ANDERSON SERANGOON JUNIOR COLLEGE

2021 JC 2 PRELIMINARY EXAMINATION

NAME:______________________________ (   ) **CLASS:** 21 /____

CHEMISTRY **9729/03**

Paper 3 Free Response **20 September 2021**

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and register number 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.

For Examiner's Use				
Paper 3	**A1**	/19	**Paper 1 (15%)**	/ 30
	A2	/18	**Paper 2 (30%)**	/ 75
	A3	/19	**Paper 3 (35%)**	/ 76
	B4*	/20	**Paper 4 (20%)**	/ 55
	B5*	/20	**Percentage**	
	*Circle the question you have attempted		**Grade**	

This document consists of **28** printed pages.

Section A

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

1 **(a)** SiH_4, PH_3 and H_2S are three compounds whose central atoms in their molecules are elements in Period 3 of the Periodic Table.

(i) State and explain the bond angles in the molecules of these three compounds. [4]

(ii) In this question, you may assume that phosphorus and hydrogen have the same electronegativity.
Draw the three molecules, SiH_4, PH_3 and H_2S and indicate for each one the polarity of each of the bonds it contains and the overall polarity of the molecule. [4]

(iii) State the properties of a gas necessary for it to approach ideal behavior. [2]

(iv) Of the three gases at 400 K, the behaviour of SiH_4 is closest to ideal gas behavior.

Suggest why H_2S deviate more from ideal behaviour than SiH_4. [1]

(b) **(i)** Define the term *lattice energy*. [1]

(ii) Use the data in Table 1.1, together with relevant data from the *Data Booklet*, to calculate a value for the lattice energy of magnesium iodide, $MgI_2(s)$. Show your working.

Table 1.1

	value / kJ mol^{-1}
electron affinity of iodine, $I(g) + e^- \rightarrow I^-(g)$	–295.4
enthalpy change of sublimation of iodine molecules, $I_2(s) \rightarrow I_2(g)$	+62.4
standard enthalpy change of atomisation of Mg(s)	+148
standard enthalpy change of formation of $MgI_2(s)$	–364

[3]

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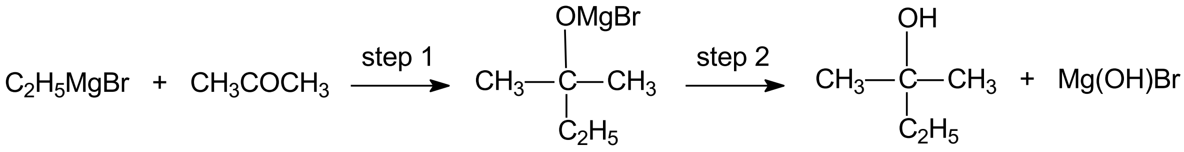
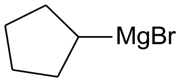
(c) Magnesium forms an important group of covalent compounds which are known as Grignard reagents. Many Grignard reagents, with different alkyl or aryl groups, have now been prepared and are widely used in organic synthesis.

A typical example of the use of a Grignard reagent is the two–step reaction of C_2H_5MgBr with propanone, CH_3COCH_3 to form 2–methylbutan–2–ol.



$$C_2H_5MgBr + CH_3COCH_3 \xrightarrow{\text{step 1}} CH_3-\overset{OMgBr}{\underset{C_2H_5}{C}}-CH_3 \xrightarrow{\text{step 2}} CH_3-\overset{OH}{\underset{C_2H_5}{C}}-CH_3 + Mg(OH)Br$$

(i) Suggest the type of reaction which occurs in step 2. [1]

(ii) Suggest the structural formula of the final organic product formed when  is reacted with ethanal, CH_3CHO, in a similar two–step process. [1]

(iii) The Grignard reagent CH_3CH_2MgBr can be readily converted into a carboxylic acid by using carbon dioxide, as shown in the two–step reaction sequence in Fig. 1.1.

$$CH_3CH_2MgBr + CO_2 \xrightarrow{\text{step 1}} \text{compound } \mathbf{A} \xrightarrow{\text{step 2}} \text{compound } \mathbf{B} + Mg(OH)Br$$

Fig. 1.1

Suggest the structural formula for compounds **A** and **B**. [2]

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(d) Two different complexes **F** and **G** can be obtained by reacting aqueous cobalt(III) chloride with ammonia under various conditions. Each complex contains a cobalt(III) ion bonded to six ligands, which can be either NH_3 or Cl^-. The cobalt(III) complexes in **F** and **G** are octahedral in shape and an octahedral arrangement is shown in Fig. 1.2.

