EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2024
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	

CIVICS GROUP	2	3	–			INDEX NUMBER		

CHEMISTRY

9729/02

Paper 2 Structured Questions

10 September 2024
2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, civics group, index number on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
Paper 2	
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This document consists of **20** printed pages.

1 This question is about different compounds of chlorine.

(a) Sodium chlorate, $NaClO$, is commonly found in household cleaning products like bleach. It is produced when chlorine, Cl_2, is mixed with sodium hydroxide, NaOH. Both $Cl^-(aq)$ and $ClO^-(aq)$ ions are produced in the reaction.

(i) By writing appropriate reduction and oxidation half equations, write an overall balanced ionic equation for the reaction.

reduction: $Cl_2 + 2e^- \rightarrow 2Cl^-$

oxidation: $Cl_2 + 4OH^- \rightarrow 2ClO^- + 2e^- + 2H_2O$

overall: $Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$

[2]

(ii) Explain, in terms of oxidation numbers, what happens to chlorine in this reaction.

Chlorine had undergone **disproportionation** since it is simultaneously reduced, as the **oxidation number decreases from 0 in Cl_2 to –1 in Cl^-**, and oxidised, as the **oxidation number increases from 0 in Cl_2 to +1 in ClO^-**. [1]

The concentration of ClO^- ions in bleach can be determined by carrying out a redox titration.

25.0 cm^3 of a commercial bleach sample was diluted with deionised water and made up to exactly 250 cm^3 in a volumetric flask. 10.0 cm^3 of the diluted bleach sample was pipetted out into a conical flask and an excess of acidified potassium iodide, KI, was added to it. The solution turns brown as iodine, I_2 was liberated.

$$ClO^- + 2I^- + 2H^+ \rightarrow I_2 + Cl^- + H_2O$$

The mixture obtained in the conical flask was titrated with 0.100 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$, using starch indicator. The average titre for the titration was 14.50 cm^3.

(iii) Calculate the amount of I_2 present in the 10.0 cm^3 diluted bleach sample.

amount of $S_2O_3^{2-}$ used $= \frac{14.50}{1000} \times 0.100 = 0.00145$ mol

$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$, $I_2 \equiv 2S_2O_3^{2-}$,

amount of I_2 in 10.0 cm^3 sample $= \frac{1}{2} \times 0.00145 = 0.000725$ mol

[1]

(iv) Hence, determine the [C*l*O⁻] in the commercial bleach sample.

$I_2 \equiv ClO^-$, amount of ClO^- in 10.0 cm^3 sample = 0.000725 mol

$$[ClO^-] \text{ in diluted sample} = \frac{0.000725}{10/1000} = 0.0725 \text{ mol dm}^{-3}$$

$$[ClO^-] \text{ in commercial bleach sample} = 0.0725 \times \frac{250}{25} = 0.725 \text{ mol dm}^{-3}$$

[2]

(b) Hydrogen chloride, HC*l*, is formed when Cl_2 is mixed with hydrogen gas. HC*l*, like other Group 17 hydrides will decompose at high temperatures.

Describe and explain the trend observed in the ease of decomposition of hydrides of chlorine, bromine and iodine.

When hydrogen halides decomposes, the H–X bond is broken. Down group 17, the **size of halogen atom increase** and **the extent of orbital overlap between H and X atoms decreases.** The bond energy of H–X bond thus decreases, and **less energy is required to break the H–X bond**. Hence, the **ease of decomposition of hydrogen halides increases** down the group. [3]

(c) 2-chlorobutane reacts with sodium hydroxide under different conditions to form four different organic products **B**, **C**, **D** and **E**.

When 2-chlorobutane is warmed with aqueous sodium hydroxide, product **B** is formed.

(i) Name the type of reaction occurring when **B** is formed from 2-chlorobutane.

Nucleophilic substitution [1]

(ii) Describe a simple chemical test to confirm the formation of **B**.

Add **I_2 (aq) and NaOH (aq)** to the test tube and **warm** the mixture. If product **B** is present, brown I_2 will decolourise and **a yellow precipitate of CHI_3 will form**.

[2]

(iii) State and explain the relative rate of reaction of 2-chlorobutane and of 2-bromobutane with NaOH(aq).

The reaction between **2-bromobutane and NaOH will be faster**. The **C–Cl bond is stronger than the C–Br bond**, hence the C–Br bond will be cleaved more easily for the reaction to occur. [1]

Compounds **C**, **D** and **E** are hydrocarbons. **D** and **E** are stereoisomers of each other.

