OCR
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

7011394988

You must have:
- the Data Sheet for Chemistry A (sent with general stationery)

You may use:
- a scientific or graphical calculator

H432/02

First name									
Last name									
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?

A $Si(CH_3)_4$

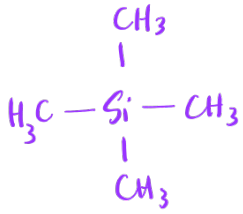
B $CDCl_3$ – no peak in ^1H NMR

C D_2O – no peak in ^{13}C NMR, no peak in ^1H NMR

D CCl_4 – no peak in ^1H NMR

D = ^2H

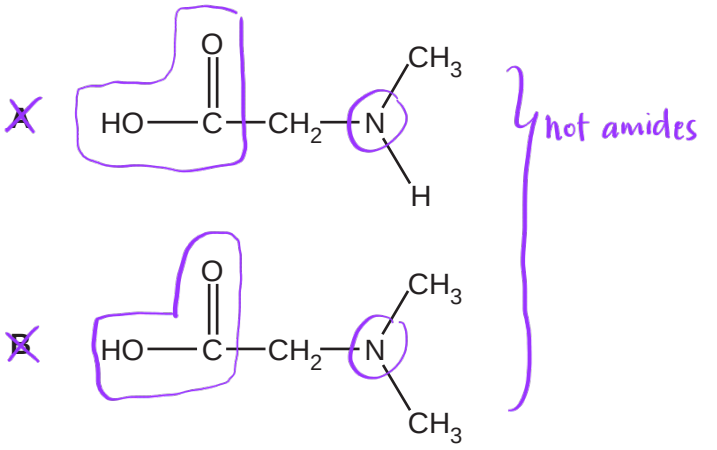
solvents



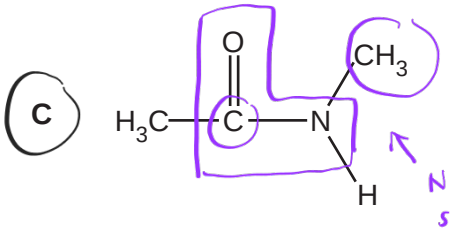
Your answer A

[1]

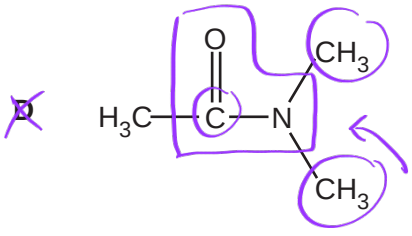
2 Which compound is a secondary amide?



not amides



N bonded to 2 carbons, so this is 2° amide

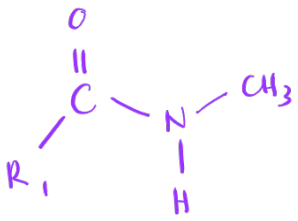


N bonded to 3 carbons, so this is 3° amide

2 carbons bonded to N

1° 2° 3°

Amide classification based on number of C bonded to amide N.



Your answer C

[1]

3

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

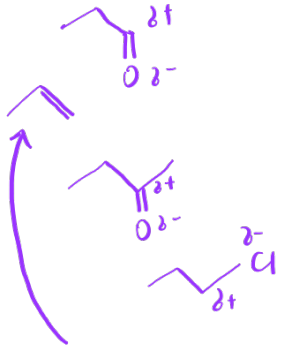
ē pair donor (eg. $:OH^-$, $\ddot{N}H_3$)

A CH_3CH_2CHO

B CH_3CHCH_2

C $CH_3CH_2COCH_3$

D $CH_3CH_2CH_2Cl$



All compounds in A, C and D have δ+ C which is a common site of attack for nucleophiles.

Your answer B

C=C in propene (B) is highly ē dense and will not elicit attack of ē dense nucleophile

[1]

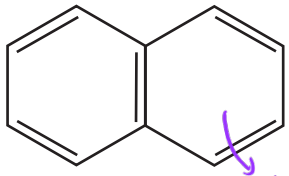
4 Which structure represents an alicyclic compound?

ali cyclic

↓ aliphatic (non-aromatic)

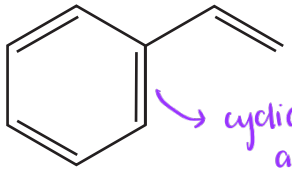
↳ ring structure

A



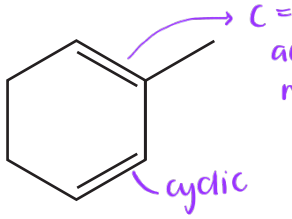
cyclic but aromatic

B



cyclic but aromatic

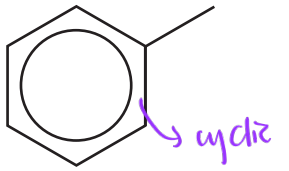
C



C=C not delocalised across whole ring so not aromatic

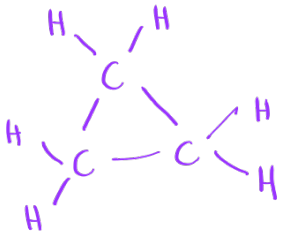
cyclic

D



cyclic but aromatic

Cyclopropane is the simplest alicyclic compound



Your answer C

[1]

planar = flat

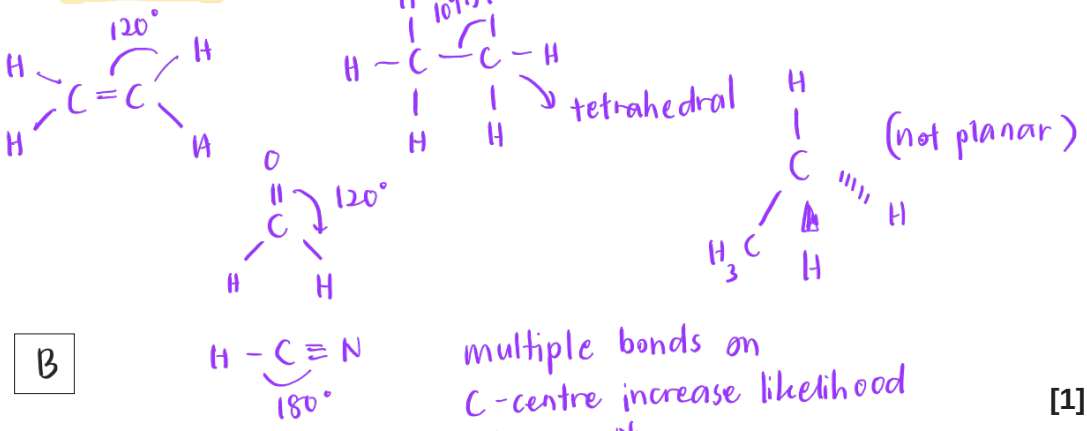
5 Which molecule is **not** planar?

A C_2H_4

B C_2H_6

C H_2CO

D HCN



Your answer B

[1]

6 What is the number of peaks in the ^{1}H NMR spectrum of $HOOCCH_2CHOHCH_2COOH$?

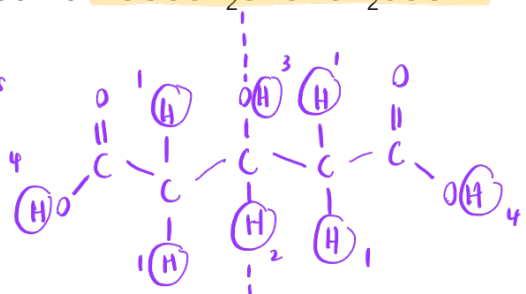
n° of peaks > n° of environments

A 3

B 4

C 5

D 6



∴ 4 environments
∴ 4 peaks

Your answer B

[1]

7 Ethanol can be prepared by different reactions.

atom economy = $\frac{\text{Mr (desired product)}}{\text{sum of Mr for all reactants}} \times 100$

Which reaction has the lowest atom economy?

~~**A**~~ $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$

~~**B**~~ $C_2H_4 + H_2O \rightarrow C_2H_5OH$ — 1 product ∴ 100% atom economy

C $C_2H_5Br + H_2O \rightarrow C_2H_5OH + HBr$ — Br is a very high Ar atom ∴ lowering atom economy

~~**D**~~ $CH_3COOC_2H_5 + H_2O \rightarrow C_2H_5OH + CH_3COOH$

CO_2 and CH_3COOH are lower Mr side products than HBr
(good approximation without using equation!)

