H

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME

CLASS

TUTOR'S NAME

CHEMISTRY

9729/02

Paper 2 Structured Questions

11 SEP 2017

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

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	
1	/13
2	/23
3	/14
4	/11
5	/14
Total	/75

This document consists of **22** printed pages.

1 Ammonium salts are commonly used in instant cold packs. The cold pack contains water and an inner pouch containing an ammonium salt. When the pack is squeezed, this inner pouch breaks and releases the salt, which quickly dissolves and lowers the pack's temperature.

To determine whether ammonium chloride or ammonium nitrate is more effective as the ingredient in the cold pack, a student decided to conduct an experiment to find out the enthalpy change of solution of the two salts, starting with ammonium chloride.

He added ammonium chloride to water and found the temperature change by plotting a suitable graph to correct for heat transfer.

In a preliminary investigation, the enthalpy change of solution of ammonium chloride was found to be approximately +15 kJ mol^{-1}.

(a) (i) Draw dot-and-cross diagram to illustrate the bonding in ammonium nitrate. Hence state the shape with respect to each nitrogen atom.

[3]

(ii) The student predicted that enthalpy change of solution of ammonium nitrate is more endothermic compared to ammonium chloride. Explain why his prediction is correct.

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……[2]

(b) (i) The student was told to use 100 cm^3 of water for conducting the experiment. Suggest a minimum mass of ammonium chloride that could be used. Given that 4.3 J is required to raise the temperature of 1.0 cm^3 of any solution by 1°C. Justify your choice with relevant calculations, stating any other assumptions you made.

[1]

The student carried out the following procedure to find the enthalpy change of solution of ammonium chloride.

1. Weigh accurately 8.00 g of ammonium chloride in a weighing bottle using a weighing balance.
2. Using a 100 cm^3 measuring cylinder, add 100 cm^3 of water into a polystyrene cup.
3. Stir the water gently using the thermometer.
4. Start the stopwatch.
5. Record the temperature of the water in the container, using a 0.1 ^oC thermometer, at 1 min interval.
6. At the 4th min, tip the ammonium chloride into the water. Do not read the temperature at this time.
7. Stir the solution gently and record the temperature of the solution at 4.5 min. Continue to stir and record the temperature at 30 s intervals until 8th min.
8. Reweigh the weighing bottle.

(ii) Draw a sketch of the graph that you expect to obtain from the experiment. Indicate clearly on the graph how the temperature change, ΔT, can be found.

[2]

(iii) Predict and explain the sign of ΔS when ammonium nitrate is dissolved in water.

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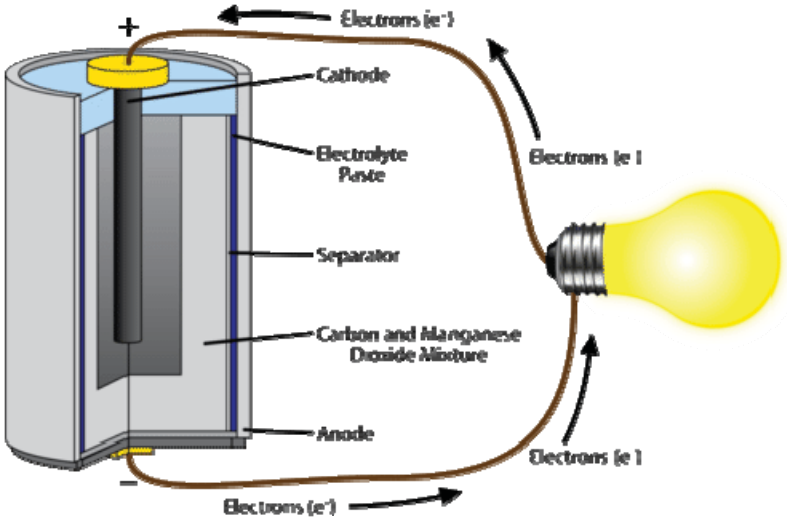
……[1]

(c) Ammonium chloride is also used as electrolyte in zinc–carbon batteries, where the outer zinc container is the negatively charged terminal and is oxidised during discharge.



The following reaction also takes place in the cell.

$$2MnO_2(s) + 2e^- + 2NH_4Cl(aq) \rightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l) + 2Cl^-(aq)$$
$$E^\ominus = +0.5\ V$$

Use the table of standard redox potentials given in the *Data Booklet* to answer the questions below.

(i) Write the overall equation for the reaction that occurs in the cell when electrons are discharged.

