NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME

SUBJECT CLASS

REGISTRATION NUMBER

CHEMISTRY

9729/03

Paper 3 Free Response

14 September 2023
2 hours

Candidates answer on Question Paper.
Additional Materials: Data Booklet

READ THE INSTRUCTIONS FIRST

Write your subject class, registration number and name on all the work you hand in.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

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.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
Section A	
1	**/20**
2	**/16**
3	**/24**
Section B	
4	**/20**
5	**/20**
Paper 3 Total	**/80**

This document consists of **32** printed pages.

Section A

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

1 **(a)** Table 1.1 list physical properties of some Period 4 elements.

Table 1.1

property	K	Ca	Fe	As	Se
relative atomic mass	39.1	40.1	55.8	74.9	79.0
atomic radius (metallic) / nm	▨	0.197	0.126	▨	▨
melting point / K	▨	1112	1808	▨	▨
density / g cm^{-3}	▨	1.54	7.86	▨	▨
1^{st} I.E. / kJ mol^{-1}	▨	▨	▨	944	941
2^{nd} I.E. / kJ mol^{-1}	3070	1150	▨	▨	▨

(i) Explain why the atomic radius of Fe is less than that of Ca. [2]

(ii) Use relevant data from Table 1.1 to explain why the density of Fe is significantly greater than that of Ca. (no calculations are required) [2]

(iii) Suggest why the melting point of Fe is significantly higher than the melting point of Ca. [2]

(iv) With reference to the electronic configuration of K and Ca, explain why the 2^{nd} I.E. of Ca is lower than that of K. [2]

(v) With reference to the electronic configurations of As and Se, explain why the 1^{st} I.E. of Se is lower than that of As. [2]

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(b) The Fischer-Tropsch process involves converting a mixture of carbon monoxide and hydrogen, known as syngas, into hydrocarbons, in the presence of catalysts.

One such reaction is shown below:

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g) \qquad \Delta H < 0$$

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

(ii) A mixture of CO and H_2 was introduced into a sealed vessel and heated to 1200 K. At equilibrium, it was found that the total pressure was 32 atm, and the mole fractions of CO and CH_4 were 0.5 and 0.12 respectively.

Calculate the equilibrium partial pressures of all gases, and hence calculate the value of K_p. [3]

(iii) Higher temperatures and higher pressures can lead to faster reactions. However, in commercial facilities that use the Fischer-Tropsch process, this was avoided. Explain why. [2]

Transition metals such as iron or cobalt, are commonly used as catalysts in the Fischer-Tropsch process.

(iv) State the type of catalysis in the Fischer-Tropsch process. [1]

(v) Outline the mode of action of the catalyst in the Fischer-Tropsch process. [2]

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2 Iodine is found naturally in compounds in many different oxidation states.

(a) Iodide ions, I^-, react with acidified H_2O_2(aq) to form iodine, I_2, and water. The resultant mixture is then shaken with cyclohexane, C_6H_{12}, to extract the I_2.

Cyclohexane is immiscible with water.

(i) Identify the role of H_2O_2(aq) in its reaction with I^- ions in acidic conditions.

Write an ionic equation for the reaction. [2]

(ii) The partition coefficient (K_{pc}) is the ratio of the concentrations of a solute in two different immiscible solvents in contact with each other when equilibrium has been established at a particular temperature.

The partition coefficient can be expressed as the following equation:

$$K_{pc} = \frac{[\text{Solute}]_{\text{Organic solvent}}}{[\text{Solute}]_{\text{Water}}}$$

15.0 cm^3 of C_6H_{12} is shaken with 20.0 cm^3 of an aqueous solution containing I_2 until no further change is seen.
It is found that 0.390 g of I_2 is extracted into C_6H_{12}.
The partition coefficient of I_2 between C_6H_{12} and water, K_{pc}, is 93.8.

Calculate the mass of I_2 that remains in the aqueous layer. [2]

(iii) Suggest how the value of K_{pc} of I_2 between hexan-2-one and water compares to the value given in **(a)(ii)**.