Your answer C

[1]

NO• must be leftover / reformed in propagation step

8 The breakdown of ozone is catalysed by NO radicals.

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

A $NO + O_2 \rightarrow N + O_3$

B $NO + O_2 \rightarrow NO_2 + O$

C $N + O_3 \rightarrow NO + O_2$

D $NO_2 + O \rightarrow NO + O_2$

overall equation : $2O_3 \rightleftharpoons 3O_2$

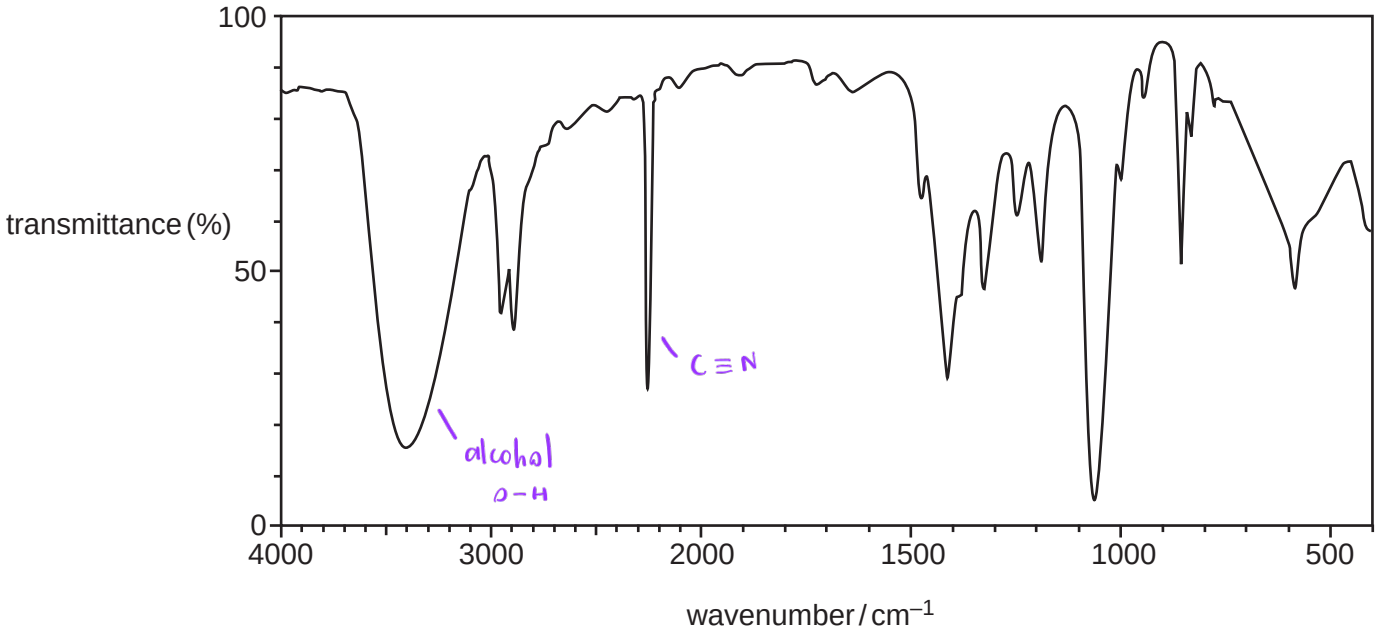
Propagation
$NO + O_3 \rightarrow NO_2 + O_2$
$NO_2 + O \rightarrow NO + O_2$

NO reformed
∴ acting as catalyst

Your answer D

[1]

9 Which compound could have produced the IR spectrum below?



A CH_3CH_2OH

B $CH_3CHOHCN$

C CH_3COOH

D CH_3CONH_2

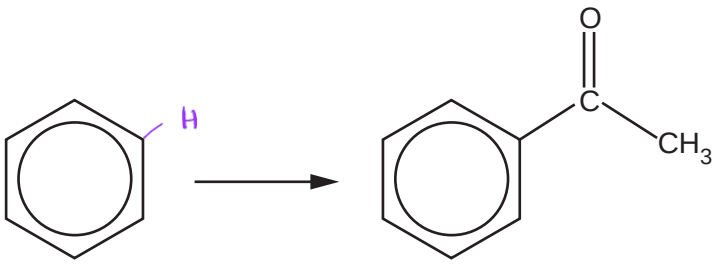
Your answer B

[1]

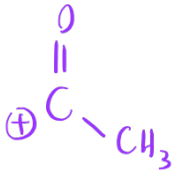
10 Benzene reacts with an organic reagent in the presence of a halogen carrier to form phenylethanone.

↳ $AlCl_3$

Electrophilic substitution



phenylethanone



Which organic reagent is required?

A CH_3CH_2OH — ⇒ H^- — too unstable

B CH_3CHO

C CH_3COCl ⇒ Cl^-

D CH_3COOH ⇒ OH^-

$HCl \rightarrow H^+ + Cl^-$

$H_2O \rightarrow H^+ + OH^-$

Cl^- more stable than OH^- as HCl is a stronger acid than H_2O

∴ Cl^- is a better leaving group than OH^-

Your answer C

[1]

11 How many straight-chain structural isomers of $C_7H_{15}Cl$ contain a chiral carbon atom?

↳ same molecular formula, different structural formula

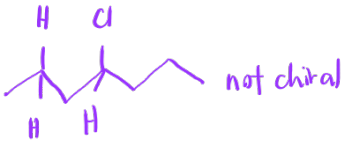
↳ carbon bonded to 4 different groups e.g.

A 1

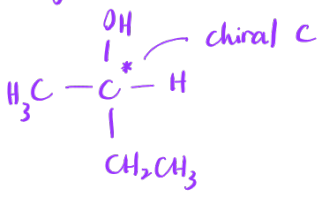
B 2

C 3

D 4



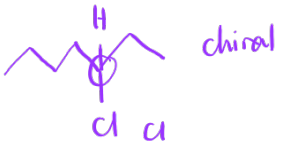
not chiral



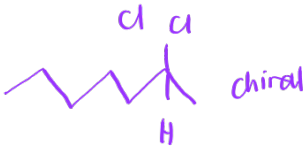
chiral C

Your answer B

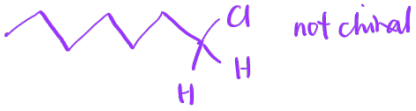
[1]



chiral

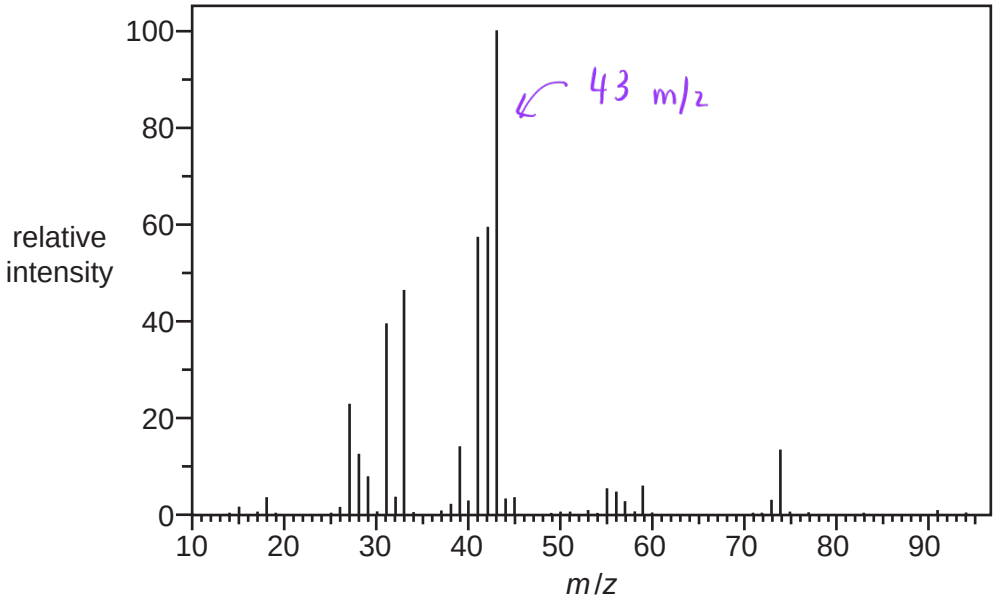


chiral



not chiral

12 The mass spectrum of $(CH_3)_2CHCH_2OH$ is shown below.



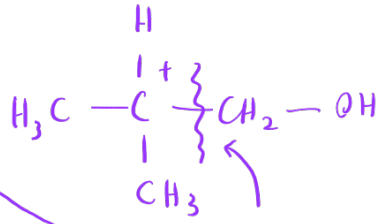
Which ion is responsible for the peak with the greatest relative intensity?

