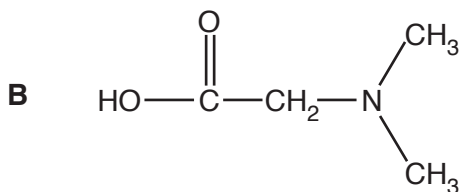
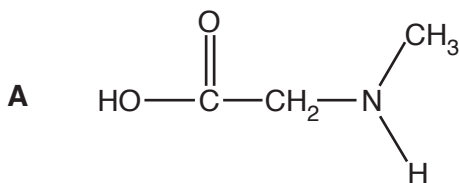


Your answer

A

[1]

2 Which compound is a secondary amide?



Your answer

C

[1]

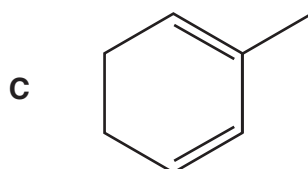
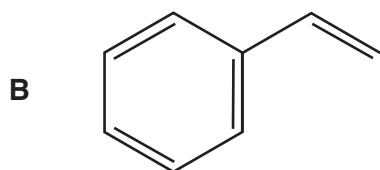
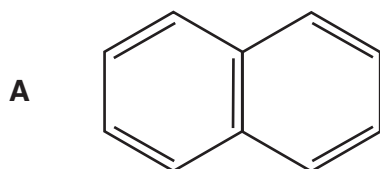
3 Which compound does **not** react with nucleophiles?

- A $\text{CH}_3\text{CH}_2\text{CHO}$
 B CH_3CHCH_2
 C $\text{CH}_3\text{CH}_2\text{COCH}_3$
 D $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$

Your answer B

[1]

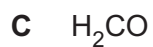
4 Which structure represents an alicyclic compound?



Your answer C

[1]

5 Which molecule is **not** planar?



Your answer

B

[1]

6 What is the number of peaks in the ^1H NMR spectrum of $\text{HOOCCH}_2\text{CHOHCH}_2\text{COOH}$?

A 3

B 4

C 5

D 6

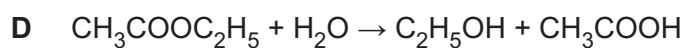
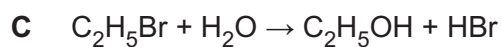
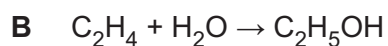
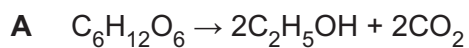
Your answer

B

[1]

7 Ethanol can be prepared by different reactions.

Which reaction has the lowest atom economy?



Your answer

C

[1]

- 8 The breakdown of ozone is catalysed by NO radicals.

Which equation is a propagation step in the mechanism for this process?

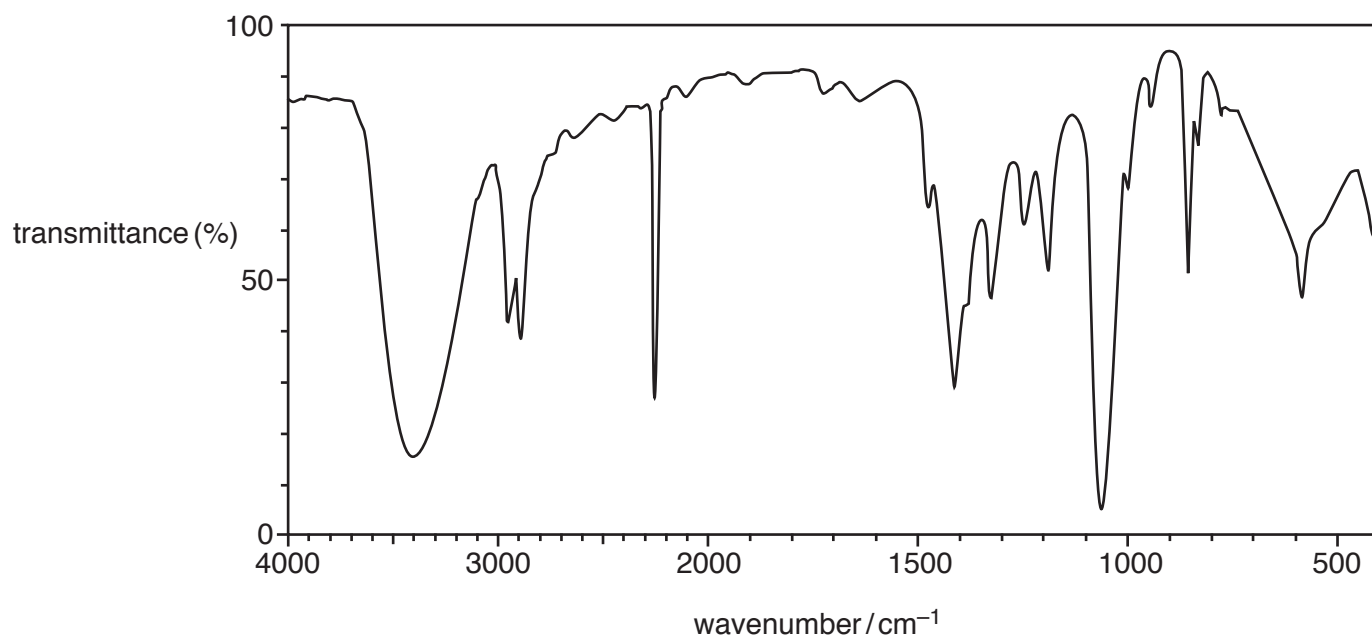
- A $\text{NO} + \text{O}_2 \rightarrow \text{N} + \text{O}_3$
 B $\text{NO} + \text{O}_2 \rightarrow \text{NO}_2 + \text{O}$
 C $\text{N} + \text{O}_3 \rightarrow \text{NO} + \text{O}_2$
 D $\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2$

Your answer

D

[1]

- 9 Which compound could have produced the IR spectrum below?



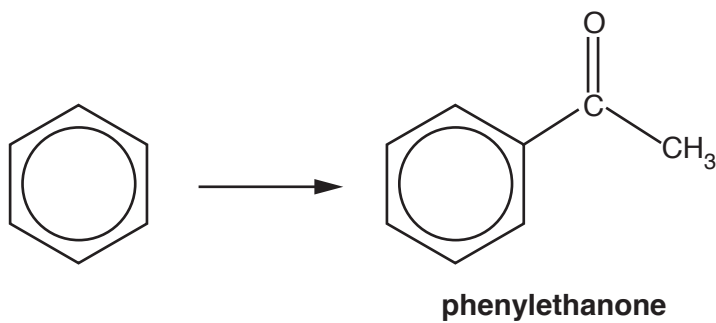
- A $\text{CH}_3\text{CH}_2\text{OH}$
 B $\text{CH}_3\text{CHOH}\text{CN}$
 C CH_3COOH
 D CH_3CONH_2

Your answer

B

[1]

- 10 Benzene reacts with an organic reagent in the presence of a halogen carrier to form phenylethanone.



Which organic reagent is required?

- A $\text{CH}_3\text{CH}_2\text{OH}$
- B CH_3CHO
- C CH_3COCl
- D CH_3COOH

Your answer

C

[1]

- 11 How many straight-chain structural isomers of $\text{C}_7\text{H}_{15}\text{Cl}$ contain a chiral carbon atom?

