HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME		**CT GROUP**	**21S**
CENTRE NUMBER		**INDEX NUMBER**	

CHEMISTRY

9729/03

Paper 3 Free Response

14 September 2022

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number, name and CT group in the spaces at the top of this page.

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. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A

Answer **all** questions.

Section B

Answer **one** question.

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

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.

No. of sheets of writing paper submitted (write 0 if none)	

For Examiner's Use	
1	**/ 16**
2	**/ 23**
3	**/ 21**
Circle your option below	
4 / 5	**/ 20**
Deductions	
Total	**/ 80**

Section A

Answer **all** the questions in this section.

DO NOT WRITE IN THIS MARGIN

1 (a) Shakudo is a Japanese alloy of copper and gold (typically 4–10% gold; the gold content is varied to control the colour of the alloy). Historically, Shakudo was used to construct or decorate Japanese sword fittings and small ornaments.

(i) A sample of Shakudo was analysed and found to contain two stable isotopes of copper.

Table 1.1

isotope	% abundance
^{63}Cu	74.1%
^{n}Cu	25.9%

Using information from Table 1.1 and the relative atomic mass, A_r, of copper from the Periodic Table, calculate the value of n. Give your answer to the nearest **integer**. [1]

(ii) Isotopes differ in their nucleon number.
What do you understand by the term *nucleon number*? [1]

(iii) Copper has electrons in the d orbitals. The d orbitals have two kinds of shapes.

Draw diagrams to illustrate the **two kinds** of shapes for the d orbitals. Include *x*, *y* and *z* axes and label the d orbitals that you have drawn. [2]

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

DO NOT WRITE IN THIS MARGIN

(b) A piece of Shakudo was suspected to contain small amounts of zinc.

In an electrolysis experiment, this piece of Shakudo was made the anode and a thin piece of pure copper was made the cathode. An aqueous solution of copper(II) sulfate was used as the electrolyte.

(i) Using the $E^{\ominus}$ data given below and relevant $E^{\ominus}$ data from the *Data Booklet*, explain what happens to the zinc and gold during the electrolysis.

$$Au^{3+} + 3e^- \rightleftharpoons Au \qquad E^{\ominus} = +1.52\ V$$

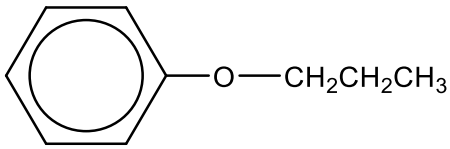
[2]

(ii) The electrolysis experiment was carried out for 12.0 minutes using a current of 1.10 A. The copper cathode increased in mass by 0.26 g.

What value of Avogadro constant, *L*, do **these figures** give? [2]

DO NOT WRITE IN THIS MARGIN

(c) Ethers have general formula R–O–R′, where R and R′ represent the alkyl or aryl groups. Propoxybenzene is an example of an ether.

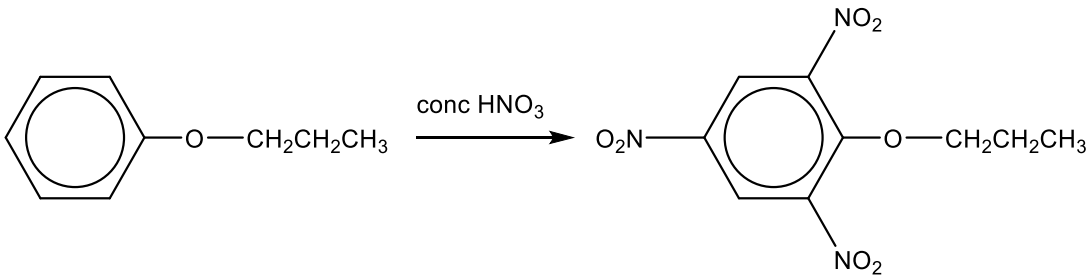


propoxybenzene

(i) The $-CH_2CH_2CH_3$ chain behaves like an alkane.

Explain why alkanes are unreactive. [1]

(ii) Propoxybenzene reacts similarly to phenol, such as in the nitration reaction shown below.



The nitration of benzene differs from that of propoxybenzene in two ways.

Describe and explain these two differences in terms of the reaction conditions and organic products. [2]

……

……

……

……

……

……

……

……

……

……

……

……

……

DO NOT WRITE IN THIS MARGIN

(d) Epoxyethane is a cyclic ether and the simplest epoxide: a three-membered ring consisting of one oxygen atom and two carbon atoms.