~~A~~ $CHCH_2OH^+$ 44

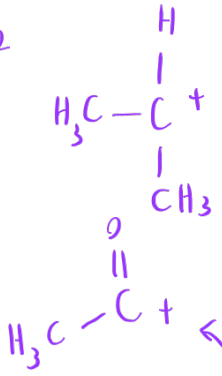
~~B~~ $CH_3CH_2CH^+$ 42

(C) $(CH_3)_2CH^+$ 43

~~D~~ CH_3CO^+ 43



Can be formed by breaking one bond



not in original molecule

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. ✓ delocalised system causes all C-C bonds to have same intermediate bond length

2 The enthalpy change of hydrogenation of benzene is less exothermic than expected. ✓ bond breaking requires more energy due to stability of delocalised ring

3 Bromine reacts with benzene less readily than with cyclohexene. ✓ delocalised ring stabilised benzene making it less likely to react with an electrophile than localised C=C

(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?

as T ↑ kinetic E of solvent ↑ ∴ easier dissolving solid ∴ solubility ↑ as temp ↑

1 ✓ The organic compound is more soluble in hot solvent.

2 ✓ The hot solution is cooled before the purified organic compound is collected.

↳ solution must be cooled to collect solid pure compound

3 ✗ The melting point of the purified organic compound is lower than the impure compound.

↳ mp of impure compound is lower than pure compound as impurities interrupt and weaken crystal lattice

A 1, 2 and 3

B Only 1 and 2

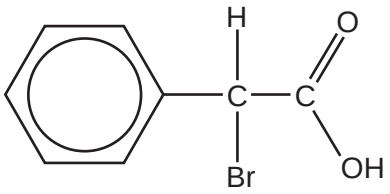
C Only 2 and 3

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 $AlCl_3$ → electrophilic sub → CH_3 substitutes H on phenyl

✓ 2 KCN in ethanol → nucleophilic sub → Br replaced by C≡N

✗ 3 CH_3OH and H_2SO_4 → esterification conditions – no C–C bond formed

A 1, 2 and 3

B Only 1 and 2

C Only 2 and 3

D Only 1

Your answer B

[1]

BLANK PAGE

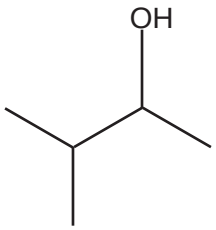
PLEASE DO NOT WRITE ON THIS PAGE

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.



alcohol A

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

3-methylbutan-2-ol

..... **[1]**

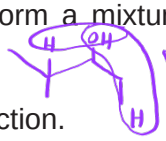
(ii) What is the structural formula of alcohol **A**?

$(CH_3)_2CHCHOHCH_3$

..... **[1]**

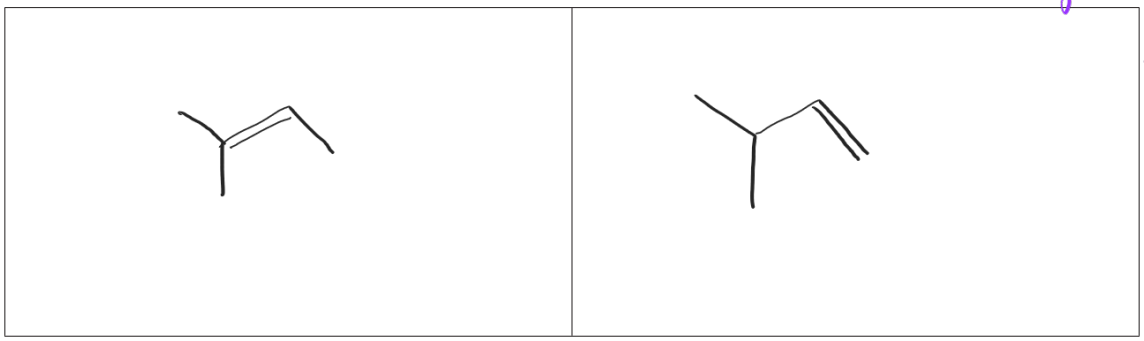
(iii) The chemist heats alcohol **A** with an acid catalyst to form a mixture containing **two** alkenes.

elimination reaction



OH is eliminated with either neighbouring H forming two structural isomers

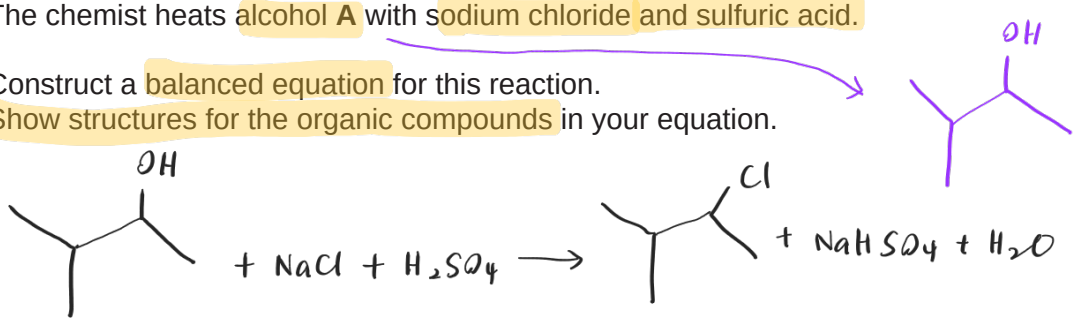
Draw the structures of the **two** alkenes formed in this reaction.



[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.

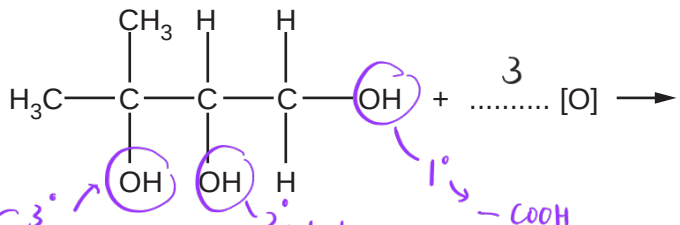


[2]

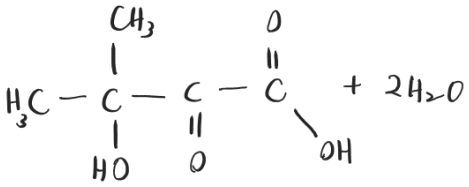
11

(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.



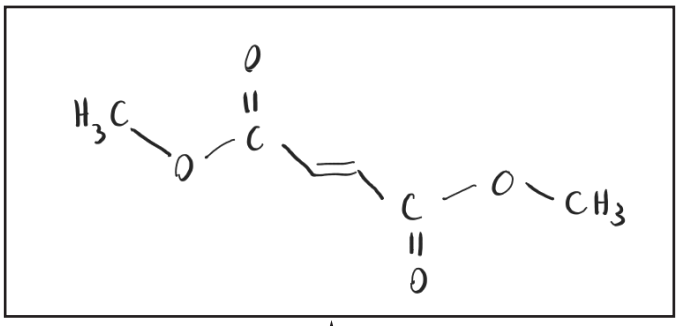
compound B



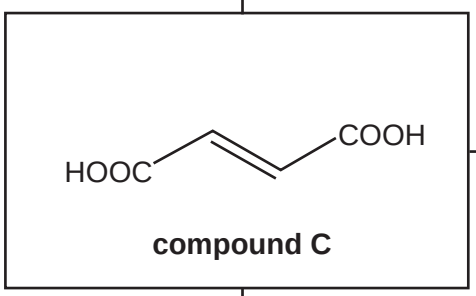
[2]

