



A Level Chemistry A

H432/02 Synthesis and analytical techniques

Sample Question Paper

Date – Morning/Afternoon

Time allowed: 2 hours 15 minutes

You must have:

- the Data Sheet for Chemistry A

You may use:

- a scientific calculator



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.
- 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

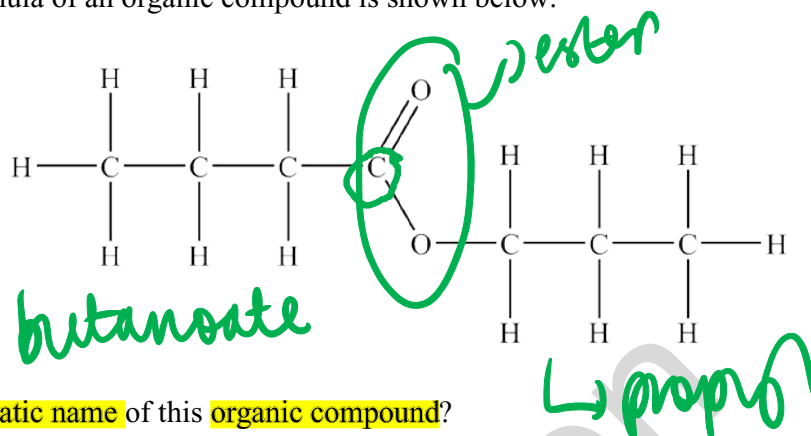
- The total mark for this paper is **100**.
- The marks for each question are shown in brackets [].
- Quality of extended responses will be assessed in questions marked with an asterisk (*).
- This document consists of **36** pages.

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

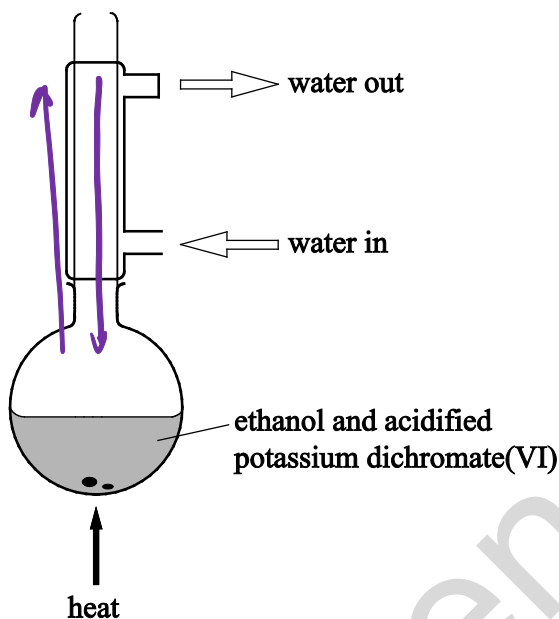
Your answer

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.

[0] Aldehyde
[0] ↓
ethanoic acid



What is the reason for heating under reflux?

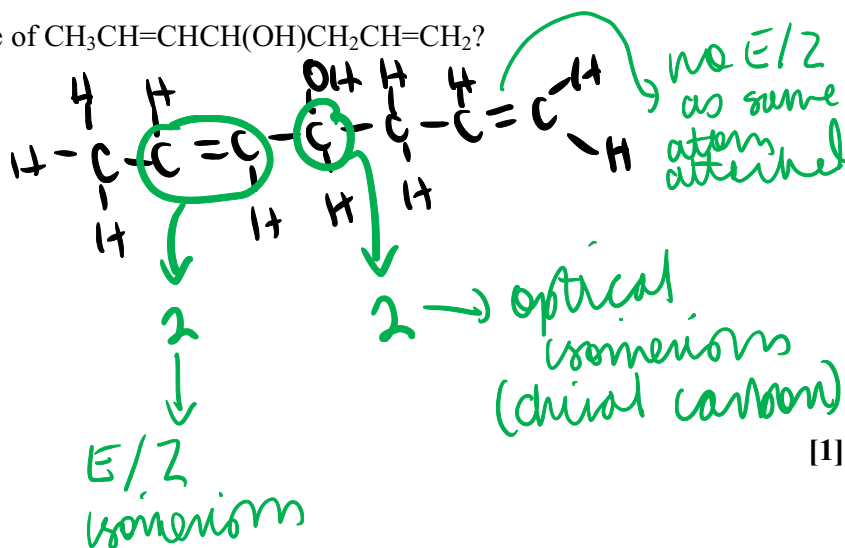
- A to ensure even heating
- B** to prevent any substances escaping → allows full oxidation
- C to boil the mixture at a higher temperature
- D to allow efficient mixing

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]

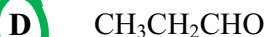
test for 1° / 2° alcohol (oxidation)
aldehyde (oxidation)

- 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

test for C=O bond.
(aldehyde or ketone)

Which compound could be **W**?



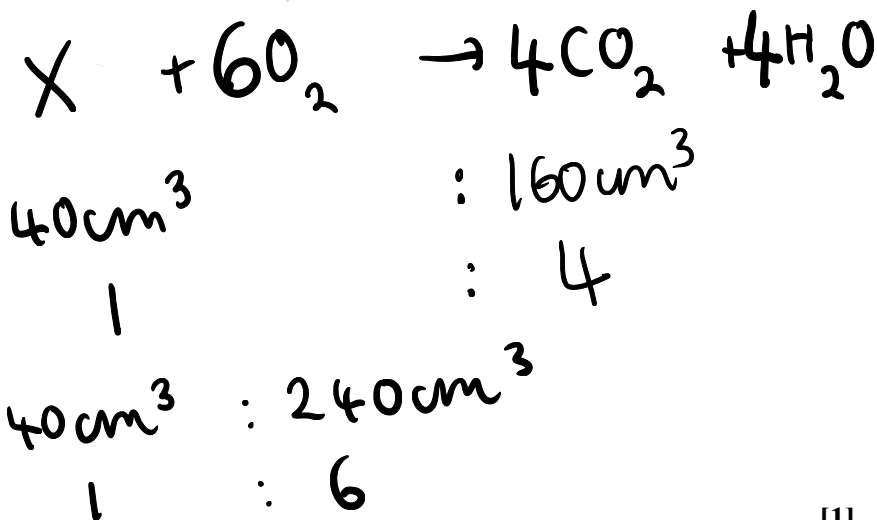
Your answer

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**?



Your answer

A

[1]

$\therefore 12$ O-atoms on LHS — 8 (O) from CO_2
 $= 4$ (O) from H_2O
 so $4 \text{ H}_2\text{O} \therefore 8$ H atoms $\rightarrow \text{C}_4\text{H}_8$.



structural isomers

- 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 \rightarrow chains can pack together closer
 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

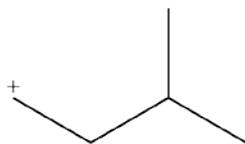
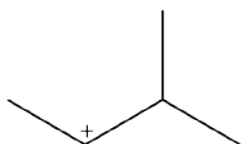
[1]

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

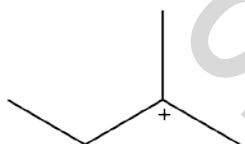
Electrophilic addition

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

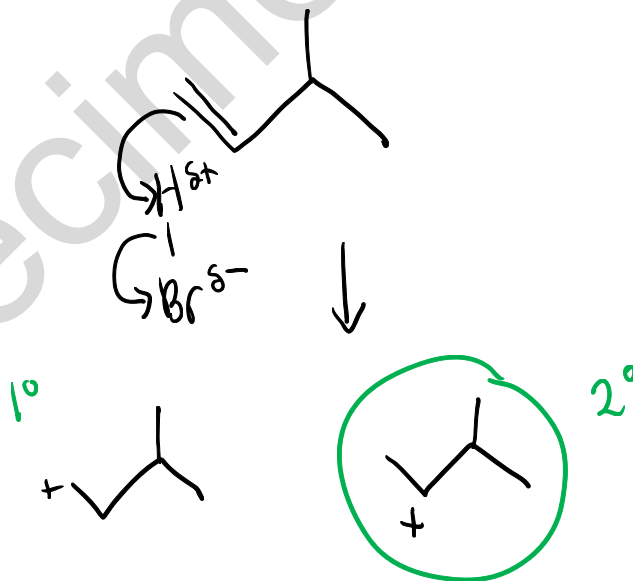
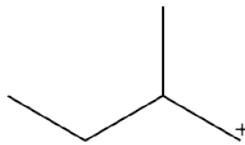
A

**B**

C



D



2° carbocations are more stable than 1° \therefore the 2° C^+ is the major intermediate.

Your answer

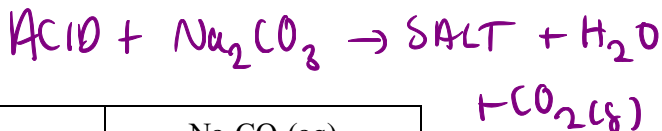
B

[1]

benzene needs a halogen carrier - it can't decolourise Br₂ as not e⁻ dense enough to induce a dipole

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.

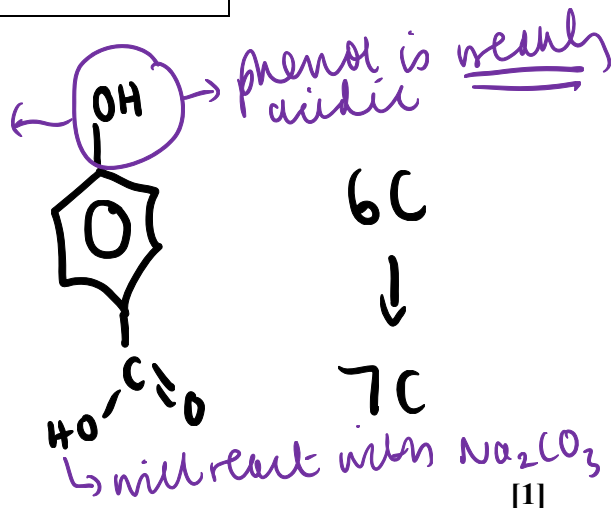


Test	Br ₂ (aq)	Na ₂ CO ₃ (aq)
Observation	decolourised	effervescence

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

- A 6
- B 7**
- C 8
- D 9

adds e⁻ density into ring so can decolourise Br₂



Your answer

B

[1]

9 **Bromine** is reacted separately with **nitrobenzene** and **phenylamine**.