(iv) State the reagents and conditions needed to favour the formation of a mixture of products **C**, **D** and **E**, rather than **B**.

Heating 2-chlorobutane with **ethanolic sodium hydroxide** [1]

(v) Draw the skeletal formulae of **C**, **D** and **E**.

 **C**	 **D**	 **E**

[2]

(d) Chlorinated phenols are good antiseptics.

(i) State and explain how the acidity of a chlorinated phenol might differ from that of phenol itself.

The acidity of phenols depends on the stability of the phenoxide ion. For a chlorinated phenol, as **chlorine is an electron withdrawing group**, it **further disperses/enhances the delocalisation of the negative charge on O into the benzene ring**. The resulting substituted phenoxide ion is **more stabilised**, causing chlorinated phenols to be dissocaited to a greater extent. Hence, a **chlorinated phenol is a stronger acid**. [2]

(ii) Unlike phenols, aliphatic alcohols, ROH, can react with carboxylic acids to form esters.

Explain why aliphatic alcohols can react with carboxylic acids to form esters.

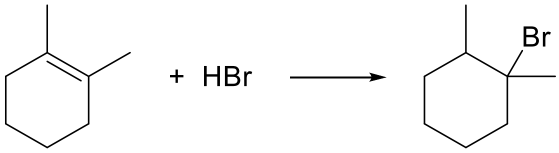
Aliphatic alcohols are stronger nucleophiles than phenols as they have an **electron-donating alkyl group** attached to the –OH group. This makes the **lone pair on O more available for donation** to the acyl C of the carboxylic acid. [1]

[Total: 19]

For Examiner's Use

2 1,2-dimethylcyclohexene can be used as a precursor for the synthesis of various flavour compounds.

When 1,2-dimethylcyclohexene is added to HBr, a reaction occurs.

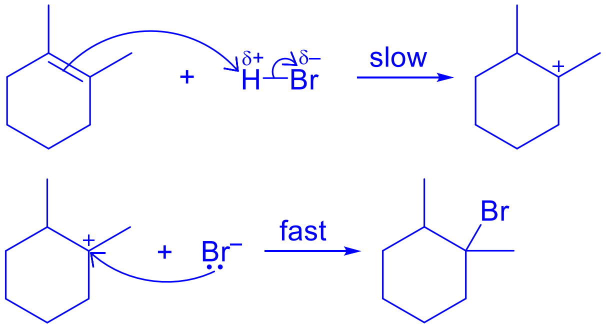


(a) **(i)** Explain why alkenes but not alkanes can react with electrophilic reagents like HBr.

Both alkenes and alkanes are **non-polar**. Alkanes are **saturated** and are thus unreactive towards electrophilic reagents. Alkenes contain the **electron rich π electron cloud in C=C that attracts electrophile**, and the weak π bond breaks easily. [2]

(ii) Describe the mechanism of the reaction, showing curly arrows, charges, dipoles and any relevant lone pairs.

Electrophilic addition



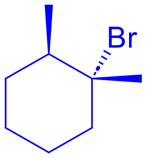
[3]

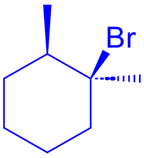
(iii) The product mixture has no effect on the plane of polarised light.

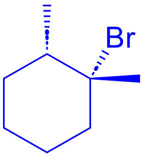
With reference to the mechanism in **(a)(ii)**, explain your reasoning.

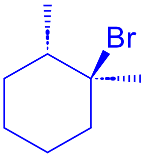
Both the **alkene C=C carbon** and the **carbon carrying the positive charge in the carbocation intermediate is trigonal planar**, there is **equal probability for the electrophile /Br^- anion to attack from either side of the plane**. As a chiral carbon is formed from each step in the mechanism, a **racemic mixture** is thus obtained as equal amounts of each enantiomer are formed. [2]

(iv) The product of this reaction, 1-bromo-1,2-dimethylcyclohexane, exists as a mixture of four stereoisomers.
Draw the structure of each stereoisomer of 1-bromo-1,2-dimethylcyclohexane.



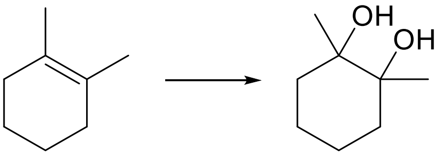






[2]

(b) 1,2-dimethylcyclohexene can be reacted to form **F**.



