RAFFLES INSTITUTION
2020 YEAR 6 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME	
CLASS	INDEX NUMBER

CHEMISTRY 9729/03

Paper 3 Free Response **18 September 2020**
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 in the spaces provided 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.

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.

For Examiner's Use					
Section A			Section B		Total
1	/ 19		(Circle the question you have answered)		
2	/ 20		4	/ 20	/ 80
3	/ 21		5	/ 20	

This document consists of **35** printed pages.

For examiner's use

Section A

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

1 In an aerosol spray, liquefied-gas propellants are sealed in a pressurised canister. Upon release into the air, the propellants instantly vaporise.

Table 1.1 shows the boiling points of some aerosol propellants.

Table 1.1

propellant	CF_2CI_2	N_2O	CH_3OCH_3
boiling point / ^oC	−30	−89	−24
M_r	121.0	44.0	46.0

(a) (i) In N_2O, the central atom is nitrogen.

Draw a dot-and-cross diagram to show the bonding in N_2O.

Include all lone pairs in your diagram. [1]

(ii) Predict and explain the shape and bond angle about the oxygen atom in CH_3OCH_3. [2]

(iii) Explain why CH_3OCH_3 has a higher boiling point than CF_2CI_2. [1]

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Question 1 continues on the next page.

For examiner's use

(b) An important property of an aerosol propellant is that it should be a gas at room temperature and pressure.

(i) State two assumptions of the kinetic theory as applied to an ideal gas. [2]

(ii) Fig. 1.1 illustrates the behaviour of 1 mol of ideal gas at 293 K.

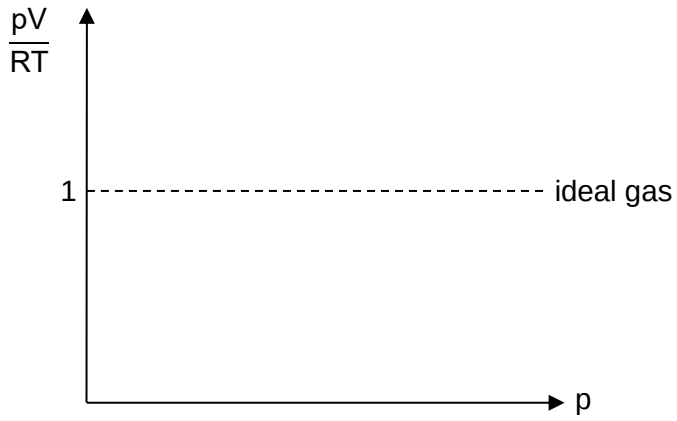

Fig. 1.1

On Fig.1.1, sketch and label the graph for 1 mol of N_2O at 293 K. [1]

(iii) On the **same** axes in Fig. 1.1, sketch and label the graph for 1 mol of N_2O at 500 K.

Explain your answer. [2]

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Question 1 continues on the next page.

For examiner's use

(c) Dimethylether, CH_3OCH_3, can be formed from the reaction between carbon monoxide, CO, and hydrogen, H_2, as shown by equation 1.

equation 1 $3CO(g) + 3H_2(g) \rightleftharpoons CH_3OCH_3(g) + CO_2(g)$ $\Delta H = -245$ kJ mol^{-1}

A mixture of CO and H_2 was introduced into a 10 m^3 sealed vessel at 500 K. The initial total pressure was 40 atm at 500 K.

After dynamic equilibrium was established, the total pressure in the vessel decreased to 28 atm at 500 K.

(i) Write an expression for the equilibrium constant, K_p, for this reaction, and state its units. [2]

(ii) *Use of the Data Booklet is relevant to this question.*

The amount of CH_3OCH_3 at equilibrium was found to be 732 mol. Show that the equilibrium partial pressure of CH_3OCH_3 in the sealed vessel is 3 atm. [1]

(iii) At equilibrium, it was found that 60% of the CO had been converted to the products. Calculate the equilibrium pressure of CO in atm. [2]

(iv) Hence, calculate the equilibrium pressure of H_2 in atm and determine the value of K_p for the reaction. [2]

(v) After dynamic equilibrium was established, some Ar(g) was added into the same 10 m^3 sealed vessel at 500 K.

