

A Level Chemistry A
H432/02 Synthesis and analytical techniques
Sample Question Paper

Date – Morning/Afternoon

Version 2.0

Time allowed: 2 hours 15 minutes

You must have:

- the Data Sheet for Chemistry A

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.
- Where appropriate, your answers should be supported with working. Marks may be given for a correct method even if the answer is incorrect.
- Write your answer to each question in the space provided.
- Additional paper may be used if required but you must clearly show your candidate number, centre number and question number(s).
- Do **not** write in the bar codes.

INFORMATION

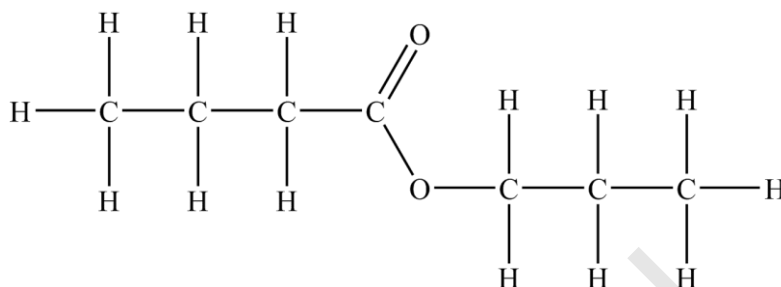
- The total mark for this paper is **100**.
- The marks for each question are shown in brackets [].
- Quality of extended responses will be assessed in questions marked with an asterisk (*).
- This document consists of **36** pages.

SECTION A

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

Answer **all** the questions.

- 1 The displayed formula of an organic compound is shown below.



What is the systematic name of this organic compound?

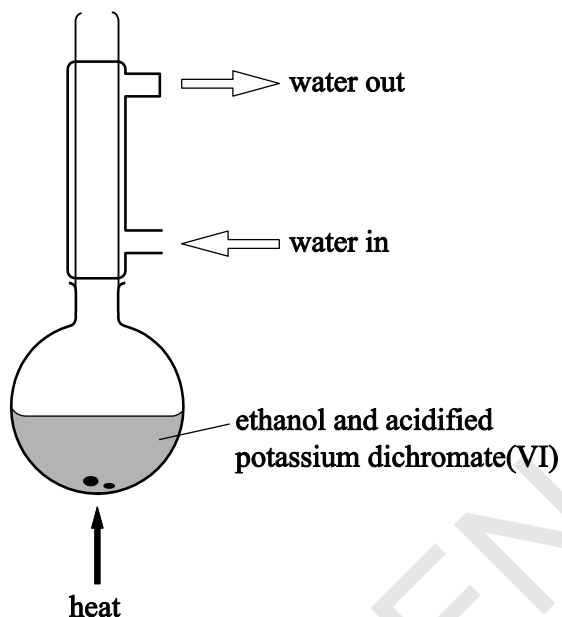
- A Propyl propanoate
- B Propyl butanoate
- C Butyl propanoate
- D Butyl butanoate

Your answer

B

[1]

- 2 Ethanol is oxidised to ethanoic acid using acidified potassium dichromate(IV) solution. The reaction is heated under reflux using the equipment shown in the diagram below.



What is the reason for heating under reflux?

- A to ensure even heating
- B to prevent any substances escaping
- C to boil the mixture at a higher temperature
- D to allow efficient mixing

Your answer

B

[1]

- 3 How many stereoisomers are there of $\text{CH}_3\text{CH}=\text{CHCH}(\text{OH})\text{CH}_2\text{CH}=\text{CH}_2$?

- A 2
- B 4
- C 6
- D 8

Your answer

B

[1]

- 4 The functional group in an organic compound, **W**, was identified by carrying out two chemical tests. The results of the tests are shown below.

Heating with acidified sodium dichromate(VI)(aq)	Addition of 2,4-dinitrophenylhydrazine(aq)
orange solution turns green	yellow/orange precipitate formed

Which compound could be **W**?

- A $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
 B CH_3COCH_3
 C $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$
 D $\text{CH}_3\text{CH}_2\text{CHO}$

Your answer

D

[1]

- 5 Complete combustion of 40 cm^3 of a gaseous hydrocarbon **X** requires 240 cm^3 of oxygen. 160 cm^3 of carbon dioxide forms. All gas volumes are at room temperature and pressure.

What is the formula of **X**?

- A C_4H_8
 B C_4H_{10}
 C C_6H_{12}
 D C_6H_{14}

Your answer

A

[1]

- 6 The boiling point of butan-1-ol is 118 °C. The boiling point of 2-methylpropan-2-ol is 82 °C.

Why is the boiling point of butan-1-ol higher than that of 2-methylpropan-2-ol?

- A butan-1-ol has stronger induced dipole–dipole interactions because it has more electrons
- B butan-1-ol has stronger induced dipole–dipole interactions because it has a straight-chain structure
- C butan-1-ol can form hydrogen bonds while 2-methylpropan-2-ol cannot
- D butan-1-ol is more stable because it is a primary alcohol

Your answer

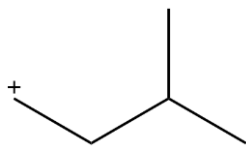
B

[1]

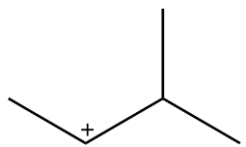
- 7 Hydrogen bromide reacts with 3-methylbut-1-ene.

What is the structure of the major intermediate formed in the mechanism?

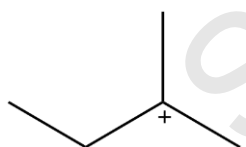
A



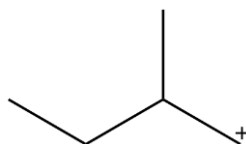
B



C



D



Your answer

B

[1]

- 8 Two chemical tests are carried out on an aqueous solution of an aromatic organic compound **Y**.

The results of the tests are shown below.

Test	Br ₂ (aq)	Na ₂ CO ₃ (aq)
Observation	decolourised	effervescence

What is the minimum number of C atoms in **Y**?

- A 6
B 7
C 8
D 9

Your answer

B

[1]

- 9 Bromine is reacted separately with nitrobenzene and phenylamine.

Which organic products are likely to form?

	Product from nitrobenzene	Product from phenylamine
A	2-bromonitrobenzene	2-bromophenylamine
B	2-bromonitrobenzene	3-bromophenylamine
C	3-bromonitrobenzene	2-bromophenylamine
D	3-bromonitrobenzene	3-bromophenylamine

Your answer

C

[1]

10 Which alcohol could be used to prepare $\text{HCOOCH}(\text{CH}_3)_2$?

- A Propan-1-ol
- B Propan-2-ol
- C 2-Methylpropan-2-ol
- D Methanol

Your answer

B

[1]

11 CN^- ions react with haloalkanes and with carbonyl compounds.

Which row gives the correct mechanisms for the reactions?