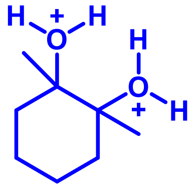
F

(i) State the reagents and condition required for the conversion.

cold $KMnO_4(aq)$, $H_2SO_4(aq)/NaOH(aq)$ [1]

(ii) **F** can undergo acid-base reaction in the presence of a strong acid such as concentrated sulfuric acid.

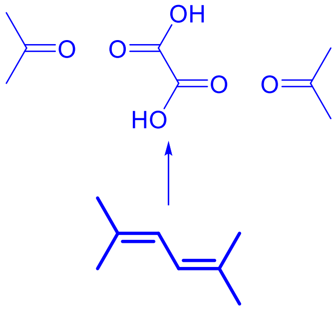
Draw the structure of the species formed when **F** reacts with concentrated sulfuric acid.



[1]

(c) **(i)** **G**, an isomer of 1,2-dimethylcyclohexene, C_8H_{14}, undergoes vigorous oxidation to produce two different organic molecules, $(CO_2H)_2$ and $(CH_3)_2CO$. One of these organic molecules is further oxidised to form CO_2.

Deduce the structure of **G.**



[1]

As CO_2 is produced, it will dissolve in the water to form a buffer mixture made up of H_2CO_3 and HCO_3^-.
This buffer is responsible for controlling the pH in blood.

(ii) Write an equation to show how the buffer system in blood helps to control pH when small amounts of OH^- ions are added to it.

$H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$ .... [1]

(iii) The pH of the human blood plasma is usually maintained at about 7.4. At this pH, the $[HCO_3^-]/[H_2CO_3]$ ratio is 20:1.
Calculate the K_a of carbonic acid.

$$\mathrm{pH} = \mathrm{p}K_a + \lg\frac{[\text{salt}]}{[\text{acid}]}$$
$$7.4 = \mathrm{p}K_a + \lg 20$$
$$\mathrm{p}K_a = 6.7$$
$$K_a = 7.96 \times 10^{-7}\ \text{mol dm}^{-3}$$

or

$$K_a = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$
$$= 10^{-7.4} \times \frac{20}{1}$$
$$= 7.96 \times 10^{-7}\ \text{mol dm}^{-3}$$

[1]

(iv) The concentration of H_2CO_3 is 0.05 mol dm^{-3} in the blood plasma.

50.0 cm^3 of 0.0100 mol dm^{-3} H_2SO_4 is added to 100 cm^3 of blood plasma.

Calculate $[HCO_3^-(aq)]$ in this solution. Show your working. Assume H_2SO_4 is fully ionised.

$$\text{Amt. of H}^+ = \frac{50}{1000} \times 0.0100 \times 2$$
$$= 0.00100 \text{ mol}$$

$$\text{Amt. of HCO}_3^- \text{ before addition of acid} = 0.05 \times 20 \times \frac{100}{1000}$$
$$= 0.100 \text{ mol}$$
$$\text{Amt. of HCO}_3^- \text{ after addition of acid} = 0.100 - 0.00100$$
$$= 0.0990 \text{ mol}$$

$$[\text{HCO}_3^-] = \frac{0.0990}{\left(\frac{150}{1000}\right)}$$
$$= 0.660 \text{ mol dm}^{-3}$$

[3]

(v) $Ca(OH)_2(aq)$ is used to detect the presence of carbon dioxide. The solubility product of $Ca(OH)_2$ is 5.62 x 10^{-6} mol^3 dm^{-9}.

Calculate the pH of a saturated solution of $Ca(OH)_2$ at 25°C.

Let solubility be x mol dm^{-3}.

K_{sp} of $Ca(OH)_2$ = $[Ca^{2+}][OH^-]^2$

$5.62 \times 10^{-6} = (x)(2x)^2$

$4x^3 = 5.62 \times 10^{-6}$

$x = 1.12 \times 10^{-2}$

Solubility of $Ca(OH)_2$ = 1.12×10^{-2} mol dm^{-3}

$[OH^-] = 2 \times 1.12 \times 10^{-2} = 2.24 \times 10^{-2}$ mol dm^{-3}

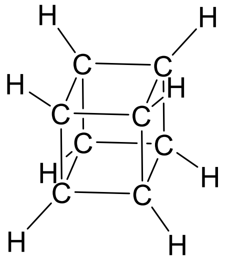
pH = $14 - \lg(2.24 \times 10^{-2}) = 12.3$

[3]

[Total: 20]

For Examiner's Use

3 **(a)** Cubane, C_8H_8, is a solid alkane under standard conditions with an interesting structure as shown.



cubane

The cubane molecule was first synthesised in 1964 by Dr. Philip Eaton. Before its synthesis, researchers believed that cubic carbon-based molecules could only exist in theory as the bonds in cubane are strained.

