RAFFLES INSTITUTION
2022 YEAR 6 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME

CLASS

INDEX NUMBER

CHEMISTRY

9729/03

Paper 3 Free Response

16 September 2022
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not open this question booklet until you are told to do so.

Write your name, class and 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. 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.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided. Do not write anything in it.
You are reminded of the need for good English and clear presentation in your answers.

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.

<table>
<tr><th colspan="7">For Examiner's Use</th></tr>
<tr><th colspan="2">Section A</th><td rowspan="4"></td><th colspan="2">Section B</th><td rowspan="4"></td><th>Total</th></tr>
<tr><td>1</td><td>/ 17</td><td colspan="2">(Circle the question you have answered)</td><td rowspan="3">/ 80</td></tr>
<tr><td>2</td><td>/ 23</td><td>4</td><td>/ 20</td></tr>
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</table>

This document consists of **40** printed pages.

Section A

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

1 Ionic chlorides have several uses such as in the manufacturing of rubber and as a dietary supplement.

(a) 20.0 cm^3 of 0.010 mol dm^{-3} $KCl(aq)$ was accidentally mixed with 20.0 cm^3 of 0.010 mol dm^{-3} $Na_2CO_3(aq)$.

To separate the chloride and carbonate ions, solid $AgNO_3$ was added to the mixture to precipitate the maximum amount of $AgCl$ without precipitating Ag_2CO_3.

[K_{sp} of $AgCl = 2.0 \times 10^{-10}$ mol^2 dm^{-6}, K_{sp} of $Ag_2CO_3 = 8.1 \times 10^{-12}$ mol^3 dm^{-9} at 25 °C]

(i) Determine the concentration of Ag^+ ions just before precipitation of Ag_2CO_3.
Hence, calculate the concentration of chloride ions remaining in the final solution. [3]

(ii) The separation of ions is considered effective if more than 98% of the chloride ions have been precipitated before the precipitation of Ag_2CO_3.

Using your answer to **(a)(i)**, determine whether effective separation has been achieved. [1]

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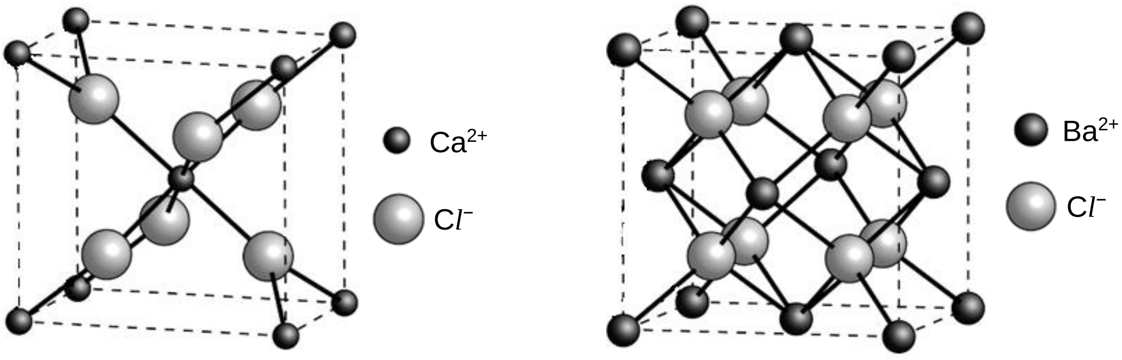
For examiner's use

(b) $\mathrm{CaC}l_2$ and $\mathrm{BaC}l_2$ have different lattice structures. Fig. 1.1 shows the structure of the repeat unit in a crystal of $\mathrm{CaC}l_2$ and in a crystal of $\mathrm{BaC}l_2$.

In $\mathrm{CaC}l_2$, the co-ordination number for Ca^{2+} is 6.
In $\mathrm{BaC}l_2$, the co-ordination number for Ba^{2+} is 8.



$\mathrm{CaC}l_2$ $\mathrm{BaC}l_2$

Fig. 1.1

(i) Suggest what is meant by the term *co-ordination number* when used to refer to a crystal lattice. [1]

(ii) Suggest why Ca^{2+} and Ba^{2+} form chlorides with different co-ordination numbers. [1]

(iii) The lattice energy of $\mathrm{CaC}l_2$ is expected to be more exothermic than that of $\mathrm{BaC}l_2$. However, the melting point of $\mathrm{CaC}l_2$ is lower than that of $\mathrm{BaC}l_2$. Suggest why. [1]

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For examiner's use

(c) Anhydrous $\mathrm{CaC}l_2$ absorbs water readily and is commonly used in the laboratory as a drying agent.