Explain the effect on the partial pressure of CH_3OCH_3. [1]

(vi) Explain the effect on the value of K_p of the reaction when the temperature is increased from 500 K to 550 K. [2]

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For examiner's use

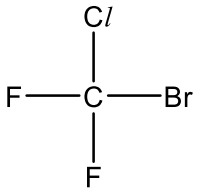
[Total: 19]

For examiner's use

2 (a) In the combustion of organic materials, C–H and C–C bonds are broken to form radicals which propagate a chain reaction until most of them form CO_2 and H_2O.

Halons are the most powerful reagents for extinguishing fires caused by the combustion of organic materials. When halons are sprayed onto the fire, halogen radicals are formed.

One of the common halons, Halon 1211, has the structure shown below.



Halon 1211

(i) Apart from depriving the fire of oxygen, suggest how Halon 1211 works to effectively suppress the fire caused by the combustion of organic materials. [1]

In the process of extinguishing the fire, Halon 1211 produces a mixture of HCl and HBr gases.

(ii) When the mixture of HCl and HBr gases is passed through aqueous Cl_2, the solution turns orange. With the aid of an equation, explain the observation. [2]

(iii) Compare the thermal stability of HCl and HBr by using relevant data from the *Data Booklet*. [2]

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(b) The extent of oxidation of iron in the reactions between iron metal and the halogens show that Cl_2 is a stronger oxidising agent than I_2.

By using relevant $E^{\ominus}$ values and considering the products formed from the reactions, explain the above statement. [3]

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For examiner's use

(c) Bush fires in Australia have sparked major concerns on global warming and scientists have been seeking alternatives to reduce greenhouse gases such as carbon dioxide, CO_2.

One method to reduce CO_2 levels in the atmosphere is to convert CO_2 to methanoic acid, HCOOH, as shown in equation 1.

equation 1 $\quad 2CO_2 + 2H_2O \longrightarrow 2HCOOH + O_2$

(i) State the type of reaction involving carbon dioxide in equation 1. Describe the change in oxidation state of carbon which occurs during this reaction. [1]

The standard electrode potentials of the two half-equations are shown below.

$$CO_2 + 2H^+ + 2e^- \rightleftharpoons HCOOH \qquad E^\ominus = -0.61\ V$$

$$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O \qquad E^\ominus = +1.23\ V$$

(ii) Calculate $E^\ominus_{cell}$ and $\Delta G^\ominus$ of the reaction in equation 1 to show that the reaction is not spontaneous and a power supply is required for the reaction to occur. [2]

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For examiner's use

(d) The Biomimetic Electrolytic Cell (BEC) shown in Fig. 2.1 can be used to convert CO_2 to HCOOH. The BEC contains porous gas diffusion electrodes which allow CO_2 gas to come into contact with the cathode and O_2 gas to depart from the anode directly without passing through the electrolyte solution. The anode is also covered with a *Nafion*™ membrane to prevent contact with the HCOOH formed.

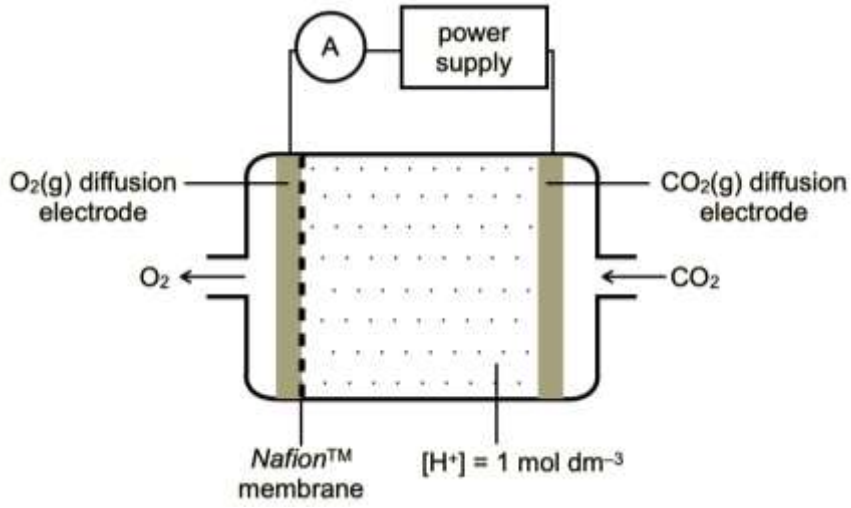

Fig. 2.1

(i) Using the information provided, suggest why

① a porous gas diffusion electrode is used at the cathode.