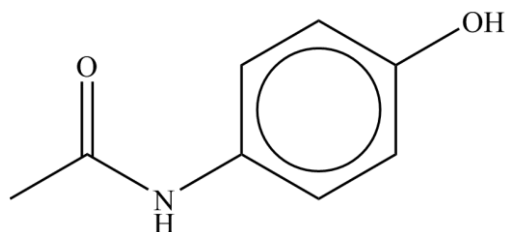
	Reaction of CN^- with haloalkanes	Reaction of CN^- with carbonyl compounds
A	Electrophilic substitution	Electrophilic addition
B	Electrophilic substitution	Nucleophilic addition
C	Nucleophilic substitution	Electrophilic addition
D	Nucleophilic substitution	Nucleophilic addition

Your answer

D

[1]

12 The structure of a molecule that is used as a pain reliever is shown below.



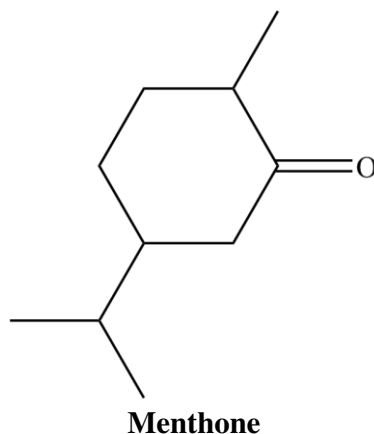
Which statement about this molecule is **not** true?

- A It has the molecular formula $C_8H_9NO_2$.
- B It reacts with bases to form salts.
- C It has a ketone functional group.
- D It can be hydrolysed with aqueous acid.

Your answer

[1]

- 13** Carbonyl compounds have distinctive smells.
Menthone smells of peppermint.



Menthone is reacted in a two-step synthesis shown below.

Step 1: A sample of menthone is added to hot acidified aqueous dichromate(VI) ions.

Step 2: The resulting mixture from **Step 1** is added to NaBH_4 in water.

What happens to the smell of the reaction mixture during the process?

	Step 1	Step 2
A	Smell of peppermint remains	Smell of peppermint is lost
B	Smell of peppermint is lost	Smell of peppermint returns
C	Smell of peppermint remains	Smell of peppermint remains
D	Smell of peppermint is lost	Smell of peppermint does not return

Your answer

A

[1]

14 Which of the following support(s) the delocalised model for benzene rather than the Kekulé model?

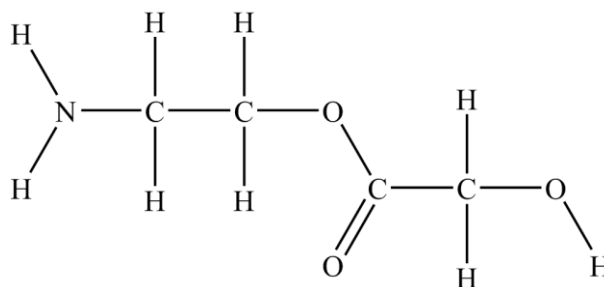
- 1:** Benzene is less reactive than cyclohexene
- 2:** A benzene molecule has a planar, hexagonal structure
- 3:** The enthalpy change of hydrogenation of benzene is more exothermic than predicted from the Kekulé structure

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

Your answer

[1]

15 The structure of molecule **Z** is shown below.



Which of the following statements is/are true?

- 1: The carbon-13 NMR spectrum of **Z** shows four peaks
- 2: The proton NMR spectrum of **Z** shows five peaks
- 3: The proton NMR spectrum of **Z** run in D₂O shows three peaks

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

Your answer

A

[1]

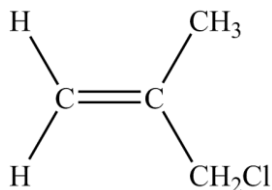
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SPECIMEN

SECTION B

Answer **all** the questions.

- 16** Methyl allyl chloride, MAC, is a chemical used in the production of insecticides. The structure of MAC is shown below.

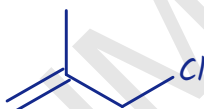


MAC

- (a) (i) Give the **molecular** formula of MAC.

..*C₄H₇Cl*..... [1]

- (ii) Draw the **skeletal** formula of MAC.



[1]

- (iii) MAC has several structural isomers.

State what is meant by *structural isomers*.

..*Compounds with the same molecular formula but different structural formulae*..... [1]

- (b) MAC is highly flammable. When MAC burns, one of the products formed is a toxic gas.

1.321 g of this gas occupies 1.053 dm³ at 100 kPa and 350 K.

Use the information provided to suggest the identity of the gas.

$$n = pV/RT = (100 \times 10^3 \times 1.053 \times 10^{-3}) \div (8.314 \times 350)$$

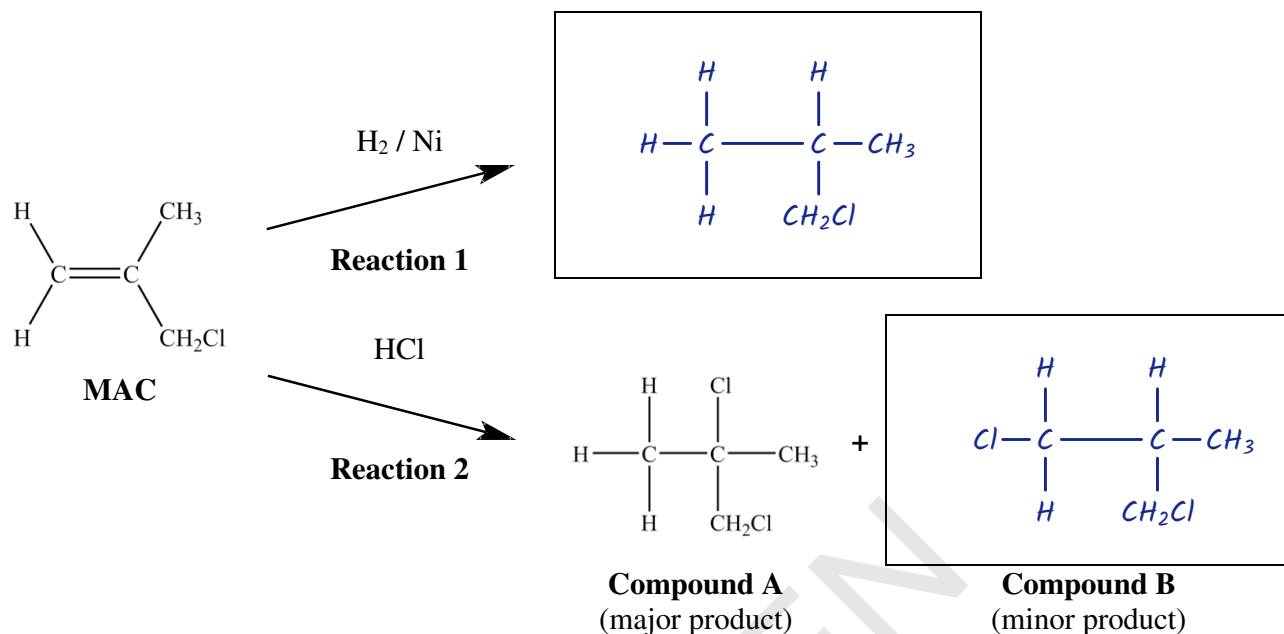
$$n = 0.0362 \text{ mol}$$

$$M = m/n = 1.321 \div 0.0362 = 36.5 \text{ g mol}^{-1}$$

$$M = 36.5 \text{ matches HCl (1.0 + 35.5), a toxic gas}$$

gas = ...*HCl*..... [4]

(c) The flowchart below shows some reactions of MAC.