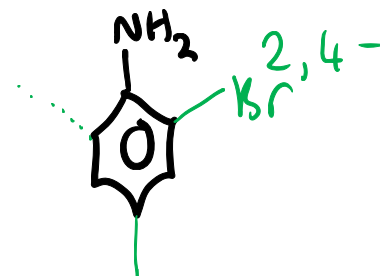
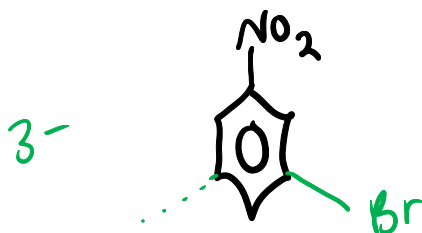
electrophilic substitution

Which organic products are likely to **form**?

	Product from nitrobenzene	Product from phenylamine
A	2-bromonitrobenzene	2-bromophenylamine
B	2-bromonitrobenzene	3-bromophenylamine
C	<u>3</u> -bromonitrobenzene	<u>2</u> -bromophenylamine
D	3-bromonitrobenzene	3-bromophenylamine

Your answer

C



[1]

-NO₂ is an e⁻ withdrawing group so deactivates ring ∴ is 3-directing

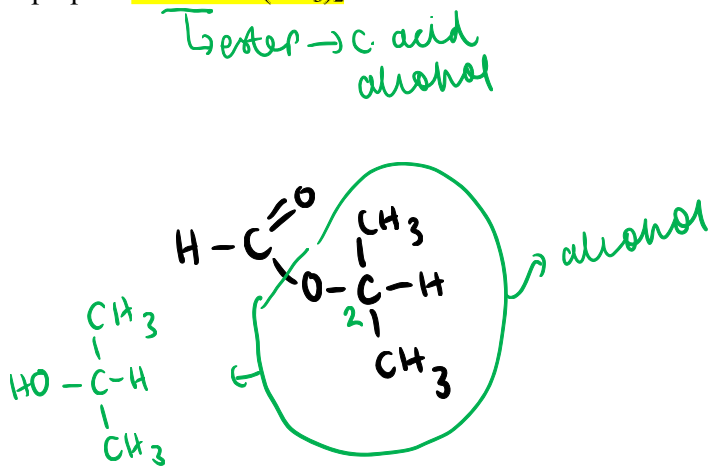
-NH₂ is an e⁻ donating group so activates the ring ∴ is 2-, 4- (+-6-) directing

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.

$\text{E} = \text{e}^-$ pair acceptor = \oplus
 $\text{Nu} = \text{e}^-$ pair donor = \ominus

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	<u>Nucleophilic substitution</u>	<u>Nucleophilic addition</u>

Your answer

D



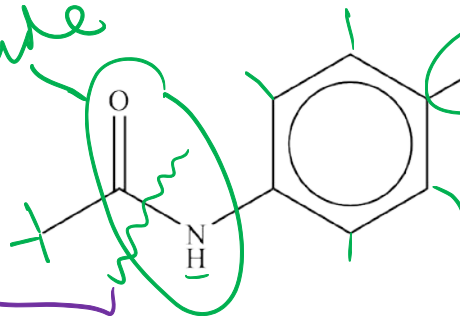
[1]

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

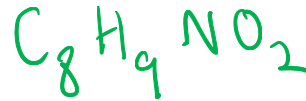
as C=O is directly bonded to N NOT a C.

can be hydrolysed with acid

amide



phenol
(weakly acidic so reacts with bases)



Which statement about this molecule is not true?

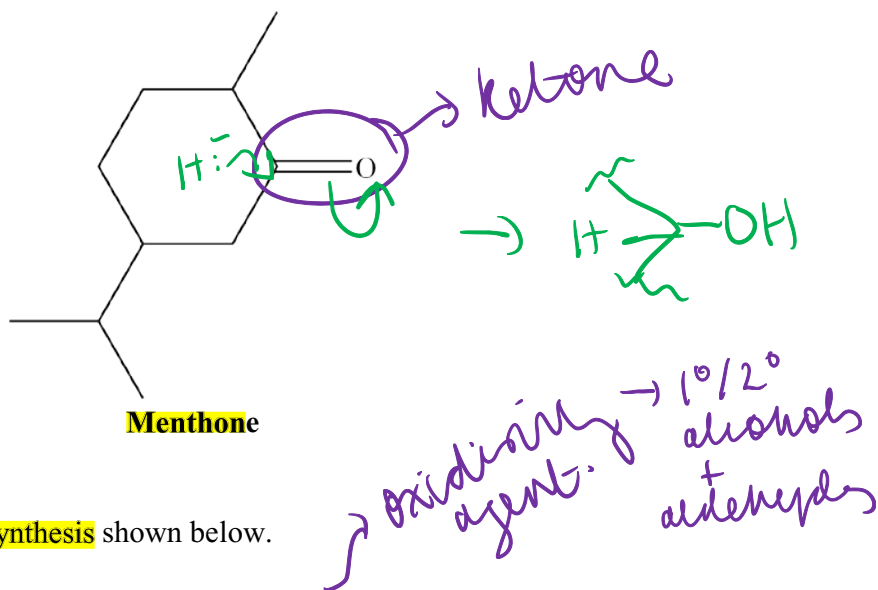
- A It has the molecular formula $C_8H_9NO_2$.
- B It reacts with bases to form salts.
- C It has a ketone functional group.
- D It can be hydrolysed with aqueous acid.

Your answer

C

[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 **NaBH₄** in water.

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

	Step 1	Step 2
<input checked="" type="radio"/> A	Smell of peppermint remains	Smell of peppermint is lost
<input type="radio"/> B	Smell of peppermint is lost	Smell of peppermint returns
<input type="radio"/> C	Smell of peppermint remains	Smell of peppermint remains
<input type="radio"/> D	Smell of peppermint is lost	Smell of peppermint does not return


Your answer

A

[1]

both are planar

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

- 1: Benzene is less reactive than cyclohexene ✓  + Br₂
- 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**

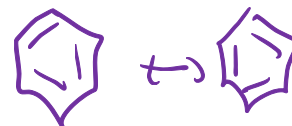
Your answer

D

Delocalised:



Kekulé:

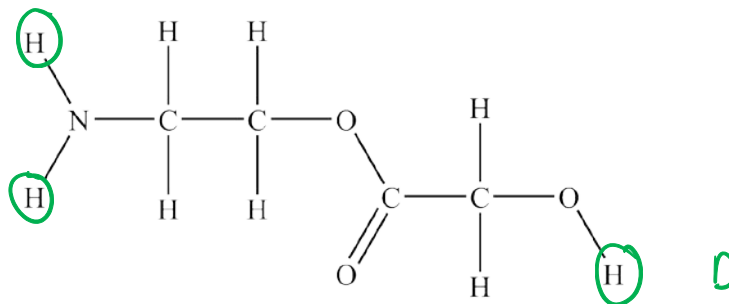


+ Br₂ , AlBr₃
 ↳ less e⁻ dense so
 needs hydrogen
 carrier / catalyst
 to react.

[1]

↳ it's less exo than predicted due to extra stability from the delocalised π e⁻ ring.

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** → 4 C environments
 ✓ 2: The **proton NMR spectrum** of **Z** shows **five peaks** → 5 H environments
 ✓ 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

5 - 2 = 3
 ↓
 O replaces H bonded to O or N so peaks no longer show in the spectrum.

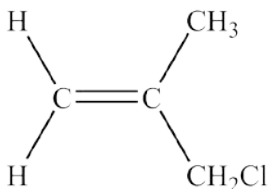
Your answer

A

[1]

SECTION B

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



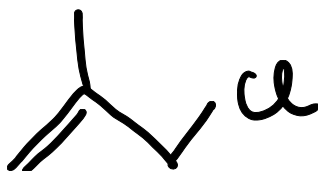
MAC

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



[1]

(ii) Draw the skeletal formula of MAC.



example of skeletal formula showing the C-C backbone. [1]

(iii) MAC has several structural isomers.

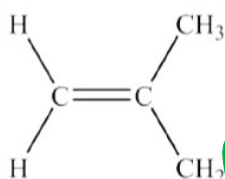
State what is meant by structural isomers.

Compounds with the same molecular formulae 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.