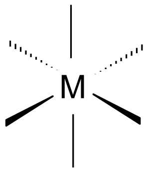

Fig. 1.2

2 mol and 1 mol of white precipitate are formed respectively when 1 mol each of the complexes **F** and **G** is treated separately with aqueous $AgNO_3$.

(i) Deduce the structural formulae of complexes **F** and **G**. [2]

(ii) The cobalt(III) complex in **G** exhibits *cis–trans* isomerism, like alkenes.

Suggest the structure of the *trans* isomer, showing clearly how the ligands are bonded to the central metal ion. [2]

[Total: 23]

Question 2 starts on the next page.

2 **(a)** Chlorine is a greenish yellow gas that was first synthesised around 1630. Chlorine forms a variety of oxides such as chlorate(VII), ClO_4^- and chlorate(V), ClO_3^-.

Chlorine gas can be produced from the electrolysis of brine (concentrated sodium chloride solution) using a diaphragm cell with inert electrodes as shown in Fig. 2.1.

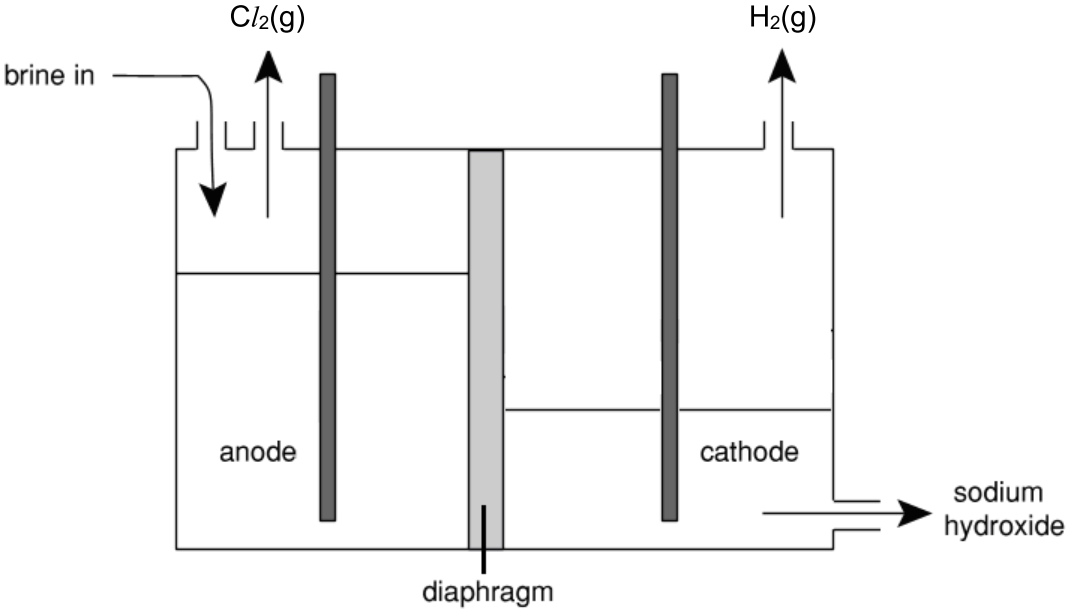

Fig. 2.1

A diaphragm is used to keep the products of electrolysis from mixing and hence, prevent the formation of undesirable by–products.

(i) Given the cathode reaction: $2H_2O + 2e \rightarrow H_2 + 2OH^-$

Write the ion-electron half-equation for the reactions taking place at the anode. Hence, construct the overall equation. You are to provide state symbols for all the equations. [2]

(ii) Calculate the mass of chlorine gas produced if a current of 5 A was passed for 7 hours through the electrolytic cell. [3]

Using relevant data from the *Data Booklet*, explain why

(iii) Dilute sodium chloride cannot be used as the electrolyte for the manufacture of chlorine in this electrolysis. [1]

(iv) Unlike chlorine, fluorine gas cannot be manufactured in a similar way using concentrated sodium fluoride. [1]

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(b) When the diaphragm in Fig, 2.1 is removed, the chlorine produced can react with the hydroxide ions to produce chloride, Cl^- and chlorate(V), ClO_3^-.