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

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



excess CH_3OH/H_2SO_4 — esterification

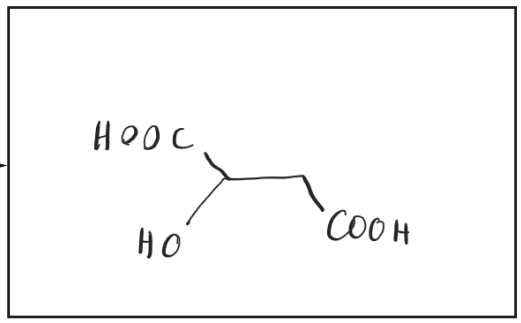


compound C

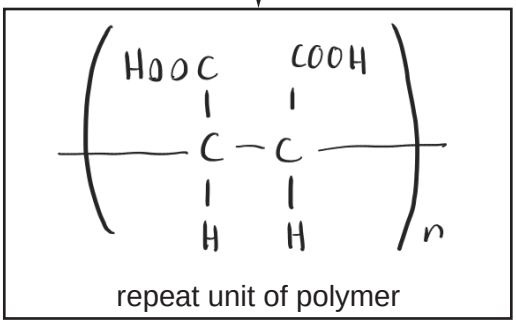
Steam

H_3PO_4

hydration



polymerisation — addition polymerisation



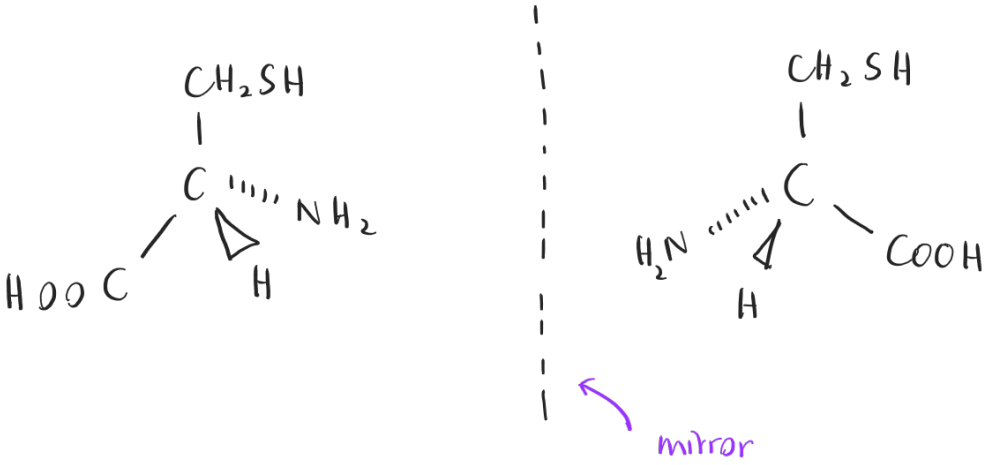
repeat unit of polymer

[3]

17 The general formula of an α-amino acid is $RCH(NH_2)COOH$.

(a) The α-amino acid cysteine ($R = CH_2SH$) shows optical isomerism.

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

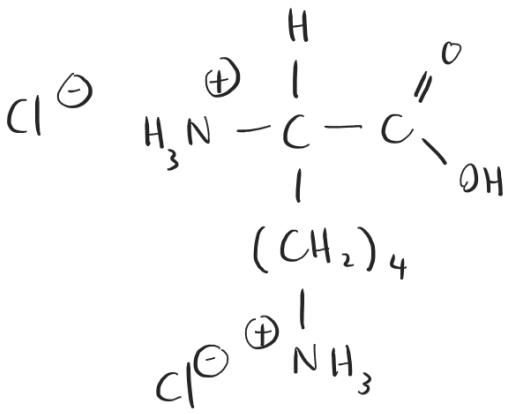


[2]

(b) The α-amino acid lysine ($R = (CH_2)_4NH_2$) reacts with an excess of dilute hydrochloric acid to form a salt.

Draw the structure of the salt formed in this reaction.

reacts with alkaline points : NH_2 groups

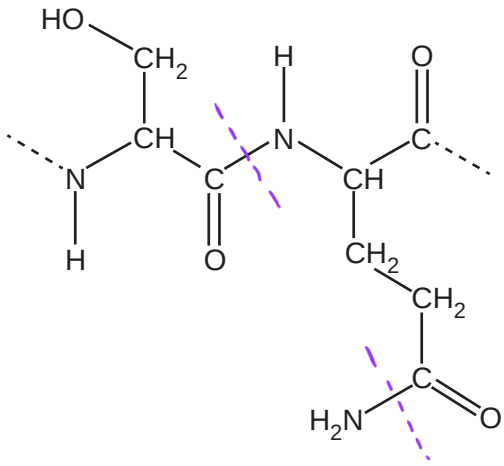


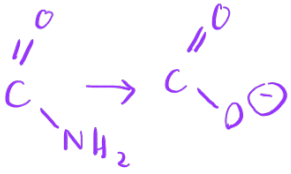
[2]

13

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

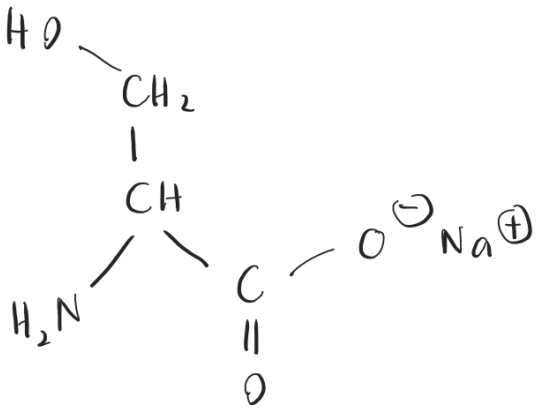
A short section of a protein chain is shown below.

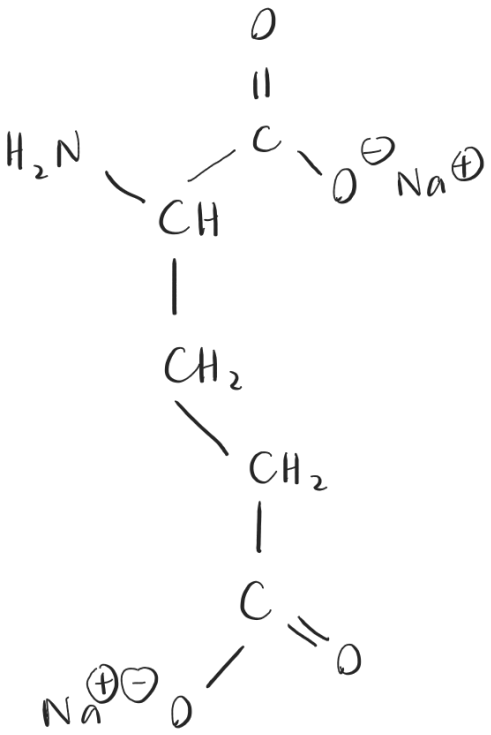




A student hydrolyses the protein with hot NaOH(aq). reacts with acidic points

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





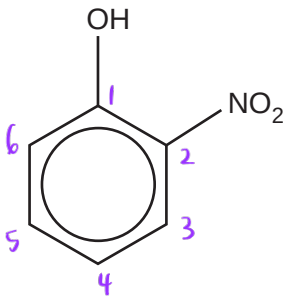
[3]

18 This question is about aromatic compounds.

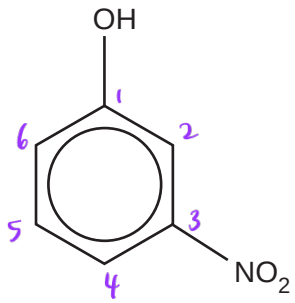
(a) Phenol undergoes nitration more readily than benzene.

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

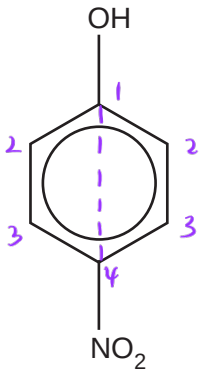
A small amount of 3-nitrophenol is also produced.



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.

2-nitrophenol and 3-nitrophenol has 6 ^{13}C NMR peaks so they aren't distinguishable.

4-nitrophenol only has 4 ^{13}C NMR peaks so it is distinguishable.

[3]

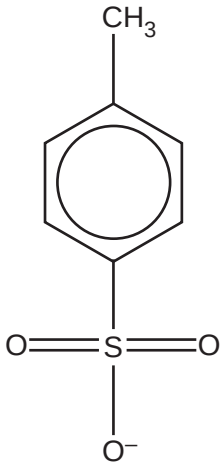
(ii) Explain why phenol is nitrated more readily than benzene.

In phenol, lone pair of electrons on O is partially delocalised into the π ring system so electron density is higher than benzene and phenol is more susceptible to electrophilic attack.