(i) The absorption of water by anhydrous $\mathrm{CaC}l_2$ is shown below.

$$\mathrm{CaC}l_2(\mathrm{s}) + x\mathrm{H_2O}(\mathrm{l}) \longrightarrow \mathrm{CaC}l_2\bullet x\mathrm{H_2O}(\mathrm{s}) \qquad \Delta H_1$$

Deduce the signs of the changes in entropy and Gibbs free energy for the above process.

Hence, state and explain the sign of ΔH_1. [2]

(ii) Define the term *lattice energy of calcium chloride*. [1]

(iii) Using the data in Table 1.1 and relevant data from the *Data Booklet*, construct an energy level diagram and calculate the lattice energy of calcium chloride. [4]

Table 1.1

standard enthalpy change of formation of anhydrous $\mathrm{CaC}l_2(\mathrm{s})$	-796 kJ mol^{-1}
standard enthalpy change of formation of $\mathrm{C}l^-(\mathrm{g})$	-242 kJ mol^{-1}
standard enthalpy change of atomisation of Ca(s)	$+177$ kJ mol^{-1}

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(d) Describe the reactions of the chlorides, $AlCl_3$ and PCl_5, with water.

Write equations for all reactions that occur and suggest the pH of the resulting solutions. [3]

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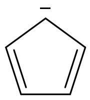
2 **(a)** A compound is aromatic if it satisfies the following two criteria.

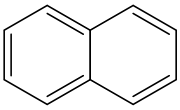
1. The compound must contain a ring comprised of continuously overlapping p orbitals.
2. The compound has (4n + 2) delocalised π electrons, where n is 0 or a positive integer (1, 2, 3 etc.)

(i) Based on the criteria above, cyclopentadienyl anion is aromatic. By considering the hybridisation of the carbon atoms, explain how cyclopentadienyl anion satisfies both criteria. [2]



cyclopentadienyl anion

(ii) Given that naphthalene is aromatic, explain why it undergoes substitution instead of addition reaction. [1]



naphthalene

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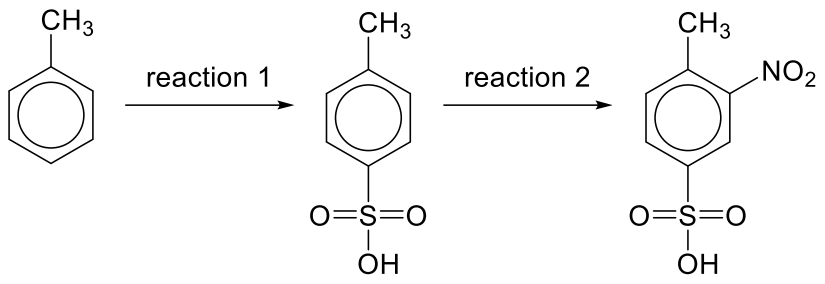
(b) Fig. 2.1 shows some electrophilic substitution reactions.



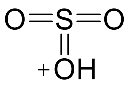
A

Fig. 2.1

In reaction 1, oleum is used as the reagent to convert methylbenzene to compound **A**. Oleum is a concentrated solution of sulfur trioxide, SO_3, in sulfuric acid, H_2SO_4.

Reaction 1 involves the following steps.

- Protonation of SO_3 by H_2SO_4 to form the HSO_3^+ electrophile. The structure of the HSO_3^+ electrophile is shown below.



$$\begin{array}{c} O{=}S{=}O \\ \| \\ {}^{+}OH \end{array}$$

- Two-step electrophilic substitution mechanism involving the reaction of methylbenzene and the HSO_3^+ electrophile, resulting in the formation of **A** and the regeneration of H_2SO_4.

(i) Write a balanced equation for the formation of the HSO_3^+ electrophile. [1]

(ii) Describe the two-step electrophilic substitution mechanism in reaction 1. Show the structure of the intermediate and all relevant charges and show the movement of electron pairs using curly arrows. [2]

(iii) State the reagents and conditions for reaction 2. [1]

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For examiner's use

(c) When 4-aminophenol is reacted with Br_2 dissolved in an organic solvent, compounds **B** and **C** are two of the products formed, as shown in Fig. 2.2.