Using oxidation numbers, construct a balanced equation for this reaction. Show your working. [2]

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(c) The standard electrode potentials, $E^⦵$, of different chlorine–containing species and hydrogen peroxide are shown in Table 2.1.

Table 2.1

	Half–equation	**$E^⦵$ / V**
1	$ClO_4^- + 2H^+ + 2e^- \rightleftharpoons ClO_3^- + H_2O$	+1.19
2	$2ClO_3^- + 12H^+ + 10e^- \rightleftharpoons Cl_2 + 6H_2O$	+1.47
3	$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
4	$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	+1.77

Predict what will happen when an excess of acidified hydrogen peroxide solution is added to a solution of Cl^-**.** [3]

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Question 2 continues on the next page.

Glucose, $C_6H_{12}O_6$, is an ideal fuel for fuel cells because it is abundant in nature, renewable, non–toxic and easy to produce. Glucose alkaline fuel cell is a promising power source for portable electronic equipment. The set–up is illustrated in Fig. 2.2.

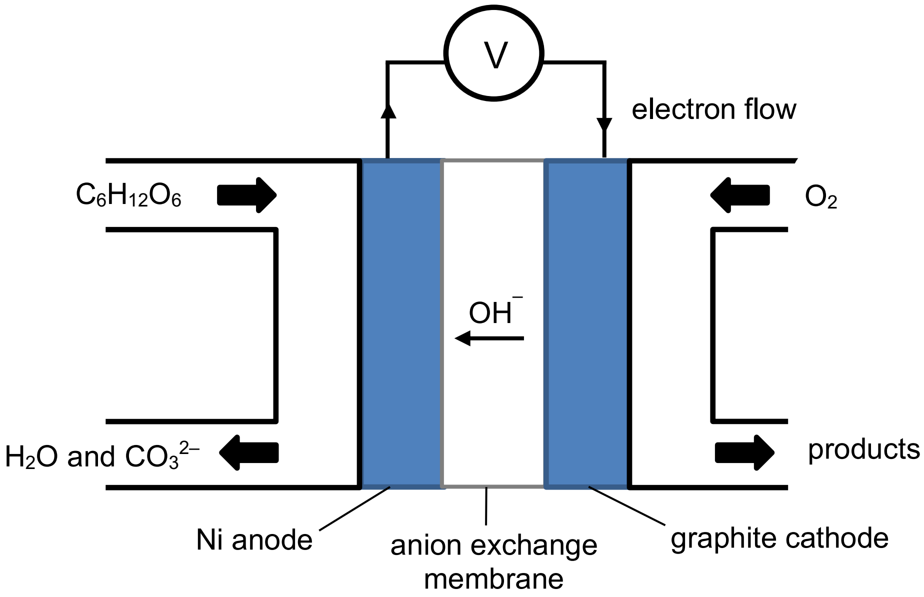

Fig. 2.2

At the anode, glucose is oxidised to carbonate ions, CO_3^{2-}, in an alkaline medium while oxygen gas is reduced at the cathode. The overall reaction occurring in the fuel cell is given below.

$$C_6H_{12}O_6 + 6O_2 + 12OH^- \rightarrow 6CO_3^{2-} + 12H_2O \qquad E^{\ominus}_{cell} = +0.85\ V$$

(d) **(i)** Calculate $\Delta G^{\ominus}$ for the overall reaction occurring in this fuel cell. [2]

(ii) Calculate the standard electrode potential for the half–equation for the reduction of CO_3^{2-} to $C_6H_{12}O_6$, using appropriate $E^{\ominus}$ value from the *Data Booklet*. [1]

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(e) In the fuel cell, glucose molecules are adsorbed on the nickel anode surface prior to oxidation to carbonate ions. Fig. 2.3 shows how the E_{cell} varies with the concentration of glucose.