② a *Nafion*™ membrane is required to prevent contact between HCOOH and the anode. [2]

(ii) With reference to the half-equations in **(c)**, explain why a higher pressure of CO_2 will lower the power supply required for the cell. [2]

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(e) The standard electrode potential of the CO_2/HCOOH half-cell in **(c)** can be determined using the standard hydrogen electrode.

Draw a fully labelled diagram for the setup and indicate the direction of electron flow. [3]

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For examiner's use

(f) A 30.0 cm^3 sample of solution containing $HCOO^-$ is reacted with excess $KMnO_4$ under alkaline conditions. The resultant mixture contains CO_3^{2-} ions and a brown-black precipitate of MnO_2.

The half-equation for the reduction of MnO_4^- is shown below.

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$

(i) Construct a balanced ionic equation for the reaction between $HCOO^-$ and MnO_4^- under alkaline conditions. [1]

(ii) 0.45 g of MnO_2 is formed in the resultant mixture**.**

Calculate the concentration of $HCOO^-$ in the 30.0 cm^3 sample. [1]
[M_r of MnO_2 = 86.9]

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For examiner's use

3 Alpha hydroxy acids (AHAs) are a class of chemical compounds that consist of a carboxylic acid with a hydroxyl group on the adjacent carbon. AHAs, such as mandelic acid, $C_6H_5CH(OH)COOH$, are well known for their use in the cosmetics industry.

(a) The K_a of mandelic acid at 25 ^oC is 3.89×10^{-4} mol dm^{-3}.

(i) Calculate the pH of the resultant solution when

① equal volumes of 0.25 mol dm^{-3} mandelic acid solution and 0.125 mol dm^{-3} aqueous sodium hydroxide are mixed. [1]

② 10 cm^3 of 0.25 mol dm^{-3} mandelic acid solution and 20 cm^3 of 0.125 mol dm^{-3} aqueous sodium hydroxide are mixed. [2]

(ii) x cm^3 of 0.125 mol dm^{-3} aqueous sodium hydroxide was added to 10 cm^3 of 0.25 mol dm^{-3} mandelic acid solution to form a buffer of pH 3.89.

Calculate the value of x. [3]

For examiner's use

For examiner's use

(b) Compounds **X**, **Y** and **Z** are isomers of mandelic acid, $C_6H_5CH(OH)COOH$.

Some information about **X**, **Y** and **Z** are given below.

- **X**, **Y** and **Z** do not form orange ppt with 2,4-DNPH.
- Only **Y** and **Z** react with aqueous Na_2CO_3 to liberate CO_2 gas.
- Only **Y** and **Z** give violet complexes with neutral aqueous $FeCl_3$.
- **Y** and **Z** both decolourise aqueous Br_2 to give different products of the same molecular formula, $C_8H_5O_3Br_3$.
- Only **X** changes hot acidified aqueous $K_2Cr_2O_7$ from orange to green.
- **X** and **Z** decolourise hot acidified aqueous $KMnO_4$ to give organic products of molecular formulae $C_7H_6O_2$ and $C_7H_6O_3$ respectively.

Suggest the structures of **X**, **Y** and **Z**. [3]

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(c) Lactic acid, $CH_3CH(OH)COOH$, is another common AHA used in pharmaceutical and cosmetics applications.

Explain why lactic acid has a significantly lower melting point than alanine, $CH_3CH(NH_2)COOH$. [2]

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For examiner's use

Question 3 continues on the next page.

For examiner's use

(d) A researcher claimed that he successfully isolated a peptide chain from an alien protein found on a meteorite. The peptide, which is made up of 11 amino acid residues, can be partially hydrolysed to form the following fragments.

his-ala-glu-thr, ala-met-his-asp, ser-phe-ala-met, thr-glu, asp-his

(i) Deduce the sequence of amino acids in this peptide chain. [1]

(ii) Over time, the researcher found that the peptide chain underwent mutation. One of the amino acid residues, phenylalanine, was converted to its isomer, compound **W**.

To better study **W** and its effect on the peptide chain, the researcher synthesised more **W** via the synthesis route shown in Fig. 3.1.

