VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATIONS
Higher 3

CHEMISTRY **9813/01**

Paper 1 **26 September 2022**

INSERT **2 hours 30 minutes**

INSTRUCTIONS

This insert contains information for Question 1. **Do not write your answers on the insert.**

This document consists of **3** printed pages and **1** blank page.

Information for Question 1

The following abstracts are adapted from "Heterogeneous and Homogenous Catalysts for Hydrogen Generation by Hydrolysis of Aqueous Sodium Borohydride Solutions" (*P. Brack et al, Energy Science and Engineering 2015 volume 3, issue 3, 174 –188.*)

Abstract 1 Sodium borohydride and ammonia borane as hydrogen storage materials

Hydrogen is more energy-dense than carbon by mass. It is an attractive alternative to the use of fossil fuels (hydrocarbons), which release carbon dioxide during their combustion, thus contributing to global warming. Cost-effective production and safe storage of hydrogen are two major hurdles to the successful inauguration of a hydrogen economy.

Sodium borohydride ($NaBH_4$) and ammonia borane (BNH_6) are the most studied chemical hydrogen storage materials.

Among the chemical hydrides considered as solid hydrogen storage materials, sodium borohydride, an ionic compound, is nontoxic, stable, and environmentally benign, and appears to be the most promising one. The hydrolysis reaction can produce pure hydrogen at temperatures as low as 298 K.

$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$ (1)
$NaBH_4 + 4H_2O \rightarrow NaB(OH)_4 + 4H_2$ (2)

Sodium borohydride undergoes self-hydrolysis upon the addition of water. The mechanism of self-hydrolysis has been described as shown below.

Step 1: $NaBH_4(s) \rightleftharpoons Na^+(aq) + BH_4^-(aq)$
Step 2: $BH_4^-(aq) + H^+(aq) \rightleftharpoons BH_3(aq) + H_2(g)$
Step 3: $BH_3(aq) + 3H_2O(l) \rightarrow B(OH)_3(aq) + 3H_2(g)$
Step 4: $B(OH)_3(aq) + H_2O(l) \rightleftharpoons B(OH)_4^-(aq) + H^+(aq)$
Step 5: $4B(OH)_4^-(aq) + 2H^+(aq) \rightleftharpoons B_4O_7^{2-}(aq) + 9H_2O(l)$

In the presence of a catalyst such as cobalt or ruthenium, the sodium borohydride hydrolysis proceeded at a uniform rate and was completed within minutes to release hydrogen gas.

Kinetic studies show that the catalytic hydrolysis of sodium borohydride is first order with respect to the catalyst, but zero order with respect to the substrate.

Ammonia borane is another appropriate hydrogen storage material because of its high hydrogen content of 19.6% by mass, high stability under ambient conditions, nontoxicity, and high solubility in common solvents. While sodium borohydride is an ionic compound, ammonia borane is a Lewis acid–base adduct.

Important Data
$\Delta H_f^\ominus[H_2O(l)] = -286$ kJ mol^{-1}
$\Delta H_f^\ominus[CO_2(g)] = -394$ kJ mol^{-1}

Solubility of $NaBO_2$ at 25 °C = 28 g per 100 g of water
Solubility of $NaBH_4$ at 25 °C = 55 g per 100 g of water
Solubility of BNH_6 at 25 °C = 33.6 g per 100 g of water

Arrhenius equation: $k = A\exp(-E_a/(RT))$ where A is a constant

Abstract 2 Direct borohydride fuel cell

A direct borohydride fuel cell (DBFC) is a device that converts chemical energy stored in borohydride ion (BH_4^-) and an oxidant directly into electricity by redox processes. A DBFC usually employs an alkaline solution of sodium borohydride as fuel and oxygen as oxidant.

DBFCs are considered attractive energy suppliers, especially for portable applications. DBFC supersedes DMFC (direct methanol fuel cell) in terms of capacity value, electrochemical activity, and power performance at ambient temperature. In addition, use of alkaline electrolytes which feature relatively low corrosion activity, opens the possibility of applying readily available and low-cost non-precious metal anode catalysts. Both borohydride ion and its oxidation product tetrahydroxyborate ion ($B(OH)_4^-$) are relatively inert and non-toxic. Tetrahydroxyborate can be recycled to produce borohydride.

There is a difference to note between sodium borohydride as a hydrogen gas generator for a hydrogen/oxygen fuel cell and sodium borohydride as a direct liquid-fed fuel cell. In the former case, the hydrolysis generates hydrogen gas, and the fuel cell is based on the oxidation of the gas subsequently. In the latter case, sodium borohydride is in an alkaline (pH > 12) solution (anodic fuel) and is fed into a DBFC and then oxidised.

The borohydride ion hydrolyses quasi-spontaneously to generate hydroxy borohydride ($BH_3(OH)^-$) and hydrogen gas on various electrode materials. Hydrolysis of hydroxy borohydride takes place through the formation of borate (BO_2^-) to generate more hydrogen gas as shown below.

$$BH_4^- + H_2O \rightarrow BH_3(OH)^- + H_2 \qquad (3)$$
$$BH_3(OH)^- + H_2O \rightarrow BO_2^- + 3H_2 \qquad (4)$$

VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 3

CANDIDATE NAME ....

CT GROUP ....