(i) Complete the flowchart above.

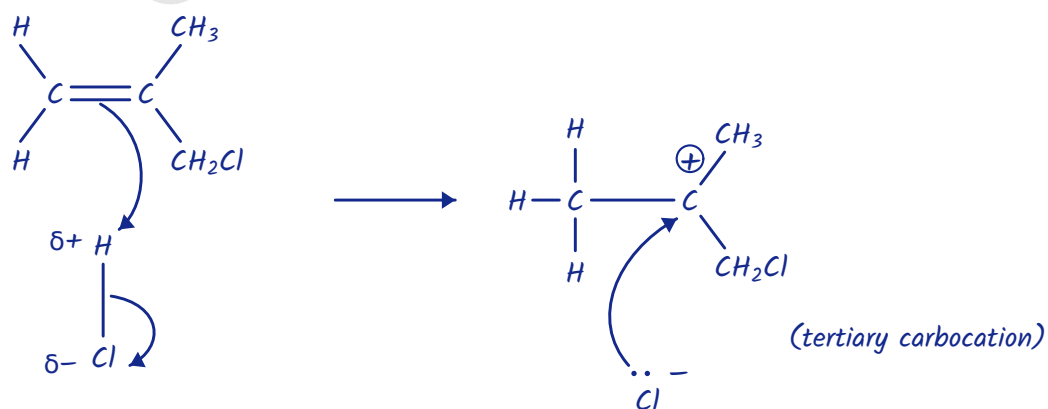
- Draw the structure of the product of **Reaction 1**.
- Draw the structure of the minor organic product of **Reaction 2** (Compound B).

[2]

(ii) **Reaction 2** creates a mixture of compounds. Compound A is the major product.

Draw the mechanism for the formation of compound A.

Use curly arrows and show relevant dipoles.



[3]

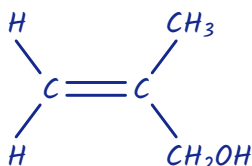
- (iii) Explain why compound **B** is the minor product of **Reaction 2**.

The carbocation intermediate that forms B is primary, which is less stable than the tertiary carbocation intermediate that forms A. [1]

- (iv) **MAC** reacts with water in the presence of $\text{AgNO}_3(\text{aq})$ and ethanol.

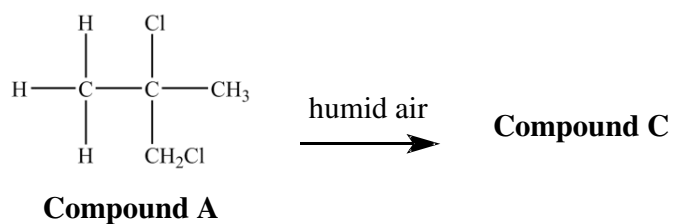
Draw the structure of the organic product of this reaction.

State what you would **observe** in this reaction and identify the compound responsible for the observation.



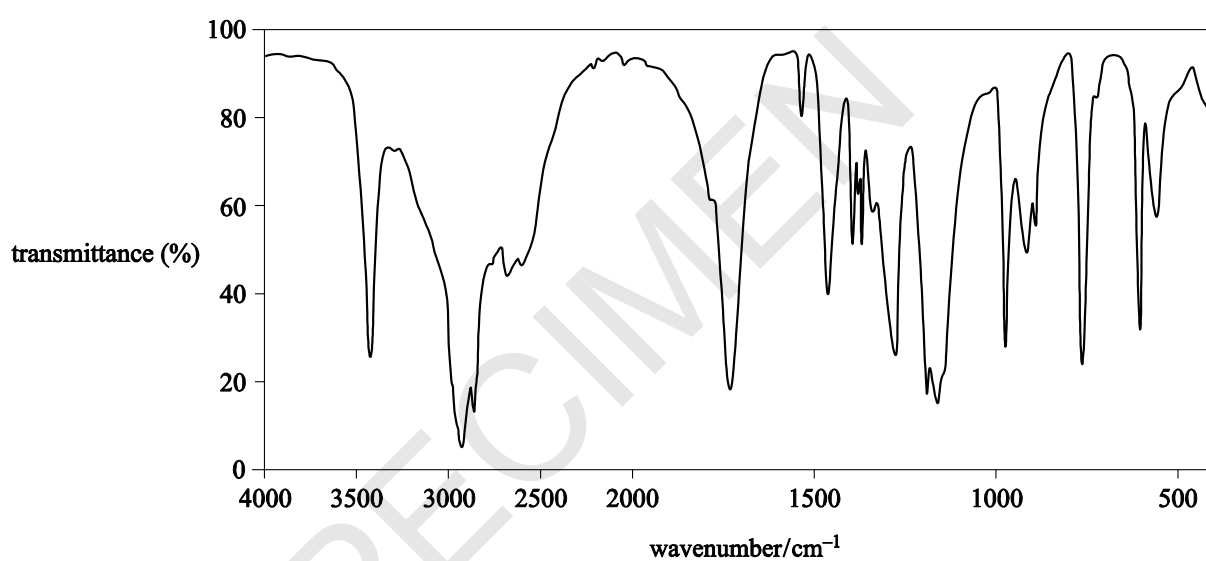
A white precipitate forms; the precipitate is silver chloride, AgCl . [2]

- (d) Compound **A** reacts slowly in humid conditions to form compound **C**.



Compound **C** contained the following percentage composition by mass:
 C, 46.1%; H, 7.7%; O, 46.2%

The infrared spectrum of compound **C** is shown below.

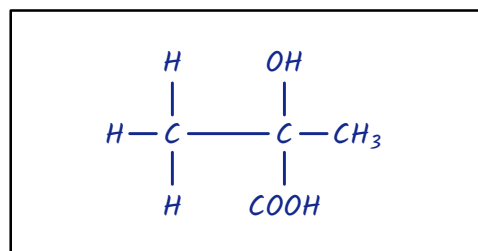


Using the information on the previous page, deduce the structure of compound C.

Give your reasoning.

$C : H : O = 46.1/12.0 : 7.7/1.0 : 46.2/16.0 = 3.84 : 7.7 : 2.89$
 $\div 2.89$ gives $1.33 : 2.66 : 1$, and $\times 3$ gives $4 : 8 : 3$, so the empirical
 formula is $C_4H_8O_3$.
 IR: very broad absorption at 2500 to 3300 cm^{-1} , O-H in COOH, and
 absorption at about 1720 cm^{-1} , C=O (1640 to 1750 cm^{-1}).
 Absorption at about 3450 cm^{-1} : O-H of an alcohol.
 So C contains -COOH and -OH in place of the two Cl-containing groups of A;
 $C_4H_8O_3$ shows no other C=O apart from the one in COOH.
 C is 2-hydroxy-2-methylpropanoic acid, $(CH_3)_2C(OH)COOH$.

structure =



[5]

17 Molecules with more than one functional group are useful chemical ‘building blocks’.

(a) Compound **D**, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{NH}_2$, is an intermediate in the synthesis of a variety of drugs.