(i) Define the term bond energy.

Bond energy is the **average energy required** to break **1 mole** of **a covalent bond** between two atoms in the **gaseous state**. [1]

(ii) Using the data given in Table 3.1, as well as information from the *Data Booklet*, calculate $\Delta H^\ominus_{\text{reaction 1}}$.

Table 3.1

standard enthalpy change of atomisation, $\Delta H^\ominus_{\text{at}}$ (C(s))	+715 kJ mol^{-1}
standard enthalpy change of sublimation, $\Delta H^\ominus_{\text{sublimation}}(C_8H_8(s))$	+554 kJ mol^{-1}
standard enthalpy change of formation, $\Delta H^\ominus_f$ $(C_8H_8(s))$	+633 kJ mol^{-1}

$C_8H_8(g) \rightarrow 8C(g) + 8H(g)$ $\Delta H^\ominus_{\text{reaction 1}}$

$$\begin{tikzcd}
C_8H_8(g) \arrow[r, "\Delta H^\ominus_{\text{reaction 1}}"] & 8C(g) + 8H(g) \\
C_8H_8(s) \arrow[u, "\Delta H^\ominus_{\text{sublimation}} = +554"] & 8C(s) + 4H_2(g) \arrow[l, "\Delta H^\ominus_f = +633"] \arrow[u, "{\begin{array}{l}8\Delta H^\ominus_{\text{at}}(C(s)) + 4B.E.(H\text{–}H) \\ = 8(+715) + 4(+436)\end{array}}"']
\end{tikzcd}$$

$$\Delta H^\ominus_{\text{reaction 1}} = -(+554) - (+633) + 8(+715) + 4(+436)$$
$$= +6280 \text{ kJ mol}^{-1}$$

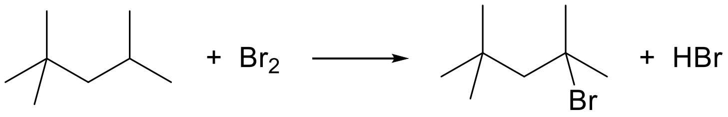
[2]

(iii) With reference to **(a)(ii)**, as well as information from the *Data Booklet*, calculate the C−C bond energy in cubane.

$$\Delta H^{\ominus}_{\text{reaction 1}} = 12\text{B.E.}(\text{C–C}) + 8\text{B.E.}(\text{C–H})$$
$$+6280 = 12\text{B.E.}(\text{C–C}) + 8(+410)$$
$$\text{B.E.}(\text{C–C}) = +250 \text{ kJ mol}^{-1}$$

[1]

(b) Similar to cubane, 2,2,4-trimethylpentane is another eight-carbon alkane. Bromination of 2,2,4-trimethylpentane produces a mixture of four different monobromoalkanes, **W**, **X**, **Y** and **Z**. Reaction of bromine with the alkane to form **W** is shown.



2,2,4-trimethylpentane **W**

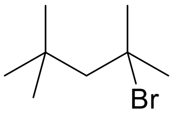
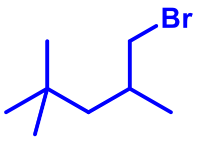
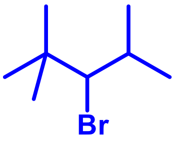
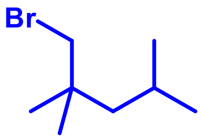
(i) Name the type of reaction between 2,2,4-trimethylpentane and bromine to form **W**.

Free-radical substitution .... [1]

(ii) The relative proportion of the four monobromoalkanes **W**, **X**, **Y** and **Z** is given in Table 3.2, assuming that the rate of substitution of any hydrogen atom in 2,2,4-trimethylpentane are equal.

Draw the structures of **X**, **Y** and **Z** in Table 3.2.