CHEMISTRY

9813/01

Paper 1

26 September 2022

2 hours 30 minutes

Candidates answer on the Question Paper.
Additional Materials: Data Booklet
Insert

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, highlighters, 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 **two** questions.

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.
You are reminded of the need for clear presentation in your ans

---

This document consists of **36** printed pages.

[Turn over

Section A

Answer all questions in this section.

The information provided in the insert is taken from a published scientific article. Other published articles may not agree with all of this information.

You should read all the above information before you start to answer any questions and use the information it contains to answer the questions.

1 **(a)** Calculate the ratio between the heat generated when H_2 is burned and the heat generated when carbon of the same mass as H_2, is burned. [1]

....

....

....

(b) Suggest why the concentration of $NaBH_4$ has to be kept low (for example below 16 g per 100 g of water) during the hydrolysis of $NaBH_4$. [1]

....

....

....

(c) State and explain the role of $B(OH)_3$ when it is reacted with water in step 4 of the mechanism regarding self-hydrolysis of $NaBH_4$. [1]

....

....

....

(d) Write an equation for the synthesis of BNH_6 from $NaBH_4$ and $(NH_4)_2SO_4$. There is a gaseous by-product in this reaction. [1]

....

(e) Draw the molecular geometry of BH_4^- and BNH_6 molecule respectively, clearly showing the shape. [2]

....

....

....

....

....

....

(f) Explain briefly how a transition metal can function as a catalyst for the hydrolysis of $NaBH_4$. [3]

....

....

....

....

....

....

....

....

....

....

....

....

(g) **(i)** Calculate the mass of ruthenium in mg used as a catalyst which must be added to 0.100 dm^3 of 1.0 mol dm^{-3} $NaBH_4$ solution to produce H_2 at a rate of 0.100 dm^3 min^{-1} at 25 °C and 1.0 atm. The rate of H_2 production per mol of ruthenium is 92 mol of H_2 min^{-1} at 25 °C. [A_r(Ru) = 101.1] [1]

(ii) For how many minutes will this reaction supply H_2 at the rate you have calculated in **(g)(i)**? [1]

....

....

....

....

....

....

....

....

....

....

(h) **(i)** H_2 used for the fuel cell is supplied from the hydrolysis of $NaBH_4$. A fuel cell is made up of three segments sandwiched together: the anode, the alkaline electrolyte, and the cathode. H_2 is used as fuel and O_2 as oxidant.

The net resultant reaction is $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

Calculate the standard Gibbs free energy for the above reaction. [1]

(ii) Calculate the volume of air in dm^3 at r.t.p. needed to generate a constant current of 2.5 A for 3.0 h in the above fuel cell. Assume that air contains 20% by volume of $O_2(g)$. [1]

....

....

....

....

....

....

....

....

....

(i) **(i)** Given that BH_4^- is oxidised to $B(OH)_4^-$ in the direct borohydride fuel cell (DBFC), write relevant equations for the reactions that take place at the cathode and anode. Hence write the equation for the overall reaction that takes place in the DBFC. [2]

(ii) The E^θ_{cell} for the reaction above is +1.64 V. Determine $E^\theta(B(OH)_4^-/BH_4^-)$. [1]

(iii) Suggest why in practice the observed anode potential is found to be between –0.83 V and the value you have calculated in **(i)(ii)**. [1]

....

....

....

....

....

....

....

....

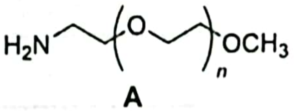
....

[Total: 18]

Name: .... CT group: ....

2 Block-copolymers, obtained by linking different polymers (blocks), have unique properties, such as the ability to self-assemble.

(a) The water soluble polymer **A** (α-methoxy-ω-aminopolyethyleneglycol) has the repeating unit –(OCH_2CH_2)–. The structure is shown below. *n* represents the number of repeating units.



A

The ^1H NMR spectrum of **A** is shown below. There are approximately 4 different chemical environments for the protons, which are named **a** to **d**.

proton	δ / ppm	peak area of signal in arbitrary units
a	2.7	0.6
b	3.3	0.9
c	3.4	0.6
d	approximately 3.5	133.7

The signal at 2.7 ppm disappears in the presence of D_2O.

(i) Copy the structure of **A** and on **every** proton label with the appropriate letters **a** to **d** that match the above spectrum. [2]

(ii) Why does the signal at 2.7 ppm disappear in the presence of D_2O? [1]

(iii) By considering the peak areas for protons **b** and **d**, calculate the value of *n*. [2]

....

....

....

....

....

....

....

....

....

....

....

....

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

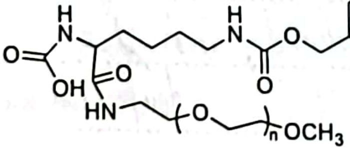
……………………………………………………………………………………

……………………………………………………………………………………

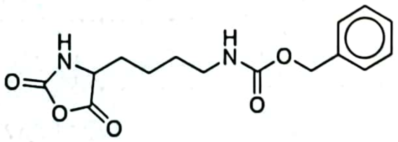
……………………………………………………………………………………

……………………………………………………………………………………

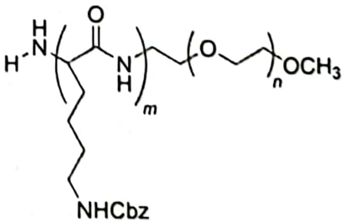
(b) The synthesis of **B** is performed through the reaction of **A** with **C**. Mild hydrolysis of **B** results in evolution of a CO_2 gas. **B** can further react to form another polymer **D** that has the repeating unit –(CONH)–. *m* represents the number of repeating units.