[3]

16

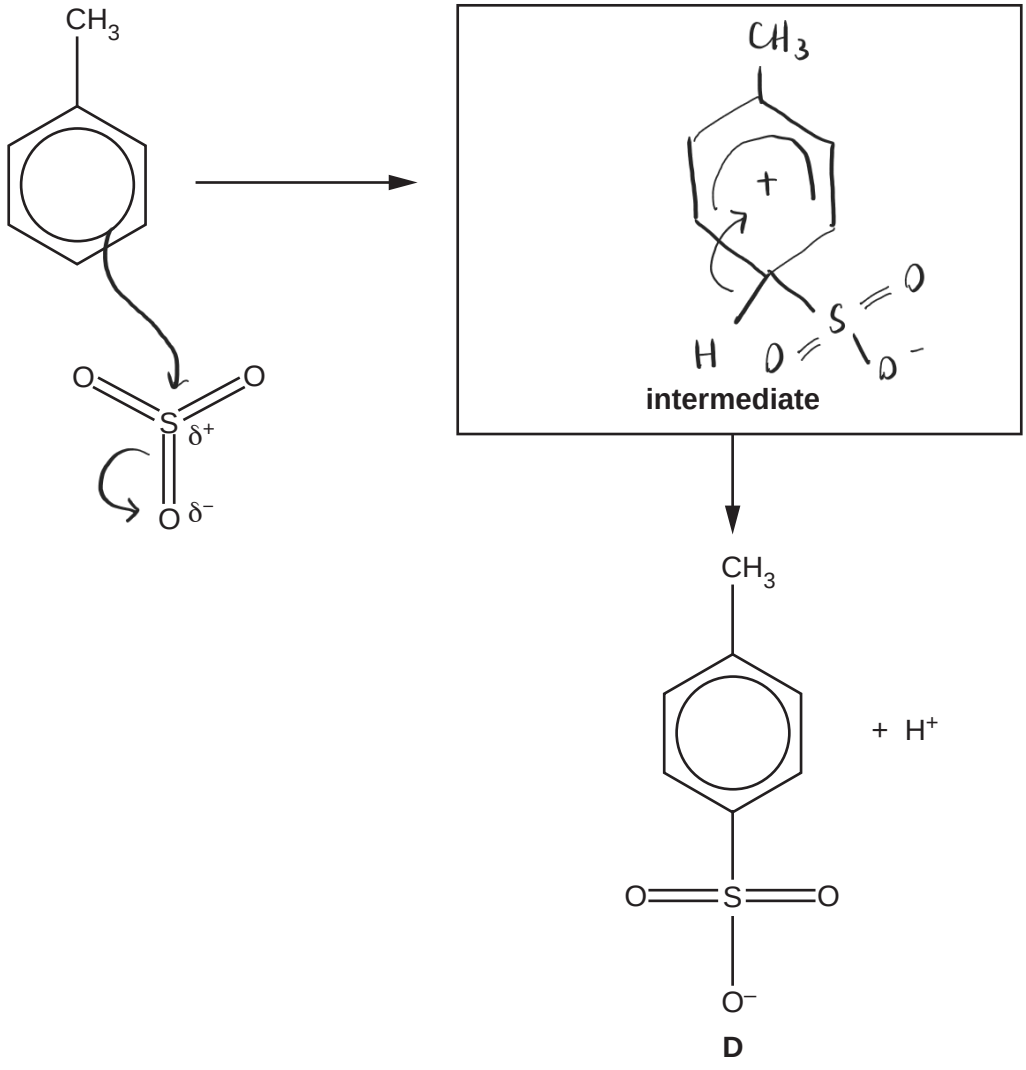
(b) Methylbenzene reacts with sulfur trioxide, SO_3, to form **D**, shown below.



D

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.



[3]

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 bond, the faster the rate of hydrolysis. For example, a C–F has the slowest rate of hydrolysis followed by C–Br and C–I has the fastest.

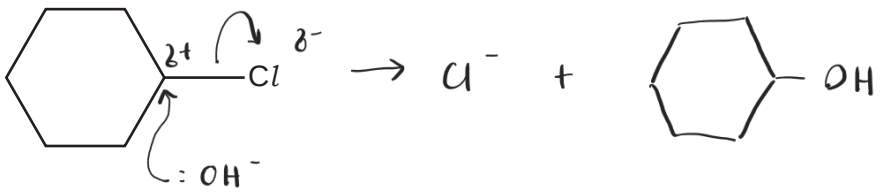
[2]

(b) Chlorocyclohexane is hydrolysed with aqueous sodium hydroxide.

haloalkane OH⁻ nucleophilic substitution

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.

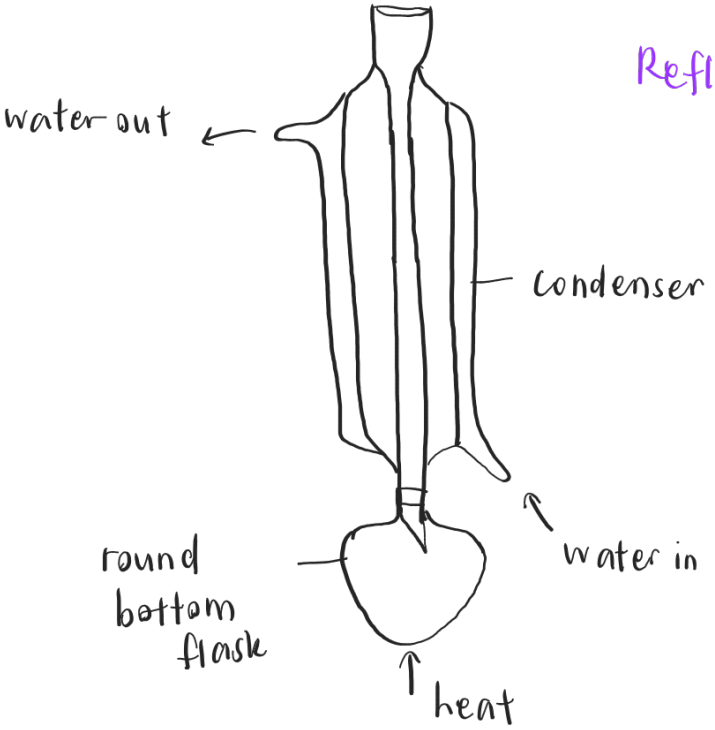
nucleophilic substitution

- 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 $AgNO_3(aq)$ 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**.

Reflux diagram



[2]

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

Show your working.

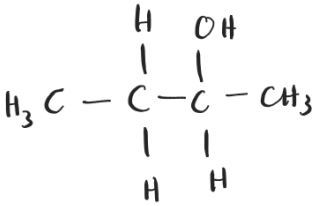
G : AgBr

$\frac{1.88}{0.01} = 188\,g\,mol^{-1}$ = RFM of G

188 − 107.9 = 80.1 = Br^-

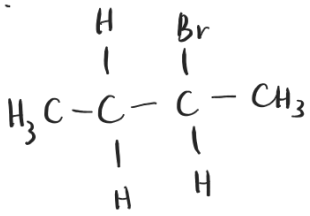
↑ RFM of Ag

F : butan-2-ol



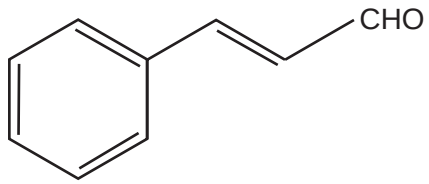
(12x4) + 9 + 16 + 1 = 74 $g\,mol^{-1}$

E :

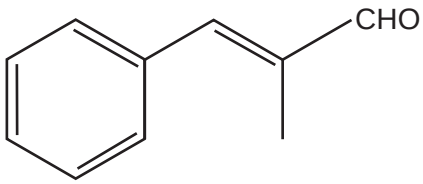


[3]

20 Cinnamaldehyde and methylcinnamaldehyde are naturally occurring organic compounds.



cinnamaldehyde



methylcinnamaldehyde

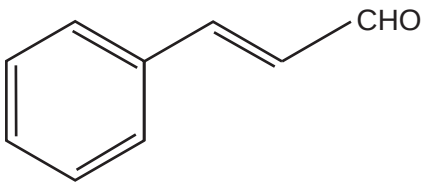
(a) Methylcinnamaldehyde is an *E* stereoisomer.

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

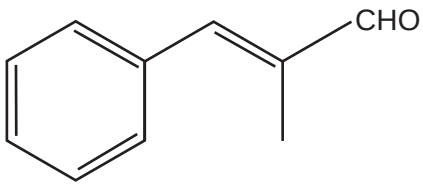
Highest priority groups : C_6H_5, CHO are on opposite sides at the C=C bond.