Table 3.2

structure	relative proportion	structure	relative proportion
 **W**	1	 **Y**	6
 **X**	2	 **Z**	9

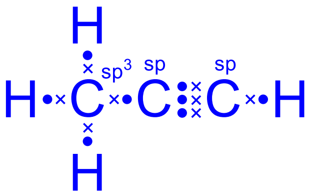
[3]

For Examiner's Use

(c) In the cracking of propane, a side product, C_3H_4, is formed.

Draw the dot-and-cross diagram of a non-cyclic isomer of C_3H_4 that contains **only one** sp^3 hybridised carbon.

Label clearly the hybridisation of all the three carbon atoms on the diagram.



[2]

(d) A Latimer diagram is a compact way to represent the standard reduction potentials of different oxidation states of an element. These diagrams show the sequential reduction potentials starting from the highest oxidation state and moving towards the lowest.

Chlorine has different oxidation states and exhibits different electrochemical behaviors in acidic and basic conditions. The Latimer diagrams for chlorine under both acidic and basic conditions are as shown.

Acidic conditions:

$$\underset{+7}{ClO_4^-} \xrightarrow{+1.19V} \underset{+5}{ClO_3^-} \xrightarrow{+1.18V} \underset{+3}{HClO_2} \xrightarrow{+1.64V} \underset{+1}{HOCl} \xrightarrow{+1.63V} \underset{0}{Cl_2} \xrightarrow{+1.36V} \underset{-1}{Cl^-}$$

Basic conditions:

$$\underset{+7}{ClO_4^-} \xrightarrow{+0.17V} \underset{+5}{ClO_3^-} \xrightarrow{+0.35V} \underset{+3}{ClO_2^-} \xrightarrow{+0.59V} \underset{+1}{ClO^-} \xrightarrow{+0.42V} \underset{0}{Cl_2} \xrightarrow{+1.36V} \underset{-1}{Cl^-}$$

(i) Explain the relative oxidising strengths of ClO_4^- under acidic and basic conditions, using the given $E^\ominus$ values in the Latimer diagram.

The oxidising strengths of chlorine species are **generally higher under acidic conditions** compared to basic conditions as ClO_4^- has a **more positive standard electrode potential** (of +1.19 V) under acidic conditions than that under basic conditions (+0.17 V). [2]

(ii) Explain why $E^\ominus(Cl_2/Cl^-)$ is the same under both acidic and basic conditions.

H^+ / OH^- is not involved in the reduction of Cl_2.

[1]

(iii) Calculate $\Delta G^\ominus$ for the disproportionation reaction of ClO_2^- in the basic medium and state whether it is spontaneous.

$$2ClO_2^- \rightarrow ClO_3^- + ClO^-$$

In basic medium, $E^\ominus_{cell}$ for disproportionation = 0.59 – 0.35 = +0.24V

$\Delta G^\ominus = -nFE^\ominus_{cell} = -2(96500)(+0.24) = -46320 \text{ J mol}^{-1} = -46.3 \text{ kJ mol}^{-1}$

Therefore the disproportionation is spontaneous.

[2]

(e) Mohr's titration is a method used to determine the concentration of chloride ions in a solution. In this titration, 25.0 cm^3 of chloride solution sample is added with 1.00 cm^3 of 1.00 mol dm^{-3} K_2CrO_4 indicator before titrating with 0.100 mol dm^{-3} $AgNO_3$ solution using. The end-point of the titration is marked by the formation of a red-brown precipitate of Ag_2CrO_4.

The relevant K_{sp} of the sparingly soluble salts are as shown.

compound	K_{sp}
$AgCl$	1.77×10^{-10}
Ag_2CrO_4	1.12×10^{-12}

(i) State the observation in the conical flask when the first few drops of titrant were added.

White precipitate is formed in the yellow solution. [1]

(ii) The $[Ag^+]$ remaining in the solution is 1.40×10^{-5} mol dm^{-3} after adding 12.00 cm^3 of $AgNO_3$ to the conical flask.

Calculate the concentration of CrO_4^{2-} ions in the solution after the addition of $AgNO_3$.

Hence, determine whether the red-brown precipitate is observed.

$$[CrO_4^{2-}] = \frac{1.00 \times \frac{1}{1000}}{\frac{25+12+1}{1000}} = 0.0263 \text{ mol dm}^{-3}$$

ionic product = $[Ag^+]^2[CrO_4^{2-}] = (1.40 \times 10^{-5})^2(0.0263) = 5.16 \times 10^{-12} > K_{sp}$

Hence, the red-brown precipitate is observed.