A reaction scheme involving epoxyethane is shown in Fig. 1.1.

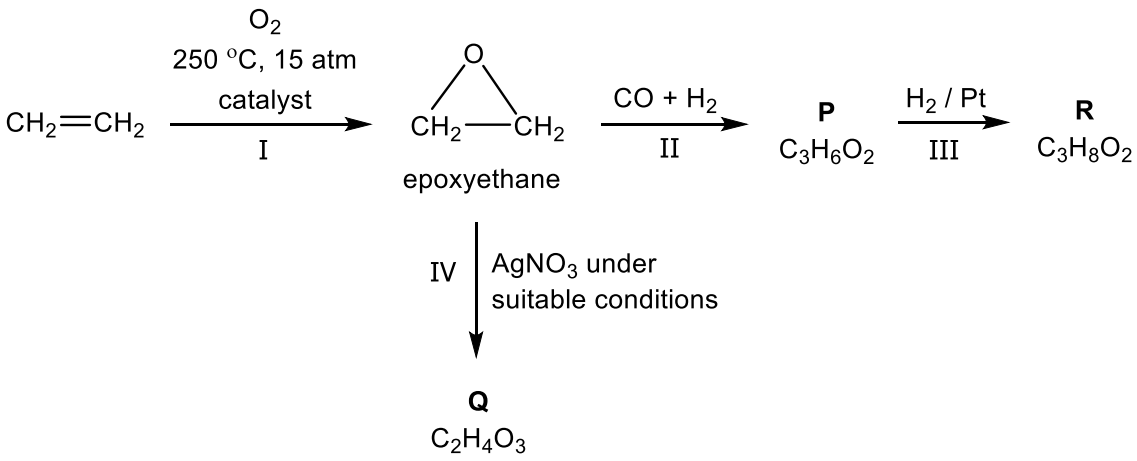


Fig. 1.1

Compounds **P** and **Q** give effervescence with sodium metal.

Both compounds do not exhibit enantiomerism.

P also gives a brick-red precipitate when warmed with Fehling's solution.

Q also gives effervescence with aqueous sodium carbonate.

Suggest the structures for **P**, **Q** and **R**. [3]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

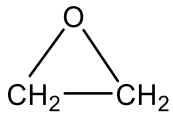
.....

.....

.....

DO NOT WRITE IN THIS MARGIN

(e) Detergents can be made from epoxyethane.



epoxyethane

The initiation step involves homolytic fission of a C–O bond in epoxyethane, giving rise to a 'double-ended' free radical.

A chain reaction then occurs.

The reaction eventually produces a molecule that contains the following structure.

——CH_2CH_2–O–CH_2CH_2–O–CH_2CH_2–O–CH_2CH_2–O–CH_2CH_2–O–CH_2CH_2–O——

Suggest equations for the **initiation step** and the **first propagation step**.
Include curly half-arrows for the initiation step. [2]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

[Total: 16]

DO NOT WRITE IN THIS MARGIN

2 (a) When solid sodium chloride reacts with concentrated sulfuric acid, white fumes of hydrogen chloride are observed as given in the equation:

$$NaCl(s) + H_2SO_4(l) \rightarrow HCl(g) + NaHSO_4(s)$$

However, when solid sodium iodide is used, very little white fumes are observed. Instead, dense purple iodine vapour and a pungent gas are formed.

(i) Solid sodium iodide is reacted with 0.00300 mol of concentrated sulfuric acid to give iodine as the only iodine-containing product. The iodine produced is dissolved in 100 cm^3 hexane.

25.0 cm^3 of this solution required 12.0 cm^3 of 0.500 mol dm^{-3} sodium thiosulfate for complete reaction.

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

Calculate the oxidation state of the sulfur-containing product in the reaction of sodium iodide with concentrated sulfuric acid. [3]

(ii) Use the *Data Booklet* to describe the relative reactivity of chloride and iodide as reducing agents. Hence, explain why different sulfur-containing products are formed when sodium chloride and sodium iodide react with concentrated sulfuric acid. [2]

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

DO NOT WRITE IN THIS MARGIN

(b) **P** and **Q** are chlorides of Period 3 elements.

P is a solid with a high melting point. It conducts electricity when molten. **P** reacts with water to form a solution of pH 6.5.

Q is a colourless liquid at room temperature. The percentage by mass of chlorine in **Q** is 83.5%. It reacts with water to form white fumes and a solution with a low pH.