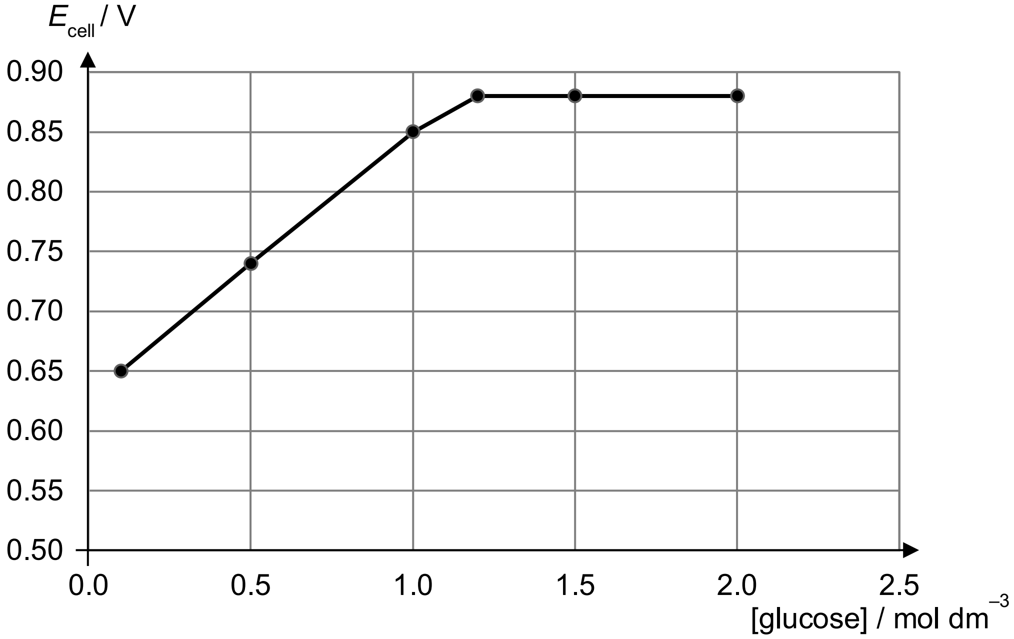

Fig. 2.3

Explain the shape of the graph. [2]

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(f) Beside the advantages mentioned in the question, suggest another possible advantage of using the glucose fuel cell compared to a hydrogen fuel cell. [1]

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[Total: 18]

3 Succinic acid, $HO_2CCH_2CH_2CO_2H$ is a diprotic acid, which serves as the precursor of certain biodegradable polymers of interest in tissue engineering applications. It is also commonly used as an acidity regulator in the food and beverage industry.

The two pK_a values associated with it are 4.2 (pK_{a1}) and 5.4 (pK_{a2}).

(a) **(i)** Butanoic acid, $CH_3CH_2CH_2CO_2H$ has a pK_a of 4.8.

With the aid of a diagram, explain why the pK_{a1} of succinic acid is lower than pK_a of butanoic acid. [2]

(ii) Calculate the pH of a 0.10 mol dm^{-3} solution of succinic acid (ignore the effect of pK_{a2} on pH). [1]

(iii) Determine the pH of the resulting solution when 30 cm^3 of 0.10 mol dm^{-3} KOH(aq) is added to 10 cm^3 of 0.10 mol dm^{-3} succinic acid. [2]

(iv) Hence using the information provided and your answers to **(a)(ii)** and **(a)(iii)**, sketch the pH–volume curve you would expect to obtain when 30 cm^3 of 0.10 mol dm^{-3} KOH(aq) is added to 10 cm^3 of 0.10 mol dm^{-3} succinic acid.
[No additional calculation is required.] [3]

(b) Succinic acid can be synthesised from bromoethanal via a series of reaction.

Bromoethanal was reacted with HCN in the presence of KCN to form **W,** C_3H_4BrNO. **W** was then reacted with reagent **U** under appropriate condition to form **X,** $C_4H_4N_2O$.

Upon heating **X** with dilute hydrochloric acid, **Y,** $C_4H_6O_5$ was generated.

Y was then heated with concentrated sulfuric acid to form **Z** which is a dicarboxylic acid with molecular formula $C_4H_4O_4$. Subsequent introduction of H_2(g) in the present of platinum catalyst will convert **Z** to succinic acid.

It is also known that when hot acidified $KMnO_4$ was added to **Z**, only an acidic gas was produced.