MAC

$n = \frac{100000 \times 1.053 \times 10^{-3}}{8.314 \times 350}$
 $n = 0.0362 \text{ mol}$

$PV = nRT$ $M_r = \frac{m}{n}$

$n = \frac{PV}{RT}$

$\rightarrow 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ (data sheet)

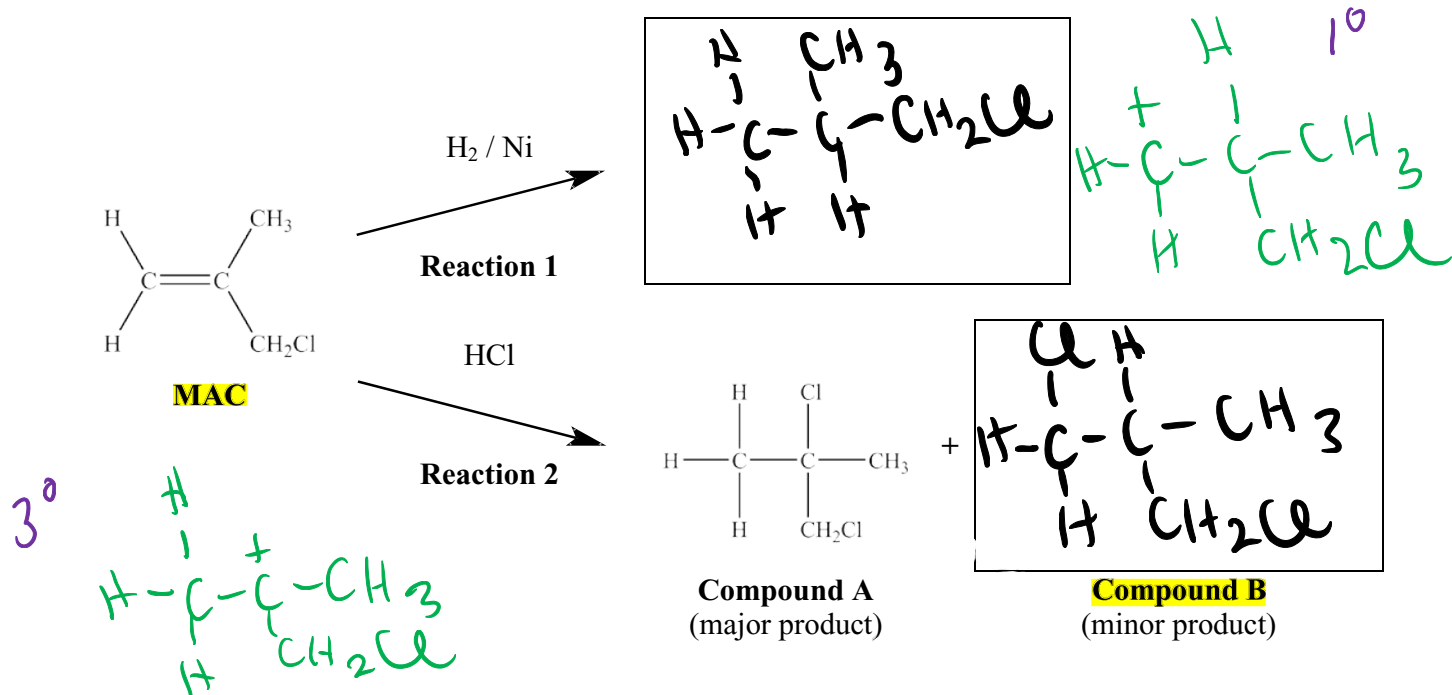
$M_r = \frac{1.321}{0.0362} = 36.5$

$\rightarrow HCl = 1 + 35.5 = 36.5$

gas = HCl [4]

Turn over

(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).

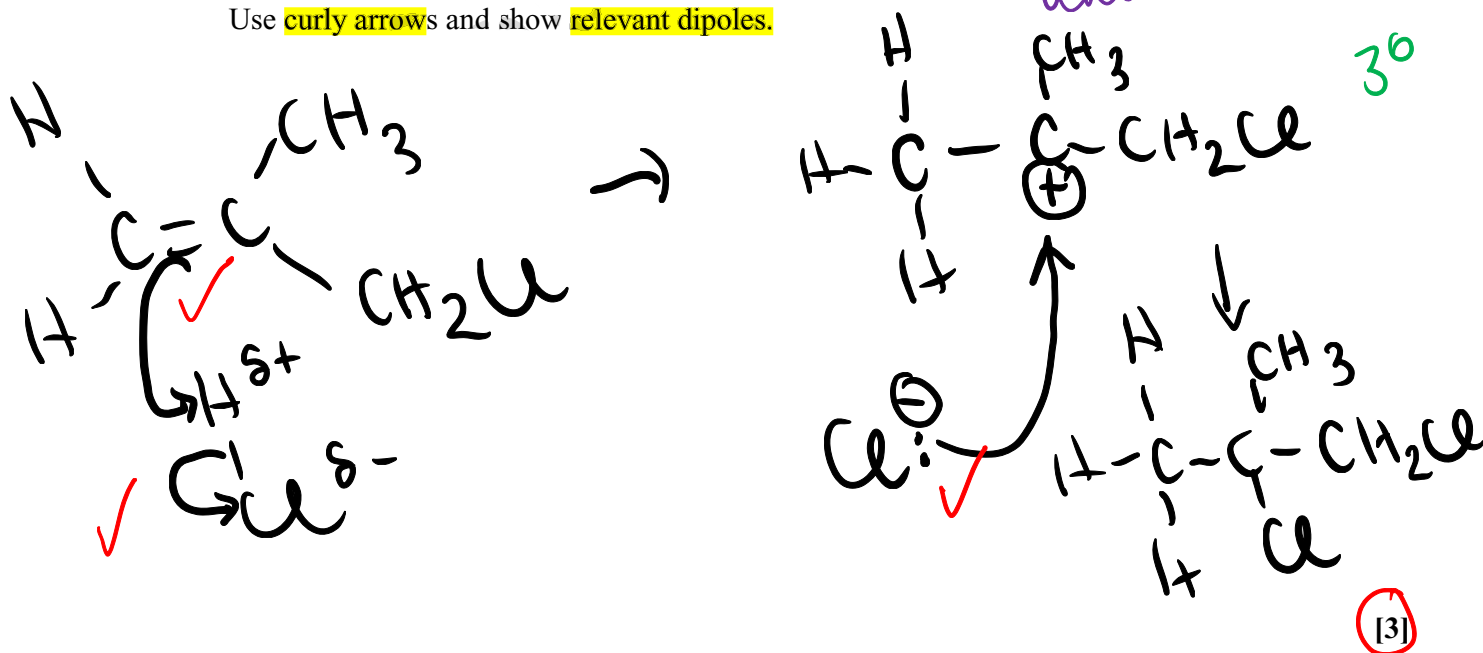
$\curvearrowright = 2e^-$

[2]

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

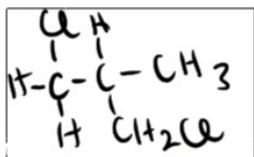
Draw the mechanism for the formation of compound A.

Use curly arrows and show relevant dipoles.



[3]

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



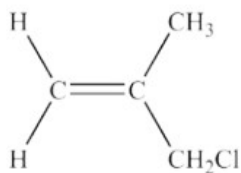
Compound B
(minor product)

Because it had the least stable carbocation intermediate. [1]

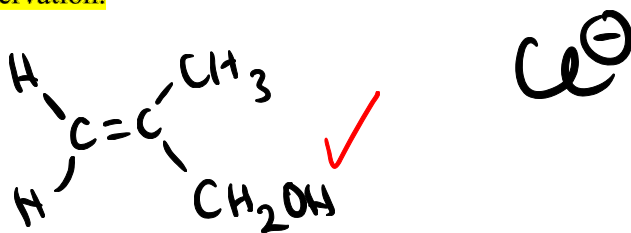
(iv) **MAC** reacts with water in the presence of $\text{AgNO}_3(\text{aq})$ and ethanol.

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**.

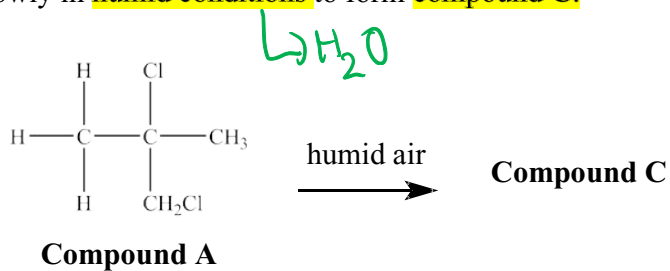


MAC



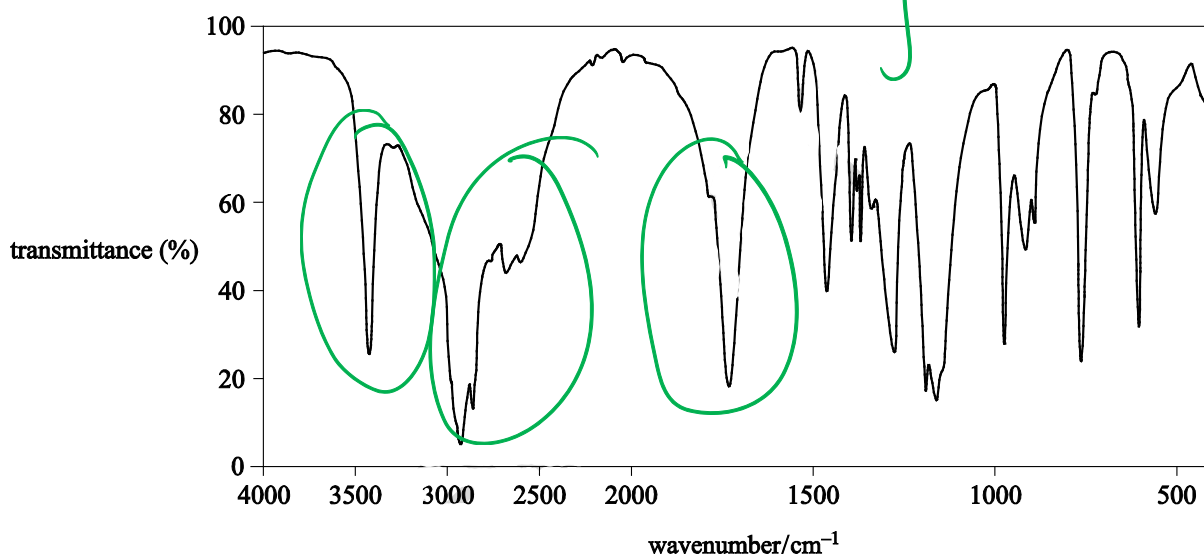
white precipitate $\rightarrow \text{AgCl}(\text{s})$ [2]

(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.

$$n = \frac{m}{A_r}$$

Give your reasoning.