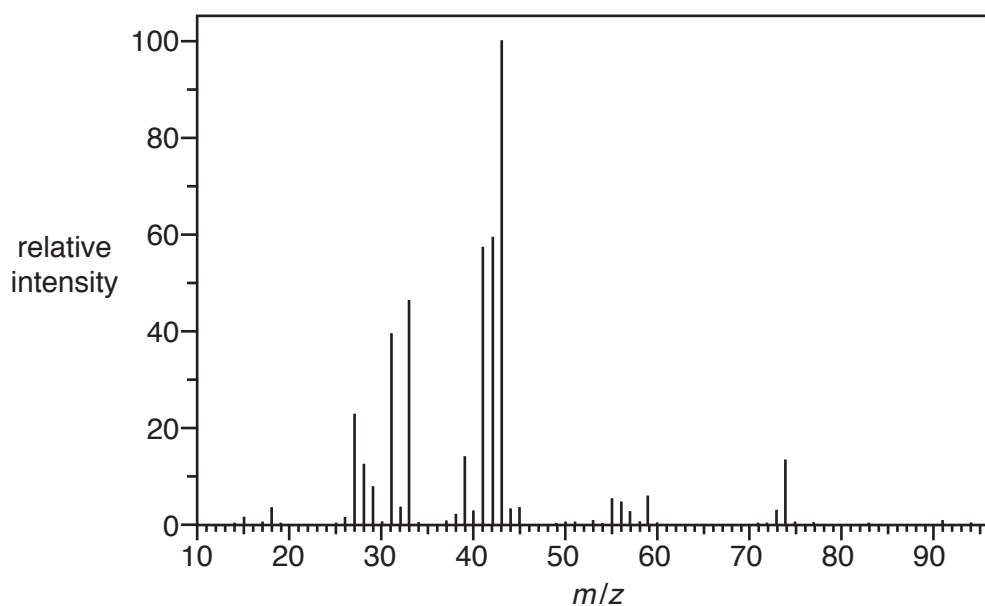
- A 1
- B 2
- C 3
- D 4

Your answer

B

[1]

12 The mass spectrum of $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$ is shown below.



Which ion is responsible for the peak with the greatest relative intensity?

- A CHCH_2OH^+
- B $\text{CH}_3\text{CH}_2\text{CH}^+$
- C $(\text{CH}_3)_2\text{CH}^+$
- D CH_3CO^+

Your answer

C

[1]

13 Which statement(s) support(s) the delocalised model for the structure of benzene?

- 1 All carbon–carbon bonds have the same length.
- 2 The enthalpy change of hydrogenation of benzene is less exothermic than expected.
- 3 Bromine reacts with benzene less readily than with cyclohexene.

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

Your answer

A

[1]

14 A solid organic compound can be purified by recrystallisation.

Which statement(s) about recrystallisation is/are true?

- 1 The organic compound is more soluble in hot solvent.
- 2 The hot solution is cooled before the purified organic compound is collected.
- 3 The melting point of the purified organic compound is lower than the impure compound.

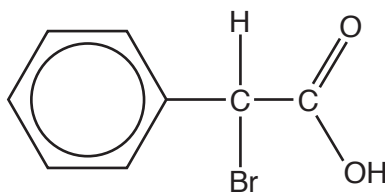
- A** 1, 2 and 3
B Only 1 and 2
C Only 2 and 3
D Only 1

Your answer

B

[1]

15 Which of the following could react with the compound below to form a carbon–carbon bond?



- 1 CH_3Cl and AlCl_3
 - 2 KCN in ethanol
 - 3 CH_3OH and H_2SO_4
- A** 1, 2 and 3
B Only 1 and 2
C Only 2 and 3
D Only 1

Your answer

B

[1]

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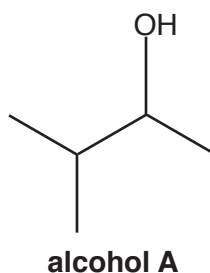
PLEASE DO NOT WRITE ON THIS PAGE

SECTION B

Answer **all** the questions.

16 This question is about reactions of organic compounds containing carbon, hydrogen and oxygen.

(a) A chemist investigates two reactions of alcohol **A**, shown below.



(i) What is the systematic name of alcohol **A**?

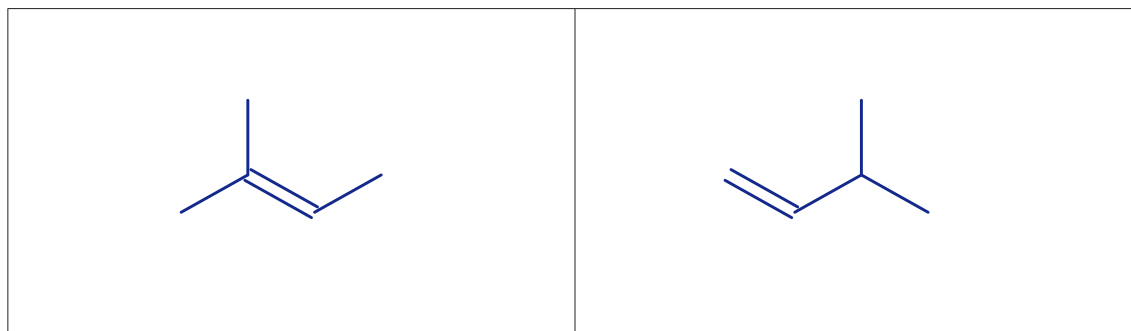
3-methylbutan-2-ol..... [1]

(ii) What is the structural formula of alcohol **A**?

(CH₃)₂CHCH(OH)CH₃..... [1]

(iii) The chemist heats alcohol **A** with an acid catalyst to form a mixture containing **two** alkenes.

Draw the structures of the **two** alkenes formed in this reaction.

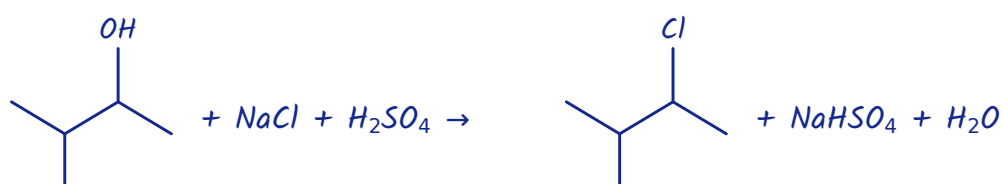


[2]

(iv) The chemist heats alcohol **A** with sodium chloride and sulfuric acid.

Construct a balanced equation for this reaction.

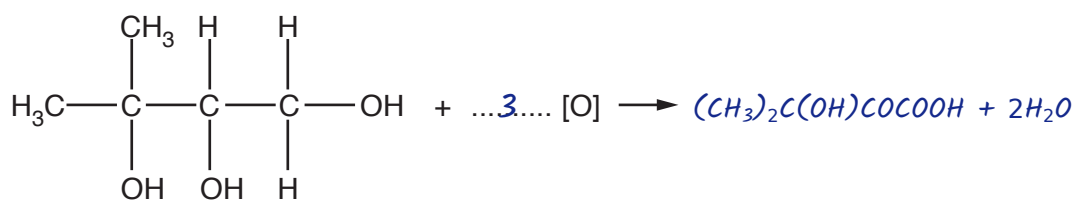
Show structures for the organic compounds in your equation.



[2]

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

Complete the equation for this reaction.