B



C

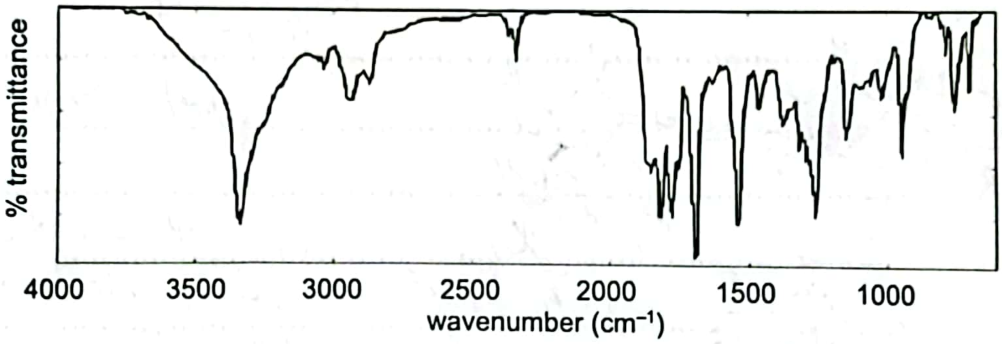


D

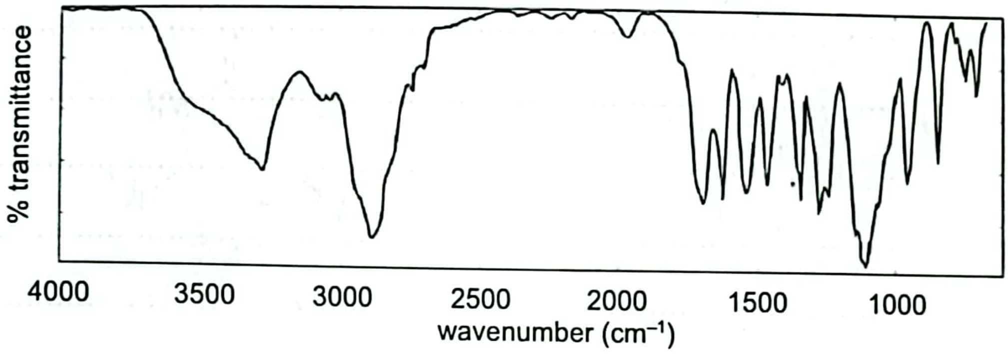
Cbz as shown in the structure of **D** represents $C_6H_5CH_2OCO$ group.

Draw the mechanism for the reaction of **A** with **C** to form **B** and identify the gas. You may represent the groups that are not involved in the reaction as R, R' etc. [3]

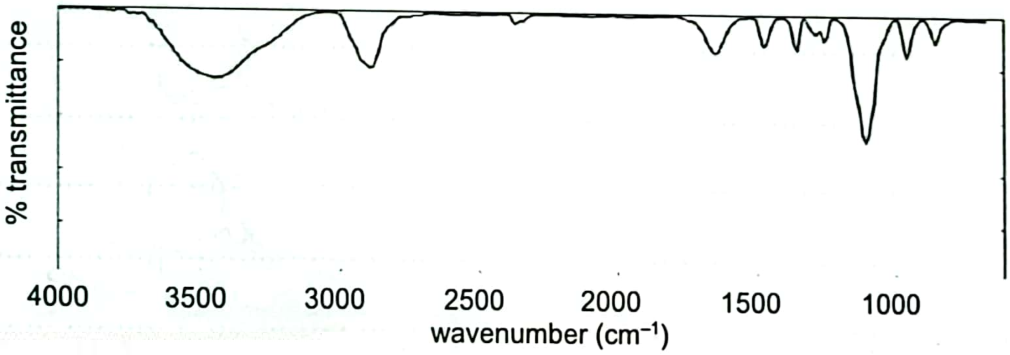
(c) The IR spectra of **A**, **C** and **D** were obtained and were labelled as **1**, **2** and **3**, not necessarily in the same order. Match the three IR spectra with **A**, **C** and **D**. Briefly explain your answer.



spectrum **1**



spectrum **2**



spectrum **3**

....

....

....

....

....

....

....

....

....

....

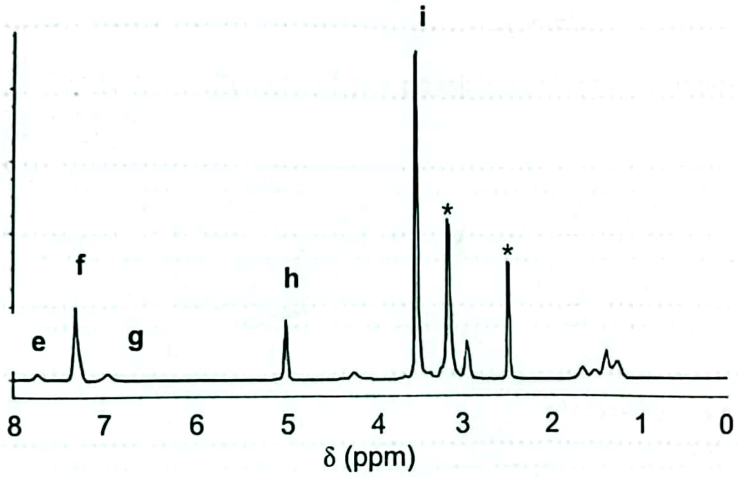
....