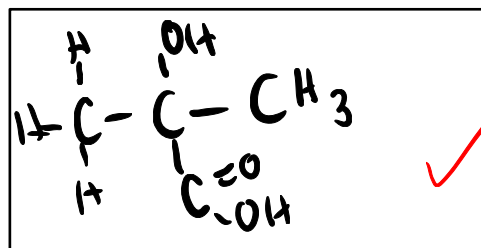
	C	H	O
%	46.1	7.7	46.2
n	$\frac{46.1}{12} = 3.84$	$\frac{7.7}{1} = 7.7$	$\frac{46.2}{16} = 2.89$
ratio	1.33	2.66	1
$\rightarrow \times 3$	4	8	3
	$C_4H_8O_3$		

$3450\text{ cm}^{-1} = \text{OH alcohol}$

$2500 - 3300\text{ cm}^{-1}$ broad absorption



$1640 - 1750\text{ cm}^{-1} = \text{C=O}$



structure =

(15)

17 Molecules with more than one functional group are useful **chemical 'building blocks'**.

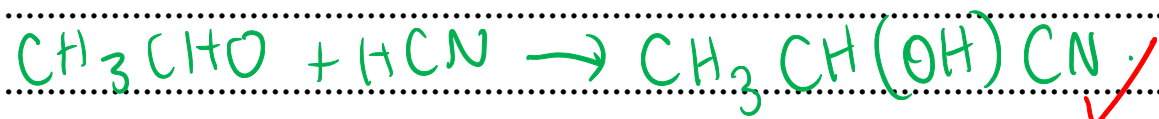
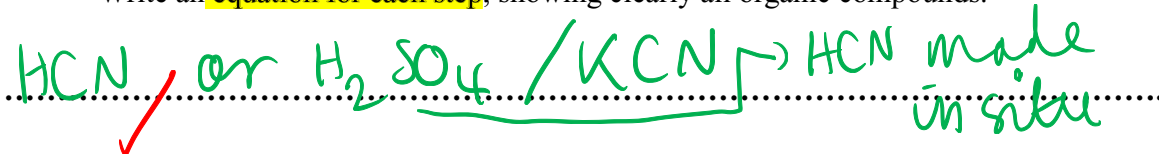
(a) Compound **D**, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{NH}_2$, is an **intermediate** in the synthesis of a variety of drugs.

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

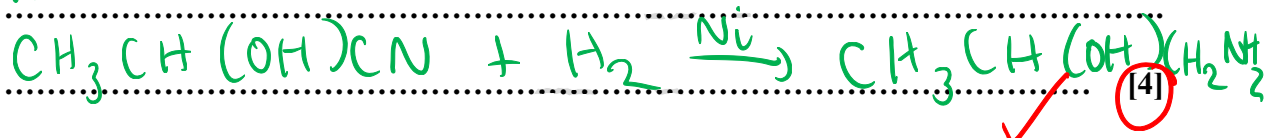
aldehyde
↳ N. addition

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.

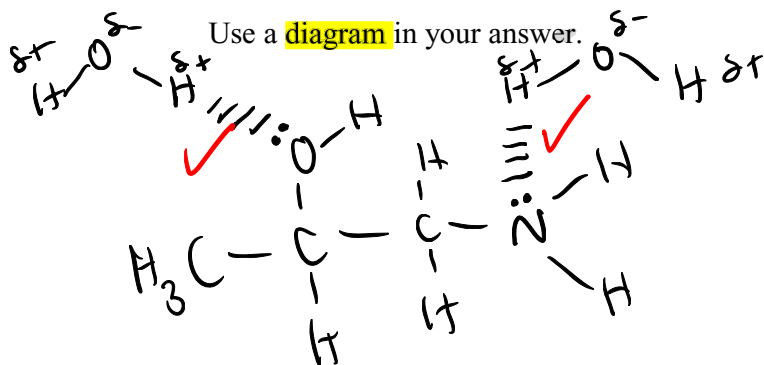


Reduction:



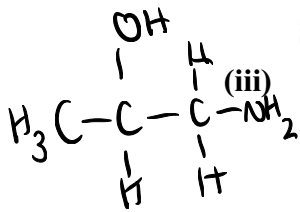
(ii) Explain why **compound D** is very **soluble in water**.

Use a **diagram** in your answer.



$-\text{NH}_2$ and $-\text{OH}$ can form H-bonds with water.

we have 2 groups which can form H-bonds with the water. [3]

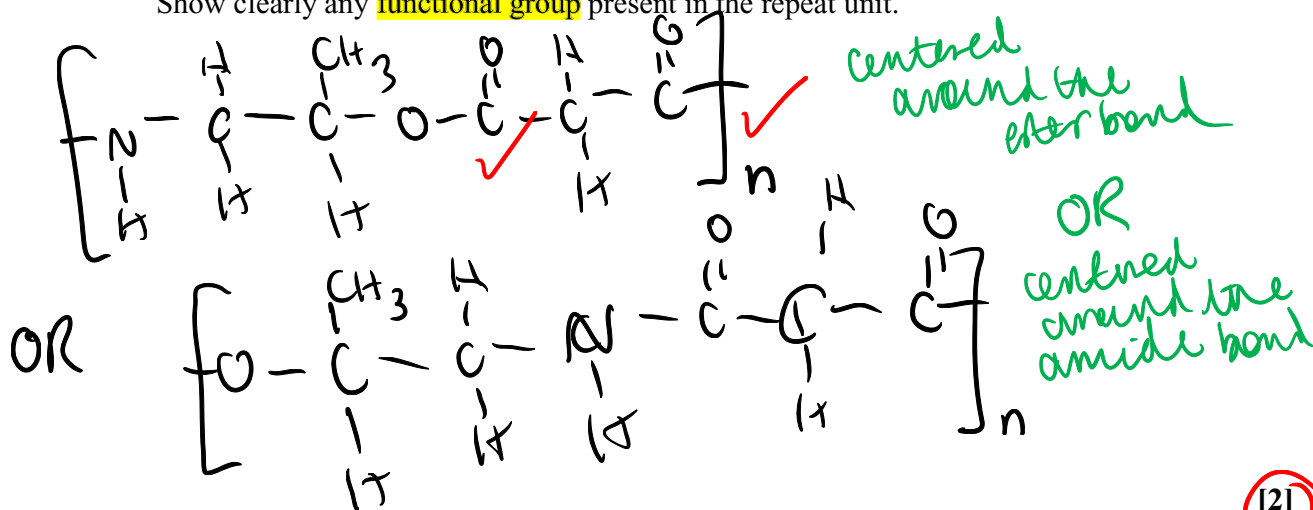


Compound D reacts with propanedioic acid, $\text{HOOCCH}_2\text{COOH}$, to form a condensation polymer.

ester ($\text{OH} + \text{COOH}$)
amide ($\text{NH}_2 + \text{COOH}$)

Draw a possible repeat unit of this condensation polymer.

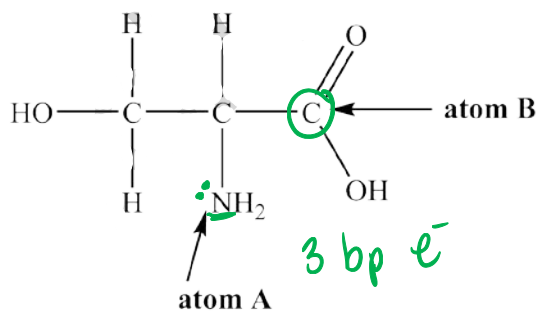
Show clearly any functional group present in the repeat unit.



[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.

A: 3 bonding pairs of e^- , 1 lone pair of e^- ✓
pyramidal, 107° ✓

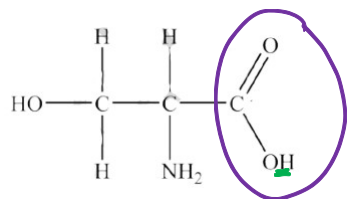
B: 3 bonding regions of e^- , 0 lone pairs of e^- ✓
trigonal planar, 120° ✓

[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**.

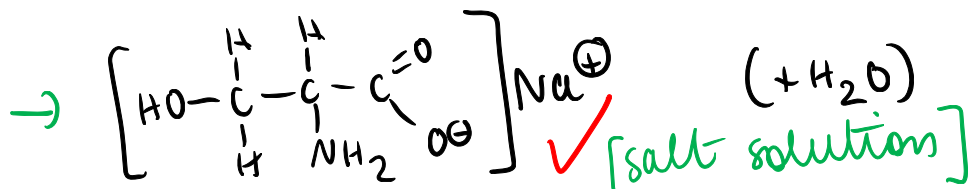
- Draw the **structure** of the **ionic organic compound** obtained.
- Outline the **steps** that the student could carry out to **obtain a pure sample** of the organic product from the reaction mixture.

NaOH



amino acid

ACID + BASE → SALT + WATER

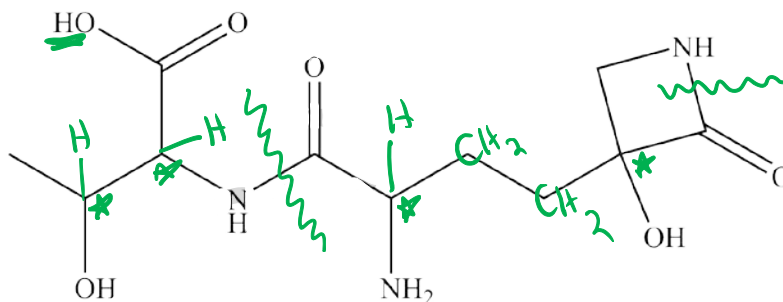


① filter the solution. ✓

② recrystallise ✓

[3]