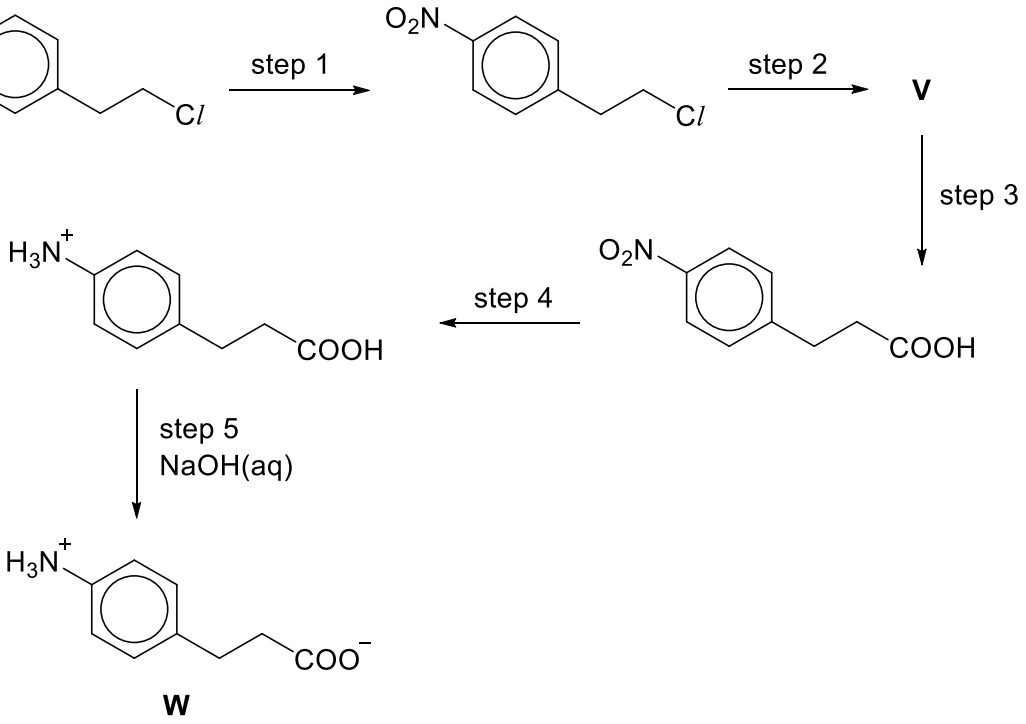


Fig. 3.1

Suggest the **displayed** formula of **V** and state the reagents and conditions for steps 1 to 4. [5]

Electrophoresis is a technique used to separate mixtures of amino acids based on the mobility of ions in an electric field.

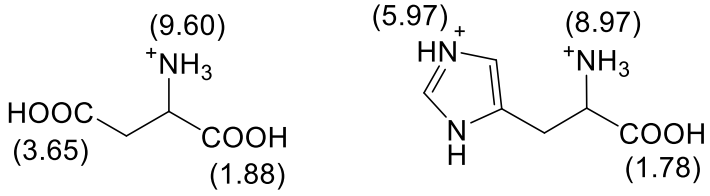
The mobility of ions depends on charge and mass.

- Ions of higher charge and/or smaller mass will migrate towards the electrode of opposite charge at a faster rate.
- Electrically neutral species will remain stationary.

Amino acids can be neutral, positively or negatively charged, depending on the pH of the solution.

For examiner's use

(iii) To separate the amino acids, the researcher hydrolysed the dipeptide fragment, asp-his, under acidic conditions to form a mixture of fully protonated amino acids. The pK_a values of the acidic groups are shown in brackets in Fig. 3.2.



aspartic acid (asp)

histidine (his)

Fig. 3.2

Using the pK_a values in Fig. 3.2, draw the major species of aspartic acid and histidine at pH 4.8. Label them as **T** and **U** respectively. [2]

(iv) The sample mixture from **(d)(iii)** was then loaded onto an electrophoresis tank buffered at pH 4.8 and an electric field was applied.

On Fig. 3.3, draw and label the relative positions of **T** and **U** after the electrophoresis. [2]

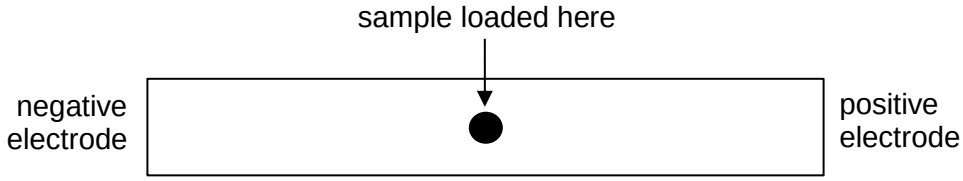


Fig. 3.3

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For examiner's use

Question 4 starts on the next page.

