YISHUN INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME			
CG		INDEX NO	

CHEMISTRY 9729/03

Paper 3 Free Response **13 September 2021**

2 hours

Candidates answer on the Question Paper
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number 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, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

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.

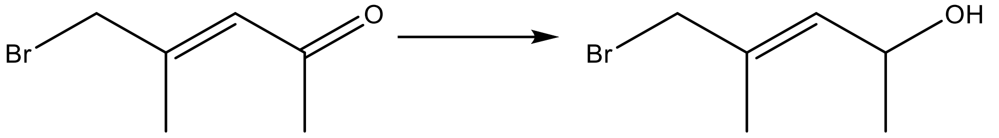
For Examiner's Use	
Section A	
1	**/21**
2	**/25**
3	**/14**
Section B	
4	**/20**
5	**/20**
Penalty	
	/80

This document consists of **34** printed pages.

Section A

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

1 5-bromo-4-methyl-3-penten-2-ol can be made from 5-bromo-4-methyl-3-penten-2-one in one step. The molecules are labelled as **A** and **B** respectively in Fig. 1.1.



A
5-bromo-4-methyl-3-penten-2-one

B
5-bromo-4-methyl-3-penten-2-ol

Fig. 1.1

(a) **(i)** State the total number of σ and π bonds in a molecule of **A**. [1]

(ii) Describe the hybridisation of the orbitals and the bonds between the carbon atoms of the C=C double bond in **A**. [2]

(iii) State the total possible number of stereoisomers that can be exhibited by **B**. [1]

(iv) Sodium borohydride is used to reduce **A** to form **B**.

Explain why only the ketone functional group in **A** undergoes reduction with sodium borohydride but the alkene functional group does not. [2]

(v) Describe a chemical test that can be used to distinguish **A** and **B**. [2]

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

Compound **E** can be made from **A** by a four-step synthesis.

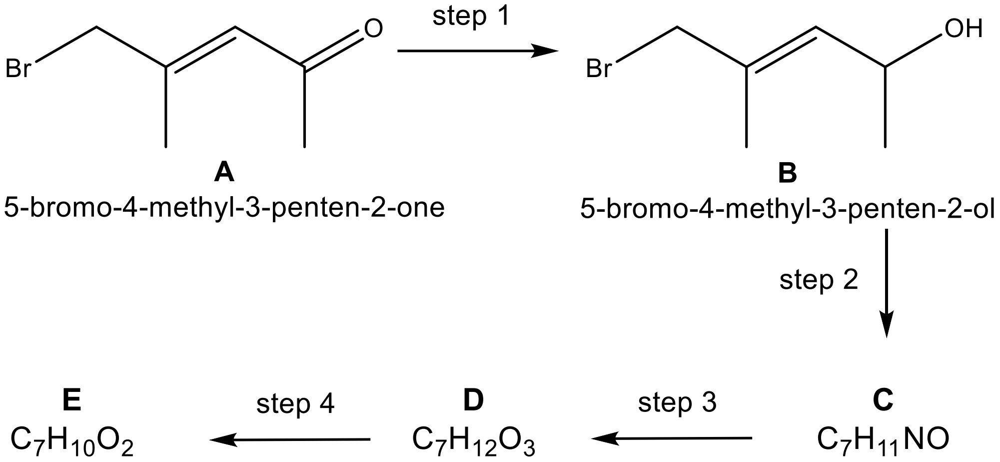


Fig. 1.2

(b) **(i)** Suggest the reagents and conditions for steps 2 and 3 in Fig. 1.2. [2]

(ii) Compound **E** is neutral and does not react with 2,4-dinitrophenylhydrazine or sodium metal.

Draw the structures for compounds **C**, **D** and **E**. [3]

(iii) 5-chloro-4-methyl-3-penten-2-ol can be used as the reactant in step 2 instead of **B** in the reaction scheme in Fig. 1.2.

Suggest how the rate of reaction will change if 5-chloro-4-methyl-3-penten-2-ol is used. [2]

……..

……..

……..

……..

……..

……..

……..