……[1]

(ii) Calculate the voltage that is generated by this cell.

……[1]

(iii) Calculate a value of $\Delta G^\ominus$ for the cell reaction, and explain the significance of its sign.

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……[2]

[Total: 13]

2 2-iodobutane can be readily converted into 2-aminobutane using ethanolic ammonia.

$$CH_3CHICH_2CH_3 + 2NH_3 \rightarrow CH_3CH(NH_2)CH_2CH_3 + NH_4I$$

In order to determine the rate equation for this reaction, an investigation was carried out at a constant temperature. 4.00 mol dm^{-3} ethanolic ammonia was first prepared by bubbling ammonia gas into ethanol.

Equal volume of 0.20 mol dm^{-3} 2-iodobutane and 4.00 mol dm^{-3} ethanolic ammonia were mixed. At suitable time intervals, 10 cm^3 of the reaction mixture was pipetted into a conical flask and quenched. Chlorine gas was bubbled into the reaction mixture and excess chlorine gas was subsequently removed. The reaction mixture was then titrated with 0.0250 mol dm^{-3} sodium thiosulfate in the presence of an indicator.

(a) Draw a labelled diagram to illustrate the bonding between ammonia and ethanol.

[2]

(b) **(i)** Suggest why the reaction must be quenched and describe how this can be done.

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……[2]

(ii) Write an ionic equation for the reaction when chlorine was bubbled through the reaction mixture.

……[1]

(iii) Hence, write an ionic equation for the reaction between the reaction mixture and sodium thiosulfate.

……[1]

(iv) Suggest a suitable indicator for the titration and describe how you would recognise the end-point during the titration.

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……[2]

(c) The table below shows the results obtained from the titration at different time intervals.

time / min	volume of sodium thiosulfate used / cm^3
5.0	12.00
10.0	20.50
15.0	26.50
20.0	30.50
25.0	33.50
30.0	35.50

(i) To determine the order of reaction with respect to 2-iodobutane, use these data to plot a suitable graph on the grid below.

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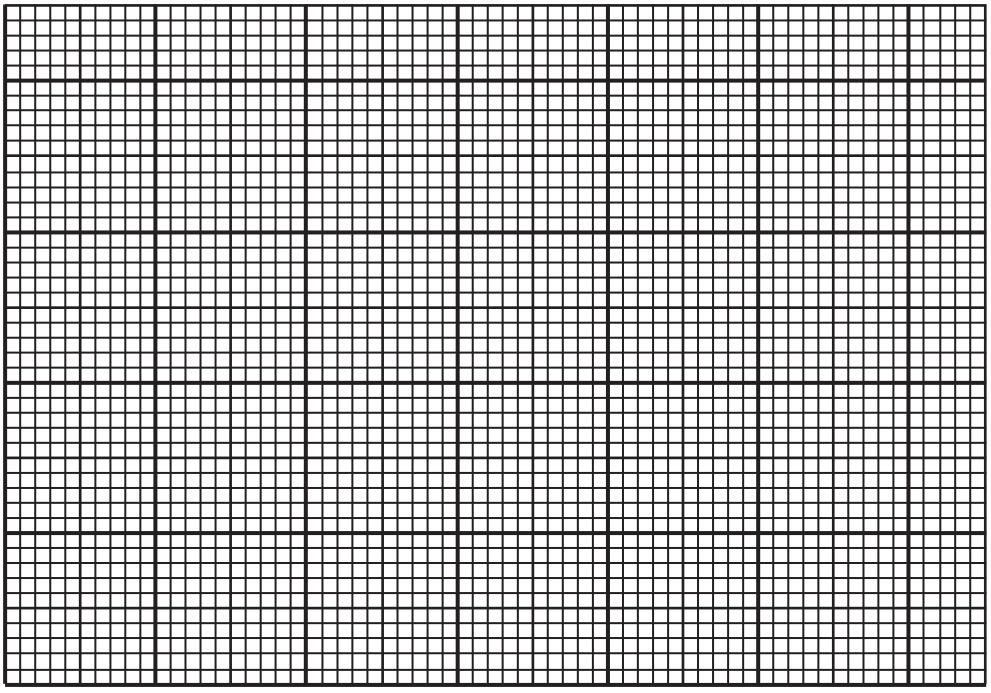

[2]

(ii) Hence, deduce the order of reaction with respect to 2-iodobutane.

[2]

(iii) The concentration of ethanolic ammonia is halved and a new series of experiments was carried out at the same temperature. When a similar graph was plotted, the gradient at each point was half that obtained from the first graph.