(i) Compound **D** can be synthesised from ethanal, CH_3CHO .

Devise a **two-step** synthesis of compound **D** from ethanal.

- Give details of appropriate reagents and relevant conditions.
- Write an equation for each step, showing clearly all organic compounds.

Step 1: add HCN (or KCN and H_2SO_4); nucleophilic addition:

$\text{CH}_3\text{CHO} + \text{HCN} \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CN}$

Step 2: react the nitrile with H_2 using a Ni catalyst (reduction):

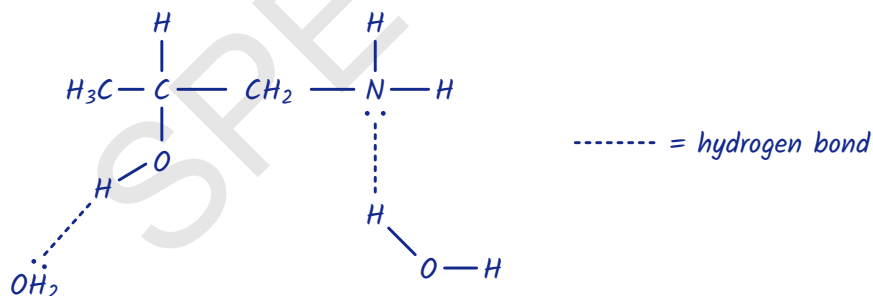
$\text{CH}_3\text{CH}(\text{OH})\text{CN} + 2\text{H}_2 \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{NH}_2$

.....

..... [4]

(ii) Explain why compound **D** is very soluble in water.

Use a diagram in your answer.



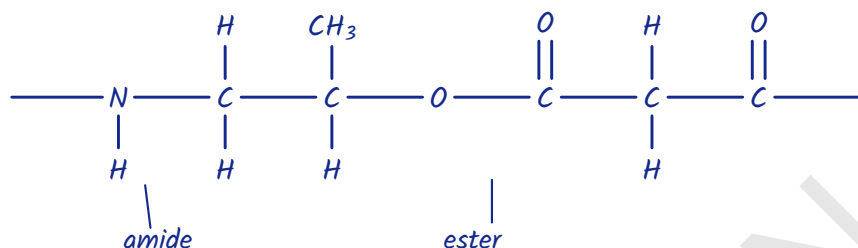
Compound D forms hydrogen bonds with water molecules, through both

its -OH group and its -NH₂ group [3]

- (iii) Compound **D** reacts with propanedioic acid, $\text{HOOCCH}_2\text{COOH}$, to form a condensation polymer.

Draw a possible repeat unit of this condensation polymer.

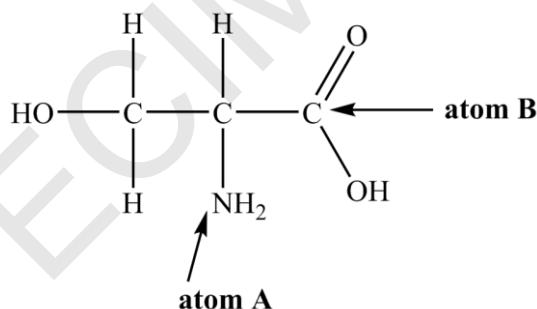
Show clearly any functional group present in the repeat unit.



[2]

- (b) Serine, shown below, is an amino acid.

(i)



Use electron repulsion theory to predict the shape of the bonds around atoms **A** and **B**.

Give relevant bond angles around atoms **A** and **B**.

Give reasons for your answers.

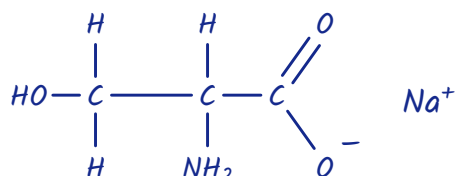
Atom A (N): 3 bonding pairs and 1 lone pair of electrons. Electron pairs repel as far apart as possible and the lone pair repels more than bonding pairs, so the shape is pyramidal, bond angle 107° .

Atom B (C): 3 bonding centres (two single bonds and a $\text{C}=\text{O}$ double bond) and 0 lone pairs, which repel equally as far apart as possible, so trigonal planar, bond angle 120° .

[4]

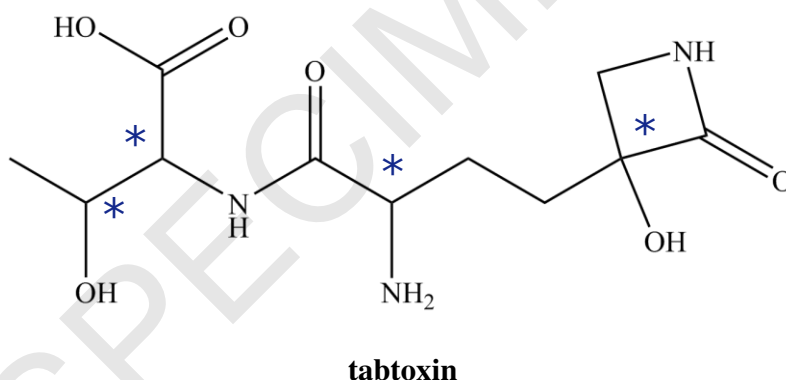
- (ii) A student adds an excess of aqueous sodium hydroxide to a sample of solid serine. The student then purifies the resulting reaction mixture to obtain a pure sample of an ionic organic product.

- Draw the structure of the ionic organic compound obtained.
- Outline the steps that the student could carry out to obtain a pure sample of the organic product from the reaction mixture.



..Filter the solution (to remove insoluble impurities), then recrystallise the
..salt: crystallise, filter off and dry the crystals..... [3]

- (c) **Tabtoxin** is a poisonous substance produced by bacteria found in lilac trees.



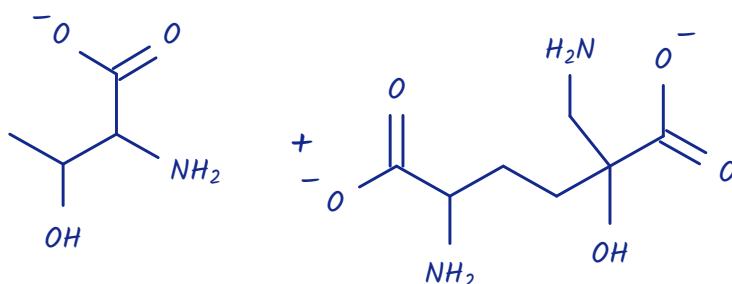
- (i) Identify the chiral centres present in a molecule of tabtoxin.

On the structure above, mark each chiral centre with an asterisk, *.

[1]

- (ii) Tabtoxin can be broken down by alkaline hydrolysis.