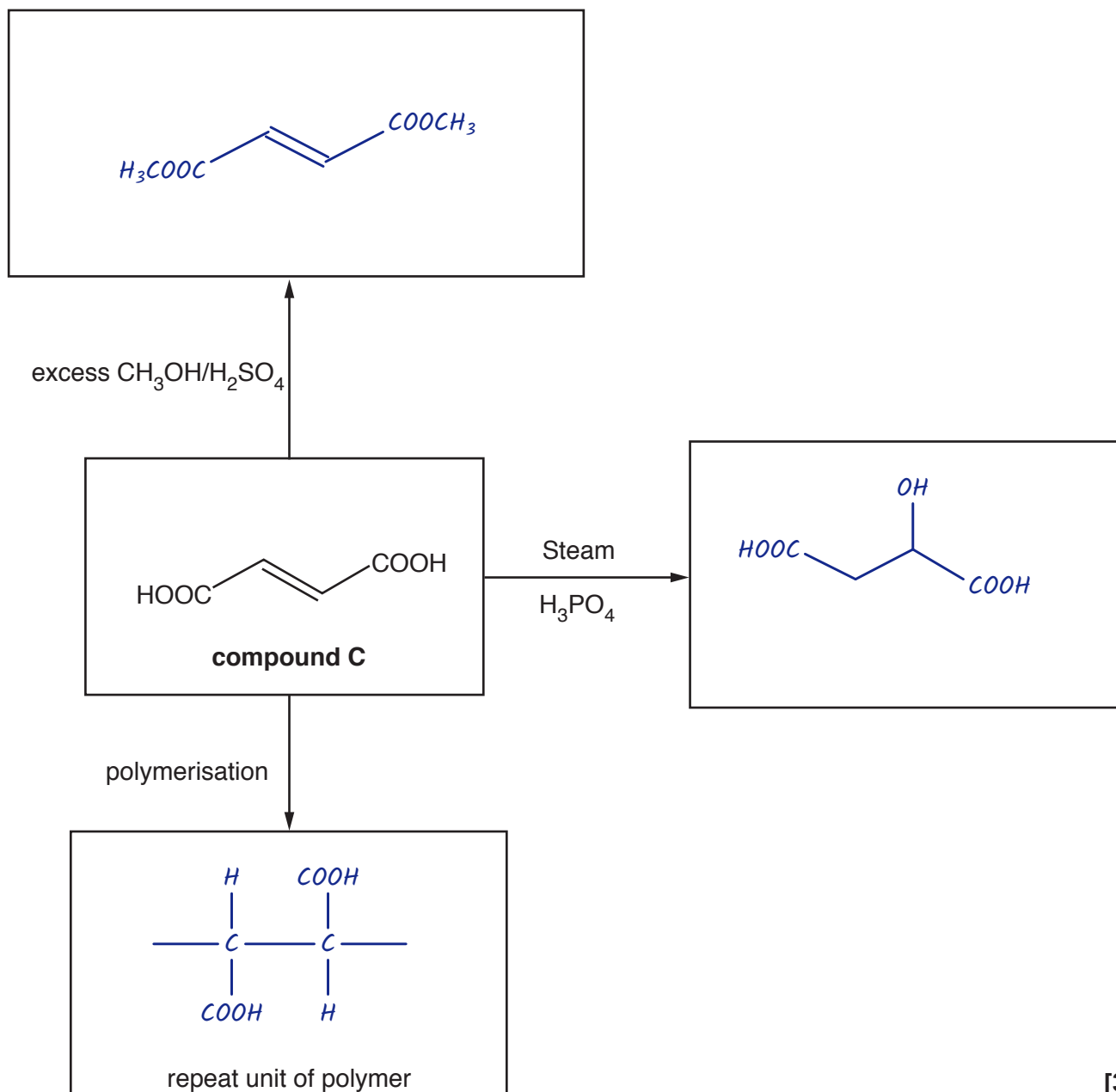


compound B

[2]

- (c) The flowchart below shows some reactions of compound **C**.

In the boxes, draw the organic products of these reactions.

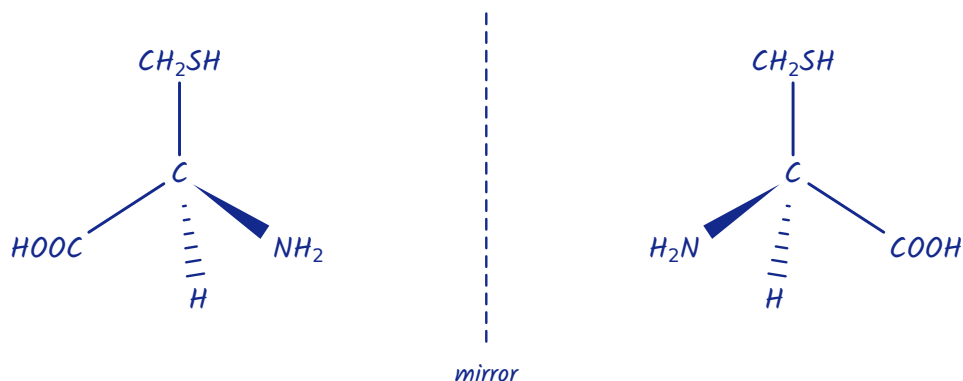


[3]

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

(a) The α -amino acid cysteine ($\text{R} = \text{CH}_2\text{SH}$) shows optical isomerism.

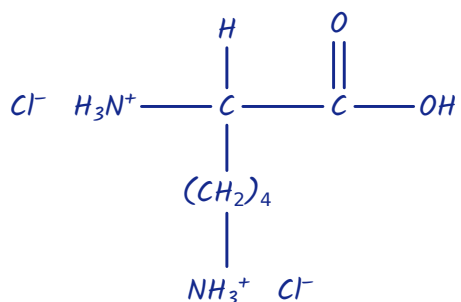
Draw 3-D diagrams to show the optical isomers of cysteine.



[2]

(b) The α -amino acid lysine ($\text{R} = (\text{CH}_2)_4\text{NH}_2$) reacts with an excess of dilute hydrochloric acid to form a salt.

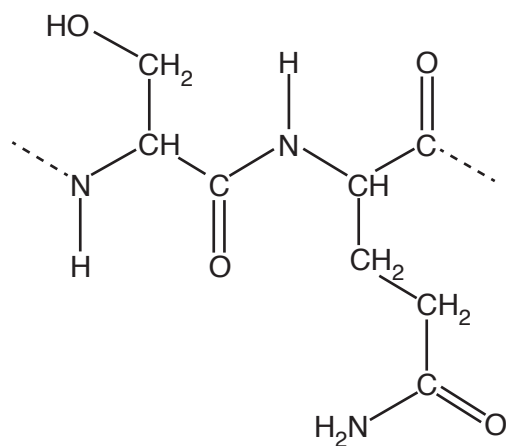
Draw the structure of the salt formed in this reaction.



[2]

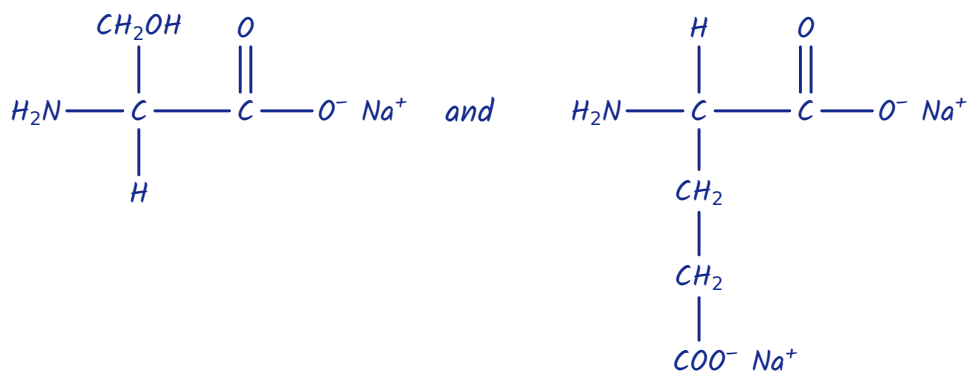
(c) α -Amino acids can react to form proteins.

A short section of a protein chain is shown below.



A student hydrolyses the protein with hot NaOH(aq) .

Draw the structures of the organic products formed from this section of the protein.



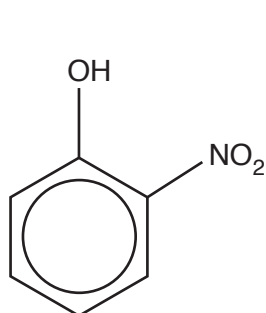
[3]

18 This question is about aromatic compounds.

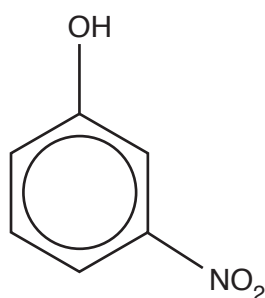
(a) Phenol undergoes nitration more readily than benzene.

- (i) A student carries out the nitration of phenol with dilute nitric acid to produce 2-nitrophenol and 4-nitrophenol.

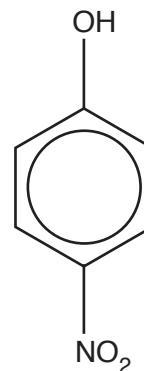
A small amount of 3-nitrophenol is also produced.