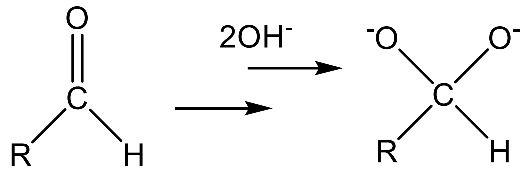
……..

[Turn over

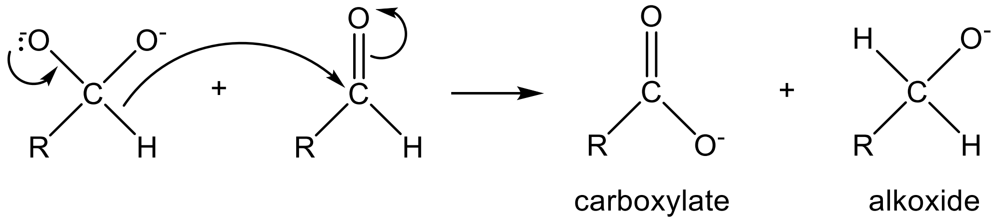
(c) The Cannizzaro reaction is a base catalysed reaction, which involves the disproportionation of aldehydes to form a carboxylic acid and an alcohol.

$$2RCHO \longrightarrow RCOOH + RCH_2OH$$

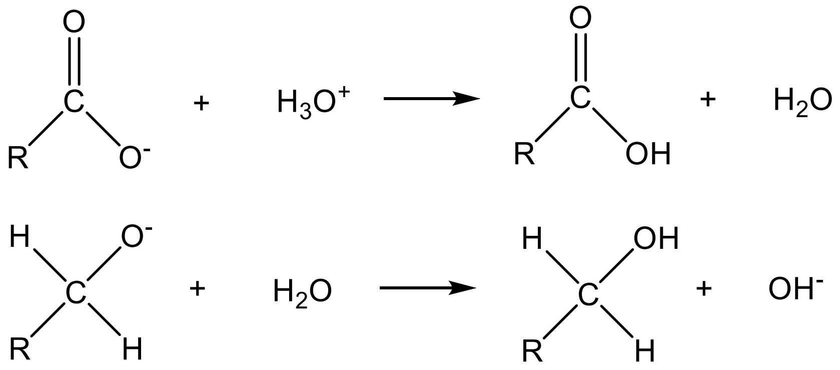
The mechanism of the Cannizzaro reaction involves 4 steps.
A nucleophilic attack on the carbonyl carbon of the aldehyde produces a dianion via a 2-step process.



In step 3, the dianion reacts with another aldehyde molecule to form the carboxylate and alkoxide ions.



In step 4, both the carboxylate and alkoxide ions are protonated to form the products.



(i) Define the term *disproportionation*, with reference to the Cannizzaro reaction. [2]

(ii) In step 1 of the mechanism, the OH^- ion acts as a nucleophile and attacks the carbonyl carbon to form an intermediate. In step 2, the second OH^- ion abstracts a proton from the hydroxyl group on the intermediate to form the dianion.

Showing any relevant lone pairs, dipoles and charges, indicate the movement of electrons with curly arrows to outline the mechanism involved in the first 2 steps of the Cannizzaro reaction. [2]

(iii) Deduce the products of the reaction when benzaldehyde undergoes the Cannizzaro reaction. [2]

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

[Total: 21]

2 **(a)** This question is about compounds of Group 17 elements and period 3 elements.

(i) Using data from the Data Booklet, state and explain how the thermal stability of the Group 17 hydrides vary down the group. [3]

(ii) Describe the reactions, if any, of $AlCl_3$ and PCl_5 with water, stating the pH of the resulting solutions. Write equations where appropriate. [4]

F, **G** and **H** are oxides of period 3 elements.

F and **H** are highly soluble in water whereas **G** is insoluble in water.

When treated with H_2SO_4(aq), only **F** and **G** reacts to form a colourless solution. When treated with NaOH(aq), only **G** and **H** reacts to form colourless solution **J** and **K** respectively.

Solution **K** forms white precipitate when treated with acidified aqueous barium nitrate.