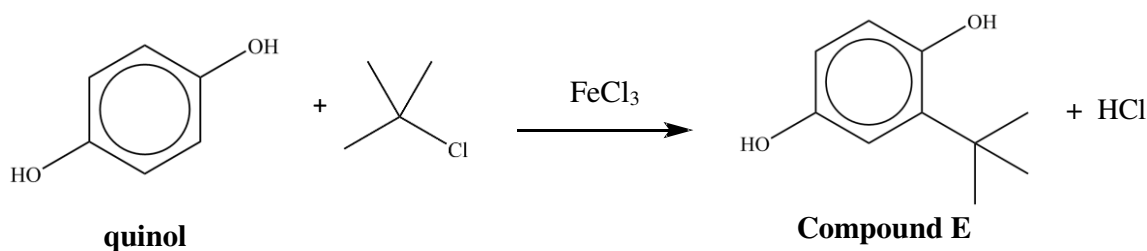
Draw the structures of **all** the organic products of the alkaline hydrolysis of tabtoxin.



[4]

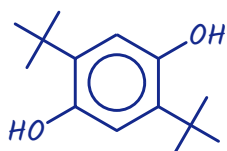
18 A student investigates reactions of aromatic compounds.

(a) The student first carries out the reaction shown below.



- (i) The student obtains a very low yield of compound E.
 The student obtains a much higher yield of a different organic product with molecular formula $\text{C}_{14}\text{H}_{22}\text{O}_2$.

Suggest an identity for the organic product $\text{C}_{14}\text{H}_{22}\text{O}_2$ and draw its structure below.



2,5-di-tert-butylbenzene-1,4-diol

[1]

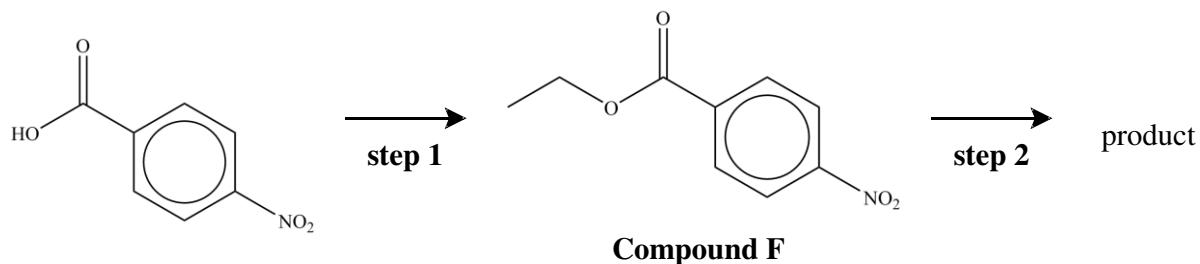
- (ii) The student is told by a friend that the FeCl_3 catalyst is not needed because quinol is more reactive than benzene.

Explain why the student's friend is correct.

You may draw a diagram to support your answer.

A lone pair of electrons on each oxygen atom (in a p-orbital) is.....
donated into, partially delocalised into, the π system of the ring.....
This increases the electron density of the ring, so quinol is much more.....
susceptible to electrophilic attack than benzene: the ring can polarise the.....
haloalkane and react without a halogen carrier..... [3]

- (b) 4-Nitrobenzoic acid is an important compound in chemical synthesis. The flowchart below shows a synthesis involving 4-nitrobenzoic acid.



- (i) State suitable reactant(s) and conditions for **step 1**.

Reactant: ethanol, $\text{CH}_3\text{CH}_2\text{OH}$

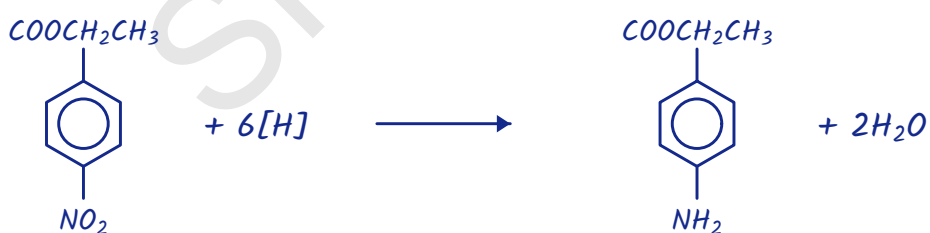
Conditions: concentrated H_2SO_4 catalyst, heat (reflux)

[1]

- (ii) In **step 2**, the $-\text{NO}_2$ group in compound **F** is reduced by tin and concentrated hydrochloric acid.

Write an equation for the reduction of compound **F**.

Show the structures of any organic compounds involved.



[2]

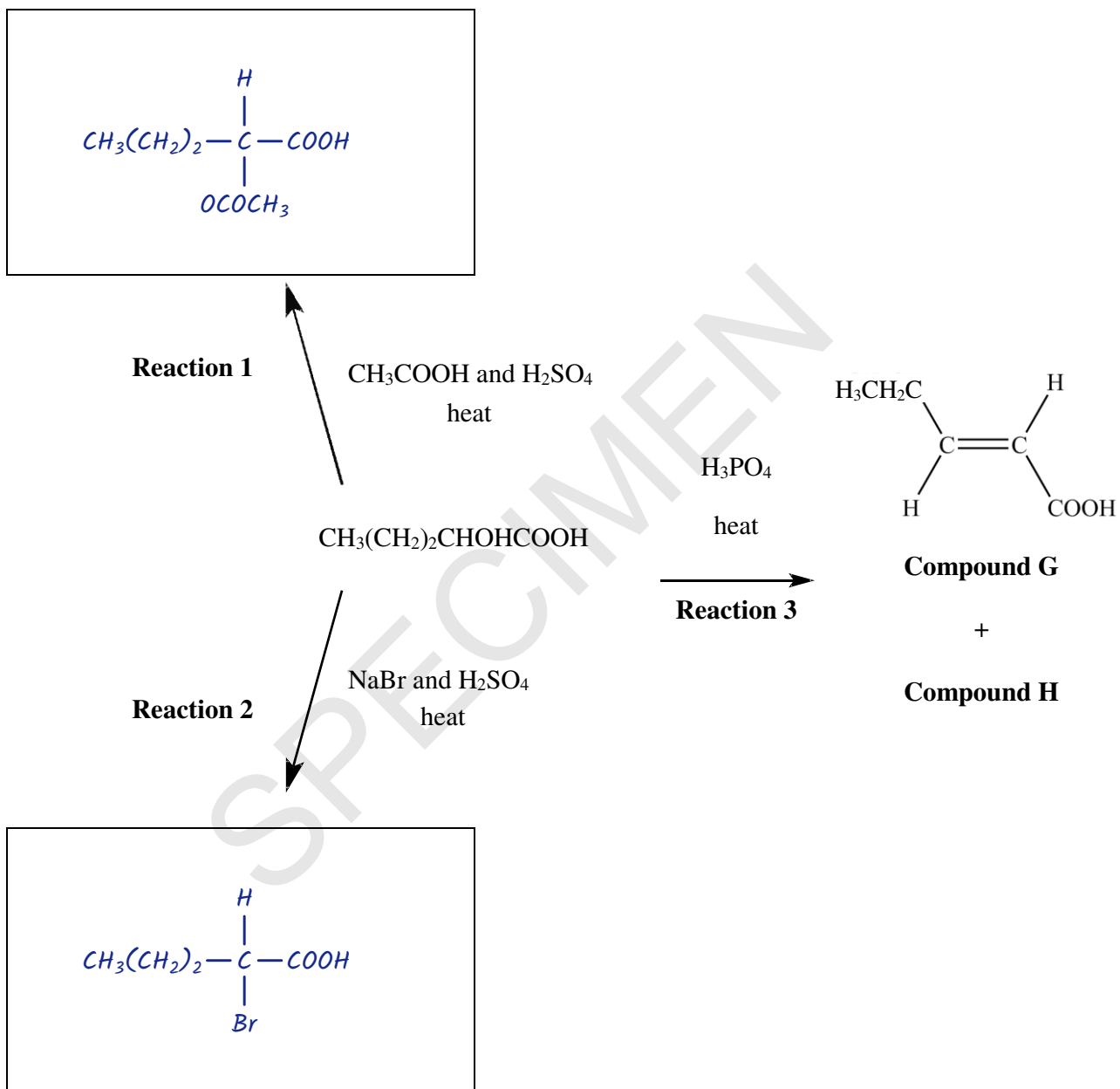
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SPECIMEN

19 α -Hydroxy acids (AHAs) are naturally occurring acids often used as cosmetics.