What is the order of reaction with respect to ethanolic ammonia? Explain your answer.

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……[1]

(iv) Hence, construct the rate equation for the reaction between 2-iodobutane and ethanolic ammonia.

……[1]

(v) Calculate the rate constant, for the reaction between 2-iodobutane and 4.00 mol dm^{-3} of ethanolic ammonia, stating its units.

[3]

(vi) Hence, describe the mechanism between 2-iodobutane and ethanolic ammonia.

[4]

(vii) Suggest and explain the effect on the rate of reaction when

I. 2-iodobutane is replaced with 2-chlorobutane.

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……[1]

II. ethanolic ammonia is replaced with ethanolic ethylamine.

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……[1]

[Total: 23]

3 The table below gives data about some physical properties of transition elements chromium, iron and cobalt.

Property	Chromium	Iron	Cobalt
First ionisation energy / kJ mol^{-1}	653	762	757
K_{sp} of $M(OH)_3$ / mol^4 dm^{-12}	6.3×10^{-31}	4×10^{-38}	1.6×10^{-44}

(a) Explain why these three metals have similar first ionisation energies.

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……[2]

(b) Equal volumes of 0.010 mol dm^{-3} chromium(III) solution and 0.010 mol dm^{-3} iron(III) solution were mixed. To separate the two metal ions, solid sodium hydroxide was added to precipitate the maximum amount of $Fe(OH)_3$ from the mixture, without precipitating $Cr(OH)_3$.

(i) Calculate the concentration of hydroxide ion in the mixture when $Cr(OH)_3$ just precipitates.

[2]

(ii) Hence, determine the concentration of iron(III) ions remaining in the solution. Evaluate if the separation is effective.

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……[2]

(iii) Alternatively, sodium hydroxide can be added until in excess to separate iron(III) and chromium(III) ions. Explain how the separation can be achieved, giving a brief procedure and the ionic equations of the reactions involved.

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……[3]

(c) (i) In the presence of ligands, the d orbitals of iron(III) complexes split into two groups. Explain how the d orbitals of an octahedral complex, such as $[Fe(H_2O)_6]^{3+}$, are arranged in the presence of ligands. Include a fully labelled diagram in your answer.

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……[2]

(ii) Hence, explain why a solution of $[Fe(H_2O)_6]^{3+}$ is yellow.

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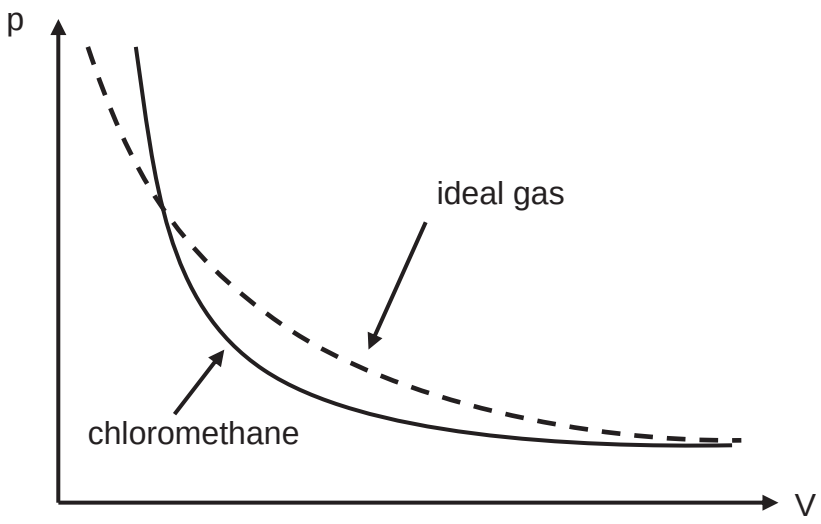
……[3]

[Total: 14]

4 (a) The following graphs show the pressure–volume relationship for 1 mole of an ideal gas and chloromethane in a syringe at temperature *T* K.



Explain why part of the graph for chloromethane is below that of an ideal gas at low pressure.