(i) Explain, in terms of the type of bonding present, the physical state of **P** and of **Q**. [2]

(ii) Identify **P** and **Q**. [2]

(iii) Explain the reactions of **P** and **Q** with water with the aid of relevant equations. [3]

DO NOT WRITE IN THIS MARGIN

(c) At high temperature, gaseous PCl_5 dissociates according to the reaction

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

(i) Write the expression for the equilibrium constant, K_p, for the reaction. [1]

(ii) Gaseous PCl_5 is added to an evacuated vessel and allowed to reach equilibrium.

The initial pressure is 70% of the equilibrium total pressure, and the equilibrium partial pressure of PCl_5 is 84 kPa. Calculate the value of K_p and state its units. [3]

(iii) The volume of the vessel is reduced at time t_1.

In Fig. 2.1, sketch how the partial pressure of PCl_5 changes from t_1, until equilibrium is re-established at time t_2. Explain your answer. [2]

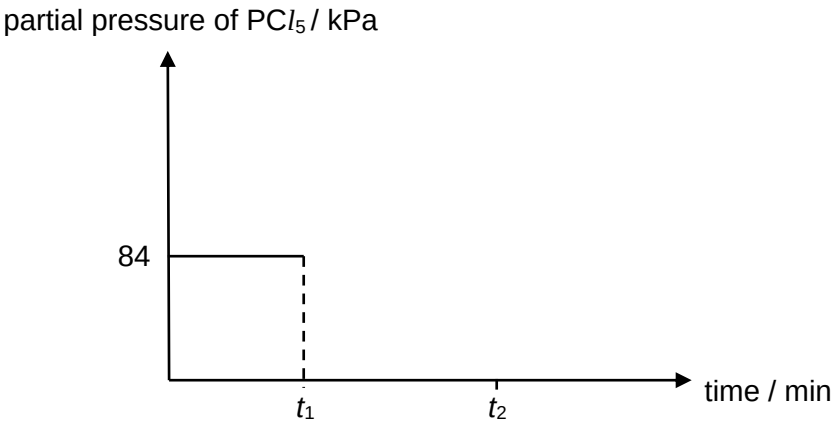


Fig. 2.1

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

DO NOT WRITE IN THIS MARGIN

……

……

……

……

(d) Compound **X** ($C_9H_{11}O_3N$) gives a yellow precipitate when warmed with alkaline aqueous iodine.

When PCl_5 is added to **X**, white fumes and compound **Y** ($C_9H_{10}ClO_2N$) are formed. **Y** is heated with tin and concentrated hydrochloric acid, followed by aqueous NaOH, to give compound **Z** ($C_9H_{11}N$).

Deduce possible structures for **X**, **Y** and **Z**, and explain the chemistry of the reactions described above. [5]

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

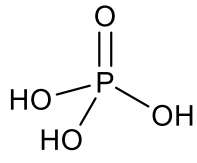
……

[Total: 23]

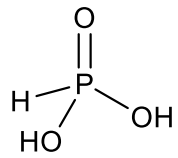
DO NOT WRITE IN THIS MARGIN

3 Phosphorus and nickel are two of the most abundant elements in the earth's crust.

(a) Phosphoric acid and phosphorus acid are two common oxo-acids of phosphorus. Phosphoric acid is a triprotic acid whereas phosphorus acid is a diprotic acid.



phosphoric acid
(H_3PO_4)



phosphorus acid
(H_3PO_3)

The phosphorus centres in these oxo-acids are sp^3 hybridised.

(i) Both nitrogen and phosphorus are in Group 15 of the Periodic Table. Explain why similar oxo-acids of nitrogen do not exist. [1]

(ii) State the number of σ bonds and π bonds in a molecule of H_3PO_3. [1]

(iii) Describe, in terms of orbital overlap, how the P–H bond in H_3PO_3 arises. Include a labelled diagram in your answer. [2]

(iv) The pK_{a1} of H_3PO_4 and H_3PO_3 are 2.1 and 1.3 respectively.

By using this information and the structures of their conjugate bases, suggest whether the –OH groups in H_3PO_4 and H_3PO_3 are electron-donating or electron-withdrawing. Explain your reasoning. [2]

……

……

……

……

……

……

……

……

……

……

……

……

……

……

DO NOT WRITE IN THIS MARGIN

(b) Nickel(II) phosphate, $Ni_3(PO_4)_2$, has potential catalytic property and has been studied extensively in recent years.