Explain your answer. [2]

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(b) The Group 1 iodides all form stable ionic lattice and are soluble in water.

(i) Define *enthalpy change of solution*. [1]

(ii) Use the data in Table 2.1 to calculate the enthalpy change of solution of potassium iodide.

Table 2.1

process	enthalpy change, ΔH / kJ mol^{-1}
$K^+(g) + I^-(g) \longrightarrow KI(s)$	−629
$K^+(g) \longrightarrow K^+(aq)$	−322
$I^-(g) \longrightarrow I^-(aq)$	−293

[1]

(iii) Suggest the trend in the magnitude of lattice energies of Group 1 iodides, LiI, NaI, KI. Explain your answer. [2]

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(c) A solution is prepared by dissolving 35.0 g of hydrated copper(II) sulfate crystals in 1 dm^3 of water. 25.0 cm^3 of the resultant solution is pipetted out and reacted with an excess of $I^-(aq)$.

reaction 1: $2Cu^{2+} + 4I^- \longrightarrow 2CuI + I_2$

The I_2 produced is titrated against a solution containing thiosulfate ions, $S_2O_3^{2-}(aq)$, using a suitable indicator.

reaction 2: $2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$

The end-point of the titration is reached when 22.30 cm^3 of 0.150 $mol dm^{-3}$ $S_2O_3^{2-}(aq)$ has been added.

(i) Calculate the mass of copper in the 35.0 g sample of hydrated copper(II) sulfate. [3]

(ii) Identify a suitable indicator for the titration. [1]

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(d) An orange precipitate of HgI_2 forms when Hg^{2+} ions are added to KI(aq). The solubility of HgI_2 at 25 °C is 1.00×10^{-7} g dm^{-3}.

Calculate the solubility product, K_{sp}, of HgI_2. [2]

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3 Halogenoalkane **Q** can be made in 2 steps from benzene as shown in Fig 3.1. In step I, compound **P** is the sole organic product formed.

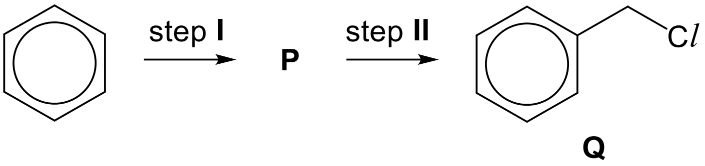

Fig 3.1

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

(ii) Suggest the reagents and conditions for step **I** and **II**. [2]

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(b) Ether can be synthesized using a halogenoalkane and phenol as shown in Fig 3.2. Phenol is first converted into phenoxide ion before reacting with halogenoalkane **Q**.