....

....

....

(d) The ^{1}H NMR spectrum of **D** is shown below. Some of the signals have been labelled as **e** to **i**.



The signals marked with * correspond to the solvent.

The table below shows the protons **e** to **i** and the peak area of each signal. Protons **e** correspond to the –(CONH)– repeating unit of **D**.

proton	peak area of signal in arbitrary units
e	22.4
f	119
g	23.8
h	47.6
i	622

Using some or all the signals, calculate the value of m, the number of –(CONH)– repeating units in **D**. You may assume the value of n is the same as found in **(a)(iii)**. Copy the structure of **D**, and on the protons you used for calculations label with the corresponding letters **f** to **i** (ignore **e** since this has been assigned) that match the above spectrum. [3]

....

....

....

....

....

....

....

....

....

....

....

....

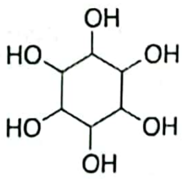
....

....

....

....

(e) The alcohol functional group is commonly found in monomers which are used to form polymers such as **A** in **(a)** and in biological molecules such as β-glucose. In this part of the question, we consider inositol and the structure is shown below.



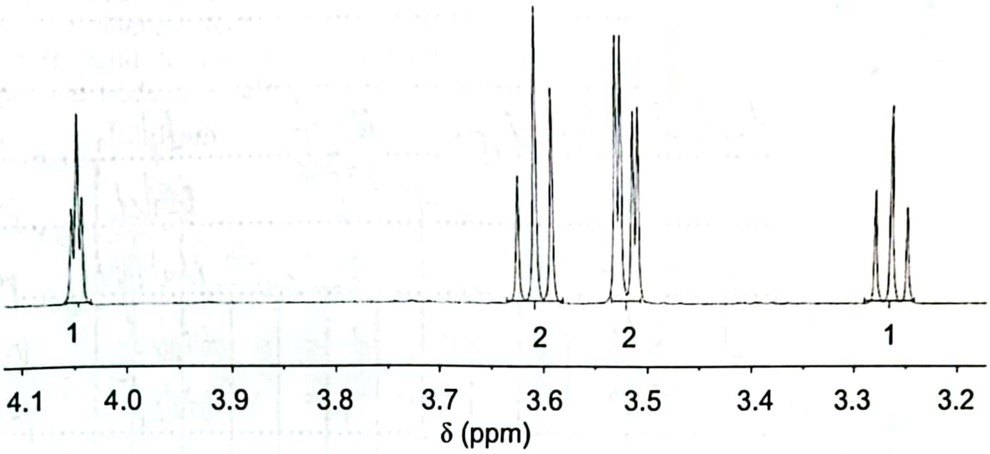
inositol

Inositol can exist as 9 different stereoisomers, including enantiomers.

(i) Draw the 2 stereoisomers of inositol that are optically active, using chair conformations. [2]

(ii) One of the above stereoisomers has a specific optical rotation of +32°. A mixture of the above 2 stereoisomers gives an optical rotation of +22° under the same conditions. Calculate the enantiomeric excess. [1]

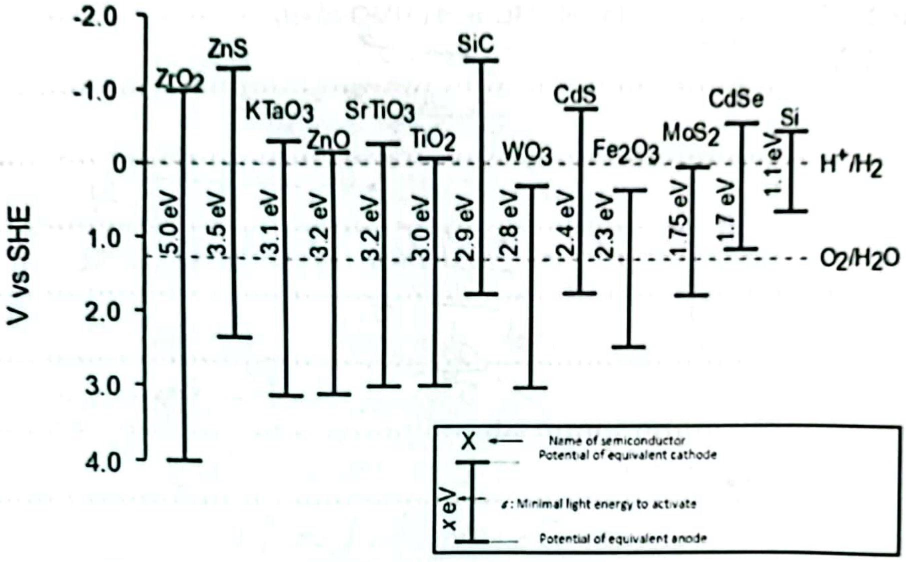
(iii) The protons on the different carbon atoms of inositol will be in different chemical environments due to the orientation of the alcohol groups. The structure of one specific stereoisomer of inositol, called *myo*-inositol which is not optically active, has the ^1H NMR spectrum in the presence of D_2O as shown below. Only one of its chair conformers is predominant. The integration is indicated on the spectrum below each signal.