(iii) Suggest the identity of the oxides **F**, **G** and **H**. [2]

(iv) Hence, write equations for the reactions of **G** and **H** with NaOH(aq). [2]

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

………

………

………

………

………

………

………

………

………

………

………

………

………

………

………

………

………

………

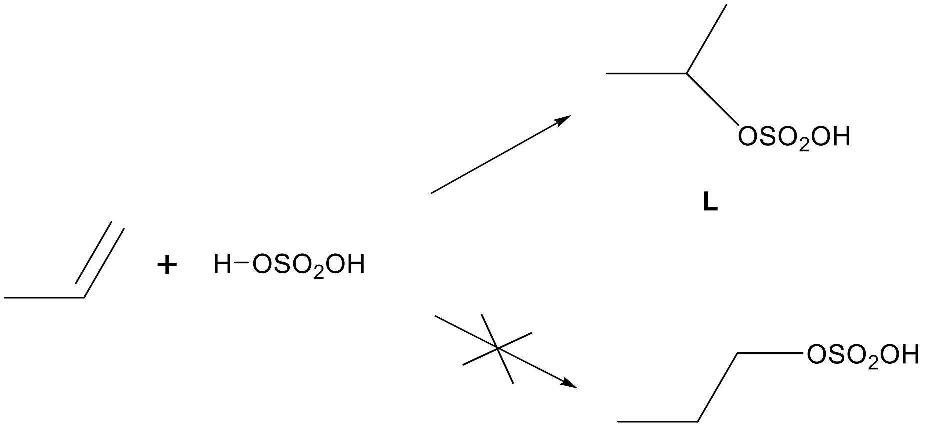
………

………

(b) Compounds of period 3 elements, such as sulfuric acid, are often used in organic reactions.

For example, sulfonation is a reaction to incorporate sulfonic acid functional group (–SO_3H) into a molecule. Both alkenes and arenes can undergo sulfonation under suitable reagents and conditions.

(i) One example of sulfonation of alkene is the reaction of concentrated sulfuric acid, H_2SO_4 with alkenes via an addition reaction. With propene, isomer **L** is produced rather than isomer **M**.

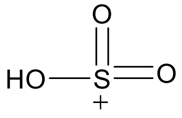


M

Fig. 2.1

By considering the mechanism and intermediates of the reaction, explain the preferential production of isomer **L**. [3]

(ii) In sulfonation of benzoic acid, sulfonium ion, SO_3H^+, generated from sulphur trioxide and fuming sulfuric acid, reacts with benzoic acid via a substitution reaction to form mixtures of aromatic mono-substituted product.



$$\mathrm{HO{-}\underset{+}{\overset{\overset{\displaystyle O}{\|}}{S}}{=}O}$$

sulfonium ion

Draw the displayed formula of the major product of the substitution reaction, and explain why it is more likely to be formed in this reaction. [2]

……

……

……

(c) Peroxyacids can be used to convert ketone to ester. An example is shown in Fig. 2.3.

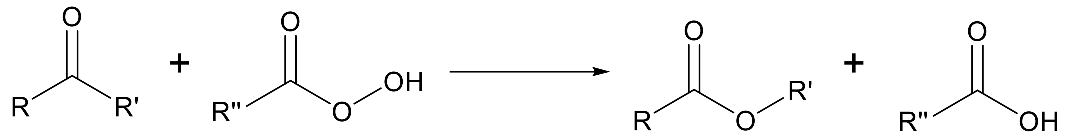


Fig. 2.3

The reaction goes through an intermediate. An example is shown in Fig. 2.4.