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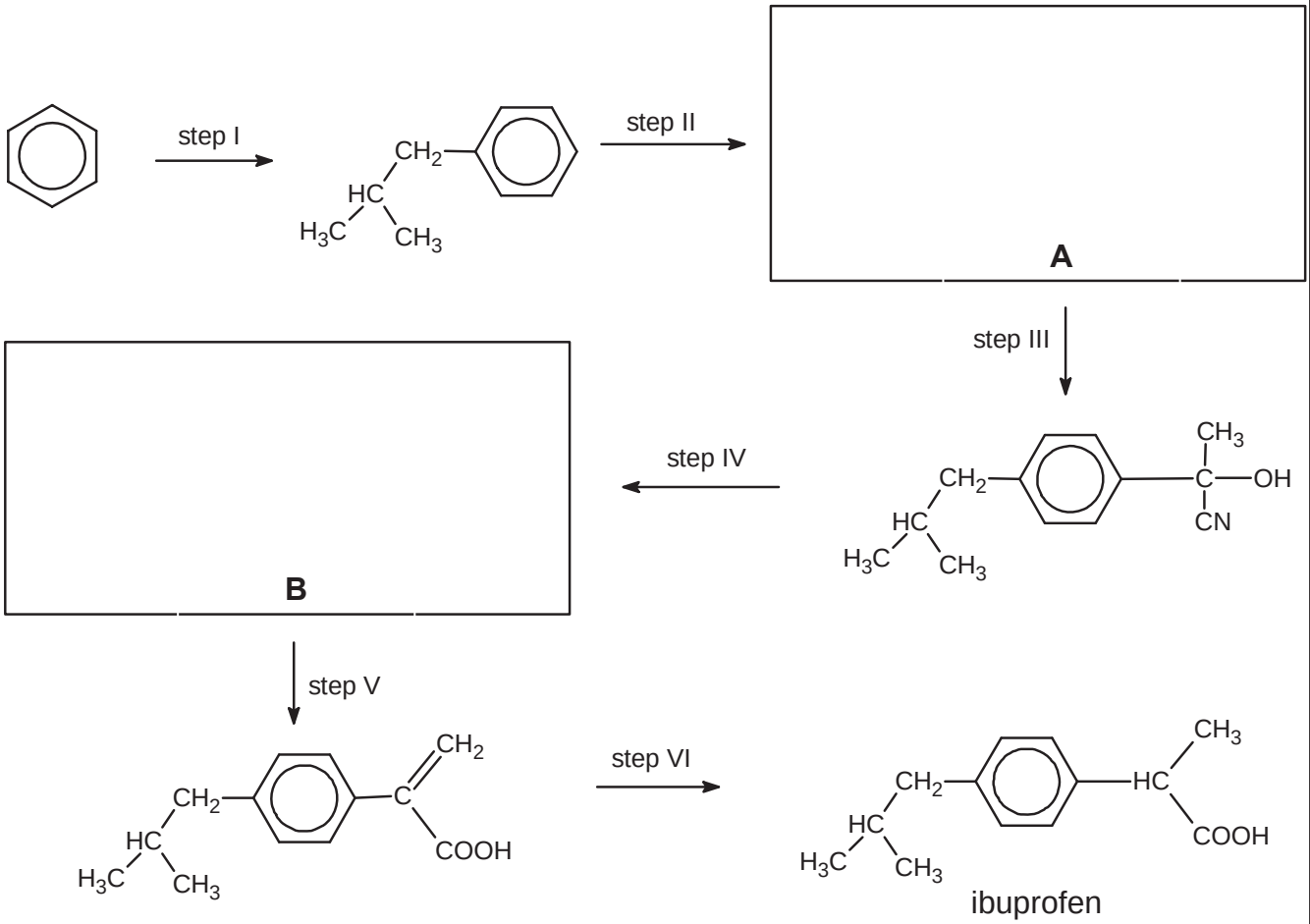
……[1]

(b) Ibuprofen is a common medication that is used to relief pain and fever. Benzene is used as the starting chemical in the production of ibuprofen according to the following synthesis scheme.



(i) State the type of reaction in step I.

.....[1]

(ii) Draw the structures of compounds A and B in the boxes above.

[2]

(iii) Suggest the reagents and conditions for step I, IV and VI.

step I: .....

step IV: .....

step VI: .....

[3]

When approving new medicine for human consumption, food and drug approving agencies require the medicine to contain only one of two enantiomers that is biologically safe.

In the production of ibuprofen, a pair of enantiomers is produced in equal quantities in step III. However, both enantiomers are used to produce ibuprofen.

(iv) Draw the pair of enantiomers and explain why 2 enantiomers are produced is step III. You may use R to represent the phenyl side chain.

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……[1]

(v) By considering the hybridisation of carbon, explain why both enantiomers can be used to produce ibuprofen?