Suggest the structure of one possible conformer of *myo*-inositol and explain your answer. [3]

(f) Much research has been made to obtain hydrogen gas by water splitting, and hence can be used as an alternative to carbon dioxide-emitting fuels. Lowering the cost of production of hydrogen gas and the environmental impact of its production is a major challenge.

One area of research is direct photocatalytic water splitting. It uses a semiconductor that can be activated by absorbing light. The diagram below shows the minimal light energy to activate in units of electron volt or eV and equivalent standard electrode potentials of different semiconductors for reaction at the cathode and anode. Dashed lines correspond to the water oxidation and reduction potentials. The standard hydrogen electrode is denoted as SHE.



(i) From the following list of semiconductors, list the semiconductors which when activated, can play both roles of anode and cathode for the water splitting reaction. Briefly explain your answer.

ZrO_2; ZnO; TiO_2; WO_3; CdS; Fe_2O_3; CdSe; Si **[2]**

(ii) Based on your answer in (f)(i), choose the semiconductor which when used both as anode and cathode is expected to be the most efficient for water splitting upon irradiating with solar energy. Briefly explain your answer. **[1]**

....

....

....

....

....

....

....

Name: .... **CT group:** ....

3 **(a)** This part of the question concerns the halogens and interhalogen compounds, which are formed between different halogens.

$1s^2 2s^2 2p^5$. $1s^2 2s^2 2p^6 3s^2$ ~~[illegible]~~ $3p^5$.

(i) Draw the molecular orbital (MO) energy level diagram for FC*l*, showing only the valence atomic orbitals of F and C*l*. Your answer should show the relative energies of the valence atomic orbitals of F and C*l*. [2]

(ii) Without drawing the MO energy level diagram for Cl_2, Cl_2^+ or Cl_2^-, predict their reactivity order. Explain and state one assumption made in your answer. [3]

(iii) Sketch and label the HOMO and LUMO of Cl_2. [1]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

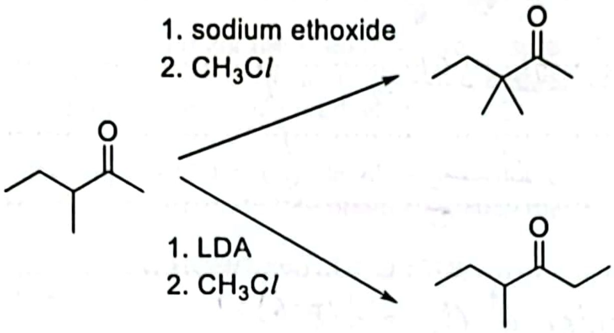
....

....

....

....

(b) $(CH_3CH_2)CH_3CHCOCH_3$ can undergo α alkylation with CH_3Cl to form two different isomeric products under different reaction conditions as shown in the reaction scheme below.



Both sodium ethoxide, $NaOCH_2CH_3$ and lithium diisopropylamide (LDA), $LiN(CH(CH_3)_2)_2$ are strong bases.

The mechanism leading to each product comprises two steps. It is known that the first step is rate determining.

(i) Draw a single energy profile diagram of the reaction above leading to formation of both isomeric products. Explain why it is possible to form both isomeric products using different reaction conditions. [3]

(ii) Suggest the structure of the **second** transition state leading to formation of $(CH_3CH_2)CH_3CHCOCH_2CH_3$. [1]

(iii) $(CH_3CH_2)CH_3CHCOCH_3$ exist as a pair of enantiomers. Explain how both enantiomers can be separated after synthesis of these compounds. [1]

(iv) Draw the *R* isomer of $(CH_3CH_2)CH_3CHCOCH_3$. [1]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

(c) **(i)** Compare and explain the difference in the wavenumber of C=O stretch in CH_3COCH_3 as well as C=S stretch in both CH_3CSCH_3 and $CH_3CSCH=CH_2$. [2]

(ii) Identify the chromophore in $CH_3CSCH=CH_2$ and state the possible electronic transitions that will be observed in its UV spectrum. [1]

(iii) Suggest how mass spectrometry can distinguish CH_3COCH_3, CH_3CSCH_3 and $CH_3CSCH=CH_2$ by identifying the major fragment ions formed. [2]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

(d) It is suggested that silver metal can reduce oxygen gas under slightly basic conditions in the presence of chloride ions according to the equilibrium below.

$4Ag(s) + 4Cl^-(aq) + O_2(g) + 2H_2O(l) \rightleftharpoons 4AgCl(s) + 4OH^-(aq)$ (*)

Given the following information
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$ $E^\theta = +0.22$ V

use relevant information from the *Data Booklet* and the relation $K_c = \exp(-\Delta G^\theta / (RT))$ to calculate the equilibrium constant of the reaction marked with * at 25 °C. [3]

....

....

....

....

....

....

....

....

....

....

....

....

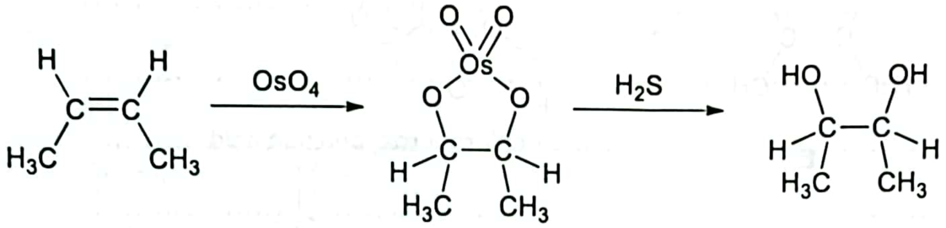
[Total: 20]

Section B

Answer **two** questions from this section.