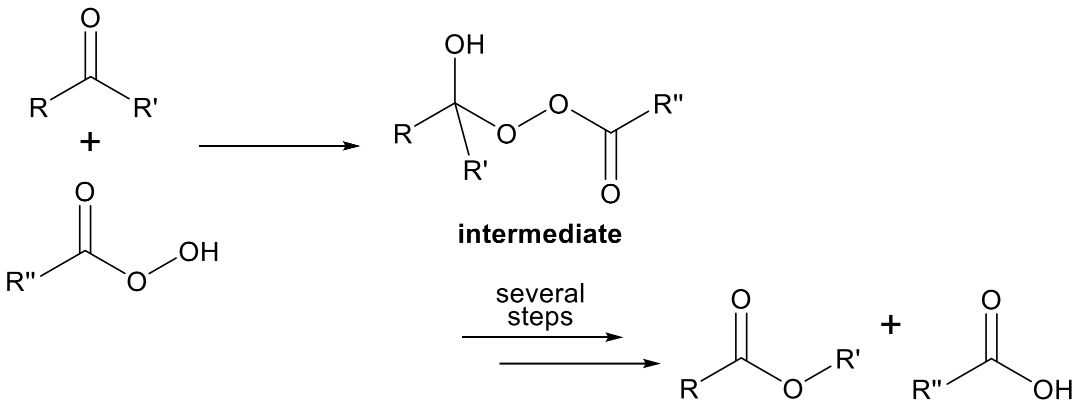


Fig. 2.4

Peroxyacids also reacts in a similar manner with aldehydes to form carboxylic acids, instead of esters. For example:

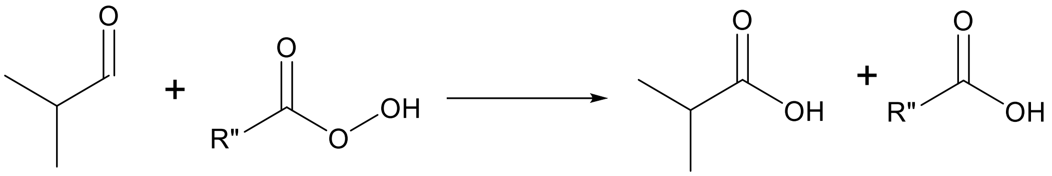


Fig. 2.5

In addition, it has been observed that aldehydes are relatively more reactive towards peroxacids than ketones.

(i) Draw the structure of the intermediate for the reaction shown in Fig. 2.5. [1]

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

(ii) Use the information given above, draw the structures of the products, **N1** and **N2**, for the reactions under the reagents and conditions shown in Fig. 2.6.

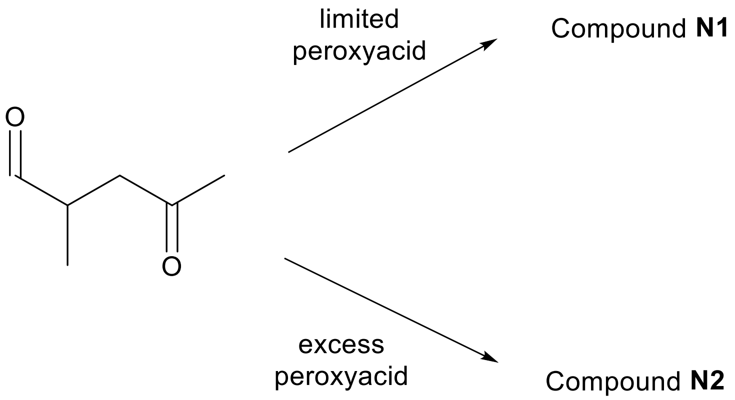


Fig. 2.6 [2]

....

....

....

....

....

....

....

....

....

....

....

....

....

(d) Salsalate, $C_{14}H_{10}O_5$, is a medication that belongs to the nonsteroidal anti-inflammatory drug classes.

When salsalate is treated with hot H_2SO_4(aq), it produces compound **P**, $C_7H_6O_3$ as the only product. **P** effervesces with Na_2CO_3(aq) and reacts with aqueous bromine to form a white precipitate with the formula $C_7H_4O_3Br_2$.

(i) State the functional groups present in **P** based on its reaction with Na_2CO_3(aq) and aqueous bromine. [1]

(ii) Suggest the two possible isomeric structures of **P** that are consistent with the information provided. Label your structures **P1** and **P2** clearly. [2]

(iii) Between the two possible structures **P1** and **P2**, the actual structure of **P** is the one with a lower first pK_a value.

Use your answer in **(ii)** to suggest which structure, **P1** or **P2**, is the actual structure of **P**. Explain your answer. [2]

(iv) Use the information given in **(d)** and your answer in **(iii)** to deduce the structure of salsalate. [1]

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

[Total: 25]

3 Manganese is a transition metal and is often used in dry cell batteries and as a black-brown pigment in paint. It is able to exhibit oxidation states from +2 to +7, which explains why it can be used as a catalyst in various reactions.