2-nitrophenol



3-nitrophenol



4-nitrophenol

The student thought that ^{13}C NMR spectroscopy could be used to distinguish between these three nitrophenols.

Explain whether the student is correct.

The student is only partly correct.

2-nitrophenol has six different carbon environments, so it gives six peaks in its ^{13}C NMR spectrum.

3-nitrophenol also has six carbon environments, so it also gives six peaks.

4-nitrophenol is symmetrical, so it has only four carbon environments and gives four peaks.

So 4-nitrophenol can be distinguished, but 2-nitrophenol and 3-nitrophenol cannot be distinguished from each other.

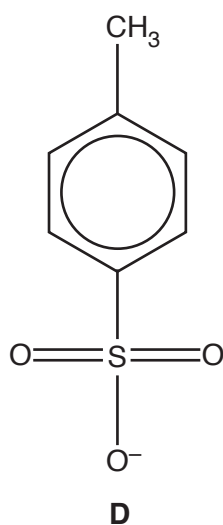
[3]

- (ii) Explain why phenol is nitrated more readily than benzene.

In phenol, a lone pair of electrons in a p-orbital on the oxygen atom is partially delocalised (donated) into the π -system of the ring. This increases the electron density of the ring compared with benzene. So phenol is more susceptible to electrophilic attack: the ring attracts and polarises the electrophile (NO_2^+ / HNO_3) more, so even dilute nitric acid nitrates phenol.

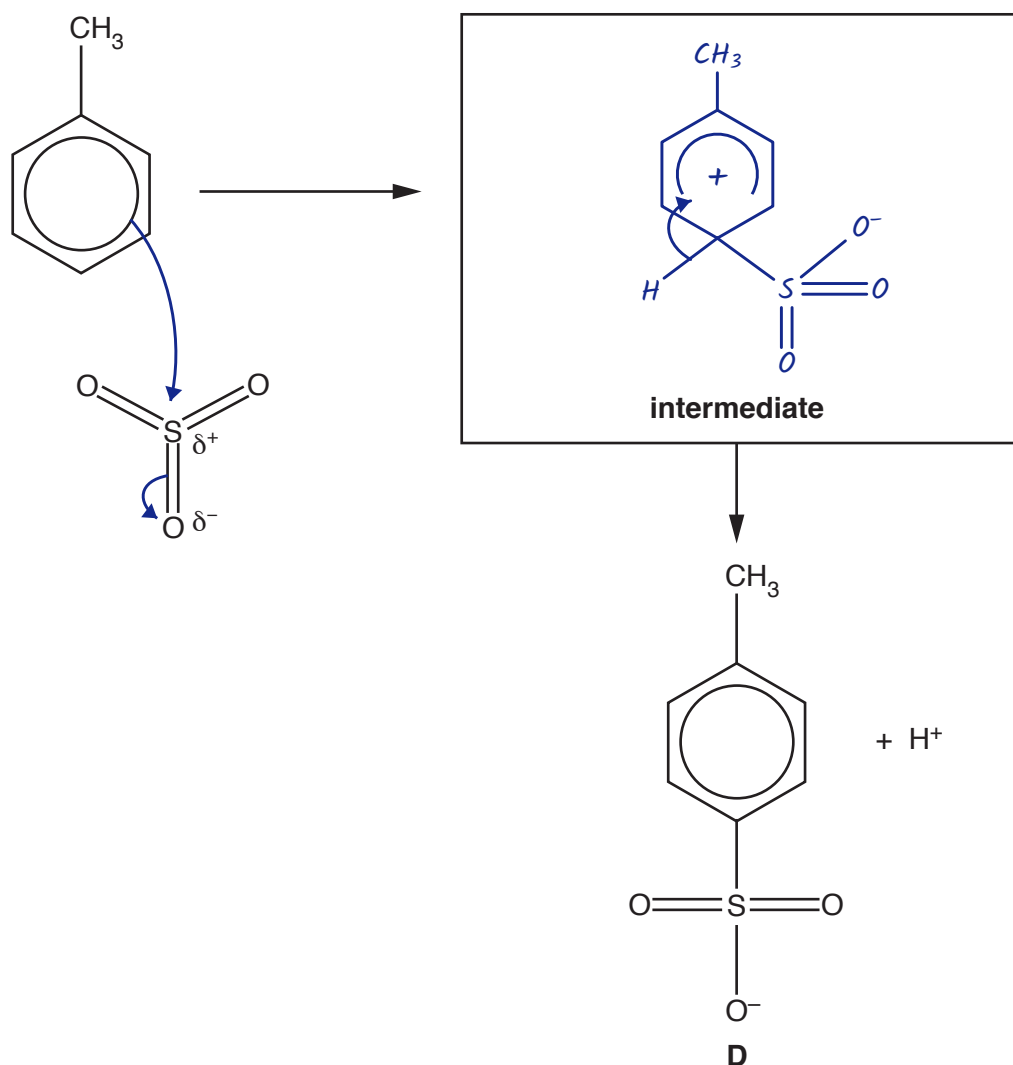
[3]

(b) Methylbenzene reacts with sulfur trioxide, SO_3 , to form **D**, shown below.



The electrophile in this reaction is SO_3 .

Complete the mechanism for the formation of **D**.
Show curly arrows and the structure of the intermediate.



19 This question is about the hydrolysis of haloalkanes.

(a) The rate of hydrolysis of a haloalkane depends on the halogen present.

State and explain how the halogen in the haloalkane affects the rate of hydrolysis.

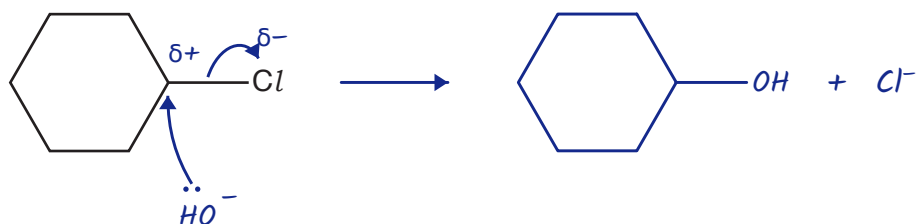
The weaker the carbon-halogen bond (lower bond enthalpy), the faster the rate of hydrolysis.

C-Hal bond enthalpy decreases down group 7: C-I is the weakest so it is hydrolysed fastest, then C-Br, then C-Cl; C-F is the strongest and is hydrolysed slowest. [2]

(b) Chlorocyclohexane is hydrolysed with aqueous sodium hydroxide.

Outline the mechanism for this reaction.

Show curly arrows, relevant dipoles and the products.



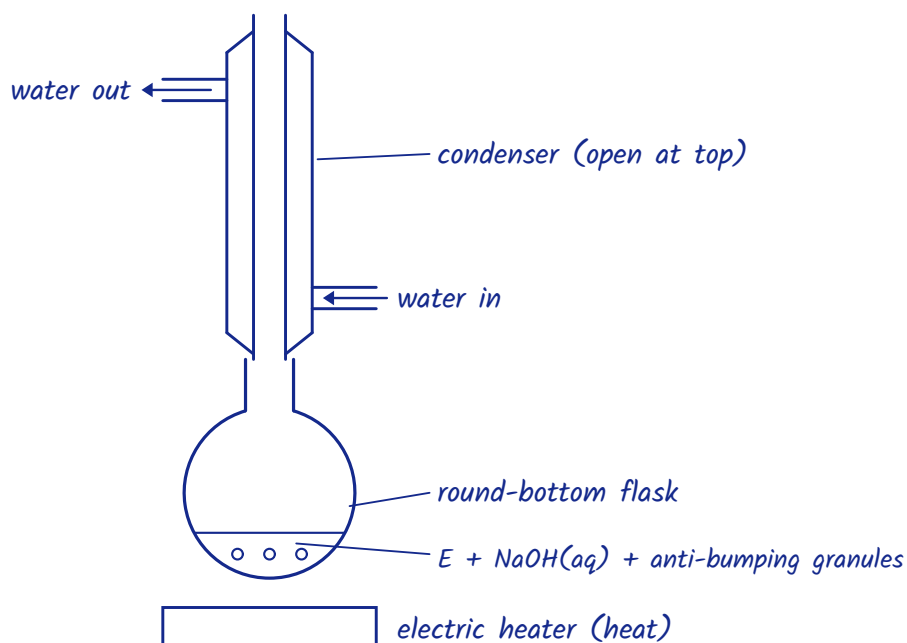
[3]

(c) A student hydrolyses a haloalkane, **E**, using the following method.