[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.

Br_2 goes 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.

Tollen's Reagent produces a silver mirror

..... **[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.

2,4-DNP produces an orange precipitate.

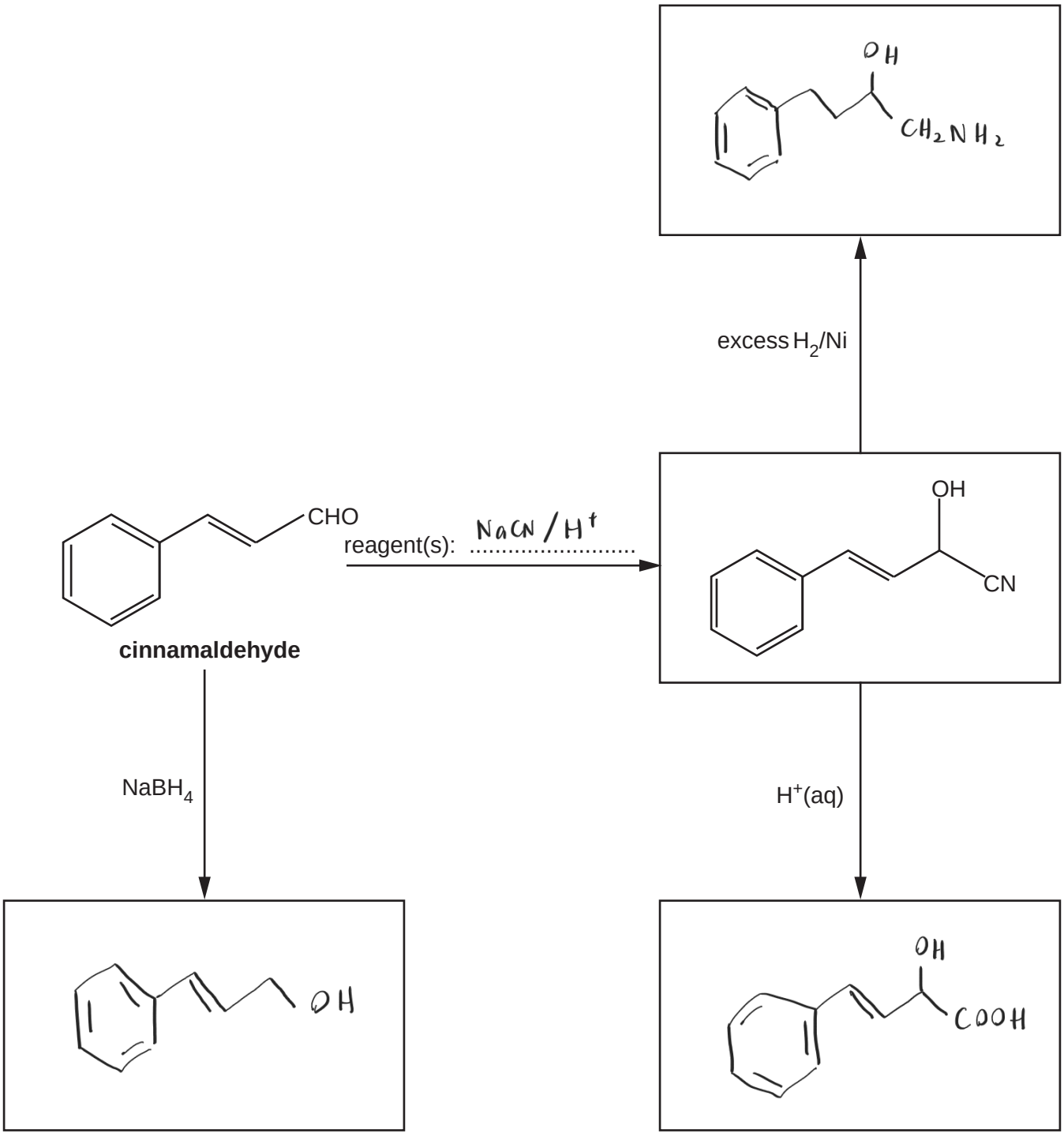
Take a melting point and compare to known values.

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

21

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

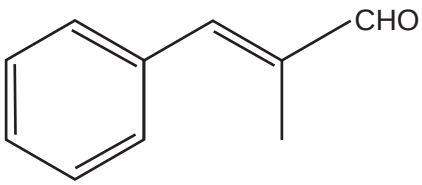
Draw the structures of the missing organic compounds in the boxes and add the missing reagent(s) on the dotted line.



[5]

22

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



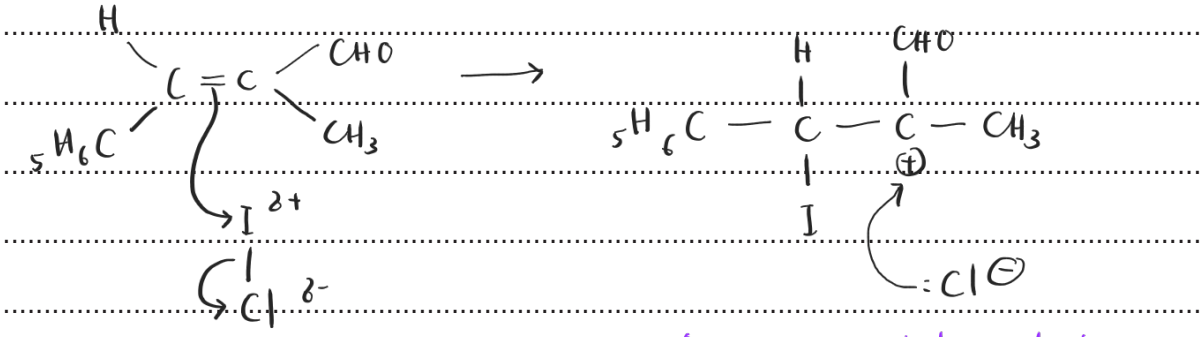
methylcinnamaldehyde

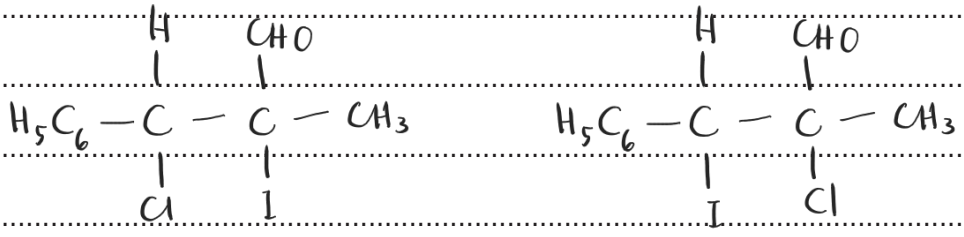
The electronegativity values of chlorine and iodine are given in the table below.

	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]**





Additional answer space if required.

.....

.....

.....

.....

.....

.....

.....

.....