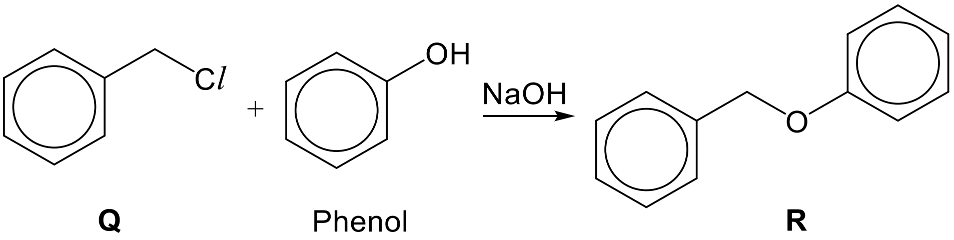
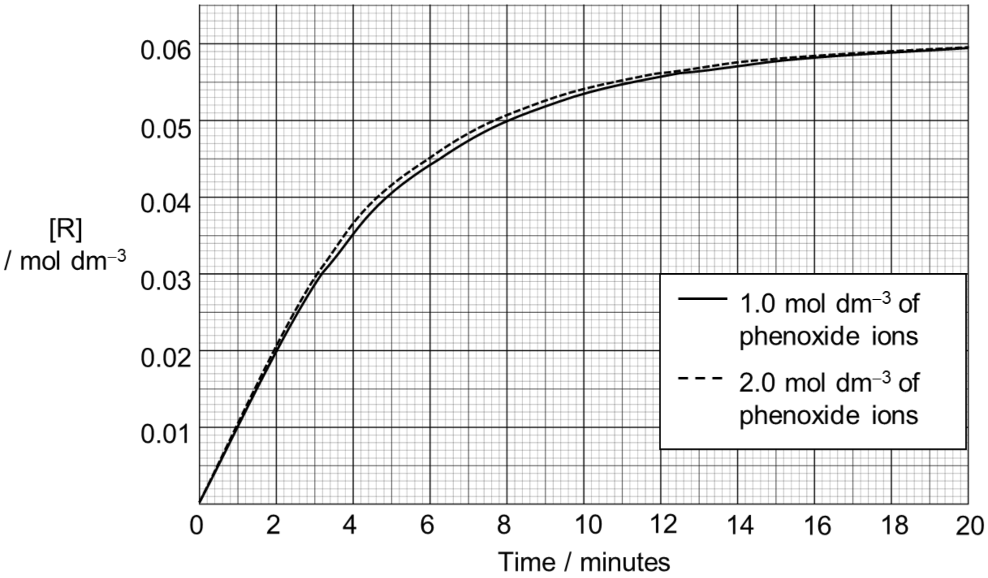


Fig 3.2

To understand the mechanism of this substitution reaction, two kinetics experiments were carried out. 1.0 mol dm^{-3} of phenoxide was reacted with 0.06 mol dm^{-3} of halogenoalkane **Q** in inert organic solvent. This experiment was then repeated with 2.0 mol dm^{-3} of phenoxide used instead.

Colorimetric method was used to monitor the concentration of compound **R** present in the solution in both experiments. The following graphs were obtained from the two experiments.



(i) Deduce the rate equation for the reaction. [3]

(ii) Hence, calculate the rate constant, for the reaction between compound **Q** and phenoxide. Give the units of the rate constant. [1]

(iii) With reference to your answer in **b(i)**, describe the mechanism of this reaction, showing curly arrows, charges, dipoles and any relevant lone pairs. [3]

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(c) Halogenoalkane **Q** can be converted into benzoyl chloride as shown in Fig 3.3. Benzoyl chloride is a reactive precursor for synthesizing other useful molecules.

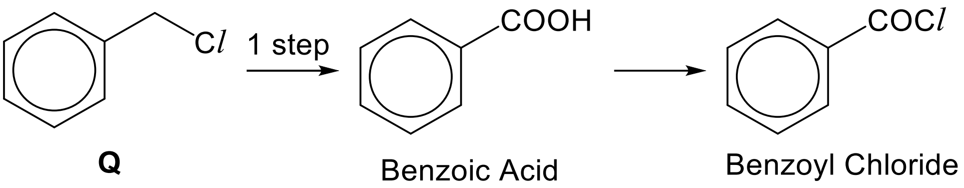

Fig 3.3

(i) State the reagents and conditions needed to convert halogenoalkane **Q** into benzoic acid. [1]

(ii) Three samples of phenol, benzoic acid and benzoyl chloride are added separately into 3 beakers containing equal volume of water.

Arrange the resultant solutions of phenol, benzoic acid, and benzoyl chloride in increasing order of pH values. Explain your answer. [3]

(iii) A pH 4.70 buffer solution was prepared by adding 0.1 mol dm^{-3} benzoic acid into a vessel containing 50 cm^3 of 0.2 mol dm^{-3} sodium hydroxide solution.

Calculate the volume of benzoic acid needed for the preparation of this buffer solution.

[pK_a of benzoic acid = 4.20] [3]

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(d) Resedine, a natural compound, is useful in the preparation of antiviral agents.

A plausible synthetic pathway of resedine from halogeoalkane **Q** is shown in Fig 3.4.