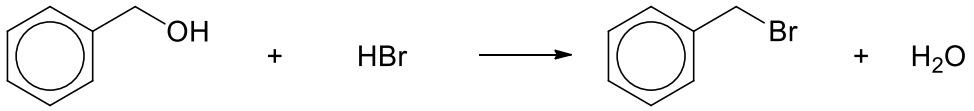
For examiner's use

Section B

Answer **one** question from this section.

4 Halogenoalkanes can be synthesised from alcohols using hydrogen halides.

Reaction 1 shows the synthesis of benzyl bromide from benzyl alcohol and hydrogen bromide.

reaction 1 

benzyl alcohol hydrogen bromide benzyl bromide

When reaction 1 was investigated kinetically, it was found that its rate was first order with respect to benzyl alcohol and with respect to hydrogen bromide.

(a) (i) Suggest a three-step mechanism for this reaction. The first step is a fast step and involves the protonation of the alcohol group in benzyl alcohol by HBr. Identify which subsequent step is the rate-determining step.

The use of curly arrows is **not** required. [3]

(ii) Describe **one** simple chemical test to distinguish between benzyl bromide, bromobenzene and benzoyl bromide. State clearly the observations for **each** compound in the test. [3]

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4-phenylbutan-2-one has a sweet and flowery smell, and is one of the most abundant attractant compounds in flowers.

Fig. 4.1 shows the synthesis of 4-phenylbutan-2-one using benzyl bromide and acetoacetic ester.