Use the data in Table 3.1, together with data from the *Data Booklet*, to calculate the standard enthalpy change of formation of $PO_4^{3-}(g)$, $\Delta H^{\ominus}_f\ PO_4^{3-}(g)$.

$$P(s) + 2O_2(g) + 3e^- \rightarrow PO_4^{3-}(g) \qquad \Delta H^{\ominus}_f\ PO_4^{3-}(g)$$

Show your working. [4]

Table 3.1

	value/ kJ mol^{-1}
standard enthalpy change of solution of $Ni_3(PO_4)_2(s)$	+179
standard enthalpy change of atomisation of Ni(s)	+431
standard enthalpy change of formation of $PO_4^{3-}(aq)$	–1277
standard enthalpy change of formation of $Ni^{2+}(aq)$	–54
lattice energy of $Ni_3(PO_4)_2(s)$	–12300

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

DO NOT WRITE IN THIS MARGIN

(c) The Mond process was developed by Ludwig Mond in 1890 to extract and purify nickel. A key step involved reacting nickel ore with carbon monoxide.

$$Ni(s) + 4CO(g) \rightleftharpoons Ni(CO)_4(g)$$

(i) State **two** physical properties of nickel, apart from the colour of the metal, in which it differs from calcium. Explain the reasons for those differences. [2]

(ii) Explain why carbon monoxide, CO, is poisonous. [2]

DO NOT WRITE IN THIS MARGIN

(d) A phosphorus-containing ligand is called phosphine and it binds to a transition metal as an electrically neutral ligand (represented as 'L' in this question part).

Fig. 3.1 shows a catalytic cycle for the synthesis of adiponitrile, an important precursor to Nylon 66.

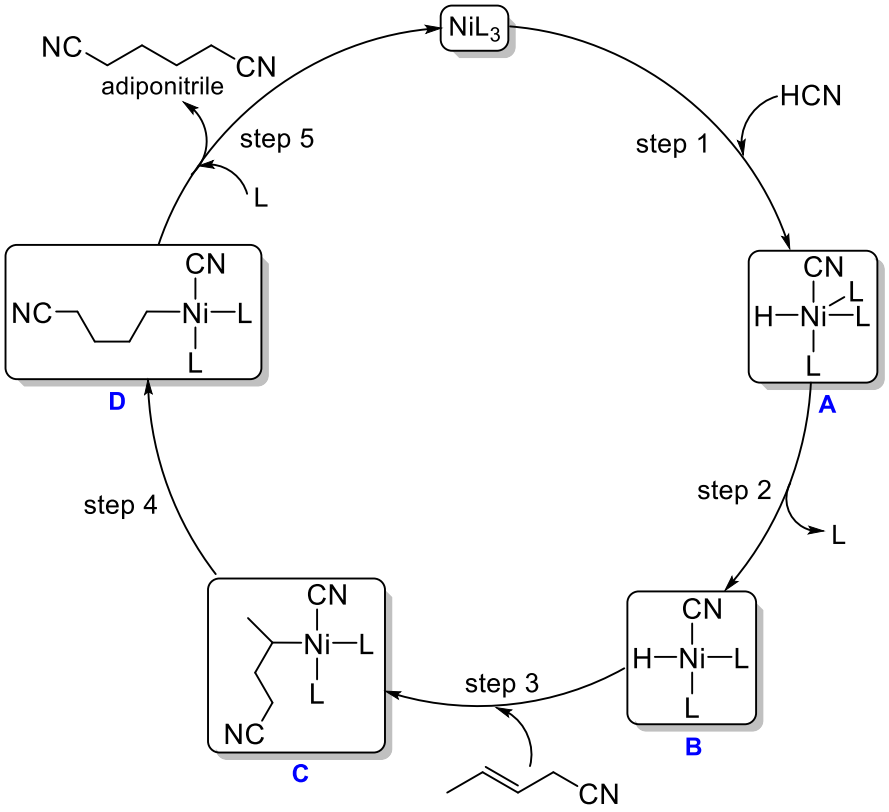


Fig. 3.1

The five steps in the above catalytic cycle can be written as five separate equations. For example, step 1 can be written as NiL_3 + HCN → **A**.

(i) Write an equation for the overall process. [1]

(ii) Besides the electrically neutral ligand L, the other two ligands bonded to Ni in **A** are hydride and cyanide.