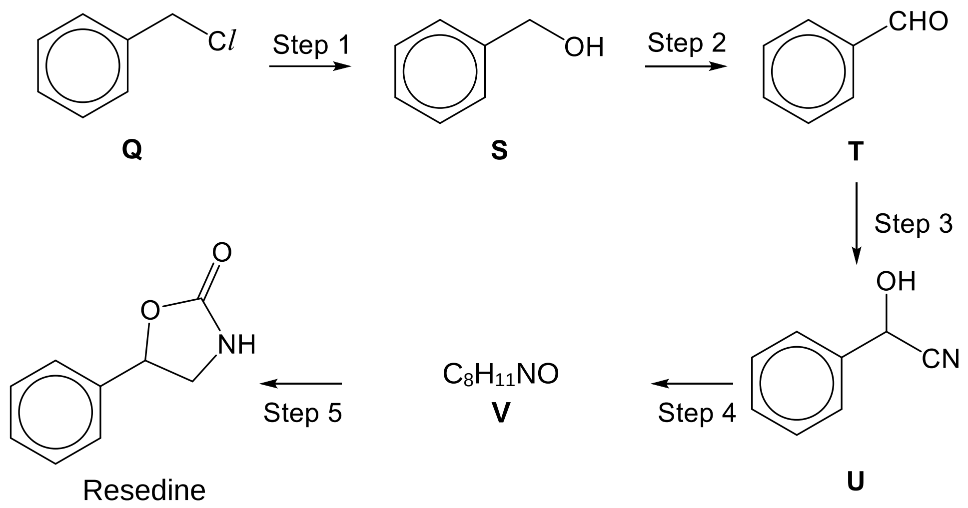

Fig 3.4

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

(ii) Suggest the structure for compound **V** and state the reagents and conditions required for step 4. [2]

(iii) Suggest the type of reaction in step 5 and hence state the reagents and conditions required. [2]

(iv) Predict the optical activity of resedine formed via the synthetic pathway proposed in **(d)**. [2]

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Section B

Answer **one** question from this section.

4 **(a)** Fig 4.1 shows an electrolytic cell that produces molten aluminium and carbon dioxide gas.

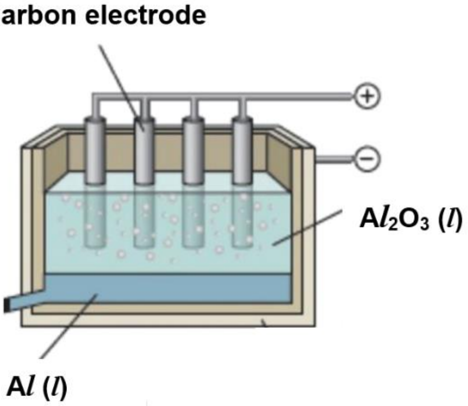

Fig 4.1

The overall equation for this reaction is:

$$2Al_2O_3(l) + 3C(s) \longrightarrow 4Al(l) + 3CO_2(g)$$

(i) Construct equations for the reactions that occur at the anode and cathode. Include state symbols in your equations. [1]

(ii) A steady current of 108 A was used to produce 185 g of $Al(l)$. Calculate the number of moles of electrons that must be transferred in the cell. Hence calculate the time needed to produce the mass of $Al(l)$. [2]

(iii) Calculate the volume of $CO_2(g)$, measured at 301 K and 1.31 atm, that is produced in the process. [2]

(iv) For the electrolytic cell to operate, Al_2O_3 must be in liquid state rather than in solid state. Explain, in terms of structure and bonding, why this is so. [2]

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(b) An Ellingham diagram shows how the Gibbs free energy change for a reaction varies with temperature, T.

The Ellingham diagram for **reaction 1** and **2** is shown in Fig 4.2.