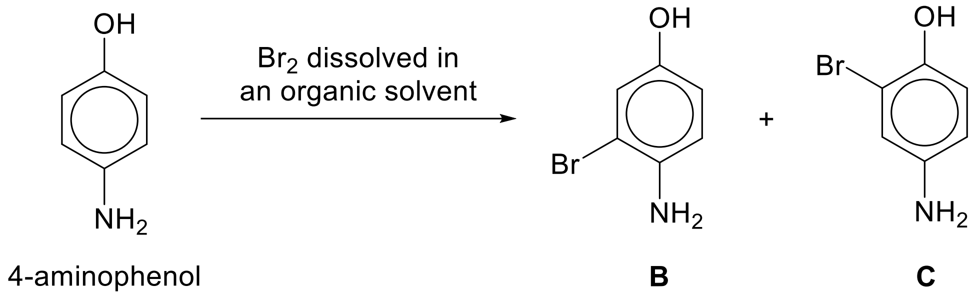

Fig. 2.2

Suggest why **B** is formed in a greater proportion compared to **C**. [2]

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(d) Fig. 2.3 shows the synthesis of compound **W**.

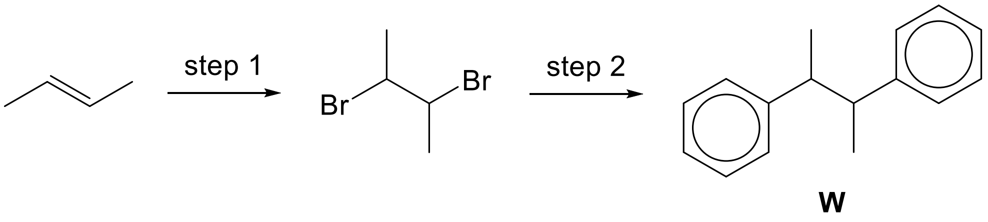

Fig. 2.3

(i) Suggest the reagents and conditions for step 2. [1]

There are three different types of compound **W** molecules.

- molecule **X** has no effect on plane-polarised light
- molecule **Y** rotates plane-polarised light by 15° clockwise
- molecule **Z** rotates plane-polarised light by 15° anti-clockwise

(ii) Draw the structures of molecules **X**, **Y** and **Z**. Suggest an explanation for the above observations. [3]

For examiner's use

(e) **(i)** Propane-2,2-diol undergoes dehydration to form propanone.

Draw the displayed formula of propane-2,2-diol. [1]

(ii) Under acidic conditions, propanone reacts to form **K**, which exists as a liquid at room temperature.

0.001 mol of **K** underwent complete combustion with 250 cm^3 of oxygen gas. The resulting gaseous mixture was passed through a tube containing anhydrous calcium chloride. The mass of the tube increased by 0.090 g. The gaseous mixture was then cooled to room temperature and the volume of the gaseous mixture was 202 cm^3. When the gaseous mixture was passed into aqueous NaOH, the volume decreased by 144 cm^3. All volumes of gases are measured at room temperature and pressure.

Use the information to show that the molecular formula for **K** is $C_6H_{10}O$. [3]

(iii) **K** ($C_6H_{10}O$) gives an orange precipitate with 2,4-dinitrophenylhydrazine but does not form a silver mirror with Tollens' reagent. When **K** is heated with acidified $KMnO_4$, **L** and propanone are formed. When **L** is heated with aqueous I_2 in dilute NaOH followed by acidification, **M** and a yellow precipitate are formed. When **M** is heated with acidified $KMnO_4$, the only product formed is a gas that gives a white precipitate with limewater.

Deduce the structures of **K**, **L** and **M**. Explain your reasoning. [6]

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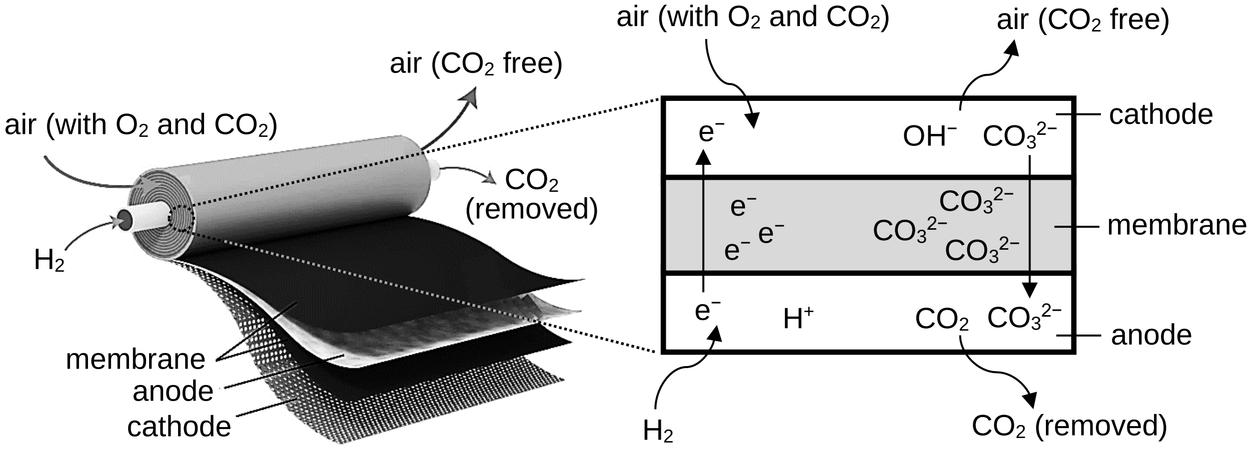
For examiner's use