(a) The flowchart below shows some reactions of an AHA, $\text{CH}_3(\text{CH}_2)_2\text{CHOHCOOH}$.

(i) Fill in the boxes to show the organic products of **Reactions 1** and **2**, clearly showing the relevant functional groups.



[2]

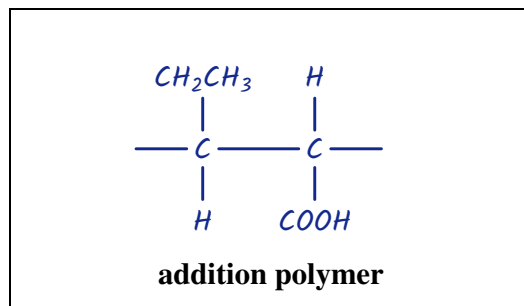
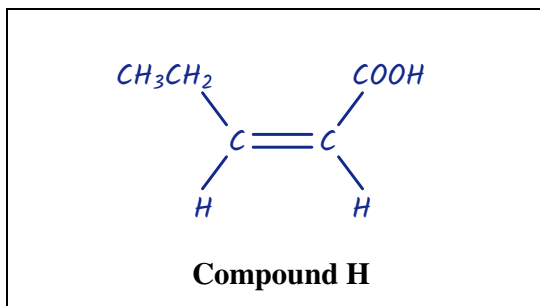
(ii) Give the **full** systematic name for compound G.

(E)-pent-2-enoic acid.....

[1]

(iii) Compound **H** is a stereoisomer of compound **G**.

- Suggest a structure for compound **H**.
- Draw the repeat unit of the addition polymer that can be formed from compound **H**.



[2]

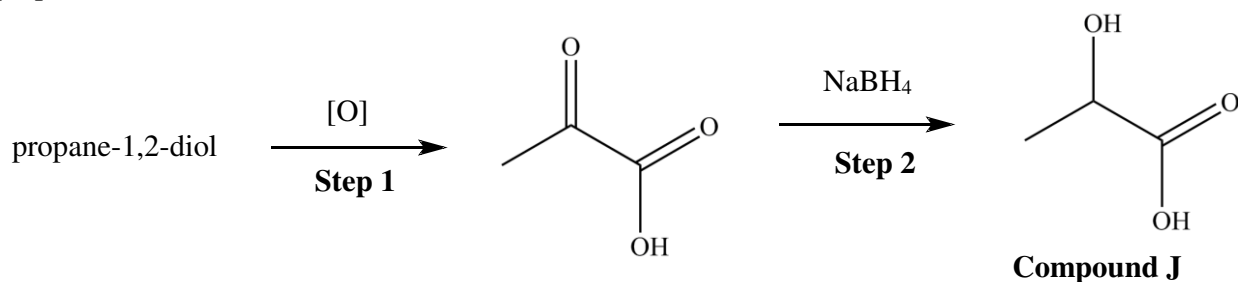
(iv) The addition polymer in (iii) is used widely in industry. Increasingly, waste polymers are being processed as a more sustainable option than disposal.

Apart from recycling, state **two** methods for usefully processing waste polymers.

..Combustion for energy production.....

..Organic feedstock to make plastics and other organic chemicals..... [2]

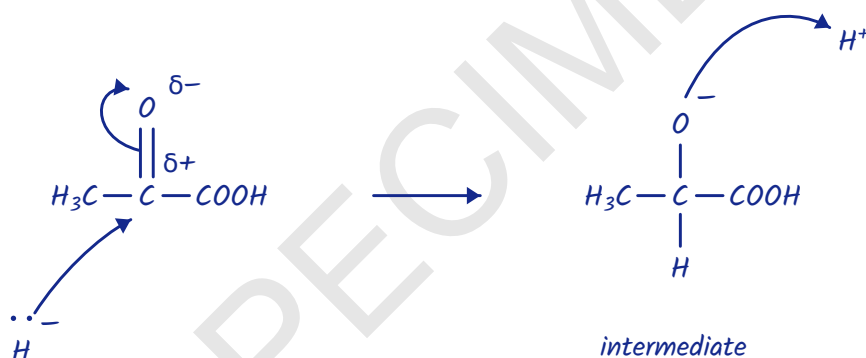
- (b) A student synthesises a sample of the AHA **J** using the following reaction scheme, starting from propane-1,2-diol.



- (i) In the space below:

- state a suitable oxidising agent for **Step 1**
- write an equation for **Step 1**
- outline the mechanism for **Step 2**, showing curly arrows and relevant dipoles.

Oxidising agent: acidified potassium dichromate(VI), $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$

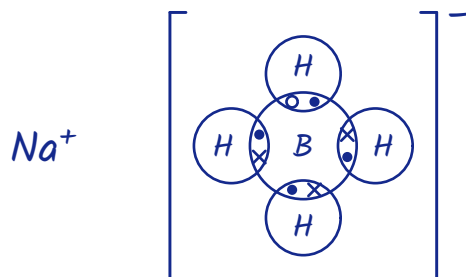


*H^- from NaBH_4 acts as a nucleophile (nucleophilic addition); the intermediate.....
takes H^+ from water.....* [5]

- (ii) The reagent used in **Step 2** of the synthesis in (i) was NaBH_4 . NaBH_4 contains the ions Na^+ and $[\text{BH}_4]^-$.

Draw a 'dot-and-cross' diagram of NaBH_4 and give the **full** electron configuration of Na^+ .

Show outer shells of electrons only.



x = B electron

• = H electron

o = electron from Na

full electronic configuration of Na^+ : ... $1s^2 2s^2 2p^6$

[2]

- (c) Compound **K** is an AHA that is often used in ‘chemical face peels’.

A student wishes to identify compound **K** from the list of compounds below.

glycolic acid	HOCH_2COOH
malic acid	$\text{HOOCCH}_2\text{CHOHCOOH}$
mandelic acid	$\text{C}_6\text{H}_5\text{CHOHCOOH}$
pantoic acid	$\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{CHOHCOOH}$

The student isolates compound **K** and analyses a sample of the compound by titration.

The student dissolves 1.89 g of compound **K** in water and makes the solution up to 250.0 cm^3 in a volumetric flask. The student titrates 25.0 cm^3 of this solution with $0.150 \text{ mol dm}^{-3} \text{ NaOH(aq)}$.