Manganese dioxide, MnO_2 is able to catalyse the decomposition of hydrogen peroxide, H_2O_2.

(a) **(i)** State the electronic configuration of the manganese ion in MnO_2. [1]

(ii) Using relevant data from the *Data Booklet* and the data given below, construct a Born-Haber cycle to determine the lattice energy of manganese dioxide, MnO_2(s).

enthalpy change of formation of MnO_2 = –504 kJ mol^{-1}
enthalpy change of atomisation of Mn = +281 kJ mol^{-1}
first and second electron affinity of oxygen atom = –702 kJ mol^{-1}

[3]

………………………………………………………………………………………………………..

………………………………………………………………………………………………………..

………………………………………………………………………………………………………..

………………………………………………………………………………………………………..

………………………………………………………………………………………………………..

………………………………………………………………………………………………………..

………………………………………………………………………………………………………..

………………………………………………………………………………………………………..

………………………………………………………………………………………………………..

………………………………………………………………………………………………………..

………………………………………………………………………………………………………..

………………………………………………………………………………………………………..

………………………………………………………………………………………………………..

The decomposition of hydrogen peroxide is found to be a first order reaction.

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

100 cm^3 of 0.1 mol dm^{-3} of hydrogen peroxide was left to decompose at a certain temperature. It was found that the concentration decreased to 0.025 mol dm^{-3} after 16 hours.

(b) **(i)** Calculate the maximum volume of oxygen produced from the complete decomposition of this sample of hydrogen peroxide at room temperature and pressure. [1]

(ii) Determine the half-life of the decomposition of hydrogen peroxide. [1]

(iii) Using your answers to **b(i)** and **b(ii)**, sketch a graph of volume of oxygen produced against time. [1]

(iv) Calculate the value of the rate constant k, stating its units clearly. [2]

…………………………………………………………………………………………………..

…………………………………………………………………………………………………..

…………………………………………………………………………………………………..

…………………………………………………………………………………………………..

…………………………………………………………………………………………………..

…………………………………………………………………………………………………..

…………………………………………………………………………………………………..

…………………………………………………………………………………………………..

…………………………………………………………………………………………………..

…………………………………………………………………………………………………..

…………………………………………………………………………………………………..

…………………………………………………………………………………………………..

…………………………………………………………………………………………………..

(c) Manganese dioxide is also used in electrochemical cells can be used to generate electricity.

The half equations for the cell are given.

$ZnO(s) + H_2O(l) + 2e^- \rightleftharpoons Zn(s) + 2OH^-(aq)$ $E^\ominus = -1.28V$
$2MnO_2(s) + H_2O(l) + 2e^- \rightleftharpoons Mn_2O_3(s) + 2OH^-(aq)$ $E^\ominus = +0.15V$

(i) Write the overall equation for when current flows. [1]

(ii) Calculate the standard Gibbs free energy change, $\Delta G^\ominus$ for this electrochemical reaction. [2]

(iii) State and explain what happens to the standard cell potential, $E^\ominus_{cell}$, when Mg^{2+} ions are added to the ZnO/Zn half-cell. [2]

……..

……..

……..

……..

……..

……..

……..

……..

……..

……..

……..

……..

……..

……..

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

[Total: 14]

Section B

Answer **one** question from this section.

4 **(a)** A fuel gas mixture consisting primarily of hydrogen gas and carbon monoxide. It can be formed from steam and carbon at high temperature.

$$H_2O(g) + C(s) \rightleftharpoons CO(g) + H_2(g) \qquad \Delta H = +131 \text{ kJ mol}^{-1}$$

In a particular experiment, steam at a pressure of 2.50 atm and a temperature of 1000K was introduced into a vessel containing an excess of powdered carbon. When equilibrium was established, the partial pressure of hydrogen was found to be 1.66 atm.

(i) Calculate the partial pressures of H_2O(g) and CO(g), and hence, the value of K_p. [2]

(ii) The experiment is repeated at a lower temperature.