(i) State reagent **U** and the conditions required to convert **W** to **X**. [1]

(ii) Deduce the structures of **W**, **X**, **Y** and **Z,** explaining the reactions described. [7]

(iii) **Z** is known to exhibit stereoisomerism. Draw and label the **skeletal** formula of the stereoisomers of **Z**. [2]

(iv) Write a chemical equation to show the reaction between **Z** and hot acidified $KMnO_4$. [1]

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Section B

Answer **one** question from this section.

4 **(a)** Cyanogen iodide, ICN exists as white crystals that react slowly with water to form hydrogen cyanide and one other acidic iodine–containing by–product. The oxidation number of iodine in the by–product is +1.

(i) State the molecular formula of the by–product. [1]

(ii) Draw the displayed structure of the by–product. [1]

(iii) Cyanogen iodide, ICN, undergoes addition reactions with alkenes. With but–1–ene, isomer **D** is produced rather than isomer **E**.

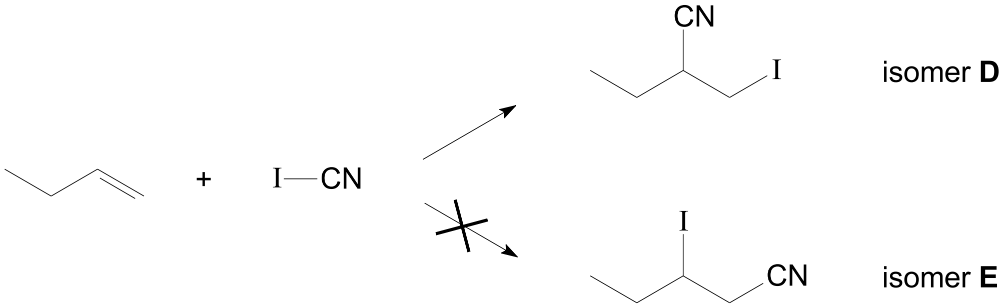

Fig. 4.1

Suggest a mechanism for this reaction. [2]

(iv) With reference to the mechanism and carbocation intermediate formed, explain the preferential production of isomer **D**. [1]

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(b) State how the reactivity of the halogens as oxidising agents varies down the group and relate these variation to relevant $E^\ominus$ value.

Hence, deduce the products formed when F_2 and Br_2 is added separately to $NaCl(aq)$. [2]

(c) Sodium, aluminium and sulfur are elements in Period 3 of the Periodic Table.

Use the oxides of these three elements to describe reactions that illustrate the variation in their acid–base behaviour. Write equations for all the reactions you describe. [5]

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(d) Table 4.1 lists the boiling points of some Period 3 oxides.

Table 4.1

compound	**formula**	**boiling point / °C**
sodium oxide	Na_2O	1950
silicon oxide	SiO_2	2230
sulfur dioxide	SO_2	–10
sulfur trioxide	SO_3	45

(i) Using structure and bonding, suggest reasons for the differences in boiling points of Na_2O, SiO_2 and SO_2. [3]

(ii) Account for the difference in boiling points between SO_2 and SO_3. [1]

(iii) SO_2 and SO_3 are sealed in separate containers and heated from room temperature to a temperature of 100 °C.

With reference to Table 4.1, explain which compound will show a greater change in entropy. [1]

(iv) When reacted with SO_3, PCl_3 produces a compound **J** with M_r = 153.5 and a by–product **K**. **J** is also produced when PCl_5 is reacted with a small amount of H_2O.

Suggest the identity of **J** and **K** and construct equations for the production of **J** from PCl_3 and PCl_5. [3]

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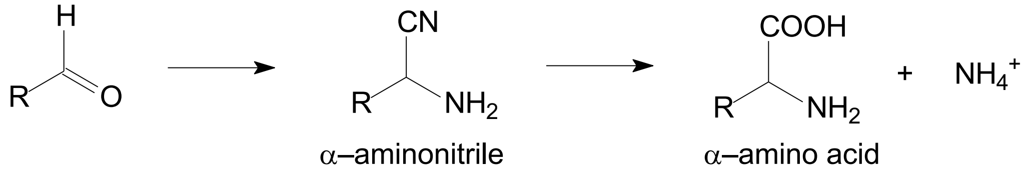
5 **(a)** The Strecker Synthesis is a preparation method for α–amino acids using aldehydes. In the process, α–aminonitriles, which are versatile intermediates to form α–amino acids via hydrolysis of the nitrile group.