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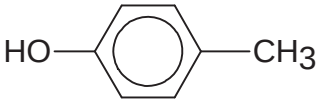
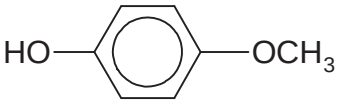
……[1]

(c) The pK_a of two substituted-phenols are given below.



pK_a = 10.26
methylphenol



pK_a = 10.21
methoxyphenol

Suggest a reason for the difference in pK_a values of both compounds.

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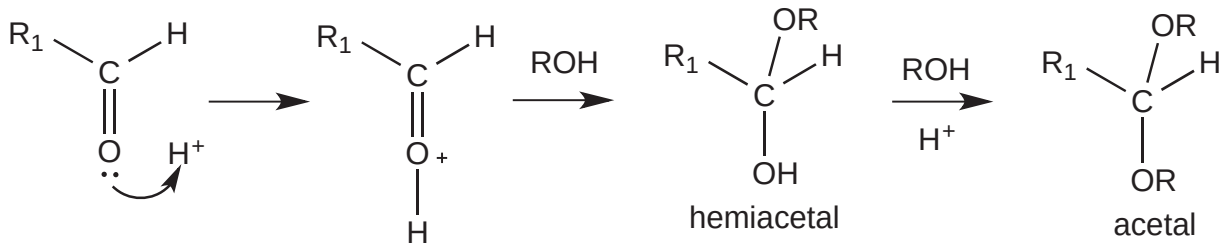
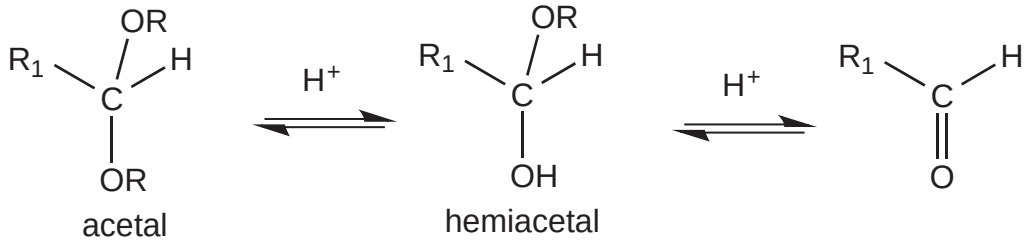
……[2]

[Total:11]

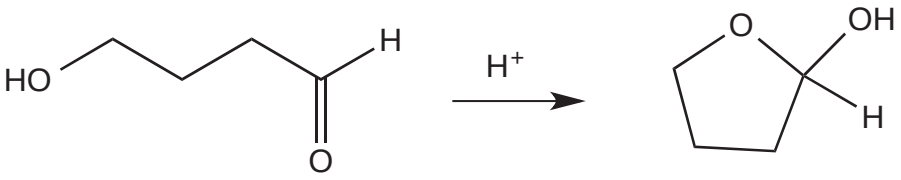
5 The synthesis of hemiacetals and acetals are acid-catalysed as shown.



However, hemiacetal and acetal formation are reversible. In the presence of acid, the acetal and hemiacetal hydrolysed back to form the aldehyde.



(a) (i) 4-hydroxyaldehyde undergoes the same mechanism in the presence of acid to form a cyclic hemiacetal, which is more stable towards hydrolysis.



Describe the mechanism for this reaction, including curly arrows showing the movement of electrons, and all charges.

[3]

(ii) Outline a simple chemical test to check if the formation of the cyclic hemiacetal is reversible.

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……[2]

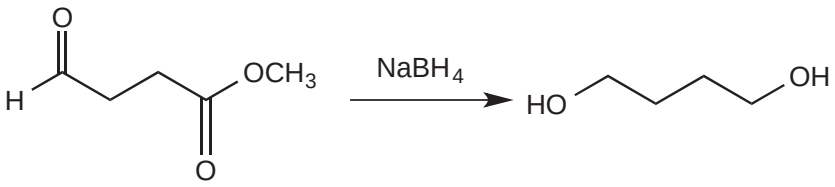
(iii) The product of this reaction, the cyclic hemiacetal, exists as a mixture of stereoisomers. Draw the displayed structure of each stereoisomer of the cyclic hemiacetal.