Step 1 is termed '*oxidative addition*'. By considering the change in oxidation state of the Ni centre, explain the terms in italics. [2]

(iii) Intermediate **C** can undergo a similar reaction as that in step 5 to give NiL_3 and **E**. Suggest the structure of **E**. [1]

……

……

……

……

……

……

DO NOT WRITE IN THIS MARGIN

DO NOT WRITE IN THIS MARGIN

(e) The rate equation for the overall reaction in Fig. 3.1 is as follows.

$$\text{rate} = k[\text{HCN}][\text{alkene}][\text{L}]^m$$

To study the order of reaction with respect to L, a large excess of HCN and alkene are used, and the rate law is simplified to the following

$$\text{rate} = k'[\text{L}]^m$$

where $k' = k[\text{HCN}][\text{alkene}]$

Taking common logarithm on both sides,

$$\lg(\text{rate}) = \lg k' + m\lg[\text{L}]$$

Fig. 3.2 summarises the results of the kinetics study.

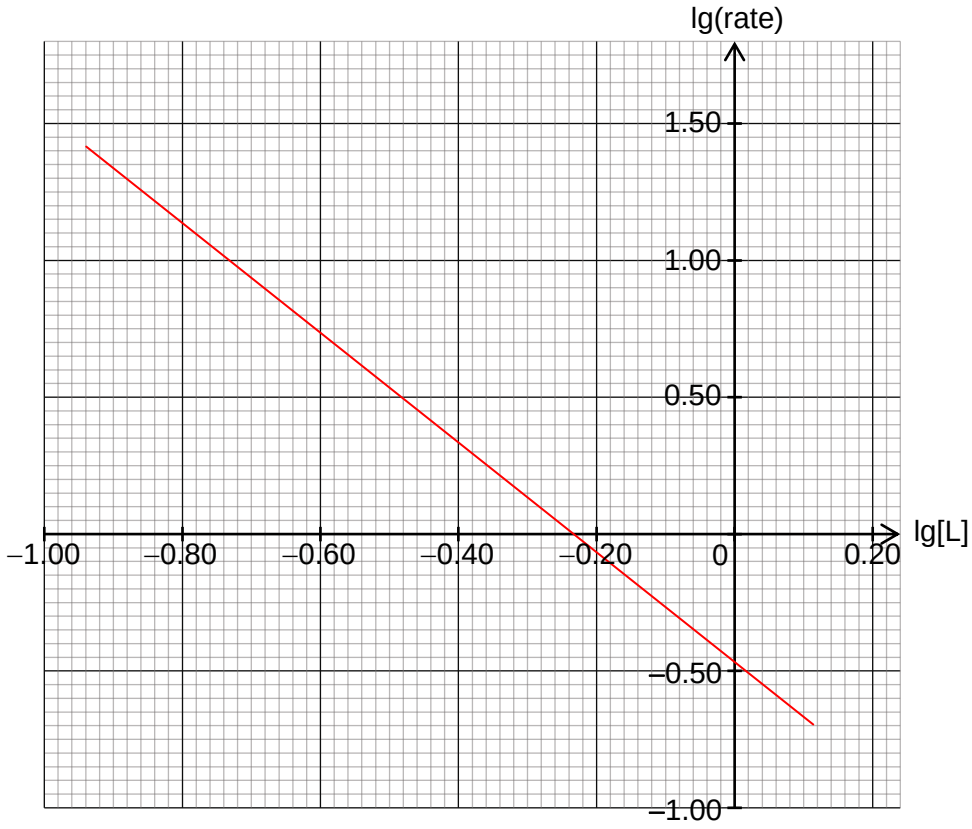


Fig. 3.2

(i) Explain why the rate law can be simplified to rate = $k'[\text{L}]^m$ in the kinetics study. [1]

(ii) Use Fig. 3.2 to determine the order of reaction with respect to L. [1]

(iii) Based on your answer in **(e)(ii)**, suggest by what factor the rate will change when [L] doubles. [1]

……

……

……

DO NOT WRITE IN THIS MARGIN

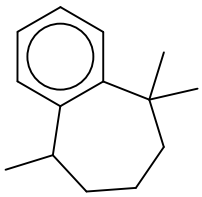
[Total: 21]

Section B

Answer **one** question from this section.

DO NOT WRITE IN THIS MARGIN

4 Users of essential oils believe that rubbing these oils onto the skin or vapourising and inhaling them are beneficial to health. A common molecule found in essential oils is ar-himachalene, which has a fused six and seven membered ring system.



ar-himachalene

(a) Human skin is waterproof and the skin glands produce protective oily secretions.

By referring to the structure and bonding of ar-himachalene, explain why it is easily absorbed onto the skin **and** is easily vapourised. [2]

.....

.....

.....

.....

.....

(b) Ar-himachalene can be synthesised from methylbenzene and compound **P** using the reaction scheme in Fig. 4.1.