Alanine, 2–aminopropanoic acid, can be prepared from ethanal via Strecker Synthesis as shown in Fig. 5.1.

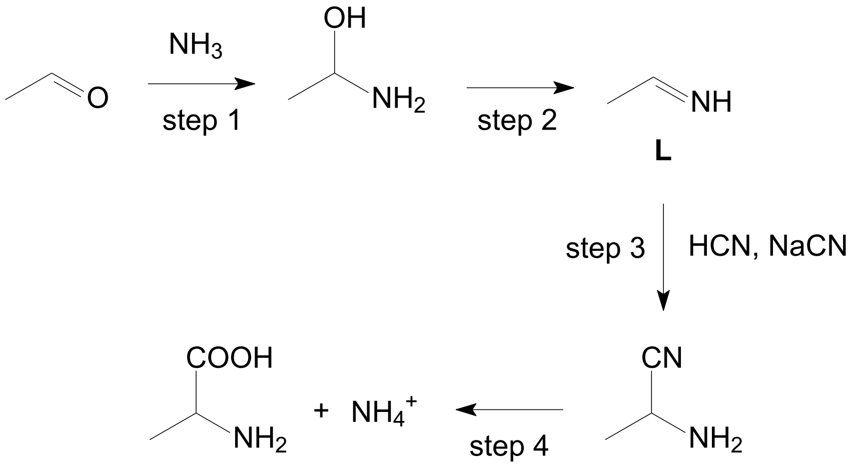


Fig. 5.1

(i) Alanine has a melting point of 213 °C while ethanal has a melting point of –124 °C. Suggest reasons for the difference in their melting points. [2]

(ii) Imines are the nitrogen analogues of aldehydes and ketones, containing a C=N bond instead of a C=O bond. Compound **L** in Fig 5.1 is one example of an imine.

Assuming the C=N bond of imines has the same reactivity as the C=O bond of carbonyl compounds, name and describe a mechanism for step 3 shown in Fig. 5.1. [3]

(iii) Explain why step 3 produces an equimolar mixture of enantiomers. [2]

(iv) Draw the enantiomers formed in step 3. [1]

(b) Fig. 5.2 shows a five–step laboratory synthesis reaction scheme of protonated alanine from ethanol.

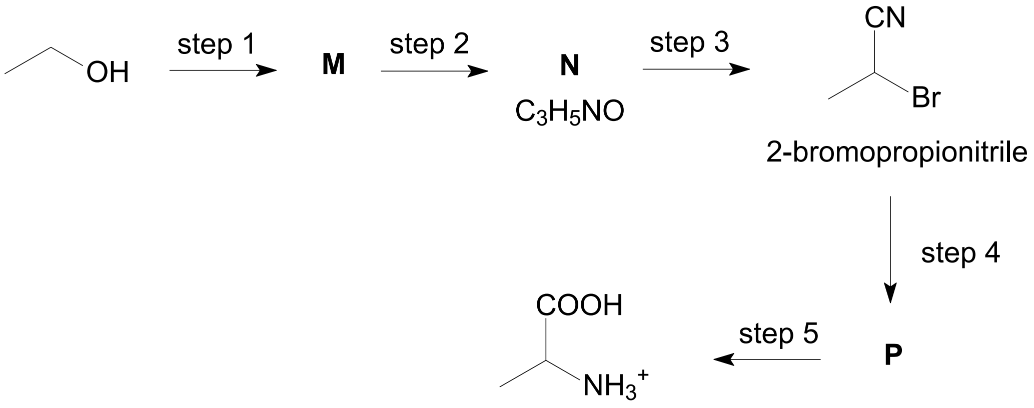


Fig. 5.2

Suggest the structures of the intermediates **M**, **N** and **P** and the reagents and conditions for steps 1 **and** 4. [5]

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(c) Ethanol can be synthesised from bromoethene with bromoethane as an intermediate.

The bromine atom in bromoethane is very reactive while the bromine atom in bromoethene is unreactive.

Suggest two reasons for the unreactivity of the bromine atom in bromoethene. [2]

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(d) Oxides of sodium and sulfur both react with water.

Write equations for these two reactions and describe the effect of the resulting solutions on Universal Indicator solution. [2]

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(e) Describe and explain how the thermal stability of hydrogen halides varies down Group 17. [3]

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Additional answer space

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