[2]

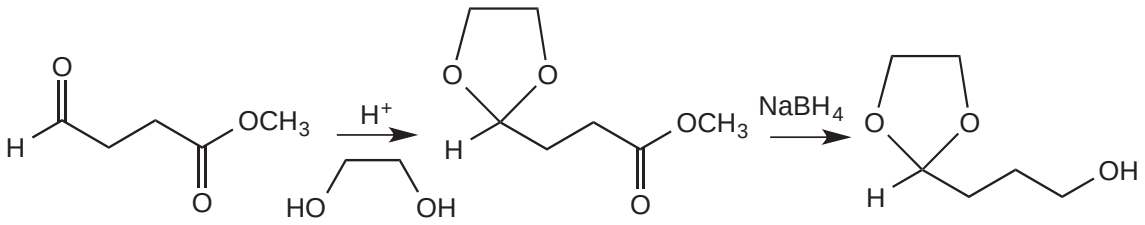
(b) Protecting groups are introduced in reactions involving complex molecules with different functional groups. This is to prevent the interfering functional groups from reacting. These functional groups in a molecule must be protected in order for reaction to proceed the desired way.

For instance, aldehyde undergoes reduction readily. The aldehyde could be converted to form acetal to protect the aldehyde against the reduction reaction.

Without protecting group:



With protecting group:



(i) Explain why sodium boron hydride, $NaBH_4$ reduces ester slowly to form primary alcohol while it reduces aldehyde more readily.

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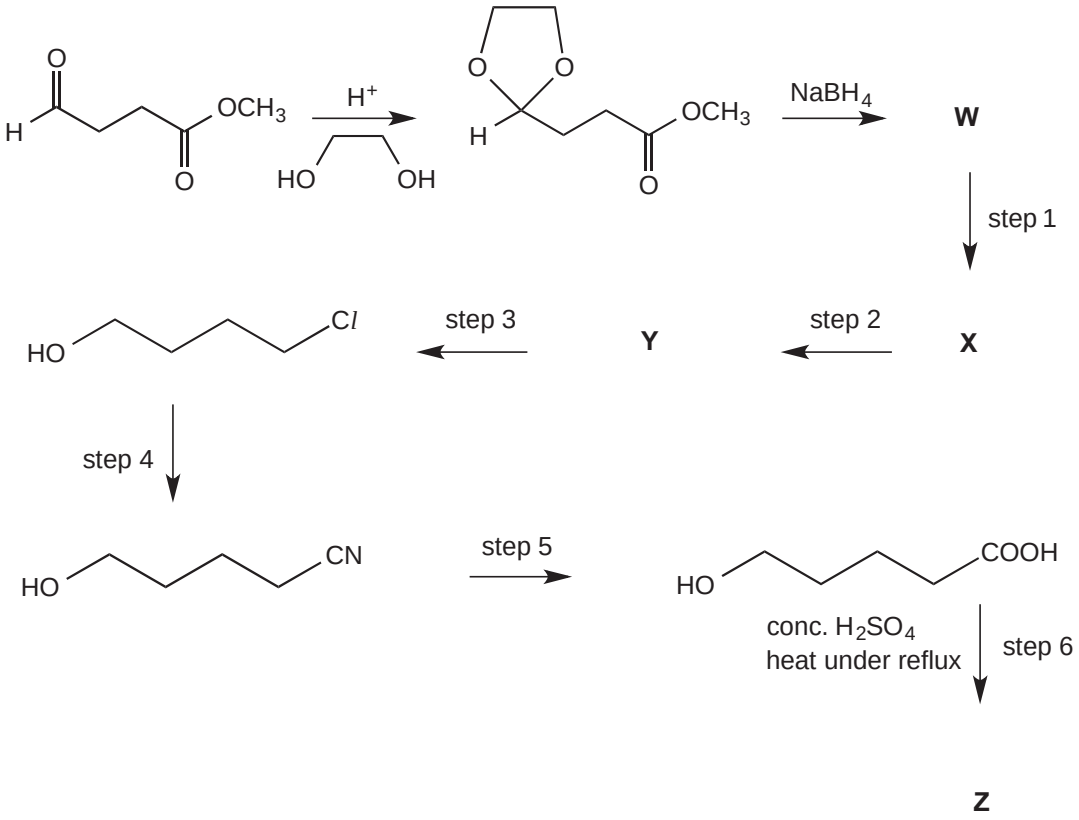
……[1]

Compound Z can be made from the following reaction scheme, where the first step involves the protection of aldehyde.



(ii) Suggest the structural formulae of W, X, Y and Z.

W	**X**
Y	**Z**

[2]

(iii) State the reagents and conditions needed for step 1, 2 and 3.

step 1: ……

step 2: ……

step 3: ……

[3]

(iv) State the type of reaction for step 4 and 5.

step 4: ……

step 5: ……

[1]

[Total:14]