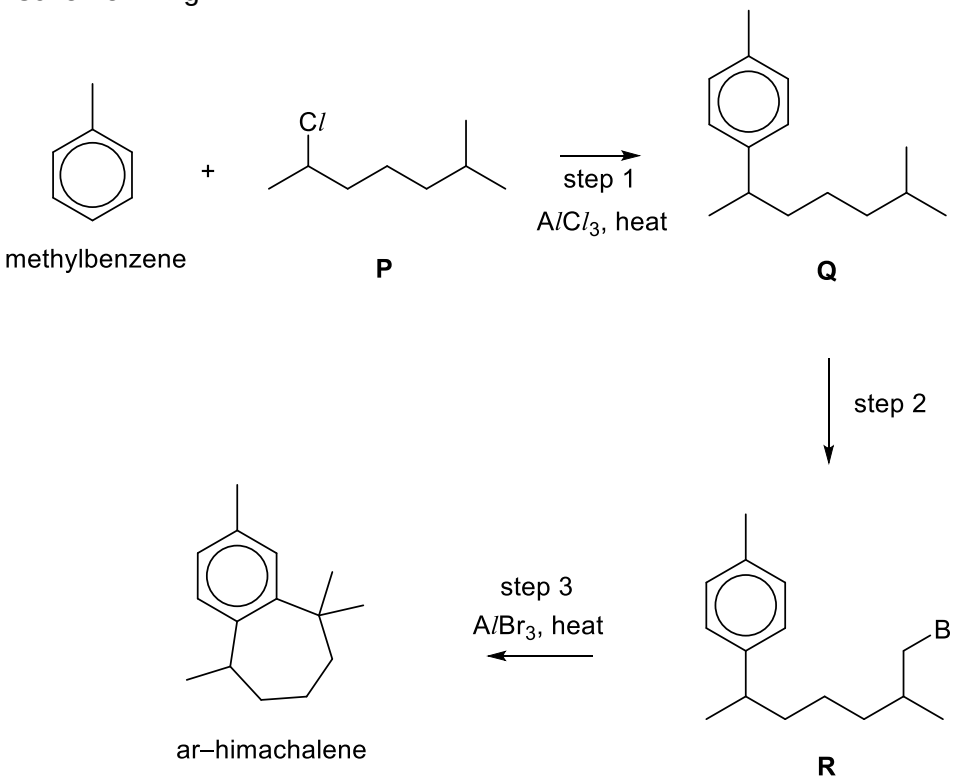


Fig. 4.1

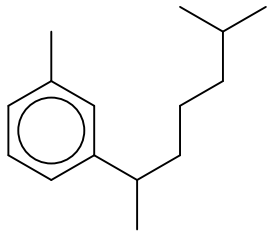
DO NOT WRITE IN THIS MARGIN

(i) State the name of compound **P**. [1]

(ii) In steps 1 and 3, A*l*C*l*$_3$ and A*l*Br$_3$ are used as Lewis acid catalysts.

Explain why A*l*C*l*$_3$ and A*l*Br$_3$ are able to function as Lewis acid catalysts. [1]

(iii) In step 1, compound **Q'** was formed as a minor product.



Q'

State the isomeric relationship between compounds **Q** and **Q'**, and explain why **Q'** was the minor product. [2]

(iv) State the reagents and conditions for step 2. [1]

(v) In step 2, bromination occurs on the terminal carbon of **Q** to produce **R** as the major product.

Explain why bromination is likely to take place at this position. [1]

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

DO NOT WRITE IN THIS MARGIN

.....

.....

.....

.....

.....

.....

.....

.....

(c) Step 3 of Fig. 4.1 produces carbocation **I** as shown in Fig. 4.2. Carbocation **I** undergoes a rearrangement reaction to form carbocation **II**.