[Total: 23]

3 *Use of the Data Booklet is relevant to this question.*

The Electrochemically Driven CO_2 Separator (EDCS) is a modified hydrogen-oxygen fuel cell used to remove CO_2 from air, as shown in Fig. 3.1.



schematic view

cross-sectional view

Fig. 3.1

The cross-sectional view of EDCS shows the transport of anions and electrons across the membrane, and the transport of gases at the cathode and anode.

The EDCS uses a membrane which acts as a salt bridge. The membrane also prevents diffusion of CO_2, OH^- and H^+ ions, but allows movement of CO_3^{2-} ions and electrons between the cathode and the anode.

Air, which contains O_2 and CO_2, enters the cathode where CO_2 is converted to CO_3^{2-} ions, which then diffuse to the anode through the membrane. H_2 is pumped into the anode and the CO_3^{2-} ions are converted to CO_2 which is removed from the anode into a separate storage.

In the EDCS, the following reactions take place at the cathode and anode.

cathode: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$ (1)
$CO_2 + 2OH^- \longrightarrow CO_3^{2-} + H_2O$ (2)

anode: $H_2 \longrightarrow 2H^+ + 2e^-$ (3)
$CO_3^{2-} + 2H^+ \longrightarrow CO_2 + H_2O$ (4)

(a) **(i)** In the absence of atmospheric CO_2, only reactions (1) and (3) occur at the cathode and anode of EDCS respectively.

Calculate the $E^\ominus_{cell}$ of the EDCS in the absence of atmospheric CO_2. [1]

(ii) By considering reactions (1) to (4), state and explain how the E_{cell} of the EDCS in the presence of atmospheric CO_2 would compare with your answer in **(a)(i)**. [3]

(iii) By considering your answer in **(a)(ii)** and the amount of CO_2 reacted per second, explain how an increase in concentration of atmospheric CO_2 affects the rate of removal of CO_2 by the EDCS. [1]

For examiner's use

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(b) In a typical hydrogen-oxygen fuel cell, both the cathode and the anode are either acidic or alkaline.

However, in the EDCS, the cathode has a high pH while the anode has a low pH.

(i) Calculate the $E^{\ominus}_{\text{cell}}$ of a typical hydrogen-oxygen fuel cell with both the cathode and the anode under

① acidic conditions,
② alkaline conditions. [2]

(ii) With reference to reactions (1) to (4), suggest why a typical hydrogen-oxygen fuel cell cannot be used in the EDCS. [2]

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(c) 3000 cm^3 of air containing 400 ppm of CO_2 passes through the cathode of the EDCS per minute at room temperature and pressure. Under these conditions, the EDCS can remove 99% of CO_2.

(i) Determine the current of the EDCS at room temperature and pressure. You may assume that the current is constant during operation of the cell. [3]

(1 ppm of CO_2 = 1 part per million by volume of CO_2 in air)

(ii) The membrane in the EDCS is flexible and can be wound up in a spiral roll to pack the largest possible area into a small compact volume, as shown in the schematic view in Fig. 3.1.

State how the rate of CO_2 removal will vary with the membrane surface area. [1]

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(d) Carbon nanotubes (CNTs), when added to the EDCS membrane, affects the membrane's electrical conductivity.

Fig. 3.2 shows the structure of a CNT.

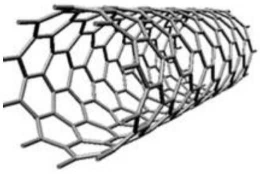

Fig. 3.2

The lattice of hexagonal rings of carbon atoms in the CNT is similar to that found in a single layer of carbon atoms in graphite.

Predict and explain how the electrical conductivity of the EDCS membrane changes with the addition of CNTs. [2]

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(e) Another method to change the electrical properties of a membrane is to include metal cations.

The metal cations can be incorporated through bonding with ionic functional groups, such as $–COO^–$ in the membrane to form $(RCOO^–)_2M^{2+}$.

Similar to carbonates, the presence of different metal ions affects the thermal stability of $(RCOO^–)_2M^{2+}$.