State and explain how this would affect the position of the above equilibrium. [2]

(iii) Sketch a suitable diagram to illustrate the effect on a lower temperature on the rate of the above reaction. [2]

………………………………………………………………………………………………………..

………………………………………………………………………………………………………..

………………………………………………………………………………………………………..

………………………………………………………………………………………………………..

………………………………………………………………………………………………………..

………………………………………………………………………………………………………..

………………………………………………………………………………………………………..

………………………………………………………………………………………………………..

………………………………………………………………………………………………………..

………………………………………………………………………………………………………..

(b) Like aluminium objects, titanium objects that have had the titanium dioxide layer removed may then be anodised.

(i) Suggest why titanium objects are anodised, and explain how anodising achieves this. [2]

(ii) The process of anodising of titanium in an acidic electrolyte is similar to that of aluminium.

Write equations for the reactions occurring at the anode during anodising of titanium object. [1]

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

(c) Titanium dioxide is also a catalyst present in the catalytic converter in vehicles. It oxidises carbon monoxide to carbon dioxide in the presence of oxygen gas.

Outline the mode of action of the catalyst in this oxidation reaction. [2]

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

(d) Electrolysis of aqueous solutions of basic sodium ethanoate, using platinum electrodes, produces ethane at the anode as shown by the following equation.

$$2CH_3COO^- \longrightarrow CH_3CH_3 + 2CO_2 + 2e^-$$

(i) Given that hydrogen gas is collected at the cathode, construct an equation for the overall reaction. [1]

(ii) Calculate the mass of ethane produced when a current of 3.0A is passed for 30 minutes, through an aqueous solution of sodium ethanoate.

The Faraday constant = 9.65×10^4 C mol^{-1} [2]

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

(e) Paterno-Buchi reaction is a photochemical reaction that forms four-membered oxetane rings.

In the presence of uv light, an excited carbonyl reacts with an alkene to form oxetane rings via a reactive intermediate as shown in Fig. 4.1.

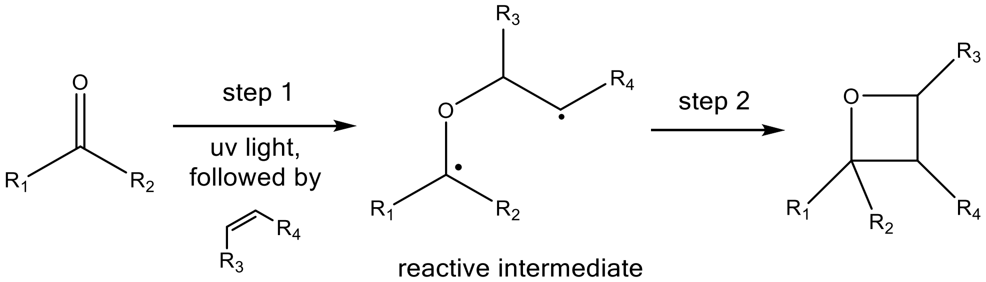
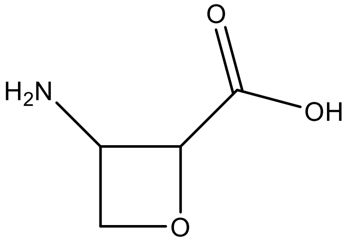


Fig. 4.1

(i) State the shape of the carbonyl carbon before and after the reaction. [2]

(ii) Copy the reactive intermediate and add curly arrows to complete step 2. [1]

(iii) Compound **Q** is an organic compound that has antibiotic properties.



Q

Q can be synthesised by the Paterno-Buchi reaction of compound **R** and compound **S**.

Compound **R** forms effervescence with aqueous sodium carbonate.

Compound **S** forms an orange precipitate **T** when reacted with 2,4-DNPH.

Use this information to suggest possible structures of **R**, **S** and **T**. [3]

…………………………………………………………………………………………………..

…………………………………………………………………………………………………..

…………………………………………………………………………………………………..

…………………………………………………………………………………………………..

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

[Total: 20]

5 **(a)** Both magnesium and calcium reacts with cold water to form hydroxides and hydrogen gas. However, the reaction with magnesium occurs very slowly whereas the reaction with calcium is more vigorous.