18.80 cm^3 of NaOH(aq) were required for complete neutralisation.

Use the results of the student’s analysis to identify compound **K** from the list above.

$$n(\text{NaOH}) = 0.150 \times 18.80/1000 = 0.00282 \text{ mol}$$

$$n(\text{H}^+/\text{COOH}) \text{ in } 25.0 \text{ cm}^3 = 0.00282 \text{ mol}$$

$$n(\text{H}^+/\text{COOH}) \text{ in } 250.0 \text{ cm}^3 = 0.00282 \times 10 = 0.0282 \text{ mol}$$

$$\text{'molar mass' of K per H}^+ = 1.89 \div 0.0282 = 67.0 \text{ g mol}^{-1}$$

None of the listed compounds has $M = 67.0$, so **K** must be diprotic

$$\text{(two COOH groups): } M = 2 \times 67.0 = 134 \text{ g mol}^{-1}$$

malic acid, $\text{HOOCCH}_2\text{CHOHCOOH}$, has $M = 134.0$, so **K** = malic acid

K = ...malic acid..... [5]

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SPECIMEN

- 20** Cyclohexanone can be prepared in the laboratory by reacting cyclohexanol with concentrated sulfuric acid and sodium dichromate.

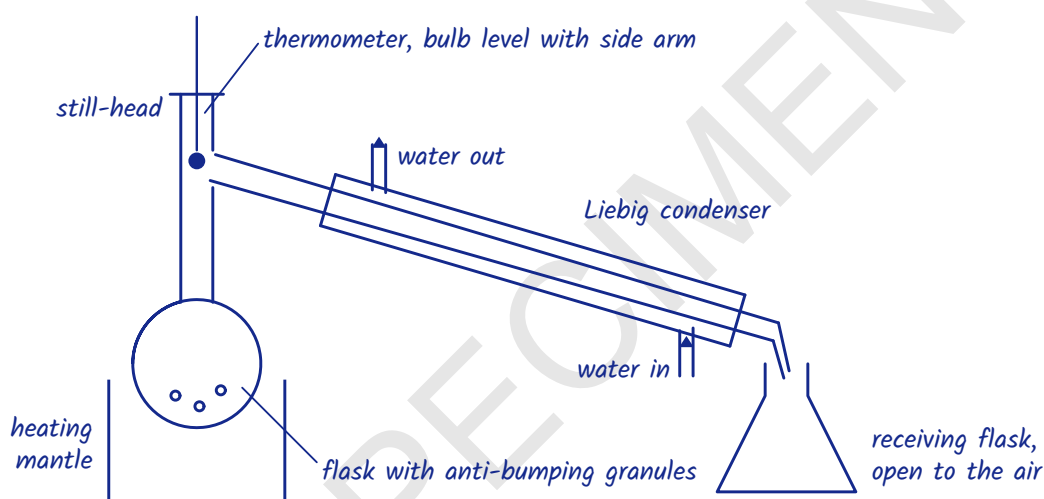
Ethanedioic acid is added to the reaction mixture to react with any excess dichromate.

The mixture is then distilled. The impure distillate is a mixture of cyclohexanone and water.

You will need to refer to some or all of the following data to answer these questions.

	Boiling point / °C	Density / g cm ⁻³	<i>M_r</i>
Cyclohexanol	161	0.962	100.0
Cyclohexanone	156	0.948	98.0

- (a)* Draw a labelled diagram to show how you would safely set up apparatus for distillation and describe a method to obtain a pure sample of cyclohexanone from the distillate. [6]



Heat with an electric heating mantle (no naked flame, as cyclohexanone is flammable), with anti-bumping granules in the flask. The apparatus must be open at the receiver end, not a sealed system. Water enters the condenser at the bottom and leaves at the top.

Purifying the distillate:

Pour the distillate into a separating funnel, shake and leave to settle into two layers. The upper layer is cyclohexanone (density 0.948 g cm⁻³, less dense than water) and the lower layer is aqueous.

Run off (top off) the lower aqueous layer and collect the organic layer in a dry conical flask.

Additional answer space if required.

Add a small amount of anhydrous magnesium sulfate (or anhydrous calcium chloride) to the organic layer to remove water; swirl, then decant or filter off the drying agent. Redistil the dried organic layer and collect the fraction that distils at about 156 °C (between about 150 and 156 °C), the boiling point of cyclohexanone. This leaves behind any cyclohexanol, which boils at 161 °C.

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- (b) Ethanedioic acid removes excess dichromate ions, $\text{Cr}_2\text{O}_7^{2-}$, as in the equation below.



Suggest how you could tell when the excess dichromate has completely reacted with the ethanedioic acid.

When adding more ethanedioic acid no longer causes effervescence (fizzing of CO_2 stops). [1]

- (c) A student monitors the course of this reaction using thin-layer chromatography (TLC).

Outline how TLC could be used to monitor the course of the reaction.

Take samples from the reaction mixture at regular intervals; spot and run each on a TLC plate alongside cyclohexanal and cyclohexanone controls. Compare R_f values; the reaction is complete when the cyclohexanal spot has gone. [2]

- (d) Plan an experiment that would allow the student to confirm the identity of the pure organic product by means of a chemical test.

React a sample of the product with 2,4-dinitrophenylhydrazine (Brady's reagent): an orange precipitate forms (carbonyl group).....

Filter off the precipitate, recrystallise it, dry it and then determine its melting point.....

Compare the melting point with the data book value for the 2,4-DNP derivative of cyclohexanone: a match confirms cyclohexanone.....

.....

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..... [3]

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SPECIMEN

- 21*** A chemist isolates compound **L**, with empirical formula $\text{C}_3\text{H}_6\text{O}$, and sends a sample for analysis. The analytical laboratory sends back the following spectra.

Mass spectrum

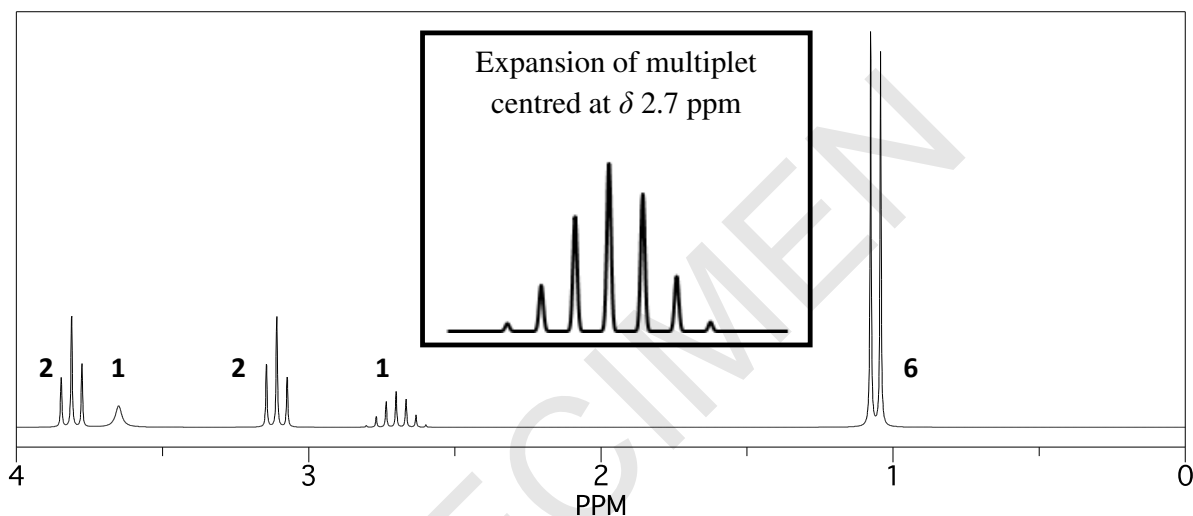
Molecular ion peak at $m/z = 116.0$.