(i) Predict and explain the relative thermal stability of $(RCOO^–)_2Mg^{2+}$ and $(RCOO^–)_2Ca^{2+}$. [3]

(ii) Write an equation for the thermal decomposition of $MgCO_3$. [1]

(iii) $(RCOO^–)_2Mg^{2+}$ decomposes similarly to $MgCO_3$. When $(CH_3COO^–)_2Mg^{2+}$ is decomposed, a liquid compound **X** is formed as one of the products.

X forms an orange precipitate with 2,4-dinitrophenylhydrazine but does not react with Fehling's solution.

Suggest an equation for the decomposition of $(CH_3COO^–)_2Mg^{2+}$. [1]

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Section B

Answer **one** question from this section.

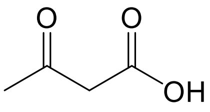
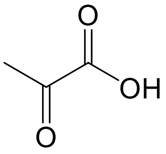
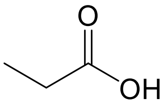
4 Many metabolic intermediates are amides and ketoacids. Ketoacids are compounds that contain both ketone and carboxylic acid functional groups.

(a) Carbon, nitrogen and oxygen are found in amides and ketoacids.

Explain the variation in first ionisation energy of these three elements. [2]

(b) The strength of an acid is measured by its K_a value. Table 4.1 shows the pK_a values for some organic acids.

Table 4.1

acid	pK_a at 25 °C
 **D**	3.58
 **E**	2.50
 **F**	4.76

Explain the differences in pK_a values of **D**, **E** and **F**. [2]

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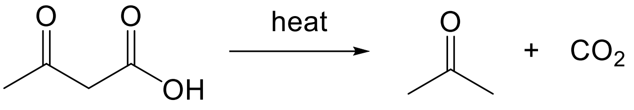
(c) When heated under acidic conditions, compound **D** undergoes decarboxylation to form a ketone and carbon dioxide, as shown in Fig. 4.1.

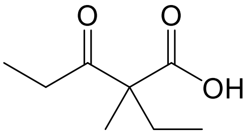


D

Fig. 4.1

(i) When heated under acidic conditions, compound **G** undergoes decarboxylation, similar to that of compound **D** shown in Fig. 4.1.

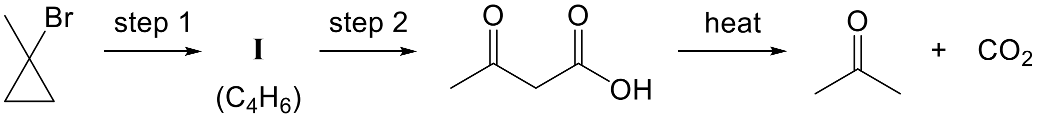
Suggest the organic product formed from the decarboxylation of **G**. [1]



G

Fig. 4.2 shows the synthesis of propanone from compound **H**.

Compound **D** was formed as an intermediate and undergoes decarboxylation to form propanone and carbon dioxide.



H **D**

Fig. 4.2

(ii) State the reagents and conditions for steps 1 and 2, and suggest the structure of compound **I**, C_4H_6. [3]

For examiner's use

(iii) Fig. 4.3 shows the three-step mechanism for the decarboxylation reaction of **D**.

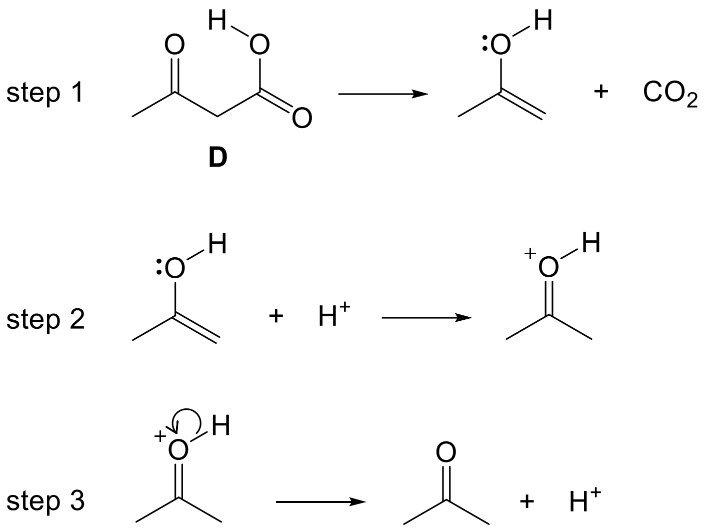
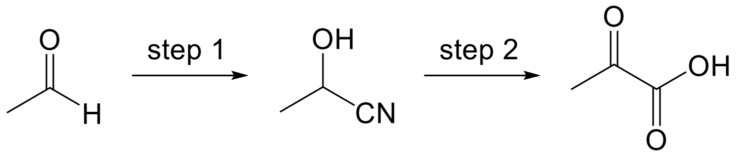


Fig. 4.3

On Fig. 4.3, draw curly arrows to show the movement of electrons for **steps 1 and 2** to complete the mechanism for this reaction. [2]

(d) Compound **E** can be synthesised from ethanal via a cyanohydrin intermediate, as shown in Fig. 4.4.