- 0.0100 mol of haloalkane **E** is refluxed with excess NaOH(aq) to form a reaction mixture containing an organic product **F**.
- The reaction mixture is neutralised with dilute nitric acid.
- Excess AgNO₃(aq) is added to the reaction mixture. 1.88 g of a precipitate **G** forms.

Organic product, **F**, has a molar mass of 74.0 g mol⁻¹ and has a chiral carbon atom.

(i) Draw a **labelled** diagram to show how the student would carry out the hydrolysis of haloalkane **E**.



[2]

(ii) Analyse the information to identify **E**, **F** and **G**.

Show your working.

$$G: n(\text{Ag}^+ \text{ halide}) = n(E) = 0.0100 \text{ mol}$$

$$M(G) = 1.88 \div 0.0100 = 188 \text{ g mol}^{-1}$$

$188 - 107.9 = 80.1$, so the halide is bromide: **G** is silver bromide, AgBr

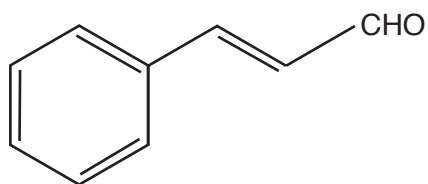
F: $M = 74.0$ is C₄H₉OH and it has a chiral carbon, so **F** is butan-2-ol,



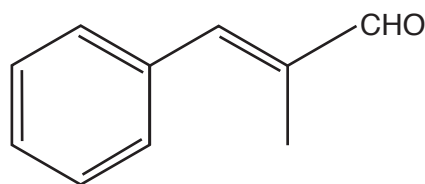
E is 2-bromobutane, CH₃CHBrCH₂CH₃

[3]

20 Cinnamaldehyde and methylcinnamaldehyde are naturally occurring organic compounds.



cinnamaldehyde



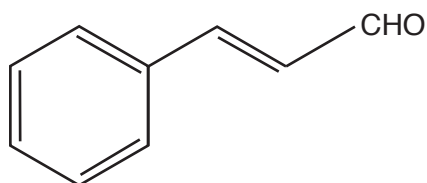
methylcinnamaldehyde

(a) Methylcinnamaldehyde is an *E* stereoisomer.

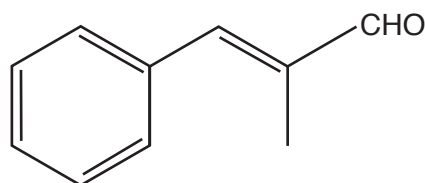
Explain this statement in terms of the Cahn-Ingold-Prelog (CIP) rules.

Using CIP rules (higher atomic number = higher priority): on one C, C_6H_5
 has priority over H; on the other C, CHO has priority over CH_3 (O has a
 higher atomic number than H).
 The two highest priority groups, C_6H_5 and CHO, are on opposite sides of the
 $C=C$, so it is the *E* isomer. [2]

- (b) A student plans to carry out some chemical tests on both cinnamaldehyde and methylcinnamaldehyde.



cinnamaldehyde



methylcinnamaldehyde

- (i) Suggest a suitable chemical test to confirm that both compounds contain an unsaturated carbon chain.

Your answer should include the reagent and observations.

Add bromine water, Br₂(aq): it is decolourised (orange to colourless).

[1]

- (ii) Describe a chemical test to confirm that both compounds contain an aldehyde functional group.

Your answer should include the reagent and observations.

Warm with Tollens' reagent (ammoniacal silver nitrate): a silver mirror forms.

[1]

- (iii) Describe a chemical test to confirm that cinnamaldehyde and methylcinnamaldehyde contain a carbonyl group.

How could the products of this test be used to distinguish between the two compounds?

Your answer should **not** include spectroscopy.

Add 2,4-dinitrophenylhydrazine (2,4-DNP, Brady's reagent): an orange/yellow precipitate forms, so both contain a carbonyl group.

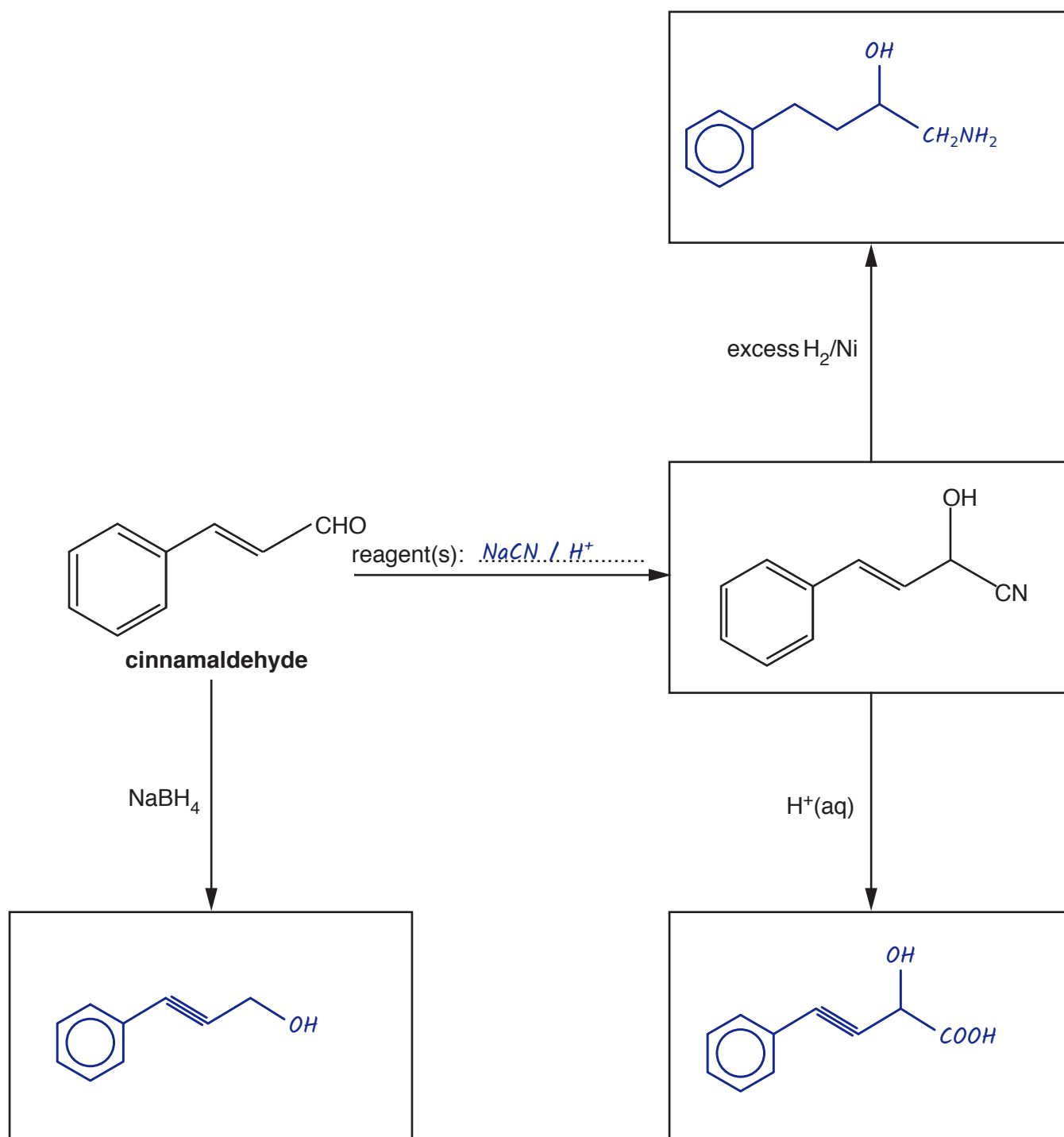
Filter off the precipitate and recrystallise it, then take the melting point of the purified crystals.