Name: .... **CT group:** ....

4 **(a)** The hydroxylation of *cis*-but-2-ene, **E** yields butane-2,3-diol **G**, via the formation of a cyclic intermediate **F**.

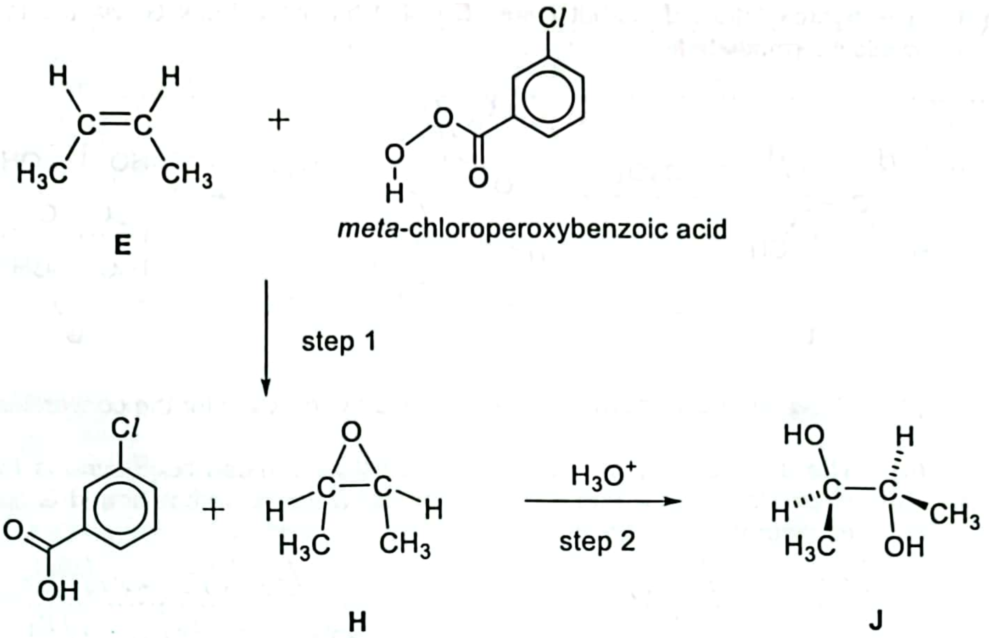


E **F** **G**

(i) Draw the mechanism and name the type of reaction for the conversion of **E** to **F**.[2]

(ii) The di-secondary alcohol **G** which exist as a meso compound is formed in this case. Using the *R* and *S* convention, draw the meso compound **G** and assign the configurations at the chiral centres. [1]

(b) The hydroxylation of *cis*-but-2-ene, **E** to yield butane-2,3-diol can occur via another synthesis with *meta*-chloroperoxybenzoic acid to form an epoxide ring, **H** in the first step, followed by acid catalysed hydrolysis as seen in the second step below. It is known that butane-2,3-diol, **J** formed has a non-superimposable mirror image.



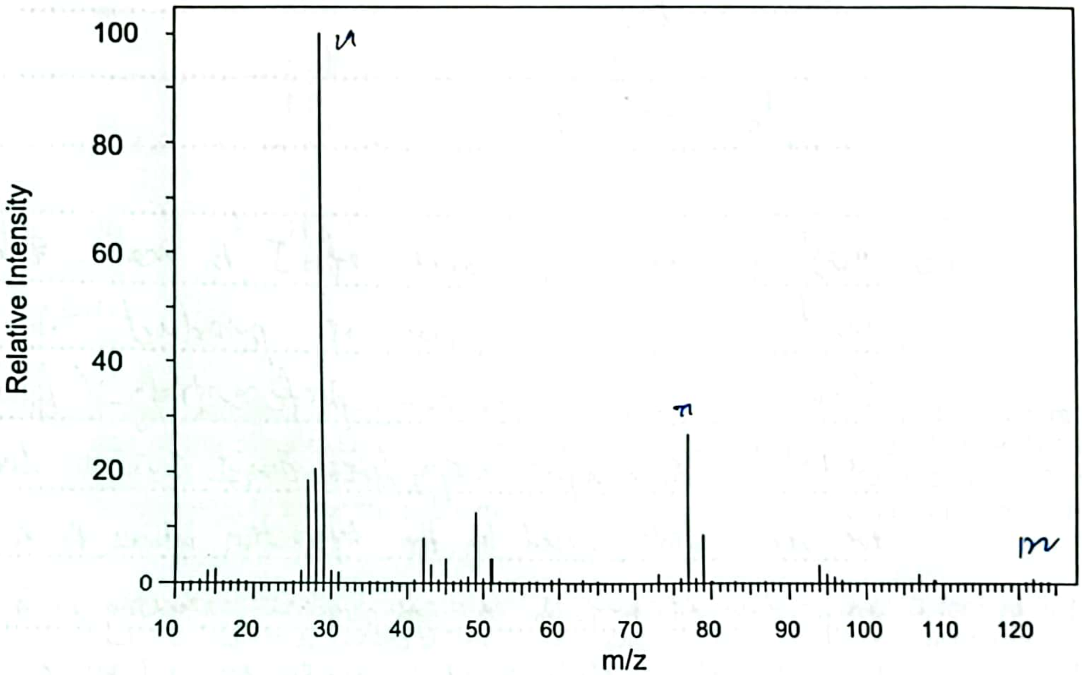
(i) In the hydrolysis of the epoxide ring in step 2, nucleophilic substitution occurs in one of the stages. Draw the mechanism for this step and state whether S_N1 or S_N2 pathway is involved in one of the stages and explain your reasoning. Your answer should show stereochemistry of all reactants, intermediates and products. [4]