E

Fig. 4.4

(i) Suggest the two types of reaction occurring in step 2. [2]

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

(e) The ketoacid-hydroxylamine (KAHA) ligation involves the reaction between a ketoacid with N-hydroxylamine to form an amide, as shown in Fig. 4.5.

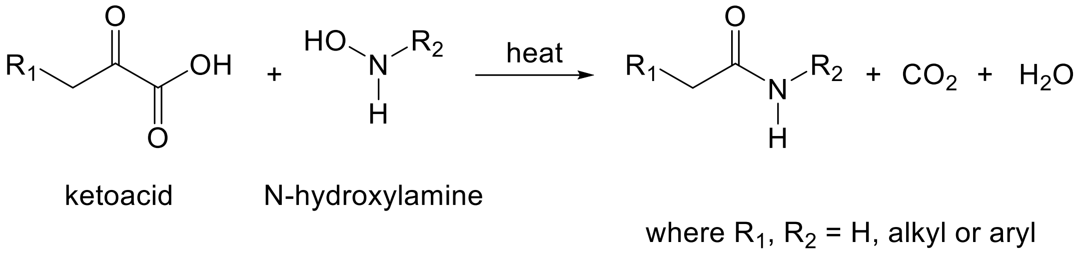


Fig. 4.5

Compound **J** undergoes KAHA ligation, as the only reactant, to form caprolactam, as shown in Fig. 4.6.

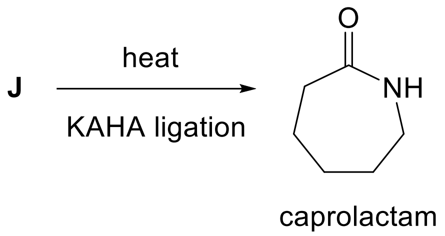


Fig. 4.6

(i) Suggest the structure of compound **J**. [1]

(ii) During the KAHA ligation of **J**, side products may form due to the polymerisation of **J**.

Suggest a condition required during the KAHA ligation to minimise the polymerisation of **J**. [1]

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(f) Ethanamide reacts under acidic conditions as shown in Fig. 4.7.

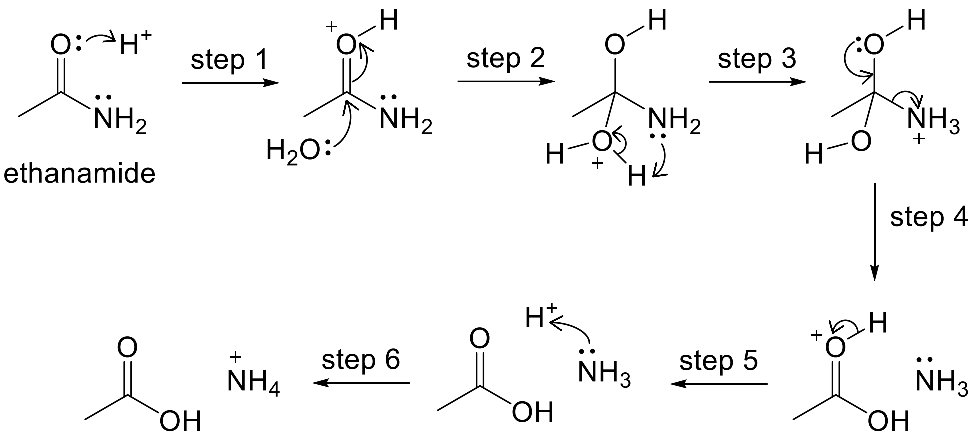
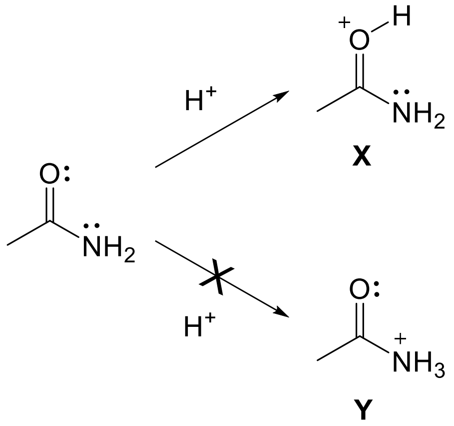


Fig. 4.7

(i) Although H^+ acts as the catalyst for the hydrolysis of amides, a catalytic amount of H^+ is **not** sufficient for the reaction in Fig. 4.7. Explain why this is so. [1]

(ii) Step 1 involves the protonation of ethanamide at the oxygen atom instead of the nitrogen atom.