Reaction 1: $2C(s) + O_2(g) \longrightarrow 2CO(g)$ $\Delta G_{1500K} = -493$ kJ mol^{-1}

Reaction 2: $2Fe(s) + O_2(g) \longrightarrow 2FeO(s)$ $\Delta G_{1500K} = -330$ kJ mol^{-1}

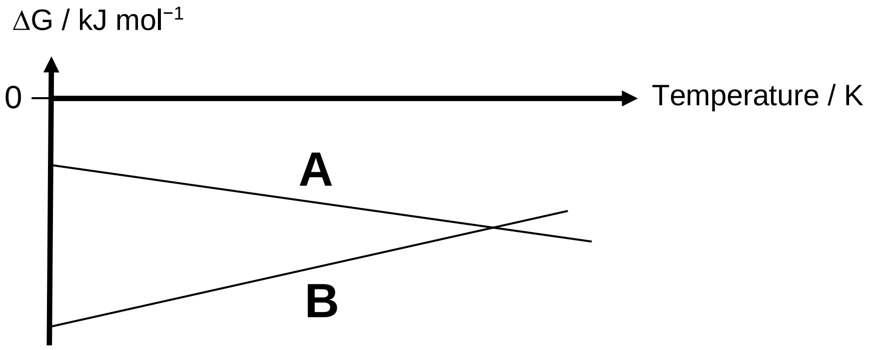

Fig 4.2

(i) With reference to the physical state of the reactants and products, explain clearly which graph in the Ellingham diagram represents **reaction 1**. [3]

(ii) The Gibb's free energy for a given reaction can be calculated in the same way as enthalpy change of reaction, via an energy cycle.

Calculate the free energy change of the following reaction at 1500 K:

$$FeO\ (s) + C\ (s) \longrightarrow Fe\ (s) + CO\ (g)$$

[1]

(iii) Molten steel is stored in a vessel saturated with oxygen at 1500 K.

Such vessels are commonly lined with aluminium oxide, which has a high melting point. Despite carbon having a high melting point, it cannot be used for the same purpose.

With reference to the information provided in **(b)**, explain why carbon cannot be used to line such vessels. [1]

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(c) Compound **Q** with the molecular formula $C_8H_9NO_2$ is found to be able to relief pain and reduce fever. At room temperature, **Q** is insoluble in water and dilute acids but soluble in aqueous sodium hydroxide. **Q** reacts with aqueous bromine to form **R**, $C_8H_7NO_2Br_2$.

On warming **Q** with dilute hydrochloric acid, compounds **S** and **T** are formed. **S** with the molecular formula of C_6H_8NOCl is soluble in water.

T, on reaction with lithium aluminum hydride, forms **U**. **U** reacts with aqueous alkaline iodine to form a yellow precipitate.

Suggest possible structures for **Q, R, S, T** and **U**. For each reaction, state the *type of reaction* described and explain what the information tells you about the functional group present in each compound. [8]

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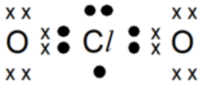
5 **(a)** **(i)** Write the balanced equation representing the standard enthalpy change of combustion of liquid C_4H_7Cl, given that gaseous ClO_2 is one of the products. [1]

(ii) The dot−and−cross diagram of ClO_2 is shown below, ClO_2 has a bond angle of 117°.



Explain, with reference to VSERP theory, why the bond angle in H_2O is smaller than that in ClO_2. [2]

(iii) *The use of the Data Booklet is relevant to this question.*

Using bond energy values, calculate the standard enthalpy change of combustion of 1−chlorobut−2−ene.

(Given: Bond energy of O=Cl is 257 kJ mol^{-1}) [2]

(iv) Explain why the theoretical value for the enthalpy change of combustion is different from your answer in **(iii)**. [1]

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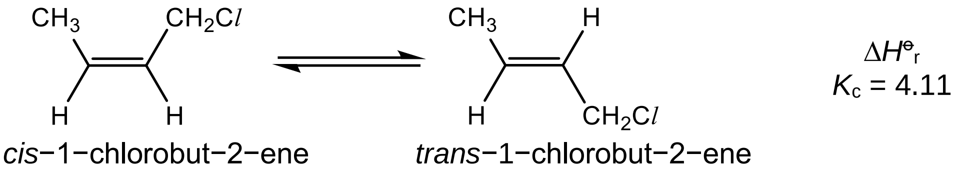
(b) The isomers *cis*−1−chlorobut−2−ene and *trans*−1−chlorobut−2−ene, C_4H_7Cl, have different stabilities.