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



tabtoxin

C with 4 different groups ✓

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

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

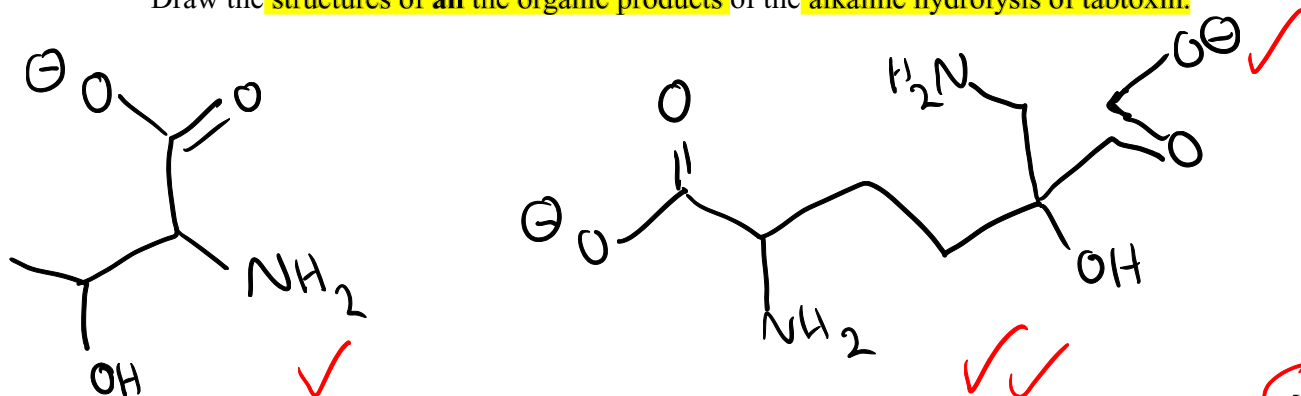
[1]

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

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

2 amide bonds ✓

will hydrolyse ester/amide bonds ✓

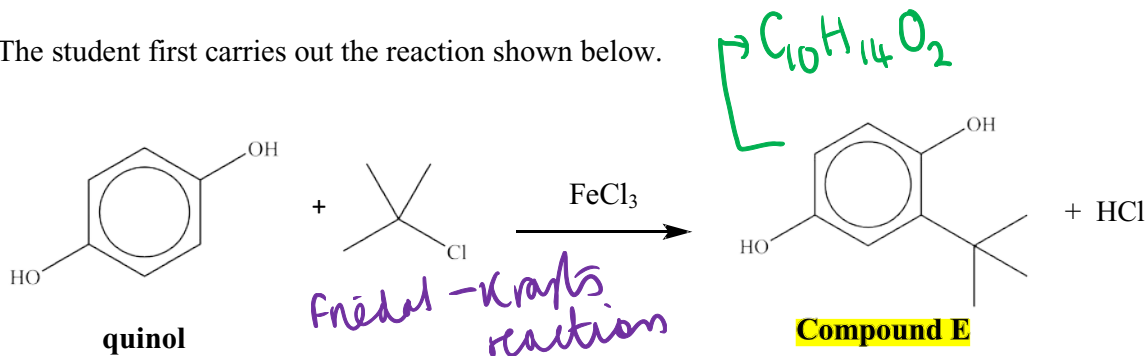


[4]

as the protons from the acid reacts with the alkali ✓

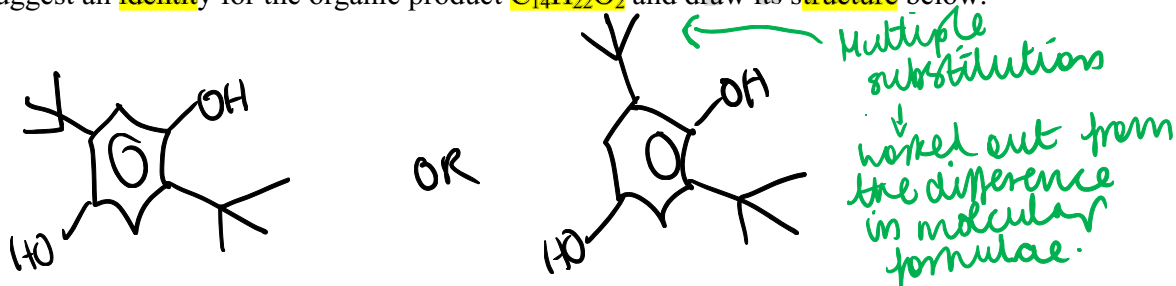
18 A student investigates reactions of **aromatic compounds**.

(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 C₁₄H₂₂O₂**.

Suggest an **identity** for the organic product **C₁₄H₂₂O₂** and draw its **structure** below.

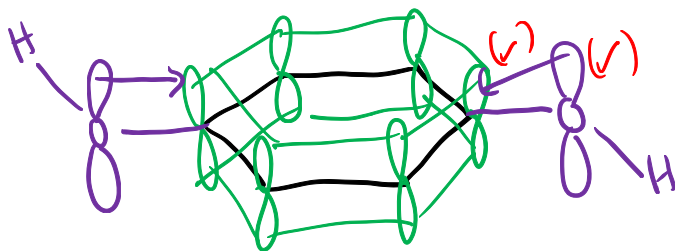
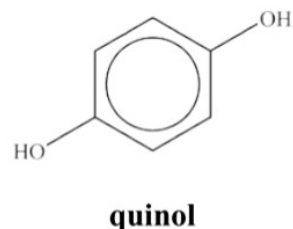


[1]

- (ii) The student is told by a friend that the **FeCl₃ catalyst is not needed** because **quinol is more reactive than benzene**.

Explain why the student's friend is **correct**.

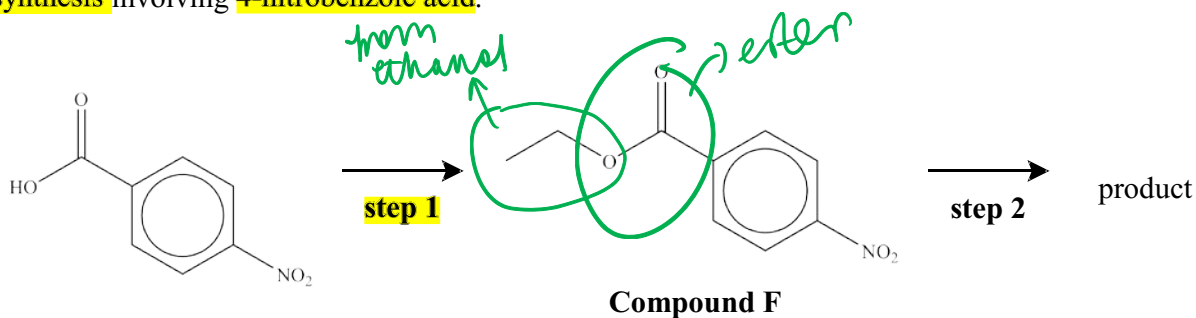
You may draw a **diagram** to support your answer.



.....
 lone pairs of e⁻ on the oxygen (OH in quinol) → partially delocalise into the ring. Adding e⁻ density, the ring ∴ making it more reactive so no catalyst is needed.....
 - ∴ quinol more susceptible to attack from an electrophile (⊕).

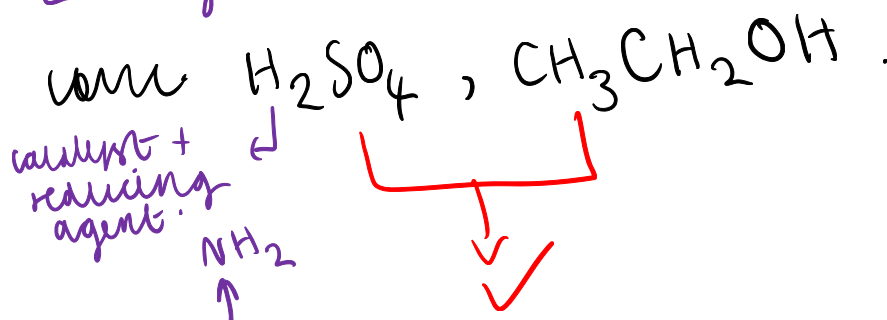
[3]

- (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.

Esterification (carboxylic acid + alcohol)

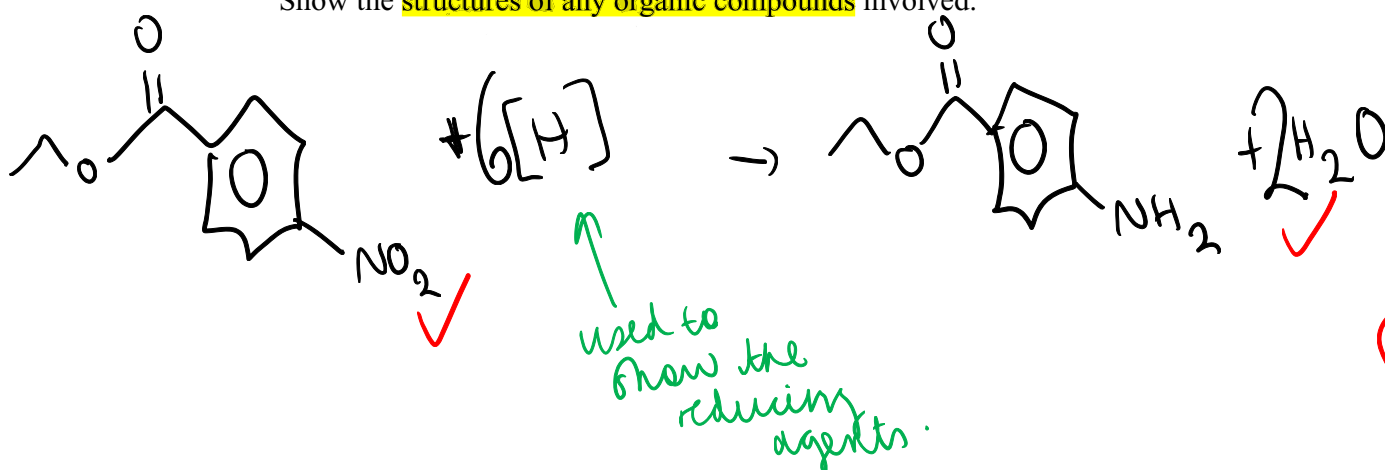


[1]

- (ii) In step 2, the -NO₂ 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.