By considering the structures of the conjugate acids **X** and **Y**, suggest why **X** is formed instead of **Y**. [2]

(iii) Using Fig. 4.7, suggest the structures of two organic products formed when ethanamide is hydrolysed with $H_2{}^{18}O$, which is water containing ^{18}O isotope. [2]

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[Total: 20]

5 Cyclohexanone is used as a solvent in the paints and printing industry. It is also a major ingredient for the synthesis of raw materials used in the production of nylon.

(a) In the presence of an acid or base catalyst, cyclohexanone exists in equilibrium with compound **P**, as shown in Fig. 5.1.

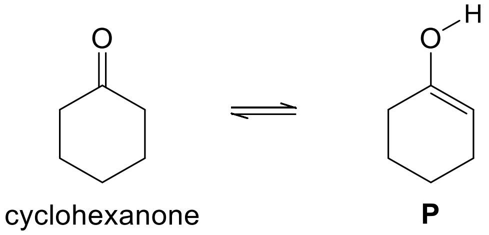

Fig. 5.1

Compared to compound **P**, cyclohexanone is more stable as the C=O bond is much stronger than the C=C bond. The equilibrium shown in Fig. 5.1 favours the formation of cyclohexanone.

(i) State the isomeric relationship between cyclohexanone and compound **P**. [1]

(ii) A similar equilibrium exists between pentane-2,4-dione and compound **Q**, as shown in Fig. 5.2. However, the equilibrium mixture contains a higher proportion of **Q** as **Q** is more stable than pentane-2,4-dione.

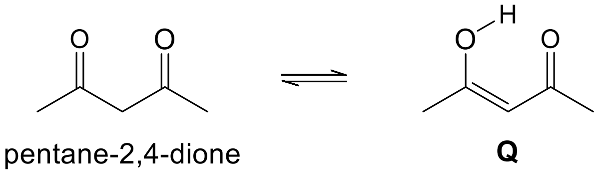

Fig. 5.2

With reference to the structure of compound **Q**, suggest **two** reasons why it is more stable than pentane-2,4-dione. [2]

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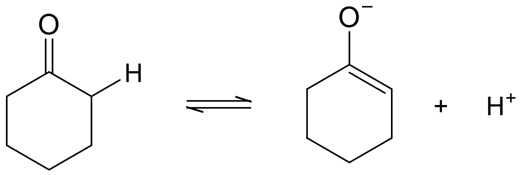
(b) The hydrogen bonded to the carbon that is adjacent to the carbonyl group is acidic because the resultant anion formed is resonance stabilised.

The acid dissociation of cyclohexanone is shown in equation 5.1.

equation 5.1

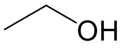
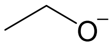
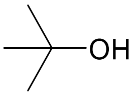
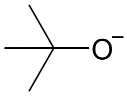
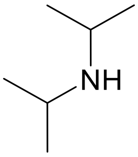
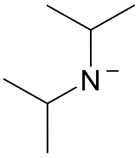


R

$pK_a = 20$

The strength of an acid is measured by its K_a value. Table 5.1 shows the pK_a values and conjugate bases of some acids. All pK_a values are measured under the same conditions.

Table 5.1

acid	pK_a	conjugate base
	16	 **I**
	18	 **II**
	36	 **III**
NH_3	38	NH_2^- **IV**

(i) Describe and explain, in terms of hybridisation and orbital overlap, why the conjugate base of cyclohexanone, **R**, is resonance stabilised.

Draw a labelled diagram, showing orbital overlap, to illustrate your answer. [2]

(ii) Conjugate base **III** is the most suitable base to deprotonate cyclohexanone to form **R**.

By considering the pK_a values and structures of the conjugate bases in Table 5.1, suggest **two** reasons why this is so. [2]

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(c) Fig. 5.3 shows the conversion of cyclohexanone to 2-propylcyclohexanone.