Compare the melting points with known values in a database: the two derivatives have different melting points, so they can be told apart.

[3]

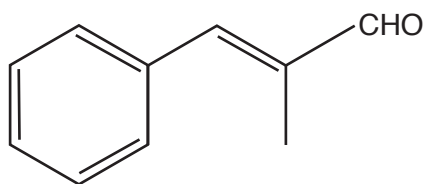
(c) The flowchart below shows some reactions starting with cinnamaldehyde.

Draw the structures of the missing organic compounds in the boxes and add the missing reagent(s) on the dotted line.



[5]

- (d)* Methylcinnamaldehyde reacts with iodine monochloride, ICl , by electrophilic addition. The reaction produces a mixture containing two different organic products.



methylcinnamaldehyde

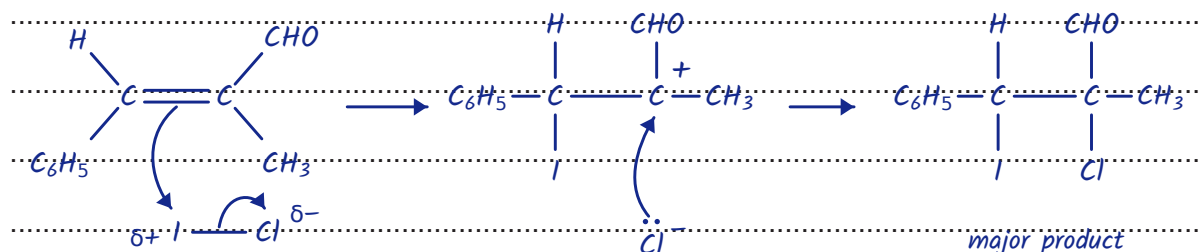
The electronegativity values of chlorine and iodine are given in the table below.

	Pauling electronegativity value
Cl	3.0
I	2.5

Outline the mechanism, using the 'curly arrow' model, for the formation of **one** of the organic products and explain which of the two possible organic products is more likely to be formed.

In your mechanism, you can show the phenyl group as C_6H_5 .

[6]



Cl is more electronegative than I, so ICl is polarised $\text{I}^{\delta+}-\text{Cl}^{\delta-}$. The

π -electrons of the $\text{C}=\text{C}$ attack the $\text{I}^{\delta+}$ atom (the electrophile) and the $\text{I}-\text{Cl}$ bond breaks heterolytically to give Cl^- .

This forms a carbocation, and a lone pair on Cl^- then attacks the positively charged carbon to give the addition product.

Two products are possible: $\text{C}_6\text{H}_5\text{CHI}-\text{CCl}(\text{CH}_3)\text{CHO}$ and

$\text{C}_6\text{H}_5\text{CHCl}-\text{Cl}(\text{CH}_3)\text{CHO}$.

The major (most likely) product is $\text{C}_6\text{H}_5\text{CHI}-\text{CCl}(\text{CH}_3)\text{CHO}$ because it forms from the more stable carbocation: the + charge is on the carbon attached

Additional answer space if required.

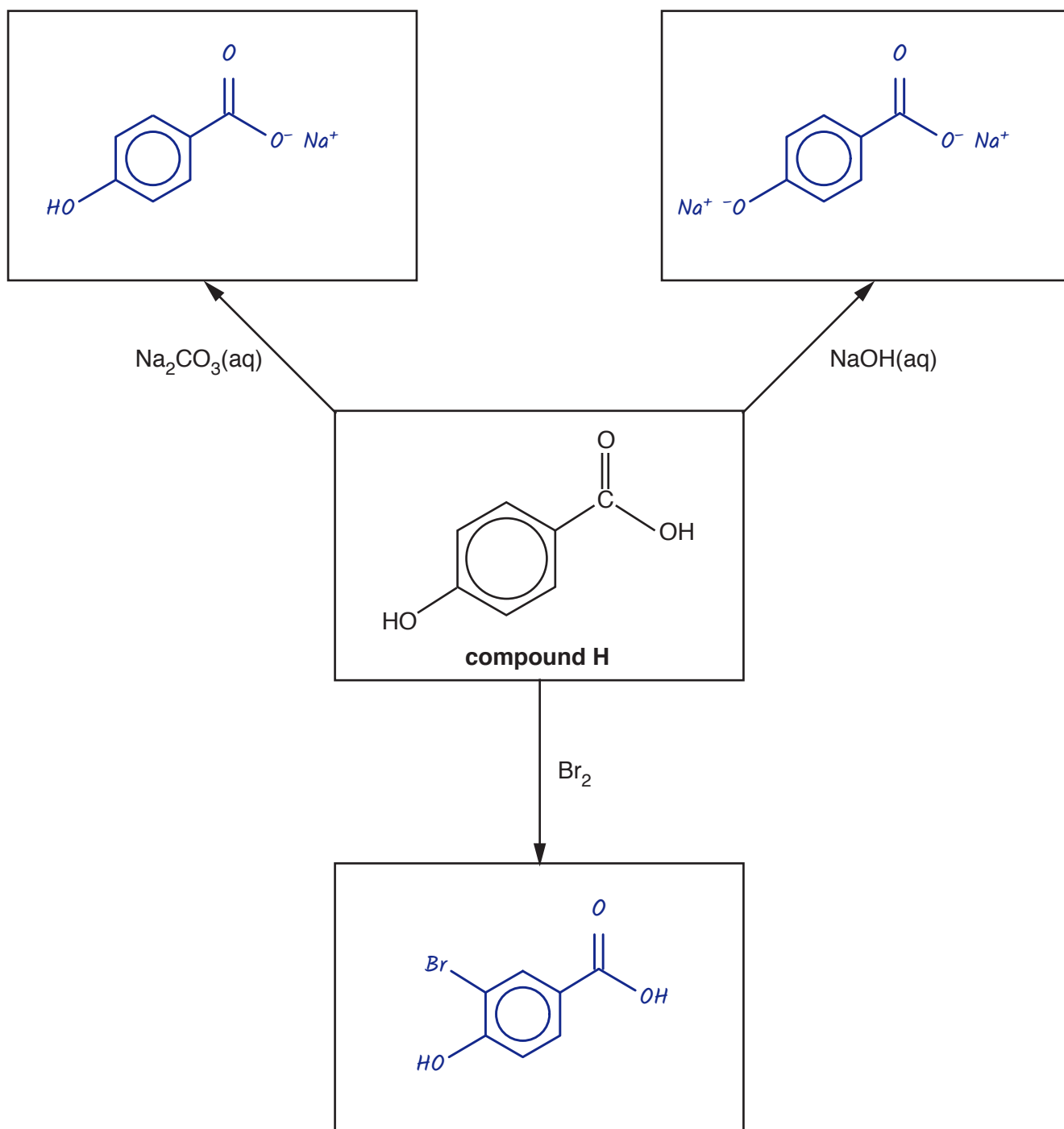
to the most carbon atoms (tertiary carbocation), and these groups donate electron density and stabilise the charge.

So in the major product Cl is attached to the carbon with the fewest hydrogen atoms and I to the carbon with the H atom. The minor product, $C_6H_5CHCl-Cl(CH_3)CHO$, forms from the less stable secondary carbocation.

21 This question is about aromatic carboxylic acids and their derivatives.

(a) The flowchart below shows some reactions of compound **H**.