By reference to the *Data Booklet*, account for the difference in reactivity of the two metals towards cold water. [2]

………………………………………………………………………………………………..

………………………………………………………………………………………………..

………………………………………………………………………………………………..

………………………………………………………………………………………………..

………………………………………………………………………………………………..

………………………………………………………………………………………………..

(b) Group 2 hydroxides decompose in a similar manner as group 2 carbonates. When subjected to strong heating, solid magnesium hydroxide decomposes to form magnesium oxide, a white solid, and a gas.

(i) Construct an equation, with state symbols, for the decomposition of magnesium hydroxide. [1]

(ii) State and explain the difference in decomposition temperature between magnesium hydroxide and calcium hydroxide. [2]

………………………………………………………………………………………………..

………………………………………………………………………………………………..

………………………………………………………………………………………………..

………………………………………………………………………………………………..

………………………………………………………………………………………………..

………………………………………………………………………………………………..

………………………………………………………………………………………………..

………………………………………………………………………………………………..

(c) **(i)** Define the term *standard enthalpy change of formation*. [1]

(ii) Use data in Table 5.1 to calculate the $\Delta H^{\ominus}_{\text{ppt}}$ for the precipitation of $Mg(OH)_2(s)$.

Table 5.1

	Value/kJ mol^{-1}
standard enthalpy change of formation of $Mg^{2+}(aq)$	–462.0
standard enthalpy change of formation of $OH^{-}(aq)$	–230.0
standard enthalpy change of formation of $Mg(OH)_2(s)$	–601.7

[2]

When a precipitate is formed, $\Delta G^{\ominus}_{\text{ppt}}$, in $Jmol^{-1}$, is given by the following expression.

$$\Delta G^{\ominus}_{\text{ppt}} = 2.303RT\log K_{sp}$$

(iii) Given that the numerical value of the K_{sp} of $Mg(OH)_2(s)$ is 7.1×10^{-12} at 298K, calculate $\Delta G^{\ominus}_{\text{ppt}}$, in $kJmol^{-1}$, for $Mg(OH)_2$. [1]

(iv) Use your answer in **(ii)** and **(iii)** to calculate $\Delta S^{\ominus}_{\text{ppt}}$, in $Jmol^{-1}$ K^{-1}, for the precipitation of $Mg(OH)_2(s)$ at 298K. [2]

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

(d) Barium hydroxide can be used to synthesise buten-3-one via a series of reactions as shown in Fig. 5.2.

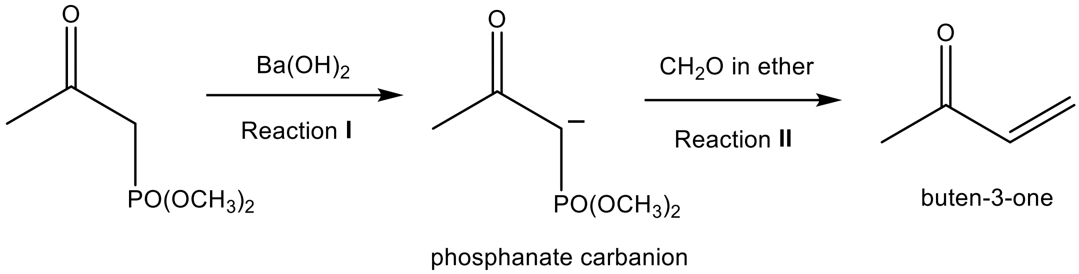


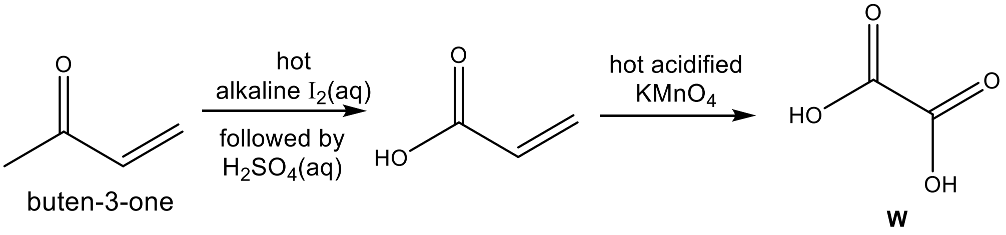
Fig. 5.2

(i) Suggest the type of reaction for reaction **I**. [1]

(ii) The phosphonate carbanion formed in reaction **I** is highly stabilised.