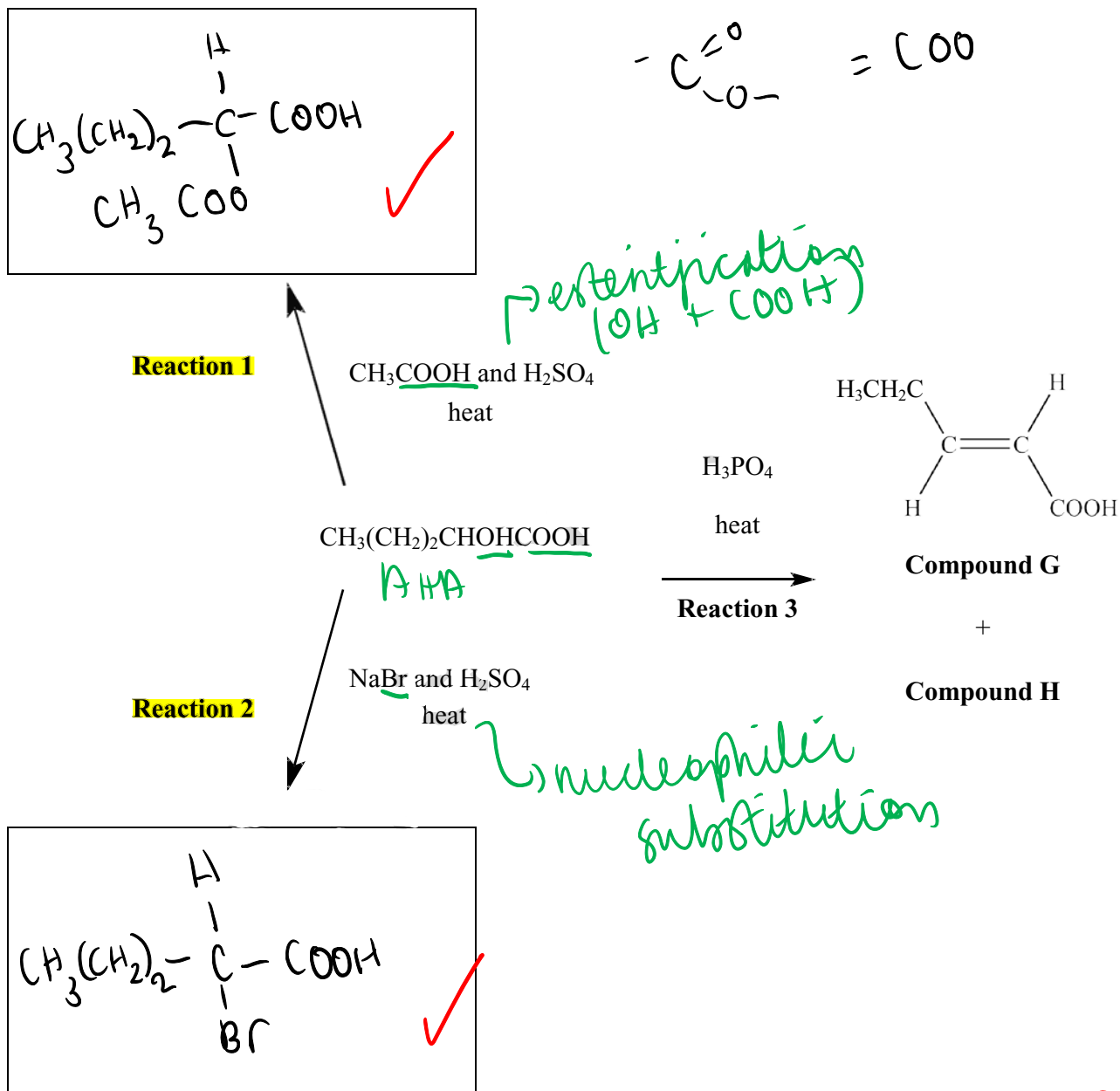


[2]

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

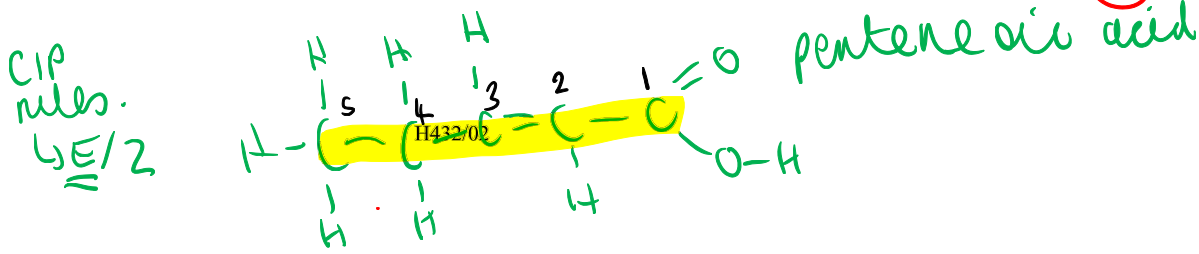
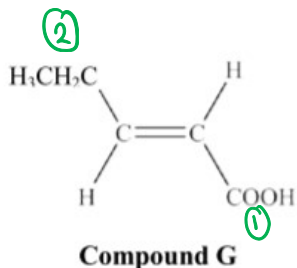
(a) The flowchart below shows some reactions of an AHA, **CH₃(CH₂)₂CHOHCOOH**.

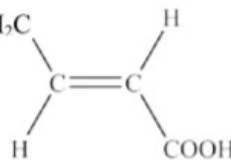
(i) Fill in the boxes to show the **organic products of Reactions 1 and 2**, clearly showing the **relevant functional groups**.



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

(E)-pent-2-enoic acid ✓



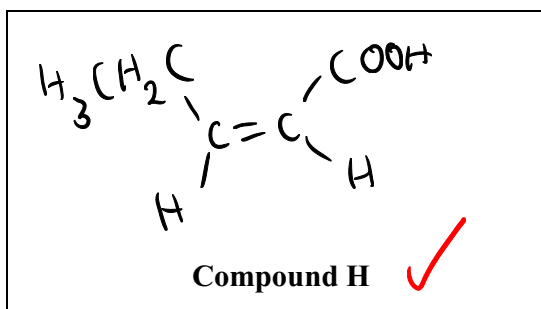


→ E-isomer

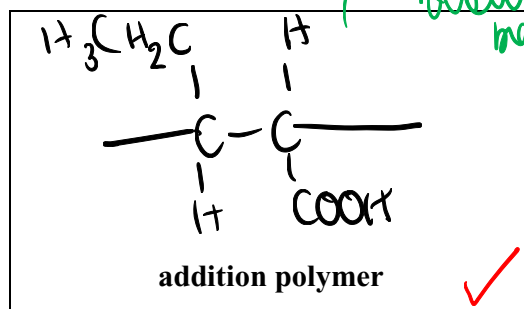
Compound G

(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.



Z-isomer



→ open up the double bond.

[2]

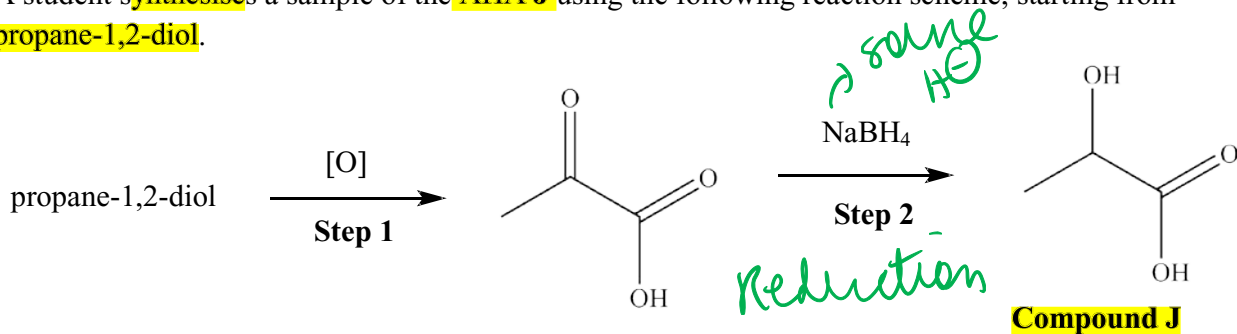
(iv) The addition polymer in (iii) is used widely in industry. Increasingly, waste polymers are being processed as a more sustainable option than disposal.

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

- combustion for energy production ✓
- use as an organic feedstock for the production of plastics/org. chemicals. ✓

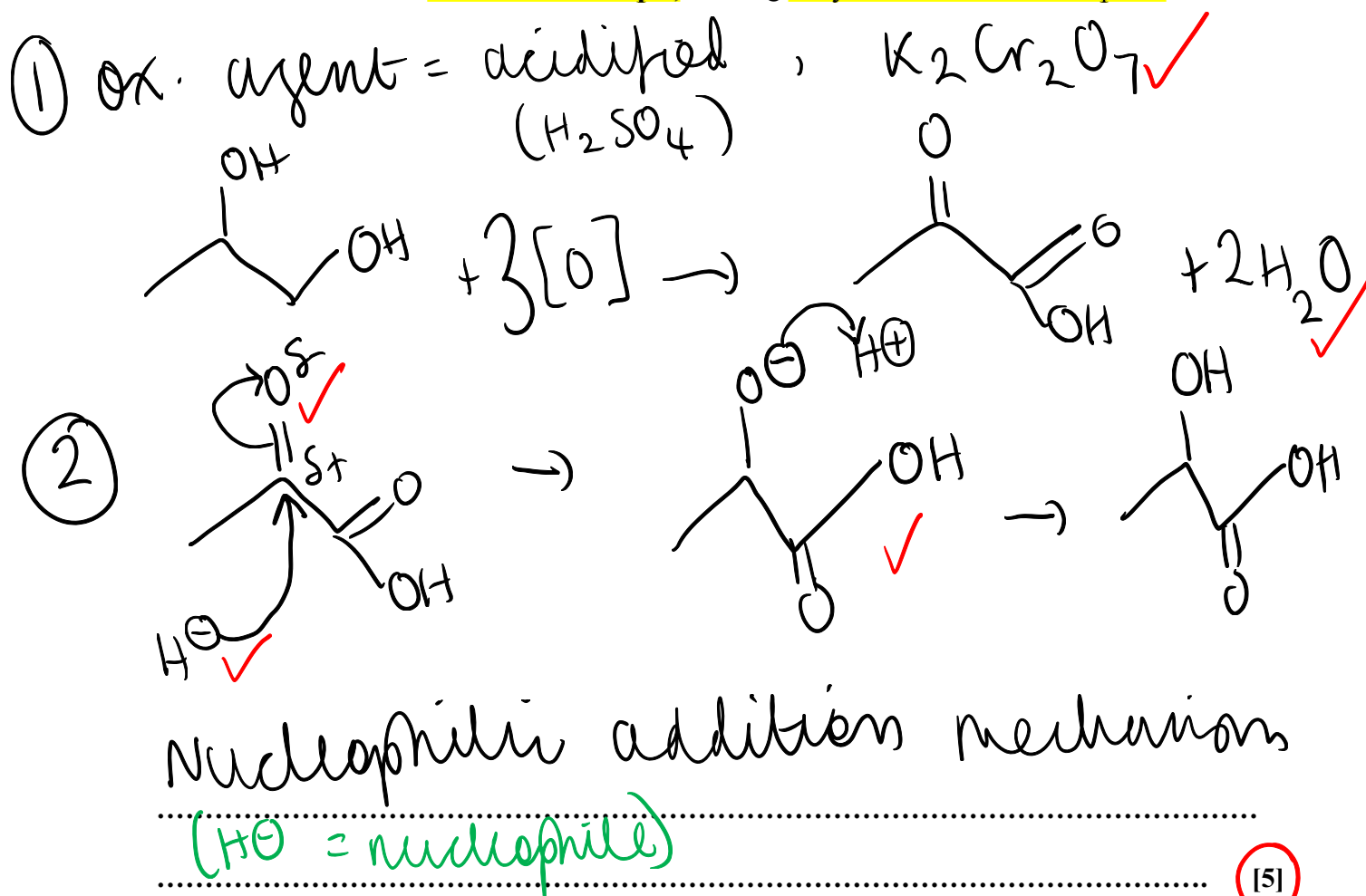
[2]