(ii) Label and draw the most unstable conformation of the product **G** formed in **(a)** and **J** formed in **(b)** using Newman projections. Explain which product formed will have a higher energy. [3]

(c) Compound **K** whose ^{1}H NMR spectrum is shown in the table below has the molecular formula $C_4H_7O_2$**L** where **L** is either Br or C*l*, and it does not react with sodium carbonate.

δ / ppm	multiplicity	number of protons
1.27	triplet	3
4.07	singlet	2
4.19	quartet	2

K has a strong IR absorption peak at 1730 cm^{-1} and has the following mass spectrum as shown below.



Deduce the structural formula of **K** and the identity of **L**. Explain your reasoning clearly. [4]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

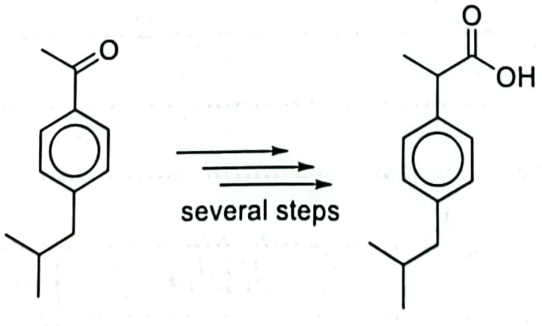
....

....

....

....

(d) Ibuprofen can be prepared using **M** and a Grignard reagent, RMgC*l* in some of the steps of its synthesis. RMgC*l* has a highly polarised C–Mg bond. RMgC*l* can be formed by the addition of magnesium metal to an alkyl halide. As the carbon atom in the C–Mg bond has a partial negative charge, it resembles a carbanion, and it reacts with electron deficient carbon centres in aldehydes, ketones, alkyl halides and carbon dioxide etc to form new carbon–carbon bonds.

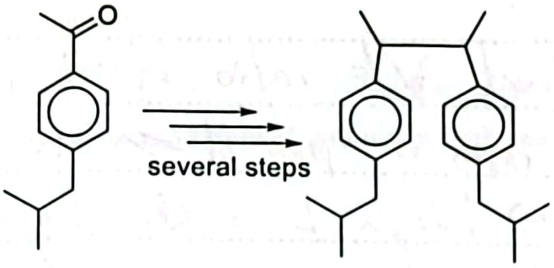


M

ibuprofen

(i) Suggest reagents and conditions in the synthesis of ibuprofen from **M**. Your answer should include the structures of the intermediates. [4]

(ii) During the synthesis of ibuprofen, a trace amount of dimer **N** can also be formed when RMgC*l* is used in one of the steps. Use the synthetic route you have proposed in **(d)(i)** to suggest how dimer **N** is formed.



M **N**

[1]

(iii) Without using any heating, suggest and briefly explain an experimental method to separate ibuprofen from the mixture containing the dimer **N** and ibuprofen only. [1]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

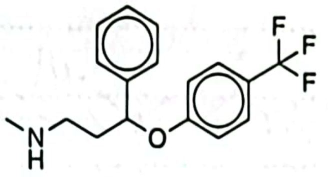
....

....

[Total: 20]

Name: .... CT group: ....

5 Fluoxetine is an antidepressant used in the treatment of major depressive disorder and obsessive-compulsive disorder, amongst many others.



fluoxetine

There are many different synthetic routes for fluoxetine. One of the first patents proposed has the following series of reactions as shown in Fig. 5.1.

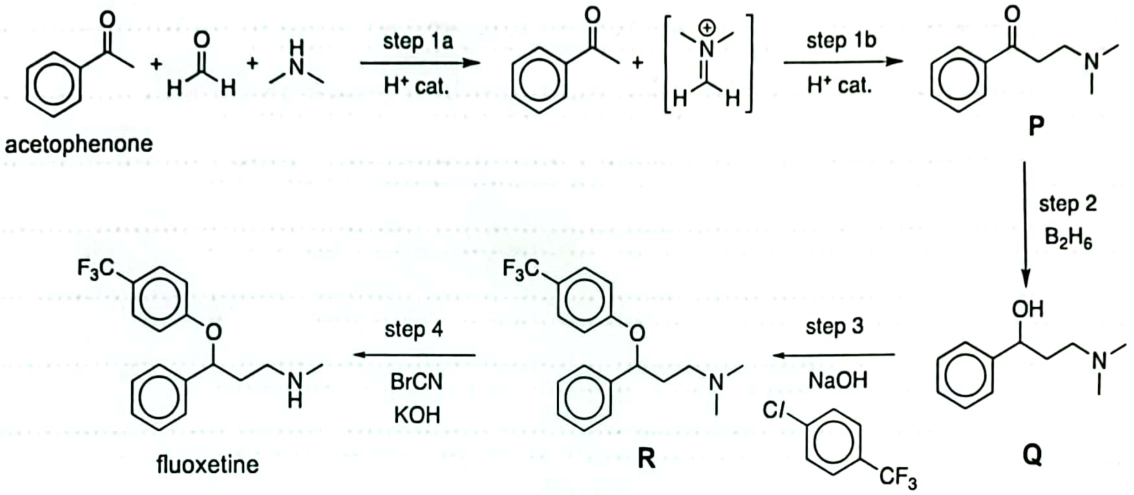


Fig. 5.1

(a) Draw a suggested mechanism for the conversion of acetophenone to **P**. [5]

....