Suggest a reason for this stability. [1]

(iii) A student proposed the following synthesis of compound **W** from buten-3-one.



Explain why compound **W** could not be obtained from the synthesis and propose how the student could modify the synthesis to obtain **W**. [2]

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……..

……..

……..

……..

……..

……..

……..

……..

……..

……..

……..

……..

……..

……..

……..

……..

……..

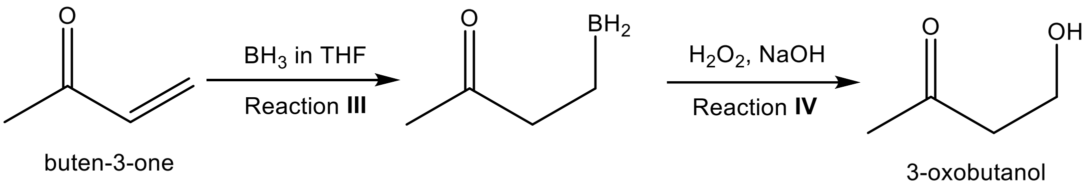
……..

……..

……..

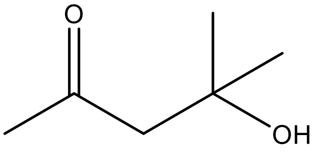
……..

(e) Buten-3-one can be converted to 3-oxobutanol using the following reactions.



(i) Suggest the type of reaction for reaction **III**. [1]

(ii) Describe a chemical test, with appropriate observations, to distinguish between compound **V** and 3-oxobutanol.



V

[2]

……

……

……

……

……

……

……

……

……

……

……

……

(f) Compound **X** can be synthesised from 3-oxobutanol as shown in Fig. 5.3.

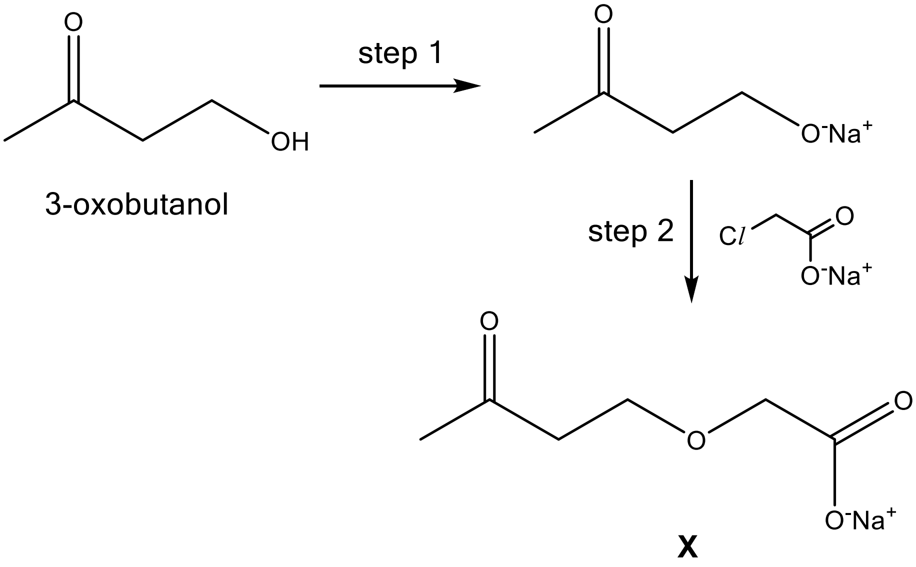


Fig. 5.3

(i) Suggest why step 1 must be carried out before reacting with the reagent in step 2. [1]

(ii) Suggest why the reaction occurs at the carbon atom of the C–C*l* bond, rather than the carbon atom of the C=O bond in step 2. [1]

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

[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.

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

………

………

………

………

………

………

………

………

………

………

………

………

………

………

………

………

………

………

………

………