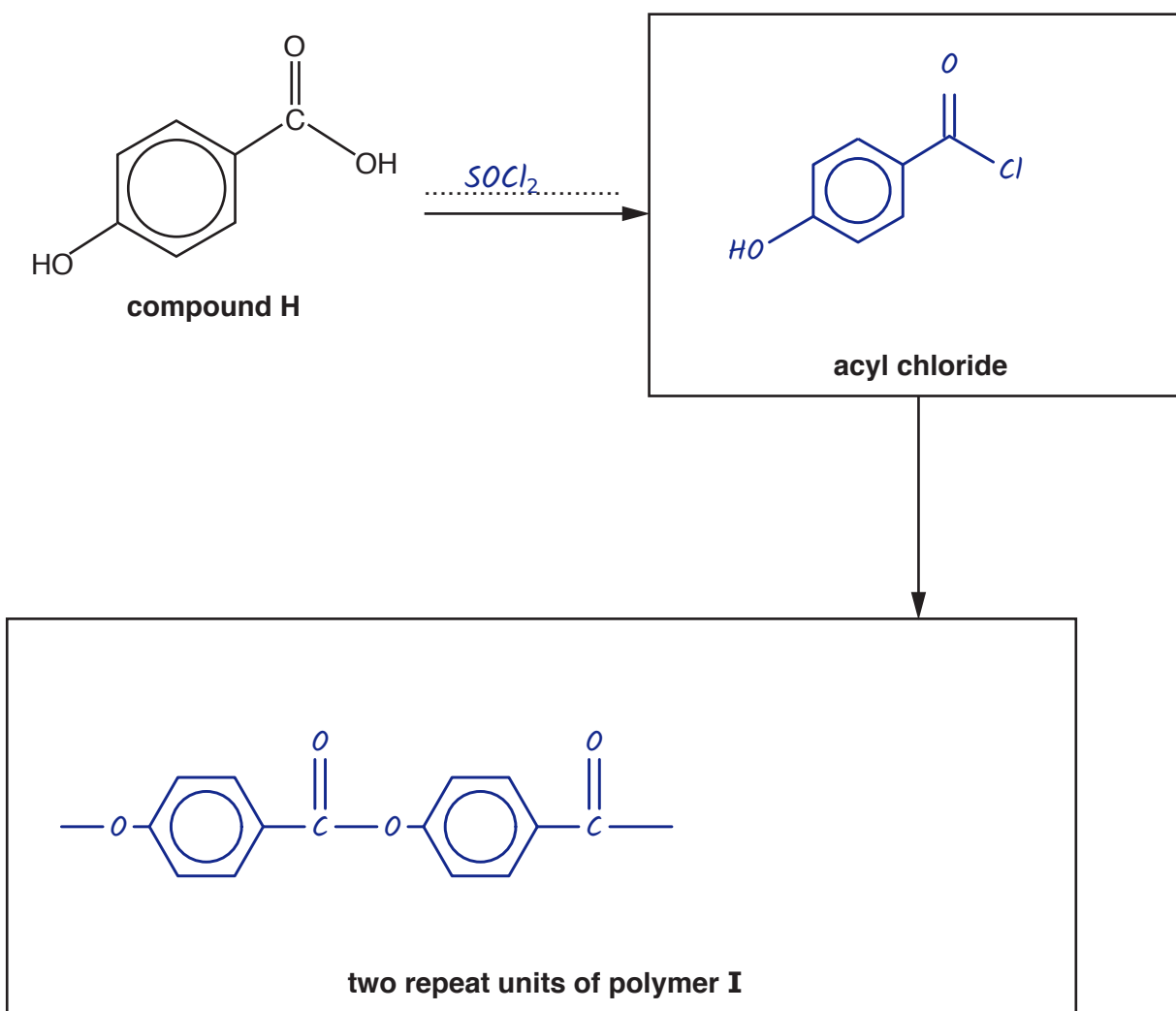
In the boxes, draw the organic products of these reactions.



[3]

(b) Compound **H** is used in the synthesis of polymer **I**, as shown in the flowchart below.

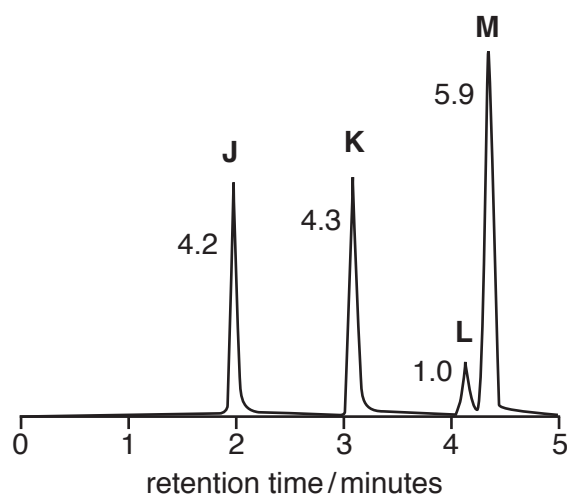
Complete the flowchart by drawing the structure of the acyl chloride and **two** repeat units of polymer **I**, and stating the **formula** of the reagent(s) required for the first stage on the dotted line.



[4]

- (c) A cosmetic product containing four esters, **J**, **K**, **L** and **M**, is analysed by gas chromatography and mass spectrometry. The results are shown below.

Gas chromatogram



The numbers by the peaks are the relative molar proportions of the compounds in the mixture.

Mass spectrometry

ester	<i>m/z</i> of molecular ion peak
J	152
K	166
L	180
M	180

- (i) The concentration of ester **K** in the cosmetic product is $9.13 \times 10^{-2} \text{ g dm}^{-3}$.

Using the results, calculate the concentration, in mol dm^{-3} , of ester **M** in the cosmetic product.

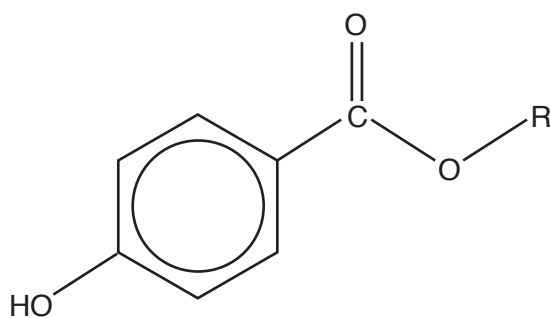
Give your answer to **two** significant figures.

$$[K] = 9.13 \times 10^{-2} \div 166 = 5.50 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[M] = 5.50 \times 10^{-4} \times 5.9 \div 4.3 = 7.546 \times 10^{-4} \text{ mol dm}^{-3}$$

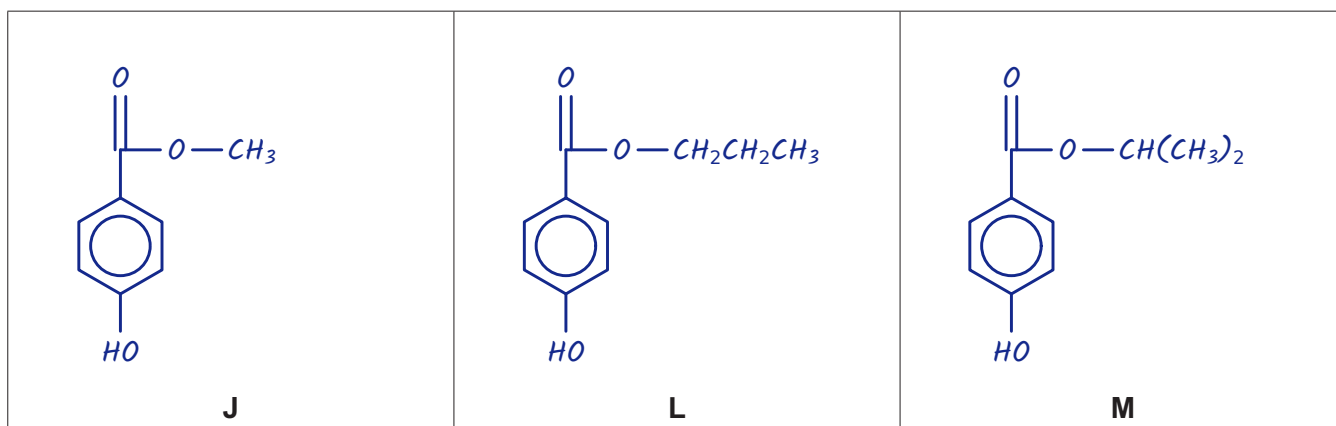
concentration of ester **M** = 7.5×10^{-4} mol dm⁻³ [2]

(ii) A general structure for esters **J**, **L** and **M** is shown below.