The standard enthalpy change for the conversion of *cis*−1−chlorobut−2−ene to *trans*−1−chlorobut−2−ene isomer is $\Delta H^\ominus_r$.



To find out the relative stability of the two isomers, standard enthalpy change of combustion, $\Delta H^\ominus_c$, of the *cis* and *trans* isomers in liquid state, (henceforth known as $\Delta H^\ominus_c$(*cis*) and $\Delta H^\ominus_c$(*trans*) respectively) will be compared.

(i) Using your answer in **(a)(i)**, and information from Table 5.1, calculate the value of $\Delta H^\ominus_c$ (*cis* – $C_4H_7Cl(l)$). Give your answer in **four** significant figures.

Table 5.1

$\Delta H^\ominus_f$ ($CO_2(g)$)	−393.5 kJ mol^{-1}
$\Delta H^\ominus_f$ ($ClO_2(g)$)	+104.6 kJ mol^{-1}
$\Delta H^\ominus_f$ ($H_2O(l)$)	−285.8 kJ mol^{-1}
$\Delta H^\ominus_f$ (*cis* – $C_4H_7Cl(l)$)	−43.1 kJ mol^{-1}

[2]

(ii) Given that $\Delta H^\ominus_c$ (*trans* – $C_4H_7Cl(l)$) is −2420 kJ mol^{-1} and using your answer in **(b)(i)**, draw an energy level diagram to calculate $\Delta H^\ominus_r$. [2]

(iii) Hence, explain how the value of K_c will change when temperature is increased. [1]

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(c) Besides alkenes, cycloalkanes can also exist as *cis*−*trans* isomers.

One example is 1,2−dimethylcyclobutane.

(i) State **two** characteristics of cycloalkanes that allow *cis*−*trans* isomerism to exist for 1,2−dimethylcyclobutane. [1]

(ii) Draw the structures of the *cis*− and *trans*− isomers of 1,2−dimethylcyclobutane. [2]

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(d) The ruthenium(II) based catalyst $RuH_2(PPh_3)_4$, where PPh_3 represents $P(C_6H_5)_3$, is able to catalyse the formation of an amide from amine and alcohol, as shown in Fig 5.1.

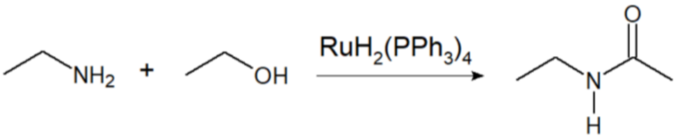


Fig 5.1

(i) Fig 5.2 shows the formation of an amide using $RuH_2(PPh_3)_4$ catalyst.

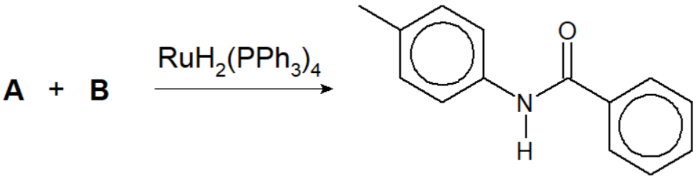
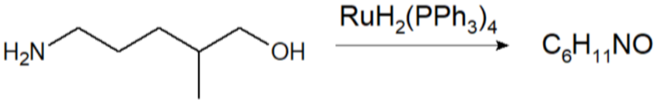


Fig 5.2

Draw the structures of compounds **A** and **B**. [2]

(ii) Hence, propose a synthetic route for the formation of compounds **A** and **B** respectively, using only methylbenzene as the starting compound in each case. [3]

(iii) Draw the structure of the product for the reaction below.



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[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.