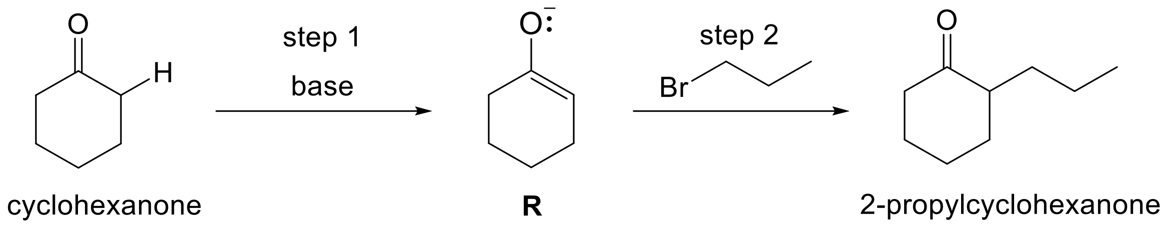

Fig. 5.3

In step 1, the base removes a hydrogen bonded to the carbon that is adjacent to the carbonyl group to form **R**.

In step 2, an S_N2 reaction occurs between **R** and 1-bromopropane to form 2-propylcyclohexanone.

(i) Suggest the mechanism for steps 1 and 2 for the conversion of cyclohexanone to 2-propylcyclohexanone. Show all relevant charges, dipoles, lone pairs and curly arrows.

You may use **B:** to represent the base used in the reaction. [3]

(ii) The solution containing 2-propylcyclohexanone synthesised from step 2 does not exhibit optical activity. Explain why. [2]

Fig. 5.4 shows the synthesis of cyclohexanone from compound **S**.

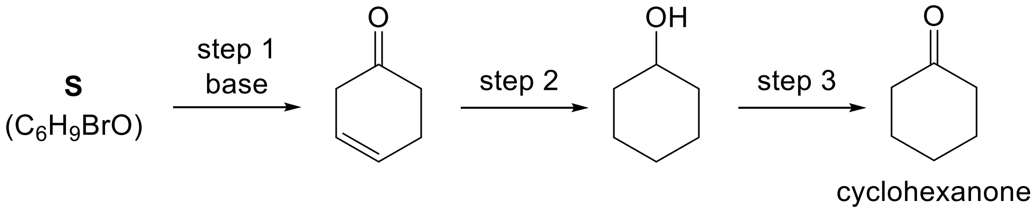

Fig. 5.4

S is a non-cyclic compound which decolourises bromine at room temperature in the dark and forms an orange precipitate with 2,4-dinitrophenylhydrazine. When heated with alkaline aqueous iodine, **S** gives yellow crystals.

(iii) Suggest the structure of compound **S**. [1]

(iv) State the reagents and conditions for steps 2 and 3. [2]

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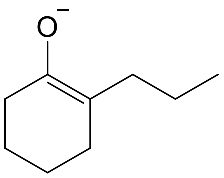
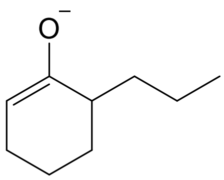
(d) Under basic conditions, 2-propylcyclohexanone can form two different conjugate base anions, **T** and **U**.



T



U

T is more stable and is formed more slowly, whereas **U** is less stable and is formed more rapidly.

Draw a labelled reaction pathway diagram to show the formation of **T** and **U** from 2-propylcyclohexanone. [2]

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(e) Nylon 6 is a polyamide commonly used in the manufacture of ropes. Fig. 5.5 shows the synthesis of nylon 6 from cyclohexanone.

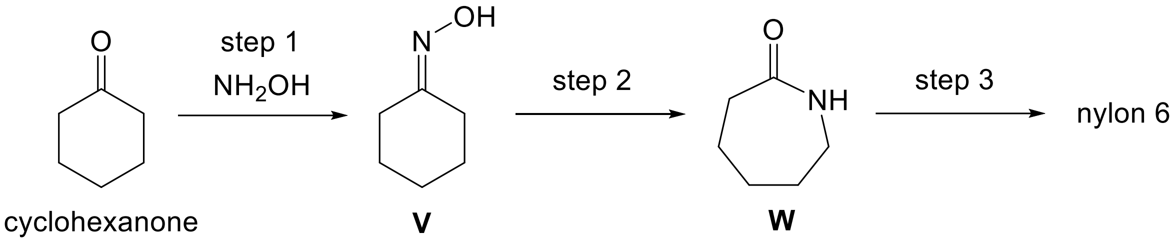

Fig. 5.5

(i) Suggest the type of reaction in step 1. [1]

(ii) Explain whether compound **V** exhibits *cis-trans* isomerism. [1]

(iii) In step 3, compound **W** undergoes hydrolysis followed by polymerisation to form nylon 6.

State the reagents and conditions for the hydrolysis of **W**. [1]

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Additional answer space

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

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