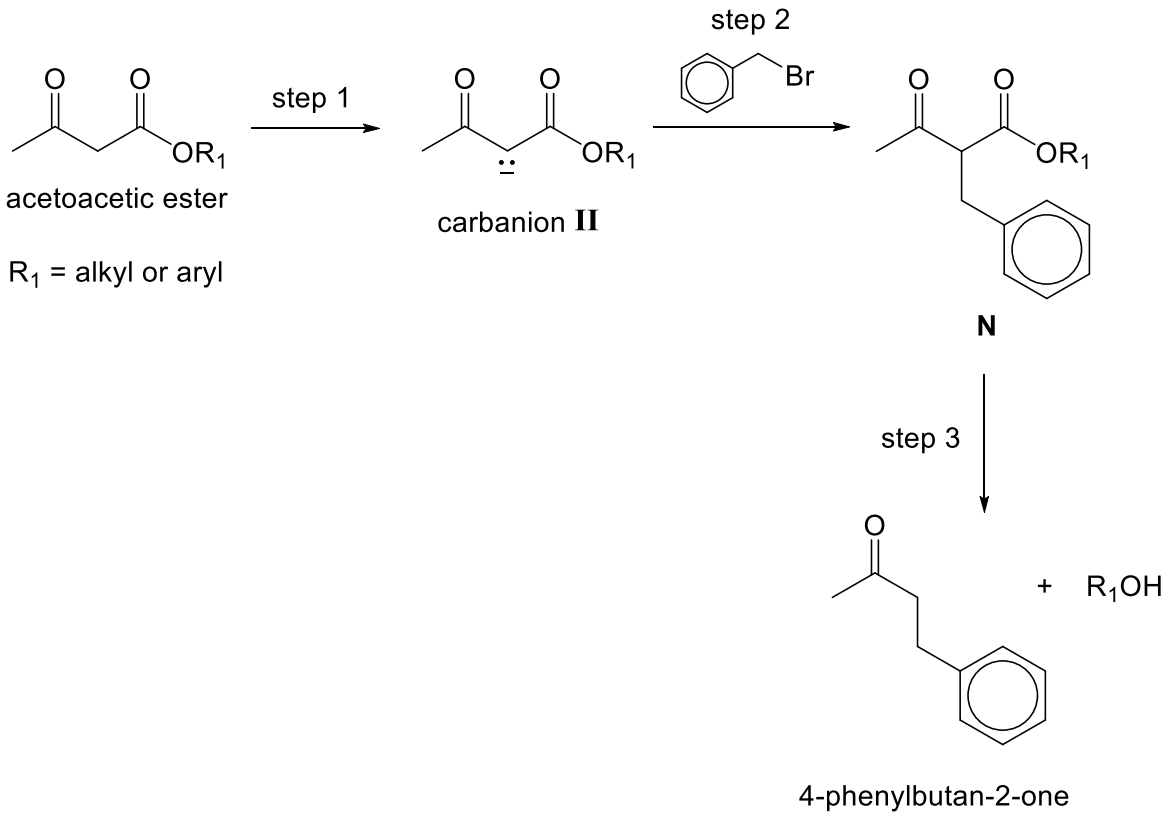

Fig. 4.1

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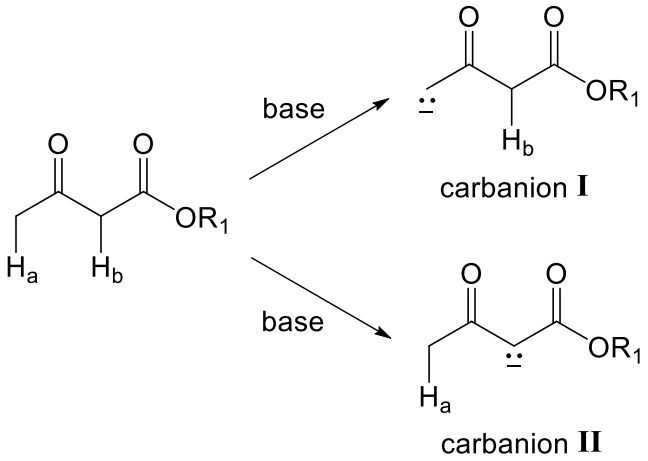
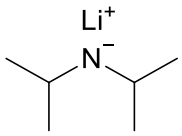
(b) (i) Step 1 involves the deprotonation of acetoacetic ester by a base. Removal of H_a and H_b results in carbanions **I** and **II** respectively, each having a trigonal planar shape around the negatively charged carbon.



Explain why carbanion **II** is preferentially formed over carbanion **I**.
Use the concepts of electronic effects and delocalisation in your answer. [2]

(ii) Lithium diisopropylamide, also known as LDA, can be used as a base in step 1 to form the carbanion. The structure of LDA is shown below.



LDA

With reference to the structure of LDA, explain why it acts as a base and not a nucleophile in step 1. [1]

(iii) Both LDA and sodium hydroxide are strong bases. However, sodium hydroxide should not be used in step 1. Suggest why this is so. [1]

(iv) Step 2 involves an S_N2 reaction between benzyl bromide and the carbanion formed from step 1.

Describe the mechanism for this reaction. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs.

You may represent the carbanion as $R:^-$. [2]

(v) In step 3, **N** undergoes hydrolysis to form an alcohol, R_1OH, and an intermediate. The intermediate spontaneously breaks down to form 4-phenylbutan-2-one and an acidic gas.

Identify the gas produced and suggest the reagents and conditions for step 3. [2]

For examiner's use

For examiner's use

For examiner's use

(c) Compound **P** ($C_7H_{11}BrO_3$) undergoes elimination to form only one alkene. **P** does not react with $SOCl_2$. When **P** is heated with aqueous sodium hydroxide, compounds **Q** ($C_4H_5O_3Na$) and **R** ($C_3H_8O_2$) are formed. Compounds **P**, **Q** and **R** give yellow precipitate with hot alkaline aqueous iodine.

Deduce the structures of compounds **P**, **Q**, and **R**, explaining the reactions described. [6]

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For examiner's use

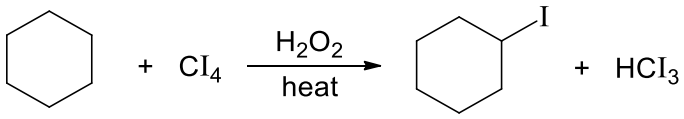
5 (a) Free radical substitution of alkanes can be initiated at moderate temperatures with the use of a radical initiator, which is a compound with a weak bond that undergoes homolytic fission easily.

One common example of a radical initiator is hydrogen peroxide, H_2O_2, which generates the hydroxyl radical, ●OH, on gentle heating.

(i) Suggest why the O−O bond in H_2O_2 is weaker than expected. [1]

Iodination of alkanes using iodine, I_2, is usually an energetically unfavourable reaction. Tetraiodomethane, CI_4, can be used as the iodine source for iodination, in the presence of H_2O_2 as the radical initiator.

Reaction 1 shows the iodination of cyclohexane using CI_4 and H_2O_2.

reaction 1 

The initiation and propagation stages consist of 2 steps each. The first step of the initiation stage is shown below.

$$HO{-}OH \longrightarrow 2\ HO\bullet$$

In the second step of the initiation stage, HOI is formed as a one of the product.