^1H NMR spectra

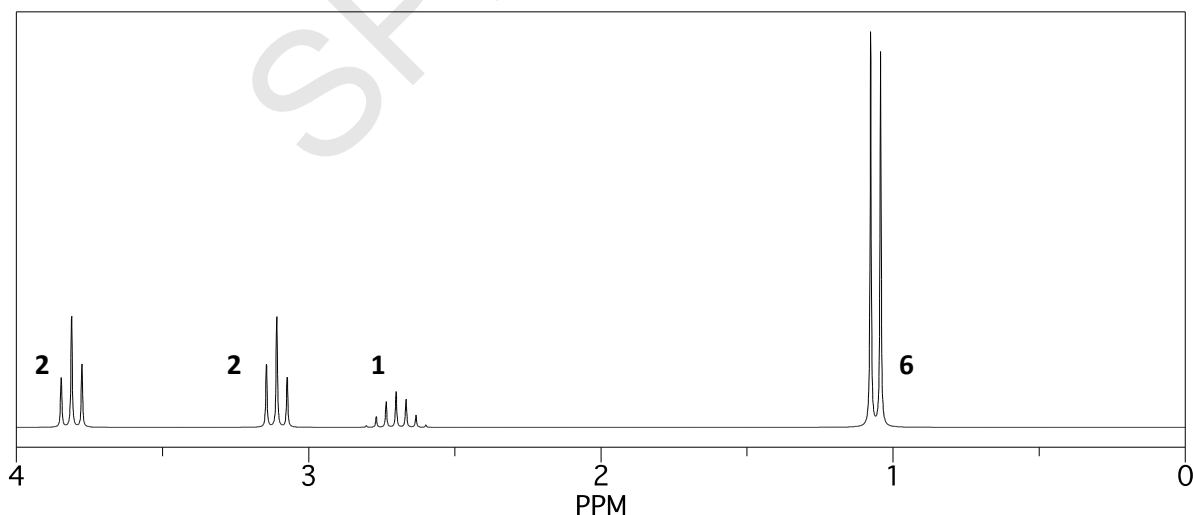
The numbers next to each signal represent the number of ^1H responsible for that signal.

Two ^1H NMR spectra were obtained: one without D_2O and one with D_2O added.

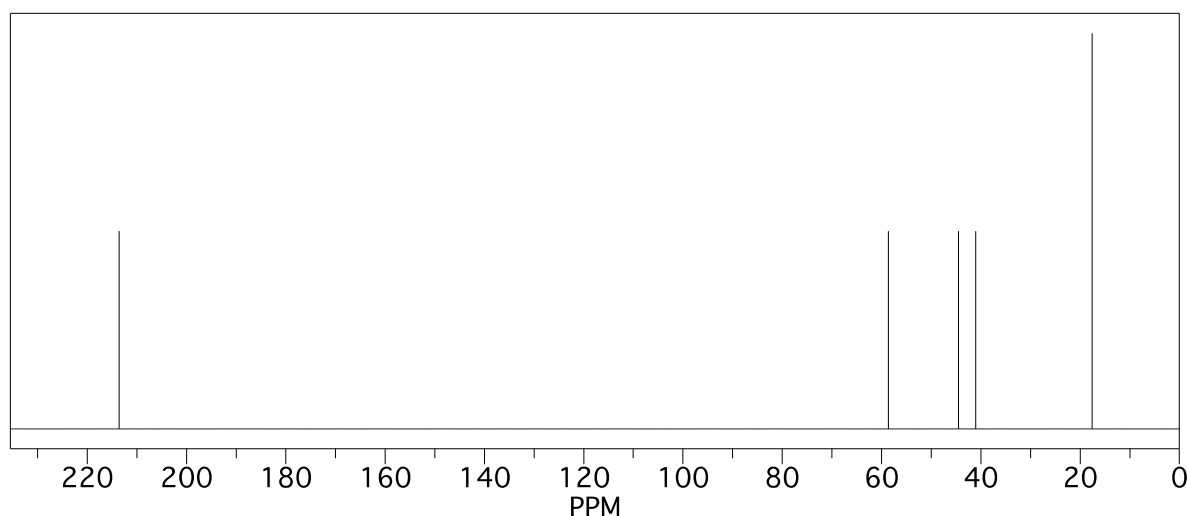
^1H NMR spectrum with no D_2O :



^1H NMR spectrum with D_2O added:



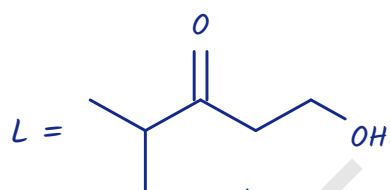
^{13}C NMR spectrum:



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

Give your reasoning.

[6]



$(\text{CH}_3)_2\text{CHCOCH}_2\text{CH}_2\text{OH}$, 1-hydroxy-4-methylpentan-3-one

Mr. of $\text{C}_3\text{H}_6\text{O} = 58.0$ and $116.0 \div 58.0 = 2$, so the molecular formula is.....

$\text{C}_6\text{H}_{12}\text{O}_2$

^{13}C NMR: 5 peaks, so 5 carbon environments (the two CH_3 carbons are.....

equivalent). The peak at about 213 ppm is a $\text{C}=\text{O}$; there is no ^1H peak at δ 9.....

to 10 ppm (no CHO), so it is a ketone, not an aldehyde. The peak at about 58.....

ppm is $\text{C}-\text{O}$ (alcohol).....

^1H NMR:.....

δ 3.7 ppm, singlet, 1H: $\text{O}-\text{H}$, because this peak is lost when D_2O is added.....

δ 3.8 ppm, triplet, 2H: CH_2 bonded to O and next to a CH_2 , so $-\text{CH}_2-\text{CH}_2-\text{O}-$

δ 3.1 ppm, triplet, 2H: CH_2 next to $\text{C}=\text{O}$ and next to a CH_2 , so $-\text{CH}_2-\text{CH}_2-\text{C}=\text{O}$

δ 2.7 ppm, septet, 1H: CH next to $\text{C}=\text{O}$, with 6 adjacent H , so $(\text{CH}_3)_2\text{CH}-\text{C}=\text{O}$

δ 1.0 ppm, doublet, 6H: two equivalent CH_3 groups next to one CH , so.....

$(\text{CH}_3)_2\text{CH}-$

So L is $(\text{CH}_3)_2\text{CHCOCH}_2\text{CH}_2\text{OH}$ (structure drawn above).....

Additional answer space if required.

END OF QUESTION PAPER

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