....

....

....

....

....

....

....

....

....

....

(b) Describe and interpret each signal in the ^1H NMR spectrum of compound **P**. Ignore any coupling involving the aromatic region. [4]

(c) **(i)** Outline the principles of IR spectroscopy. [2]

(ii) Describe how the IR spectrum of acetophenone and **Q** would differ. [2]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

(d) **(i)** Step 3 involves a nucleophilic substitution of an aryl chloride. Explain why this reaction is unusual. [2]

(ii) Draw the mesomeric (resonance) forms of the intermediate formed in step 3. [2]

(iii) **Q** can be converted to **R** using an alternative synthetic route. Suggest reagents and conditions for the synthesis of **R** from **Q**. Include the structure of intermediates in your answer. [3]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

[Total: 20]

Name: .... **CT group:** ....

6 In the presence of a strong base such as NaH, alcohols can react with alkyl halides to form ethers. This is known as the Williamson ether synthesis.

$$CH_3CH_2OH + CH_3Br + NaH \rightarrow CH_3CH_2OCH_3 + NaBr + H_2$$

(a) **(i)** Suggest why the more common bases such as NaOH could **not** be used for this synthesis. [1]

(ii) Draw a suggested mechanism for the reaction above. [2]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

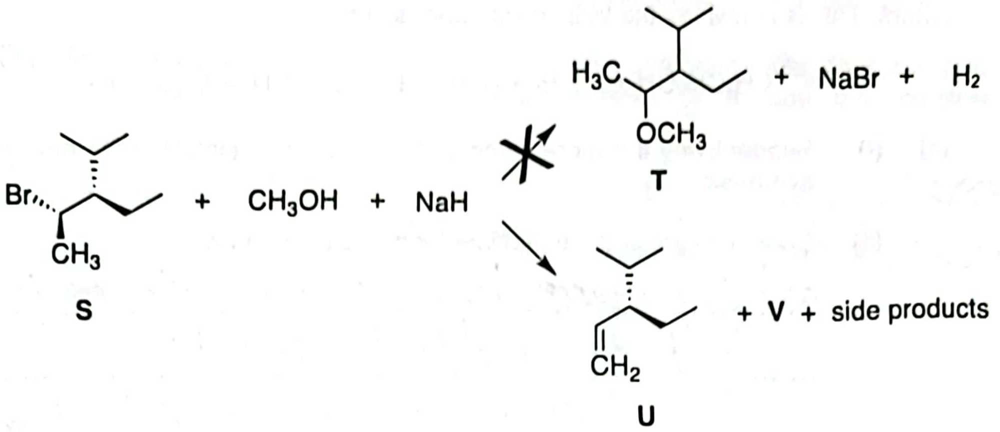
....

....

....

....

(b) When compound **S** reacts with methanol in the presence of NaH, **T** is not formed. A mixture of **U** and its isomer **V** are obtained instead.



(i) Suggest why **U** is formed instead of **T**. Hence identify and propose the mechanism for the formation of **U** from **S**. [3]

(ii) With the aid of Newman projection(s), propose the structure of isomer **V**, clearly indicating its stereochemistry. Briefly explain your answer. [3]

....

....

....

....

....

....

....

....

....

....

....

....

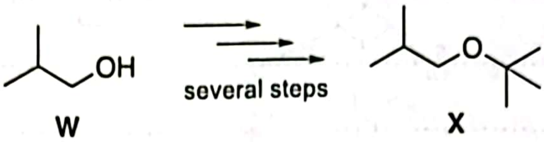
....

....

....

....

(c) Compound **X** can be prepared in a multistep process using **W** as the **only** organic reagent. Using information from **(a)** and **(b)**, suggest reagents and conditions in the synthesis of **X** from **W**. Include the structure of intermediates in your answer.



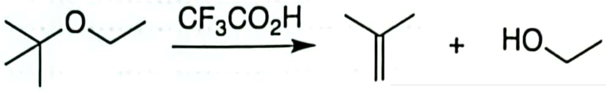
[4]

(d) The main reaction that ethers undergo is a cleavage to form their respective alcohols and alkyl halides in the presence of a strong acid such as hydrogen iodide.

(i) Propose a mechanism for the above reaction. Suggest a reason why the reaction proceeds via your proposed mechanism. [3]

(ii) Suggest an organic side product in the above reaction in the presence of excess hydrogen iodide. [1]

(iii) When the acid is replaced with CF_3CO_2H, it was observed that the following reaction takes place instead as shown below.



Suggest a reason for this observation. [1]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

[Total: 20]

Name: .... **CT group:** ....

Additional answer space

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