(ii) Outline the initiation and propagation steps in the mechanism for reaction 1, labelling the steps clearly. [4]

(iii) Suggest why only a trace amount of H_2O_2 is required in reaction 1. [1]

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For examiner's use

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(b) Fig. 5.1 shows how optically pure samples of each enantiomer of 3-methylhexan-3-ol can be obtained from an optically pure sample of 3-methylhexane.

Bromination of an optically pure sample of 3-methylhexane followed by treatment with hot aqueous NaOH yields racemic mixtures I and II respectively.

To separate the enantiomers in racemic mixture II, a chiral resolving agent is used. One such resolving agent is Mosher's acid chloride.

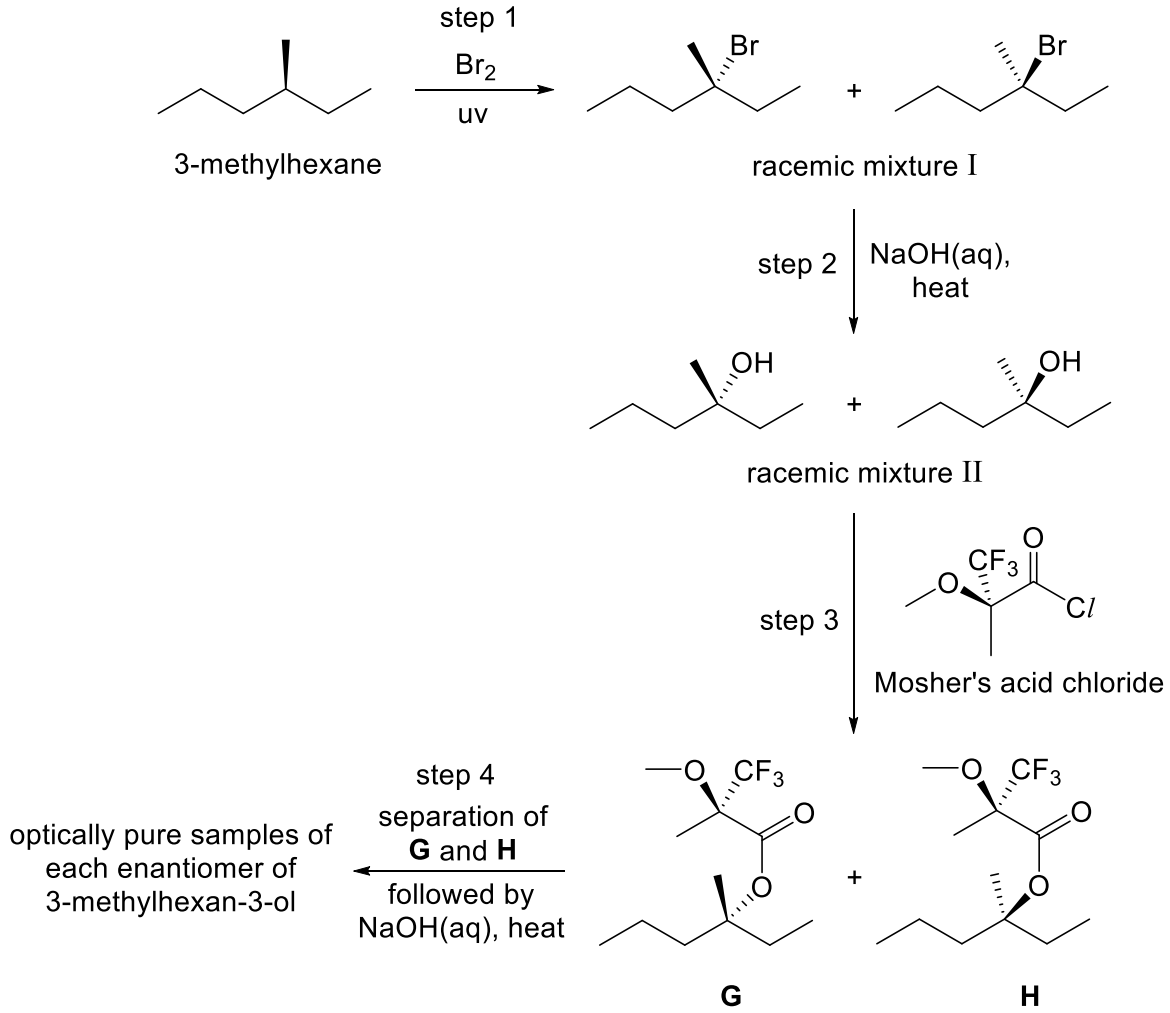

Fig. 5.1

(i) Explain why the reaction of an optically pure sample of 3-methylhexane with Br_2 gives racemic mixture I. [1]

Compounds **G** and **H** are formed from the reaction between racemic mixture II and Mosher's acid chloride in step 3.