- (b) A student synthesise 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**.

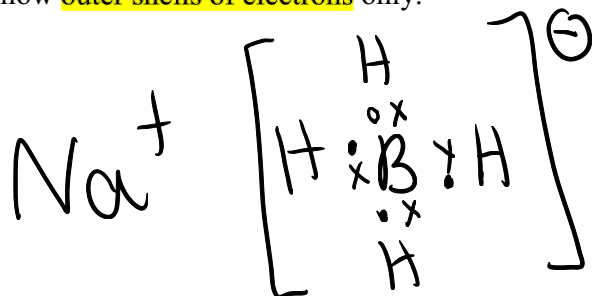


[5]

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

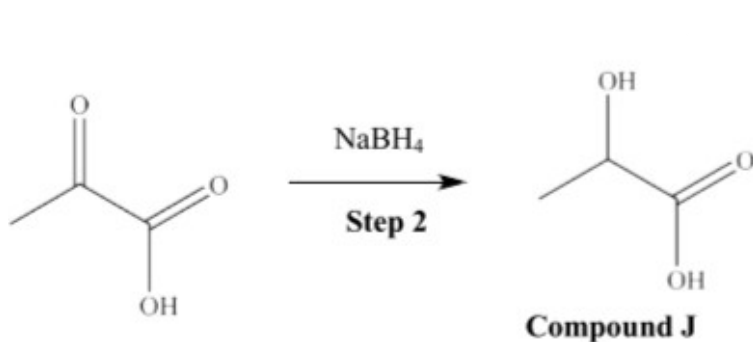
Draw a 'dot-and-cross' diagram of NaBH_4 and give the full electron configuration of Na^+ .

Show outer shells of electrons only.



$\circ = e^-$ from Na
 $\times = e^-$ from H
 $\bullet = e^-$ from B
 3 different symbols needed for the mark.

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



(21)
 $\text{Na } 11e^- : 1s^2 2s^2 2p^6 3s^1$

(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.

<i>76 g mol⁻¹</i>	glycolic acid	<u>HOCH₂COOH</u>
	malic acid	<u>HOOCCH₂CHOHCOOH</u>
	mandelic acid	<u>C₆H₅CHOHCOOH</u>
	pantoic acid	<u>HOCH₂C(CH₃)₂CHOHCOOH</u>

Molar mass (K) needed.

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

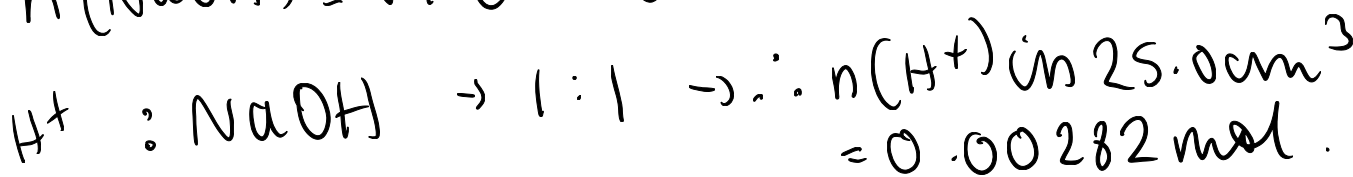
The student dissolves **1.89 g of compound K in water** and makes the **solution up to 250.0 cm³** in a volumetric flask. The student **titrates 25.0 cm³** of this solution with **0.150 mol dm⁻³ NaOH(aq).**

18.80 cm³ of NaOH(aq) were required for **complete neutralisation.**

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

Show **all of your working.**

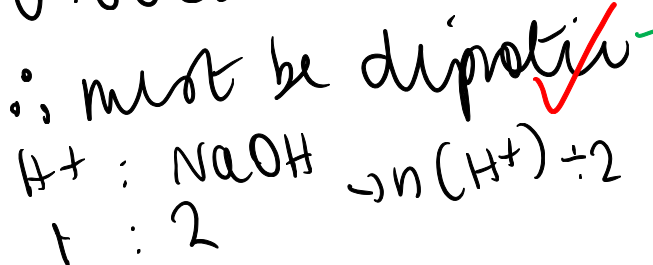
$$n(\text{NaOH}) = v \times c = \frac{18.80}{1000} \times 0.150 = 0.00282 \text{ mol.}$$



$25 \text{ cm}^3 \xrightarrow{\times 10} 250 \text{ cm}^3$
 $0.00282 \times 10 = 0.0282 \text{ mol.}$

$$M_r(\text{K}) = \frac{m}{n} = \frac{1.89}{0.0282} = 67.0 \text{ g mol}^{-1}$$

$\downarrow \times 2$
 134 g mol^{-1}



K = Malic acid (5)

*Because none of the molar masses of the monoprotic acids are 67.
 ↳ only one diprotic acid = malic acid.*

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.

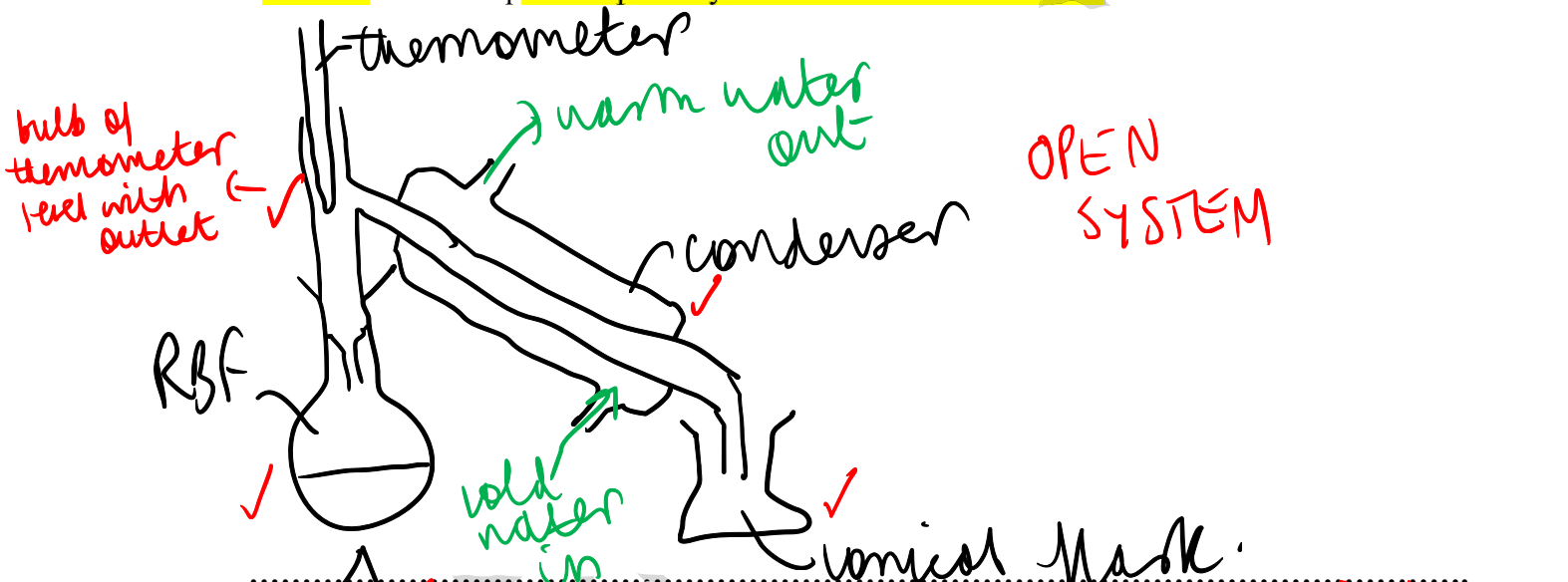
	Boiling point /°C	Density /g cm ⁻³	M _r
Cyclohexanol	161	0.962	100.0
Cyclohexanone	156	0.948	98.0

QWC

water

l

(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.