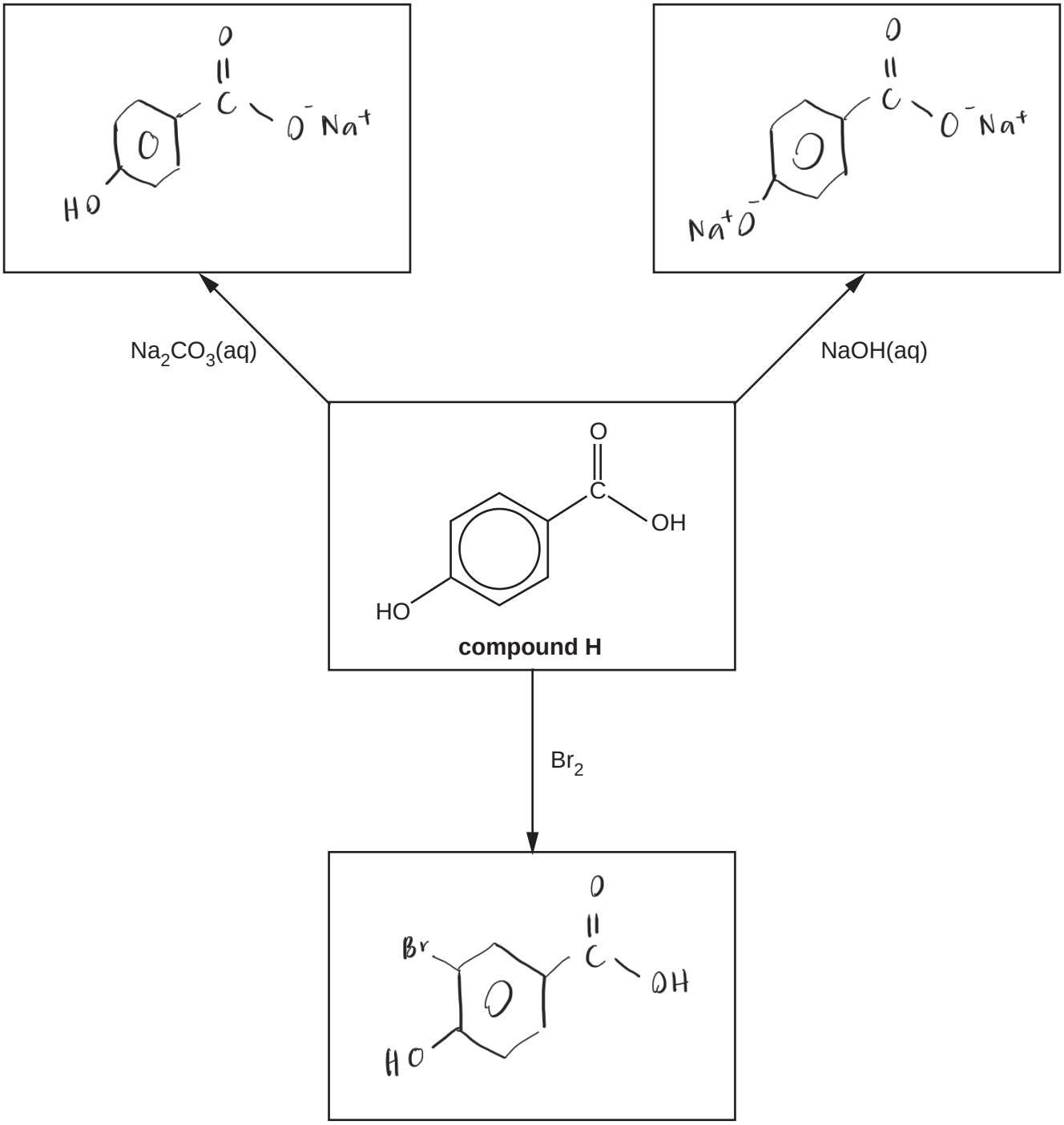
.....

.....

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

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

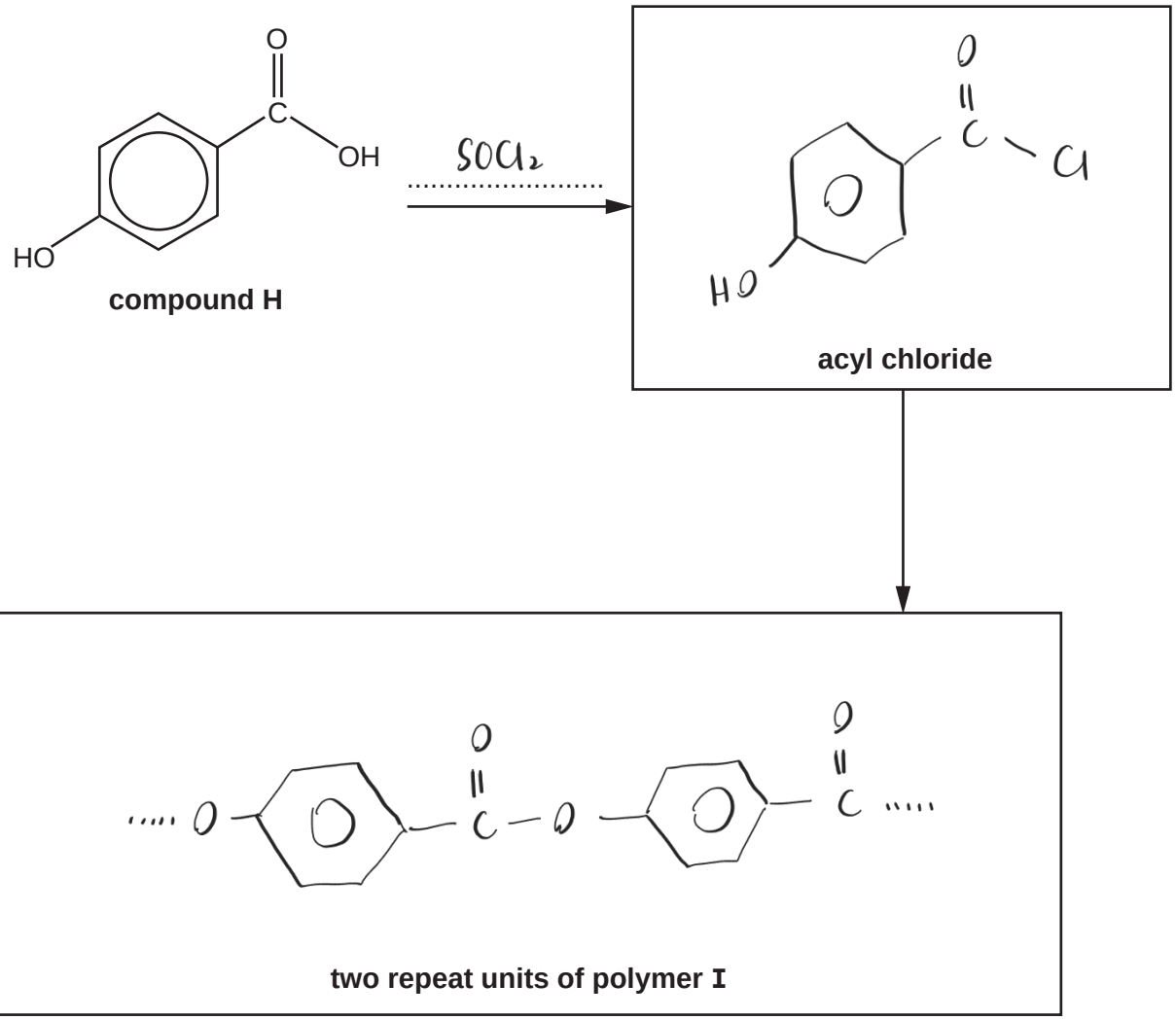
In the boxes, draw the organic products of these reactions.



[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.



compound H

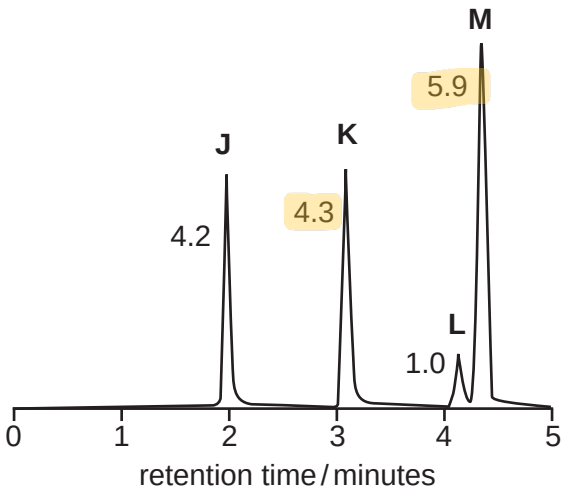
acyl chloride

two repeat units of polymer I

[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	*m/z* of molecular ion peak
J	152
K	166
L	180
M	180

$152 - 137 = 15$

166

$180 - 137 = 43$

$180 - 137 = 43$

$\frac{g\,dm^{-3}}{g\,mol^{-1}} = mol\,dm^{-3}$

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

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

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

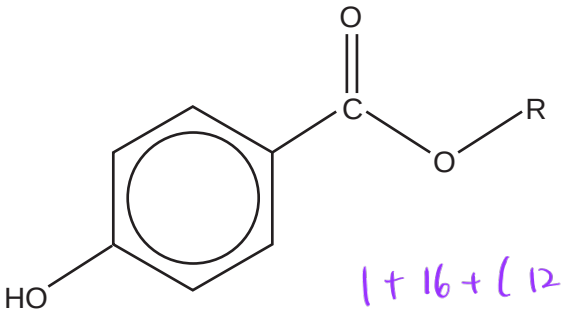
$$\frac{9.13 \times 10^{-2}}{166} = 5.50 \times 10^{-4}\,mol\,dm^{-3}$$

$$5.50 \times 10^{-4} \times \frac{5.9}{4.3} = 7.5 \times 10^{-4}\,mol\,dm^{-3}$$