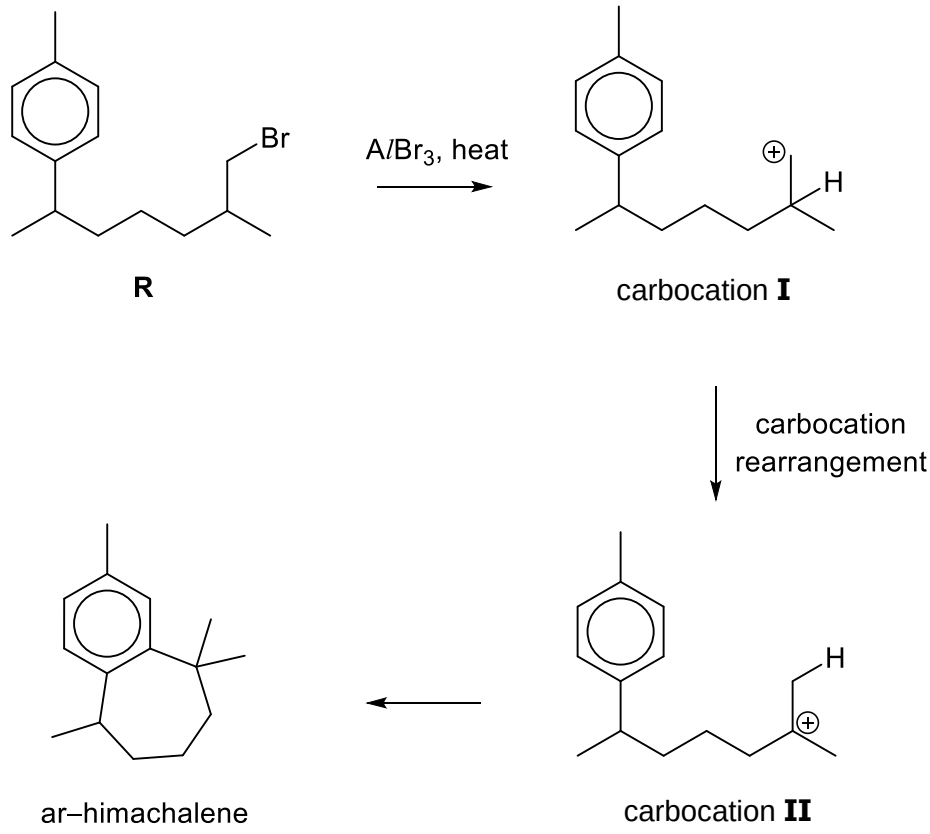


Fig. 4.2

In this rearrangement reaction, a hydrogen atom from the tertiary carbon atom is transferred to the terminal carbon atom. This is known as a *hydride shift*.

(i) Draw curly arrow(s) on Fig. 4.2 to suggest a mechanism for this *hydride shift*. [1]

(ii) By comparing the structures of carbocations **I** and **II**, explain why there is a tendency for this carbocation rearrangement to occur. [2]

DO NOT WRITE IN THIS MARGIN

(iii) Carbocation **II** undergoes an intramolecular reaction to form ar-himachalene.

State the type of reaction that occurs and describe this mechanism by using curly arrows to show the movement of electron pairs. [3]

.....

.....

.....

.....

.....

.....

.....

.....

.....

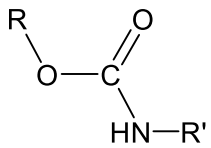
.....

.....

.....

.....

(d) Carbamates are organic compounds with the –OCO–NH– functional group as shown below. They are commonly used as insecticides.



carbamate

When the carbamate above was heated with dilute acid, ROH, R'–NH_3^+ and carbon dioxide gas were produced.

(i) State the type of reaction that occurred and write a balanced ionic equation for the reaction. You may use R and R' in your equation. [2]

(ii) The carbamate functional group resembles two other functional groups. By considering the similarities, or otherwise, suggest why the carbamate functional group is able to undergo the reaction in **(d)(i)**. [1]

.....

.....

.....

DO NOT WRITE IN THIS MARGIN

.....

.....

.....

.....

.....

.....

.....

.....

.....

(e) Compound **S** ($C_{10}H_8N_2O_2$) has the following properties.

property 1	Like ar-himachalene, it contains a fused six and seven membered ring system.
property 2	It contains the carbamate functional group and liberates NH_3 when heated with NaOH(aq).
property 3	It exhibits optical activity.

When **S** was heated with acidified $KMnO_4$(aq), the purple $KMnO_4$ was decolourised and effervescence occurred. Compound **T** ($C_8H_6O_4$) was obtained.

(i) By considering the molecular formula of **S** and property 2, suggest which other nitrogen-containing functional group is present in **S**. [1]

(ii) Suggest the structures of **S** and **T**. [2]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

[Total: 20]

DO NOT WRITE IN THIS MARGIN

5 (a) (i) Propene undergoes an electrophilic addition reaction with aqueous bromine. Suggest a mechanism for this reaction and use it to predict the major product formed. [2]

(ii) Propene can be synthesised from butanone in three steps as shown in Fig. 5.1.