[2]

(iii) Mohr's titration should be carried out under conditions of pH 6.5–9.

Suggest a reason to account for why the pH cannot be higher than 9.

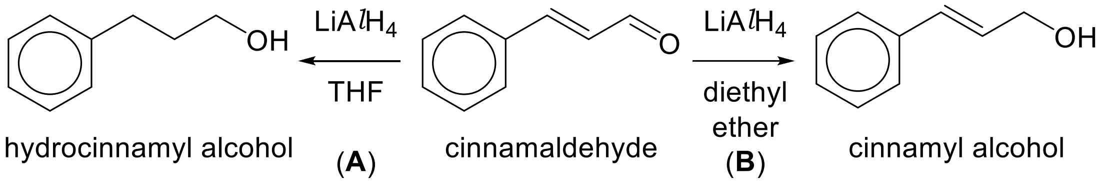
If pH is high, **Ag^+ will be precipitated out** (as Ag_2O).

As a result, the end-point with the formation of the reddish-brown precipitate cannot be accurately determined/titre value cannot be accurately determined. [1]

[Total: 19]

For Examiner's Use

4 It is possible to control the reactivity in $LiA\mathit{l}H_4$ reduction by altering the mode of addition. This can be demonstrated by the reduction of cinnamaldehyde to either hydrocinnamyl alcohol or cinnamyl alcohol as described below.



Data about the compounds including the two solvents, diethyl ether and THF, are given in Table 4.1.

Table 4.1

compound	melting point$^{\Delta}$ / °C	boiling point$^{\Delta}$ / °C	density / g cm^{-3}	M_r	solubility in water
cinnamaldehyde	–7.5	248	1.05	132	slightly
cinnamyl alcohol	33	250	1.04	134	slightly
hydrocinnamyl alcohol	–18	235	1.04	136	slightly
$LiA\mathit{l}H_4$	150*	–	0.917	38	react
THF	–108	66	0.89	72	soluble
diethyl ether	–116	35	0.71	74	slightly

* decomposes $^{\Delta}$ under atmospheric pressure

Procedure **A** : **Reduction of cinnamaldehyde to hydrocinnamyl alcohol**

<u>Synthesis</u>

1. Dry, in an oven, a three-necked flask, an addition funnel and a condenser.
2. Weigh out 2.9 g (0.0763 mol) of $LiA\mathit{l}H_4$ and introduce it into the three-necked flask.
3. Add in 20 cm^3 of dry THF and quickly fit a stirrer, condenser and addition funnel and set up the apparatus as in Fig. 4.1.
4. Pass a stream of purified argon gas into the reaction flask, switch on the stirrer and heat the flask to a gentle boil.
5. From the addition funnel add a solution of 5 g cinnamaldehyde (0.0379 mol) in dry THF very slowly to maintain the gentle boil.

<u>Isolation</u>

6. When the reaction is completed, cool the flask in an ice bath and cautiously add saturated aqueous sodium sulfate dropwise to the stirred reaction mixture.
7. Add aqueous sulfuric acid.
8. Shake the resultant mixture with diethyl ether in a separating funnel and separate the aqueous layer from the organic layer. Reject the aqueous layer.
9. Add anhydrous calcium chloride to the organic layer.

<u>Purification</u>

10. Filter and evaporate the solvent under reduced pressure and distil the residual oil under reduced pressure. Isolate the hydrocinnamyl alcohol (boiling point 120–121 °C under reduced pressure).