(ii) State the type of reaction occurring in step 3. [1]

(iii) Unlike racemic mixtures I and II, **G** and **H** can be easily separated. Explain why this is so. [1]

For examiner's use

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(c) Hydrocarbons undergo reactions with chlorine under different conditions. Compare and account for the differences in conditions used in the chlorination of cyclohexene and benzene. [3]

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For examiner's use

(d) Ethers are compounds with the general formula R–O–R' where R and R' may be alkyl or aryl groups.

Allyl phenyl ethers can undergo the Claisen rearrangement to form *o*-allylphenol, as shown in Fig. 5.2. When allyl phenyl ether is heated, the aromatic ring is initially destroyed to form the intermediate **J**. **J** then undergoes a tautomerisation process to give *o*-allylphenol with the aromatic ring restored.

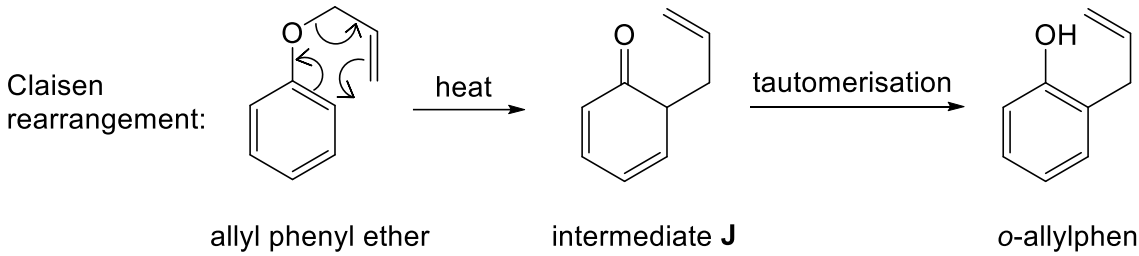

Fig. 5.2

(i) Suggest a simple chemical test to distinguish between intermediate **J** and *o*-allylphenol. [2]

Fig. 5.3 shows a reaction scheme involving the Claisen rearrangement.

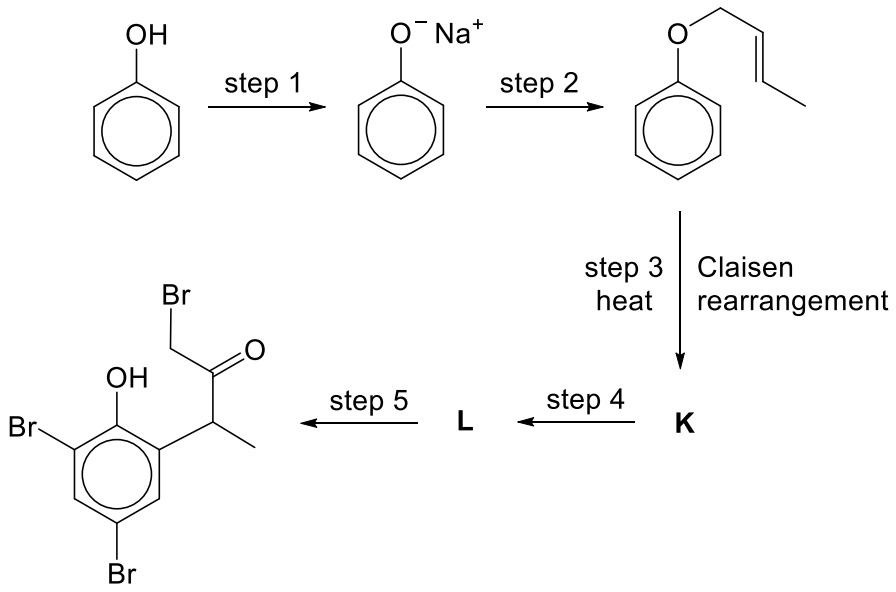

Fig. 5.3

(ii) State the reagents and conditions for steps 1, 2, 4 and 5. [4]

(iii) Suggest the structures of compounds **K** and **L**. [2]

For examiner's use

[Total: 20]

For examiner's use

Additional answer space

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

For examiner's use