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

27

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



$1 + 16 + (12 \times 6) + 4 + 12 + (16 \times 2) = 137$

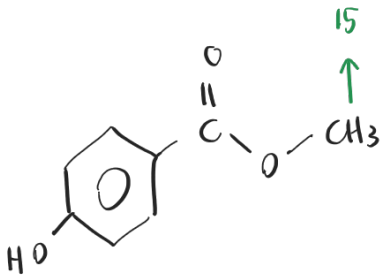
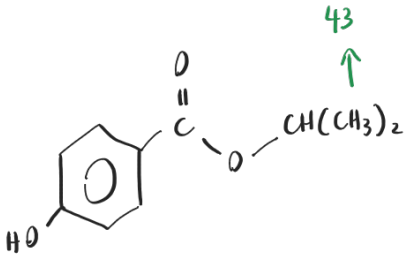
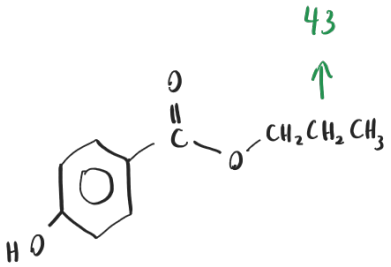
Where 'R' is an alkyl group.

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

$\frac{43}{12} = 3.6$

$12 \times 3 = 36$

$43 - 36 = 7$

 **J**	 **L**	 **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

C_nH_{2n+2} = general alkane

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

$C_7H_{16} + 7\frac{1}{2}O_2 \longrightarrow 7CO + 8H_2O$ **[1]**

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

- heptane is a longer carbon chain than hexane so has more points of contact
- heptane has stronger induced dipole - dipole interactions
- pentan-1-ol has hydrogen bonds which are stronger than induced dipole - dipole interactions
- more energy is required to break these hydrogen bonds

[4]

29

(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.

$CO_2 : \frac{2.97}{12 + (16 \times 2)} = 0.0675 \text{ mol}$

$H_2O : \frac{1.62}{1 + 1 + 16} = 0.0900 \text{ mol}$

$CO_2 : H_2O$

$3 : 4$

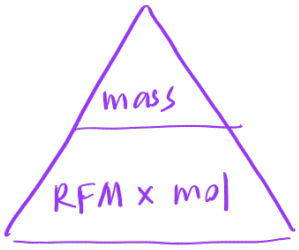
$C : H$

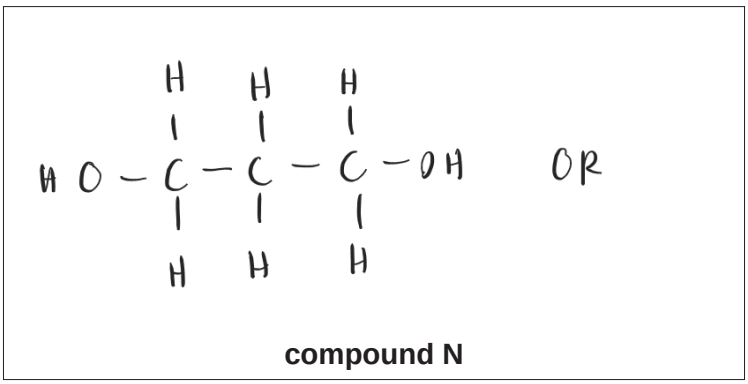
$3 : 8$

$C_3H_8O_2$

$76 - ((12 \times 3) + 8) = 32$

$\frac{32}{16} = 2 = 2O's$



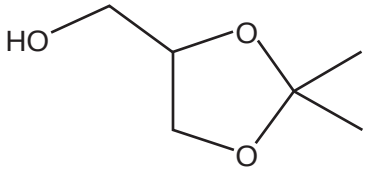


compound N

[5]

30

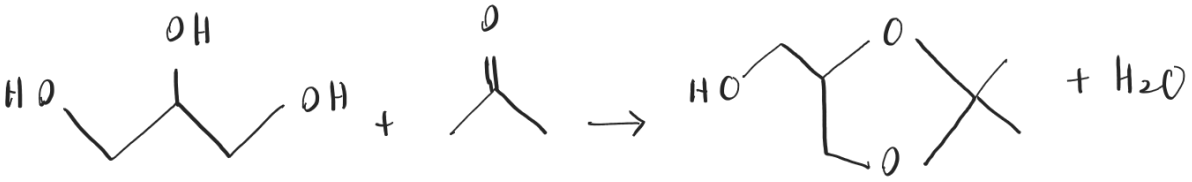
(ii) Solketal has been investigated as a potential fuel additive.



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.



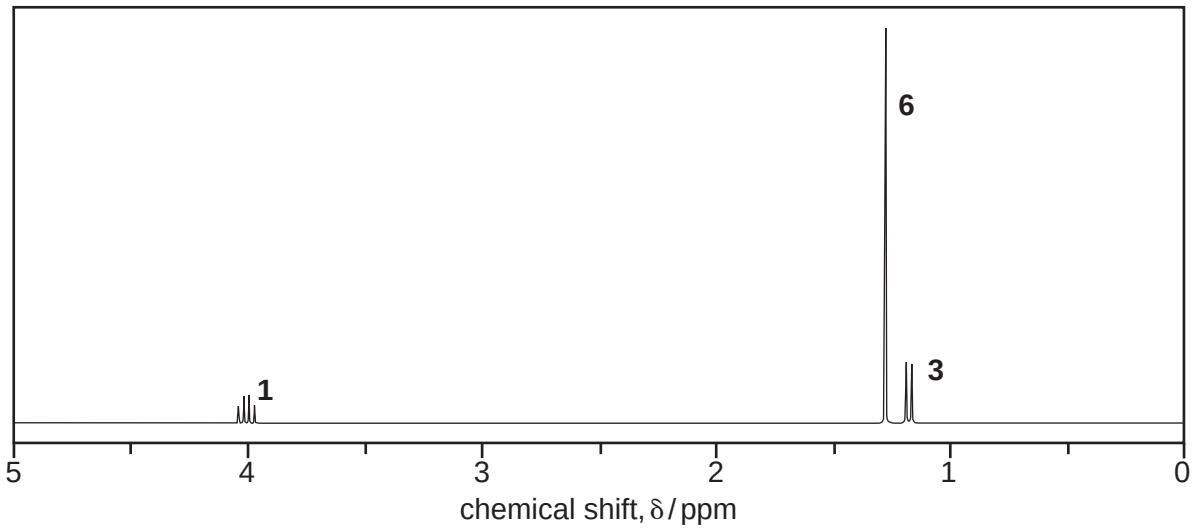
[2]

(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

^{1}H 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.

31

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

Show **all** your reasoning. **[6]**

$\frac{54.54}{12}$: $\frac{9.10}{1}$: $\frac{36.36}{16}$

= $\frac{4.545}{2.273}$: $\frac{9.10}{2.273}$: $\frac{2.273}{2.273}$

= 2 : 4 : 1

empirical formula : C_2H_4O

$(12 \times 2) + 4 + 16 = 44$

$132 \div 44 = 3$

molecular formula = $C_6H_{12}O_3$

δ = 4.0 ppm, quartet, 1H $CH_3 - CH - O$

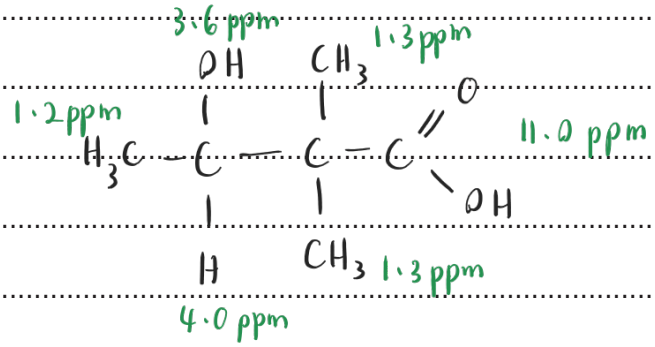
δ = 1.3 ppm, singlet, 6H $(CH_3)_2 - C$

δ = 1.2 ppm, doublet, 3H $CH_3 - CH$

δ = 11.0 ppm = COOH

δ = 3.6 ppm = OH

Additional answer space if required.



END OF QUESTION PAPER

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).