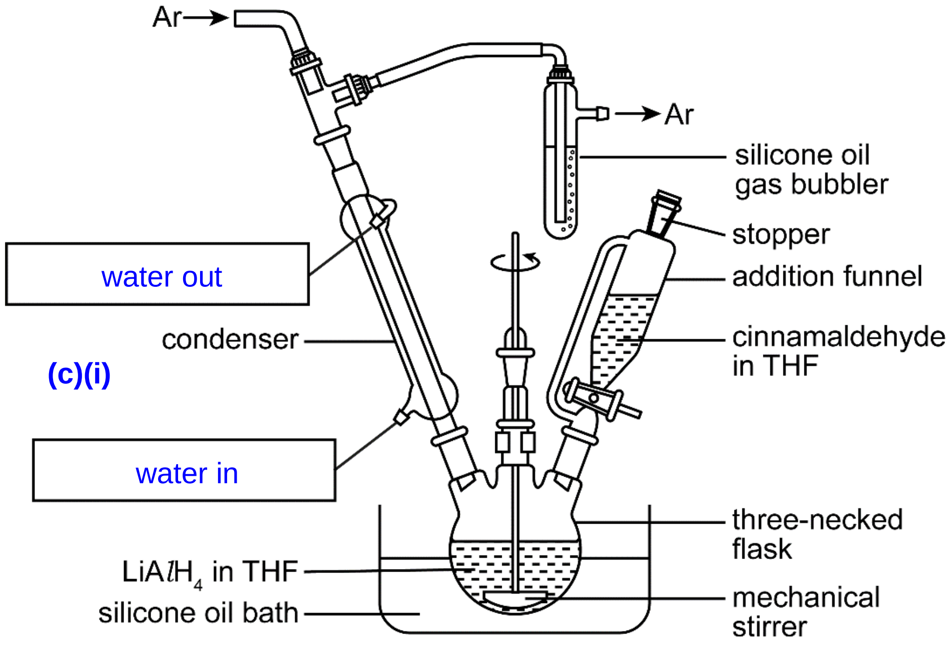


Fig. 4.1

(a) Explain why the apparatus and solvent used must be dried.

$LiAlH_4$ is **highly moisture sensitive** and is destroyed by **reaction with water**. [1]

(b) **(i)** Suggest the purpose of passing purified argon gas into the reaction flask.

To maintain a **moisture-free, inert atmosphere** within the reaction vessel. [1]

(ii) Suggest a function of the silicone oil gas bubbler.

- **Prevent air/moisture** from **getting into** the reaction **vessel**, if there were an under pressure in the reaction vessel (such as when heat is removed).
- **Visibly confirm** that the **system is being flushed** with argon gas.
- **Prevent built up of pressure** within the vessel, while preventing air/moisture from getting into the reaction vessel. [1]

(c) **(i)** Label the direction of "water in" and "water out" for the condenser, in the two boxes in Fig. 4.1. [1]

(ii) Suggest why the solution of cinnamaldehyde in THF must be added slowly in step 5 to maintain the gentle boil.

The reaction between $LiAlH_4$ and cinnamaldehyde is **highly exothermic**.

If the solution is added too quickly, a **large amount of heat** will be generated which can cause the **low boiling THF solvent** to vaporise too quickly / **explosion** / **decompose the $LiAlH_4$ and the desired product**. [2]

(d) With reference to Table 4.1, explain why diethyl ether is used to extract the organic compounds from the mixture in step 8 instead of THF.

As THF is **miscible with water / soluble in water**, it is **not possible to extract** the organic compounds into THF and **obtain two separate layers**. [1]

(e) State the purpose of adding the anhydrous calcium chloride in step 9.

As water is slightly soluble in diethyl ether, the anhydrous calcium chloride serves to **remove residual water from the solvent extract**. [1]

(f) Suggest why the residual oil is distilled under reduced pressure to isolate pure hydrocinnamyl alcohol, rather than under atmospheric pressure.

The high boiling point of over 200 ºC under atmospheric pressure would require **heating the residual oil to a high temperature**, which would lead to possible **decomposition of the desired product**. [1]

(g) Describe a simple chemical test to show the **absence** of cinnamaldehyde in the distillate obtained.

Dissolve the distillate in a little THF and add **2,4-dinitrophenylhydrazine**. The **absence of an orange precipitate** confirms the absence of unreacted cinnamaldehyde. [2]

Procedure **B** : **Reduction of cinnamaldehyde to cinnamyl alcohol**

Synthesis

1. Dry, in an oven, a three-necked flask, an addition funnel and a side arm adapter (see Fig. 4.2).
2. Make up a suspension of 0.72 g of $LiAlH_4$ (0.0189 mol) in 50 cm^3 of dry diethyl ether in the addition funnel.
3. Set up the dried apparatus as in Fig. 4.2 with a solution of 10 g of cinnamaldehyde (0.0758 mol) in 25 cm^3 of dry diethyl ether in the flask.
4. Switch on the stirrer, cool the flask with an ice-salt bath until the internal temperature is –10 °C.
5. Add the suspension of $LiAlH_4$ in diethyl ether over 30 minutes so that the temperature remains below +10 °C.