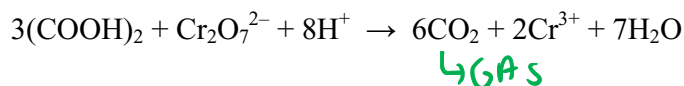


- ✓ Separating funnel (aq. + org. layer)
 - ↳ tap off the layers ✓
- Add a small amount of MgSO₄ to our cyclohexanone (drying agent to remove H₂O)
- Re-distil cyclohexanone, collect fractions distilling at 156°C. ✓

Full marks :- Full, annotated diagrams
 - At least two detailed points describing further purification.

[6]

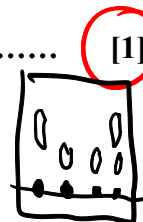
- (b) Ethanedioic acid removes excess dichromate ions, $\text{Cr}_2\text{O}_7^{2-}$, as in the equation below.



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

lack of further effervescence.
(Fading/bubbling 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 on a TLC plate, with cyclohexanone + cyclohexanone control. ✓ (R_f values) [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.

→ cyclohexanone
↓
KETONE

(Brady's reagent)

- Reacting our sample 2,4-DNP → orange ppt. ✓
- Recrystallise the ppt, determine the melting point. ✓ (both points needed for mark)
- Compare the mp to known value for cyclohexanone. ✓

2,4-DNP = 2,4-dinitrophenylhydrazine. [3]

21* A chemist isolates **compound L**, with **empirical formula C₃H₆O**, and sends a sample for analysis. The analytical laboratory sends back the following spectra.

$(12 \times 3) + 6 + 16 = 58$

Mass spectrum

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

$\rightarrow = Mr$
 $\frac{116}{58} = 2 \rightarrow C_6H_{12}O_2$ ✓

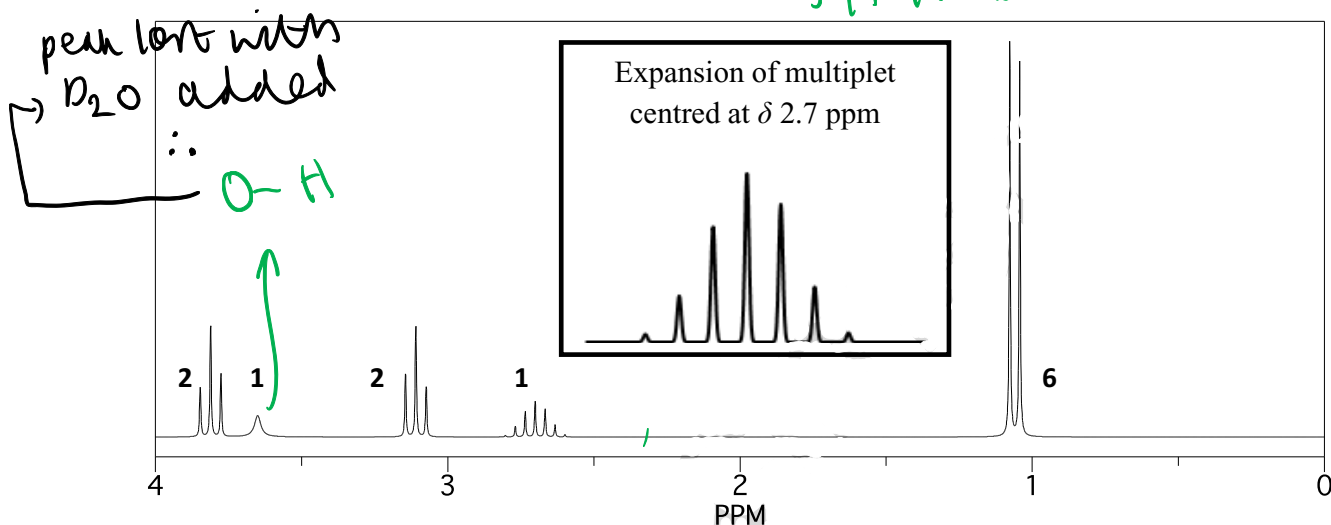
¹H NMR spectra

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

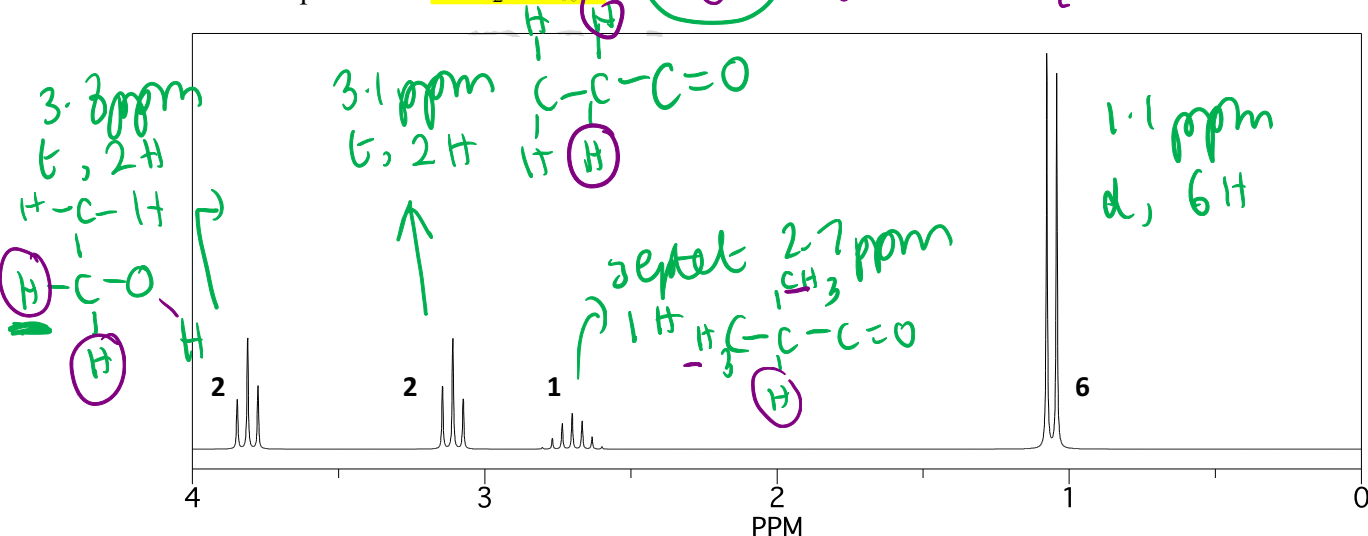
Two ¹H NMR spectra were obtained: one without D₂O and one with D₂O added.

(n+1) rule.
 $\rightarrow \neq$ H bonded to adjacent C.

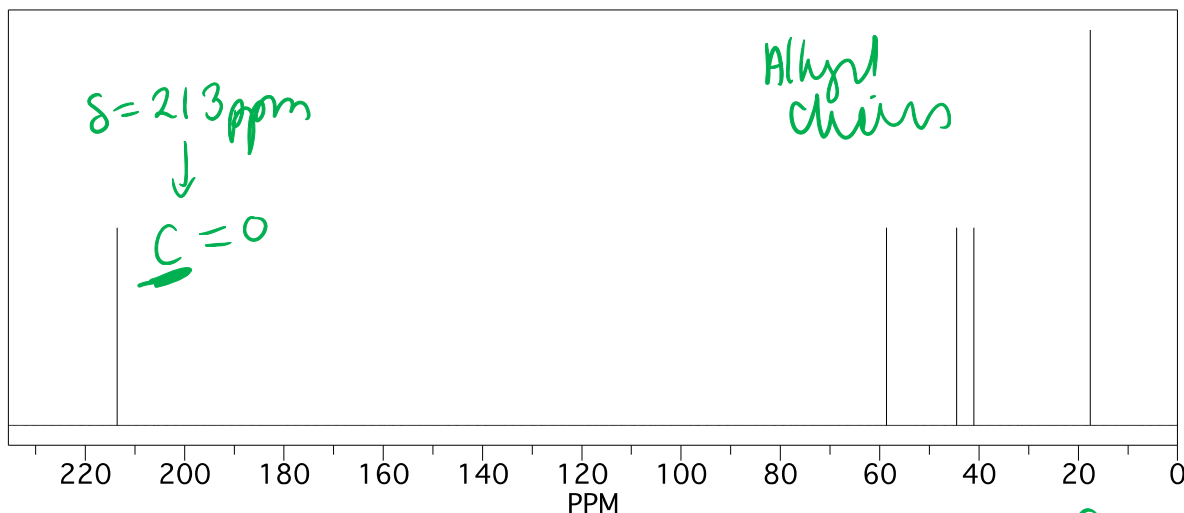
¹H NMR spectrum with **no D₂O**:



¹H NMR spectrum with **D₂O added**:



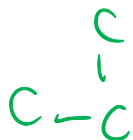
¹³C NMR spectrum:



peaks = # C environments

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

Give your reasoning.



↓
5 peaks

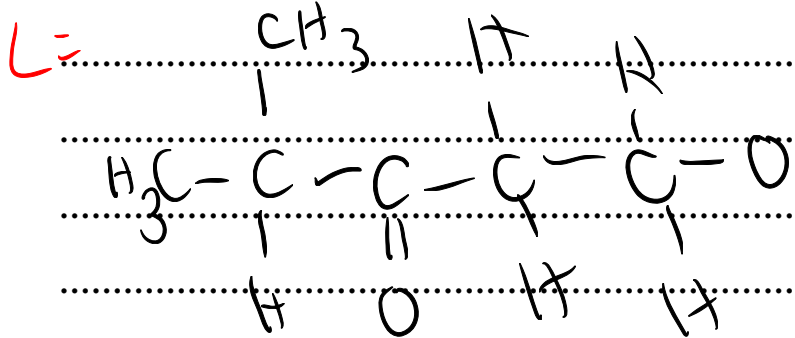
Molecular formula = $\text{C}_6\text{H}_{12}\text{O}_2$ ✓

5 C environments, C=O bond peak

@ 213 ppm (¹³C NMR).

Ketone, no $\delta = 9-10$ ppm

on ¹H NMR (aldehyde).



(H) → peak lost (¹H NMR) added O₂.

- peak environment, splitting, integration needed (shown on previous page) for full marks.

[6]

END OF QUESTION PAPER