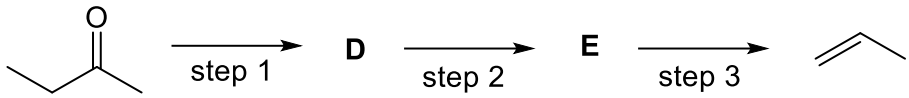
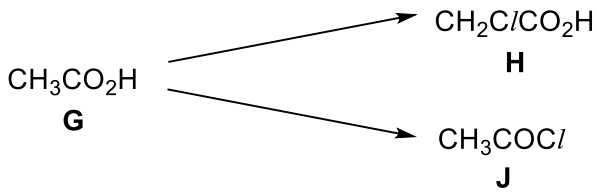


Fig. 5.1

Suggest reagents and conditions for each of the steps 1, 2 and 3. Draw the structures of the intermediate compounds **D** and **E**. [3]

DO NOT WRITE IN THIS MARGIN

(b) Two chlorine-containing compounds can be made from ethanoic acid by the following routes.



(i) Warming **G** with $SOCl_2$ produces **J**.
Draw a dot-and-cross diagram to show the bonding present within a $SOCl_2$ molecule.
Predict its shape and bond angle. [2]

(ii) When separate portions of water are added to compounds **G**, **H** and **J**, solutions with pH values of 0.5, 2.5 and 3.0 are formed (not necessarily in the order of **G**, **H** and **J**).
When aqueous silver nitrate is added to these three solutions, two solutions show no reaction, but the third solution produces a thick white precipitate.

Suggest, with explanations, which pH value is associated with each of **G**, **H** and **J**.
Explain the formation of white precipitate in terms of relative reactivity of the organic functional groups present. [5]

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

DO NOT WRITE IN THIS MARGIN

DO NOT WRITE IN THIS MARGIN

(c) The concentration of Cl^- ion in a water sample can be determined by titrating the sample with a solution of $AgNO_3(aq)$ of known concentration.

A student carried out this experiment by titrating 25.0 cm^3 of a water sample containing unknown concentration of Cl^- ion against a solution of 0.0500 mol dm^{-3} $AgNO_3(aq)$. The concentration of Ag^+ ion in the water sample is monitored and recorded as the titration progresses.

A sketch of the titration curve obtained is shown in Fig. 5.2. The concentration of Ag^+ ion is expressed in terms of pAg, where pAg = $-\log_{10}[Ag^+]$.

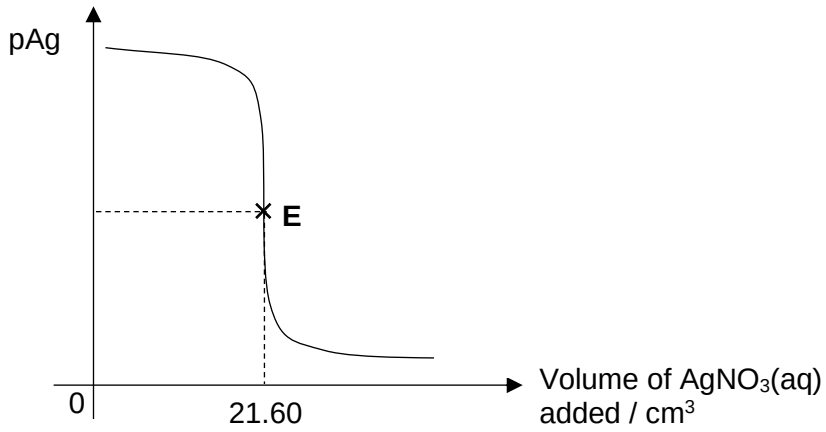


Fig. 5.2

The solubility product, K_{sp}, for $AgCl$ is 1.80×10^{-10} mol^2 dm^{-6}.

(i) Calculate the concentration of Cl^- ions in mol dm^{-3} in the water sample, assuming that all Cl^- ions in the water sample have reacted with $AgNO_3(aq)$ at point **E**. [1]

(ii) Show that a precipitate will be observed when 0.100 cm^3 of $AgNO_3(aq)$ is added to the water sample during the titration. Show your working clearly. [2]

(iii) Given that the pAg at point **E** is 4.87, calculate the concentration of Cl^- ions in mol dm^{-3} at this point. [1]

(iv) Explain why the gradient of the curve is gentle at first and becomes steeper when passing through point **E**. [2]

(v) Predict and explain how your answer in **(c)(i)** will be affected if the water sample is contaminated with a small amount of $NH_3(aq)$. [2]

……

……

……

……

……

……

DO NOT WRITE IN THIS MARGIN

[Total: 20]

Additional answer space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.

DO NOT WRITE IN THIS MARGIN

DO NOT WRITE IN THIS MARGIN

DO NOT WRITE IN THIS MARGIN