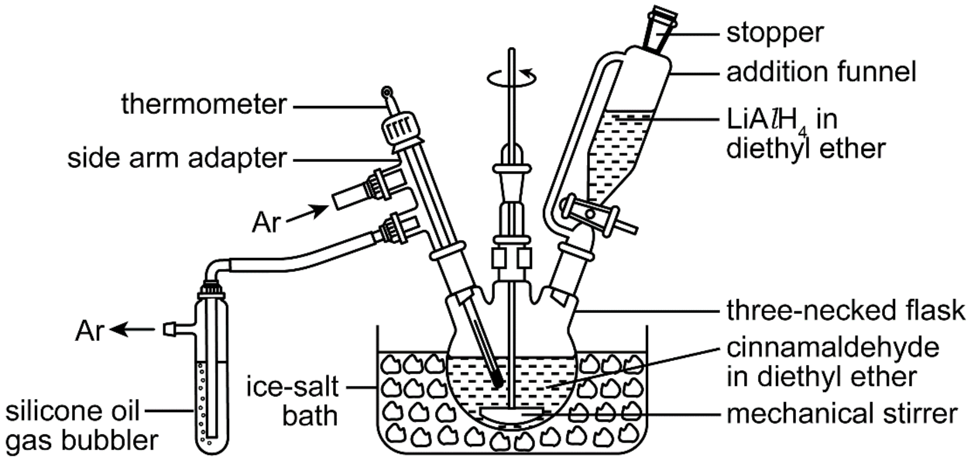


Fig. 4.2

Isolation

6. When the reaction is completed, add water.
7. Add aqueous sulfuric acid.
8. Separate the diethyl ether layer from the aqueous layer.
9. Shake the aqueous layer with fresh diethyl ether in a separating funnel and separate the aqueous layer from the diethyl ether layer. Reject the aqueous layer.
10. Add anhydrous calcium chloride to the combined diethyl ether layers.

Purification

11. Filter and evaporate the diethyl ether under reduced pressure and distil the residual oil under reduced pressure. Isolate the cinnamyl alcohol (boiling point 139 °C under reduced pressure).

(h) Cinnamaldehyde (RCHO) is first reduced to the corresponding alkoxide (RCH_2O^-), which acts as a ligand to form an anionic complex with aluminium in $LiAlH_4$.

(i) $LiAlH_4$ and cinnamaldehyde reacts in a 1:4 ratio and forms the complex as the only product.
Write an equation for the reaction between $LiAlH_4$ and cinnamaldehyde. You may use RCHO to denote cinnamaldehyde.

$LiAlH_4 + 4RCHO \rightarrow Li^+Al(RCH_2O)_4^-$ .... [1]

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Water is added in step 6 of Procedure **B** to break down the complex by protonating the alkoxide to liberate cinnamyl alcohol and two metal hydroxides, one of which is insoluble.

(ii) Suggest the identity of the insoluble metal hydroxide.

$Al(OH)_3$ .... [1]

(iii) Considering the answer to **(h)(ii)**, explain how the addition of aqueous sulfuric acid in step 7 allows a solution to be obtained for steps 8 and 9.

To **dissolve** the **insoluble $Al(OH)_3$** precipitate so that a homogeneous solution is obtained for extraction. .... [1]

$LiAlH_4$ reacts with the aldehyde functional group in cinnamaldehyde expectedly. However, reaction with the alkene functional group is unexpected.

(i) **(i)** Explain why $LiAlH_4$ is expected to react with the aldehyde functional group but not with the alkene functional group.

$LiAlH_4$ reduces via action of the nucleophilic hydride, H^- ion. The carbonyl carbon in the aldehyde functional group is **electron-deficient** hence susceptible to **nucleophilic attack** by H^-, while the alkene functional group is **electron-rich, repelling the H^- nucleophile** resulting in very high activation energy.

.... [2]

(ii) With reference to both Procedure **A** and Procedure **B**, suggest a reason why Procedure **A** is able to give the unexpected product, hydrocinnamyl alcohol.

$LiAlH_4$ is always **in excess** in Procedure **A** when cinnamaldehyde is added dropwise to $LiAlH_4$ in the flask, hence enabling further reduction of the C=C to occur. ***or*** Procedure **A** is carried out at a **much higher temperature** of 66 °C compared to at most 10 °C in Procedure **B**, **providing more energy** for the reduction of C=C to occur. .... [1]

[Total: 17]