Where 'R' is an alkyl group.

Use the mass spectrometry results to deduce possible structures for esters **J**, **L** and **M**.



[3]

22 The relative molecular masses and boiling points of some fuels are shown in **Table 22.1**.

Fuel	Relative molecular mass	Boiling point/°C
hexane	86	69
pentan-1-ol	88	138
heptane	100	98

Table 22.1

(a) Write an equation for the incomplete combustion of heptane.



(b) Explain the difference in the boiling points of the fuels in **Table 22.1**.

Heptane has a longer chain than hexane (more electrons), so there are more points of contact (more surface interaction) between its molecules. So heptane has stronger induced dipole-dipole interactions (London forces), and more energy is required to break them, so heptane boils higher than hexane.

Pentan-1-ol has an O-H group, so it forms hydrogen bonds between molecules as well as London forces.

Hydrogen bonds are stronger than induced dipole-dipole interactions, so more energy is required to break them and pentan-1-ol has the highest boiling point despite its lower M_r . [4]

(c) Fuel additives are often used to improve the combustion of a fuel.

(i) Compound **N** is a fuel additive containing carbon, hydrogen and oxygen only.

Complete combustion of 1.71 g of compound **N** produces 2.97 g of CO_2 and 1.62 g of H_2O . The relative molecular mass of compound **N** is 76.0.

Calculate the molecular formula of **N** and suggest a possible structure for the compound.

$$n(\text{CO}_2) = 2.97 \div 44.0 = 0.0675 \text{ mol, so } n(\text{C}) = 0.0675 \text{ mol}$$

$$n(\text{H}_2\text{O}) = 1.62 \div 18.0 = 0.0900 \text{ mol, so } n(\text{H}) = 0.180 \text{ mol}$$

$$\text{mass of C} = 0.0675 \times 12.0 = 0.810 \text{ g}$$

$$\text{mass of H} = 0.180 \times 1.0 = 0.180 \text{ g}$$

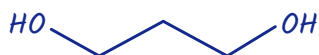
$$\text{mass of O} = 1.71 - 0.810 - 0.180 = 0.720 \text{ g}$$

$$n(\text{O}) = 0.720 \div 16.0 = 0.0450 \text{ mol}$$

$$\text{C} : \text{H} : \text{O} = 0.0675 : 0.180 : 0.0450 = 3 : 8 : 2$$

$$\text{empirical formula } \text{C}_3\text{H}_8\text{O}_2, M = 76.0 = M_r$$

$$\text{so molecular formula of N} = \text{C}_3\text{H}_8\text{O}_2$$

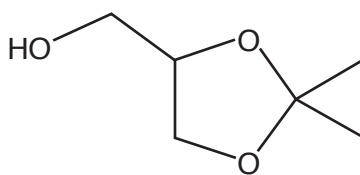


propane-1,3-diol

compound N

[5]

- (ii) Solketal has been investigated as a potential fuel additive.

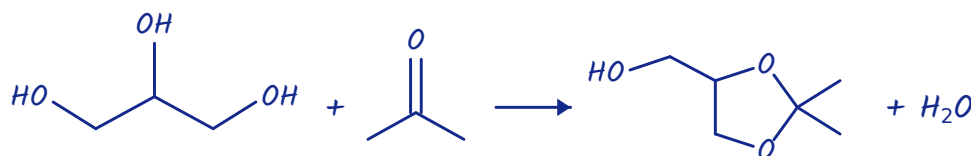


solketal

Solketal is synthesised from propane-1,2,3-triol and a carbonyl compound.

Construct a balanced equation for this synthesis.

Show structures for the organic compounds in your equation.



[2]

- (d)* A scientist is researching compounds that might be suitable as fuel additives. One of the compounds gives the analytical results below.

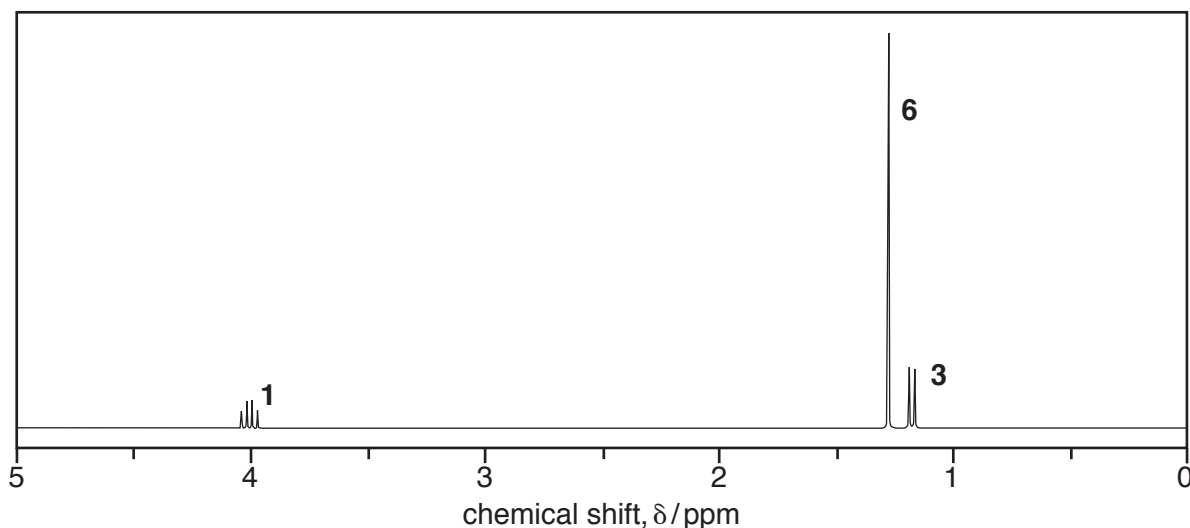
Elemental analysis by mass:

C: 54.54%; H: 9.10%; O: 36.36%

Mass spectrum:

Molecular ion peak at $m/z = 132.0$

^1H NMR spectrum in D_2O



The numbers by the peaks are the relative peak areas.

When the spectrum is run without D_2O , there are **two** additional peaks with the same relative peak areas at 11.0 ppm and 3.6 ppm.

Use the information provided to suggest a structure for the compound.

Show **all** your reasoning.

[6]

$$C : H : O = 54.54/12.0 : 9.10/1.0 : 36.36/16.0 = 2 : 4 : 1$$

Empirical formula C_2H_4O (44.0); $132.0 \div 44.0 = 3$, so $C_6H_{12}O_3$.

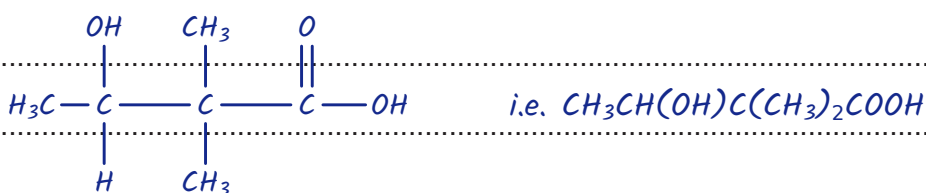
δ 4.0 ppm, area 1, quartet: one H on a C bonded to O (H-C-O), next to a CH_3 (3 adjacent H, $n+1 = 4$).

δ 1.2 ppm, area 3, doublet: CH_3 next to a C with one H, so CH_3-CH .

δ 1.3 ppm, area 6, singlet: two equivalent CH_3 groups on a C with no H, so $(CH_3)_2C$.

Without D_2O the two extra peaks (area 1) are O-H protons that exchange with D_2O : 11.0 ppm is COOH and 3.6 ppm is an alcohol OH.

6 C, 12 H and 3 O fits $C_6H_{12}O_3$, so the compound is:



Additional answer space if required.

END OF QUESTION PAPER

[illegible]

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